National Programme on **Materials** and **Structure Research**

SECOND PROGRESS REPORT

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ISBN 951-715-402-X (print)
ISBN 951-715-403-8 (pdf)

Painopörssi Oy, Helsinki 2002

Preface

The National Programme on Materials and Structure Research (MATRA), launched by the Academy of Finland in 1993 to promote re-industrialisation, has been special in many respects: the total funding of around EUR 31.0 million and several rounds of applications, the long duration of the programme (1994-2000), its interdisciplinarity and the large number of research projects involved (a total of 48 projects or consortia). In addition, the programme was pioneering cooperation between the Academy of Finland and the National Technology Agency, Tekes (the Academy allocated EUR 24.0 million and Tekes EUR 7.0 million). The goal of the programme was to promote research collaboration both within and between academia and industry in the rapidly developing areas in the field of material science.

The first progress report of the Programme was published in 1996. It consisted of reports of the consortia accepted in the first and second rounds of application. If the consortia applied for further funding their progress reports were sent to the evaluators. Accordingly, the research conducted by the consortia was thoroughly reviewed. Similar reports were asked from the consortia which were funded in the later stages of the programme: in the third and fourth rounds of application. The same procedure was carried out with the projects funded by Tekes. All these reports are collected in this book. The progress reports, in addition to other material, were used for the evaluation of the whole research programme. This evaluation was conducted by an external expert panel: Professor Jan-Otto Carlsson (University of Uppsala, Chair), Professor Anders Liljas (University of Lund) and Professor Etienne Schacht (Ghent University). The evaluation report is available at the Academy's web site and can be ordered from the Communications Unit of the Academy of Finland.

I would like to see that the experience and knowledge achieved through this research programme would advance materials and structure research in the future.

Helsinki, March 13, 2002

Marja-Liisa Riekkola

Chair of the Programme Committee of the MATRA
Vice-Chair of the Research Council for Natural Sciences and Engineering

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RESEARCH PROJECTS ACCEPTED IN THE THIRD ROUND OF APPLICATION 1997 -1999

STRUCTURE, FUNCTION AND ASSEMBLY OF BIOLOGICAL MACROMOLECULE COMPLEXES

Dennis Bamford[1], Esko Ukkonen[2] and Stephen Fuller[3]

Abstract

The objectives of the proposed results were to obtain quantitative data on two bacterial virus systems that both have a membrane as a structural component. The principal approaches used were spectroscopy, cryo electron microscopy combined with image reconstruction methods, crystallography and electrochemistry. In all fronts the research advanced mostly as indicated in the research proposal Several new EM based structures were obtained on virus particles at medium resolution and one high resolution X-ray based structure was also solved. Based on these results new biological insights to virus evolution was achieved. It seems that the studied viruses (phi6 and PRD1) belong to virus lineages where viruses infecting hosts from different domains of life have a common ancestor, even though no nucleotide or amino acid sequence similarity can be detected. and tables in place.

1 Partners and Funding

1.1 Institute of Biotechnology and Department of Biosciences, University of Helsinki

The research group consisted of subproject leader senior researchers Jaana Bamford, Sarah Butcher and Roman Tuma, post postgraduate students Jarmo Juuti, Anja Paatero, Minna Poranen, Pia Rydman , Marika Grahn.

1.2 Department of Computer Science, University of Helsinki

The research group consists of grad students K.Fredriksson, J.Ravantti, and undergraduate students T.Kivioja and S.Sihvo.

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[1] Institute of Biotechnology and Department of Biosciences, University of Helsinki, P.O.Box 56, FIN-00014 University of Helsinki

[2] Department of Computer Science, University of Helsinki, P.O.Box 26, FIN-00014 University of Helsinki

[3] European Molecular Biology Laboratory, Meyerhofstr. 1, 69117 Heidelberg, Germany

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1997-1999 from MATRA. Other sources were available but difficult to identify for this particular structural project as there were also other scientific production than the one reported here. It is also evident that MATRA funding supported only partially the production reported.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
	Academy	341	342	343	-	**1.026**

2 Research Work

2.1 Objectives and Work Plan

To obtain structural and dynamic quantitative information on two bacterial virus systems that both contain a biological membrane. The methods in use were cryo electron microscopy, crystallography, spectroscopic methods as well as electrochemistry.

2.2 Progress Report: Common Themes

The three involved research groups have published five primary research articles together. Two of them [6,15] focus on the assembly intermediates and symmetry mismatch in the RNA dependent RNA polymerase complex of phage phi6, a molecular machine capable of RNA packaging, replication and transcription. One [11] describes the vertx structure of icosahedral dsDNA phage PRD1. Associated with the DNA delivery. Two works [10,17] deal with novel algorithms in the EM-based image reconstruction process. Based on these and additional works commercial applications are designed on the phi6 polymerase.

2.3 Progress Report: Progress by the Bamford laboratory

The objectives of the proposed project included the usage of spectroscopic methods to study the different viral particles and their subassemblies. These results have been described in detail in the primary publications [1,2,7,8,13,]. Also proposed electrochemical approaches to dissect mostly virus cell interactions yielded intriguing results on the behaviour of cell membranes [3,4,5,14,22]. In addition we were able to proceed either in solving high resolution structures or obtaining diffracting crystals of a number of proteins [12,18,19]. In addition a mass spectroscopic method for to determine protein multimericity was developed [9]. RNA secondary structure determination for viral packaging sites is described in [16] and SAXS and genetics based structural analysis of the PRD1 spike complex was described [20,21].

2.4 Progress Report: Progress by the Ukkonen group

The main achievements were the new combinatorial approach to pattern matching [23] and developing of an architecture for 3D virus reconstruction.

2.5 Progress report of the Fuller Group

Fuller group did not obtain funding from this program and thus their other than collaborative efforts are not described here.

3 International Aspects

The work described is and has been highly international. Fifteen out of the 22 reported primary articles are done as an international collaboration. We have had also an EU funded projects on the structures of dsRNA viruses running simultaneously with the Matra funding. The partners were D.Stuart (Oxford), Bamford (Helsinki), Fuller (Heidelberg), Mertens (Pirbright) and Skoglund, (Stockholm).

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 5.1, refereed conference papers in Section 5.2, monographs in Section 5.3 and theses in Section 5.4.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
BIO	Ref. journal art.	6	1	8	7	**22**	1-6, 7,8-15,16-22
	Ref. conf. papers	-	1	-	-	**1**	23
	Doctoral dissert.	2	-	1	-	**3**	24-26
	Master degrees	-	-	2	-	**2**	27-28

5 Publications

5.1 Refereed Journal Articles

[1] J.T. Juuti and D.H. Bamford (1997). Protein P7 of phage f6 RNA polymerasecomplex,acquiring of RNA packaging activity by *in vitro* assembly of the purified protein onto deficient particles. *J. Mol. Biol.,* 266, 891-900.

[2] J.M. Benevides, M. Tsuboi, J.K.H., Bamford and G.J. Thomas, Jr.(1997). Polarized Raman spectroscopy of double-stranded RNA from bacteriophage f6: local Raman tensors of base and backbone vibrations. *Biophysical J.,* 72, 2748-2762.

[3] R. Daugelavicius, E. Bakiene, J. Berzinskiene and D. H. Bamford (1997). Binding of lipophilic anions to microbial cells. *Bioelctrochemistry and Bioenergetics,* 42, 263-274.

[4] R. Daugelavicius, J.K.H. Bamford, A.M. Grahn, E. Lanka, and D.H. Bamford (1997). IncP plasmid encoded cell envelope-associated DNA Transfer complex increases the cell permeability. *J. Bacteriol.*, 179, 5195-5202.

[5] R. Daugelavicius, J.K.H. Bamford, and D.H. Bamford (1997). Changes in host cell energetics in response to bacteriophage PRD1 DNA entry. *J. Bacteriol.*179, 5203-5210.

[6] S. Butcher, T. Dokland, P. Ojala, D.H. Bamford and S.D. Fuller (1997). Intermediates in the assembly pathway of the double stranded RNA virus phi6. *EMBO J.* 14, 4477-4487.

[7] J.T Juuti, D.H. Bamford, R. Tuma, and G.J. Thomas, Jr. (1998). Structure and NTPase activity of the RNA translocating protein (P4) of the bacteriophage f6. *J. Mol. Biol.* 279, 347-359.

[8] R.H. Jenkins, R. Tuma, J.T. Juuti, D.H. Bamford and G.J. Thomas, Jr. (1999) A novel Raman spectrometric method for quantitative measurement of nucleoside triphosphate hydrolysis. *Biospectroscopy*, *5, 3-8.*

[9] J. Helin, J. Caldentey, N. Kalkkinen and D.H. Bamford (1999). Analysis of the multimeric state of proteins by matrix assisted laser desorption/ionization mass spectrometry after cross-linking with glutaraldehyde, *Rapid Communications in Mass Spectrometry,* 13, 185-190.

[10] J. Ravantti and D.H. Bamford (1999). A data mining approach for analyzing density maps representing macromolecular structures. *J. Structural. Biol.* 125, 216-222.

[11] P.S. Rydman, J. Caldentey, S. J. Butcher, T. Rutten, S. Fuller, and D.H. Bamford (1999). Bacteriophage PRD1 contains a labile receptor-binding structure at each vertex. *J. Mol. Biol*. 291, 575-587.

[12] S.D. Benson, J.K.H. Bamford, D.H. Bamford and R.M. Burnet (1999). Viral evolution revealed by bacteriophage PRD1 and human adenovirus coat protein structures. *Cell*, 98, 825-833.

[13] R. Tuma, J. K. H. Bamford, D.H. Bamford, and G.J. Thomas, Jr.(1999). Assembly dynamics of the nucleocapsid shell subunit (P8) of bacteriophage phi6. *Biochemistry*, 38, 14644-14652.

[14] M.M. Poranen, R. Dagelavicius, P. M. Ojala Michael W. Hess and D.H. Bamford (1999). A novel virus-host cell membrane interaction: membrane voltage dependent endocytic-like entry of bacteriophage phi6 nucleocapsid, *J. Cell. Biol.* 147, 671-681.

[15] F. DeHaas, A. Paatero, L. Mindich, D.H. Bamford and S.D. Fuller (1999). The role of symmetry mismatch in RNA packaging by the polymerase complex of dsRNA bacteriophage phi6. *J. Mol. Biol.* 294, 357-372.

[16] M.J.T Pirttimaa and D.H. Bamford (2000). RNA secondary structures of the bacteriophagephi6 packaging regions. *RNA*, 6, 880-889.

[17] T. Kivioja, J. Ravantti, A. Verkhovsky, E.Ukkonen and D.H. Bamford (2000). Local average Intensity-based method for identifying spherical particles in electron micrographs, J. Structural. Biol. 131, 126-134.

[18] S.J. Butcher, E. Makeyev, J.M. Grimes, D.I. Stuart and D.H. Bamford (2000). Crystallization and preliminary X-ray crystallograpich studies on the bacteriophage phi6 RNA-dependent RNA polymerase. Acta Cryst. Ser. D 56, 1473-1475.

[19] X. Lan, S.J. Butcher, S.D. Benson, D.H. Bamford and R.M. Burnett (2000). Crystallization and preliminary X-ray analysis of receptor-binding protein P2 of bacteriophage PRD1. J. Structural Biol., 131, 159-163.

[20] J. Caldentey, R. Tuma and D.H. Bamford (2000). Assembly of bacteriophage PRD1 spike complex: role of the multidomain protein P5. *Biochemistry*, 39, 10566-10573.

[21] J.K.H. Bamford and D.H. Bamford (2000). New mutant class, made by targeted mutagenesis, of phage PRD1 reveals that protein P5 connects the receptor binding protein to the vertex. *J. Virology*, 74, 7781-7786.

[22] R. Daugelavicius, E. Bakiene and D.H. Bamford (2000). Stages of polymyxin B interaction with the Escherichia coli cell envelope. Antimicrobial Agents and Chemotherapy, 44, 2969-2978.

5.2 Refereed Conference Papers

[23] AK.Fredriksson and E. Ukkonen (1998). A rotation invariant filter for two-ddimensional string matching. In: Proc. Combinatorial Pattern Matching (CPM'98), LNCS 1448, pp118-125, Springer-Verlag 1998.

5.3 Monographs

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5.4 Doctoral, Licentiate, and Master Theses

[24] J. Juuti. Bacteriophage phi6 RNA polymerase Complex: Structure, Assembly and Functions of the component proteins. PhD dissertation, Department of Biosciences, University of Helsinki, 1997.

[25] M. Grahn, dsDNA Bacteripphage PRD1: Interaction with Cell Surface Receptor, the DNA Transfer Complex Encoded by a Conjugative IncP plasmid. PhD dissertation, Department of Biosciences, University of Helsinki, 1997.

[26] T. Kivioja. Automatic picking of viral particles from electron micrographs (in Finnish). Masters thesis, Department of Computer Science,.raport C-1999-53, University of Helsinki, 1999.

[27] S. Sihvo. Data base for three dimensional objects (in Finnish), Masters thesis, Department of Computer Science, report C-1999-62, University of Helsinki, 1999.

CONTENTS

THE TERNARY COMPLEX BETWEEN HEPARAN SULPHATE, FIBROBLAST GROWTH FACTOR RECEPTOR AND FIBROPLAST GROWTH FACTOR: STRUCTURE AND STRUCTURE-BASED DRUG DESIGN

Adrian Goldman[1], Kari Alitalo[2], Markku Jalkanen[1], Mark Johnson[3] and Ari Koskinen[4]

Abstract

Coordination and regulation of cell growth and differentiation is the fundamental question in developmental biology. The regulation in space and time of cellular behaviour by growth factors and their receptors is obviously a key part of this. Although much is already known, even in terms of atomic structures, about signalling events inside the cell, the events that occur outside the cell are not as well understood. Yet defects in the receptors or their growth factors lead to many different problems, from developmental abnormalities to cancer.

Our major objective was solving the structure of a ternary complex of fibroblast growth factor receptor (FGFR) with its two ligands, acidic fibroblast growth factor (aFGF) and proteoglycans, as represented by heparan sulphate. We then wished to connect structure and functional behaviour and to use that knowledge to design structure-based agonists and antagonists.

In parallel, we will continue to analyse the binding of FGFR to its effectors using plasmon resonance and other analytical techniques. We have recently discovered an FGF-inducibile Response Element (FiRE) that allows us to trace signal transduction from molecular events at the cell surface all the way to the target gene. By analysing FiRE activation, we will be able to correlate functional studies with the structure and binding of FGFR to either or both of its ligands: FGFs and oligosaccharide.

Finally, molecular modelling will be used to dissect the ternary complex: to understand what interactions switch the ternary complex “on”, what switch it “off”. Here, site-directed mutagenesis and the knowledge of the binding interactions described above will be very powerful. Recent findings in other systems also indicate that this type of approach should lead

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[4] Department of Chemistry, University of Oulu, Linnanmaa, PO Box 191, FIN-90101 Oulu

to new, non-toxic, oligosaccharide-based bioactive materials. The applications range from implants and drug delivery devices to novel pharmaceuticals.

During the course of the project, we have managed to produce large amounts of FGFR from various sources, including baculovirus/insect cells, *P. pastoris* and, in unfolded form, *E. coli*. We determined the glycosylation pattern of FGFR by proteolysis/MALDI-TOF mass spectrometry and determined that FGFR senses the degree of sulphonation of heparan sulphate, but not the actual positions of sulphonation.

1 Partners and Funding

1.1 Macromolecular Structures Group, University of Turku/University of Helsinki (MSG-UTU)

The research group consists of subproject leader professor Adrian Goldman, postgraduate students Heidi Tuominen, students Jan-Josef Filén and Suvi-Katri Leivonen, as well as support from postdoctoral associate Heikki Heimo, technician Raija Andersen (in Turku 97-98) and programmers Dan-Johann Still and Zuhair Iftikhar.

1.2 Molecular/Cancer Biology Laboratory, Haartman Institute, University of Helsinki (FGFR-HU)

The research group consists of subproject leader professor Kari Alitalo and graduate student Sirpa Vainikka.

1.3 Syndecan Group, Turku Centre for Biotechnology, University of Turku (SG-UTU)

The research group consists of subproject leader professor Markku Jalkanen, graduate student Britt-Marie Loo and postdoctoral associate Kamel Darwish.

1.4 Molecular Modelling Group, Åbo Akademi University, Department of Biochemistry and Pharmacy (MMG-ÅA)

The research group consists of subproject leader professor Mark Johnson and postdoctoral associate Sari Helin and programmer Dan-Johann Still (joint with MSG-UTU).

1.5 Organic Chemistry Group, Department of Chemistry, University of Oulu (OCG-UO)

The research group consists of subproject leader professor Ari Koskinen and graduate students Leina Otsomaa and Teijä Hyppönen.

1.6 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table. Amounts in italics are estimates.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
MSG-UTU	UTU	300	300	200		**800**
	Academy	456	457.5	458.7		**1372.2**
FGFR-HU	HU	200	200	200		**600**
	Academy	114	114	114		**342**
SG-UTU	UTU	200	200	200		**600**
	Academy	360	360	360		**1080**
	EU	400	400	400		**1200**
MMG-ÅA	ÅA	200	200	200		**600**
	Academy	259	259	259		**777**
OCG-OU	OU	200	200	200		**600**
	Academy	381	391	399		**1171**
Total		**3070**	**3081.5**	**2990.7**		**9142.2**

2 Research Work

2.1 Objectives and Work Plan

The original objectives defined in the work plan were as follows:

1. aFGF production
2. FGFR-4ed production
3. Syndecan-1ed production

4. Crystallisation of FGFR4-ed
5. FGFR-4ed and syndecan-1ed binding analysis
6. Crystal structure analysis of FGFR4-ed
7. Modified syndecan-1ed
8. Modified FGFR-4ed.
9. Oligosaccharide production scale-up
10. Homology molecular modelling
11. Modified oligosaccharides
12. Rational design of inhibitors

Initially, more attention was to be placed on scale-up of production of the various components for the ternary complex (aFGF, FGFR-4ed, synthetic oligosaccharides, syndecan-1ed), on continued analysis of the binding requirements of the complex, and on crystallisation, with an aim to shift resources towards the end of the grant period towards crystallographic structure analysis, molecular modelling, and design and synthesis of glycomimetics.

During the course of the grant, it became clear that the level of our effort on production of FGFR4-ed was not sufficient, and so more effort was devoted to that than to crystallisation and crystallography on the ternary complex.

2.2 Progress Report: Common Themes

During the grant period, progress was made on defining the binding motifs and length of required for binding oligosaccharides to FGFR4, as well as which FGFs bound FGFR4 best. The results showed that the extracellular domain of FGFR4 (FGFR4ed) fromed complexes with FGF-1 and FGF-2 in the presence and absence of heparin, and that heparin alone induced receptor dimerisation on the Biacore plasmon resonance chip. 12 sulphated sugar residues are required to bind FGFR4-ed in a wild-type manner, with 8 being the minimal length. FGFR4ed binding saccharides always contain both 2-O-sulphated iduronic acid and 6-O- sulfated N-sulfoglucosamine residues. The affinity did not seem to depend on the position of the 6-O-sulphates, but on how many of them there were.

2.3 Progress Report: Progress by the Macromolecular Structures Group

During the current grant period, we achieved the following:

1) A purification of C-terminal His-tagged wild-type fibroblast growth factor 4 (extracellular domain) (FGFR4-ed) produced in Baculovirus/insect cells.
2) Production of wt FGFR4-ed with N-terminal His-tag and tomato etch virus protease (rTEV) site for one-step tag removal.

3) Demonstration by protease digestion and MALDI mass spectrometry that FGFR4-ed as produced in Baculovirus/insect cells is variably N-glycosylated on Asn88, 234 and 266, but not on the other three Asn in the protein, and it is not O-glycosylated.
4) Construction of single, double, and triple variants (N88D, N88/234D, N88/234D, N234/266D and N88/234/266D).
5) Production of the N-terminal His-tagged deglycosylated triple variant in Baculovirus/insect cells, demonstrating glycosylation is not required for correct folding of FGFR4-ed
6) Binding studies (gel shift assay, and BiaCoreX) of the C-terminal and N-terminal His-tagged wild-type protein and N-terminal His-tagged triple variant, demonstrating:
    a) glycosylation is not required for wild-type receptor binding
    b) heparan sulphate (HS) binds to the His-tag, complicating interpretation of HS results on His.tagged proteins.
7) Production of triple mutant and wild-type FGFR4-ed, both N- and C-terminally His-tagged into inclusion bodies in *E. coli* in large yields (as much as 70 mg/l).
8) Partial refolding of the *E. coli*-produced FGFR4-ed, but unfortunately the material was aggregated (RMM> 1 MegaDalton), even though it was soluble at 25 mg/ml.
9) Demonstration that *E. coli*-produced refolded material did not bind FGF nor HS.
10) A demonstration that monoclonal antibody F85 GC5 selects for native-folded FGFR4-ed over SDS-denatured and SDS-denatured, reduced FGFR4-ed.

2.4 Progress Report: Progress by the Molecular/Cancer Biology Laboratory, Syndecan Group, Molecular Modelling Group, and the Organic Chemistry Group.

No reports by the other laboratories were received.

3 International Aspects

There were numerous research contacts from the Jalkanen group to Professor Ulf Lindahl’s group in Sweden, and the Jalkanen group was a member of the EU BRIGSH consortium. Professor Ralf Pettersson’s group (Sweden), donated the FGF-1 that we used for binding studies. The members of the consortium presented their work at various international conferences and gave seminars abroad.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1997	1998	1999	2000-1	**Total**	Publication numbers
MSG-UTU	Ref. journal art.	-	-	-	2	**2**	19,25
	Master degrees	-	1	-	1	**2**	
FGFR-HU	Ref. journal art.	-	2	-	1	**3**	5,10, 19
	Doctoral Dissert	-	-	1	-	**1**	
SG-UTU	Ref. journal art.	4	3	4	5	**16**	1-4, 6,7,911,14-16, 18-23, 25
MMG-ÅA	Ref. journal art.	-	-	1	-	**1**	13
OCG-OU	Ref. journal art.	-	1	-	2	**3**	9, 12, 24
	Master degrees	2	-	-	-	**2**	

5 Other Activities

Joint meetings of all the groups were held once a year; pairwise interactions, especially among the groups in Turku, occurred more frequently than that. There was regular electronic mail contact.

6 Publications

6.1 Refereed Journal Articles

[1] Jaakkola, P., Vihinen, T., Maatta, A., and Jalkanen, M., Activation of an enhancer on the syndecan-1 gene is restricted to fibroblast growth factor family members in mesenchymal cells, *Mol Cell Biol, 17*, 3210-3219 (1997).

[2] Kaukonen, J., Alanen-Kurki, L., Jalkanen, M., and Palotie, A., The mapping and visual ordering of the human syndecan-1 and N-myc genes near the telomeric region of chromosome 2p, *Hum Genet, 99*, 295-297 (1997).

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THEORY AND SIMULATION OF MATERIALS SOLIDIFICATION

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Abstract

The basic goal of the project was to develop a new theory of dendritic solidification and to apply and develop models to describe and simulate practical casting processes of multicomponent metal alloys, concrete, polymers, ice etc.

The prevailing solidification theory was expanded to multicomponent steels by using a thermodynamic solution model and equations of thermodynamic equilibrium as well as the general theories of interdendritic and constrained dendritic solidification (HUT). Thermodynamic descriptions for a number of systems were assessed as well. Based on a thermodynamic, kinetic and heat transferal consideration and combining with the solidification theories new solidification models were developed, as specified for different steels or other alloys and for different casting methods.

When developing a dendritic growth theory, a thorough analysis was performed on the basic role of the solid/liquid surface energy generally described by the Gibbs-Thomson equation (VTT). It was concluded that the Gibbs-Thomson equation can be used for the purpose, while e.g. the surface component theory and the Equation of State approach provide results that deviate up to two orders of magnitude from the G-T derivations. Theoretical work was done to directly solve the Ivantsov's paradox by introducing an additional mechanism that controls solidification within the capillary nano-layer at the interface. The results suggest that it may be possible to explain the dendrite velocity and tip scale selection by considering the diffusion of surface energy in the phase change. An important application is in more accurate prediction of the icing rate of various structures, such as ships, aircraft and communication towers.

A two-scale model for liquid-solid phase transition with equiaxed dendritic microstructure in binary material in the case of slow solute diffusion was presented (JU). The model consists of a macroscopic energy transport equation and, for each point of the macroscopic domain, of a local cell problem describing the evolution of the microstructure and the microsegregations. It is formally derived by homogenisation of a sharp interface model including the Gibbs-Thomson law and kinetic undercooling. Based on the two-scale model, a numerical two-scale

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method for the simulation of phase transitions with dendritic microstructure was developed, and numerical examples were performed.

1 Partners and Funding

1.1 Laboratory of Metallurgy, Helsinki University of Technology (HUT)

The research at the laboratory of Metallurgy (HUT) was done by Dr. Jyrki Miettinen, Senior Research Scientist (responsible scientist), M.Sc. Heli Kytönen and M.Sc. Mia Pohjola. Dr. Seppo Louhenkilpi from HUT and Martti Vilpas from VTT, Manufactoring Technology, participated in the research as experts of continuous casting and welding technology, respectively. The research was supervised as well as the whole project was led by prof. Lauri Holappa, D. Sc. (Tech.).

In addition, Dr. Andy Howe (British Steel, Swinden Laboratories) and Dr. Bengt Hallstedt (ETH, Zürich) participated in the research.

1.2 VTT Building Technology, Technical Research Centre of Finland (VTT)

The research at VTT was done by Dr. Lasse Makkonen, Senior Research Scientist (responsible scientist), Dr. Tuomo Kärnä, Head Research Scientist, Mrs. Heli Viirola, project research scientist, and Mr. Kari Kolari, research scientist.

In addition, Dr. Ryan Blackmore (The King’s University College, Edmonton, Canada) and Prof. K. Szilder (Kitami Institute of Technology, Japan) participated in the work.

1.3 University of Jyväskylä, Department of Mathematical Information Technology (JU)

The research at the University of Jyväskylä was done by Prof. Pekka Neittaanmäki, (responsible scientist), Tuomo Räisänen (research assistant) and Dr. Sergey Korotov.

In addition, Prof. Michal Krížek (Acad. Sciences, Prague, Czech Republic), Prof. Ronald Hoppe (Univ. Augsburg, Germany), Dr. Irina Erunova (Northwest Polytech. St.Petersburg, Russia), Dr. Ljudmila Rivkind (Univ. Heidelberg, Germany), Prof. Peter Knabner (Univ. Erlangen, Germany) and Dr. Christof Eck (Univer. Erlangen, Germany) participated in the work.

1.4 Funding

Table 1. Funding of the project in 1000 FIM in 1997-1999 (2000), Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
HUT	HUT	25	25	30		**80**
	Academy	270	280	290		**840**
	Tekes	94				**94**
VTT	VTT	75	240	200	128	**643**
	Academy	84	116	107		**307**
	Tekes/Matra	22	223	105	217	**567**
JU	Math. depart.	20	20	20		**60**
	Academy	188	232	205		**625**
	COMAS	45				**45**
	INTAS	20				**20**
	Univ. Erlangen			60		**60**
	Academy/ Matra					**1772**
	Tekes/Matra					**567**
	Tekes/Other					**94**
	Institutes					**783**
	Others					**125**
Total		**843**	**1136**	**1017**	**345**	**3341**

2 Research Work

2.1 Objectives and Work Plan

The basic goal of the project was to develop a new theory of dendritic solidification and to apply and develop models to describe and simulate practical casting processes e.g. multicomponent metal alloys, concrete, polymers, ice etc.

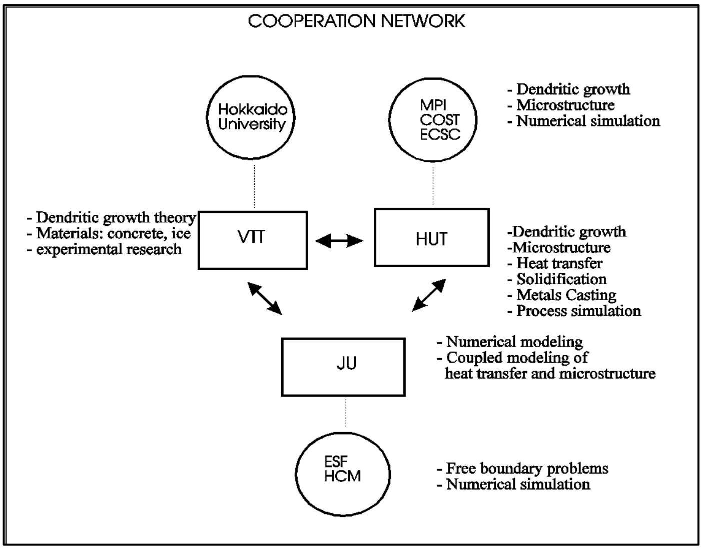
The objective of the project in **VTT** was to develop a general theory of dendritic solidification and to study the role of dendritic growth in hydration of concrete and on this basis, develop new, high strength concrete materials with minimum shrinking and cracking problems. The theory would provide a basic tool for simulating the microscopic solidification process of concrete and metallic alloys (steels), as well as some other materials, such as polymeric materials, ice crystals and biological cells.

It was also aimed to extend the dendritic theory developed in **VTT** to multicomponent metallic alloys, such as steels, in **HUT**. In addition, special semiempirical formulas were aimed to be developed to predict the grain size in as-cast structures of steels. These theories of microstructure should then be incorporated into a special solidification analysis package (IDS) developed earlier in **HUT**, and this improved model package should be coupled to an earlier developed heat transfer model of **HUT** and **JU**, in cooperation between **HUT** and **JU**. This new, coupled model of microstructure and heat-transfer should then be applied to real casting processes (e.g. continuous casting) of metallic alloys, and especially of steels. These simulations reveal the effect of process parameters on the microstructure, thus, allowing a better control of microstructure and its properties during the proper casting process.

Finally, the aim was to educate new researchers to maintain the knowledge of the methods to be developed for future applications. Education of researchers took place in each of the institutions, **VTT**, **HUT** and **JU**.

2.2 Progress Report: Common Themes

The essential features of the collaboration between the three main partners and the few external partners can be seen in the previous chapter and the following schematic picture. The results shown in the next chapter are addressed to the main responsible partner of each task but are, in most cases, based on quite solid and lively co-operation.



2.3 Progress Report: Laboratory of Metallurgy (HUT)

During solidification of a metallic alloy, a high cooling rate, typically, results in a fine dendritic structure with good mechanical properties although it also leads to higher solute and impurity microsegregations between the dendrite arms, thus reducing the hot ductility of the structure, Moreover, fast solidification causes strong solute accumulation ahead of the advancing dendrite tips decreasing the temperature for the start of local solidification and affecting the primary structure (solid phase) to be formed. Particularly, this phenomenon is essential in welding processes. In addition, the dendritic structure, together with alloying and cooling, affects the grain formation after solidification. This grain structure has a special influence upon the following solid state phase transformations (e.g., austenite decomposition in steel) affecting the shrinking behaviour (and thus, the cracking sensitivity) of the strand, as well as the mechanical properties of the final product. Hence, in order to control the solidification event and to get a good product quality, one should know how different casting parameters, such as cooling rate, growth rate and temperature gradient, affect the formation of microstructure. This implies the modeling of macroscopic heat transfer in a real casting process affected by the proper process parameters.

The prevailing theory of solidification was developed to multicomponent steels. The solidfication was considered from a thermodynamic, kinetic and heat-transferral point of view, and by combining the theories, a new theory composite was created. As a result, five solidification models were obtained for educational and research purposes. The study was divided into three fields of equal progress in each during the project:

1. <u>Expansion of solidification theory</u>. Using a thermodynamic solution model and equations of thermodynamic equilibrium, the general theories of interdendritic and constrained dendritic solidification were expanded to multicomponent steels. The deviation in the thermodynamic equilibrium during rapid growth, caused by solute trapping, capillarity and interface friction, is included in the calculations.

2. <u>Creation of thermodynamic descriptions.</u> For the effective use of a thermodynamic solution model, thermodynamic descriptions of certain systems had to be reoptimized. The superiority of the new descriptions to earlier ones were shown in seven international articles Calculated thermodynamic properties, phase equilibria and solute partitions agreed well with measured data. Due to the laborious nature, the thermodynamic descriptions as such are often subjects of projects (e.g., in European COST actions). In this study, however, they were formed as a byproduct.

3. <u>Development of solidification models</u>. Five solidification models, IDS, SAC, SFC, CDG and MDM, were developed and each model was verified with experimental data. A description and a user-manual is available for each model in the form of an international article or a laboratory report. The tasks of the models are the following:

- IDS (interdendritic solidification of steels, further development). The model is used to study the effect of composition and cooling on the microstructure and to calculate thermophysical material properties to SAC and SFC models. New features in the model are the simulation of eutectic ferrite and proeutectoid cementite.

- SAC (heat transfer, solidification and decomposition of austenite in continuous casting of low-alloyed steels). The model is used to study the effect of cooling conditions of a true cc-process on the strand microstructure and to optimize a safe combination of cooling and composition, to confirm a good quality for the final product.

- SFC (heat transfer, solidification and ferrite controll in continuous casting stainless steels). The model is used to study the effect of cooling conditions of a true cc-process on the ferrite content in the strand and to optimize a combination of cooling and composition resulting in an optimal ferrite profile in the strand.

- CDG (constrained dendritic growth in steels). The model is used to study the effect of composition and growth conditions on the microstructure and the properties of the solidification front. The thermodynamic-kinetic approach of the model was commended by the reviewing committee of the ”Metallurgical and Materials Transactions” journal. Particularly, the model is well applicable to study the rapid solidification processes (welding, laser melting).

- MDM (interdendritic solidification of copper and brasses). The idea of the model is analoguous to the IDS model. The model was applied in the study of modelling of up-casting process, which was classified as an outstanding ”pioneer study” by the reviewing committee of the ”Metallurgical and Materials Transactions” journal.

In addition, the models have been used in connection to earlier developed cc-models, TEMPSIMU and CASIM. Due to the strong emphasis put on the modelling work in the study, its possibilities for further applications are excellent. The work, indeed, will continue after this project.

2.4 Progress Report: Technical Research Centre of Finland (VTT)

In the beginning of the project, previous Academy-funded theoretical and experimental work on understanding the peculiar nature of the surface of ice was continued. It was found out that the contact angle of water on ice is well above 0 degrees, which means that the conventional explanation of the liquid-like-layer on ice below its melting point is fundamentally incorrect. Another mechanism of surface premelting of ice, namely pressure melting due to surface capillary pressure, was then proposed and showed to quantitatively explain the premelting range. The theoretical concept was developed further, showing that the proposed mechanism, whereby the equilibrium melting temperature of the surface differs from the bulk melting temperature, also explains regelation of ice. Moreover, this theory explains why water reaches a density maximum above its freezing temperature. These results developed in the project /10/ have, inspite of their unorthodox nature, already been accepted by the scientific community as shown by the way they are referred to in a recent text-book “Ice Physics” (Petrenko, F.V. & Whitworth, R.W., Oxford Univ. Press, 373 p.).

Experimental studies and a literature review /23/ on dendritic growth in hydration of concrete were another early part of the project. The morphological features were found to consist mostly of needles, and no evidence of truly dendritic growth forms were found. Therefore, the coordinating group of the project decided already in 1997 to shift the emphasis out of this problem to other topics of the project.

When developing a dendritic growth theory, which must be based on the solid/liquid surface energy, a fundamental discrepancy was found in the surface energy results from different kind of experiments. It was considered that such a fundamental problem should first be solved, in particular as it transpired that the methods based on the Gibbs-Thomson equation, generally used in dendrite studies, might be incorrect. A thorough analysis of this aspect /22, 11/ resulted in the conclusion that the Gibbs-Thomson equation can be used for the purpose. While this may eventually have no implications on dendrite studies, other than providing more confidence in the methods used, it dramatically affects surface science in those fields where e.g. the Fowkes equation, Oss-Chaudry-Good equation or the Equation of State have been used for determining surface energies of various materials. The study in this project reveals that both the surface component theory and the Equation of State approach provide results that are incorrect by up to two orders of magnitude. An indication of the significance of this finding in surface science is that the principal researcher was requested to present an invited paper in the 2nd International Conference on Contact angle, Wettability and Adhesion, June 2000, NY, USA.

It has been suggested in recent scientific literature that, in directional solidification, the dendrite tip scale would be determined by the dendrite primary spacing. This would solve the so called Ivantsov’s paradox, i.e. that only the product VR of the growth velocity V and tip scale R is given by the thermal diffusion theory, but not V and R separately (however, in experiments it is found that certain R and V are always selected at any supercooling).

The analysis of the dendrite primary spacing in this project /12/ not only provides a new better predictor equation for the spacing and explains the hysteresis of it, but also shows the above mentioned suggestion of the tip scale selection to be unfounded. It was shown in this project that the equation for the spacing can be derived for any arbitrarily short dendrite tip; this result excludes the recent proposal that R would be determined by the shape of tale region of the dendrites and thus by the spacing.

Theoretical work was done to directly solve the Ivantsov's paradox by introducing an additional mechanism that controls solidification within the capillary nano-layer at the interface. The results suggest that it may be possible to explain the dendrite velocity and tip scale selection by the considering the diffusion of surface energy in phase change. Comparisons with the recent microgravity data on dendritic growth on the NASA's Space Shuttle missions seem promising.

Attention has been paid in the project to applications of the results. In the field of metallurgy these will be considered at HUT. As far as the results of dendritic growth in ice are concerned, an important application is in more accurate prediction of the icing rate of various structures, such as ships, aircraft and communication towers. Two reviews on those subjects /13, 14/ have been prepared upon invitation by the Royal Society. These reviews include the aspect of explaining ice sponginess (liquid fraction) by the dendrite growth theory.

2.5 Progress Report: University of Jyväskylä (JU)

In liquid-solid phase transitions as e.g. the casting of metals often a specific dendritic microstructure of the phase interface is observed. The microstructure has a profound influence on the properties and the quality of the material. It affects in particular the grain structure and the microsegregation (small scale variations of the composition of the material). The microstructure is the consequence of an instability of a "flat" liquid-solid interface with respect to small perturbations. Its scale must be limited by surface energy terms. The phenomenologically simplest models capable to describe the evolution of microstructure on the microscopic scale are sharp interface models with surface tension given by the Gibbs-Thomson law and possibly kinetic undercooling. The numerical simulation of single crystal growth is a well-studied task, numerical techniques range from interface-tracking methods over level-set methods to phase field methods. However, these methods need a very detailed resolution of every crystal in order to give reliable results, therefore they are not directly applicable to the simulation of a whole macroscopic structure as e.g. a cast. In the past decade there has been considerable effort in developing purely macroscopic models for the microstructure evolution in castings. However, these models usually need evolution laws for certain parameters of the microstructure which can be derived only in the case of very simple model problems with a limited range of validity; and the results of purely macroscopic models are still not satisfactory.

As our contribution, a new two-scale model for the evolution of equiaxed microstructure in binary material with "fast" heat and "slow" solute diffusion is presented. The model is based on a decomposition of the process into two scales, the macroscopic scale having the size of the whole domain and the microscopic scale of single crystals. This is done by coupling a macroscopic homogenized energy transport equation with microscopic cell problems describing the evolution of the single crystals and the microsegregation. The model is derived by homogenization via formal asymptotic expansion of a sharp interface model for binary material involving surface energy and kinetic undercooling.

3 International Aspects

The HUT subproject had a close connection with a European project “Improvement of internal quality by controlling the micro-structure of microalloyed cast steels” (ECSC Research project P 3508, 1996-1998) with Max Planck Institute in Düsseldorf, SAG Dillinger Hütte in Dillingen and Imatra Steel, Finland as partners. Fruitful collaboration was also performed with Dr. B. Hallstedt, ETH Zürich and Dr. A. Howe, BSC Swinden Laboratories, Rotherham U.K. in thermodynamic assessment and estimation of liquidus temperatures, respectively /2, 8/.

The principal researcher of the VTT subproject (L. Makkonen) spent two months as a Visiting Professor with Graduate School of Engineering, Hokkaido University, Japan. Prof. K. Szilder from Kitami Institute of Technology, Japan stayed at VTT for one month to work in the project. Co-operation with Dr. Ryan Blackmore at the King’s University College, Edmonton, Canada has been by e-mail. Dr. R. Gagnon from National Research Council of Canada payed a one week visit at VTT. Project results were presented in the Annual Meeting of the Adhesion Society in Panama Bay, U.S.A. and in the international journals as listed in the publication list of the project.

JU had ectensive of international co-operation a.o. with Prof. D. Tiba at Academy Science Bucharest, Romania, Dr. L. Rivkind at University Heidelberg, Germany and University of Erlangen (Dr. Korotov’s stay).

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
HUT	Ref. journal art.	-	3	4	2	**9**	
	Ref. conf. Papers	1	1	1		**3**	
	Monographs				1	**1**	
	Licentiate degrees				(1)	**1**	
VTT	Ref. journal art.	1	-	-	4	**5**	
	Ref. conf. papers	-	1	-	-	**1**	
	Monographs	-	-	-	1	**1**	
JU	Ref. journal art.				4	**4**	
	Conf. talks				3	**3**	

( ) in the year 2001

5 Other Activities

At VTT: An article for the general publicity; Makkonen, L., 1998: Jään olemus kirkastui (The essence of ice cleared up). **Tiede 2000** (Science 2000), 1/98: 46-48 (in Finnish), and an interview of L. Makkonen in the TV science program “Prisma” (Finnish Broadcasting Co., Channel 1) in March 1998

6 Publications

6.1 Refereed Journal Articles

[1] J. Miettinen, Reassessed thermodynamic solution phase data for Fe-Si-C system, CALPHAD, 22 (1998), 231-256.

[2] J. Miettinen and B. Hallstedt, Thermodynamic assessment of the Fe-FeS-MnS-Mn system, CALPHAD, 22 (1998), 257-273.

[3] J. Miettinen, Approximate thermodynamic solution phase data for steels, CALPHAD, 22 (1998), .275-300.

[4] K. Härkki and J. Miettinen, Mathematical modeling of copper and brass upcasting, Metall. Mater. Trans., 30B (1999), 75-98.

[5] J. Miettinen, Thermodynamic description of Cr-P and Fe-Cr-P systems at low phosphorus contents, CALPHAD, 23 (1999), 141-54.

[6] J. Miettinen, Thermodynamic assessment of Fe-Cr-Ni system with emphasis on the iron-rich corner, CALPHAD, 23 (1999), 231-248.

[7] J. Miettinen, Thermodynamic description of solution phases in systems Fe-Cr-Si and Fe-Ni-Si with low silicon contents and with application to stainless steels, CALPHAD, 23 (1999), 249-262.

[8] J. Miettinen and A. Howe, Estimation of liquidus temperatures for steels using a thermodynamic approach, Ironmaking and Steelmaking, 27(2000), 212-27.

[9] J. Miettinen, Thermodynamic-kinetic simulation of constrained dendrite growth in steels", Metall. Mater. Trans.B, 31B (2000), 365-79.

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[12] L. Makkonen, Spacing in solidification of dendritic arrays. Journal of Crystal Growth, 208 (2000) 772-778

[13] L. Makkonen, Models for the growth of rime, glaze, icicles and wet snow on structures. Philosophical Transactions of the Royal Society, A 358 (2000) 2913-2939

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[15] Ch. Eck, D. Knabner and A. Korotov, Two-Scale Method for the Computation of Solid-Liquid Phase Transition with Dendritic Microstructure, to appear in Journal of Computational Physics.

[16] Faragó, S. Korotov and P. Neittaanmäki, Galerkin Approximations for the Linear Parabolic Equation with the Third Boundary Conditon, to appear in Application of Mathematics.

[17] S. Korotov, M. Krížek and P. Neittaanmäki, Weakened Acute Type Condition for Tetrahedral Triangulations and the Discrete Maximum Principle, Mathematics Computation, 70 (2001), pp. 107-119.

[18] S. Korotov and M. Krížek, Acute Type Refinements of Tetrahedral Partitions of Polyhedral Domains, SIAM Journal at Numerical Analysis, 39 (2001), pp. 724-733.

6.2 Refereed Conference Papers

[19] K. Härkki, J. Miettinen and L. Holappa, Mathematical modelling of heat transfer and solidification in brass upcasting. Proceedings of the Conference on Numerical Methods for Thermal Problems, Swansea, UK, 496-507, 1997.

[20] S. Louhenkilpi, J. Laine, J. Miettinen and T. Hätönen: "CASIM software for on-line calculation of liquid pool end position in continuous casting", In Proceedings of the 3rd European Conference of Continuous Casting, Madrid, 1041-1044, 1998.

[21] J. Miettinen, H. Kytönen, S. Louhenkilpi and J. Laine: "IDS, TEMPSIMU, CASIM, Three Windows Applications for Continuous Casting of Steel", conference pesentation in the 12th IAS Steelmaking Seminar and 2nd ISS Argentina Section Meeting, Buenos Aires, 1999.

[22] L. Makkonen, Controversy on methods to estimate surface energies - Is the Gibbs-Thomson equation applicable? Proceedings, 22nd Meeting of the Adhesion Society (USA), Panama City, FL, USA: 131-133, 1999.

6.3 Monographs

[23] H. Viirola.&P. Raivio, Hydration of Portland cement. VTT Research Notes, 2041, 61 p. (in Finnish with English summary), 2000.

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CONTENTS

DEVELOPMENT OF NON-PEPTIDE AGONISTS OF SOMATOSTATIN

Pekka Häyry[1]

Abstract

The vasculoprotective effects of certain hormones, particularly of somatostatin and estrogen, are well established. Both hormones have, however, pleiotropic actions on multiple tissues. We generated a paradigm that the multiple effects in multiple tissues, may be regulated by multiple subsets of hormone receptors and that each tissue in health and disease, expresses only a limited receptor repertoire. Five distinct somatostatin receptor (SSTR) genes have been descirbed that encode receptor proteins of the 7-transmembrane domain class within the superfamily of G-protein coupled receptors. Both structural and functional information indicate that the receptors can be divided into two groups: one group includes SSTR2, (SSTR3) and SSTR5 and the other group SSTR1 and SSTR4. These two groups can be differentiated both by their selectivity in binding to synthetic SST analogs, as well as on the basis of their amino-acid homologies. We first investigated the pattern of SSTR subtype expression in rat thoracic aorta in resting state and at 15 min, 3, 7, 14 and 28 days after vascular injury by RT-PCR, and localized the receptor protein in the tissue by immunohistochemistry using our own subtype-specific rabbit antisera. After injury, the SSTR1 mRNA was increased on days 3 and 7, coinciding with the proliferative response of SMC, and declined to basal level by day 14. SSTR4 mRNA displayed a delayed and more gradual increase beginning on day 3-7 and remaining elevated thereafter. SSTR2 and 5 mRNAs were constitutively expressed at very low level, and showed no or only minimal change post injury. By immunohistochemistry, SSTR1 and 4 proteins were expressed during the proliferative burst and SSTR4 when SMC migration into the intima continued. Thereafter, we syntetized a SSTR1.4 reactive peptide, (DesAA1,2,5(D-W8,IAmp9)Somatostatine-14. The peptide dose-dependently inhibited intimal hyperplasia after rat carotid denudation injury. The SSTR1,4 selective peptide was more efficacous than somatostatin-14, having equal affinity to all 5 subtypes. Although relavively high dosages were used for complete inhibition, no toxic effects were observed. Thus, *targeting to subtype 1 and 4 (possibly to subtype 1 alone) completely abolishes intimal hyperplasia after denudation injury*. Although the results need to be confirmed in primates, they suggests that agonist ligands targeting to subtype 1 and 4 should be synthetized when developing somatostatin-based vasculoprotective drug therapies in man.

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1 Partners and Funding

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1.1 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1997	1998	**Total**
UH	Academy	295	295	**590**
McGill*				
Juvantia*				
Total		**295**	**295**	**590**

* These partners funded their own part of the work, McGill the RTPCR assays and development of rabbit antisera to the SSTR subsets and Juvantia the synthesis of peptides.

2 Research Work

2.1 Objectives

Characteristic to the pathophysiology of coronary reocclusion and chronic allograft rejection, is endothelial cell (EC) activation, proliferation of vascular smooth muscle cells (SMC), their migration into the intima and thickening and remodeling of the vessel wall. Common molecular pathways in dysplasias of different etiologies, are synthesis of growth factors and cytokines by activated EC and inflammatory cells, change of the SMC phenotype from contractile to secretory, expression of growth factors and growth factor receptors by activated SMC, and changes in SMC interactions with the extracellular matrix (upregulation of integrin b3 etc.). As in all these dysplasias, the problem ultimately focuses on the regulation of SMC replication and migration, also therapies should be aimed at these events.

Our first objective is to understand what SMC-specific genes are induced in response to proliferative signal(s), how they are regulated and which of these genes are rate limiting. Based on these results, our second objective is to design new drugs to inhibit pathological SMC migration and proliferation.

2.2 Results

Because only 20% of the requested funding was provided, we concentrated on the somatostatins only.

Aim #1: Only a limited reperetoire of SSTRs are expressed in the vascular wall after injury:

Treatment of restenosis after angioplasty with octapeptide somatostatin (SST) analogs has met with variable success. These analogs bind with high affinity to only two SST receptor (SSTR) subtypes (2 and 5), display moderate affinity for SSTR3, and low affinity for SSTR1 and 4. To optimize the vasculoprotective effect of SST, we have investigated the pattern of expression of all five SSTRs in rat thoracic aorta in the resting state and at 15 min, 3, 7, and 14 days after balloon endothelial denudation. SSTR1-5 were analyzed as mRNA by semiquantitative reverse transcriptase-polymerase chain reaction and as protein by immunocytochemistry. All five SSTRs were expressed in rat aorta both as mRNA and protein and displayed a time-dependent, subtype-selective response to endothelial denudation. mRNA for SSTR1 and 2 increased acutely (SSTR1 > SSTR2) on days 3 and 7, coincident with smooth muscle cell (SMC) proliferation, and declined to basal levels by day 14. SSTR3 and 4 displayed a different pattern with a delayed, more gradual increase in mRNA beginning at days 3–7 and continued to increase thereafter. SSTR5 mRNA was constitutively expressed at a low level and showed no change during the 2 wk postinjury period. By immunohistochemistry, SSTR1-5 antigens were localized predominantly in SMC that were present in the media or had migrated into the intima; antigen expression correlated with receptor mRNA expression. Notably, only SSTR1,3,4 were expressed in the intima: SSTR1 and 4 during the proliferative burst and SSTR3 and 4 after proliferation, when SMC migration into the intima continues. These results demonstrate dynamic changes in SSTR1-5 expression after vascular trauma localized to areas of vascular SMC migration and replication. In view of their early and prominent induction, SSTR1 may be the optimal subtype to target for inhibition of myointimal proliferation, and SSTR3 and 4 for migration and remodeling.

—Khare, S., Kumar, U., Sasi, R., Puebla, L., Calderon, L., Lemström, K., Häyry, P., Patel, Y. C. Differential regulation of somatostatin receptor types 1-5 in rat aorta after angioplasty. FASEB J. 13, 387–394 (1999)

Aim #2: Targeting to SSTR subtype 1,4 entirely inhibitits intimal hyperplasia after endothelial denudation injury:

Somatostatin analogs, octreoptide and lanreotide, selective to receptor subtypes 2,and 5, failed clinical efficacy in prevention of restenosis after percutaneous transluminal angioplasty. One possiblility for the lack of effect, was that a wrong subset of receptors was targeted. As recently shown, subtype 1 and 4, rather than 2 and 5, are expressed in the vascular wall of both rat and man. The expresion subtype 1 increases after endothelial denudation injury in rat, but expression of 2 and 5 remains low, and subtype 1 is nearly exclusive subtype in atherosclerotic human vessels. Here we demonstrate that a peptide, CH-275 (DesAA1,2,5(D-W8,IAmp9)Somatostatine-14, having high affinity to subtype 1 and 4, but none to 2 and 5, dose-dependently inhibits intimal hyperplasia after rat carotid denudation injury. CH-275 was more efficacous than somatostatin-14, having equal affinity to all 5 subtypes. Although relavively high dosages were used for complete inhibition, no toxic effects were observed. Thus targeting to subtype 1 and 4 (possibly to subtype 1 alone) completely abolishes intimal hyperplasia after denudation injury. Although the results need to be confirmed in primates, they suggests that agonist ligands targeting to subtype 1 and 4 should be synthetized when developing somatostatin-based vasculoprotective drug therapies in man.

-Aavik, E., Aavik, S. Patel Y and Häyry P. Elimination of vascular fibrointimal hyperplasia by somatostatin reseptor 1,4 selective agonist in rat FASEB J. Submitted.

3 International Aspects

Publications of the research work has been done in top-level international journals.

The project leader has attended as speaker in the following international conferences.

1997
Keystone Atherosclerosis Symposium. Keystone, Colorado, USA. Speaker.

Fourth Banff Conference on Allograft Pathology. Banff, Alberta, Canada. Invited Speaker.

Second International Course on Organ Transplantation. University of Rome ’’La Sapienza’’, Rome, Italy. Invited speaker.

Symposium on Chronc Graft Dysfunction, University of London, London, UK . Invited Speaker.

Hesperis, European College of Transplantation Helsinki, Finland. Chairman, Invited Speaker.

XIVth International Congress of Nephrology Sydney, Australia. Speaker.

Current Problems in Heart Failure and Cardiac Transplantation. Assessment of Acute Rejection & Allograft Coronary Disease. Thun, Switzerland. Invited Speaker.

1. Argentinan Meeting on Organ Procurement Buenos Aires, Argentina. Invited Speaker.

Progress in Transplantation Medicine: Research, Laboratory Monitoring and Clinical Perspectives Nice, France. Invited Speaker.

IVth Congress of the Turkish Transplantation Society, Ankara, Turkey. Invited Speaker.

1998
American Association of Transplant Physicians, San Juan PR, Invited Speaker.

New Trands in Immunosuppressions, Geneve, Switzerland, Invited Speaker.

New Dimensions in Transplantation, Florence, Italy. Invited Speaker.

Transplant Infectious Disease, Orlando, Florida. Invited Speaker.

European College of Transplantation, Birmingham, UK. Invited Speaker.

Meeting of the Spanish Society of Transplantation, Madrid, Invited Speaker.

Congress of the Argentinan Society of Transplantation, Buenos Aires, Invited Speaker.

International Meeting of the Transplantation Society, Montreal, Canada, Chairman, Invited Speaker.

Meeting of the Mexican Society of Transplantation, Aguascalientes, Mexico, Invited Speaker.

3rd International Meeting on Transplantation Education, Praque, Chech Republic, Invited Speaker.

Meeting of the German Transplantation Society , Munich, Germany, Invited Speaker.
Imperial College of Science, Technology and Medicine Meeting on Transplantation, London, UK, Invited Speaker.

Participation in EU projects

- BMH4-CT95-1160: Adenovirus mediated gene transfer and biological active peptides: new potential approaches to the treatment of intimal hyperplasia fter vascular injury.
- SMT4-CT98-7514: Convergence of Euroopean renal transplant pathology assessment procedures (CERPAP)

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Patents

Häyry, P., Patel, Y. A method for the prevention of a patient's fibroproliferative vasculopathy. United States, US 6,124,256, filed 27.3.1998. The patent covers use of somatostatin receptor subype 1 or 4 selective agonists for treatment of vascular wall thickening after surgical or atherosclerotic trauma, which are present in vascular restenosis and chronic allograft rejection. International PCT application is now on the national level.

Canada, Japan, USA WO 99/49884 23.3.99 PCT/FI99/00222. Filed on the national stage according to phase I or II.

Canada 23.3.99 2,323,748. Filed on the national stage of PCT/FI99/00222, no office action yet

Japan 26.9.00 2000-540847. Filed on the national stage, based on US 09/049,020 (27.3.98), national stage initiated, no office action yet

United States 6,124,256 27.3.98 26.9.00 US 09/049,020. Priority patent.

EPO EP 1064017 26.9.00 3.1.01 99910396.3. Filed on the national stage of PCT/FI99/00222 according to phase I or II.

DESIGN OF NOVEL POLYMERIC MATERIALS OF NEXT GENERATION

Barbro Löfgren[1], Markku Leskelä[2], Tuula Pakkanen[3], Lauri Niinistö[4] and Jarl B. Rosenholm[5]

Abstract

Through the single site catalyst technology novel functionalized polyolefins have been produced both by using new catalytic systems and by commercial metallocene catalysts. The fact that metallocenes are quite thoroughly studied has been a motive for studies on alternative catalyst systems. Another reason has been the aim to develop catalyst systems, which are more suitable for polymerization of polar comonomers.

Development of a series of aminopyridinato complexes of tantalum (V) has been done in cooperation with the research groups of University of Helsinki and Helsinki University of Technology, Polymer Technology. Several tantalum (V) aminopyridinato complexes were synthesized and two of them, bis(2-benzylaminopyridinato)trichlorotantalum(V) and trichlorobis[2,6-di(phenylamino)pyridinato-N,N`]tantalum(V) were studied in polymerizations at HUT. These complexes are considerably active in ethene polymerization when activated with methylaluminoxane, and are producing a polymer with moderate molar mass and narrow molar mass distribution comparable to the values obtained with metallocenes.

In the collaboration between the research groups at University of Joensuu and Helsinki University of Technology, Polymer Technology, the catalyst dibromo-N,N`-1,2-acenaphthylenediylidenebis[2,6-bis(1-methylethyl)benzeneamine]Ni(II) was synthesized and used in ethene polymerization to obtain a specific microstructure. The Ni(II) diimine/methylaluminoxane(MAO) catalyst system produces in situ highly branched polyethene and the polymer behaves like an elastomer, even though no comonomer is added. The structure and properties of the produced polyethene are controlled through the polymerization conditions. An increase in the polymerization temperature gives a more branched structure, whereas an increase in the monomer concentration lowers the degree of branching. The polymers are further characterized by an extremely high molar mass but fairly narrow molar mass distribution. Another feature of the Ni (II) diimine/MAO catalyst is its high

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activity. In the solid state, the Ni diimine bromide complex is dimeric, but in solution in the presence of MAO, the complex dissociates to a highly active, monomeric four-coordinated Ni (II) complex of the Brookhart type.

The mechanism of nickel-catalysed ethene polymerization was also the object in the cooperation of the research groups of University of Helsinki and Helsinki University of Technology, Polymer Technology. Nickel (II) complexes bearing the unsymmetric didentate 2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine ligand in which one side contains the pyridine ring and the other side consists of a 2,6-dialkylphenylimino group was synthesized in order to study steric and electronic effects on the oligomerization-polymerization interface. These nickel- based catalyst precursors have also a dimeric structure, but when the catalytically active complex is generated in the reaction of MAO, its dimeric structure is broken once the bridging halides are removed. Hence no significant difference in polymer properties was observed between the dibromo and dichloronickel(II)-based systems. As for the above mentioned Ni(II) diimine complexes, the activity, the degree of branching, unsaturation selectivity, and the molar mass of the produced polyethenes are highly dependent on polymerization conditions.

Studies of interactions between metallocene catalyst and carrier were conducted in cooperation with the research groups of University of Joensuu, Helsinki University of Technology, Laboratory of Inorganic and Analytical Chemistry, and Helsinki University of Technology, Polymer Technology. Heterogeneous metallocene catalysts were prepared by adsorbing racemic ethylenebis(1-indenyl)zirconium dichloride on trimethylaluminum (TMA) vapour modified silica surface using atomic layer chemical vapour deposition (ALCVD) technique. In the reaction of TMA with silica, a saturated surface was formed consisting of different $(\text{–O})_{4-n}\text{Si(CH}_3)_n$ and –AlCH_3 groups. When the metallocene was adsorbed onto the carrier it seemed to react with the surface –AlCH_3 groups and possibly –ZrCH_3 groups were formed. The heterogeneous catalysts produced similar polyethenes and polypropenes as the corresponding homogeneous catalyst, but with lower activity.

In the collaboration between the research groups at Åbo Akademi University and Helsinki University of Technology, Polymer Technology the effect of the structure and surface properties of commercial mesoporous silicate, MCM-41 (Grace), and aluminium modified MCM-41 on metallocene (zirconocene) adsorption and catalyst activity was investigated. The highest amount of zirconocene was adsorbed on Al-modified MCM-41 (Si/Al=32), providing the most reactive sites for attachment of the active component on the support surface. This support gives also the highest activity in ethene polymerization. The high surface area of MCM-41 could not be proved to have a large effect on the ethene polymerization reaction compared to lower surface area material. However, due to the insufficient variation of the physico-chemical parameters during the polymerization experiments, the special features of the MCM-41 support could not be evaluated to the full extent.

Another collaboration between the research groups at Åbo Akademi University and Helsinki University of Technology, Polymer Technology, focused on the investigation of the sterical hindrance of the bulky metallocene catalysts immobilized directly on silica supports. Therefore the silica supports were treated with ?-aminopropyltrimethoxysilane or ?-mercaptopropyl-trimethoxy-silane as spacer molecules displacing the catalyst further away from the surface. All of the supported complexes were catalytically active in ethene polymerization and produced normally polymers with higher molar masses than the corresponding homogeneous catalyst.

Another important research topic of the group headed by Prof. M. Leskelä, University of Helsinki, in this consortium, has been synthesis of new metallocenes of group four metals. The aim of the work has been finding of new active catalysts capable to produce both polyethene and polypropene and copolymers with different alkenes. The metallocene research is also important in terms of understanding the mechanism in catalysis and catalyst structure-polymer property relation. The main emphasis has been in acenaphthyl and different benzyl substituted zirconocene dichlorides. Acenaphthyl zirconocene is very active catalyst for polyethene and many ethene copolymers. One important reason for the synthesis of a series of benzyl-substituted zirconocenes was to study the electronic and steric effects caused by substituents in 1-position of indenyl. The results showed that the intramolecular interaction between one carbon atom of the benzyl substituents and the cationic zirconium ceneter plays an important role in polymerization.

The group headed by Prof. Tuula Pakkanen, University of Joensuu has focused on well-characterized chemically tethered heterogeneous metallocene catalysts prepared by a stepwise synthesis. The partially dehydroxylated silica surface was transformed by an ALCVD method in the first step to a cyclopentadiene-bearing surface using $(EtO)_3SiCH_2CH_2CH_2Cp$. Anchoring of a transition metal complex, for example $MCl_4(THF)_2$ (M=Zr, Hf), $CpMCl_3$ or Cp^*MCl_3 ($Cp^* = C_5Me_5$, M= Ti, Zr, Hf) onto the Cp-ligand surface of SiO_2 produced supported half-metallocene or metallocene complexes. The chemically tethered constrained-geometry catalysts were prepared using the same assembling method. Silica was first modified with an amino silane and the amine-bearing surface was then reacted with $Me_2Si(C_5Me_4H)Cl$, $MeHSi(C_5Me_4H)Cl$, or $Me_2Si(C_5H_5)Cl$, to obtain a bifunctional ligand surface having amino and cyclopentadienyl groups in the same ligand molecule. In the final step, a Group 4 metal amide ($(M(NMe_2)_4$ M = Ti, Zr, Hf) was anchored onto the ligand surface of SiO_2 by amine elimination reaction. The surface structures of the synthesized catalysts were proved with solid state FT-IR, ^{13}C and ^{29}Si CP/MAS NMR. All of the supported metal complexes when activated with MAO polymerized ethene, especially in the case of zirconium and hafnium with a moderate activity. The high-density polyethenes produced had narrow molar mass distributions indicating the single-site nature of the synthesized heterogeneous catalysts.

The project group, headed by Prof. L. Niinistö, Helsinki University of Technology, has studied the modification of silica support by surface-controlled atomic layer deposition (ALD) and developed practical methods for the determination of hydroxyl groups on the silica support. In addition to experimental studies, theoretical aspects related to the factors affecting the activity of heterogeneous metallocene catalysts and the properties of polyethene products were also studied. For the determination of aluminium in aluminium chloride and oxide modified porous silica, analytical method based on X-ray fluorescence spectrometry (XRF) was developed. Modification of silica was focused on the deposition of catalytically active species onto unmodified silica support. The precursor used was commercial zirconocene, Cp_2ZrCl_2. The ALD method seemed to be a feasible way to adsorb zirconocene in a controlled way onto the support. The surface of silica supports was studied in detail in order to understand the modification reactions on silica. For the determination of surface hydroxyl groups on silica two practical methods were developed: the first is based on DRIFT spectrometry, which was calibrated with multivariate techniques, and the second on thermogravimetry (TG). Both methods were found to be simple and fast techniques for the determination of hydroxyl groups in several silica samples with a sufficient accuracy. Multivariate models for the activities of the polymerization catalysts, as well as, for some properties of polyethene products: molar masses, polydispersities and melting points, were developed using chemometrics. The properties were modelled with separate models, and the prediction ability was found to be good for most of the models. The models developed were able to predict the activities of the catalysts and the properties of the polyethene products starting from the polymerization parameters.

As agreed in the project proposal the group headed by Prof. Jarl B. Rosenholm, Åbo Akademi University has focused on three topic areas: the synthesis and chemical modification of the catalyst support, the heterogenization of the catalyst by immobilization and on the characterization of the heterogenized catalyst. A mesomorphous catalyst support was synthesized with a surface area exceeding 1000 m^2/g and it was doped with different amounts of alumina and titania to adjust its surface properties. A siliceous support material commonly used for catalyst immobilization was used as a reference material. An extensive investigation including probe adsorption, NH_3-gas adsorption and thermal (TGA) methods were used to determine both the Lewis and the Brönsted acidic and basic sites on the support surface. Moreover, the pores of the support were thoroughly characterized with sorptometry and the pore structure modelled with the corrugated pore structure model. This is necessary in order to evaluate the influence of the transport of the monomer reactants to the catalytic surface sites and the removal of the polymer from the active sites (catalyst poisoning). The inclusion of aluminium into the silica support surface was investigated with ^{27}Al-NMR and the structure with TEM. The support was also modified with spacer molecules in order to investigate whether the bulky catalyst experiences steric hindrance if immobilized directly to the surface. The catalyst was immobilized on the various both traditional and chemically surface modified support materials. The attachment of the catalyst to the support was confirmed with different techniques, including ^{13}C-CPMAS NMR. Finally the catalyst activity was tested with a few standard polymerization experiments. Unfortunately the physico-chemical conditions were not sufficiently systematically varied in order to fully evaluate the special features of the heterogeneous catalysts. To a great extent this work was performed through an extensive European collaboration.

The group headed by Doc. B. Löfgren, Helsinki University of Technology, Polymer Technology, has continued to study the chemical modification of polyolefins in order to enhance their chemical and physical properties by incorporation of polar comonomers by direct copolymerization. The copolymerization has been expanded from oxygen-functional monomers to nitrogen-functional vinylic comonomers. Addition of polar comonomers causes a decrease in the ethene and propene polymerization rates, which seems to be dependent on both the catalyst geometry and on the reactions of the comonomer with the cocatalyst. The steric conditions influencing the activity in copolymerizations have been studied using molecular modelling. A small addition of a functional comonomer causes a remarkable improvement in the processability of metallocene catalysed polyolefins. The functionalized polyolefins have been used as effective, new compatibilizers in immiscible polymer blends. Theses metallocene catalysed copolymers improved the toughness of the blends significantly and furthermore they surprisingly increased the stiffness and strength, which is not common with compatibilizers in general.

The five research groups cover the progresses of the consortium in detail.

1 Partners and Funding

1.1 Laboratory of Inorganic Chemistry, University of Helsinki (UH)

The research group consisted of subproject leader professor Markku Leskelä, postgraduate students Timo Repo (1997-99), Mika Polamo (1997-99), and Marina Gustafsson (1998-99).

1.2 Materials Chemistry Laboratory, University of Joensuu (UJ)

The research group consisteds of subproject leader professor Tuula Pakkanen, postgraduate students Anne-Marja Uusitalo, Sari Timonen (15.12.1997- 31.8.1999) and Hannele Juvaste (15.8.1998-31.12.1999, stipend from University of Joensuu), Kari Mönkkönen (1.4-31.8.1997) Harri Lasarov (1.1-28.2.1997) as well as student Mauno Miettinen (1.1-31.3.1997).

1.3 Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology (HUT/Inorg.Lab.)

The research group consisted of subproject leader professor Lauri Niinistö, postgraduate students Minna Kröger-Laukkanen (1.1.1997-31.10.1998, 1.9-31.12.1999), Marko Peussa (1.10.1997-31.7.1999) and Satu Ek (née Härkönen) (1.1-31.7.1999), and student Aki Havulinna (22.6-30.12.1999).

1.4 Department of Physical Chemistry, Åbo Akademi University (ÅA)

The research group consisted of subproject leader professor Jarl B. Rosenholm, postgraduate students Hanna Rahiala (1997-1999), Tom Eklund (1997-1998 (7 months)), Janne Puputti (1998 (2 months)-1999), Jan Bäckman (1997 (3 months)) and the summer trainee Liisa Sinervo (1998 (3 months)).

1.5 Polymer Technology, Polymer Science Centre, Helsinki University of Technology (HUT/Pol.Tech.)

The research group consisted of subproject leader docent Barbro Löfgren, postgraduate students Päivi Aaltonen (4months in 1997) Kimmo Hakala (1997-99), Tuulamari Helaja (1.9.99-31.12.99), Santeri Paavola (1.10.98-31.12.99) and Ulla Hippi (nèe Anttila) (part time in 1999).

1.6 Funding

Table 1. Funding of the project in 1000 FIM in 1997-99.

Partner	Funding organization	1997	1998	1999	**Total**
UH	UH	150	150	150	**450**
	Academy	518.1	619.6	622.3	**1760**
UJ	UJ	-	29	78	**107**
	Academy	399	409	412	**1220**
HUT/	HUT	20	40	41	**101**
Lab.Inorg	Academy	398	475	451	**1324**
HUT/	HUT	100	100	150	**350**
Pol.tech.	Academy	274.7	369.2	356.1	**1 000**
ÅA	ÅA	20	25	30	**75**
	Academy	407	411	412	**1 2030**
Total		**2286.8**	**2627.8**	**2702.4**	**7617**

2 Research Work

2.1 Objectives and Work Plan

The goal of this research was to produce novel functionalized polyolefins through metallocene catalyst technology and to get a deep knowledge of the relations between the structure of the catalytic system, the microstructure of the polymer formed and the end properties of the final material.

Realization of the work plan fell into following parts:

* to synthesize new early transition metal complexes
* to synthesize novel metallocenes of group 4 metals
* to design new late transition metal catalysts with lower Lewis acidity, which allows both the polymerization and the addition of polar comonomers
* to heterogenize the homogeneous catalysts

* to prepare new supported catalysts by reacting the catalytic metal molecule directly to the silica surface and to coadsorb the cocatalyst, *e.g.* Methylaluminumoxane (MAO) onto the metal
* to modify silica and alumina catalyst supports with atomic layer epitaxy (ALE) technique
* to modify porous silica particles by coprecipitation or by overlayers of various oxides
* to perform detailed characterization of the new catalytic systems at molecular level utilizing all modern techniques available
* to compare the effect of catalyst supports, on the structure of the final polymer
* to conduct polymerizations with functionalized comonomers
* to study polymerization of dienes
* to characterize the structural features and the rheological properties of the copolymer formed
* to study the effect of polymerization conditions on processing parameters to obtain good processability of the polymers
* to create a broader fundamental research in the field through cooperation between the universities
* to develop small scale testing methods for polymers, which correlate to application tests

According to the art of the work to be done, the research program was divided into five separate subprograms:

I " New polymerization catalysts"(UH)
This program focused on the design of new catalyst precursors, which are based on complexes of both early and late transition metals. Late transition metals are rich in *d*-electrons and have lower Lewis acidity than the traditional metallocenes. One part of the early transition metal complex studies was synthesis of novel dual-site metallocenes and study their steric and electronic effects in polymerization.

II " Development of catalysts for production of new polymeric materials" (UJ)
In this program the key factor was to heterogenize homogeneous metallocene catalysts. New approach for construction of heterogeneous single site catalysts was the introduction of the transition metal and ligand components separately onto the support and their surface reaction to produce the active site.

III " Modified supports" (HUT/Inorg.Lab.)
The aim was to produce new and improved catalyst supports and to bind active catalytic species onto them. The atomic layer epitaxy (ALE) technique was employed to modify alumina or silica catalyst supports.

IV " Preparation and characterization of the catalyst system and the surface properties of the polymer" (ÅA)
The aim was to investigate whether the chemical modification or an enhanced porosity of the silica catalyst support influences the properties of the heterogeneous

catalyst. The catalyst was modified through coprecipitation by transition metal oxides or by adsorbed spacer molecules reducing the steric hindrance of the catalyst immobilized directly on the support surface.

V " Design of tailor made materials to suit specific applications" (HUT/Pol.Tech.)
The focus was on testing the performance of the new catalytically active compounds suitable for copolymerizations with functional groups and on evaluating the polymers produced.

2.2 Progress Report: Common Themes

2.2.1 Aluminum alkyl modified silica carriers in heterogeneous catalysts.

Metallocenes supported on silica were investigated in the collaboration between the research groups at HUT/Inorg.Lab. UJ and HUT/Pol.Tech. Requirements for commercial metallocene catalysts are good morphology, high activity and single-site nature. To achieve these characteristics, the silica carrier must be modified before adsorption of the metallocene complex in order to remove the Si-OH groups, which may lead to decomposition of the catalyst [30].

In this study the modified silica carriers were prepared at HUT/Inorg.Lab.using atomic layer chemical vapour deposition (ALCVD) technique. Onto the silica carrier, pretreated with TMA, *rac*-$Et(Ind)_2ZrCl_2$ was adsorbed by the group at UJ. Relatively little metal complex (Zr=0.35-0.45 wt-%, Al/Zr ca 40) was attached to the TMA/SiO_2 carriers, which is typical for metallocene complexes adsorbed on TMA modified silica. The Cl/Zr mole ratio of 1.8-1.9 suggests that metallocene either retains its structure in the mobilization on the surface or the chlorines are bonded to Lewis acidic cites.

Heterogeneous *rac*-$Et(Ind)_2ZrCl_2/TMA/SiO_2$ catalysts were tested in the polymerization of ethene and propene using methylalumoxane (MAO) cocatalyst at HUT/Pol.Tech. Polyethene and polypropene were produced with narrow molar mass distribution, and with similar molar masses as with the homogeneous *rac*-$Et(Ind)_2ZrCl_2$. The activities were about one-eighth that of the homogeneous one both in ethene and propene polymerizations.

2.2.2 MCM-41 and silica supported metallocene catalysts

Support materials were thoroughly characterized and modelled as collaboration between the ÅA and the HUT/Inorg.Chem.[37]. A special focus was laid on the surface sites. Both the Brönsted (proton exchange) and the Lewis (electron exchange) type of surface groups were evaluated. Moreover the pore structure of the highly porous MCM-41 material was modelled.

The effect of the structure and surface properties of support material on zirconocene chloride adsorption and catalyst activity in ethene polymerization was studied in the cooperation between the research groups at ÅA and HUT/Pol.Tech. [37,40].

The zirconocene dichloride Cp_2ZrCl_2 was immobilized on commercial Grace mesoporous silicate MCM-41 and aluminium modified MCM-41 at ÅA. The highest amount of zirconocene dichloride was adsorbed on Al-modified MCM-41 (Si/Al=32), providing the most reactive sites for attachment of the active component on the support surface. The ^{13}C-CPMAS NMR studies proved that Cp_2ZrCl_2 was bound to the support surface. Also the highest activity in ethene polymerization, performed at HUT/Pol.Tech., was obtained using this support as can be seen from Table 2.

Table 2. Results of ethene polymerizations promoted by silica supported Cp_2ZrCl_2 catalysts.

Catalyst	m cat mg	n Zr µmol	Activity kg PE/mol Zr*h	T_m C°	M_w kg/mol	M_w/M_n
Cp_2ZrCl_2-Grace SiO_2[a]	3.4	0.46	10 000	137.3	450	2.2
Cp_2ZrCl_2-Si-MCM-41	2.4	0.43	6 100	135.5	430	2.3
Cp_2ZrCl_2-Si/Al=32	1.4	0.41	15 800	137.9	450	2.2
Cp_2ZrCl_2 (homog.)	0.1	0.30	29 900	137.5	475	2.5

Polymerization conditions: T_p=50C°, $p(C_2H_4)$=2.5 bar, Al/Zr=2000, and t_p=30 min.
[a] Cp_2ZrCl_2 was immobilized at 70C°.

Due to the restricted variations of the physico-chemical parameters used in the standard polymerization experiments the special features of the chemically modified MCM-41 could not be evaluated to a full extent. Instead, although the surface properties were superior, the effect on the ethene polymerization reaction was much the same as the less porous reference standard support material, Grace silica. The melting temperature, around 135C°, indicate the formation of linear high-density polyethene.

2.2.3 Introduction of new metals in catalyst synthesis

One important part of the common studies in the consortium was introduction of new metals, e.g. Ni, Co and Ta into the field of polymerization catalysts. The catalysts were synthesized in UH and in UJ and the polymerization experiments were carried out in HUT (Pol.Tech.) [12,13,32,52].

2.2.3.1 Nickel (II) and cobolt (II) pyridinylimine complexes

Nickel (II) and cobolt (II) complexes bearing the unsymmetric didentate 2,6-bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine ligand in which one side contains the pyridine ring as found in bipyridine-type alkene oligomerization catalysts and the other side consists of a 2,6-dialkylphenylimino group resembling the bulky structures of the 1,4-diazabutadiene ligands were synthesized at UH.

These novel catalyst precursors were used in ethene polymerizations conducted in HUT (Pol.Tech.). The nickel complexes treated with MAO were active in the polymerization of ethene, while, in turn, the cobalt compound showed only marginal activity which is in accordance from earlier results from diazabutadiene systems. In the nickel catalysed reactions both the activities and product molar masses are highly dependent on the polymerization temperature. Besides yield of polymer and its chain length also degree of branching and unsaturation selectivity are highly dependent on the polymerization conditions.

2.2.3.2 Nickel (II) Diimine complexes

Dibromo-*N,N′*-1,2 acenaphthylenediyllidenebis[2,6-bis(1-methylethyl)benzene-amine]Ni(II) catalyst was synthesized and its solid state structure was characterized by crystallographic methods in UJ. The catalyst consisted of two centro-symmetrically related monomeric moieties, where Ni atoms were bridged by two bromide ligands. The Ni atom was five-coordinated, with a square pyramidal coordination polyhedron. The sixth coordination site of the octahedral geometry was effectively blocked by the isopropyl groups of the 2,6-C_6H_3(*i*-Pr) substituents of the diimine ligand. In solution, in the presence of MAO, the longer bridging Ni-Br bonds broke, and the complex dissociated to a monomeric four-coordinated complex of the Brookhart type catalyst.

The polymerizations carried out in HUT (Pol.Tech.) demonstrated that in particular, different kinds of branches in the main chain could be achieved through variations in the polymerization conditions. Such behaviour is very typical for this kind of catalysts. Dynamic mechanical thermoanalysis showed that polyethene behaved like an elastomer, even though no comonomer was added. Depending on the degree and type of branching, polyethene was either quite amorphous or highly crystalline with a high melting temperature.

2.2.3.3 Tantalum aminopyridinato complexes

Bis(2-benzylaminopyridinato)trichlorotantalum(V) (**1**) and trichlorobis[2,6-di(phenylamino)pyridinato-*N,N′*]tantalum(V) (**2**)were prepared in UH, and their capability as catalysts activated by MAO were studied in HUT (Pol.Tech.). The results obtained from ethene polymerizations with **1**/MAO and **2**/MAO catalyst systems are presented in Table 3. The results show that both Ta (V) complexes are considerably active in ethene polymerization. The activities increase with increasing polymerization temperature. The activity of **2**/MAO at 80°C (23 900 kg PE/mol Ta*h) is close to the activities obtained with metallocene/MAO systems. The molar masses are only moderately high and are decreased when polymerization temperature is raised.

Table 3. Results of ethene polymerizations promoted by catalyst systems **1**/MAO and **2**/MAO.

Cat.	Ta µmol/dm^3	T_p °C	t_p min	Activity kg PE/mol Ta*h	T_m °C	M_w kg/mol	M_w/M_n
1	44.7	30	20	800	137.7	201	2.5
1	22.3	60	7	5 000	135.4	94	2.0
2	3.7	30	30	900	136.3	115	1.9
2	3.7	60	30	5 800	135.3	85	1.9
2	3.7	80	7	23 900	133.9	66	1.8

Polymerization conditions: p_{Et}=5 bar, Al/Ta=2000

2.3 Progress Report: Progress by the Laboratory of Inorganic Chemistry, UH

2.3.1 Introduction

The aim of research was to synthesize and study new olefin polymerization catalysts. The target was to find new alternatives to metallocenes and these new catalysts should have the advantages of metallocenes: structurally known, highly active, single site behaviour and possibility to tailor the catalyst properties by tailoring the ligand structure. The drawback of metallocenes and all early transition metal complexes, the high Lewis acidity, was tried to avoid in studies of late transition metal complexes. The lower Lewis acidity should allow the use of polar comonomers.

The synthesis and structural characterization, as well as, the first polymerization experiments were carried out in UH. Heterogenization of some the complexes were carried out in UJ. More polymerization experiments were done in HUT/(Pol.Tech.), where also the polymer materials were characterized. The results from polymerization experiments both from early (Ta) and late transition metal (Ni) complexes have been presented in 2.2. Here the early transition metal complexes are briefly described.

One of the synthetic targets was dealing with metallocenes. The aim was to synthesize new substituted zirconocenes and study the intramolecular electronic and steric interactions, which may affect polymerization. One of the aims was to design a dual site metallocene.

2.3.2 Complexes with nitrogen as donor atom

Aminopyridinato complexes were studied for early transition metals from groups four (Ti, Zr, Hf), five (Nb,Ta) and six (W). The novelty in the research was both in ligands and metals (Nb,Ta,W). Aminopyridinates represent ligands where nitrogen is the donor atom. The focus in the work was in didentately acting ligands, since they were assumed to form complexes rigid enough for single site type behaviour after activation with MAO. New efficient one-step methods, based on direct reflux reaction between metal halides and 2-(phenylamino)pyridines and melt reaction between metal halides and less reactive 2-(benzylamino)pyridine ligands, were developed. Totally 13 different complexes were crystallized and their structures were determined [3,5,8,89]. In this study tantalum complexes were for the first time showed to be active in olefin polymerization. Especially, trichlorobis [2,6-di (phenylamino) pyridinato-N,N'] tantalum (V) showed interesting polymerization behaviour and high activity when activated with MAO (Table 3).

In later transition metal complexes the focus was also in ligands bearing nitrogen as donor atoms. The compounds studied were unsymmetric diimine complexes of Ni, Pd and Co. Ni complexes showed best activity and the forming polymer was linear and slightly branched polyethene (2.3.2.1). The complexes have been presented in more detail in the report "Coordination Compound Catalysts".

2.3.3 Metallocene Dichlorides

Several different types of metallocenes have been prepared, the main emphasis being in the preparation of zirconocene dichlorides. The main focus in the ligand design has been in the combining of traditional bis(indenyl) type ligands [9, 17,18] with substituents, which facilitate further control on the polymerization. In our research one of the most promising series of compounds was based on the benzyl substituent in the 3-position (Figure 1) [15, 19, 21, 22, 24, 26-28]. This kind of substitution pattern allows novel control of the molar mass distribution by varying the reaction conditions e.g. monomer pressure.

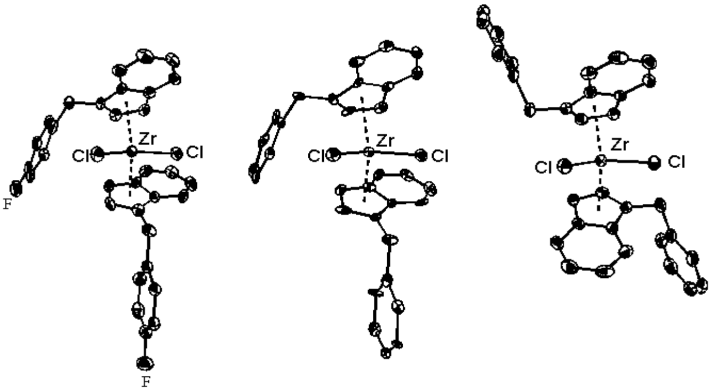


Figure 1. Different benzylic substituted bis indenyl zirconium dichlorides. From the left: para-fluoro benzyl substituted rac-like bis(indenyl)zirconium dichloride, benzyl substituted rac-like bis(indenyl)zirconium dichloride and right benzyl substituted meso-like bis(indenyl)zirconium dichloride.

Further on, basic ligand structure of the bis(indenyl) zirconium dichlorides has been modified by designing and addition of the new ligand moieties. Replacement of one or two chlorines by substituted phenoxy group facilitates modifications on the catalytic structures, but the catalytic activities remains on the very high level [11]. Also novel cyclopentadienyl moieties have been prepared, resulting in sterically bulky metallocenes bearing cyclopenta- acenapthtadiene as a ligand. The major chain termination reaction in the polymerization with these catalysts is methyl elimination, thus resulting high molar mass polymers (Figure 2) [10,13,39].

2.3.3.1 New Polymer materials

Copolymerizations of ethene, propene, hexene, hexadecene, dienes, norbornene, and phenyl norbornene were studied using zirconocene- and hafnocene/MAO catalysts. Catalysts with different symmetry, ligand framework and *ansa*-bridge were used. Homo- and copolymerization of unsymmetric dienes e.g. isositronellene, results in novel chemically active polymers, which can be further modified by epoxidation, bromination and radical reactions [16]. Ethene-hexene and ethene-hexadecene copolymerizations were carried out with metallocenes bearing bulky acenapthtyl and fluorenyl ligands and phenyl group in the *ansa*-bridge (Figure 3). Activation was made with MAO. By this catalyst system very high molar mass copolymers were produced with excellent catalytic activity. Synthesis of poly(propene-co-phenylnorbornene) was also studied using *ansa*-bridged zirconocenes with different symmetry and ligand structure.

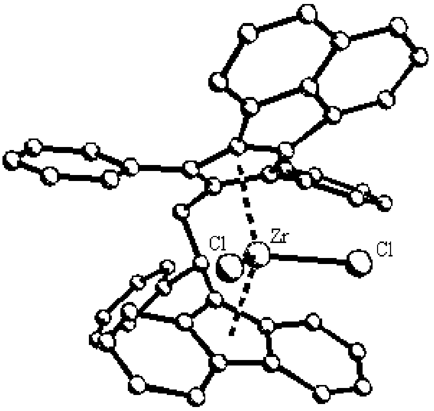


Figure 2. Catalyst precursor for the preparation of high molar mass ethene-hexene copolymers.

2.4 Progress Report: Progress by Materials Chemistry Laboratory, UJ

2.4.1 Introduction

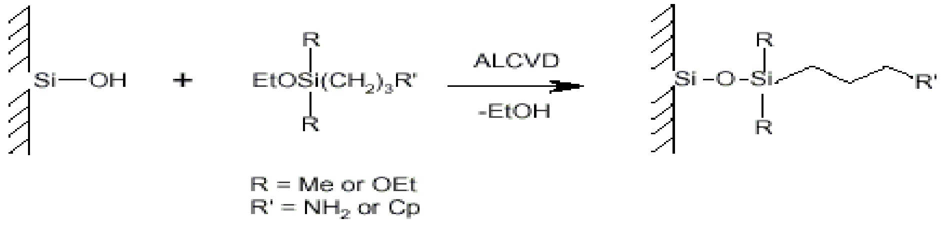
For many industrial applications the insoluble supported metallocene catalysts are desirable allowing for example the control of morphology of the polymer product in the particle forming processes. In addition, the supported metallocenes may be utilized in cheaper gas-phase and bulk propene processes and they may permit the use of less

MAO, while still offering the control of structure and properties of polymeric materials using ligand variation.

The target in the research project *Development of Catalysts for Production of New Polymeric Materials* was to develop new methods for preparation of heterogeneous metallocene-type catalysts. In general, a direct adsorption of the metallocene complex on the surface of inorganic oxide carrier produces a heterogeneous catalyst, from which the metal complex rather easily leaches out. Therefore an assembling method involving anchoring of a cyclopentadienyl ligand through a spacer on the carrier surface and immobilizing of the metal compound on the ligand surface with a chemical reaction was chosen [21-22,24-29,31,33].

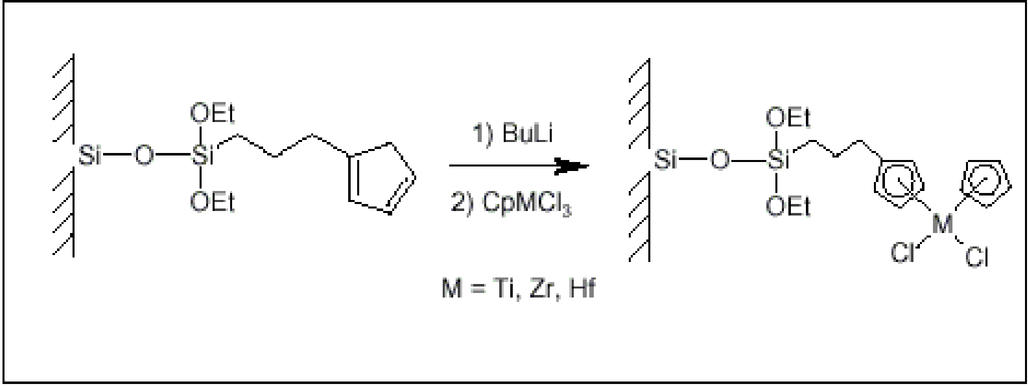
2.4.2 Stepwise preparation of heterogeneous catalysts

We have studied stepwise preparation of heterogeneous metallocene-type catalysts using gas phase - solid state as well as liquid phase – solid state reactions. This research has aimed at preparation of chemically tethered metallocene catalysts on an inorganic oxide support. The fundamental strategy in this research has been to functionalize the surface of the silica support with a silicon compound containing one or two organic functional groups, which can be used for attachment of the transition metal complex (Scheme 1).



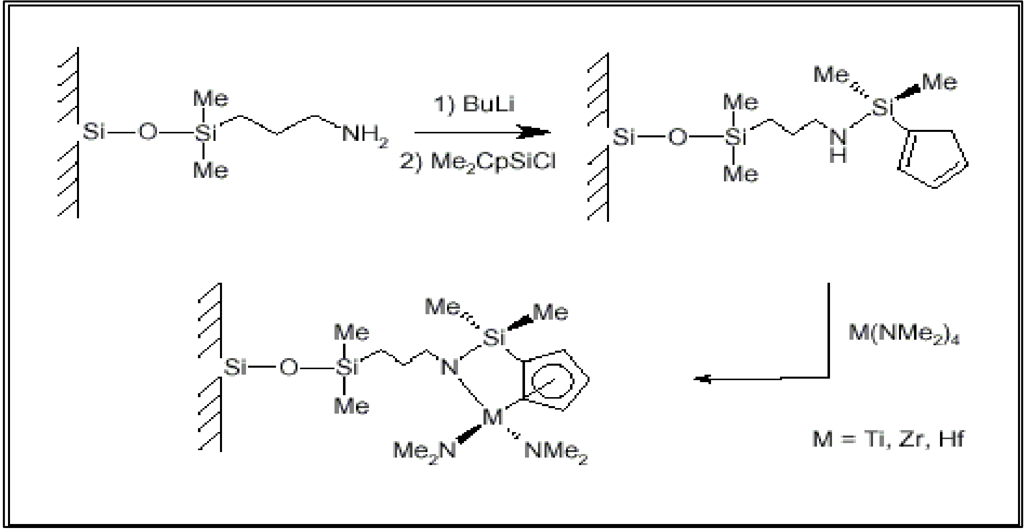
Scheme 1

Chemical modification of a partially dehydroxylated silica surface was accomplished with a coupling agent, $(EtO)_3Si(CH_2)_3Cp$, using an ALCVD-technique (Atomic Layer Chemical Vapour Deposition). The Cp-ligands of the SiO_2 surface were transformed to the cyclopentadienyl anions by a reaction with BuLi. The cyclopentadienyl surface on silica carrier was used for immobilizing of Ti-, Zr-, Hf- and Cr-compounds: $MCl_4(THF)_2$ (M= Zr, Hf), $CpMCl_3$ and Cp^*MCl_3 (Cp*= C_5Me_5, M= Ti, Zr, Hf), $M(NMe_2)_4$ (M = Ti, Zr) and $CrCl_3(THF)_4$ (Scheme 2). All of the supported metal complexes polymerized ethene in the presence of MAO. Especially zirconium and hafnium catalysts showed a good polymerization activity and the polyethenes produced had on the basis of GPC-measurements narrow molar mass distributions (polydispersity < 3), which indicates that these catalysts act as single-site catalysts, which is a typical feature of the homogeneous metallocene catalysts.



Scheme 2

In addition, bifunctional ligand surfaces were prepared on silica by a reaction of $Me_2Si(C_5Me_4H)Cl$, $MeHSi(C_5Me_4H)Cl$, or $Me_2Si(C_5H_5)Cl$ with the amine-bearing surface (Scheme 3). The two functional groups for coordination of metal compounds were cyclopentadienyl (or tetramethyl cyclopentadienyl) and amine, which were bridged by either dimethyl or methylsilyl groups. Ti-, Zr- and Hf-amides were immobilized on these surfaces using amine elimination reaction producing the first well-characterized supported forms of the constrained–geometry catalysts. The zirconium and hafnium based catalysts were found to be moderately active in ethene polymerization using MAO as a cocatalyst. The polyethenes produced under the used reaction conditions were linear high-density material and possessed narrow molar mass distributions indicating the single-site nature of these supported constrained-geometry catalysts.



Scheme 3

The comprehensive characterization of the ligand surfaces of the silica support as well as the immobilized metal complexes was done using solid-state FT-IR and ^{1}H, ^{13}C and ^{29}Si CP/MAS NMR methods. The polymerization activities of the prepared catalysts were routinely studied in ethene polymerization using MAO as a cocatalyst and under non-optimized conditions.

In conclusion, the ALCVD method was found to produce highly uniform and defined ligand surfaces. The assembling method, as a whole, constituted a convenient method for preparation of supported single-site catalysts. The surface densities of the ligand as well as the metal complex could be controlled by the calcination conditions of the silica support. The polymerization activities of these chemically tethered metal complexes remained low compared to those of the corresponding homogeneous metallocene catalysts. Optimization of the activation conditions for this type of heterogeneous single-site catalysts would require an in-depth understanding of the activation mechanism.

2.5 Progress Report: Progress by the Laboratory of Inorganic and Analytical Chemistry, HUT

The main goal of the project was to provide novel well-characterized supports for polymerization catalysts of enhanced activity. At the beginning of the project, the modification of silica support with aluminium oxide thin films and the possibility to use these modified catalyst supports for the polymerization processes were studied. The modified aluminium oxide films were deposited onto porous silica by the atomic layer deposition (ALD) technique, also referred to as atomic layer epitaxy (ALE). Analytical method based on X-ray fluorescence spectrometry (XRF) was developed to determine aluminium in $AlCl_3$- and Al_2O_3- modified silica catalyst supports [34]. Instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) were used as reference methods to determine the aluminium content of supports. Correlation factors for the calibration graphs were 0.984 for $AlCl_3/SiO_2$ and 0.995 for Al_2O_3/SiO_2 samples in the aluminium content range 0-2.6 g Al/100 g of sample.

Besides support modification by the surface-controlled ALD process and subsequent characterization by analytical techniques, active catalytic species, such as metallocenes, were deposited by ALD on the surface sites of the unmodified support. The deposition of catalytically active species onto silica support was performed with commercial zirconocene, Cp_2ZrCl_2. The ALD method seemed to be a feasible way to adsorb zirconocene in a controlled way onto the support [20]. The studies on reactions of Cp_2ZrCl_2 vapour on the silica surface at 300 °C showed that the reaction mechanism depends on the nature of silica surface. Therefore preheating temperature of the silica had a significant effect on the reaction. ^{13}C NMR spectra revealed that there was triply, doubly and singly bonded zirconium on the silica support which was preheated at 350 °C, while on the silica preheated at 600 °C the zirconium was mainly singly bonded.

The surface hydroxyl groups on catalyst supports are of crucial importance for the adsorption reactions on the support [111,112]. Thus, the surface of silica supports was studied in detail in order to understand the modification reactions of silica. For the determination of surface hydroxyl groups on silica two practical methods were developed [35,36,101]. The first is based on DRIFT spectrometry and the second on thermogravimetry (TG). Both methods were found to be simple and fast techniques for the determination of hydroxyl groups in silica. In the DRIFTS method thermogravimetry was used as a reference method and the calibration was performed with the help of multivariate techniques. Data pre-treatment was performed with orthogonal signal correction (OSC) and it was followed by subsequent partial least squares projection for latent structures (PLS) modelling [35]. The calibration model was validated by predicting the hydroxyl content of samples not used in the construction of the models. The OSC-PLS model was able, with a sufficient accuracy (the goodness of predictability Q^2=0.988), to predict the hydroxyl content of several silicas with different physical properties. In the TG method the measurements were performed by heating the silica samples (15-30 mg) at a rate of 5 °C/min from room temperature to 1250 °C in an argon flow [36]. The dehydration and dehydroxylation phenomena were distinguished with the help of the differential TG curve (DTG). The total hydroxyl group content was calculated from the total mass loss of the second step. When comparing the total OH group content and the OH group content at 550 °C determined by the TG method with the results of calcined samples measured by the reference method (^{1}H MAS NMR), they were found to be in a good agreement with each other.

In addition to experimental studies, theoretical aspects related to the factors affecting the activity of heterogeneous metallocene catalysts and the properties of polyethene products were also considered [101]. Judging from literature, considerable effort has been placed to study metallocene catalysts immobilized on different supports. Although many articles have been published in this field, most of the investigations concern only the authors'own data. No investigation appears to have been done to combine the results of several different studies into a single model that would give a correlation between various parameters used in the experiments and the resulting polymerization properties of the catalysts. The aim of the present study was to create multivariate models by chemometrics for the activities of the catalysts, molar masses, polydispersities and melting points of polyethene products. The properties were modelled with separate models with good results. The prediction ability was good for all the models, except for the model concerning the melting points. The melting points could not be modelled due to unavoidable inaccuracy of the melting point measurements. On the other hand, the models developed were able to predict the activities of the catalysts and other properties than melting points of the polyethene products from the polymerization parameters.

2.6 Progress Report: Progress by Department of Physical Chemistry, ÅA

2.6.1 Introduction

A basic knowledge of the surface properties of the support material is essential in order to produce highly active heterogeneous catalysts. E.g. the number, type and binding strength of the surface sites, the porosity and the total surface area are all determinative for the amount of catalyst and spacer molecules adsorbed on the support. It is also known that the (re)activity of the adsorbed organic catalyst may be enhanced by small variations in the acid and base strength of the inorganic support which is achieved through a coprecipitation of transition metal oxides into the silica support matrix. A variation of the pore size, pore volume and surface area has been found to control the transport of reactant monomers to the catalytic sites and the removal of the polymer product. Finally, spacer molecules may be used to displace the catalyst further from the support surface thus reducing the possible steric blockage of the bulky catalyst attached directly to the surface.

As agreed in the project application the focus of this subproject was laid on three topic areas:

1. Synthesis and chemical modification of the catalyst support
2. Heterogenization of the catalyst
3. Characterization of the heterogenized catalyst

Moreover, the FT-Raman characterization procedure developed in the previous project to quantify the isotacticity of the polymers [113] was made available for the research partners if enough of polymer had been produced in the experiments.

2.6.2 Synthesis and chemical modification of the catalyst support

A highly porous silica model monolith was synthesized with the support of EU-TMR research program denoted, “Mechanisms of the formation of ordered mesomorphous, inorganic materials from organized molecular assemblies” (MESOP). This silica support had a surface area exceeding 1000 m^2/g, which ensured a large site area and a controlled mass transport. Its properties were compared with a standard silica support material for catalyst immobilization.

The surface (re)activity was adjusted by coprecipitating different amounts of titania and alumina which are known to change the acid and base properties, both in the Lewis (electron exchange) and the Brönsted (proton exchange) sense [37]. The surface acid and base properties were carefully characterized with a number of methods as described below.

In order to investigate whether the bulky catalyst was sterically hindered, when adsorbed directly to the surface, different spacer molecules were adsorbed to the surface sites in a controlled way [38,39]. The adsorption was characterized by recording the adsorption isotherms enabling an evaluation of both the number of surface sites occupied and the energy of adsorption from alternative solvents.

2.6.3 Heterogenization of the catalyst

The catalyst was immobilized directly on the activated supports and its catalytic activity was tested in a restricted number of standard polymerization experi-ments [37,40,41]. The preparation of the immobilized catalysts was made in collaboration with Dr. Leanne Britcher (University of South Australia), who has a broad experience in this field. The polymerization reactions were made in collaboration with B. Löfgren at HUT/Pol.Tech. Unfortunately the physico-chemical conditions were not sufficiently systematically varied in order to fully evaluate the special features of the different heterogeneous catalysts. Moreover insufficient amount of polymer was produced in order to make a more thorough characterization of the polymer produced. The evaluation of the influence of the porosity thus remained incomplete.

2.6.4 Characterization of the heterogenized catalyst

Both the supports and the immobilized catalysts were characterized thoroughly, including a modelling of the pore structure. First both the Lewis and the Brönsted acidic and basic surface sites were characterized with probe adsorption, with ammonia adsorption and through thermal desorption [42,43]. As a result, very accurate information of the influence of the chemical modification was achieved. The Brönsted activity was further analysed by investigating the freezing behaviour of water adsorbed into the pores and by the evaluation by the hydroxyl group density on the surfaces [35,42-44] in collaboration with P. Pomonis at the University of Ioannina and L. Niinistö at HUT/Inorg.Lab. The change in hydroxyle groups upon the surface modification was also quantified, as was the NMR-analysis of the degree of true incorporation of alumina into the silica walls [37,43] in collaboration with R. Harris at the University of Durham. Finally, the pore structure characterized through gas sorptometry was modelled with the corrugated pore structure model [45].This work was a collaboration with G.P. Androutsopoulos at the National Technical University of Athens. As mentioned, the adsorption of the spacer molecules were characterized by recording the adsorption isotherms and comparing the number of sites with the site occupancy and the energetics of adsorption with the probe adsorption. The catalyst activity was characterized with standard polymerization reactions.

2.7 Progress Report: Progress by Polymer Technology, HUT

2.7.1 Introduction

The aim in our polymerization research was the incorporation of functional groups into hydrocarbon polymers, which enhance their chemical and physical properties. The production of functionalized polyolefins on a commercial scale is currently based on high-pressure free radical processes in which comonomers like vinyl acetate and methyl- or butylacrylates are used. Another extensively utilized route for adding polar groups to polyolefins is the post polymerization modification, which is usually performed by free radical grafting in reactive extrusion.

The most straightforward way to produce functionalized polyolefins is the direct polymerization of functional monomers by Ziegler type catalysts. The constraint in this approach is the poisoning of catalyst components by polar groups. The polymerizations of functional groups containing vinyl monomers are, however, reported to be possible with both Ziegler-Natta and metallocene catalysts. This succeeds when the Lewis basicity of the monomers is reduced by masking with aluminum alkyls or by adding silyl or other kinds of protecting groups into the heteroatom.

2.7.2 Synthesis of Functional Polyolefins with Metallocene Catalysts

During the first three years of this program we studied the synthesis of functional polyolefins through direct polymerization of ethene or propene and some polar oxygen functionalized comonomers with soluble zirconocene-MAO catalysts. The catalyst deactivation was observed to vary depending on the structural features of a polar monomer utilized in the copolymerization [46,47,107]. In the search for functionalized alkenes with superior comonomer properties, a qualitative approach of inspecting interactions between alkene derivatives and the catalyst components was undertaken [51]. Thus several alkenols, aminoalkenes and carbonyl-functionalized alkenes were synthesized and subsequently screened by NMR to find suitable candidates for copolymerizations with ethen or propene by T. Helaja in the UH/Org.Lab. [53,110].

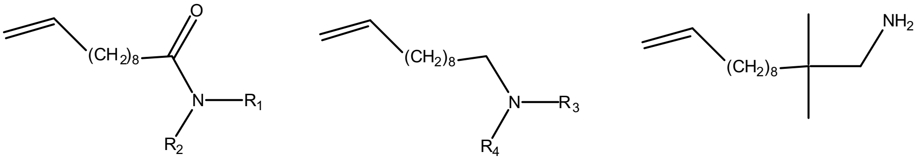
The studied alkenols formed aluminum alkoxides with MAO even in the case of a substantial steric hindrance around the OH group. The NMR studies suggest that stronger interaction between comonomers and the catalyst system is involved in the case of a- or ß-branched rather than straight chain alkenols. In fact, the decomposition of the aluminium alkoxide was observed only for the straight chain alkenol (10-undecen-1-ol) [54,56].

2.7.3 Copolymerizations with oxygen- and nitrogen-functionalized long-chain olefins

The objective has been to investigate the influence of molecular structure around the oxygen atom on the comonomer incorporation in copolymerizations with ethene using an $Et(Ind)_2ZrCl_2/MAO$ catalyst. The comonomers [(**I**) 10-undecen-1-ol, (**II**) 10-undecenyl methyl ether, (**III**) 10-undecenyl trimethyl silyl ether, and (**IV**) 1-undecene] were chosen so that the chemical environment around the oxygen atom was different in each comonomer. The alcohol comonomer, 10-undecen-1-ol (**I**), contains a free hydroxyl group with the active hydrogen [55].

The polymerization results showed that the substitution of the hydrogen atom in the hydroxyl group of comonomer **I** with larger methyl or trimethylsilyl groups did not affect the magnitude of catalyst deactivation. The trimethylaluminium (TMA) included in the composition of MAO is known to react with primary alcohols like comonomer **I** to form aluminium alkoxides. In contrast, our NMR studies have shown that the ether derivatives **II** and **III** mostly remain as free comonomers in the presence of MAO. Nevertheless, alcohol **I,** and ethers **II** and **III** did not show any noteworthy differences in their ability to copolymerize. This indicates that the formation of aluminium alkoxides, as in the reaction between the hydroxyl group and MAO, is not a prerequisite for comonomer incorporation.

The adding of non-functionalized 1-undecene, (**IV**) to the reaction medium resulted in the increase in the polymerization activity. This phenomenon is well known as the positive comonomer effect.



1 $R_1 = H, R_2 = Me$
2 $R_1 = H, R_2 =$ *tert*-Bu
3 $R_1 = R_2 = Me$
4 $R_1 = R_2 = Et$
5 $R_1 = R_2 =$ *i*-Pr

6 $R_3 = H, R_4 = Me$
7 $R_3 = H, R_4 =$ *tert*-Bu
8 $R_3 = R_4 =$ *i*-Pr
9 $R_3 = R_4 = H$
10 $R_3 = Bz, R_4 =$ *tert*-Bu
11 $R_3 = R_4 =$ *sec*-Bu
12 $R_3 = R_4 = Me$

13

Scheme 4.

Along with oxygen-functional monomers, nitrogen-functional vinylic comonomers are among the most widely studied functional comonomers in copolymerizations with ethene, propene or other α-olefins. The range of comonomers studied is presented in Scheme 4 [58].

Table 4. Data of copolymerizations of amides 1-5 with ethene and propene[a]

Monomers	$c_{com.}$ mmol/dm^3	Al/Com. mol/mol	A[b]	Com. in Polymer mol %	M_w kg/mol	M_w/M_n	T_m °C
Ethene	-	-	14 400	-	188	3.2	137
Et/**1**	1.7	40.0	3 800	0.24	107	3.2	130
Et/**2**	1.3	50.0	2 900	0.33	69	2.7	133
Et/**3**	1.7	40.0	< 30	n.d.	n.d.	n.d.	n.d.
Et/**4**	1.7	40.0	190	0.43	18	3.0	127
Et/**5**	1.7	40.0	130	0.58	10	2.4	126
Propene	-	-	5 800	-	68	2.1	148
Pr/**1**	1.7	80.0	1 500	0.04	43	2.1	146
Pr/**2**	1.7	80.0	460	0.24	26	2.2	144
Pr/**3**	1.7	80.0	200	0.40	31	2.2	142
Pr/**4**	1.7	80.0	870	0.14	35	2.1	145
Pr/**5**	1.7	80.0	230	0.45	22	2.1	142

[a] Polymerization conditions, for ethene polymerizations: catalyst $Et(Ind)_2ZrCl_2/MAO$, $[Zr] = 1.7 \cdot 10^{-5}$ mol/dm^3, Al/Zr = 4000 mol/mol, T_p = 60°C, p_{et} = 1.5 bar; for propene polymerizations: catalyst $Me_2Si(2\text{-}MeInd)_2ZrCl_2/MAO$, $[Zr] = 6.7 \cdot 10^{-5}$ mol/dm^3, Al/Zr = 2000 mol/mol, T_p = 50°C, p_{pr} = 1.5 bar; [b] Activity of the catalyst in kg of polymer/ (mol Zr ·h).

The results of the copolymerizations of the five differently substituted amides of 10-undecenoic acid (1-5) in Table 4 show that the activity decreased drastically relative to the homopolymerization, even though concentrations of the comonomer were low and Al/comonomer molar ratios high. The comonomers 1 and 2 seemed to be slightly less poisonous to the catalyst than were comonomers 3-5. A possible explanation is that comonomers with acidic hydrogen are capable of reacting with MAO (or with the trimethylaluminium), which reduces their reactivity towards the active catalyst. No significant differences were observed among dimethyl-, diethyl-, and diisopropyl-substituted amides in either reactivity or the activity of the catalyst.

To further study the possibility of preparing nitrogen-functionalized polar olefin copolymers, a number of primary, secondary and tertiary amines were used as comonomers in copolymerizations with ethene. The results are summarized in Table 5. Judging by the values of polymerization activity, amine comonomers as a whole are much better tolerated by metallocene catalyst than are the corresponding amide comonomers. The higher comonomer concentrations could be used without increasing the concentrations of catalyst or cocatalyst, and moderate ethene polymerization rates were still achieved.

The reactivity of the comonomer, determined by the incorporated functionality in the copolymer, was decreased when the bulkiness of the ligands around the nitrogen atom was increased. At the same time the productivity of the catalyst was slightly increased. A plausible explanation is that the steric hindrance due to the larger groups joined to nitrogen prevents the free electron pairs from forming complexes with the active catalyst.

Table 5. Data of copolymerizations of amines 6-13 with ethylene[a]

Comonomer	$c_{com.}$ mmol /dm^3	Al/Com. mol/ mol	A[b]	Com. in Polymer mol %	M_w kg/ mol	M_w/M_n	T_m °C
-	-	-	14 400	-	188	3.2	137
9	16.7	4.0	950	0.92	13	2.1	122
13	6.7	10.0	2 200	0.28	26	2.4	128
6	16.7	4.0	1 700	0.84	14	1.6	124
7	16.7	4.0	1 400	0.65	16	2.3	124
12	16.7	4.0	2 100	0.92	17	2.2	121
8	16.7	4.0	1 400	0.70	12	2.0	125
11	16.7	4.0	1 500	0.60	21	2.3	124
10	16.7	4.0	2 500	0.49	23	2.1	124

[a] Polymerization conditions, catalyst $Et(Ind)_2ZrCl_2$/MAO, Al/Zr = 4000, T_p = 60°C, p_{et} = 1.5 bar; [b] Activity of the catalyst in kg of polymer/ (mol Zr ·h)

Despite the different mode of reactivity, both alkenols and amines appeared to follow a common trend when copolymerized with ethene or propene *i.e.* catalyst activities improved in the order *prim* <*sec*<*tert* derivative. Moreover, the bond formation between the heteroatom of the comonomer and Al of MAO appears not to be decisive for the diminished catalyst spoiling in copolymerizations. The carbonyl functionalized alkenes deactivated the catalyst system to a larger extent compared with the other alkenes investigated. This finding suggests that the functional group itself is more crucial for the catalyst deactivation than the steric hindrance in the heteroatom vicinity of an alkene.

Steric studies on some comonomers and metallocene catalysts using molecular modelling have been performed in cooperation with L. Ahjopalo in Technical Research Centre of Finland. The theoretically obtained results have been in agreement with the experimental results as to the polymerizability of different comonomers [50].

2.7.4 Application of functionalized polyethene copolymers as compatibilizers in PE/PA6 blends

Blending of polyolefins with engineering plastics offer an interesting route to polymers with new property combinations. Desired combination of properties is not achieved simply by melt mixing, but a compatibilizer is required as well. Functionalized copolymers can be used as new effective compatibilizer alternatives for immiscible polymer blends. Copolymers with hydroxyl or carboxyl functionalities were used as compatibilizers in PE/PA6 blends. Toughness as well as surprisingly stiffness and strength increased significantly with these new compounds used as compatibilizers. Crystallization and melting behaviour changed and improvement in adhesion was clearly observed in SEM micrographs [48].

3 International Aspects

Many foreign graduate students and post docs have worked in the polymerization catalyst group of UH. Prof. Leskelä has presented the list of the visitors in the report “Coordination Compound Catalysts”. The most active collaboration has existed with University of Ulm (Professor B. Rieger) via a DAAD - Academy of Finland exchange program. Every year graduate students (1-3) have spent 3 months in the partner’s laboratory. In addition, two post docs (G. Jany and A. Abu-Surrah) have spent 1.5 years at UH. In metallocene studies collaboration has been made with Prof. H.-H. Brintzinger (Konstanz) and in aminopyridinato complexes with Prof. Kempe (Rostock). Some theoretical studies on bonding in catalyst molecules have been carried out with University of Granada (Prof. J. Molina).

The laboratory of Inorganic and Analytical Chemistry at HUT started co-operation in catalyst research during the project with the Institut de Recherches sur la Catalyse (CNRS) in Lyon, France. Two posters based on the research results obtained during the project were presented 15-19-8.1999 in the 6th Scandinavian Symposium on Chemometrics (SSC6) in Porsgrunn, Norway and 4-7.7.2000 in the Calorimetry and Thermal Effects in Catalysis (CTEC), Lyon, France.

Department of Physical Chemistry at ÅA has been several years a member of EU-TMR research program denoted “Mechanisms of the formation of ordered mesomorphous, inorganic materials from organized molecular assemblies” (MESOP).

As a part of the collaboration between ÅA and University of South Australia, Dr. Leanne Britcher’s expertise in preparation of immobilized catalysts was utilized. In the field of characterization of catalyst surfaces ÅA collaborated with the University Ioannina and with the University of Durham. In modelling of pore structures ÅA had collaboration with National Technical University of Athens.

Barbro Löfgren together with Jukka Seppälä are the Finnish members of the Management Committee for the COST Action D17 “Oligomers, Polymers and Copolymers via Metal Catalysis.

4 Publications and Academic Degrees

Table 6. Publications and academic degrees produced in the project.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
UH	Ref. journal art.	14	2	-	2	**18**[a]	1-20
	Ref. conf. Papers	1	3	2	3	**9**	59-67
	Doctoral dissert.	2	-	1	-	**3**	89-91
	Master degrees	-	1	1	3	**5**	92-96
UJ	Ref. journal art.	4	-	3	5	**12**[a]	1, 21-33
	Ref. conf. Papers	2	2	1	2	**7**	68-74
	Doctoral dissert.	-	-	1	1	**2**[b]	98-100
	Master degrees	1	-	-	-	**1**	97
HUT/	Ref. journal art.	-	-	1	2	**3**[a]	20,30,34-36
Inorg	Doctoral dissert.	-	-	-	-	[b]	103
	Licentiate degrees	-	-	-	-	[b]	101
	Master degrees	-	-	-	1	**1**	102
ÅA	Ref. journal art.	-	-	2	2	**4**[b]	37-45
	Ref. Conf. Papers	1	1	-	-	**2**	75,76
	Doctoral dissert	-	-	-	-	[b]	104,105
	Licentiate degrees	-	-	1	-	**1**[b]	105,106
HUT/	Ref. journal art.	5	1	8	4	**18**[b]	1,12,13,23,30,32,37, 40,46-58
Pol.	Ref. Conf. Papers	1	7	2	2	**12**	65,75,77-86
	Monographs	-	1	-	1	**2**	87,88
	Doctoral dissert.	1	-	1	-	**2**	107, 110
	Licentiate degrees	-	-	-	1	**1**	108
	Master degrees	-	-	1	-	**1**	109

[a] 2 publ. in 2001, [b]Finished year 2001.

5 Other Activities

5.1 Patents, Patent applications and Invention Disclosures

PA 1 M. Polamo, M. Leskelä, K. Hakala & B. Löfgren: Chloro-(2-amonopyridine derivative) Complexes of Early Transition metals (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W) as Homogeneous Polymerization Catalysts. **Finn. Pat. 102 476; PCT Int. Appl. WO 97 45,454.**

PA 2 T. Repo & M. Leskelä: Metallocene Compounds for the Polymerization of Ethylenically Unsaturated Monomers. **Finn. Appl. 97 2946; PCT Int. Appl. WO 9902540.**.

5.2 Joint meetings of the subproject groups

The participating groups have met each other regularly 3-4 times/year, where the results have been discussed and the consolidated plans for the next period have been settled.

5.3 Participation in conference arrangement

Nordic Polymer Days, Helsinki May 2000 (Barbro Löfgren member of the org. committee, member of the advisory board and chairman)

6 Publications

6.1 Refereed Journal Articles

[1] T. Repo, M. Klinga, M. Leskelä, A.-M. Uusitalo, T.T. Pakkanen, K. Hakala, P. Aaltonen and B. Löfgren, Ethylenebis-(salicylideneiminato)zirconium Dichloride: Crystal Structure and Use as a Heterogeneous Catalyst in Polymerization of Ethylene. Macromolecules **30** (1997) 171-175.

[2] M. Polamo and M. Leskelä, Formation of Tetrahydrofuran Adducts in the Reaction of $Li(NPh_2)_4$ and $ZrCl_4$: Crystal Structures of $[Li(thf)_4]$ $[ZrCl_5(thf)]$ and $Li(thf)_3$-μ-Cl-$ZrCl_4(thf)$. Acta Chem. Scand. **51** (1997) 44-48.

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[9] G. Jany, T. Repo, M. Gustafsson, M. Leskelä, I. Mutikainen, M. Polamo, M. Klinga, U. Dietrich and B. Rieger, Synthesis, Characterization and Polymerization Behaviour of {(1R,S)-2-(^{5}-9-Fluorenyl)-1-[^{5}-1(R,S)-indenyl]-1-phenylethane}zirconium Dichloride and {1(R,S)-Cyclohexyl-2-(^{5}-octahydro-9-Fluorenyl)-1-[^{5}-tetrahydro-1(R,S)-indenyl]ethane} zirconium Dichloride. Chem. Ber. **130** (1997) 747-751.

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[11] T. Repo, G. Jany, M. Salo, M. Polamo and M. Leskelä, Phenoxy Substituted Zirconocenes in Ethylene Polymerization. J. Organomet. Chem. **541** (1997) 363-366.

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ADVANCED EPITAXIAL COMPOUND SEMICONDUCTORS FOR OPTOELECTRONICS (EPI-2)

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Abstract

The *EPI*-2 research project, carried out by the Consortium of five partners,[5] was a part of "*Electronics and Telecommunications Materials*" of the National Programme in Materials and Structure Research (*MATRA*) for the years 1.1.1997 – 31.12.1999. The estimated budget was FIM 12,906,000 (Euro 2,170,633), of which the Academy of Finland carried the cost of FIM 8,270,000 (Euro 1,390,914). The total manpower spent was 415.5 MM.

The main purpose of *EPI-2* was to study the physics of epitaxial compound semiconductors. The objectives were to improve the understanding of structural, electrical, and optical properties of semiconductors and develop related technologies for optoelectronics. The methodology used to achieve the objectives was a definition of well-defined but interconnected technical workpackages and the overall co-ordination that ensured the smooth running of the Project, reviewing the targets, and handling deviations from the work-plan.

EPI-2 resulted in 82 journal articles and 29 conference papers. Of these publications 25 were inter-partner works, indicating a productive collaboration of the partners. Students involved in this Project received 13 Doctoral Degrees and 27 Master of Science Degrees. The Partners had a world-wide co-operation with universities and companies, which contributed to the success of the Project and helped disseminate the results.

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To re-capitulate, *EPI-2*

(i) improved the overall scientific and technological knowledge of semiconductors and had breakthroughs in the areas of main interest, as highlighted in Section 7.3 and also evidenced by the impressive list of publications, Section 9

(ii) educated and trained a large number of students and researchers

(iii) contributed to the foundation of new production plants and spurred other industrial take-ups of the results

(iv) paved the way to the creation of a new research centre in Finland.

EPI-2 strengthened the Finnish share in the semiconductor market by producing results that were of interest to industry. Moreover, it played a seminal role in establishing two new semiconductor companies in Finland. It also trained students and researchers, many of whom are now serving industry or acquiring further expertise in universities. It also addressed a long discussed issue of whether Finland needs a research institute that would be dedicated to the R&D of optoelectronics and optical communications. The discussions led to the foundation of Optoelectronics Research Centre (ORC) in 1999.

1 Partners

TUT. Research Staff of Tampere University of Technology. Total person-months of work funded by Academy of Finland in *EPI-2*: 141,5.

Name	Degree	Job Title	Sex
Pessa Markus	**Professor, Dr.**	**P.I. of EPI-2**	**M**
Aho Riku	M.Sc.	Researcher	M
Aarik Jaan	Ph.D.	Senior Researcher	M
Dekker James	Ph.D.	Researcher	M
Dumitrescu Mihail	Ph.D.	Senior Researcher	M
Guina Mircea	M.Sc., Post-Graduate Student	Researcher	M
Hirvelä Tommi	Undergraduate Student	Research Assistant	M
Kazantsev Andrey	M.Sc.	Researcher	M
Koskinen Mervi	M.Sc.	Researcher	F
Kuuslahti Tiina	M.Sc.	Researcher	F
Köngäs Jukka	M.Sc.	Researcher	M
Jaakkola Reino	M.Sc.	Researcher	M
Laukkanen Pekka	M.Sc.	Researcher	M
Lehkonen Sami	M.Sc.	Researcher	M
Leinonen Pirjo	FM, Post-Graduate Student	Researcher	F
Leinonen Tomi	Undergraduate Student	Research Assistant	M
Melanen Petri	Undergraduate Student	Research Assistant	M
Nurmi Tero	Undergraduate Student	Research Assistant	M
Nurminen Maria	Undergraduate Student	Research Assistant	F
Orsila Seppo	M.Sc.	Researcher	M
Rinta-Möykky Ari	M.Sc.	Researcher	M
Saarinen Mika	M.Sc., Post-Graduate Student	Researcher	M
Sahrakorpi Seppo	M.Sc., Post-Graduate Student	Researcher	M
Savolainen Pekka	Ph.D.	Researcher	M
Toikkanen Lauri	M.Sc., Post-Graduate Student	Researcher	M
Toivonen Mika	Ph.D.	Researcher	M
Tukiainen Antti	M.Sc., Post-Graduate student	Researcher	M
Turpeinen Jani	M.Sc.	Researcher	M
Uusimaa Petteri	Ph.D.	Researcher	M
Wartak Marek	Professor	Researcher	M
Vilokkinen Ville	M.Sc.	Researcher	M
Xiang Ning	Ph.D.	Senior Researcher	M

HUT-1. Research Staff of Helsinki University of Technology. Total person-months of work funded by Academy of Finland: 70.

Name	Degree	Job Title	Sex
Hautojärvi Pekka	**Professor**	**P.I. of HUT-1**	**M**
Aavikko Reino	Undergraduate Student	Research Assistant	M
Arpiainen Sanna	M.Sc.	Researcher	F
Hassel Juha	Undergraduate Student	Research Assistant	M
Havukainen Eeva-R.	Undergraduate Student	Research Assistant	F
Jääskeläinen Juha	FM	Researcher	F
Kauppinen Hannu	Ph.D.	Researcher	M
Kivioja Jani	Undergraduate Student	Research Assistant	M
Laakso Antti	M.Sc.	Researcher	M
Laine Tatu	Ph.D.	Researcher	M
Nissilä Jaani	M.Sc.	Researcher	M
Oila Juha	M.Sc.	Researcher	M
Pelli Antti	Undergraduate Student	Research Assistant	M
Ranki Ville	Undergraduate Student	Research Assistant	M
Seppälä Pekka	Undergraduate Student	Research Assistant	M
Sihto Sanna-Liisa	Undergraduate Student	Research Assistant	M
Storgås Jan	Undergraduate Student	Research Assistant	M
Tahvanainen Kaarlo		Mechanician	M
Väisänen Jaakko	Undergraduate Student	Research Assistant	M

HUT-2. Research Staff of Helsinki University of Technology. Total person-months of work funded by Academy of Finland: 106.

Name	Degree	Job Title	Sex
Nieminen Risto	**Professor**	**P.I. of HUT-2**	**M**
Astala Roope	M.Sc.	Researcher	M
Herrgård Markus	M.Sc.	Researcher	M
Jääskeläinen Anna	M.Sc.	Researcher	F
Kaukonen Markus	Ph.D.	Researcher	M
Lee Young-Joo	Ph.D.	Researcher	M
Lento Juha	M.Sc.	Researcher	M
Mattila Tomi	Ph.D.	Researcher	M
Pesola Marko	Ph.D.	Researcher	M
Pöykkö Sami	Ph.D.	Researcher	M
Sammalkorpi Ville	M.Sc.	Researcher	M

UH. Research Staff of University of Helsinki. Total person-months of work funded by Academy of Finland: 78.

Name	Degree	Job Title	Sex
Räisänen Jyrki	**Professor**	**P.I. of UH**	**M**
Ahlgren Tommy	Ph.D.	Researcher	M
Keinonen Juhani	Professor	*Researcher*	M
Nurmeal Arto	Ph.D.	Researcher	M
Pusa Petteri	M.Sc.	Researcher	M
Rajatora Marko	M.Sc.	Researcher	M
Rauhala Eero	Ph.D.	Researcher	M
Rydman Walter	Undergraduate Student	Research Assistant	M
Salonen Reeta	M.Sc.	Researcher	F
Seppälä Anni	Ph.D.	Researcher	F
Slotte Joonatan	Ph.D.	Researcher	M
Väkeväinen Kyösti	Ph.D.	Researcher	M

VTT. Research Staff of VTT Chemical Technology. Total person-months of work funded by Academy of Finland: 20.

Name	Degree	Job Title	Sex
Likonen Jari	**Ph.D.**	**P.I. of VTT**	**M**
Ahlgren Tommy	Ph.D.	Researcher	M
Lehto Sari	Lic. Tech.	Researcher	F

2 Funding

Breakdown of funding of *EPI-2* in FIM in 1997-99. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland is also shown in the Table.

Partner	Funding Organisation	1997	1998	1999	Total (FIM)
TUT	Academy	1.104.090	1.106.800	1.109.046	3.319.936
	TUT	540.000	560.000	580.000	1.680.000
HUT-1	Academy	447.000	643.800	698.500	1.789.300
	HUT-1	420.000	300.000	300.000	1.020.000
HUT-2	Academy	571.200	566.300	569.500	1.707.000
	HUT-2	520.000	540.000	580.000	1.640.000
UH	Academy	338.000	294.998	421.840	1.054.828
	UH	777.000	737.000	1.012.000	2.526.000
VTT	Academy	130.400	130.700	138.900	400.000
	VTT	200.000	198.000	77.000	475.000
Total		**5.047.690**	**5.077.588**	**5.486.786**	**15.612.064**

3 International co-operation within EPI-2

3.1 Participation in International Research Projects

Partner	*Project*
TUT	EU Esprit 22477 BLUES Blue European Semiconductor Laser
TUT	EU Esprit 24997 SMILED Semiconductor Microcavity Light Emitting Diodes
TUT	READY 1&2 Research and development of red laser diodes for the wavelength of 630 and 650 nm by solid-source MBE
HUT-2	EU TMR Network CT-98-0178 Electronic Structure Calculations of Materials Properties for Industry and Basic Science
HUT-2	COST Action P3 Simulation of Physical Phenomena in Technological Applications
HUT-2	ESF-PESC Programme Electronic Structure Calculations Elucidating the Complex Atomistic Behaviour of Solids and Surfaces

3.2 Foreign Visiting Researchers (minimum stay of one month)

Partner	Visitor	From Country of	Duration
TUT	*Kusrayev Yuri, Ph.D.*	Russia, IOFFE Inst.	May 1997
TUT	Cooper Graig, Ph.D.	U.K., Univ. Wales Cardiff	May 1997
TUT	Dahl Siegrid, Student	Canada, Polytech. Montréal	02.06.-15.08.1997
TUT	McCotter Daimien, Student	Canada, Queen´s Univ.	15.06.-15.09.1998
TUT	Beatriz Rosero Herrera, M.Sc.	Spain, Univ. Politecn. Madrid	September 1998
TUT	Renee Diehl, Ph.D.	USA, Pennsylvania Univ.	29.12.98–19.2.1999
TUT	Barnes Colin, Ph.D.	Ireland, Dublin City Univ.	03.05.-15.08.1999
TUT	Ladstädter Florian, Student	Austria, Karl-Franzens Univ.	28.06.-19.09.1999
TUT	Scholz Stefan, Ph.D.	Germany, DLR	01.08.-31.12.1999
TUT	Okhotnikov Oleg, Ph.D., Prof.	Portugal, Univ. do Porto	August 1999
TUT	Rangel Kuoppa Victor M.Sc.	Mexico, Inst. Politecnico	20.08.1999 -
HUT-1	Desgardin Pierre, Ph.D.	France, C.N.R.S.	9 months 1997-98
HUT-1	Laurent Henry, Ph.D.	France, C.N.R.S.	9 months 1998
HUT-2	Mozos Jose-Luis, Ph.D.	Spain, Univ. Barcelona	15.09.97 – 30.8.00
HUT-2	Lee Young-Joo, Ph.D.	Korea, KAIST	01.03.1999 -
HUT-2	Staab Torsten, Ph.D.	Germany, Univ. Halle	01.05.1998 -

3.3 Visits of Partner´s Researchers (Minimum stay of one month)

Partner	Visitor	To Country of	Duration
HUT-1	Oila Juha	Holland, Delft Univ. of Techn.	2 months 1998
HUT-2	Jääskeläinen Anna	Italy, Politecnico Milan	01.01.98 - 30.06.1998
HUT-2	Kaukonen Markus	UK, Univ. Exeter	01.08.99 - 31.03.2001
HUT-2	Astala Roope	UK, Univ. Cambridge	01.11.99 -

4 Academic degrees received within EPI-2

Altogether 13 Doctoral and 27 Master Theses were received by students who worked full-time or part-time in *EPI-2*

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Partner	Degree	Sex	Name	Year
TUT	Ph.D.	M	Toivonen Mika	1997
TUT	Ph.D.	M	Savolainen Pekka	1999
TUT	Ph.D.	M	Uusimaa Petteri	1999
TUT	M.Sc.	M	Toikkanen Lauri	1997
TUT	M.Sc.	M	Aho Riku	1998
TUT	M.Sc.	M	Köngäs Jukka	1998
TUT	M.Sc.	M	Mäkelä Timo	1998
TUT	M.Sc.	F	Kuuslahti Tiina	1999
TUT	M.Sc.	M	Orsila Seppo	1999
TUT	M.Sc.	M	Saarinen Mika	1999
TUT	M.Sc.	M	Sipilä Pekko	1999
TUT	M.Sc.	M	Laaksonen Sami	2000
TUT	M.Sc.	M	Laukkanen Pekka	2000
TUT	M.Sc.	M	Rinta-Möykky Ari	2000
TUT	M.Sc.	M	Tukiainen Antti	2000
TUT	M.Sc.	M	Turpeinen Jani	2000
TUT	M.Sc.	M	Vilokkinen Ville	2000
HUT-1	Ph.D.	M	Laine Tatu	1997
HUT-1	Ph.D.	M	Kauppinen Hannu	1998
HUT-1	M.Sc.	M	Oila Juha	1998
HUT-1	M.Sc.	M	Väisänen Hannu	1998
HUT-1	M.Sc.	M	Kivioja Jani	2000
HUT-1	M.Sc.	M	Ranki Ville	2000
HUT-2	Ph.D.	M	Mattila Tomi	1997
HUT-2	Ph.D.	M	Pöykkö Sami	1998
HUT-2	Ph.D.	M	Kaukonen Markus	1999
HUT-2	Ph.D.	M	Pesola Marko	2000
HUT-2	M.Sc.	M	Lento Juha	1997
HUT-2	M.Sc.	M	Herrgård Markus	1998
HUT-2	M.Sc.	F	Jääskeläinen Anna	1999
HUT-2	M.Sc.	M	Astala Roope	1999
HUT-2	M.Sc.	M	Sammalkorpi Ville	1999
UH	Ph.D.	M	Väkeväinen Kyösti	1997
UH	Ph.D.	M	Ahlgren Tommy	1998
UH	Ph.D.	M	Slotte Jonatan	1999
UH	Ph.D.	F	Vainonen-Ahlgren Elizaveta	2000
UH	M.Sc.	M	Nurmela Arto	1997
UH	M.Sc.	F	Salonen Reeta	1997
UH	M.Sc.	F	Seppälä Anni	1997
UH	M.Sc.	M	Pusa Petteri	1999

5 Statistics of publications and academic degrees

Publications and academic degrees (from Section 4), broken by Partners. The list of the refereed journal articles and conference papers are given in Section 9.

Partner	Type of Publicatin	1997	1998	1999	2000	Total
Inter-partner	9.1.1 Ref. journal articles	3	3	7	6	19
Publications	9.1.2 Ref. conference papers	3	1	1	1	6
Independent Publications						
TUT	9.2.1 Ref. journal articles	1	8	4	2	15
	9.2.2 Invited conference papers	1	2			3
	9.2.3 Ref. conference papers	1		1		2
	Doctoral dissertations	1		2		3
	Master degrees	1	3	4	6	14
	Patents / patent applications	1				1
HUT-1	9.2.1 Ref. journal articles	2	4	3	5	14
	9.2.2 Invited conference papers					
	9.2.3 Ref. conference papers	2		2		4
	Doctoral dissertations	1	1			2
	Master degrees		2		2	4
HUT-2	9.2.1 Ref. journal articles	5	7	8	2	22
	9.2.2 Invited conference papers	1	1	2		4
	9.2.3 Ref. conference papers	3	1	1		5
	Doctoral dissertations	1	1	1	1	4
	Master degrees	1	1	3		5
UH	9.2.1 Ref. journal articles	3	6	2	1	12
	9.2.3 Ref. conference papers	2	1	2		5
	Doctoral dissertations	1	1	1	1	4
	Master degrees	3			1	4
VTT	Inter-partner Publications only: 11 refereed journal articles 4 refereed conference Papers					
TOTAL		**37**	**43**	**44**	**28**	**152**

6 Awards, prizes, scientific honours

Markus Pessa: 1999 *Honorable mentioning* of education and training post-graduates, awarded by the Tampere University of Technology

Markus Pessa: 1998 *Professor of the Year*, awarded by the Union of University Professors in Finland

Tomi Mattila: 1998 *Best Contributed paper by a Young Researcher*, 20th International Conference on Defects in Semiconductors, Aveiro, Portugal, 1998

7 Research work

7.1 Recap of Aims and Objectives and Their Realisation

The aim of *EPI-2* was to provide deep insight into the physics and technology of epitaxial semiconductors, and produce results that would have potential applications upon completion of the project.

The objectives were

(i) Grow and optimise wide-band-gap $Ga_xIn_yAl_{1-x-y}(As)P$ semiconductors using a solid-source molecular beam epitaxy (SS-MBE) method

(ii) Develop an MBE compatible method for doping ZnSe

(iii) Develop an MBE compatible method for growth of GaN-based alloys

(iv) Improve the understanding of defects, impurity doping, diffusion, and surface and interface structures of compound semiconductors

(v) Optimise and grow quantum-well device structures for green ZnSe-based and red AlGaInP-based laser diodes

(vi) Optimise and grow quantum-well structures for blue GaN LEDs

(vii) Prepare state-of-the-art lasers and LEDs and assess their performance characteristics

The methodology used to achieve the objectives was a definition of five technical workpackages, each including a number of Tasks.[1] These workpackages naturally fit the objectives, and they were further divided into Tasks.

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[1] Project Proposal, May 1996

WP1	Novel aspects of growth and doping of wide-gap semiconductors
WP2	Physics of wide-gap semiconductors and growth of layered structures
WP3	Characterisations of materials
WP4	Theory and modelling of semiconductor materials and devices
WP5	Fabrication and assessment of visible-light lasers and LEDs.

7.2 Overview

The workparts were carried out quite rigorously. The overall co-ordination of *EPI-2* ensured that the project ran smoothly, reviewed the targets and handled changes in the technical parts. The co-operation between the partners was useful, since a large part of the project was truly new and had strategic potential for many applications, which would require concentrated efforts. *EPI-2* had, indeed, the mechanism in use to control the project and what changes were necessary, disseminate the information obtained, and quickly assess its scientific or technological importance at each stage of the research.

The Consortium held five review meetings: June 1997, October 1997, March 1998, March 1999 and September 1999. Workshops on particular problems were held frequently.

Two major changes were made. First, we ceased the development of ZnSe lasers and leveraged the relieved growth capabilities to introduce wide-band-gap GaN. This was necessary because optical degradation of the "soft" ZnSe lasers appeared inevitable. Degradation analyses showed that the basic problem arose from heteropolar lattice-mismatched nucleation of ZnSe on GaAs,[1] leading to threading dislocations and other defects that deteriorated the active region when biased. Another problem was a difficulty to achieve a high enough *p*-type doping to produce stable low-resistivity ohmic contacts. Second, the Consortium had to ramp up MBE capacity to cope with explosive demand for $Ga_xIn_yAl_{1-x-y}As_zP_{1-z}$ wafers. Funds for purchasing a new reactor were raised (Euro 800,000), and an all-solid-source MBE system was acquired. Later, this system proved indispensable for the preparation of complex devices with vertical architecture as well as high-power edge-emitting lasers.

7.3 Summary of Highlights

7.3.1 Theoretical and Computational Efforts

Theoretical, computational, and experimental work on physical properties of semiconductors, notably heterostructures, provided a deep understanding of the MBE method, the nature and formation of defects, the doping, and the electrical compensation.

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[1] G. Kiriakidis *et al.*, Thin Solid Films 360, 195 (2000)

Extensive modelling of the electronic and atomic structures of the compound semiconductors and Si and SiC was performed by first-principles calculations. Most accurate ground-state calculations were made using a major electronic structure code, *Finger*, [1] based on plane-wave-pseudopotential techniques within the density-functional theory. Large supercells, containing up to 512 atoms, could be employed together with ultra-soft pseudopotentials. This work (corresponding to WP 2 and WP 4) made it possible to interpret in many cases quantitatively the results of experimental observations.

Photon confinement in planar microcavities was studied within the framework of the cavity quantum electrodynamics and by experimentation (WP 2). To design microcavity optical sources – RC-LEDs and VCSELs – several modelling tools were applied, making use of radiation-enhanced quantum confinement effects. The electrical properties of vertical emitters were explored using a commercial software code, *Lastip / Pics3d.* The results were exploited by demonstrating groundbreaking operational performances of resonant cavity red light emitting diodes and preliminary VCSELs.

7.3.2 Joint Efforts to Use Multiple Characterisation Methods

Crucial for conclusive results on structural defects and doping properties was the use of powerful spectroscopic methods (WP 2 and WP 3): the positron annihilation spectroscopy,[2] Rutherford backscattering (RBS) and elastic recoil analyses,[3] particle x-ray emission measurements (PIXE) and nuclear resonance broadening (NBR) ion beam techniques combined with channelling measurements,[4] and the secondary ion mass spectrometry (SIMS).[5] Other methods to be mentioned here were the scanning electron microscopy (SEM), photoluminescence (PL), Hall-effect measurement method, and high-precision X-ray diffraction (XRD).

7.3.3 Growth Methods Used for preparing ZnSe- and GaN-based Semiconductors

Growth and doping of II-VI semiconductors (WP 1) by molecular beam epitaxy (MBE) concerned with ZnSe, ZnS_xSe_{1-x}, $Cd_yZn_{1-y}Se$, $Mg_zZn_{1-z}S_{z'}Se_{1-z'}$, and $Mn_zZn_{1-z}S_{z'}Se_{-z'}$. These compounds were building blocks for green LEDs and lasers.

Another wide-gap compound of interest was GaN. This and related materials were prepared by MBE at TUT and by MOCVD in the University of Warsaw, CNRS

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[1] R.M. Nieminen, Current Opinion in Solid State and Materials Science 4, 493 (1999)

[2] K. Saarinen *et al*, in *Semiconductors and Semimetals* (ed. M. Stavola) 51 A, Academic Press, New York, 1998, pp. 209-285

[3] T. Ahlgren, Phys. Rev. Lett. 81, 842 (1998)

[4] E. Rauhala *et al.*, J. Appl. Phys. 83, 738 (1998)

[5] J. Oila *et al.*, Phys. Rev. B 59, R12736 (1999)

Valbonne and the University of Montpellier. In addition, some bulk GaN samples were available from Unipress Ltd., Warsaw.

7.3.4 ZnSe and Related Compounds

In ZnSe-on-GaAs, the stacking-fault density as low as 1×10^4 cm^{-2} was demonstrated, which was remarkably lower than a stacking-fault density often reported in the literature. This was achieved by depositing a GaAs buffer layer onto a GaAs substrate, prior to growth of ZnSe, in a twin-MBE system equipped with separate III-V and II-VI growth chambers and an intermediate chamber, which allowed transferring the samples from one chamber to another without exposing into air thus avoiding surface contamination. Migration enhanced epitaxy (MEE) growth of ZnSe on GaAs further improved a quality of the heterointerfaces. The GaAs surface exposed to 5-20 cycles of Zn and Se pulses in MEE mode of operation significantly improved the subsequent layers of ZnSe and ZnSSe which were grown by ordinary MBE. The MEE resembled a vacuum atomic layer epitaxy (ALE),[1] but because it was not a self-regulatory process a careful control of the duration and intensity of molecular beams was necessary.

The highest *p*-doping level obtained was 1×10^{18} cm^{-3} (with nitrogen, the best *p*-type dopant), representing the state-of-the-art. The novelty in this case was to employ MEE for growth of the topmost atomic layers of ZnSe to maximise the carrier concentration. Mastering the MEE enabled δ-doping of a sub-lattice digitally – one layer at the time.

Studies of MBE-grown *p*-ZnSe:N by the low-energy positron annihilation spectroscopy and SIMS and ECV experiments revealed that only 20-40 % of all N atoms were electrically active N_{Se}^- acceptors at relatively low concentration [N]. The rest of nitrogen formed negative $V_{Se}N_{Se}$ pairs or positive defect complexes. With increased [N] the compensation became even more pronounced. Typically, 10 % of N were active when [N] $\approx 10^{19}$ cm^{-3} in ZnSe. No problem was found in *n*-type doping with chlorine.

The top *p*-metal contacts were Te/Pd/Pt/Au, fabricated by e-beam evaporation. Using RBS together with the atomic force microscopy the diffusion of metals into ZnSe could be determined. It turned out that annealing the samples caused only minor changes in depth profiles of Au, but tended to form Au grains on the surface. Channelling experiments[2] showed that about 30 % of diffused Au were close to substitutional sites in ZnSe with an average displacement of 0.2 Å. For Pt, no specific lattice site was observed. SIMS showed that for as-grown samples Pd diffused into ZnSe far deeper than other metals. When the samples were annealed, Pd and Te diffused outwards into the Au layer through the Pt layer, but the depth profiles of Au and Pt remained quite unchanged.

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[1] C.H.L: Goodman and M. Pessa, J. Appl. Phys. 60, R65-R81 (1986)

[2] A. Seppälä *et al*, Nucl. Instr. & Meth. B 161, 673 (2000)

Despite the problems of the defect density and the low *p*-type doping level it was possible to process green lasers, which emitted at around 570 nm. The lifetimes were short, 30 seconds or so, when the devices were operated in *cw* mode at room temperature – an achievement in Europe at that time, though.

7.3.5 GaN and Related Compounds

GaN samples were mainly grown by MBE on GaN / sapphire templates. MOCVD GaN samples grown abroad were also investigated. The MBE samples could be doped *n*-type (Si) and *p*-type (Mg) up to $n = 7 \times 10^{19}$ cm^{-3} and $p = 3 \times 10^{18}$ cm^{-3}.

Although the band-gap of GaN is on the UV, broad yellow emission centred at 550 nm may be intensive, depending on the growth method and conditions. Yellow emission was generally attributed to the presence of Ga vacancies,[1] [2] [3] [4] but whether they were in the form of vacancy clusters or paired complexes, $V_{Ga} - O_N$, $V_{Ga} - Si_{Ga}$, could not be solved. Experiments revealed that when GaN was *p*-doped and deposited onto GaN / sapphire templates at high temperature (> 800 °C) by MBE under slightly Ga-rich growth conditions, yellow emission was almost undetectable. Positron annihilation experiments found no Ga vacancies in these samples above the sensitivity limit of 10^{16} cm^{-3} of this technique, while a vacancy concentration up to 1×10^{18} cm^{-3} was measured for undoped and *n*-type samples. SIMS indicated that all the samples contained some oxygen, on an order of 5×10^{17} cm^{-3}, likely due to a gradual dissociation of sapphire and diffusion of relieved oxygen from the substrate into nitride.[5] At low growth temperatures (< 800 °C) resulting in poorer crystal structures, yellow emission always appeared concomitant with an increase in oxygen level (according to SIMS), suggesting that yellow emission was associated with the presence of oxygen and Ga vacancies. It was also found that using an indium surfactant, i.e., a floating indium layer on the growing front, band-edge emission improved significantly even at low growth temperature with respect to yellow emission. The improvement in layer quality was assigned to enhanced migration of incident Ga atoms and, hence, to a likely reduction in Ga vacancies. Positron measurements on undoped MOCVD GaN (on Si substrates) revealed a large number of Ga vacancies, $10^{17} - 10^{18}$ cm^{-3}, while PL of this sample exhibited a strong yellow band. Heavily *p*- doped (Mg) MOCVD-grown samples showed reduced Ga vacancies.

Work on multiple quantum wells and double heterostructures containing GaInN and GaN led to demonstrations of blue MQW LEDs and DH LEDs (WP) at the

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[1] T. Mattila and R.M. Nieminen, Phys. Rev. B 55,9571 (1997)

[2] Ch. Manz *et al.* Appl. Phys. Lett. 74, 3993 (1999)

[3] U. Kaufman *et al.¸Phys. Rev. b 59, 5561 (1999)*

[4] J. Oila *et al.*, Phys. Rev B 63, 45205 (1999)

[5] J.E. Van Nostrand, *et al.* J. Appl. Phys. 87, 8766 (2000)

wavelengths of 447 and 472 nm, respectively. The maximum light power obtained was about 0.2 mW.

7.3.6 $Ga_xIn_yAl_{1-x-y}As_zP_{1-z}$

A choice of MBE growth parameters (WP 1) is always a multi-variable optimisation problem. A countless number of growths with different nucleation parameters were carried out to find out a trade-off choice for the variables. Quite an accurate control of growth was obtained for generic $Ga_xIn_yAl_{1-x-y}As_zP_{1-z}$ compounds, either lattice-matched or mismatched to GaAs or InP substrates. In this research, diffusion of the dopants Si and Be was also considered. Diffusion of Be appeared to be concentration-dependent, and post-growth annealing strongly affected the depth profile resulting in diffusion down to 200 nm in GaAs. Diffusion of Si had two components, namely, the concentration-dependent and concentration-independent ones,[1] and the diffusion length was short compared to that of Be.

7.3.7 $Ga_xIn_yAl_{1-x-y}As_zP_{1-z}$ –based Devices

EPI-2 greatly improved the understanding of the physics of complex heterostructures and helped develop state-of-the-art light emitters (WP 5). Undoubtedly, the main achievement was a demonstration of the viability of monolithic microcavity / DBR structures as planar ultra-high-efficiency light sources. Operation up to 85 °C and a 622 Mbit/s error-free data transmission in a 1-metre long polymer optical fibre (POF) was demonstrated at an optimal wavelength of 650 nm where POF has a local attenuation minimum. A peak quantum efficiency of 9.5 %, close to the theoretical limit of about 11 %, and the light power up to 15 mW were obtained. This quantum efficiency was much higher than 2 %, typical of a conventional planar GaAs LED. Another important result was a demonstration of 650-670 nm edge-emitting lasers launching record-high 3 W *cw* output. The threshold current density was 400 A/cm^2, the T_0 value was 110 K, and the slope efficiency was 0.58 W/A per facet.

7.3.8 Education and Training of Researchers

EPI-2 offered a useful training period for students and researchers in the semiconductor physics, technology, and metrology. 26 students received MA Degrees and 14 PhD Degrees, and altogether 101 scientific papers were published. Upon completion of the project, a number of researchers who acquired their expertise in *EPI-2* moved to industry providing an efficient route to commercialisation of the strategically important ideas and results.

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[1] T. Ahlgren *et al.*, Phys. rev. B 56, 4597 (1997)

7.3.9 Take-up of Results by Industry

EPI-2 played a seminal role in the establishment of a spin-off company (year 2000), which now manufactures epitaxial semiconductor wafers and devices. Furthermore, the development of RC-LEDs in this and other projects gave birth to yet another company (2001), which plans to commercialise RC-LEDs and VCSELs. These companies are exploiting the SS-MBE-based $Ga_xIn_yAl_{1-x-y}As_zP_{1-z}$ technology. Several other companies, domestic and foreign, are working in co-operation with ORC. Such a take-up of results by industry was an outstanding achievement in our views and totally unforeseeable in the beginning of *EPI-2*.

HUT-2 participated in the software development of first-principles electronic structure codes, which have been commercialised by several companies and which are being widely used in industry. HUT-2 also contributed to the *Castep* code distributed by Molecular Simulations Inc., and to the *Wien97* code and to the *Vasp* code. The latter is now distributed by Materials Design srl.

HUT-2's modelling work on silicon crystal growth and processing is currently being utilised by Okmetic Ltd., a leading European silicon wafer manufacturer.

7.3.10 Establishment of A New Research Institute

The results of *EPI-2*, on their part, urged upon politicians the necessity of founding a new research centre in Finland, ORC (1999). Today, ORC is working on epitaxial III-V semiconductors, optoelectronics, and optical fibre communications.

Judging from the results summarised in Sections 7.3.1 - 7.3.10 we may suggest that the objectives of *EPI-2* have been reached in all major fields of interest.

8 Partners actions

8.1 Progress Report: TUT

8.1.1 Layer growth and doping by SS-MBE and MBE

ORC contributed to the development of SS-MBE for phosphides. SS-MBE is now matured to the point where commercial interest is very high. It has displaced the former gas-source MBE and challenges MOCVD to grow phosphides with complex heterostructures. On the other hand, it may not be the most favorite method for preparing simple structures because of its slow growth rate and high investment costs.

Be and Si have become established in use as *p*- and *n*-type dopants for $Ga_xIn_yAl_{1-x-y}As_zP_{1-z}$. (Amphoteric) carbon was not attempted, due to limited resources available.

ORC also studied ZnSe and GaN. To produce nitrogen for these materials, i.e., doping ZnSe *p*-type and growing GaN, nitrogen *rf*-plasma sources were applied. Cl and Si were the *n*-dopants for ZnSe and GaN, respectively, and Mg was a *p*-dopant for GaN. Though the preparing of reasonable material quality was feasible, and the light emitters of $Zn_xMg_{1-x}S_ySe_{x1-y}$ / $Zn_xCd_{1-x}Se$ / ZnSe (green)[1] and $Ga_xIn_{1-x}N$ / GaN (blue)[2] were demonstrated, it turned out that ZnSe as a “soft” ionic compound could hardly be used to make robust light emitters by any technique. GaN LEDs, on the other hand, do not suit the MBE technology for many reasons. To achieve high-quality GaN, no matter what substrate would be used, one should grow it at high temperatures, over 1000 °C, which is very hard to be realized by any modification of MBE. Furthermore, the Ga-to-N ratio must be kept close to 1:1 for hours and do it repeatedly from one growth to another at 1000 °C, suggesting a huge consumption of Ga and In and rapid precipitation of these metals all over the deposition chamber. Also, the growth rate of MBE-GaN decreased rapidly when the growth temperature was increased over 850 °C. Our experiments indicated that MBE growth of GaN LEDs and lasers to an optically and electrically device-graded quality in a competitive way is almost impossible.

8.1.2 Device modelling and simulations

To design and optimise light sources with microcavity concepts, i.e., RC-LEDs and VCSELs, ORC employed various modelling and simulation tools. Most of the tools were developed at ORC. The modelling and simulation were mainly based on the transfer matrix method. We also applied commercially available software codes, *Lastip / Pics3d*, to analyse electrical properties of the devices. This computational work yielded information that was useful for optimisation of the device parameters as follows.

- Reflectivity analysis used for determining the reflectivity dependence on layer contrast (i.e., material composition), layer thickness, a number of periods of layers for DBR mirrors to achieve desired reflectivity, and the optical field wavelength for stopband investigations
- Determination of spectral and angular positions and extension of the cavity mode, enabling the analysis of the cavity mode / quantum well resonance and guiding a choice of cavity detuning
- Determination of the optical field distribution inside the devices, enabling the analysis of QW coupling to the optical field and optimisation of the doping profile.
- Determination of the angular far field profile, enabling studies of the extraction efficiency and light coupling efficiency into an optical fibre.

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[1] Green ZnSe laser diodes operating at room temperature in *cw* mode had short lifetimes, not more than 30 seconds – although this was an achievement in Europe at that time (1997-98).

[2] Blue GaInN / GaN MQW- and DH-LEDs were made. The turn-on voltage was little over 3 V, and the maximum output was 0.2 mW.

8.1.3 RC-LEDs and VCSELs

The main achievement in the device physics of WP 5 was the demonstration of a resonant microcavity concept for spontaneous emission. An RC-LED operating at 650 nm was prepared and analysed.[1] This work received a world-wide attention. For example, *Opto & Laser Europe* *83, 2001,* wrote a cover story of our RC-LEDs entitled "The Best of Both Worlds". Europe is one step ahead of Asia and the US when it comes to developing high-speed spontaneous light sources, but warned, justifiably, that Europe must work hard to keep its lead, or countries like Taiwan, which has expertise in LED production, will take this lead from us.

The monolithic RC-LEDs had usually a cosine-type 1-λ cavity, containing multiple quantum wells centred at the antinode of an F-P mode for the best exciton / cavity coupling. Cavity detuning was designed to maximise the extraction efficiency and light output. Due to strong commercial interest in this area, ORC considers some elements of design to be a background material not accessible to the public. Hence, we are forced to refrain from disclosing all information in this Report.

Resonant-cavity LED at 650 nm shining bright and exhibiting a record signal modulation speed of over 300 MHz. Courtesy: ORC / TUT

Another challenging task was to develop high-power red edge-emitting lasers. This work hinged on successful device design and good control over growth and processing. A variety of lasers were calculated and tested in attempts to determine the most viable solutions for the beam aspect ratio, differential external quantum efficiency, optical field confinement, and many other features. The lasers operating at 630 – 670 nm were investigated. The output power of 3 W *cw* and the differential quantum efficiency up to 0.58 W/A per facet were demonstrated for broad-area single oxide-stripe chips.

Other devices made by ORC were green (570 – 580 nm) ZnSe lasers and blue (450 – 470 nm) GaInN / GaN MQW and DH LEDs. ZnSe lasers operated for 30 seconds at room temperature in *cw* mode, launching an output of about 0.5 mW. The GaN LEDs launched a 0.2-mW output.

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[1] Several research projects were performed at the same time to collect expertise available in the principles of RC-LEDs, one of them was *EPI-2* that contributed to the materials research and understanding of the device theory.

8.2 Progress report: HUT-1

Materials of major interest in this project and the EPI-2 consortium have been ZnSe and GaN. They both are wide-band-gap semiconductors and thus potential for blue-green light emitting devices. They are, however, difficult to grow and dope. We have applied positron spectroscopy to characterise ZnSe, GaN, GaAs, Si, and CdF2 materials and to study their defect and doping properties.

Crucial for conclusive results has been the use of SIMS by the VTT group. During the period of this project the SIMS was calibrated for quantitative analysis of various dopant impurities in GaN. Reference samples for SIMS experiments were prepared by the UH group, using their ion beam techniques.

8.2.1 Vacancies and compensation in ZnSSe layers

Fundamental problems exist in the doping: ZnSe can be easily doped *n*-type, e.g., by Cl impurities, but the fabrication of *p*-type material is difficult. With nitrogen doping the active acceptor concentration saturates at about 10^{18} cm^{-3}, although more than 10^{19} cm^{-3} N atoms have been incorporated during the growth.

We have applied a new approach to study the electrical compensation of ZnS_xSe_{1-x}:N by combining the results of SIMS, ECV, and positron annihilation experiments. By using the negative vacancy and the negative ion concentrations calculated from positron data and the total nitrogen and the hole concentrations from SIMS and ECV experiments, we have estimated the concentrations of various nitrogen related defects in ZnS_xSe_{1-x}. As a result, we conclude that only 20 - 40 % of all nitrogen atoms are situated as electrically active isolated N_{Se}^- acceptors. The rest of the N impurities are situated in negative $V_{Se}N_{Se}$ pairs or in positive defect complexes. In some samples the majority of N atoms occur in electrically neutral form.

8.2.2 Vacancy defects in GaN

Bulk GaN crystals grown in UNIPRESS in Warsaw under 1.5 GPa nitrogen pressure at 1,500 °C have been studied by positron lifetime and Doppler broadening techniques. The undoped *n*-type crystals contain Ga vacancies in the range of 10^{18} cm^{-3}. In lightly Mg-doped crystals, the Ga vacancies are still observed but at reduced concentration. Heavily Mg-doped semi-insulating crystals show no signal of vacancies indicating that their concentration is less than 10^{16} cm^{-3}. Combination of positron and SIMS results indicates that Mg atoms are at negative charge state. The compensation is due to the interplay between the Mg acceptors and O impurities acting as shallow donors.

Epitaxial layers grown by MOCVD on sapphire substrates in the University of Warsaw, CNRS Valbonne, and University of Montpellier have been characterised by a low-energy positron beam. The results show that Ga vacancies are present at concentrations of 10^{17} - 10^{18} cm^{-3} in undoped n-type layers. Their concentration correlates with the intensity of the yellow luminescence and with the V/III molar ratio. On the other hand, the layers grown in oxygen-free condition by MBE on Si(111) do not show Ga vacancies nor the yellow luminescence.

The experimental findings can be understood in the light of theory. The calculations suggest that Ga vacancies and V_{Ga}-oxygen pairs are the most abundant native defects in highly n-type material and that the acceptor levels of the Ga vacancy are involved in the yellow luminescence transition.

8.3 Progress Report: HUT-2

The mission of HUT-2 within EPI-2 has been to carry out extensive modelling work for several physical problems encountered in the growth, processing and characterisation of novel semiconductor materials and structures. In particular, we have performed first-principles calculations for the electronic and atomic structures of compound and elemental semiconductors, using large-scale, state-of the-art methods. Much of the work has focussed on the questions related to the role of native defects and unintentional impurities in the doping of III-V and II-VI compounds. We have worked in close collaboration with the experimental groups and provided theoretical and computational support in the identification of atomistic defects and their reactions.

The problems of special interest have been

- atomistic structures and band offsets at III-V/II-VI interfaces
- factors contributing to the doping limits of compound semiconductors (solubilities, self-compensation, background defects and complexes)
- self-diffusion mechanisms in compound semiconductors
- analysis of positron-lineshape and lifetime experiments in the identification of defects and decorated complexes
- metastable defects
- defect dynamics and vibrational spectra
- the role of defect complexes in unwanted broadband luminescence
- annealing kinetics of defect complexes during processing (in particular, oxygen clustering in silicon)

Within the project, we have extensively used and developed a major electronic structure code, FINGER, for accurate ground-state calculations. This code uses plane-wave-pseudopotential techniques within the density-functional theory. Large supercells can be used together with ultra-soft pseudopotentials. The code is fully parallelized (at the Fast-Fourier-Transform level) for the Cray T3E, and can thus run extremely effectively. This enables calculations with supercells containing up to 512 atoms. Moreover, we have developed and implemented new methods to surpass the limitations of the local-density-approximation (LDA), which can be severe in the gap region of semiconductors. Specifically, we have implemented the screened-exchange method, which does provide accurate values for the band gap and localised states within the gap.

We have developed new methods for calculating the line shapes of annihilation radiation from positrons trapped in lattice defects. These line shapes can be measured accurately with the coincidence technique over a large energy (momentum) scale, and reveal detailed information of the defect and its atomistic composition. The computational methods are indispensable for proper analysis of experimental results.

We have also performed extensive molecular-dynamics simulations using both first-principles interatomic forces and more approximate tight-binding methods. The dynamical simulations have elucidated both the growth mechanisms and the microscopic dynamics of complexes. The latter can be correlated with vibrational spectra.

The following specific systems have been studied within EPI-2 (see also the publications listed below):

- Structures and band offsets in GaAs/ZnSe interfaces, including the alloying effects of both sides of the junction
- Doping of ZnSe with Cl and Zn (complexes and compensation)
- Divacancies and self-diffusion in GaAs
- Native defects in SiC (vacancies and antisites)
- Defect complexes and broadband luminescence in GaN and AlN
- Oxygen complexes and their annealing kinetics in Si and GaAs.

8.4 Progress Report: UH

8.4.1 Diffusion of atoms in semiconductors

The diffusion studies have been related to (a) metals suitable for preparing ohmic contacts and (b) elements used as dopant atoms. In these studies the interest has been focused on the ZnSe material.

Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) are very important tools for depth profiling in semiconductor physics. Therefore, the development of the methods is essential. It is well known that surface roughness can make the interpretation of RBS spectra difficult. For example, in studies of diffusion in thin films, the annealing often causes grain formation on the sample surface. The changes in the surface topography can cause diffusion-like broadening of RBS spectra.

A method for determining correct depth profiles from samples with rough surfaces has been devised. The method combines RBS with atomic force microscopy. The topographical information obtained by atomic force microscopy was used to calculate the effect of the surface roughness on the backscattering spectrum.

As an example of the method developed, annealed metal/semiconductor heterostructures have been studied in collaboration with TUT and HUT-1. Au and Pt are contact materials having small contact resistanceand used commonly on semiconductor devices. The thermal stability of the contact/semiconductor interface is of prime importance. The diffusion of gold into ZnSe has been studied, the semiconductor was grown in TUT by molecular beam epitaxy. Gold grains were observed on the surfaces of the annealed samples. The annealing also caused diffusion of gold into ZnSe. A scanning nuclear microprobe was used to verify the results by measuring backscattering from grains and from areas of the samples where no grains had been formed during annealing. An empirical model for calculating the diffusion coefficient for different quality of crystal ZnSe is presented.

The diffusion of platinum in molecular beam epitaxy grown ZnSe was investigated as an inter-partner study with TUT. The diffusion coefficients were determined by fitting a concentration independent solution of the diffusion equation to the experimental depth profiles obtained by RBS. The activation energy and pre-exponential factor of the diffusion process were found to be 1.7 eV and 6.4×10^{-6} cm^2/s, respectively

The study of concentration dependent and independent silicon diffusion in ion implanted GaAs has been realised in collaboration with VTT. As a result, a new diffusion model was developed which better explains the experimental concentration profiles than the earlier models suggested in the literature.

As a joint study with VTT, the diffusion of As into Ge from a GaAs overlayer deposited on p-type Ge substrates has been investigated by means of secondary ion mass spectrometry (SIMS). Arsenic atoms are shown to diffuse through Ge vacancies with the charge states 2- and 0. No presence of the singly negatively charged vacancies was observed, indicating that Ge vacancy could be a negative U-centre. The identification of point defects in semiconductors is of fundamental interest, and diffusion of impurity atoms can be a powerful tool to investigate point defects in semiconductors. The increasing importance of Ge in applications such as multi-junction GaAs/Ge and GaInP/GaAs/Ge solar cells necessitates further studies on diffusion in Ge.

8.4.2. Determination of dopant atom lattice sites

The determination of lattice location and charge state of impurities in semiconductors is of fundamental interest and important in investigating the diffusion mechanisms and in designing device structures.

The lattice location and diffusion of silicon has been studied in <100> GaAs implanted with 40-keV 30-Si ions. As the main n-type dopant, the study of silicon in GaAs is important. Fitting a concentration dependent diffusion model to the annealed silicon depth profiles, measured with secondary ion mass spectrometry, made it possible to identify silicon interstitials. In the diffusion model presented, in addition to silicon located on Ga and As sites and $Si_{\{Ga\}}$- $Si_{\{As\}}$ pairs, also interstitial silicon is taken into account for the first time. The charge state of the silicon interstitial was calculated to be +1.

The channeling phenomenon can be used to determine lattice sites of impurity atoms in crystalline materials. The lattice location of diffused gold and platinum in ZnSe epitaxial layers was studied using the RBS channeling technique. The channeling angular scan measurements and comparisons to Monte Carlo simulations revealed that about 30% of the Au atoms were close to substitutional site, with an average displacement of about 0.2 Å. The displacement could be due to formation of small clusters or pair formation of vacancy and Au atoms. In the case of Pt, no specific lattice site was observed.

An experimental apparatus was developed for the simultaneous use of RBS, particle induced x-ray emission (PIXE) and nuclear resonance broadening (NRB) ion beam techniques combined with the channeling measurements. The aim of the studies conducted with the apparatus is to get insight into the diffusion mechanisms involved in the impurity atom migration. The characteristics of the PIXE method in channeling experiments of ZnSe have been investigated and compared with RBS channeling. The effect of various experimental parameters, especially the effect of the analysis depth and ion energy on the PIXE channeling minimum yield, was studied and compared with Monte Carlo simulations. The effect of secondary fluorescence on PIXE channeling was studied in ZnSe/GaAs heterostructures.

8.4.3 Ion-matter interactions

To successfully utilise the techniques of ion beam characterisation, accurate basic data on ion-matter interactions are necessary. Such data have been determined systematically within the EPI-2 project.

Scattering cross sections for the light ions used for analyses in the scattering of project ions, ^{1}H, ^{4}He, ^{6}Li, ^{7}Li and ^{11}B, by low- and medium-mass elements have been measured. Both excitation functions and angular distributions have been experimented. These results are of importance in applying the RBS and ERDA techniques for depth profiling and detecting impurities and for compositional analysis of elements in semiconductors. In general, the scattering of ions by target atoms can not be predicted theoretically above the Rutherford energy region. Therefore, theoretical methods of nuclear physics, such as the optical model and R-matrix theory have been applied to these data sets. Parameters of the theoretical methods thus derived enable us to extrapolate the experimental cross section data for all relevant scattering angles in the given projectile – target system. Deep depth profiling of dopant atoms at high energies requires the knowledge of non-Rutherford scattering cross sections obtained by these theoretical models. The studies of scattering cross sections have been published in four articles.

The knowledge of the slowing down of ions in matter is the basis of all depth information obtained by the ion beam techniques. The theoretical models to calculate the stopping powers are, however, inaccurate and experimental data are thus essential. The stopping cross sections of the ZnSe material for 0.4 – 2.2 MeV ^{1}H, ^{4}He and for 1.6 – 8.9 MeV ^{7}Li ions have been measured by the RBS technique. For helium and lithium, the results show 4 – 10% and 1 – 9% smaller ZnSe stopping than those calculated by the most up-to-date theoretical predictions. Correction factors for the depth scale measurements in ZnSe should be adopted accordingly.

Light charged particle induced gamma-ray emission spectroscopy has been well established as a tool for analytical work. The potentials of the heavier ions, commonly used as projectiles in heavy ion RBS and ERDA, have been investigated within the project. These reactions can be used for the detection of elements simultaneously with the RBS and ERDA techniques. For this purpose, thick target gamma-ray yields for 25 elements in the range Z = 3 – 30 at ^{12}C, ^{14}N and ^{16}O ion energies of 22, 28 and 33 MeV have been determined.

8.4.4 Irradiation of compound semiconductor materials and implantation of samples

In the irradiation of semiconducting materials, the main interest has been the investigation of the damage produced and annealing behaviour of InP, bombarded by nitrogen and aluminium. These efforts were a common theme with HUT-1 and VTT. They were initiated during the preceding EPIMATTER project and finished during EPI-2. The RBS channeling method was used to provide information about interstitials and displaced atoms, NRB and SIMS yielded nitrogen depth profiles while the positron beam spectroscopy was used to determine the vacancy-type defects. The InP material was the subject of two articles, published jointly with HUT-1 and VTT.

^{15}N ions of 50 keV, implanted to doses of 10^{14} – 10^{16} N/cm^{2} into n-type (100) InP were first used. The annealing behaviour of the damage and vacancy concentration distributions at temperatures of 450 – 650 °C were found to correlate with the implanted N distribution in the case of the highest implantation dose. This indicates that disorder annealing and loss of nitrogen behaved in like manner with increasing temperature. For the lower doses, however, almost no redistribution or loss of nitrogen arose despite structural damage and vacancy annealing. Two types of vacancies were identified – monovacancies were formed in the In sublattice at low doses, highest doses produced divacancies. Annealing tended to convert monovacancies into divacancies.

Also the annealing behaviour of aluminium was investigated in single-crystal InP implanted with 40-keV and 120-keV ^{27}Al ions. The aluminium concentration profiles were determined by two techniques. SIMS was used for depth profiling especially of the low dose implanted samples. The high dose samples were measured by NRB by taking advantage of the narrow 992 keV resonance in the reaction ^{27}Al(p, γ)^{28}Si. The implanted samples were subject to annealing in argon atmosphere in the temperature range 400 - 600 ^{o}C. Redistribution and a significant aluminium surface enrichment took place with the 40 keV -implanted samples.

In an other line of studies of the irradiation effects on semiconductors, solar cell materials were irradiated with 3.0 MeV protons. The experiments are related to a TUT's subproject, which aims at the development of radiation resistant solar cells for space applications. In a joint effort with the TUT, we investigated the degradation characteristics for molecular beam epitaxy (MBE) grown GaInP, GaAs single junction, and GaInP/GaAs tandem solar cells.

The 100-kV isotope separator of UH accomplished the implantation of III –V and II – VI semiconductor samples for the needs of other Partners. UH provided standards for the quantitative calibration of the SIMS measurements at VTT. The list of deliveries of the implanted samples is given in the Table below.

Table. Delivery of implanted samples by UH to other Partners within EPI-2.

Partner	Sample	Dopant	Energy (keV)
VTT	Si	^{11}B	20
		^{12}C	15
		^{16}O, ^{18}O	20
	Ge	^{69}Ga	100
		^{75}As	100
	GaN	^{12}C	100
		^{16}O, ^{18}O	25
		^{24}Mg	35
		^{29}Si	120
	GaAs	^{9}Be	20
	ZnSe	^{48}Ti	75
		^{58}Ni	100
	InP	^{9}B	30
		^{16}O, ^{18}O	80
		^{29}Si	40
	GaInP	^{16}O, ^{18}O	80
	MgZnSSe	^{14}N	30
TUT	GaAs	^{9}Be	30
	GaInP	^{9}Be	30
	AlInP	^{9}Be	30

8.5 Progress Report: VTT

8.5.1 Diffusion and annealing behaviour of atoms in compound semiconductors

Diffusion and annealing behaviour of nitrogen and aluminium in InP, beryllium in GaAs, AlInP and GaInP, silicon in GaAs, and arsenic in Ge have been studied in close collaboration with TUT and UH. In addition, interdiffusion of metallic contact layers has been investigated. The metal contacts included In/Au on GaAs, and Ti, Ni and Te on ZnSe as well as Td/Pd/W/Au on ZnSe.

Studies on annealing effects on nitrogen-implanted InP samples were started in the EPIMATTER project and were finished in EPI-2. These samples were analysed using the NRB and RBS methods at UH, positron annihilation at HUT-1 and SIMS at VTT. Doses above 10^{15} N atoms cm^{-2} were found to produce amorphous layers extending from the surface to depths beyond the deposited energy distribution, up to 110 nm. The depth of an amorphous layer was observed to depend on the implantation dose. The damage and vacancy concentration distributions were correlated with the implanted nitrogen distribution in the case of the highest implantation dose at 10^{16} N atoms cm^{-2}. For the lower doses, however, almost no redistribution or loss of nitrogen arose despite structural damage and vacancy annealing. Interpretation of the positron data allowed an identification of two types of vacancies, as discussed in previous Section.

Diffusion of thin grown-in Be layer in III-V compound semiconductors GaAs, AlInP, and GaInP has been carried out in collaboration with TUT and UH. MBE-grown samples were annealed using rapid thermal annealing (RTA) in the temperature range of 550 - 850 °C. A boxed-shaped diffusion profile for Be was obtained for all materials studied. This is an indication of concentration dependent diffusion.

Diffusion of ion implanted silicon in GaAs has been studied using SIMS and RBS techniques. The implanted samples were subjected to annealing in argon atmosphere in the temperature range 650 - 850 °C. Two silicon diffusion mechanisms were observed, namely, concentration independent and concentration dependent diffusion. Concentration independent diffusion, observed as a broadening of the initial implanted distribution, is very slow and is assigned to Si atoms diffusing interstitially. Concentration dependent diffusion with low solubility and extending deep into the sample is quantitatively explained by diffusion via vacancies of Si atoms in the Ga and As sublattices. Diffusion coefficients together with carrier concentration as a function of Si concentration have been calculated at different temperatures.

Diffusion of As into Ge will be utilised in making triple junction solar cells to create a *p-n* junction in Ge. Arsenic will diffuse from a GaAs layer into a Ge substrate during RTA. Diffusion of As into Ge from a GaAs overlayer deposited on *p*-type Ge substrates has been studied by means of SIMS in collaboration with UH and TUT. The SIMS results show that diffusion is concentration dependent. A steep diffusion front was observed in the SIMS analyses. A concentration-dependent diffusion of As atoms was observed in addition to the concentration-independent diffusion of Ga and As atoms. The concentration dependence is explained by a Fermi-level-dependent diffusion model. Arsenic atoms are shown to diffuse through Ge vacancies with the charge states 2- and 0. Doping and diffusion of Ga have also been investigated. In addition to As diffusion from GaAs overlayer, diffusion of ion implanted As has also been investigated. The diffusion of arsenic has been studied in < 100 > Ge implanted with 10^{15}, 120-keV As ions/cm^2. The implanted samples were subjected to annealing in argon atmosphere in the temperature range of 450 – 550 °C. The annealing times varied between 0.5 and 91 h. The As concentration profiles were measured by SIMS. A Fermi-level-dependent diffusion of As atoms was observed, which is quantitatively explained by diffusion via Ge vacancies with charge states 0 and 2-. The activation energies and pre-exponential factors for As diffusion through neutral Ge vacancies was found to be 3.4 ± 0.3 eV and 2.02×10^{20} nm^2/s respectively and through doubly negatively charged vacancies 2.9 ± 0.3 eV and 1.89×10^{16} nm^2/s, respectively. The solid solubility limit of As increases with temperature from about 1×10^{19} cm^{-3} at 450 °C to about 5×10^{19} cm^{-3} at 550 °C.

The annealing behaviour of aluminium has been studied in single-crystal InP implanted with 40 and 120 keV ^{27}Al$^+$ ions. The implantation doses were 1 x 10^{15} and 1 x 10^{16} cm$^-$

^{2}. The aluminium concentration prooles were determined by two techniques, SIMS and the nuclear resonance broadening technique (NRB) which was used for checking purposes. The usability of the SIMS technique for profiling Al rich layers was studied. Significant inconsistencies were observed in the SIMS profiles with the high dose implanted samples. The 120 keV, 1 x 10^{16} cm^{-2} implanted samples were subject to annealing in argon atmosphere in the temperature range 380 - 600°C. Redistribution and a significant aluminium surface enrichment took place. The coefficients of Al migration were determined by fitting a concentration independent solution of the diffusion equation to the experimental depth profiles. The deduced activation energy and frequency factor for aluminium migration in implanted InP are 0.78 eV and 5.5 x 10^5 nm^2/s, respectively. Rutherford backscattering (RBS) spectra measured along <100> channeling direction for 120 keV, 10^{16} cm^{-2} implanted samples indicated a loss of crystalline structure near the surface both in the as-implanted and in the annealed samples.

Metallic In/Au layers on GaAs were annealed using RTA. The annealing temperature was between 100 and 600 ^{o}C. Both In and Au were observed to diffuse into the GaAs substrate during annealing. Studies on Ni, Ti and Te diffusion into ZnSe were performed.

Ohmic multilayer Te/Pd/Pt/Au contacts on ZnSe material and interdiffusion of elements have been studied using SIMS. Analyses were made from a small metal pad. One sample was annealed at 200 ^{o}C and Pd and Te was observed to diffuse outwards into the Au layer through the Pt layer. Oxygen was, also observed to diffuse during annealing. Work on metallic layers and ohmic multilayers was done in collaboration with TUT and UH.

8.5.2 Dopant analyses in compound semiconductors

Various impurity and dopants in II - VI and III - V compound semiconductors have been analysed with SIMS technique. In II - VI materials the total concentration of nitrogen was determined quantitatively using ion implanted standard samples obtained from UH. The effect of plasma parameters in SPS source on N concentration was investigated. Typically N concentration was in the range of 10^{18} - 10^{20} cm^{-2}. These samples were highly compensated. Nitrogen doping of MgZnSSe was investigated. Mg concentration was varied in the range of 5.5 - 11.5 %. For each material with different Mg concentration an ion implanted standard sample was obtained from UH. Nitrogen concentration was in the range of 10^{18} - 10^{19} cm^{-3}. These samples were also highly compensated. In addition to dopant analyses, hydrogen, carbon, oxygen and chlorine impurities have been analysed in ZnSSe materials in collaboration with HUT-1.

In the case of III-V materials various laser and solar cell structures have been analysed, and doping of Be and Si have been investigated. Be and Si in GaAs, GaInP and AlGaInP have been analysed quantitatively using ion implanted standard samples. In the case of solar cells, diffusion of Be is of great interest.

Studies on effect of oxygen incorporation on electrical and optical properties of Be- and Si-doped InP and GaInP grown by solid source molecular beam epitaxy were started in collaboration with TUT. Oxygen impurity was mainly from the phosphorus source and could be reduced by using lower phosphorus cracker temperature.

In addition to the quantitative dopant analyses, various impurities (H, C, 0, and Cl) have been analysed qualitatively for AlGaInP laser structures. Even though no ion implanted standard samples were available in this case, the data obtained for different samples could be compared with each other.

Impurities (C, O) and dopants (Mg, Si) have been analysed quantitatively in GaN. This work has been done in collaboration with HUT-1 and TUT. Impurity concentrations in GaN films deposited at TUT have typically been in the range of $10^{17} – 10^{20}$ cm^{-3}. In the case of undoped and Mg-doped GaN bulk crystals the concentration of negative ions correlates with that of Mg impurities determined by SIMS. According to positron lifetime spectroscopy the negative ions can be attributed to Mg_{Ga}^{-}. The negative charge of Mg suggests that Mg doping converts *n*-type GaN to semi-insulating mainly due to the electrical compensation of O_N^{+} donors by Mg_{Ga}^{-} acceptors.

9 Publications

9.1 Inter-Partner Publications

9.1.1 Refereed Journal Articles

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VTT

Publications of VTT are given in the Inter-partner Publications sections 9.1.1 - 9.1.2.

Co-author in 11 Inter-partner refereed journal articles
Co-author in 4 Inter-partner refereed conference papers.

SYNTHESIS AND FUNCTIONALISATION OF POROUS CERAMIC OXIDES

With Focus on Porous Structures: *Membranes, Filters and Bioceramcis*

Jarl B. Rosenholm[1], Tapio Mäntylä[2] and Antti Yli-Urpo[3]

Abstract

Porous bioactive materials and porous layered membranes have been manufactured from ceramic oxides. Opposite to the common practice of concentrating the attention only on the final processing step, such as tape casting, the project team has investigated all the processing steps of importance for the properties of the final product:

Synthesis ⇒ Raw materials ⇒ Intermediates ⇒ Processing ⇒ Products

In this way the influence of the chemicals used even in minute amounts (impurities) have been evaluated. The options of using dopants for the chemical modification of the surface properties in the synthesis have been monitored. The nucleation of particles and the control of their stability has been investigated with a variety of advanced instrumental techniques such as synchroton SAXS, revealing the developent of the gel structure. The initial rate determining step of aluminium hydroxide has been theoretically modeled in order to understand the influence of solvation on the ion species formed before nucleation. The pore structure of the intermediates and the final products have been characterized and modeled by e.g. gas adsorption and permeability studies. The sol-gel process has not been restricted to the synthesis of nucleis, but has also included the utilization and modification of commercially available ceramic oxide powders as intermediates. The conditions and properties controlling the colloidal sol-gel processing of the final products have been characterized. With the exceedingly intense collaboration between the project partners the results obtained are, as a rule, indistinguishable as a contribution of a certain group. Instead the results provide a compre-hensive and fundamental picture of the interactions involved in the manufacturing chain illustrated above. The results encompass interaction-structure, interaction-sol-gel transition, interaction-product properties relationships of particular value when dealing with precious functional materials with gradient porous structures.

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1 Partners and Funding

Not all, but a few of the researchers indicated have been employed for the full three year period.

1.1 Department of Physical Chemistry, Åbo Akademi University (DPC/ÅAU)

The research group consisted of project co-ordinator and subproject leader Professor Jarl B. Rosenholm, senior researchers Professor Marek Kosmulski and PhD Mika Lindén, postgraduate students Mika Jokinen, Patrik Ågren, Pasi Mikkola, Jan Gustafsson, Alf Pettersson, Patrik Eriksson, Reeta Viitala, Juha Päivärinta, Mats Graeffe, Kurt Gunnelius, Eklund Tom and summer laboratory assistants Sandra Bihlmaier and Jessica Rosenholm.

1.2 Institute of Materials Science, Ceramic Materials and Surface Engineering, Tampere University of Technology (IMS/TUT)

The research group consisted of subproject leader professor Tapio Mäntylä, postgraduate students Erkki Levänen, Faranak Shojai, Lars Grönroos, Mika Kolari and Jarkko Leivo.

1.3 Institute of Dentistry, Bioceramic Applications, University of Turku (ID/UT)

The research group consisted of subproject leader professor Antti Yli-Urpo, Ph.D. Ilkka Kangasniemi, students and postgraduate students Timo Peltola, Marko Pätsi and Reeta Viitala and temporary workers Ulla Pesonen, Sherri Kothari, Christian Müller-Mai, Jouni Heikkilä, Elina Larmas, Kimmo Vähätalo and Manja Ahola.

1.4 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000.

Partner	Funding Organisation	1997	1998	1999	2000	**Total**
DPC/ÅAU	Academy of Finland	587	620	653	NA	**1860**
IMS/TUT	TUT	100	100	150	260	**610**
IMS/TUT	Academy of Finland	620	641	579	NA	**1840**
IMS/TUT	Industry	971	1134	1041	270	**3416**
ID/UT	Academy of Finland	230,4	229,1	NA	NA	**459,5**
Total		**2508,4**	**2724,1**	**2423**	**530**	**8185,5**

2 Research Work

2.1 Background

There is an increasing interest to harness the exceptional properties offered by the III A-B and IV A-B group oxides (e.g. SiO_2, TiO_2, ZrO_2, Al_2O_3, Y_2O_3, etc.) as matrix elements as such or as mixtures in the development of advanced functionalized materials. The extensive occurrence of SiO_2 and Al_2O_3 puts them, however, in a priority position as matrix materials in composite structures.

The special properties of these pure and mixed oxides provide an ideal basis to produce materials of particular interest for both the biomaterials,- as well as the industrial materials community. For the first group the functionalization of siliceous biomaterials through chemical and physical processing techniques to monoliths, films and fibers enables the manufacturing of tailor made materials for implants with bioactive properties or drug doped porous materials to inhibit, e.g. inflammatory reactions after surgery. Oppositely, the aim of the structural biomaterials is to remain intact after implantation but possessing ideal tissue-implant adherence for simultaneous toughness and biocompatibility.

The colloidal sol-gel processing technique has proven to be particularly successful when manufacturing nanomatertials with a demanding structure. Typically such structures are hierarchic with a gradient transport of the substances of importance for the process (catalysis, separation, delayed drug release, etc.). The sol-gel synthesis also allows for a functionalisation of the porous structure following the standard synthesis protocol. Finally, the sol-gel technique can take advantage of organized assemblies and polymeric networks to prepare predetermined pore structures. The sol-gel technique encompasses both the synthesis of gels or particles as well as colloidal processing of powder matrices by slip or tape casting. All in all it relies on the traditions of the surface and colloid science in which framework functionalized nanomaterials have been prepared by sol-gel technique for about hundred years.

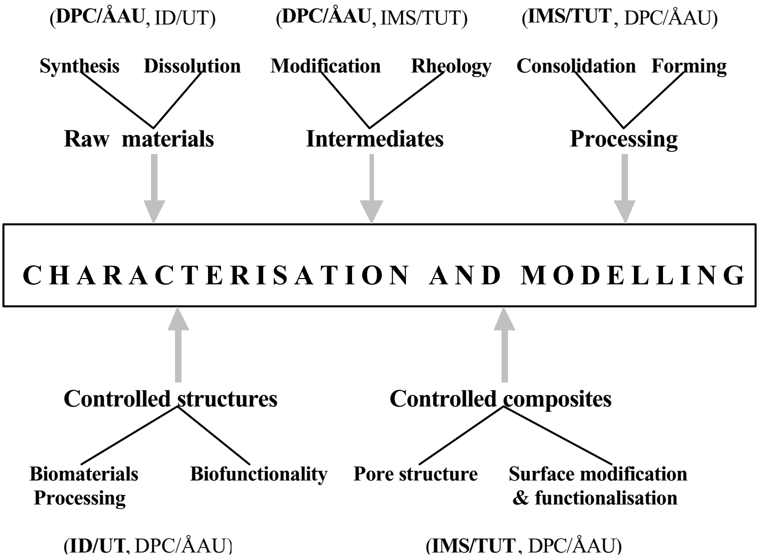
2.2 Objectives and Work Plan

The overall objective of the project is documented in the heading, i.e. to synthesise porous ceramic oxides with hierarchic structures and demanding functionalities. The manufacture of defect free products is ensured by applying chemical surface modifications and the colloidal sol-gel processing technique. The functionality is introduced by dopants in the synthesis stage, by the particular transport properties provided by the hierarchic structure, or by post surface modification of the intermediates or the products.

The comprehensive understanding of the factors governing each step in the manufacturing of the hierarchic functional composite materials requires the knowledge of the interrelationship between each step of the chain:

Synthesis ⇒ Raw materials ⇒ Intermediates ⇒ Processing ⇒ Products

Obviously, the investigation relies on an extensive characterisation of the systems used with advanced experimental techniques and on a sufficient theoretical modelling supporting the data analysis. Each partner contributed to the characterisation. The interrelationship of the themes can be visualised with the flow sheet shown below, where the groups mainly participating in the activities are given within parenthesis. As shown, the thorough characterization provides experimental data, which may be used in the design of recipes for the synthesis of materials and for theoretical modeling of the interrelationship between properties and structure. In this way the conclusions drawn from the experimental results are evaluated in a strict way.



A special feature for this project is the exceedingly intensive collaboration between all the members of the research groups. It must therefore be stressed that the results of the project are to a great extent common for two or more research partners. The reporting on the progress of research is presented by the group in principal charge of the task, independent of which partner contributed the most to a particular subproject. In this way a repetitive reporting is avoided for the benefit of clarity of the progress report.

2.3 Progress Report: Department of Physical Chemistry, Åbo Akademi University (DPC/ÅAU)

As indicated in the flow chart above the primary aim for the research group was to develop new synthesis routes to produce the raw materials needed and to evaluate the amount of substance dissolved from the raw materials used. Moreover, the rheology of the slips were controlled by chemically modifying the particle surfaces. In particular, the research team took a leading role in the characterization and modelling of the systems studied. Beside of the themes reported in this section the researchers have been actively involved in the development of stable sols suitable for slip or tape casting (A23, A28-A44, A48-A59, M18-M30) and for the preparation of thin TiO_2 films (A24-A26, A45). The research team has also been involved in the synthesis of bioactive materials (A1, A18-A21, A25-A27, A46-A47, A56). The results of this research are reported by the other partners.

2.3.1 Synthesis of powders and monoliths (P. Ågren, Thesis, A1-A7)

The influence of a non-ionic polymer, polyethylene glycol (PEG), on an acid-catalysed sol-gel synthesis of silica has been extensively investigated. PEG is a biocompatible, non-toxic polymer, which makes it suitable for biological applications. Both the amount and the molecular weight of the PEG were changed and the gelation time was studied as a function of these two parameters. Figure 1 shows the dependence of the gelation time as a function of wt-% of PEG. The gelation time for sample PEG0, which did not contain any PEG, was 505 minutes. The gelation times were reduced for samples that contained low amounts of PEG compared to sample PEG0.

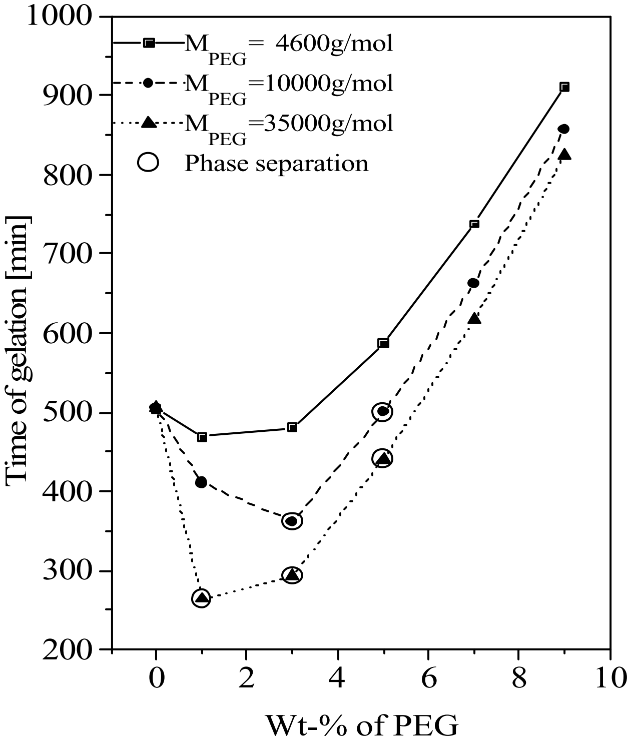


Fig. 1. Visually determined gelation times as a function of wt-% of PEG, for PEG M_w = 4600, 10000 and 35000 g/mol.

A comparison of the gel time with the flow properties of the gel nicely show that the PEG sterically hinders fast condensation of silica. Additionally, the sol viscosity increases at high PEG amounts, thus preventing fast diffusion of silica clusters to collide and con-dense, hence decreasing the reaction rate and increasing the gelation time.

In order to quantitatively determine the particle size during the sol-gel synthesis dynamic light scattering, DLS, was utilized. Furthermore, the radius of gyration, R_g, of the fractal aggregate was determined by small angle X-ray scattering, SAXS. In order to compare the particle sizes for stable and for phase separated samples both types of samples were measured. Figure 2.a shows the evolution of the mean particle size, as a function of sol-gel synthesis time, for sample PEG0. Initially, the mean particle size was only a few nanometers and increased to about 15 - 20 nm after 322 minutes of the reaction. The particle distribution curves were broad, implying that the particle size range was quite disperse, which is expected for a sol-gel synthesis. At longer reaction times, this gelling system was not suitable for DLS. On the other hand, at longer reaction times, the rapidly increasing viscosity, shown in Figure 2, provide good evidence of a growing giant spanning cluster. This behavior is very commonly observed in gelling systems. Furthermore, the R_g of the fractal aggregate starts to grow much faster at the point where the viscosity starts to increase, thus indicating the growth of a giant spanning cluster. In accordance, the particles were growing during the process, thus forming a gel.

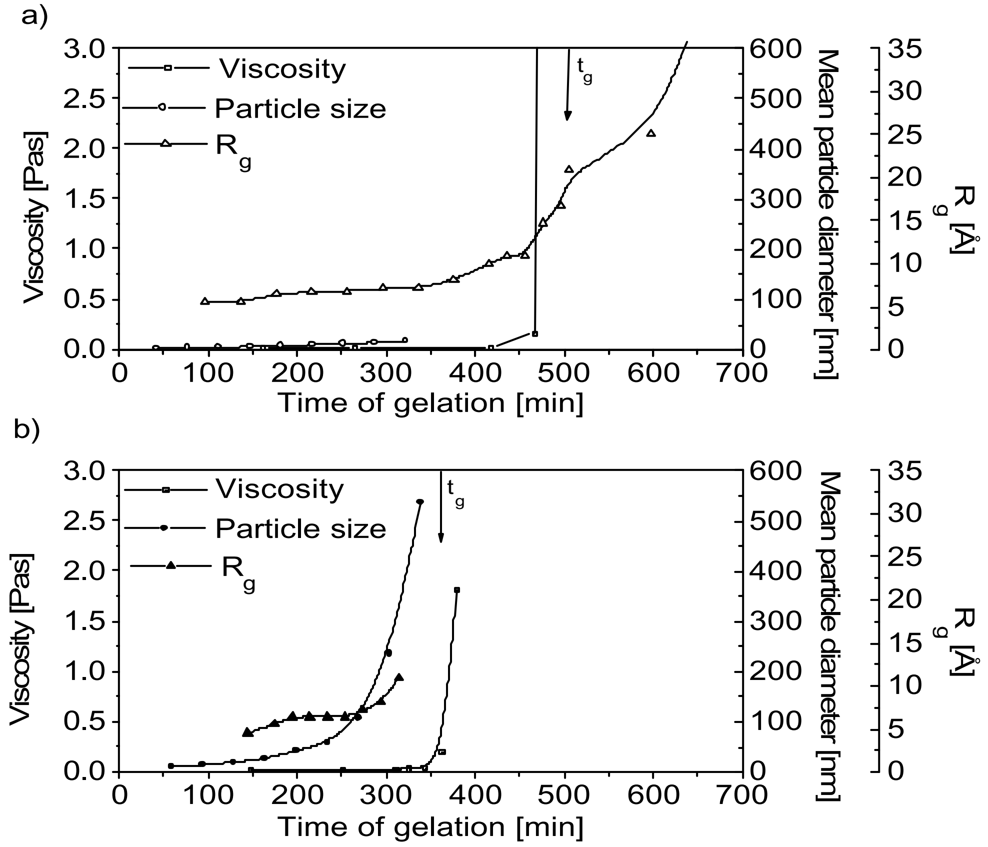


Fig. 2. Dynamic viscosity (measure at a shear rate of 3.67 s^{-1}), mean particle size and radius of gyration of a fractal aggregate for samples a) PEG0 and b) PEG103.

The gels made in the presence of PEG resulted in fairly large particles at the end of the sol-gel process. This observation holds true for all the stable samples investigated.

Figure 2.b, on the other hand, shows the particle size evolution as a function of time of a phase-separated sample; this example provides a good illustration of all investigated phase separated samples. Already at the early stages of the reaction the mean particle size was approximately 10 nm, indicating a faster growth rate. Further, the particles were growing progressively, attaining sizes close to 1000 nm, which is the upper detection limit for the technique used. In fact, there was a bimodal particle size distribution, where the smaller particles were in the same size range as the ones measured in Figure 2.a and the larger ones were large flocculates in solution. It seems that the small particles act as primary particles for the large flocculates.

Frequency dependence curves of storage and loss modulus have been measured, in order to gain information about the gel structure from the critical exponent n. At the gelation point the storage and the loss modulus become parallel to each other confirming the power law behavior, and thereby yielding the value for n. The critical exponent yields information about the extent of branching of the gel. If the value is high a less branched gel was formed and vice versa. Table I summarizes the values obtained for n, showing that most of the obtained values are approximately $n = 0.74$. Since the n value is large for the phase-separated gels they are less branched than the others, which is easy to understand since they consist of large coagulates. Among the stable samples investigated the highest and lowest values were obtained for samples PEG359 and PEG101, respectively, suggesting a clear distinction in the degree of branching. The fractal dimension values obtained for the phase separated samples were clearly lower than obtained for any other sample.

Table I. Values for the critical exponent *n,* fractal dimension d_f at gelation point, fractal dimension d_f after three days of aging, specific secondary micropore and mesopore volume, specific total pore volume and specific BET surface area. The nomenclature used to describe the samples is as follows: samples having the codes PEG461, PEG463, PEG465, PEG467 or PEG469 contain PEG M_w = 4600 g/mol of the amount of 1, 3, 5, 7 or 9 wt-% per total mass. The same nomenclature applies also for PEG M_w = 10000 and 35000 g/mol. An organic silica precursor, tetraethylortosilicate, TEOS, was used in all cases.

Sample	*N*	d_f at t_g	d_f after aging	Tot. pore vol. [ml/g]	BET [m^2/g]
PEG0	0.74	1.80	2.15	0.35	657
PEG461	0.74	1.85	2.26	0.356	643
PEG463	n.m.	1.97	2.48	n.m.	n.m.
PEG465	0.73	2.00	2.45	0.37	624
PEG467	n.m.	2.03	2.47	n.m.	n.m.
PEG469	0.74	1.96	2.20	0.344	577
PEG101	0.71	2.02	2.45	0.447	689
PEG103	0.83	1.67	1.34	n.m.	n.m.
PEG105	0.83	1.71	1.97	0.307	628
PEG107	0.75	2.14	2.60	n.m.	n.m.
PEG109	0.75	2.09	2.58	0.359	603
PEG351	-	1.70	1.97	0.358	644
PEG353	n.m.	1.45	1.33	n.m.	n.m.
PEG355	0.83	1.51	1.51	0.282	610
PEG357	n.m.	1.84	2.10	n.m.	n.m.
PEG359	0.78	1.95	2.46	0.364	605

n.m. = not measured

The fractal dimension obtained, from the small-angle X-ray scattering curve, offers information about the structure of the gel and possibly about the reaction mechanism that took place during the sol-gel reaction. On the whole, the measurements revealed that the fractal dimension and the length scale, over which self-similarity was observed was increasing during the entire sol-gel reaction. Furthermore, this behavior still proceeded during the aging process of the gel. At the gelation point the fractal dimension had attained a value of d_f = 1.80 for sample PEG0. This is more or less the value one would expect for diffusion limited cluster-cluster aggregation (DLCCA), since it agrees well with simulated values. Moreover, the rheological data shows that the condensation reactions still continued after the gelation point. This further increases the fractal dimension, attaining a value of d_f = 2.15 after three days of aging and d_f = 2.21 after eight days of aging, respectively. The condensation reactions cause compaction and rearrangement of the gel. By computer simulations a value of d_f = 2.25 for the fractal dimension has been obtained that takes into account rearrangements of the gel. However, the reaction forming the gel is assumed to be a reaction limited cluster-cluster aggregation (RLCCA). That is probably why the simulated value is higher than the one experimentally obtained for sample PEG0.

Nitrogen adsorption-desorption isotherms obtained from the heat-treated gels, *i.e.,* ceramics, revealed that all samples consisted of micropores. Furthermore, all samples prepared in the presence of PEG showed a hysteresis loop in the desorption branch, indicating the presence of mesopores as well. This is not surprising since the DLS results showed that all the samples prepared in the presence of PEG consisted of somewhat larger particles. Therefore, it is feasible to claim that the mesopores are formed of voids between these particles. The mesopore size distribution analysis showed that the samples which phase separated had a much broader mesopore size distribution than the others. This is not surprising, as the visual and DLS results proved the existence of very large particles. However, all the pores formed between these particles are not detected since the pore system, formed between the large particles, extends way beyond the mesopore size range. Therefore, it is not detectable with nitrogen adsorption. The micropore size distribution is narrower for all samples containing PEG as compared to the reference sample PEG0. Generally, the effect was more pronounced the higher the amount of PEG.

The micropore size distribution analyses were somewhat inconclusive due to the lack of a maximum in the effective width distribution. However, the information gained showed that the micropore width distribution under 1 nm is quite broad and that hardly any micropores having widths above 1 nm exist. This coincides nicely with the results gained from the α_S plots, which all indicated a small filling swing associated with the presence of primary micropores. Also secondary micropores and mesopores evidently composed a part of the pore structure. However, their sizes coincide with each other making a separate pore volume assignment of them difficult even from an α_S plot. Thereby, the pore volume from both type of pores has been reported in Table I. The interesting feature for those two pore types is that the lowest values were found for the phase separated samples. Addition of the primary, secondary and mesopore volumes gives the total pore volume. From the pore size distribution, the BET analysis and the pore volume data in Table I, it becomes evident that the thermally removed PEG did not leave any additional holes, which would have increased the porosity of the ceramic material. Apparently, the phase behavior caused by PEG has a greater effect on the porosity than the imbibed PEG.

The structure information from the rheological and small angle X-ray scattering (SAXS) measurements correlated nicely for the phase separated samples, *i.e.,* the degree of branching was lower for those samples. If, for fractal systems, the mass and surface scale equally, the system may be assigned to a mass fractal. If the entire surface is accessible for adsorption, surface area and porosity should correlate with the fractal dimension. Therefore, the fractal dimensions recorded for the gels (green state ceramic materials) provided valuable structural information. However, the limitation of fractal analysis is that a single value for the fractal dimension cannot provide information about the precise nature of the porosity. In an ideal practical case of interest, the porosity and the fractal dimension are known for one ceramic sample and the fractal dimension for all the green state ceramics. This already offers structural information (mainly relative information) about how porous the green state ceramics would be if processed to ceramic materials, which saves time and effort. However, according to the data in Table I, the surface area does not correlate at all with the fractal dimensions obtained. The reason for the discre-pancy may be the uncertainty in determining the BET surface area for microporous solids. Anyhow, for the phase separated samples, the physisorption data of the specific secondary micropore plus mesopore volume seems to correlate with the rheological and small angle X-ray scattering data, *i.e.*, they have the lowest values. The reason for this correlation might be that the fractal aggregate did not grow as large in size and number for the phase separated samples as for the stable samples. Therefore, the phase separated samples would not have a significant pore volume contribution from larger micropores and mesopores. Consequently, one has to make the assumption that the primary micropores are formed at the initial stages of the synthesis and larger micropores and mesopores are formed at later stages.

2.3.2 The silicate-surfactant system (A8-A14)

Porous silicates were also synthesized in the presence of hexadecyltrimethylammonium bromide (CTAB). The materials formed were silicate-surfactant composite aggregates, consisting of silicate walls organized in a regular pattern. First, the amount of ammonia used as catalyst and the prehydrolysis time were altered in order to synthesize materials consisting of both textural and framework-confined porosity. Secondly, the phase behavior of the silicate-surfactant mesophase was changed by polar additives, *i.e.*, butanol and hexanol. Finally, the hexagonally ordered material was swelled by apolar additives, *i.e.,* hexane, octane and toluene.

The N_2 adsorption-desorption isotherms for the samples made at different pH values, clearly showed that the samples consisted of two kinds of porous networks. This became evident as two marked uptakes were observed in the isotherm. In fact, a gel structure was observed when the synthesis pH was low in comparison to the ill-defined particles formed at all the other pH values. The gel structure indicates that smaller particles are formed. The TEM micrographs showed that the particles consisted of framework-confined meso-pores. Furthermore, a correlation between the synthesis pH and the particle size was found; the sample made at the lowest pH produced the smallest particles. Consequently, a clear correlation between the synthesis pH and the textural porosity was found; the sample made at the lowest pH had the highest textural porosity. A relation was also found between the prehydrolysis times and the textural porosity, the highest textural porosity being found for the samples having the longest prehydrolysis times. Furthermore, a comparison of the physisorption and XRD data suggested an increase in the pore wall thickness for samples allowed to prehydrolyze for the longest time period.

Synchrotron SAXS was utilized in order to receive detailed information about the formation of silicate-surfactant mesophases. At the initial stages of the synthesis, diffuse scattering of micelles were observed. However, the data from the diffuse part of the scattering curve could not be used for a more detailed study of the micelles. On the other hand, the Bragg reflection appearing after about 80 s of mixing reveals valuable information about the reaction taking place. The peaks in the X-ray diffractogram could be indexed assuming a two-dimensional hexagonal symmetry. Moreover, the peaks shifted to higher two theta angles with increasing reaction time. Therefore, a contraction of the mesophase with increasing reaction time could be established. The driving force for the contraction is a decrease in interaggregate electrostatic repulsion between the composite aggregates upon condensation. Furthermore, the intensity of all reflection peaks increased with reaction time, which is indicative of an increased ordering and higher solid content of the solution. Finally, the intensity of the 200 reflection was initially higher than that of the 110 reflection, but the opposite was observed at longer reaction times. This effect can also be explained by means of a decrease in interaggregate electrostatic repulsion, since the amount of good scatterers will increase along the 110 axis upon condensation.

The addition of short-chain alcohols, *i.e.*, butanol and hexanol, in the synthesis mixture, had a quite dramatic effect on the phase behavior of the composite mesophase. All the features brought up in the previous section holds true for these systems as well. However, some interesting additional features could be observed when using an alcohol as the additive. First, a slightly swollen hexagonal structure could be observed in the diffractogram when small amounts of alcohol were added to the synthesis mixture. However, another smaller (“normal”) hexagonal structure could be observed in the diffractogram shortly after. Thereby, two coexisting hexagonal structures could be observed simultaneously in the diffractogram. Increasing the added amount of alcohol further, led to the formation of a coexisting swollen hexagonal and a lamellar phase. Again, another hexagonal structure was observed at longer reaction times. Finally, at relatively high amounts of alcohol added, only a lamellar phase could be observed.

The addition of different oils, *i.e.*, hexane, octane and toluene, in the synthesis mixture, produced bimodal silicate-surfactant composite mesophases. The composite mesophases have different *d*-spacings depending on the amount and type of oil. This coincides nicely with the fact that oil can be solubilized in the micellar core, thus increasing the size of the micellar aggregate. Aromatic compounds, like toluene, are solubilized in larger amounts in aqueous solutions of ionic surfactants. This effect originates both from the smaller molecular volume and the higher polarity of aromatic compounds. Due to the higher polarity, aromatic compounds can solubilize both in the micellar core and in the palisade layer. As a result, the micellar core-water interaction energy will decrease and lead to an increase of the solubilization of aromatic compounds in micellar aggregates, compared to the corresponding saturated hydrocarbons. In our study, the well-ordered hexagonal phase expanded only slightly with increasing reaction time and amount of oil, in the presence of hexane and octane. However, a pronounced swelling of the well-ordered hexagonal phase in the presence of toluene was observed with both increasing reaction time and increasing amount of toluene. The effect of swelling, both in time and amount, increased in the order octane

< hexane << toluene, *i.e.*, toluene being the most effective one. The pronounced swelling with time of the whole hexagonal structure can be seen in Figure 3. The same sequence holds true for the water solubility of the oils, *i.e.*, toluene being the most water soluble oil in the investigated series. Therefore, it seems like it is the availability of the oil into the structure that is the key parameter. The reason for this is that the time available for oil to solubilize in a silicatropic hexagonal phase is limited since the ongoing condensation reactions will gradually render the structure rigid.

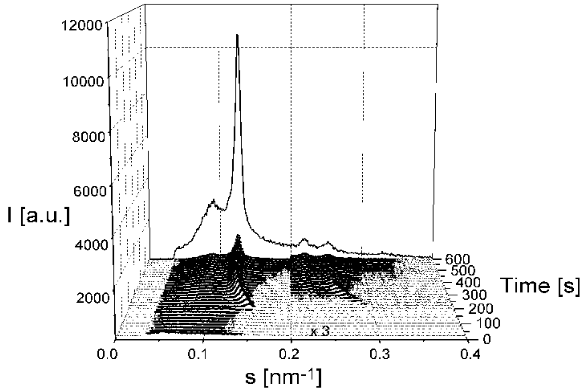


Fig. 3. An *in situ* synchrotron XRD pattern of the development of a silicate-surfactant composite mesophase in the presence of toluene, $m_{toluene}/m_{CTAB} = 5.85$. Note the multiplication of the intensity scale in the s range 0.2 – 0.4 1/nm.

2.3.3 Doped silicates (A15-A21)

Highly porous MCM-41 gels were chemically modified by incorporating Al and Ti into the silica network. The change in the acidity and basicity was evaluated with a number of techniques, e.g. by using thermally programmed ammonia desorption (TPD). Moreover, Lewis and Brönsted active probes were adsorbed from cyclohexane and the data fitted to Langmuir, Freundlich and Henry corrected Langmuir isotherms. The results were checked using FTIR spectroscopy and potentiometric titration. The original structure was found to remain, but the Al and Ti introduced medium and weak acidic sites. The adsorption studies (UV-Vis and microcalorimetry) using probe molecules showed that adsorption strength was enhanced. The influence of the modified pore surfaces were also investigated by ^{1}H-NMR. It was then found that the core water confined in the pores freezes at about 225-230 K leaving a melted water sheet at the pore surfaces. This water sheet undergoes a countinuous transition as the temperature drops. The activation energy of the transition (14-19 kJmol^{-1}) was found to be dependent on the acid sites. The activation energy becomes zero when the distance between the sites becomes about 5.5Å.

The pore structure was modeled with the newly reported Corrugated Pore Structure Model (CPSM) based on the nitrogen adsorption isotherm data. The model produced tortuosity factors in the range of 1.0-2.35. These values are lower than tose of typical catalysts (3-10) and reflect the ordered structure of the MCM-41 material. Addition of Al caused a pore size distribution towards the micropore region, while Ti shifted it towards the mesopore region. Lower additions of Al and Ti caused a pore surface area reduction, but not a substantial shift of the intrinsic pore size distribution.

In order to illustrate the preparation of the multicomponent systems by the sol-gel method, six different ternary samples containing $CaO-P_2O_5-SiO_2$ expressed as oxides were synthesized. This particular ternary system is interesting from the bioceramics point of view. The doped Ca and P in the system could raise the calcium and phosphate concentration in solution (body fluid) and in the vicinity of the materials surface and thus have an influence on the hydroxyapatite formation. Independently of the molar ratios $CaO-P_2O_5-SiO_2$ the power law behavior observed ($G' \propto G'' \propto \omega^n$) gives approximately the same scaling exponent (*n*) suggesting that the aggregation proceeds like an ideal percolation process.

The results suggest that the silica species alone aggregate and form the gel. The calcium and phosphorus remain as soluble species, salts, in the structure. An additional leaching test supports this conclusion: when the gels are washed in water/ethanol solutions, all the calcium and phosphorus has disappeared from the structure when it is analyzed after drying and calcination. The phase containing calcium and phosphorus is soluble in water. Due to the high solubility of the salts, they remain in the solution encapsulated in the pores of the silica gel structure.

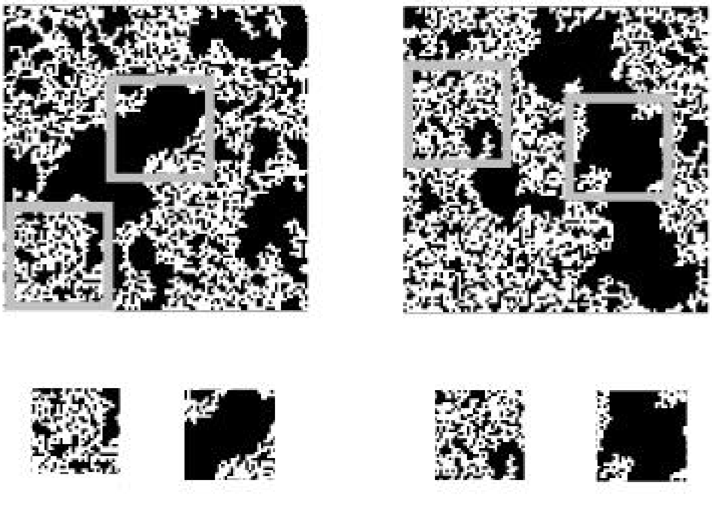


Fig. 4. Spanning clusters (the white cluster describing an infinite silica aggregate) and the black areas that represent voids including calcium, phosphorus, other ions and liquid. Two cuts from the clusters are shown beneath indicating the reason for the heterogeneity.

In Figure 4, two different simulated spanning clusters are illustrated (a white cluster forming an infinite silica aggregate from the particles in the sol according to percolation). The black areas represent voids (calcium, phosphorus, other ions and liquid). Two different spanning clusters show that the clusters have an arbitrary form. Two cuts of each image are shown underneath and they indicate why two different samples from the same batch may give different results when the composition is measured. However, one should remember that they are taken at the sol-gel transition point and the liquid still remains in the structure. After drying and heat treatment, the amount of the solid matter is not as great as the black areas, but the reason for formation of possible calcium- and phospho-rus-rich gradients can be seen. The structure is already heterogeneous after the sol-gel transition and dehydration causes further heterogeneity by migration of ions and contraction of the gel structure. As discussed in the biomaterials section the surface structure formed during gelation has a particular importance for the bioactivity. The formation of apatite (HCA) crystals on the silica surface seems to be induced by the peaks in the gels acting much as surface crystal nuclei (D9, D11, D14, D15, D23). The apatite nucleation was also favoured by a critical mesopore size in the gel (D9).

2.3.4 Theoretical modelling of the crystallization of AL(OH)$_3$ (A22, A23)

The Bayer process is used for extraction of aluminium hydroxide from bauxite in hot caustic solutions. The final product is aluminiumtrihydroxide, $Al(OH)_3$. It has been shown that $Al(OH)_4^-$ is dominant species in the caustics solution. This has also been proved by theoretical methods (Gerson,A.R., Ralston J., Smart R. St.C.; *Colloids and surfaces A*, 110, 105-117 (1996)). Assuming a co-ordination number of four we find:

$$Al[(OH)_4]^- + H^+ \rightarrow Al[(OH)_3(OH_2)]^o \qquad (1)$$

Although the Bayer process has been used for a long time, the exact mechanism of the reaction is still unknown. It is also unknown whether or not the nucleation proceeds via $Al[(OH)_4]^-$. Based on semiempirical quantum chemical calculations, Gearson et al. suggested that the reaction might occur via minor species like $Al[(OH)_3(OH_2)]^o$. In our opinion, *ab initio* calculations are needed to describe aluminium reactions.

The dimers and trimers, tetramers investigated in this study are -$(OH)_2Al(OH)_2Al(OH)_2$-like structures where each pair of aluminium is bridged by two hydroxyl groups. This is also the main block in the crystal line Gibbsite. Harmonic vibrations were calculated for all the structures calculated to ensure that the structure is at minimum. The formation of a dimer from $Al[(OH)_3(OH_2)]^o$ by releasing two water molecules is exothermic by -68.8 kJ/mol according to our HF calculation. At the MP2 level of approximation the dimerization energy is almost the same, -69.9 kJ/mol. However, the formation energy calculated with DFT method differs markedly from the MP2 and HF results. In the formation of the trimer, where $Al[(OH)_3(OH_2)]^o$ reacts with a dimer and one water is removed the HF reaction energy is -118.5 and again the MP2 energy is close to the HF one, -119.6 kJ/mol. The DFT reaction energy, -109.1 kJ/mol, does not differ as much in the formation of the dimer. In the formation of the tetramers the DFT energy, -131.0 kJ/mol, is almost the same as the HF reaction energy, -133.7 kJ/mol. At the MP2 level of approximation computer time needed to optimize tetramer was prohibitively large. The whole recrystallization reaction path with structures and energies are described in figures 2.8 and 2.9. The PCM model changes only slightly the reaction energies for formation of the dimers. Reactions are about 2 kJ/mol more favorable when using PCM model as expected because the effect is pronounced only in reactions of small ions like $Al(OH)_4^-$. Both $Al[(OH)_4]^-$ and $Al[(OH)_3(OH_2)]^o$ species were found to be stable.

2.4 Progress Report: Institute of Materials Science, Ceramic Materials and Surface Engineering, Tampere University of Technology (IMS/TUT)

The parameters controlling the properties of the porous oxide films during different manufacturing steps were modeled. The manufacturing steps included slip preparation, consolidation, sintering and surface modifications. The parameter versus property relations were studied for alumina and zirconia structures with different pore sizes. The porous oxide films were further developed for different applications.

2.4.1 Fine alumina layers

Layers having pore diameter from 70 to 300 nm were prepared from submicron alumina powders. Several different powder types were studied. The consolidation of particles by particle packing was modeled. The processing and resulting structures were found to be very dependent on the raw material type. The deflocculation, consolidation, and sintering depend on the particle size distribution, the particle morphology, and the impurities of the powder. Even small amount of impurities can affect on the deflocculation behavior and result in unwanted grain boundary films after sintering.

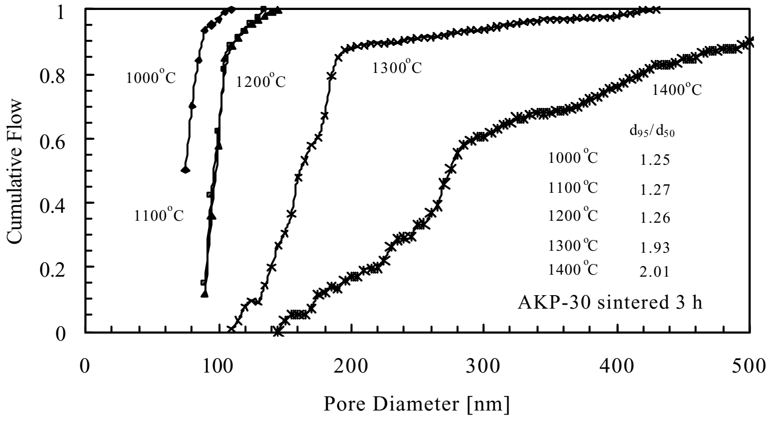
Additive selection has strong effect on layer growth dynamics. Additives may adsorb on the surface of particles and cross-link during drying resulting in strong bonds between particles. Cross-linking of binder also results in loose packing of particles and therefore large pore size and high porosity. Additives may not adsorb on the surface of particles, when the binder effect is weaker, but the achieved packing is more uniform. The additives have strong effect on the viscosity of the solution [M1-M3, M24-M25, M35-M38].

Additives also affect on the surface tension of solution, the wetting behavior between substrate pores and solution and therefore to the capillary pressure. The capillary pressure is the driving force of consolidation during dip coating based on particulate filtration mechanism. The effect of the additives is not straightforward, since the filtrate penetration into substrate pores may occur at different velocities. The adsorption velocity of molecules make the the wetting behavior time dependent.

Polyvinylalcohol (PVA) and sodium polymetacrylicacid (Na-PMAA) have different effect on the capillary pressure. PVA addition reduces significantly the capillary pressure by decreasing the surface tension without having effect on the wetting angle. Wetting angle does not decrease according to equilibrium Young equation since PVA adsorbs slowly on the oxide surfaces. Na-PMAA adsorbs fast on the oxide surface and improves therefore wetting. Improved wetting with slightly lower surface tension increase the capillary pressure. Na-PMAA follows the equilibrium Young equation [M1].

The effect of additive systems on the dip coated layer growth kinetics and the layer properties were studied with model developed for coating on the two-layered substrate. The layer growth rate, porosity and permeability were found to be strongly dependent on the degree of deflocculation and additive system. [M2, M3].

Sintering of thin, supported films differs considerably from the sintering of free standing structures. When sintering is performed at temperatures where sintering shrinkage occurs, the substrate restrict the shrinkage in directions parallel to surface. This restriction leads to small volume shrinkage and significant pore coarsening broadening of pore size distribution as shown in Figure 1 [M4].



	d_{95}/d_{50}
1000 °C	1.25
1100 °C	1.27
1200 °C	1.26
1300 °C	1.93
1400 °C	2.01

Fig. 1. Cumulative flow pore size distribution of supported alumina layer after various sintering temperatures. Pore size increases and the distribution broadens when sintering temperature was raised to temperatures where significant shrinkage should occur [M4].

Due to coarsening and broadening of the pore size distribution occur at high temperatures, sintering should be done at temperature, where the surface diffusion is the main mass transport mechanism leads to a small shrinkage. The sintering time should be long enough to allow the growth of strong necks between particles. Sintering of films for long times at low temperature leads anyhow to the low hardness values.

The choice between narrow pore size distribution and higher hardness depends on the application [M4].

The permeability of the supported structure increases when the sintering temperature was increased. The pore size coarsening combined with the small decrease of porosity resulted in high permeability values. The microstructural features such as pore smoothening and decrease of tortuosity, also increase the permeability [M4].

The sintering studies showed that if the uniform structure is needed, a special care should be put on the careful deflocculation of the slip. It is difficult to achieve uniform densification of a film on a substrate even in the case of the almost ideal packing of spherical particles. If larger or smaller pore size with narrow pore size distribution are needed, the raw material powder must be changed to different size instead of raising the sintering. The uneven densification was found to be independent on the material and particle size. Similar phenomena were observed also with coarser and finer alumina powders and with zirconia powders [M4, M10].

2.4.2 Fine zirconia layers

A good deal and deep understanding of the desired powder characteristics and the way they influence the processing of membranes either in slip processing or in heat treatment was developed during this research program. It enables us to select the right powder available in the market or to modify the powder in order to produce the membrane with desired properties for a certain application. Processing variables in slip processing were well recognized which is a good base for preparing slips different slip casting methods [M6, M8-M10, M35].

Results of the durability of 3Y-ZrO_2 membranes in aqueous solutions of acids and bases at room temperature and 80°C showed that although the porous structure suggested higher damage in water environment compared to the dense ceramic due to high surface area, but 3Y-ZrO_2 membrane retained a good structural integrity after corrosion tests. Although the dissolution of yttria could be a problem in highly acidic solutions, the performance of zirconia membranes in basic and more neutral solutions was quite satisfactory [M12, M13]. The possibility to produce monoclinic zirconia membranes was also demonstrated [M14].

2.4.3 Very fine alumina layers

Alumina structures with very fine pore sized (6…15 nm) were prepared. The effect of processing parameters and sintering on the resulting structure were studied [M34]

Slip preparation from a very fine powder has different parameters compared with a coarse powders. At high solid content, the slip (sol) tends to form very high viscosity gel. Gelling prevents the close packing of particles leading to high porosity and also to high drying shrinkage. Gelling can be used for film preparation so that gel is formed from very diluted sol by filtration on the supporting structure. This gel layer has low permeability and the layer growth is very slow allowing precise control of the gel layer thickness. High drying shrinkage requires careful selection of binder system in order to prevent cracking during drying. Large sintering shrinkage and very small capillaries also require precise control of sintering parameters. The pore properties of structure are strongly dependent on the sintering temperature since several phase transformations of alumina occur when the sintering temperature is increased.

In the film preparation the relation between solid load, binder concentration and film thickness was found. The thickness should be limited under 10 μm, since thicker films are sensitive for cracking even with binders. If thicker layer is needed, the layers should be prepared by multiple coating cycles having heat treatment after each coating cycle. Multiple coating also reduces the amount of defects. Two coating cycles were found to reduce the amount of defects almost to zero. Further coatings only increased the thickness of layer.

Phases in series γ-, δ-, θ- and α-Al_2O_3 were found when sintering temperature was increased from 500°C to 1200°C. Phase transformation to α-Al_2O_3 increased the grain size significantly, caused great reduction of surface area, and had significant volume change due to α-Al_2O_3 phase transformation. The phase transformation to α-Al_2O_3 is reconstructive phase transformation, which does not cause cracking if the heating rate is slow enough. The pore size of transition alumina layers can be varied from 6 nm to 15 nm by varying the sintering temperature. The α-Al_2O_3 phase increased the pore diameter up to 70 nm.

The water permeability of the layer increased with the sintering temperature. Mechanisms were similar to those of the coarser structures. The permeability increased from 40 to 250 l/hm^2bar for transition aluminas when sintering temperature was increased from 500°C to 1100°C. The phase transformation to α-Al_2O_3 increased the permeability further to 350 l/hm^2bar.

The transition alumina layers have major drawback in the poor chemical resistance. The dissolution studies showed that the transition alumina layers can withstand water-based solutions at pH range from 5 to 9. The higher or lower pH values rapidly destroy the structure.

2.4.4 Surface modifications

The surface of porous alumina layers were modified in order to vary the surface charge and surface energy. The structures were modified with TiO_2, SiO_2 and MgO in order to control the isoelectric point of pore wall. Silanes and fluoropolymers were used for surface energy reduction. The binding of surface energy modifiers to oxide was done through the –OH groups and heat treatments leading to strong oxygen-modifier bond. This type of bond can withstand aggressive environments without degradation. The surface energy of silanes can be further varied by heat treatment. The use of fluoropolymers led to very low surface energies. The use of low energy surfaces in water filtration applications anyhow is limited, since overpressure is needed to impregnate water into pores of the membrane [M5, M15, M16].

2.4.5 Applications

The porous ceramic structures were prepared and tested for several applications in corrosive environments and high temperatures at different fields of industry. In these applications the functionality of structures was tested as well as the durability in different environments [M7, M17-M23, M26-M30, M34-M36, M39].

Alumina membranes and modified alumina membranes were used in pilot filtration apparatus for filtration tests to treat pulp and paper mill waste waters. Tests were done in collaboration with the Pirkanmaa Regional Environment Centre [M5, M11, M15, M16, M19, M21, M31-M33, M40-M41]. The results suggested that industrial waste waters usually consist of several compounds that may cause the fouling of the membrane layer. The key factor seems to be how strong is the adhesion of compound on surface and is it possible to remove the compound by shear, backflushing, cleaning procedures etc.

The adsorption behavior of different compounds were studied with VTT-Energy (Technological Research Centre of Finland) by developing surface modified porous granules for removal of chemical compounds from pulp and paper mill waste waters. The pore morphology and surface properties were varied within large scale to obtain good adsorption behavior. The best adsorption of the hydrophobic species on the granules were found with hydrophobic surfaces having isoelectric point at high pH values.

The resistance of the membrane against ultrasonic treatment was studied with VTT-Energy. The ultrasonic treatment of fouling layer requires mechanical durability of the membrane. The cavitation produced by ultra sonic vibration induces high local stresses to the structure. The sintering additive system and the sintering cycle of the membranes were developed so that the structure is durable in the ultrasonic treatment.

The electronic conductive layers of TiN on porous alumina were prepared by Physical Vapor Deposition (PVD) method. The conductive layers were tested as electrodes during flitration. In Figure 2 is shown the evolution of resistance, layer thickness, and impregnation time of water drop (describes the permeability) as a function of deposition time. After long deposition time the conductive TiN layer formed impermeable, dense structure. In Figure 2 can be observed that the optimum deposition time exists, which gives conductive layer without affecting the permeability.

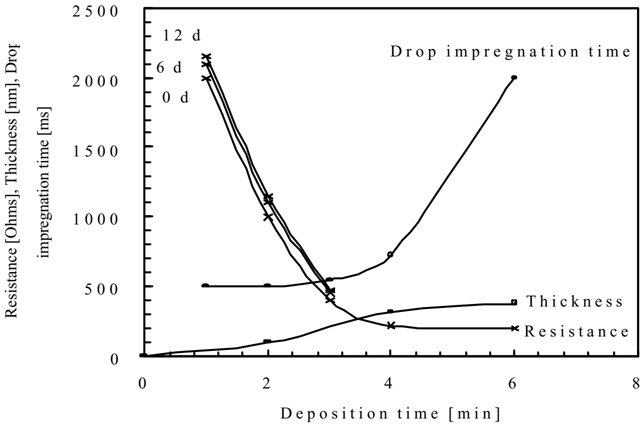


Fig. 2. Evolution of TiN layer properties during deposition. Optimum deposition time exist resulting adequate conductivity without blocking the pores. The increase of resistance after 12 days water impregnation was neglible.

2.5 Progress Report: Institute of Dentistry, Bioceramic Applications, University of Turku (ID/UT)

The main aim of the subproject was to produce new information on some biologically important processes occuring on ceramic biomaterials by adjusting their nanoscale structural dimensions. The studies were mostly performed in simulated in vitro conditions. Specific aims were biocompatibility, adjustable biodegradation and good bioactivity. In this project, bioactivity means a materials' property to form a bond with a living tissue, in the first place with bone. The main method of characterisation was utilisation of a widely used, specific in vitro-solution, a simulated body fluid (SBF). The ability of sol-gel derived ceramics to form a bone-like mineral, hydroxyapatite on their surfaces, was studied with SBF. This ability is generally considered to be a prerequisite for a material to be able to bond to the bone. Materials were also tested in minor extent by protein adsorption and in vivo with test animals.

The main preparation method of biomaterials in this subproject, the sol-gel process, proceeds via hydrolysis and condensation of a liquid precursor to formation of nanoscale particles, whose properties (particle size, aggregation behaviour) are adjusted to form desired gel structures that are further dried and calcined to ceramics. These bioceramics have been prepared and characterised in different morphologies (porous monoliths, thin films by dip coating and fibres) in collaboration with other subprojects. The common property in all of these materials is the variation of structural dimension in nanoscale.

2.5.1 TiO_2-Based Thin Films

The potential advantages of the thin sol-gel derived titania coatings over other coatings (bioactive glass, glass-ceramic and other ceramic coatings) are addressed to the simpler production processes, thinner coatings (typically 40-200 nm) and reduced dissolution rates. The possibility to modify the surface topography, adsorption capacity, and composition in producing coatings makes the sol-gel derived bioactive materials very attractive in the field of medicine and dentistry. Thin titania coatings can be deposited by aerosol condesation or dip coating onto substrates of large dimensions and complex geometries. However, although the influence of TiO_2 coating is preferable with respect to bone bonding (”bioactivity”), another factor is introduced; a major problem with the bioactive ceramic coatings have been their poor adherence to titanium which has also been noticed with the bioactive hydroxyapatite-titania composite coatings.

Inaerosol coating the solvent fume transported sol is deposited on the surface. Depending on the deposition time different TiO_2 layer thicknesses are obtained. The surface properties can be tuned by heating the substrate during deposition (D16, D17, A24, A45).

In dip-coating, the main parameters affecting film properties are composition of sol, aggregation of particles in sol, viscosity of sol, (dry) oxide content of sol, dipping speed, number of subsequent coating layers, drying and heat-treatment. These parameters were applied to prepare films with varying surface characteristic (D21).

Coatings were prepared by dipping the titanium substrate into the sol and then withdrawing it at the speed of 0.30 mm/s. The coated substrates were generally sintered for 10 min at 400-600°C. After sintering, the coatings were cleaned ultrasonically in acetone for 5 min and in ethanol for another 5 min and, finally dried at ambient temperature. This dipping, heating and washing cycle was repeated so many times as the coating layers were needed. Sols were characterized by measuring viscosity and changes in particle size as function of time with capillary viscometer or rotational rheometer and dynamic light scattering, respectively. Atomic force microscopy was used to analyze nanoscale properties of films and scanning electron microscopy was used to support the surface analysis. In addition, *in vitro* analyses in the simulated body fluid as well as pilot *in vivo* analysis were made for the sol-gel derived films (D5-D7,D11,D22).

Bond strength (tensile) of TiO_2 gel films to titanium substrate were studied using different pretreatments; sodium hydroxide corroding, plasma cleaning and titanium nitride coating. In addition, effects of heating temperature, heating vacuum and titanium surface roughness were studied. Samples were analyzed by scanning electron microscopy (SEM), AES, AFM and tested by a pull off test, where steel cylinders were glued to the TiO_2 coated titanium plates (D5).

The surface topography of the titania films can be modified by carefully controlling the sol properties as a function of the aging time and by changing the number of the coating layers. The surface analysis revealed the topography of the outermost surface of films varied clearly on nanoscale and it is suggested to have an influence both on the physical and chemical properties. It has locally also an influence on the surface charge density (D6-D7,D11,D22).

The bonding strength of the sol-gel derived TiO_2 coatings to titanium substrate was found to be sufficiently high for implant coatings. Different pretreatments could be used to adjust the bonding strenght to over 24 MPa; grinding, titanium nitride coatings and sodium hydroxide corroded substrate structures (D5).

2.5.2 Fibres

Biomedical fibres of silica are novel materials and the flexibility of the sol-gel process creates possibilities to prepare various functional materials. The easy introduction of drugs and other related substances into the porous structure provides one example. Biodegradable and non-toxic biomedical materials that are able to work directly and locally in the human body would often be beneficial, for example as implants used as drug delivery devices or temporary implants in bone repairs. The sol-gel derived silica fibres can be prepared to fulfil these requirements.

In the case of the sol-gel derived silica fibres, there are two main parameters determining the fibre bulk structure. By controlling the degree of branching of silica clusters, more or less condensed green fibre structures are achieved. The heat treatment of the fibres is another and more efficient way to condense the bulk structure. Depending on the application of the sol-gel derived biodegradable silica fibres, the optimum balance between mechanical properties and biodegradation may vary. If the fibres are used for drug delivery in soft tissue, the mechanical properties are of minor importance. However, the mechanical properties must allow processing of the obtained fibres to a desired form after spinning. If better mechanical properties are needed, it has to be remembered that biodegradation ceases after heat-treatment at high temperatures. The identification of the optimal mixture of mechanical properties and biodegradation is the main challenge for research.

The aim of studies were to prepare different alkoxy-derived biodegradable silica fibres using the sol-gel method by controlling the functionality of the silica precursor (tetraethyl orthosilicate, TEOS) and the structure of the polymeric silica clusters. Both the sols and the green state fibres were characterised to determine factors in the fibre bulk structure that define the fibre solubility (biodegradation) and ability to form calcium phosphate in a simulated body fluid.

Dry spinning was used to prepare the sol-gel fibres. The spinning solution was kept in a container. When the spinning solution reached a certain level of viscosity, spinning was started. A rotational viscometer with a disc shaped spindle (Brookfield LVDV II+)

was used to define the point where the spinning could be started. Nitrogen gas was led into the closed container to push the spinning solution to a gear pump. The gear pump (Zenith 958736) with a capacity of 0.6 ml/revolution metered the spinning solution to the spinning head. The spinneret is made of a gold/platinum alloy. The diameter of the holes was 0.065 mm and the l/d ratio was 1. The number of the holes was 6. The distance between the spinneret and the wind-up roll was adjusted to meet the demands of each fibre.

Transmission electron microscopy (TEM) is used to illustrate the inner bulk structure of the green body of the fibre and AFM is used to probe the surface properties. In addition, the fibers were characterised for bioactivity and biodegradation in the simulated body fluid (D10,D12-D14,D22).

The fine adjustments of the recipes had a slight influence on the biodegradation, but the sol-gel process stage had a much stronger influence. The fibres spun in the early stage of the spinnability degrade more slowly in the SBF. The spinnability is achieved by controlling the viscosity level by enhancing or lowering the temperature of the sol. Addition of NH_3 into the sol pre-catalysed by an acid did not destroy the spinnability, but the reaction time is reduced remarkably. Evaporation of ethanol or enhanced reaction temperature did not have an influence on the spinnability as compared to the corresponding samples kept in closed vessels, only reaction times were reduced. This provides a good way to control the total time of the preparation process. If the fibres are heat-treated at temperatures below 300°C, the differences in the fibre bulk structures are remarkable. By combi-ning the concentrations of substances, process stage, reaction circumstances and the viscosity of the sol properly, different green state fibre structures with adjustable biodegradation can be prepared. The results indicate that the surface structure in the nanometer scale varies clearly as the fibers are spun at various spinning moments (D10,D12-D14,D22).

The *in vitro* bioactivity and solubility tests were performed using a simulated body fluid (SBF). In these studies the term “bioactivity” signifies the ability of different materials to form calcium phosphate on its surface. It is considered that the essential condition for an artificial material to bond to a living bone is the formation of a certain type of calcium phosphate, bone-like apatite on its surface in body environment**.**

Fig. 1. A cross section of a sol-gel derived SiO_2 fiber after being immersed in the simulated body fluid for two weeks. Lighter area has been identified to be hydroxyapatite (HA).

Thus, it is expected that it is possible to evaluate bone-bonding ability of a material by *in vitro* tests in which apatite formation on surface is examined in different solutions simulating the body fluid. One commonly used solution which is able to reproduce *in vivo* surface structure changes is the simulated body fluid (SBF).
A general reason to use simulated body fluids, e.g. SBF, is to predict possible bioactivity and to save time and money when the basic tests are made *in vitro* before the expensive and time consuming *in vivo* experiments. In addition, the *in vitro* tests also enable a fast way to design new biomaterials or improve the properties of existing materials.

The calcium or phosphate required for apatite generation on the different oxide surfaces were extracted from SBF. The reduction of the concentration of phosphorus or calcium in SBF indicates the possible apatite layer precipitation on the different surfaces (described in Figure 1 and 2). In addition, SiO_2 concentration was monitored when needed (D4-D15,D22).

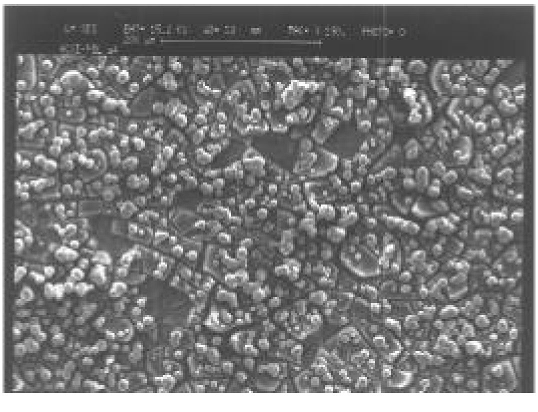


Fig. 2. Hydroxyapatite granulates on sol-gel derived SiO_2 monolith.

2.5.3 Preparation of Simulated Body Fluid (SBF)

The simulated body fluid (SBF) was prepared by dissolving reagent chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$ and Na_2SO_4 into deionised water. The fluid was buffered at physiological pH 7.40 at 37°C with tris(hydroxymethyl) aminomethane and hydrocloric acid.

In different experiments, three specimens from each studied materials were used to investigate the reactions of the materials in SBF. Each specimen was immersed in 50 mL of SBF in a closed polyethylene container. Three samples of SBF enclosed in bottles without a specimen were used as controls to examine the solution stability. The specimens were immersed in the SBF fluid for 2-6 weeks, the bottles being placed in a shaking water bath (Heto SBD 50 (160 strokes pr. minutes with stroke amplitude 36 mm)) having a constant temperature at 37°C (D4-D15,D22).

2.5.4 Ion Concentration Analysis

Depending on the experiments, the differences in the solubility of the different SiO_2 substrates were determined by the silicon released in the SBF. Sample solutions were monitored for silicon concentrations as a function of the immersion time (Figure 3). The silicon concentrations were also analysed by a molybdenum blue–method with UV-Vis spectrophotometer (Pharmacia LKB. Novaspec II or Hitachi Model 100-60). The silicon analysis was based on reduction with 1-amino-2-naphthol-4-sulfonic acid. All sample solutions were tested three times each (D4-D15,D22).

In addition, sample solutions were monitored for calcium or phosphorus concentrations as a function of immersion time in the SBF to routinely determine if the possible apatite layer is formed on the different surfaces (Figure 5). Calcium concentrations were determined with atomic absorption spectrophotometer (AAS, Perkin-Elmer 460, Figure 4). Phosphorus concentrations were analysed by a molybdenum blue -method (which is different as in the case of the silicon analysis) with UV-Vis spectrophotometer (Pharmacia LKB. Novaspec II or Hitachi Model 100-60). The phosphorus concentrations was analysed by the Lowry-Lopez method.

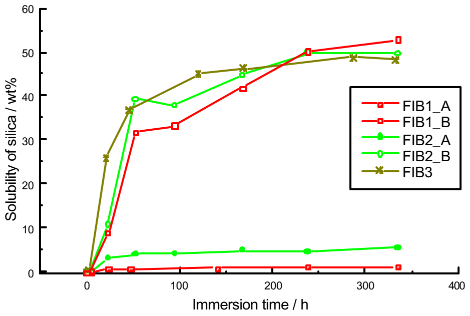


Fig. 3. Clear changes in SiO_2 solubility for sol-gel derived fibers being immersed in SBF.

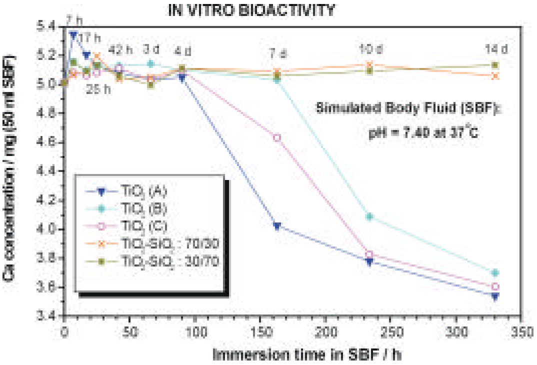


Fig. 4. Routine measurements to determine *in vitro* bioacitivity by measuring Ca concentration in the simulated body fluid as a function of immersion time.

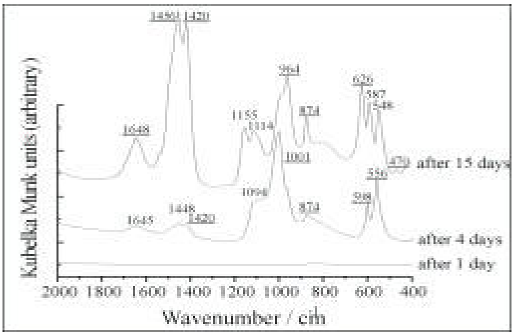


Fig. 5. A typical "fingerprint" of carbonate-containing hydroxyapatite formed on sol-gel derived TiO_2 film surface after being immersed in the simulated body fluid (15 days).

2.5.5 Nanoscale Structure and Bioactivity *In Vitro*

The structure, especially the surface structure of the sol-gel derived materials has been analysed more closely in the nanometer scale. The correct proportions between the peaks and peak distances has been observed to be important with respect to the *in vitro* bioactivity. Typical non-bioactive and bioactive surfaces are described in Figure 6. The results are analogous for all morphologies studied, monoliths, films and fibers. The results indicate that the peak distance distribution between 5-50 nm, especially between 5-20 nm, together with the peak height ≥ 1 nm are most favourable for the calcium phosphate formation. Typical distributions for non-bioactive and bioactive surfaces are described in Figure 6. The dimensions of a continuous oxide surface below 5 nm cannot be reliably measured by AFM. However, the pore structure measurements performed for SiO_2 monoliths show that the most important dimensions are above 5 nm.

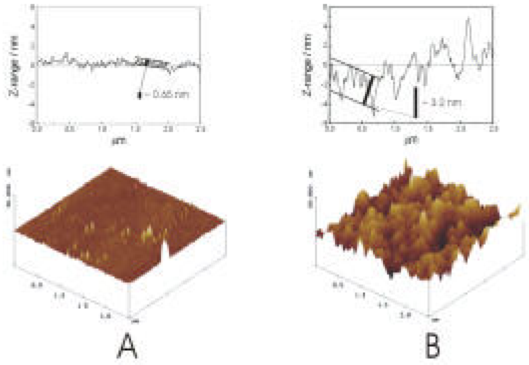


Fig. 6. AFM images with corresponding line profiles describing topography of a non-bioactive (A) and bioactive (B) SiO_2 surface.

The peak distances greater than 50 nm did not have any significant effect on the *in vitro* bioactivity. In the region of 15-50 nm, the narrower the peak distance was the greater was the number of them. It is also interesting to notice, that the bone in general, is made up of microscopic plate-like calcium phosphate crystals (20 by 3-7 nm) formed within and between fibrils of collagen. In other words, the surface dimensions of our sol-gel derived SiO_2 or TiO_2 materials for rapid *in vitro* calcium phosphate formation seems to be quite similar with the dimensions of the calcium phosphate crystals in the bone. This gives rise for an interesting thought about the role of the surface and its relation to the heterogeneous nucleation, supersaturation and optimal thermodynamic conditions. In summary, the most favorable dimensions on the materials surface to form HCA match with the natural size of calcium phosphate crystals in bone (D9,D11,D14-D15,D22).

The pore structure or the textural features of the sol-gel-derived SiO_2 monoliths have also been examined. It was found that a great mesopore volume and a wide mesopore size distribution (5-50 nm), preferably above 5 nm favoured the HCA nucleation and a great surface area was not needed. However, this study report about the bulk structures, only giving indirect information about the surface structures and dimensions (D9).

The amount of released silica (in SBF) could not be shown to be in correlation with the *in vitro* bioactivity, because both slowly and fast dissolving SiO_2 samples were bioactive. Anyway, it is possible that some kind of silica solubility is also needed together with the optimum surface structure for rapid calcium phosphate formation on the fiber surfaces (D9,D13-D14,D22).

The surface structure before immersion in SBF does not represent exactly the real surface characteristics of the surface, just before the calcium phosphate nucleation occurs in the SBF. Many of these materials have a good *in vitro* bioactivity, i.e., they have similar ability to form calcium phosphate rapidly, although TiO_2 samples are rather insoluble, some of the SiO_2 samples have dissolved a lot, some of them only slightly. The structure of the surface before immersion in SBF is similar in these cases, but there are great differences in the solubility. In the case of highly soluble materials, it is assumed that dimensions of the gel surfaces in the nanometer scale resemble the dimensions of the original surfaces (D9,D11,D14-D15,D22).

2.5.6 Protein Adsorption on Sol-Gel Derived Materials

When studying the effects of protein adsorption on apatite formation on coatings titania coatings were produced on quartz glass cover-slips. To get better attachment between the standard coating and the quartz glass the sol properties had to be improved. Sol properties were tried to improve with valeric acid addition. All procedures were compared with standard procedure. Valeric acid : $Ti(OR)_4$ and $H_2O:Ti(OR)_4$ molar ratios were maintained at 0.50 and 1.5.

Coated and non-coated samples were incubated in human plasma in order to obtain a simulated protein adsorbed surface of an implant. Three pieces of each material were immersed in SBF as such or after 1 h pretreatment in human plasma. Human plasma incubated materials were analysed using sodium dodecyl sulfate, polyacrylamide gel electrophoresis (SDS PAGE). All solutions was monitored for change in both calcium and phosphate concentration as a function of immersion time. Calcium concentration was determined by using AAS. The surfaces were analyzed using SEM-EDX, thin-film X-ray diffraction (TF-XRD) and optical microscopy.

TiO_2 films without protein adsorption and sintered at 500°C formed apatite on their surface fastest of all coatings in this study. Protein adsorption seems to slow down the apatite formation on the active coatings somewhat. On the other hand proteins adsorbed on any surface nucleate apatite formation after two weeks. On the control samples (with no Ti-coating) apatite formed after 3 weeks with protein adsorption and not at all without. Although protein adsorption *in vitro* has a marked effect on apatite formation it is not known if the effect is similar in *in vivo* conditions. Ca and P doped Ti-coatings were not cabable of inducing apatite formation sintered at any temperature up to 600°C. This effect is probably caused by densification of the Ti-coating by these additives (D4).

2.5.7 *In Vivo* Analysis

In the first experiment, TiO_2-coated titanium implants were implanted press-fit in the distal epiphysis of both femurs of 20 rabbits perpendicularly to the long axis behind the patellar sliding plane. The specimens were prepared for light microscopy and histomorphometry was carried out evaluating total length, length of bone, osteoid, chonroid and soft tissue. A bony frame was observed around the implants after 84 and 168 days of implantation. SEM analysis showed a continuity of the mineralised material between the implant and bone. The amount of bone on the coated cylinders was higher than in normal, non-coated c.p. titanium (D3).

Another test was done on the sol-gel derived TiO_2 films. Eight adult New Zealand White female rabbits, weighing 3-4 kg, were used. The rabbits were anaesthetized by intramuscular (i.m.) injections of Hypnorm® at a dose of 0.3 mL/kg body weight (b.wt.). Implantation was made unilaterally in the femural bones. After incision through the skin and periosteum, a flap was raised to expose the bone area. After low-speed drilling three conical implants were inserted in rabbits femural bone with press-fit technique. The animals were killed with an overdose of Hypnorm intravenously (i.v.) and fixed by ethanol (70%). The implants and femural bone were removed together. Animals were followed 17, 28, 61 and 90 days. Calcium phosphate deposits were observed on the TiO_2 film surfaces after the implantation period of 28 and 90 days. Corresponding control samples (c.p. titanium) did not show any calcium phosphate deposition within the 90 days of implantation (D11).

2.5.8 Main Conclusions for Characterisation of Bioapplications

Different materials obtained clearly different *in vitro* bioactivities as well as the biodegradation could be varied within a large range. The results indicate that the surface structure before immersion in SBF in the nanometer scale is the most important factor controlling the *in vitro* bioactivity of the sol-gel derived films and fibers. The peak distance distribution between 5-50 nm, especially between 5-20 nm, together with the peak height ≥ 1 nm are the most favourable dimensions for the calcium phosphate formation. Same analogy was observed for monoliths, as the best results were obtained for the samples having a mesoporous (by definition d = 2-50 nm) structure. These dimensions match also with the natural size of calcium phosphate crystals in bone. The inner structure as well as the surface structure of SiO_2 could be varied so that biodegradation could be adjusted to be about 20 times faster in the most soluble samples as compared to slowest dissolving samples.

Addition of calcium and phosphorus species in the sol-gel derived SiO_2 and TiO_2 did not have unambiguous effects on the bioactivity. As they strongly affected the formed structure both in the case of monoliths and films, it is hard to distinguish between the effects caused by the varying structure and varying chemical composition. In the case of monoliths, one sample with mole ratios 35% Ca and 5 % P in SiO_2 obtained good *in vitro* bioactivity results, but all the other Ca- and P-doped samples were worse than pure sol-gel derived SiO_2 samples. In the case of TiO_2 films, the highest bioactivity was observed for undoped TiO_2 coatings. The bioactivity of the doped coatings was inversely proportional to the dopant level; no bioactivity was observed for coatings with a dopant level of 2.5 mole % or higher.

Protein adsorption seems to slow down the apatite formation on the active coatings somewhat. It is obvious, as the proteins always adsorb very fast on any surface, that they change the surface structure and chemistry and introduce thus new parameters to be studied in the *in vivo* conditions.

Our preliminary *in vivo* experiments gave proof that the *in vitro* bioactivity test gives an reliable indication of the *in vivo* calcium phosphate forming ability which may lead to the osteoconduction and further to the bone bonding (D3-D15,D22).

3 International Aspects

The project has benefited from the collaboration of the partners with the following formal networks:

* EU-TMR research program, "Mechanisms of the formation of ordered meso-morphous, inorganic materials from organized molecular assemblies"(MESOP).
* ESF research program, "Vapor-pgase synthesis and processing of nanopartcle materials" (NANO).
* Ministry of Education, Finland, Graduate School of Materials Research

Bilateral collaboration with the following research units has provided support for the project members:

* Ian Wark Research Institute, University of South Australia (Prof. J. Ralston, Dr. J. Matison)
* Max-Planck Institut fur Kohlenforschung (Prof. Ferdi Schuth)
* Institute of Biophysics and X-ray Structure Research, Austrian Academy of Sciences (Prof. P. Laggner).
* Japan Fine Ceramic Center, Nagoya (JFCC, Dr. H. Matsubara)
* Department of Pathology, Free University of Berlin (Dr. C. Muller-Mai)
* Department of Clinical Dentistry, Sheffield University (Dr. Paul Hatton)

3.1 Positions in international organisations

* Jarl B. Rosenholm has been acting as a president of the European Colloid and Interface Society (ECIS)
* Jarl B. Rosenholm has beenacting at the council of the International Association of Colloid and Interface Scientists (IACIS)
* Jarl B. Rosenholm has been acting as a Titular member at the International Association of Pure and Applied Chemistry (IUPAC, CI6)
* Jarl B. Rosenholm has been acting at the standing International Board for the European Colloid and Interface Conferences (ECIC)
* Jarl B. Rosenholm has been acting at the standing International Advisory Board for the Electrokinetic Phenomena Conferences (ElKin)
* Jarl B. Rosenholm has been holding the chair of the National Graduate School of Materials Research

4 Publications and Academic Degrees

Table 4.1. Publications and academic degrees produced in the project by each partner listed in the sequence DPC/IMS/ID for all publications to which group members have contributed. Each type is listed separately in section 6.

Partner	Type of publication	1997	1998	1999	2000	2001	**Total**
DPC/IMS/ ID	Ref. Journal art.	3/2/2	6/1/4	9/1/1	18/3/4	16/9/6[a]	**52/16/17**
	Ref. Conf. papers	11/13/3	2/7/-	2/-/1	1/2/-	N/A	**16/22/4**
	Monographs	-	-	1	-	-	**1**
	Doctoral dissert.	-/-/-	/-/-	2/-/-	-/1/1	3/1/-[c]	**5/2/1**
	Licentiate degrees	-/1/-	-/-/-	-/-/-	-/-/-	1/-/-	**1/1/-**
	Master degrees	/-/1	2/1/-	-/-/-	-/-/-	-/-/-	**2/1/1**
	Other activities	-/1/-	-/2/-	1/1/-	-/-/-	-	**1/4/-**
	Patents or appl.			1/2/1	1/-/1		**2/2/2**

a) Including publications in press and submitted
b) Due to the large number, only a few are listed
c) Those under preparation included

5 Other Activities

5.1 Patents, Patent Applications and Invention Disclosures

Jokinen M., Peltola T., Veittola S., Ahola M. and Kortesuo P., US. Provisional Patent Application No. 0627.6006 (22.2.1999), PCT-Application No. FI00/00131 (22.2.2000), Biodegradable Ceramic Fibres From Silica Sols

Leivo J., Nikkilä A-P., Levänen E., Mäntylä T., Filter Element Produced by A Reaction-Sintering Process, US-patent application 09/297,882, 1999.

Leivo J., Nikkilä A-P., Levänen E., Mäntylä T., Filter, PCT-patent FI103644, 1999.

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6 Publications

It is not possible to assign a publication appearing after the termination of a project reliably as being produced only within the framework of the project. Therefore, for simplicity all publications related to results produced during the project period are reported as publications without restriction. Due to the large number of conference papers only a fraction of representative papers are reported here but are mainly included in the numbers given in the Table 4.1.

6.1 Refereed Journal Articles

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NANO-OPTICS AND ELECTRONICS

M. Salomaa, G. Aminoff, M. Lindberg, J. Sinkkonen and J. Tulkki.

No information provided.

STUDIES ON BIOABSORBABLE, BIOACTIVE POLYMERIC COMPOSITES

P. Törmälä [1]

Abstract

The purpose of this project has been to develop and study novel, biomimetic, synthetic, high performance, bioabsorbable materials and implants. Biomimetic behaviour of the material means that the material has chemical and physical properties imitating the behaviour of living tissues. Bioactive composites were developed from bioabsorbable polymers (lactide copolymers, polyorthoesters and pseudopolyaminoacids), fibrous reinforcements (organic and inorganic fibers), ceramic fillers (bioglass and calcium phosphate particles), ceramic coatings and bioactive molecules, like growth factors.

The cellular and tissue responses and bioabsorption of biomimetic composites were studied with animal studies in musculoskeletal applications. The cellular reactions caused by the bioabsorption of biomimetic materials and implants were studied in detail both with histological, immunohistochemical, electronmicroscopical and with *in vitro* cell cultural methods.

Membranes and plates were studied for guided tissue regeneration in connection with implantology, in calvarial bone fracture fixation and in guided bone regeneration.

Cell cultures, animal experiments and clinical trials were done with bioabsorbable stents manufactured from bioabsorbable composites. In cell cultures toxicological behaviour of stent materials was studied. In animal studies and in clinical trials the performance of bioabsorbable stents in urethral, in ureter and in biliary and in cardiovascular applications were studied.

1 Partners and Funding

The partnership of the project has based on cooperation between material researchers and surgical research groups. Funding of research work has been obtained from Academy of Finland (AF), National Technology Agency (NTA), universities and industry.

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1.1 Institute of Biomaterials, Tampere University of Technology (“Tampere”-group), Tampere, Finland. (Abbr. IB-TUT)

The MATRA research group has consisted of project leader Academy Professor P. Törmälä, and of 6 postgraduate students.

1.2 Department of Orthopaedics and Traumatology, Helsinki University, Helsinki, Finland. (Abbr. DOT-HU)

The research group has consisted of subproject leader Prof. (mer.) P. Rokkanen, 12 senior researchers (at least MD or VMD and PhD) and 10 junior researchers (MD, VMD, BMS).

1.3 Department of Oral and Maxillofacial Surgery, Helsinki University, Helsinki, Finland. (Abbr. DOMS-HU)

The research group has consisted of subproject leader Prof. C. Lindqvist and of two senior researchers.

1.4 Department of Surgery, Oulu University Central Hospital, Oulu, Finland. (Abbr. DS-OUCH)

The research group has consisted of subproject leader Docent T. Waris, three senior researchers and four postgraduate students.

1.5 Department of Urology, Tampere University, Tampere, Finland (Abbr. DU-TU)

The research group has consisted of subproject leader Prof. T. Tammela and one postgraduate student.

1.6 Funding

Table 1. Funding of different research partners (kFIM)

Partner	Funding organisation	1997	1998	1999	**Total**
IB-TUT	TUT	400	400	400	**1200**
	AF	500	500	500	**1500**
	Industry	600	600	600	**1800**
	NTA	500	500	500	**1500**
DOT-HU	HU	150	150	150	**450**
	AF	300	300	300	**900**
DOMS-HU	HU	200	200	200	**600**
DS-OUCH	OU	100	100	100	**300**
	NTA	300	300	300	**900**
Total		**3050**	**3050**	**3050**	**9150**

2 Research Work

2.1 Objectives and Work Plan

Goals of the project have been the development of new biomimetic bioabsorbable composite materials by processing new bioabsorbable polymers, fiber reinforcements, particle fillers and/or bioactive organic molecules with modern melt-molding and solid state processing methods to the desired compositions with the desired mechanical properties and hydrolysis behaviour.

Studies of interactions between degrading implants and the surrounding cells and tissues are targeted to give new scientific information of the mechanisms of reactions leading to the fragmentation, digestion and dissolution of implant materials in relation to tissue healing, reconstruction and regeneration.

Technological goals of the project have been to apply the scientific basic information created in the project in practically oriented research and development projects to develop full-scale composite implant manufacturing methods and new generations of biomimetic implants which open new application possibilities in surgical practice.

By using biomimetic materials and coatings new generations of biocomposites can be developed with minimal tissue reactions and with better tissue tolerances and at best such materials contribute actively to tissue healing and regeneration and to new tissue formation.

2.2 Progress Report: Common Themes

2.2.1 Bioactive Character of Bioabsorbable Polymers and Composites

Research collaboration between several partners has shown that bioabsorbable polymers and implants express bioactive behaviour in different tissue environments. The bioactive behaviour was manifested in studies of:

- Bone or connective tissue healing after osteotomy fixation with bioabsorbable implants in comparison to the fixation with metallic implants [17, 29, 32, 34, 125]
- Development of bone mineral density after fracture/osteotomy fixation [55]
- Guided bone-defect healing with membranes or plates [8, 34, 77, 80, 111, 115, 206]
- Reconstruction of small joints with bioabsorbable joint scaffolds [35, 52, 97, 104]

The bioactive behaviour of bioabsorbable implants is evidently a consequence of their mechanical properties and of the bioabsorption process.

Because the modulus of self-reinforced bioabsorbable fracture fixation implants is the same order of magnitude as the modulus of cortical bone, these materials do not cause such a stress protection atrophy which high stiffness metal cause. The “natural” stiffness of bioabsorbable implants evidently accelerates internal callus formation and ossification in the fracture line and prevents the reduction of bone mineral density typical for the metallic (stainless steel) implants.

The bioabsorption process of poly-α-hydroxy acids releases acidic monomeric and oligomeric degradation products, which evidently are the reason to the antibacterial effects of implants made of them.

The results of this project have shown that bioabsorbable implants, when exhibiting advantageous mechanical and bioabsorption properties and proper geometrical forms, can act as bioactive scaffolds contributing in a positive way to regeneration and reconstruction of damaged tissues.

2.2.2 Enhanced Bioactivity

Although bioabsorbable implants in favourable compositions and geometries express bioactive behaviour, their bioactivity can be enhanced significantly with bioactive additives, like drugs, ceramics or growth factors. Therefore one objective of this project has been to develop bioabsorbable polymeric carriers and composites with bioactive molecules. Such materials will release bioactive additives, like drugs, growth factors etc. typically some weeks or months. Following bioactive additive releasing systems have been developed and studied in this project:

- Antibiotic releasing composites [66, 101],
- Polylactide-hydroxyapatite composites [47, 227],
- Poly-α-hydroxy acid- $BaSO_4$ composite (x-ray positive) stents [51, 120, 128],
- Bioabsorbable, bone morphogenic proteins (BMP) releasing systems [70, 93, 132, 164, 186],
- Bioabsorbable polymer – bioactive glass composites [116, 124, 214, 216],
- PLLA stents coated with silver nitrate and oxofloxazine for antibacterial effects [179],
- ε-caprolactone/lactide-tricalcium phosphate composite [143, 183, 221],
- Polyactive™ -bioactive glass composite [217,218].

2.2.3 Conclusions

Several of the above bioactive, bioabsorbable composites have expressed bioactive additive releasing behaviour, which may further be applied clinically to enhance the efficiency and performance of bioabsorbable implants. Some of the most interesting results were:

- Ultrasonically molded polylactide – ciprofloxazine composites release therapeutic doses of ciprofloxazine over several months *in vitro* [66, 101],
- BMP released from bioabsorbable bone osteotomy fixation pins enhances callus formation in healing cancellous bone, however, not in distal femur [70, 93, 132 164, 186, 203]

- Bioabsorbable glass dissolves *in vitro* from composites with bioabsorbable polymers and the precipitation of hydroxyapatite (HA) crystals on composite surfaces can be seen. The new HA precipitations evidently are osteopromoting enhancing osteoconductive character of bioabsorbable implants [116, 124, 214-218],

- Bioabsorbable stents coated with silver nitrate and oxofloxazine may be applied clinically as antibacterial urethral stents [179].

2.3 Progress Report: Partner IB-TUT

In Institute of Biomaterials (TUT) the research work has been focused to processing, structural and property studies of bioabsorbable polymers and to the development of composite materials, especially bioactive composites, and implant prototypes of these polymers to the studies of other partners.

The polymers have been lactide polymers and copolymers [16, 20, 22, 23, 37, 46, 50, 69, 96], polyglycolide [24, 83], caprolactone copolymers [13, 36], polyorthoesters [95], tyrosine polycarbonates [122], Polyactive™ [36] and starch derivatives [189]

Polymer materials have been processed with melt molding techniques, like extrusion [35], with ultrasonic molding [4, 6, 25, 66], with compression molding and with solid state deformation techniques [5, 33, 39, 43, 67]. The processed material geometries have been fibers, films, plates, rods, and more sophisticated forms, like screws, tacks and stents.

In these studies we have developed further so-called self-reinforcing (oriontrusion) technique, where solid polymer billets are oriented by deformation in solid state [68, 71, 88, 91, 110, 170]. This orientation increases many times the strength and ductility of bioabsorbable polymers. The technique was applied first time in biomaterials research by our group in 1980's and nowadays also many other research groups as also some companies in Europe, USA and in Japan apply this method in biomaterials technology.

Based on development of bioabsorbable materials, the research group has also developed several bioabsorbable implants and their installation instruments for musculoskeletal, CMF, cervical, tracheal, urological and cardiovascular applications [3, 30, 31, 49, 52, 63, 65, 85, 90, 97, 104, 107, 117, 123, 133, 162, 171, 174, 180, 194-197, 202, 204, 213].

This work has yielded also several patents and patent applications describing bioabsorbable and/or bioactive composites and implants and surgical installation instruments [3, 30, 31, 85, 87, 90, 98, 100, 131, 153, 158-161, 181, 182, 191, 196, 197, 208-212].

2.4 Progress Report: Partner DOT-HU

This group has continued the studies on bioactive and bioabsorbable materials, like: biodegradation of polyglycolide membrane *in v*ivo, callus transplant as a bone graft, fixation of osteotomies and fractures, intraosseous plating, ligament augmentation, cellular response of bone to polyglycolide and polylactide materials, guided bone healing with bioabsorbable membranes, and experimental model to study the tissue reactions [1, 7, 8-11, 17, 26, 29, 32, 38, 41, 42, 44, 45, 53-56, 76, 81, 82, 84, 86, 92, 94, 102, 113-115, 125, 130, 137, 140, 141, 156, 163, 167, 184, 187, 198- 200, 205-207].

The other main objectives of experimental and clinical studies have been the development of bioactive and osteogenic implants to enhance fracture repair and guided restoration of bone defects. Transforming growth factor beta1 has been applied to accelerate the healing process of certain fractures, delayed unions and bone defects [70, 93, 132, 164, 186].

2.5 Progress Report: Partner DOMS-HU

This partner has studied the non-specific foreign body reaction caused by implantated bioabsorbable materials (polylactides, polyglycolides, polyorthoesters) or biostable materials (titanium) and clinical applications of bioabsorbable implants in CMF-surgery [72-75, 143-148, 220-228].

A long term clinical trial of fixation of split sagittal osteotomies with self-reinforced polylactide screws has been continued. Ca. 50 patients have been treated during 4 years, with as a rule uneventful healing. The group has also done clinical studies of using small polylactide screws and plates in fixation of maxillofacial fractures.

2.6 Progress report: Partner DS-OUCH

In this subproject bone tissue regeneration, reconstruction and healing processes have been studied experimentally and clinically in craniofacial surgery using as models polyglycolide and polylactide plates, screws and membranes [27, 28, 34, 77, 80, 89, 108, 111, 112, 134-136, 138, 139, 154, 155, 157, 165, 166, 168, 169, 188, 192, 201].

2.7 Progress Report: Partner DU-TU

This partner has studied toxicological behaviour of bioabsorbable polymers and composites, bacterial adherence to bioabsorbable polymers and antibacterial composites and the use of bioabsorbable stents as urological implants with animal experiments and clinical trials [2, 12-15, 18, 19, 21, 48, 57, 58, 60-62, 64, 78, 79, 103, 105, 118-121, 126-129, 142, 172, 173, 176-178, 193, 196].

3 International Aspects

The researchers of the partner institutions have given every year tens of lectures in domestic and in international meetings.

The publication list of this report shows that lot of the results of this project have been published in prominent international medical journals or materials science journals.

4 Publications and Academic Degrees

Partner	Type of publication	1997	1998	1999	**Total**	Publication numbers
IB-TUT	Ref. journal art.	5	2	6	**13**	16,19,33,66,71,91,130,174, 175,190,193,195,219
	Ref. conf. papers	23	17	16	**56**	12,13,21,22,35-37,39,40,43, 46-52,57,58,63,67-70,88,95-97,104,107,110,116,118, 121-124,126,129,132,133, 162,173,176,177,180,185, 194,201-204,214-218
	Monographs	-	1	1	**2**	117,213
	Patents and patent applications	10	10	16	**36**	3-6,20,23,25,30,31,65,83,85, 87,90,98-100,103,105,131, 153,158-161,181,182,189,191, 196,197,208-212
	Master degrees	2	2	3	**7**	
DOT-HU	Ref. journal art.	6	2	2	**10**	1,29,32,38,55,56,76,86,156, 164
	Ref. conf. papers	12	12	7	**31**	7-9,11,24,26,41,42,44,45,53, 54,81,82,84,92-94,102,113, 115,137,140,141,184,186, 187,198-200,206
	Monographs	2	1	-	**3**	10,17,125
	Doctoral dissert.	1	3	1	**5**	
DOMS-HU	Ref. journal art.	2	5	6	**13**	72,73,145-148,183,220-223, 227,228
	Ref. conf. papers	2	7	3	**12**	74,75,109,143,144,149-152, 224-226
	Doctoral dissert.	-	-	1	**1**	
	Masters degrees	-	-	1	**1**	
DS-OUCH	Ref. journal art.	3	2	1	**6**	27,28,77,80,89,188
	Ref. conf. papers	1	9	14	**24**	34,108,111,112,114,134-136, 154155,157,163,165-171, 192,205,207
DU-TU	Ref. journal art.	3	2	-	**5**	2,18,64,78,79
	Ref. conf. papers	6	5	3	**14**	14,15,59-62,119,120,127, 128,138,142,172
	Monographs	1	-	-	**1**	
	Doctoral dissert.	-	-	1	**1**	

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RESEARCH PROJECTS ACCEPTED IN THE FOURTH ROUND OF APPLICATION 1998 - 2000

IMPROVING THE WEAR AND CORROSION RESISTANCE AND FIXATION OF IMPLANTS BY AMORPHOUS DIAMOND COATING. EVALUATION OF BIOLOGICAL HOST RESPONSE TO NEW MATERIALS.*

Asko Anttila[1] and Seppo Santavirta[2]

Abstract

The main barrier to the progress of diamond coatings has been adhesion. To overcome this barrier, we have developed a new, superior, simple method (unique in the world) based on pulsed accelerator units and graded structures at the interface between the substrate and diamond coating. This technique enables the preparation of highly adherent thick diamond coating on any substrate material. Therefore, the excellent wear results, e.g. in the case of hip joint prosthesis were obtained. The wear rate measured in a commercial 6-channel hip simulator for 15 million walking cycles (requires to about 15 years of clinical use) in serum lubrication was negligible, i.e. even 1,000,000 times lower than the clinical values for commercial hip prostheses (polyethylene-metal or metal-metal pairs).** The coatings remained smooth throughout the tests without delamination. Furthermore, diamond is fully biocompatible and offers low coefficient of friction. It can be concluded that high quality amorphous diamond coatings should offer superior stability (minimal wear and corrosion debris release in surrounding tissues) and good biomechanical performance in clinical use. Elimination of wear debris should correspond to a substantial improvement of the longevity of the total hip replacement. In a more broad basic research view, by studying plasmas used in the deposition unit new useful knowledge of energetic non-equilibrium plasmas was obtained, e.g. from the energy and the ionization behaviour of plasma.

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* This title is somewhat misleading, because Prof. S. Santavirta's group did not get funds from Academy (MATRA) for the second period. However, we continue the co-operation with Prof. Santavirta's group in the National Excellence Group.

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** In our application for MATRA funds, we promised "to develop amorphous diamond coatings to achieve nonwearing and biocompatible total hip and knee prostheses, with radically improved clinical survival potential." This goal has been achieved.

1 Participants and Funding

1.1 Plasma Research Laboratory, University of Helsinki

The research group consists of project leader Emer. Professor Asko Anttila, Professor Reijo Lappalainen (present address University of Kuopio), senior researchers Panu Pekko PhD (at present working at VTT, Technical Research Centre of Finland), postgraduate students Veli-Matti Tiainen MSc, Esa Alakoski MSc, Mirjami Kiuru MSc and Mikko Selenius MSc (University of Kuopio) and students Antti Soininen and Leena Uusipaikka.

1.2 Funding

Table 1. Funding of the project in 1000 FIM in 1998-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Funding Organisation	1998	1999	2000	**Total**
Academy	160	460	160	**780**
Tekes*	160	160	160	**480**
UH**	400	400	400	**1200**
UK***		50	150	**200**
Total	**720**	**1070**	**870**	**2260**

*The National Technology Agency
**University of Helsinki
*** University of Kuopio

2 Research Work

2.1 Objectives and Work Plan

Almost all effort was aimed to the preparation of the well working artificial hip joint pairs. The cleaning and fitting techniques of the hip joint pairs were developed. The sample holder which enables the use of the complicated deposition process was constructed. The process consist of four successive steps: argon sputtering, tantalum deposition with magnetron sputtering, high energy carbon plasma deposition and final low energy carbon plasma deposition. The research and development of this project is continued as a part of national excellence group (Tissue Engineering and Medical, Dental and Veterinary Biomaterial Research Group).

2.2 Progress Report: Progress by the Plasma Research Laboratory

At present the most recent publication of the project is that of R. Lappalainen et.al [22]. It gives a detailed description of the main results, i.e. the simulator wear testing of the diamond coated hip joint pairs. Simulator testing procedures were approved in a large international comparison study.

3 International Aspects

The results of the research have been shared internationally via normal publishing procedures, i.e. articles and presentations on international forums. The articles of the group have been published in scientific journals with highest impact factors on the field of the materials science (Advanced Materials, Diam. Relat. Mater.). The members of the group have given presentations as invited speakers in international conferences, including the leading conference on tedrahedral amorphous carbon (ta-C) coatings, Specialist Meeting on Amorphous Carbon (SMAC 2000). The group has used its internet home page as an active channel of the scientific communication.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
UH	Ref. journal art.	6	8	2	-	**16**	1-6,7-14, 15-16
	Ref. conf. Papers	-	-	-	1	**1**	24
	Monographs	1	-	-	-	**1**	25
	Doctoral dissert.	-	-	-	1	**1**	26
	Licentiate degrees	-	-	-	-	**0**	
	Master degrees	2	5	1	4	**12**	27-38

5 Other Activities

Three patent applications have been submitted. If they will be accepted, the commercial breakthrough would be earlier. A member of the group was in television in a science program (Prisma) presenting our method. Members of our group have been as invited speakers in several conferences. Pictures of coatings manufactured in our laboratory have been in the covers of different series, e.g. the Annual Report of the University of Helsinki and in the Annual Report of Physics Department.

6 Publications

6.1 Refereed Journal Articles

[1] L. Yu. Khriachtchev, R. Lappalainen, M. Hakovirta, and M. Räsänen, Raman diagnostics of amorphous diamond-like carbon films produced with a mass-separated ion beam, Diamond and Related Materials 6(1997)694-699 .

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6.2 Refereed Conference Papers

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6.3 Monographs

[25] L. Yu. Khriachtchev, M. Räsänen, R. Lappalainen and M. Hakovirta, Raman spectroscopy of amorphous diamondlike carbon films produced with a mass-separated ion beam and pulsed arc discharge,in NATO ASI Series, Diamond based composites and related materials, M.A. Prelas et al. (eds.), Kluwer Academic Publishers, 1997, p. 309-321.

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[36] S. Lehti, Tekonivelpinnoitteiden väsymiskäyttäytyminen, Master thesis, Department of Physics, Univ. of Helsinki, Helsinki, 2000.

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CARDIAC TROPONIN C, STRUCTURE AND DYNAMICS

T. Drakenberg and I. Kilpeläinen

No information provided.

MATERIALS FOR MOLECULAR ELECTRONICS: CONDUCTING POLYMERS WITH WELL-DEFINED MORPHOLOGY

Jouko Kankare[1] , Henrik Stubb[2] and Ari Ivaska[3]

Abstract

In the Laboratory of Analytical Chemistry, University of Turku (UT), the main goal has been to develop new well-defined organic electroactive films by synthesizing new monomers, optimizing procedures for fabricating films and developing new techniques for characterizing them. A new method for making self-assembled thiol films on gold was developed, as well as new mathematical models for their adsorption and desorption processes. Electropolymerization and redox processes of polypyrrole and various polythiophene derivatives have been studied. New polyelectrolyte type water-soluble anionic and cationic polythiophene derivatives were synthesized and the first "all-thiophene" film was prepared by the layer-by-layer technique.

The overall goal of the research programme of Department of Physics, Åbo Akademi University (ÅAP) is to develop new organic materials and structures for molecular electronic devices. The focus is on charge carriers, their transport and redistribution (mobility, accumulation, trapping, etc.). Light emitting diodes (LED) and field effect transistors (FET) are our target devices. Active materials are primarily thiophenes, phenylenevinylenes and anilines. Langmuir-Blodgett, spincoating and spincasting techniques are used for making thin films. Special characterization methods have been developed: photomodulation spectroscopy (photoconductivity, photoinduced absorption, electroabsorption, time-of-flight TOF) and charge extraction in a linearly increasing voltage (CELIV, for the first time applied to organic materials)..

In the Laboratory of Analytical Chemistry, Åbo Akademi University (ÅAA), the concept of using conducting polymers as the ion-to-electron transducer has been developed further and applied to several new potentiometric ion-sensors. Amperometric ammonia sensors based on reduction of polypyrrole in presence of ammonia was developed. Spectroelectrochemical methods have been used in studying polymerization and redox reactions of several conducting polymers. Copolymerization of poly(paraphenylene) and poly(3-octylthiophene) have been studied as well as combination of fullerenes with conducting polymers.

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1 Partners and Funding

1.1 Laboratory of Analytical Chemistry, University of Turku (UT)

The present research group consists of project leader professor Jouko Kankare, also leader of the consortium, senior researchers docent Jukka Lukkari, docent Igor Vinokurov and Dr. Natalia Kotcharova, postgraduate students Mr. Mikko Salomäki, Mr. Tatu Hellström, Mr. Antti Viinikanoja, Mr. Timo Ääritalo, Mr. Janne Ahonen and Mr. Kari Kleemola and a student Ms. Hanna Paloniemi. During the years 1996-2000 the postgraduate students Mr. Markku Rajamäki, Ms. Mia Lindström and Ms. Eeva-Liisa Kupila (PhD 1996) have participated in the project, as well as students Ms. Janika Paukkunen, Ms. Minna Meretoja, Ms. Anna-Maija Ouwehand, Ms. Vuokko Lauerma, Ms. Hanna-Kaisa Kyyrönen. Mr. Matti Sillanpää, Ms. Tiina Kokko, Ms. Eija Toivanen and Ms. Heli Santalahti.

1.2 Department of Physics, Åbo Akademi University (ÅAP)

The following persons have participated in the research group: subproject leader prof. Henrik Stubb, Laboratory Manager Kjell-Mikael Källman, Postdoc (Academy of Finland) R. Österbacka, postgraduate students P. Granholm, H. Sandberg, and T. Ääritalo and student T. Bäcklund. Mr. Ääritalo has served as a synthesist both for the UT and ÅAP groups. Several visiting scientists have also contributed to the work (see Section 3).

Within MATRA, the ÅAP group has also participated in a consortium headed by prof. H. Lemmetyinen “Organic Thin Films with Functional Activity“. There is a division of tasks for ÅAP within these consortia, emphasizing electrical conduction and transport phenomena in the present one and optical transitions and charge transfer in Lemmetyinen’s consortium. A strict separation is still impossible as the two fields are intertwined.

1.3 Laboratory of Analytical Chemistry, Åbo Akademi University (ÅAA) (1998-2000)

The research group consists of subproject leader Professor Ari Ivaska, senior research personal: Professor Andrzej Lewenstam, docent Johan Bobacka, docent Carita Kvarnström, Dr. Li Niu (1999-2000), Dr. Tomasz Sokalski (2000), postgraduate students Ms Pia Damlin (PhD 2001), Ms Rose-Marie Latonen (PhD 2001), Ms Pia Sjöberg, Ms Mercedes Vazquez, Ms. Beatriz Meana Esteban, Ms Ann-Sofi Nybäck (Lic. 1999), Mr. Tom Lindfors (PhD 1999) and students (MSc) Mr. Tomas Asplund (1998-99), Mr. Patrik Grönholm (1998), Mr. Fredrik Sundfors (2000), Mr. Peter T. Lingenfelter, Mr. Petter Danielsson (2000), Ms. Marika Käldström (2000) and Ms. Johanna Nordman (2000).

1.4 Funding

Table 1. Funding of the project in 1000 FIM in 1998-2000.

Partner	Funding organisation	1998	1999	2000	**Total**
UT	UT	50	50	50	**150**
	Academy	550	680	670	**1900**
ÅAP	ÅAU	90	90	90	**270**
	Academy	300	450	450	**1200**
	Tekes	150	150	175	**475**
	Grad.school &doc grants	110	50	50	**210**
ÅAA	ÅAU	50	50	50	**150**
	Academy (MATRA+post-doc)	654	920	826	**2400**
	Industry	50	50	50	**150**
	Tekes	200	200	200	**600**
Total		**2204**	**2690**	**2611**	**7505**

2 Research Work

2.1 Objectives and Work Plan

The original research proposal (1994) concerned the synthesis, characterization and applications of electrically conductive polymers with the emphasis on the development of high-quality and well-characterized materials suitable for use in molecular electronics. The three research groups were not new in the field of conductive polymers; as a matter of fact, their research had already continued several years prior to the establishment of the consortium. The division of research was planned according to the previous expertise of the groups, i.e. optimization of conductive polymer film formation and spectroelectrochemical characterization of films (UT), physics of conductive polymer films and their use in semiconductive devices (ÅAP) and analytical applications of conductive polymers as sensor materials (ÅAA). This principle of division has not appreciably changed during the years of cooperation.

In the original research plan several issues were emphasized. The study of the mechanism of electropolymerization and nucleation in the procedure of preparing polymer films as well as the study of alternative methods of film preparation were considered as important issues. Completely new electrically conductive polymer materials were also planned to be synthesized, new characterization methods developed, and applications for molecular electronics studied. Preliminary studies on the applicability of the materials to the semiconductor devices, selective ion sensors and biosensors were planned.

As the second funding period started (1998), the plans remained essentially unchanged. However, some new issues appeared and somewhat different emphasis was laid on previous goals. During the later funding period the role of applications was more strongly stressed in the research plan. The application categories were *sensors* and *electrically light emitting materials*. On the other hand, the importance of self-assembled monolayers and multilayers had generally grown and this development was taken into account.

2.2 Progress Report: Common Themes

The anticipated benefits of consortium were listed in the first research proposal in 1994. The similarity of materials used in the research means that principally similar fabrication and characterization processes are needed and consequently the possibility to use the instrumentation and expertise available in these three groups was considered very important.The need for a *synthetic organic chemist.* was considered most urgent, and from the very beginning of the project a synthesist common to the whole consortium was hired.

Although instrumentation and expertise in each other's laboratories were extensively exploited and regular common seminars were arranged on a monthly or bimonthly basis, the number of common publications remained rather modest. However, this cannot be seen as the lack of synergism of the consortium.

Presently the most important conductive polymer in the commercial sense is perhaps PEDOT (poly-(3,4-ethylenedioxythiophene)) used in large quantities e.g. as an antistatic agent. This polymer has aroused also academic interest due to its extaordinary stability, and both the UT and ÅAA groups have been working on it. The joint research on the electrochemical properties of this polymer has resulted in two publications [8, 57].

Studies on electrical conductivity and luminescence have been common themes in the cooperation of ÅAP with the other two participants. ÅAP has received a selection of materials from the two other participants: PPV (poly-*p*-phenylenevinylene), polyfluorenes and polyelectrolytes from UT [94, 90] and electrochemically prepared PPV [53] from ÅAA. The latter polymer was used in novel LEDs.

2.3 Progress Report: Progress by the Laboratory of Analytical Chemistry, University of Turku (UT)

The tasks in this joint consortium project were divided in such a way that the synthesis of new materials, their characterization and development of new methods of film formation and characterization were given to the group in University of Turku. During this reported period 1996-2000 the main results of UT group can be considered as follows:

- Studies of the polymerization mechanisms and redox processes in polythiophene and its derivatives. This work has been mainly done in close collaboration with prof. Visy's group (University of Szeged) [1-5,77,83,89,93].
- Studies of one of the most important conducting polymers poly(3,4-ethylenedioxythiophene), its doping processes especially in the cathodic region, and its preparation in aqueous solution. Corresponding structural analogs in the benzene and thiophene series were also studied [7-10,73,75,79,84,92].
- The use of polyaniline as a sensor material for oxygen in aqueous solution. In this study a novel mechanism of a potentiometric sensor was presented based on the formation of charge-transfer complexes between the analyte and conductive polymer [11].
- Isosbestic points in the absorption spectra of conductive polymers recorded at different potentials are commonly used as criteria for the number of species in the polymer film. Our study shows that erratic conclusions are easily drawn because of nonlinear effects due the local field of light wave [12].
- Preparation of covalently bound redox polymer on gold surface using the technique of alternating reagents. This “molecular wire“ composed of alternating diamine and benzoquinone moieties shows promises as an anchoring agent for biological molecules [13].
- Studies of self-assembled monolayers (SAM) were started during this period. The most important results in this field are (a) the invention of Bunte salts (alkyl and aryl thiosulfates) as a new source for thiol-covered gold-SAMs [14], (b) the study of post-self-assembly reactions of an important SAM reagent, 4-aminothiophenol, on gold surface [15], and (c) the development of new mathematical models for the general mechanism of the adsorption process [16] and the special mechanism of electroreductive desorption process of gold-SAMs [17].

- Synthesis of new water-soluble polythiophene derivatives. Altogether 8 new anionic and one cationic derivatives of 3-hydroxythiophene were prepared and characterized. The most important result of this study is the observation that high-quality conducting layers could be prepared from these newly synthesized polyelectrolytes by using the layer-by-layer techniques [18-20]. The reliable and reproducible preparation of films of conducting polymers was one of the main goals of this research consortium and this new technique more or less seems to fulfill these goals. To the best of our knowledge, we are among the first who have developed this technique to the level where all polyelectrolyte layers are of the same type of electronically conductive polymers [20]. This technique is now under intense research in our laboratory, the intention being to develop thin-film sensors using electroactive polyelectrolyte nanolayers and appropriate receptor groups.

In addition, a comprehensive evaluation of various factors on the quality and electrical conductivity of electrosynthesized polypyrrole was accomplished as a Ph.D. thesis [120], partly published as separate publications before 1996. New characterization methods were developed for organic thin films such as electromodulated reflectance spectroscopy [20] and a new method for measuring the quartz crystal impedance and hence the viscoelasticity of films [148].

2.4 Progress Report: Progress by the Department of Physics, Åbo Akademi University (ÅAP)

2.4.1 Electrooptical properties of LEDs

The basic idea in the group has been to study thin organic films with potential applications in molecular electronics. We have especially tried to clarify and model the electro-optical response of the materials and structures used. We have been using well-known model materials for both charge transport properties and luminescence. The materials used have mostly been polythiophenes (PT), poly(*p*-phenylenevinylenes) (PPV) and polyaniline (PANI). Our group was actually the first to demonstrate monomolecular layer FETs [J. Paloheimo et al, APL 1990] and LEDs [22], as well as ac-LEDs based on molecularly thin multilayer structures [26].

What became apparent during this research period was that the electric field, previously considered to be uniform within the film, is redistributed when applying a voltage pulse [36]. This phenomenon was clarified by using the novel integral mode time-of-flight (TOF) technique. We found that the photosignal can be used as a measure of the electric field in the generation region. This led to the model of the electric field redistribution schematically shown in Fig. 1.

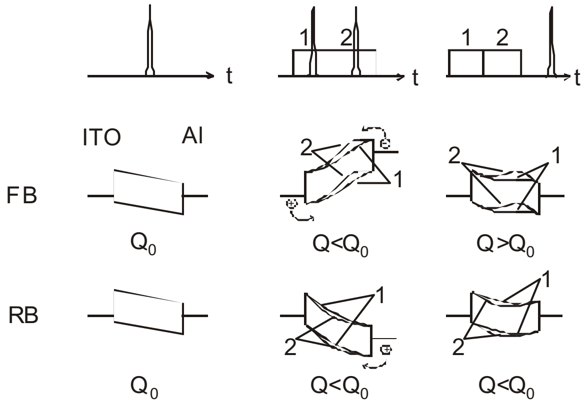

Fig.1 Schematic picture of the time evolution of the electric field near the aluminum electrode in a PHT LED. FB and RB means forward bias and reverse bias, respectively.

From the frequency response of alternating current LEDs [36, 33] we could show that the interfaces become more important the thinner the films are. The result was at first very surprising, but we were able to determine that large amounts of charges are trapped at the polymer/polymer interfaces [34], as shown in Fig. 2.

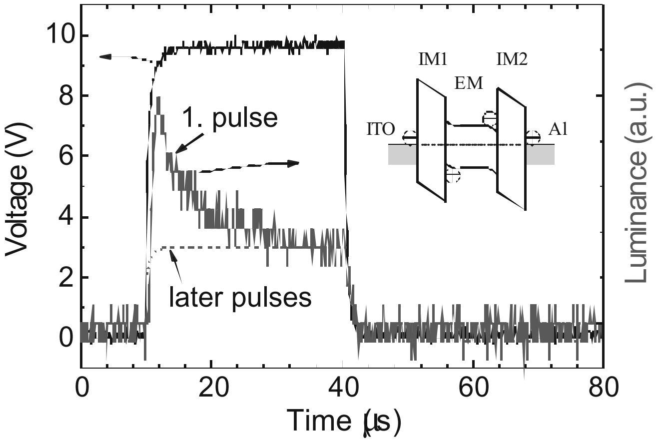

Fig. 2. The role of interfaces in multilayer LEDs. Injected and trapped charges at the polymer/polymer interfaces are readily available to recombine when applying the first pulse.

Charge transport studies in thin polymeric films were a common theme during the whole project. A novel method of preparing molecularly thin, conducting polyaniline films, and a model for the transport in these films were developed [27, 30, 101]. These thin films were later used in the ac-LED devices presented above. More recently, corresponding studies on P3HT-films have been performed [113], a work which is now continued by H. Sandberg during his visit at University of Cambridge.

To study the charge transport through the films has been a very difficult task, because of the dispersive transport in the polymer films. In collaboration with University of Vilnius we have applied a novel TOF method that has proven very useful in organic semiconductors [31, 105, 110]. We have also introduced a new and technically simple method to study the equilibrium charge carrier transport in LED devices. From this technique, called charge extraction in a linearly increasing voltage (CELIV, see schematic view in Fig. 3) we can get information about the charge carrier mobility, number of trapping states, and the underlying nature of the charge transport for equilibrium charge carriers [41, 110]. This is in contrast to the TOF method, where we only can study photogenerated carriers. The use of these two techniques will, no doubt, be very useful for future studies of charge transport in organic semiconductors.

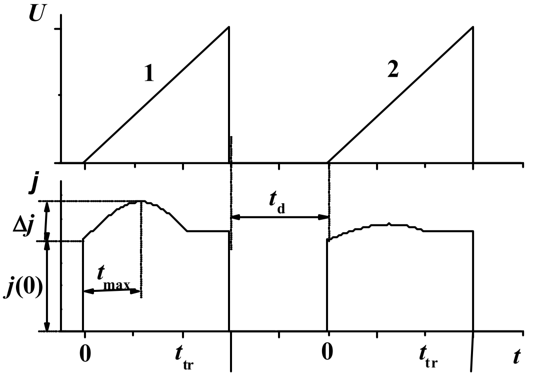

Fig. 3 Schematical view of the observed current when applying a linearly increasing voltage $(U=At)$. $J(0)$ is the displacement current associated with the geometrical capacitance, while Δj is the extraction current.

2.4.2 Optical properties

We have extended our optical measuring techniques to include photomodulation spectroscopies, such as photoinduced absorption (PA) [39, 40, 106, 107], electroabsorption (EA) [106], steady state photoconductivity [108] and their action spectra [39, 106-108]. Also new phenomena such as spectral narrowing and lasing in PPV devices have been studied [106,107].

In order to further understand the light emission in electroluminescent devices, photomodulation (PM) spectroscopies offer a useful tool in order to clarify the nature of the excited states [39, 40]. Furthermore, the discovery of higher dimensionality of charged excitations [40] in the new, improved polymers such as regioregular poly(3-alkylthiophenes) has opened up possibilities of studying new physics. In this respect, the synergism of having both electrical and optical measuring possibilities in the same setups are starting to pay off.

2.5 Progress Report: Progress by the Laboratory of Analytical Chemistry, Åbo Akademi University (1998-2000)

One of the main research lines in our project has been the application of conducting polymers in potentiometric and amperometric chemical sensors. An other line closely related to the sensor research has been characterization of different conducting polymers.

The chemical sensor work is continuation of the work done in the group already during the previous MATRA project: 1995-97. The main concept in the potentiometric sensors has been the use of the conducting polymer as an ion-to-electron transducer. The chemical information of species in solution is mainly in the ions and their concentrations. In conventional ion-selective electrodes this information is converted to electronic signal in the internal reference electrode and the internal solution. In our concept this is done in a layer of conducting polymer between the electronic conductor and the ion-selective membrane. Results are reported in references [55], [58], [63], [64], [71], and [141]. Then we have also continued the study of single-piece-electrodes where soluble conducting polymers are dissolved directly in the PVC based cocktail for preparation of ion-selective electrodes. These results are reported in the references: [46], [51], and [56]. Then we have also developed the concept in such a way that the ionophore is directly dissolved in a soluble polymer without any PVC or plastisizer: [50], [47], [48], [139]. A microelectrode based on the solid-contact concept has been developed and tested [47]. The tip of the electrode was ca 20 µm. The earlier studies on ion transfer accompaying charging-discharging of polypyrrole and potentiometric selectivity and sensitivity of polypyrrole have been continued: [62], [65], [72], [140], [142], [143], [144]. Polypyrrole has also been used as the sensitive membrane in amperometric sensor for dissolved ammonia [69]. The studies were carried out in a FIA-system. In presence of ammonia oxidized polypyrrole is chemically reduced and then immediately electrochemically reoxidized by the potentiostat. The oxidation current is a measure of the concentration of ammonia in the sample.

3 International Aspects

The UT group has tight contacts of collaboration with the Institute of Physical Chemistry, University of Szeged (formerly József Attila University). Since 1988 every year professor Csaba Visy and occasionally professor Mihaly Novák have made one to several months visits to the UT group under the auspices of the Academy of Finland or the Hungarian-Finnish Science and Technology Programme. This Finnish-Hungarian connection is important for both parties. A considerable number of scientific publications – all of them directly related to this project – have been published as a result of this cooperation. In September 1996 József Attila University conferred the title of Doctor Honoris Causa to prof. Jouko Kankare for this collaboration.

In 1999 the UT group started collaboration with Dr. Mario Morin's group in the University of Ottawa. Dr. Morin is an expert in single crystal electrodes and SAMs and has access to an SHG (second harmonic generation) instrumentation which is very useful in studying the structure of interfaces. So far this collaboration has produced one joint publication.

The UT group has participated in the EU Human Capital and Mobility network programme *"Electron and energy transfer in model systems and their implication for molecular electronics"* (ERB 4050PL93-2376) (1995-98), in which nine European research institutes (University of Turku, Université Paul Sabatier, University of Ferrara, Aristotelian University, Bristol University, University of Innsbruck, Université Louis Pasteur, University of Leuven , Institut de Ciència de Materials de Barcelona) collaborated in trying to synthesize and characterize simple model systems for molecular electronic devices.

The following scientists from ÅAP have stayed longer than 4 weeks abroad: R. Österbacka, Dept.of Physics, Univ. of Utah (USA) for a total of 13 months and 3 weeks; H. Sandberg, Cavendish Laboratories, Univ. of Cambridge (UK) for a total of 3 months and 2 weeks (ongoing).

The following scientist have visited ÅAP for periods longer than 2 weeks: Dr. D. Bhattacharjee, CAT, Indore, (India) 3 months; Doc. A. Alexeev, General Physics Institute, Moscow State University (Russia), total of 10 months 3 weeks; Dr. A. Aleshin, A.F. Ioffe Physico-Technical Institute, Russian Academy of Science (Russia) 3 months; M.Sc. A. Chowdhury, IACS, Calcutta (India) 2 months 2 weeks; Prof. G. Juška, Dept. of Solid State Electronics, Univ. Vilnius (Lithuania) 2 weeks; Doc. K. Arlauskas, Dept. of Solid State Electronics, Univ. Vilnius (Lithuania) 2 weeks, M.Sc. K. Genevicius, Dept. of Solid State Electronics, Univ. Vilnius (Lithuania) 4 months.

The ÅAP group is actively involved in cooperation between Dept. of Solid State Electronics, Univ. of Vilnius (Lithuania), Dept. of Physics, Univ. of Utah (USA), Indian Association for the Cultivation of Science, Calcutta (India), and CNR, Milano (Italy).

The research of the ÅAP group has been presented in numerous international conferences, including 2 invited papers and 15 oral presentations.

The Academy of Finland and Deutsche Academische Austausdienst DAAD, bilateral agreement financed cooperation between ÅAA and Institut für Festkörper- und Werkstofforschung, Dresden, Germany, 1998-99. In connection of the project a common seminar: "Conducting Polymers and Fullerenes-Leitfähige Polymere und

Fullerene“ was held in Turku in May 22-23, 2000 Docent Carita Kvarnström and Ms Pia Damlin have been few times to Dresden to do measurements with special equipments.

Cooperation with the research group of Professor N.S. Sariciftci, University of Linz, Austria: Docent Carita Kvarnström did research work in Linz from September 1997 to September 1998. Ms Pia Damlin spent two months in Linz in fall 1998. Dr. H.Neugebauer spent one month in Turku in fall 1999.

Cooperation with the University of Mining and Metallurgy, Krakow, Poland: professor Lewenstam has the position of visiting professor and has a research team in Krakow. He has been to Krakow, regularly over the years. Dr. Kubiak from Krakow has been to Turku for two months, August-September, both in 1998 and 1999.

Cooperation with University of Warsaw, Warsaw, Poland: Dr. Krzysztof Maksymiuk and Dr. Agata Michalska worked in the ÅAA group for two months both in 1998 and 1999. Dr. T.Sokalski has been in Turku since February 2000.

Cooperation with the Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, China: Dr. L.Niu has been in Turku since February 1999. Professor Ivaska has visited the Institute both in 1999 and 2000.

Cooperation with the Institute of Analytical and General Chemistry, Budapest Technical University, Budapest, Hungary: docent Carita Kvarnström, Ms Pia Sjöberg, Ms Ann-Sofi Nybäck have been doing research at the institute during 1998-2000. Professor K.Toth from Budapest was the opponent in the PhD dissertation of Tom Lindfors in 1999.

Professor Ari Ivaska, Professor Andrzej Lewenstam and docent Johan Bobacka have been invited to present plenary and keynote lectures in several international conferences.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. ÅAA has given only data between 1998-2000. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1996	1997	1998	1999	2000-	**Total**	Publication numbers
UT	Ref. journal art.	2	4	3	3	8	**20**	1-20
	Ref. conf. papers	2	6	2	6	5	**21**	73-93
	Monographs			1			**1**	119
	Doctoral dissert.	1					**1**	120
	Master degrees			3	1	4	**8**	121-128
ÅAP	Ref. journal art.	2	10	5	2	5	**24**	21-44
	Ref. conf. papers	3	4	4	5	7	**23**	94-116
	Doctoral dissert.			1	1		**2**	129,130
	Licentiate degrees		1	1			**2**	131,132
	Master degrees	2		2	1	0	**5**	133-137
ÅAA	Ref. journal art.			3	16	9	**28**	45-72
	Ref. conf. papers				2		**2**	117,118
	Doctoral dissert.				1		**1**	138
	Licentiate degrees				1		**1**	139
	Master degrees				1	5	**6**	140-145

5 Other Activities

ÅAA has filed two patent applications related to this research project during the period 1998-2000 [146,147]. UT has filed one patent application dealing with a new method for measuring the impedance of a quartz resonator for the determination of e.g. viscoelasticity of conducting polymers [148].

In connection of this research project and the cooperation with the Institut für Festkörper- und Werkstofforschung, Dresden, Germany a common seminar was arranged in Turku, May 22-23, 2000: "Conducting Polymers and Fullerenes -

Leitfähige Polymere und Fullerene" with 30 participants from Germany and the Consortium.

During the entire funding period starting from 1995 regular seminars between the participants of the consortium were arranged on a monthly or bimonthly basis. In these seminars the researchers told about their latest studies and also gave tutorial lectures on new techniques. All the seminars have been kept in English and also foreign researchers have been regular visitors in most meetings. The last seminar was arranged in December 2000. In that connection a press conference was arranged and an article was published in Turun Sanomat [149] about our work and conducting polymers in general, referring to the recent Nobel prizes of professors Heeger, MacDiarmid and Shirakawa.

6 Publications

6.1 Refereed Journal Articles

[1] Csaba Visy, Jukka Lukkari & Jouko Kankare, Electrochemical Polymerization of Tetrathienyl Derivatives of the Carbon Group Elements. - J.Electroanal.Chem. 401 (1996) 119-125.

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ORGANIC THIN FILMS WITH FUNCTIONAL ACTIVITY: PREPARATION, PROPERTIES AND APPLICATIONS

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Abstract

The present report describes the results obtained by the consortium during the period 1998-2000. Each team presents their own achievements separately.

The main focus of the research group at the **Institute of Materials Chemistry**, Tampere University of Technology (IMC), is photodynamic studies of molecular systems. The most important results of the group in the field of the molecular DA systems can be summarised as follos: a) *Spectroscopy studies of the photodynamic of DA systems* in solution. The instrumentation available allows recording both emission and absorption changes of the samples with femtosecond time-resolution. Primary steps of intramolecular energy and electron transfer have been resolved in a series of covalently linked DA compounds. *b) Organised molecular systems*. An important step in utilisation of our fundamental knowledge in the field of photoinduced electron and energy transfer is fabrication of the organised molecular systems utilising electron transfer function of a single molecule. This can be achieved by application of Langmuir-Blodgett technique. The laboratory has developed and studied numerous molecular mono- and multilayer systems, which can perform energy and charge transfer functions including vectorial charge transfer across the film. c) *Time-resolved Maxwell displacement charge measurements of organised molecular films*. A unique method was developed for the investigation of the ultra-thin molecular films. Application of the method allowed to resolve and to monitor the charge transfer processes in monomolecular LB films.

The overall goal of the research programme of **Department of Physics**, Åbo Akademi University (ÅAP) is to develop new organic materials and structures for molecular electronic devices. In our physics environment this is done by modeling and solving central physical problems. The focus is on charge carriers, their transport and redistribution (mobility, accumulation, trapping, etc.). Light emitting diodes (LED) and field effect transistors (FET) are our target devices. For LEDs the mechanism of luminescence and the charge accumulation/trapping at interfaces are crucial. For FETs the latter is also important, but even

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more so, properties affecting the carrier mobility. Our active materials are primarily thiophenes, phenylenevinylenes and anilines, some being commercially purchased some prepared by our collaborators. The structures are often in the form of thin films. Here we have Langmuir-Blodgett, spincoating and spincasting techniques at our disposal, the former giving true molecular thickness control.

Beyond the basic electrical and optical measurements we have developed our special characterization methods during the project period: photomodulation spectroscopy (photoconductivity, photoinduced absorption, electroabsorption, time-of-flight TOF) and charge extraction in a linearly increasing voltage (CELIV, for the first time applied to organic materials). Especially the latter two have given new information on the role of charge carrier accumulaton and the corresponding field redistribution.

At the **Department of Physical Chemistry**, Åbo Akademi University (ÅAPC), novel biofunctional lipids have been synthesized for specific bioaffinity measurements. Two different thin film techniques, the Langmuir-Blodgett and self-assembly techniques, have been used to prepare a biofunctional surface on a solid substrate. Versatile surface and structural characterisation has been carried out in order to unambiguously demonstrate the characteristics, quality and functionality of the films. The main goals were reached: the homogeneity and mechanical stability as well as the biofunctional specificity of the prepared films were shown to be clearly improved compared with the starting level. The best results were obtained for a film representing a combination of Langmuir and self-assembly monolayers.

The main objective of the research performed by the group of **Sensing Materials** at VTT Automation (VTT) has been to develop an immobilisation method based on the coupling of antibody Fab′-fragments to linker lipids in a monolayer matrix. The Langmuir-Blodgett technique has been used in order to obtain a homogeneous, oriented, stable and reproducible layer on the transducer interface. Antibody Fab′-fragments of polyclonal anti-human IgG have been covalently attached to previously synthesised lipids with terminal linker groups as a means to obtain an oriented immobilisation and thus a highly sensitive immunoassay. Most efficient coupling with the highest response to antigen was achieved with a maleimide linker embedded in phosphatidylcholine. The layers exhibit a low non-specific binding and a high antigen binding capacity. Atomic force microscopy images of the films showed that the position of the Fab′-fragments depends on the fluidity of the host matrix – a more fluidic layer gives more slanted Fab′-fragments, whereas the fragments are standing right up on a condensed layer. The lipid layers could be stored dry and the layers can be regenerated and used repeatedly. The detection limit of the assay for hIgG was below 1ng/ml. More recently an even more promising immobilisation method with oriented antibodies and a very low non-specific binding has been investigated. Human IgG concentrations below 10 pg/ml have been measured with surface plasmon resonance.

1 Partners and Funding

1.1 Institute of Materials Chemistry, Tampere University of Technology

The following persons have participated in the research group: project leader prof. H. Lemmetyinen, Senior Researchers Nikolai Tkachenko and Elina Vuori-maa, postgraduate students Tapio Jussila, Andrei Tauber, Tero Kesti and Visa Vehmanen.

1.2 Department of Physics, Åbo Akademi University

The following persons have participated in the research group: subproject leader prof. Henrik Stubb, Laboratory Manager Kjell-Mikael Källman, Post-doc (Academy of Finland) Ronald Österbacka, postgraduate students Henrik Sandberg and Markus Westerling and student Tomas Bäcklund. Several visiting scientists have also contributed to the work (see Section 3)

Within MATRA, the ÅAP group has also participated in a consortium headed by prof. Jouko Kankare “Conductive Polymers with Well-Defined Morphology”. There is a natural divison of tasks for ÅAP within these consortia, emphasizing optical transitions and charge transfer in the present one and electrical conduction and transport phenomena in Kankare’s consortium. A strict separation is still impossible as the two fields are intertwined.

1.3 Department of Physical Chemistry, Åbo Akademi University

The research group consisted of the subproject leader docent Jouko Peltonen, postgraduate students Tech.Lic. Erika Györvary, Phil.Lic. Tapani Viitala and M.Sc. Petri Ihalainen and the graduate student Dimitar Valtakari. M. Sc. Annette Andersson and students Risto Korpinen, Hanna Koivula and Heli Hartikainen have also paerticipated the work.

1.4 VTT Automation, Measurement Technology, Sensing Materials

The research group consists of subproject leader PhD Inger Vikholm, senior researcher PhD Janusz Sadowski, researcher Martin Albers and student Leena Vuori. Researchers Hannu Helle and Hannu Välimäki have also participated the work.

1.5 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
TUT/IMC	TUT	-	250	300	300	**850**
	Academy	-	490	505	505	**1500**
	TEKES	-	350	350	-	**700**
	Grad. Sch. & Doctoral stipends	-	-	150	150	**300**
ÅAU/ÅAP*	ÅA	-	90	90	90	**270**
	Academy	-	280	460	310	**1050**
	TEKES	-	150	150	175	**475**
	Grad sch. & Doctoral stipends	-	110	50	50	**210**
ÅAU/ÅAPC	ÅA	-	100	100	100	**300**
	Academy	-	490	470	490	**1450**
	TEKES	-	-	-	400	**400**
	EU/SMT	-	30	30	10	**70**
VTT	VTT	302	341	348	369	**1360**
	Academy	304	-	-	-	**304**
	TEKES	-	519	523	551	**1593**
Total		**607**	**860**	**870**	**920**	**3257**

*The funding from the other sources beyond the Academy of Finland has been considered shared equally between the two consortia.

2 Research Work

2.1 Objectives and Work Plan

The main focus of the research group of **IMC** has been photodynamic studies of molecular systems. The group has long-term experience in fabrication and investigation of the highly ordered solid molecular films prepared using different types of techniques, of which the most important has been the Langmuir-Blodgett technique. The main aimss of the group in the field of the molecular DA systems can be summarised as followed:

a) *Spectroscopy studies of the photodynamic of DA systems* in solutions. The instrumentation available allows recording both emission and absorption changes of the samples with *femtosecond* time resolution. Primary steps of intramolecular energy and electron transfer have been resolved in a series of covalently linked DA compounds.
b) *Organised molecular systems*. An important step in utilisation of our fundamental knowledge in the field of photoinduced electron and energy transfer is *fabrication of the organised molecular systems* utilising electron transfer function of *a single molecule*. This can be achieved by application of Langmuir-Blodgett technique. During the past decade the laboratory has developed and studied numerous molecular mono- and multilayer systems, which can perform energy and charge transfer functions including vectorial charge transfer across the film.
c) *Time-resolved Maxwell displacement charge measurements of organised molecular films*. A unique method was developed for the investigation of the *ultra-thin molecular films*. Application of the method allowed to resolve and to monitor the charge transfer processes in monomolecular LB films.

The main goal of the **ÅAP** group was to develop (semi)conducting organic thin films and structures applicable in molecular-electronics and optoelectronic applications. To achieve the goals, the main research was divided into the following topics:

a) *Materials* (PANI, PT derivatives, PPV, novel materials both for luminescence and bioapplications such as molecular donor-acceptor pairs).
b) *Thin film preparation* (LB deposition, spincoating, self-assembly etc).
c) *Structures and devices* such as field-effect and LED structures.
d) *Electrical properties* (dc-conductivity, ac-frequency response, steady-state photoconductivity). And finally
e) *Optical properties* (electroluminescence, PL, photoconductivity).

The objective of **ÅAPC** has been to study biosensing organic thin films. As a result of the basic research in the first MATRA project during years 1995-1997 novel surfactants were synthesized and monomolecular thin films prepared thereof for protein immobilization. Versatile characterisation was carried out regarding both structural and functional properties of the films. The main focus of the current project during 1998-2000 has been to concentrate on the optimization of the monolayer composition and functionality. This has included the minimization of phase separation of the two-component lipid monolayer, optimization of the density of protein binding sites and enhancement of the mechanical stability of the solid-supported film structure.

As a novel approach, self-assembled films were studied in parallel with the Langmuir-Blodgett films. The work proceeded consistently from surfactant immobilisation studies and determination of the immunological activity further on to a comparison of the film prepation techniques (LB films vs. self-assembly monolayers).

The main objective of the **VTT** group was to develop an immunosensing method based on the coupling of fragmented antibodies to linker lipids in a monolayer matrix. The Langmuir-Blodgett technique was to be used in order to obtain a homogeneous, oriented, stable and reproducible layer on the transducer interface. The coupling was studied *in situ* with a quartz crystal microbalance, QCM and by surface plasmon resonance, SPR.

2.2 Progress Report: Common Themes

One of the common themes between IMC and ÅAP was the study of charge transport between molecular donor-acceptor (DA) pairs and charge transporting polymers, such as regioregular polythiophenes [ICP 59, ÅAP 23]. It was shown that the polymer acts as an efficient secondary donor to the DA pairs, with increased lifetime of the charge carriers. Both the film fabrication procedure (Langmuir-Blodgett, LB) and measurement methods are well known for both groups.

The cooperation of the ÅAPC group has been most active with the VTT group, dealing with the studies of biofunctional thin films. The films that have been studied differ somewhat between the two groups but regarding characterisation both groups have crosswise taken advantage of the resources available. This fruitful collaboration has lead to 6 joint publications (including a review article) and it has clearly added to the body of knowledge we now have about the biofunctionality of the films.

The cooperation between the groups of ÅAPC and IMC has also been reported in two joint articles dealing with the film forming properties of dye molecules and thienoviologens.

2.3 Progress Report: Progress by the Institute of Materials Chemistry, TUT

2.3.1 Basic Photochemical Phenomena of the Donor-Acceptor Dyads in Solutions

A series of the DA dyads has been synthesized and studied by the group. The recent examples are pyropheophytin-anthraquinone (PQ) and phytochlorin-fullerene (PF) dyads (Fig. 1). Both molecules undergo Photo Induced Electron Transfer (PET) [IMC 3, IMC 4], but PF does it faster and with higher efficiency. The primary events in the relaxation of the photoexcitation in the PF dyad reveal the formation of an intramolecular exciplex between the phytochlorin and fullerene moieties [IMC 26]. It was found that the exciplex is a precursor of the charge separated state and plays an important role in the electron transfer function of the dyad. It was proposed that the reason for the exciplex formation is the close proximity of the ? -conjugated electron subsystems of the donor and acceptor. This assumption was recently confirmed when an exciplex-like emission was observed for a porphyrin-fullerene dyad [IMC 26]. The quantitative analysis of the emission and absorption spectra allowed the estimation of the principal ET parameters, such as reaction free energy, reorganization energies, DA vibrational frequencies and DA electronic couplings.

2.3.2 Functional Organic Molecules in Solid LB Films

Placing the functional molecules in solid mono- and multilayer LB films may change the properties of the compounds drastically as compared to the liquid phase. One reason is intermolecular interaction, e.g. any aggregation of the dye molecules, which may lead to gradual decrease in the lifetime of the excited state from several nanoseconds to a few picoseconds. For example, for chlorophyll *a* LB films the deactivation mechanism of the excited state is the intermolecular electron transfer [IMC 23] taking place between similar molecules in the chlorophyll aggregate. Thus the system cannot be used to construct molecular devices (MD) performing vectorial PET.

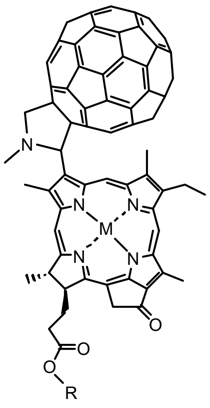


Fig. 1. Phytochlorin-fullerene (PF) DA dyads.

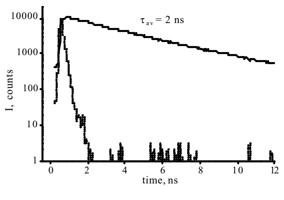


Fig. 2. Fluorescence decay of TBP:ODA = 1:6 LB film.

The aggregation can be diminished artificially by placing the functional molecules in a passive lipid matrix or/and designing molecules with special groups preventing the aggregation. This can be illustrated by the example of hydrophobically shielded porphyrin, 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (TBP) [IMC 9]. In LB films mixed with octadecylamine (ODA) the lifetime of the excited state remained as long as 2 ns even at high concentration of porphyrin (Fig. 2). This compound can be used as a light antenna and primary electron donor in design of MD.

The aggregation does not always lead to a faster dissipation of the excitation energy. The aggregates of pentafluorophenylporphyrin (PFP) are characterized by an unusually long lifetime of the fluorescence (>2 ns at PFP:ODA = 1:3) and can be used for the light harvesting in complex LB films [IMC 16].

The aggregation of dissimilar molecules can also result in the formation of the DA pairs. This was observed for the porphyrin-fullerene mixed films [IMC 42], where the close proximity of the donor and acceptor results in the formation of emitting charge separated state.

2.3.3 Vectorial Photo Induced ET in LB Films

The PQ and PF dyads can be used for deposition of the LB films with uniform orientation of the functional groups. The PQ samples can perform the vectorial PET [IMC 22]. But even better results were achieved with PF dyads (Fig. 1) [IMC 33], where the vectorial PET can be detected by using time-resolved Maxwell displacement charge measurements (Fig. 3). The important property of the charge transfer state in the LB film is its relatively long lifetime (>30 ns for PF) as compared to that in solutions (less than 1 ns). These compounds can be used as primary charge separating centers in the MD design.

An alternative approach to PET in LB films is the design of separate donor and acceptor compounds, which can interact with each other and form DA heterodimers. This can be achieved by the use of the electrostatic interaction of donor and acceptor, as it was demonstrated by the example of porphyrin-phthalocyanine heterodimer [IMC 3]. Photo-voltage response of the heterodimer in LB film showed a fast formation and recombination of the charge separated state (<10 ns).

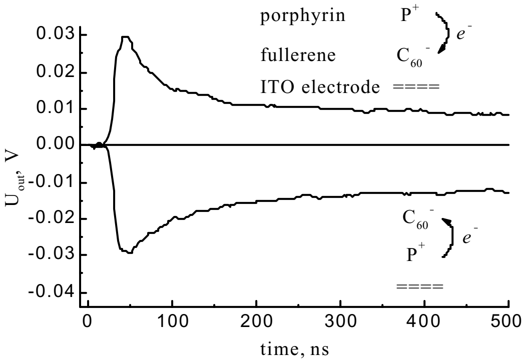


Fig. 3. Photovoltage response of the PF films. Direction of the ET can be switch by changing deposition direction of the active layer.

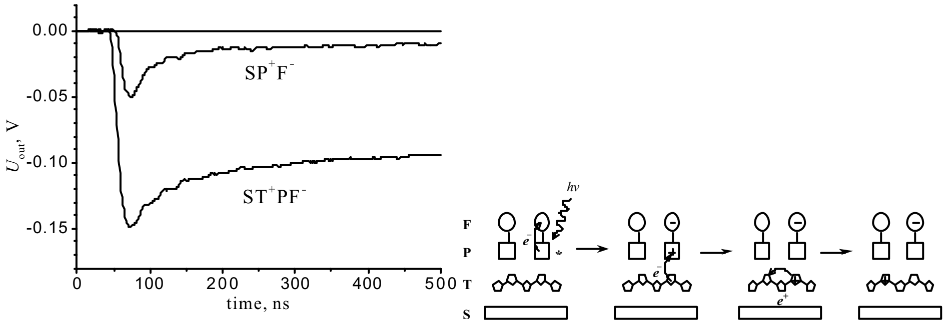


Fig. 4. Photovoltage responses of PF monolayer and PF-polythiophene bilayer films. The scheme show reactions leading to formation of long-lived and long distance charge separated state.

Heterodimers can be formed due to a weak inter-chromophore interaction. This can be illustrated by the example of the pair of TBP and Zn complex of TBP [IMC 42]. In the ODA matrix the porphyrins form heterodimers with predominant position of the Zn porphyrin on the top of the freebase compound. As the result the films perform vectorial PET in a controllable way and can be used to accomplish primary charge separation function in the MD design.

All the examples mentioned above illustrate a single step electron transfer, which is followed by charge recombination. Experiments were also carried out to demonstrate the improvement of the ET function. The layer of the phytochlorin-fullerene dyad (capable for the PET reaction) was deposited on top of the layer of polythiophene, which can operate as a secondary electron donor. As the result, the amplitude and the lifetime of the photovoltage response increased gradually (Fig. 4), indicating that the second step of the interlayer electron transfer takes place [IMC 59, ÅAP 23]. This is a promising result, which proves the design goals of the project.

2.3 Progress Report: Progress by the Department of Physics, ÅA

2.4.1 Electrooptical properties of LEDs

The basic idea in the group has been to study thin organic films with potential applications in molecular electronics. We have especially tried to clarify and model the electro-optical response of the materials and structures used. We have been using well-known model materials for both charge transport properties and luminescence. The materials used have mostly been polythiophenes (PT), poly(p-phenylenevinylenes) (PPV) and polyaniline (PANI). Our group was actually the first to demonstrate monomolecular layer FETs [J. Paloheimo et al, APL 1990] and LEDs [ÅAP 2], as well as ac-LEDs based on molcularly thin multilayer structures [ÅAP 6].

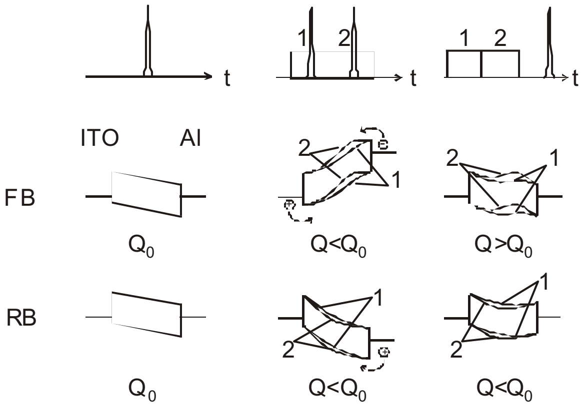


Fig.5. Schematic picture of the time evolution of the electric field near the aluminum electrode in a PHT LED. FB and RB means forward bias and reverse bias, respectively.

What became apparent during this research period was that the electric field, previously considered to be uniform within the film, is redistributed when applying a voltage pulse [ÅAP 16]. This phenomenon was clarified by using the novel integral mode time-of-flight (TOF) technique. We found that the photosignal can be used as a measure of the electric field in the generation region. This led to the model of the electric field redistribution schematically shown in Fig. 5

From the frequency response of alternating current LEDs [ÅAP 6, ÅAP 13] we could show that the interfaces become more impor-tant the thinner the films are. The result was at first very surprising, but we were able to determine that large amounts of charges are trapped at the polymer/polymer interfaces [ÅAP 14], as shown in Fig. 6.

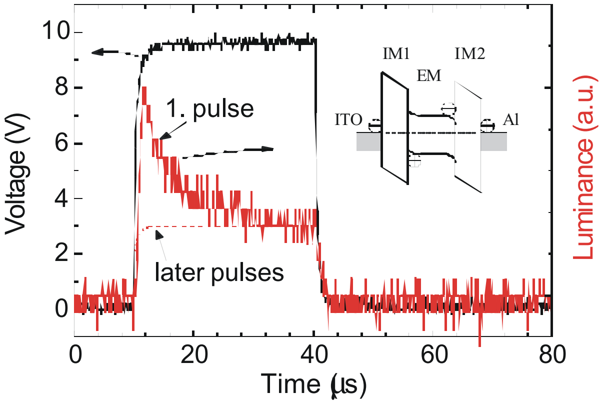


Fig. 6. The role of interfaces in multilayer LEDs. Injected and trapped charges at the polymer/ polymer interfaces are readily available to recombine when applying the first pulse.

Charge transport studies in thin polymeric films were a common theme during the whole project. A novel method of preparing molecularly thin, conducting polyaniline films, and a model for the transport in these films were developed [ÅAP 7, ÅAP 10, ÅAP 32]. These thin films were later used in the ac-LED devices presented above. More recently, corresponding studies on P3HT-films have been performed [ÅAP 44], a work which is now continued by H. Sandberg during his visit at University of Cambridge.

To study the charge transport through the films has been a very difficult task, because of the dispersive transport in the polymer films. In collaboration with University of Vilnius we have applied a novel TOF method that has proven very useful in organic semiconductors [ÅAP 11, ÅAP 36, ÅAP 41]. We have also introduced a new and technically simple technique to study the equilibrium charge carrier transport in LED devices. From this technique, called charge extraction in a linearly increasing voltage (CELIV, see schematic view in Fig. 7) we can get information about the charge carrier mobility, number of trapping states, and the underlying nature of the charge transport for equilibrium charge carriers [ÅAP 21, ÅAP 41]. This is in contrast to the TOF method, where we only can study photogenerated carriers. The use of these two techniques will, no doubt, be very useful for future studies of charge transport in organic semiconductors.

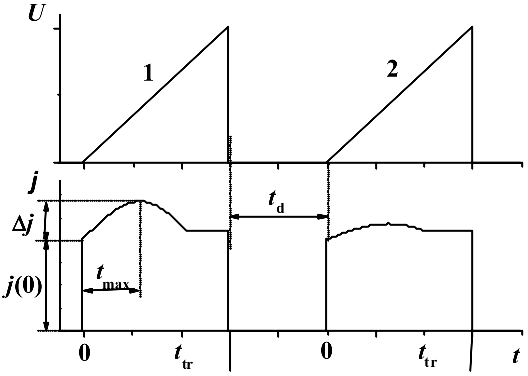


Fig. 7. Schematical view of the observed current when applying a lineary increasing voltage (U=At). J(0) is the displacement current associated with the geometrical capacitance, while Δj is the extraction current.

2.4.2 Optical properties

We have extended our optical measuring techniques to include photo-modulation spectroscopies, such as photoinduced absorption (PA) [ÅAP 19, ÅAP 20, ÅAP 37, ÅAP 38], electroabsorption (EA) [ÅAP 37], steady state photoconductivity [ÅAP 39] and their action spectra [ÅAP 19, ÅAP 37, ÅAP 38, ÅAP 39]. Also new phenomena such as spectral narrowing and lasing in PPV devices have been studied [ÅAP 18, ÅAP 37].

In order to further understand the light emission in electroluminescent devices, photomodulation (PM) spectroscopies offer a useful tool in order to clarify the nature of the excited states [ÅAP 19, ÅAP 20]. Furthermore, the discovery of higher dimensionality of charged excitations [ÅAP 20] in the new, improved polymers such as regioregular poly(3-alkylthiophenes) has opened up possibilities of studying new physics. In this respect, the synergy between having both electrical and optical measuring possibilities in the same setups are starting to pay off.

2.5 Progress Report: Progress by the Department of Physical Chemistry, ÅA

In the first part of this MATRA-project (1995-1997) the basic knowledge was established for the production of polymer or polymerizable biofunctional monolayers. The polymerization of the Langmuir-Blodgett (LB) films tranferred from the air/water interface onto a solid substrate was demonstrated, as well as their ability to immobilize proteins. In the second part of the project (1998-2000) the main focus has been to improve the mechanical stability of the films and to carry systematic studies on protein adsorption. In addition, self-assembly films and their combination with LB films have been studied with the same final application of protein adsorption.

The reaction mechanism of polymerizable lipid LB films was investigated in detail and AFM was used to demonstrate the clearly enhanced mechanical stability of the polymer films as compared with the monomeric system. AFM studies furthermore revealed the optimal polymerization time beyond which the film started degrading and became inhomogeneous. For the lipids with non-conjugated double bonds as reaction sites in the hydrocarbon chains, a general equation for the first order reaction kinetics was applied to a two-dimensional system. It was important to take into account the time-dependent area variation and availability of monomers able to react. For diacetylenic lipids representing a typical topochemical polymerization reaction, on the contrary, a first order consecutive reaction kinetic model was successfully applied.

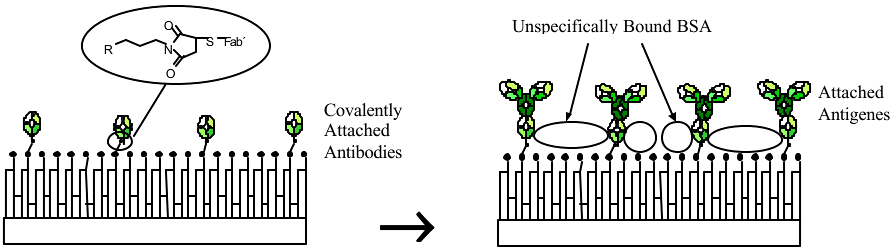


Fig. 8. A schematic illustration of a polymerized biofunctional film on a solid substrate. BSA is used to block unspecific binding sites of the antigens.

As a next step a biofunctional lipid was mixed in the polymerizable matrix film. For this purpose, a novel lipid was synthesized which contained both reactive sites in the non-polar chains for 2D-polymerization of the made up monolayer, and a linker unit in the polar headgroup for protein binding (Figure 8). The fact that the floating mixed monolayer could be polymerized at a non-crystalline state minimized the phase segregation of the two lipid components. The stability of the UV-cured film was clearly better than that of the corresponding monomer film.

A problem remained for the polymer monolayer in that the binding of the film to the solid substrate was through physisorption, causing long-term instability. In the next evolution, also the matrix lipid was derivatized such that the monolayer could be chemisorped to the solid substrate. Hence, the duty of one of the synthesized components, 1-palmitoyl-2-(15-(S-methyldithio)-penta-decanoyl)-sn-glycero-3-phosphocholine (DSDPPC), was to covalently bind the film to the solid substrate during deposition, whereas the other component, 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPGL), was responsible for the biofunctionality of the film. DSDPPC was derivatized from DPPC substituting a disulphide group at the end of one of the hydrocarbon chains, to enable covalent binding to a gold substrate. The mixture formed a Langmuir monolayer and phase separation between the components was found to be minor.

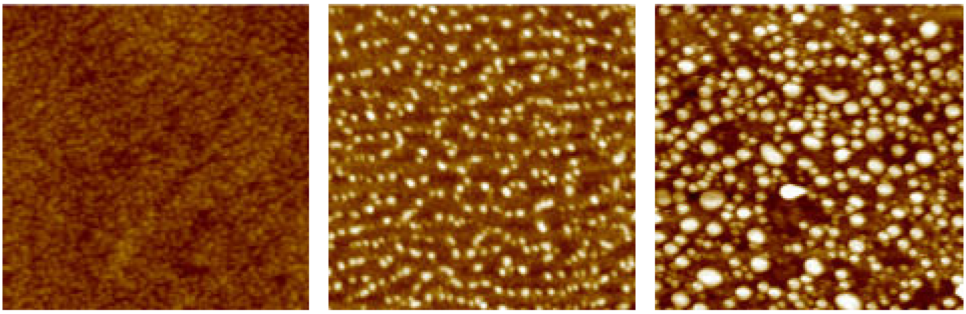


Fig. 9. AFM topographs of a pure binary film of DSDPPC:DPPGL (95:5) horizontally deposited on a gold substrate (image to the left), and the same sample with Fab'-fragments immobilized on the film (image in the middle). The image to the right illustrates Fab-binding to a monolayer with 80:20 ratio of DSDPPC:DPPGL, i.e. with increased linker lipid concentration. The image size is 2 x 2 μm^2 and height scale 10 nm. The roughness values from the left are 0.3 nm, 1.2 nm and 1.9 nm.

Biofunctional purely self-assembly films were studied, as well. We studied alkanethiols which adsorb spontaneously from solution onto a gold surface. In an adsorbed silver alkanethiol, the terminal silver was changed to a maleimide group through a substitution reaction, to biofunctionalize the surface. The successful preparation of these films was demonstrated by AFM and ESCA measurements.

Clear differences were observed between the studied films regarding their ability to specifically immobilize model proteins (Fig. 8). Three different analytical techniques where used to determine the amount of adsorbed proteins: quartz crystal microbalance (QCM), surface plasmon resonance (SPR) and AFM. The polymer films prooved to show less nonspecific binding of fragmented antibodies (Fab'-fragments) than the monomer films (Figure 9). However, the linker lipid DLiPE-EMC turned out to be chemically less stable than DPPGly. Furthermore, compared with the DLiPE-based polymer films, the unspecific protein binding was further decreased for the DSDPPC/DPPGL films. The self-assembly films were the most simple ones to prepare but the linker concentration in the film still needs to be fine-tuned in order to optimize the orientation and amount of immobilized Fab-fragments.

A spin-off project has already been started (TEKES-project in the POTRA-programme) where the obtained results are applied. The aim is to develop a diagnostic test for prenatal screening in collaboration with industry. The films have already shown great sensitivity and specificity for protein adsorption.

Altogether 13 articles have been published by the group sofar, and 2 doctoral theses, which both were even granted the highest marks. Several of the publications are joint works within the consortium. The altogether 6-year MATRA project has clearly shown its power in giving results on long term through collaboration. This type of continuity has been of special importance for postgraduate training and by that way for the production of experts in the field. The size of the team during the six years has increased from 3 to 9 members, demonstrating increased and evolved expertise not only in the field of thin films research but also more generally in the field of surface characterisation.

2.6 Progress Report: Progress by VTT Sensing Materials

In order to obtain a controlled orientation of antibodies on the sensor surface, the studies performed by VTT mainly involved the incorporation of saturated linker lipids (EMC-DPPE, and DTP-DPPE) in binary systems of phosphatidylcholine and in ternary systems of phosphatidylcholine and cholesterol [ÅAPC 7, ÅAPC 12, VTT 1, VTT 2]. Lipid monolayers were formed at the air-water interface and transferred onto hydrophobic slides by horisontal deposition. Cholesterol made the monolayers more condensed. Antibody Fab´-fragments of human IgG was covalent attached through the thiol exposed on the Fab´-fragment opposite to the antigen binding domain. The procedure is schematically illustrated in Figure 10.

In situ measurements with QCM at the air-monolayer interface showed that EMC-DPPE was more reactive towards Fab´ than dithiopyridine, DTP-containing layers [VTT 2]. This could be explained by a more optimal orientation of the EMC-linking group. The binding of Fab´-fragments was dependent on both the concentration of

Fab´-fragments and the amount of linker embedded in the monolayer. Only small amounts of Fab´-fragments adsorbed

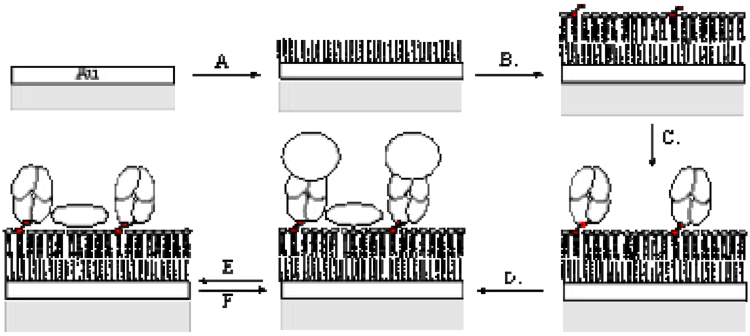


Fig. 10. A simplified schematic illustration of the immobilization procedure and the subsequent immunological interaction taking place on a gold coated glass slide. A) Self-assembly of octadecylmercaptan, B) horizontal deposition of a lipid/linker monolayer, C) attachment of Fab´-fragments to linker lipids, D) non-specific binding of BSA, E) binding of human IgG and F) regeneration of the layer.

onto the AFM images of EMC-DPPE embedded in dipalmitoylphosphatidyl-choline, DPPC host matrix and this amount did not vary much when low linker lipids at low ratios were embedded. However, when more than 7 mole% linker lipids were embedded in the layer a monolayer of Fab´-fragments was attached at high antibody concentrations. The Fab´-fragments attained an optimal antigen-binding capacity at a certain degree of packing. If the surface concentration of the immobilised antibodies was too high the interaction with antigens decreased due to steric hindrance. Binding efficiencies of antibodies and fragments attached the linker lipids in the various monolayer matrices is given in Table 2. The efficiency of the whole antibody or antibody $F(ab)_2$ fragments adsorbed onto polystyrene was only 3 – 10%. A binding efficiency of 60% was obtained for Fab´-fragments on DPPC/EMC-DPPE with all the used methods. When cholesterol was included in the matrix the efficiency was between 20 – 60%. The variation was most probably due to the much higher amount of non-specific binding to this matrix. A large variation in binding efficiency was also obtained for DTP-DPPE (4-71%), whereas binding efficiencies between 22 – 53% were obtained when cholesterol was included in this matrix. Deposition of the layer may affect the orientation of the linking group and influence the binding capacity.

Table 2. Binding efficiencies, η, of antibody Fab′fragments coupled to various surfaces

η_a [%]

Film type	QCM	SPR	RIA	AFM*
Polystyrene/whole antibody			3	
Polystyrene/$F(ab)_2$			10	
DPPC/EMC-DPPE	63	66	60	50
DPPC/CHOL/EMC-DPPE	59	37	24	55
**DLiPE/EMC-DLiPE monomer	50-90	20		
**DLiPE/EMC-DLiPE partially polymerised	70-80	55		52
DPPC/DTP-DPPE	4		71	
DPPC/CHOL/DTP-DPPE	50		22	56

*AFM measurements were performed at ÅAPC and ** films formed at ÅAPC

The fluidity of the host layer seemed to be of importance for binding of the Fab′-fragments. Cholesterol makes the DPPC layer more condensed and affects the orientation of the Fab′s but, on the other hand, increases the amount of non-specific adsorption. We have therefor also studied the unsaturated phospholipid dioleoylphosphatidylcholine, DOPC as a host matrix. The Fab′fragments have a more slanted orientation in the DOPC matrix and take a more standing position as the condensation of the host matrix increases [ÅAPC 12].

As a typical example, Figure 11 shows the SPR intensity change of the interaction of Fab′-fragments with a monolayer of DOPC/DPPE-EMC (in a molar ratio of 19/1) transferred at a surface pressure of 30 mN/m and stored dry one week at room temperature [ÅAPC 12]. The SPR intensity decreased on injection of buffer onto the monolayer, indicating swelling and/or reorganization of the monolayer. A steady state was obtained after about 10 minutes in contact with buffer. This time is dependent on how long the film has been stored. Layers stored only for one day show no swelling/reorganisation behaviour. A sudden increase in intensity was observed on injection of Fab’- fragments. The intensity decreased on rinsing with buffer and a further decrease was observed on interaction with BSA. The intensity, however, increased again on rinsing with buffer indicating a reorganisation of the layer. The surface was regenerated with a glycine-HCl aqueous solution at a pH of 2.8. Human IgG interacts with the Fab′-fragments for several regene-ration cycles. The binding of hIgG to a DOPC/EMCDPPC/Fab′mono-layer previously regenerated with a glycine-HCl solution is shown in Figure 12. These measurements indicate that concentrations below 1 ng/ml could be obtained with SPR.

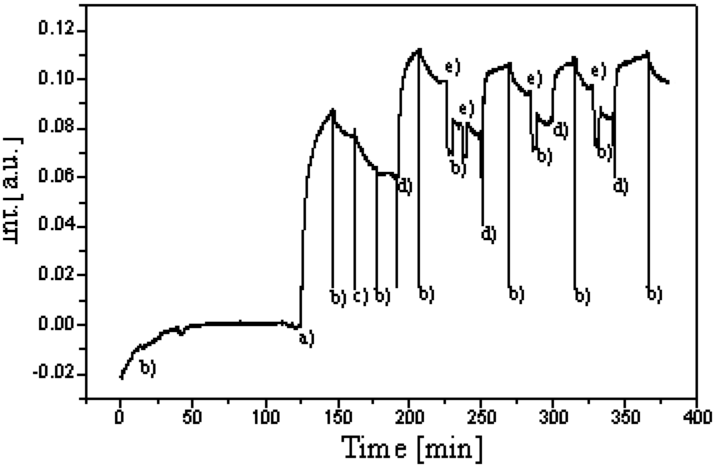


Figure 11. Shift in SPR light intensity at a fixed angle upon binding of 50 µg/ml Fab′-fragments, 100 µg/ml BSA and 100 µg/ml hIgG to a monolayer of DOPC/DPPE-EMC 19/1. The consecutive steps can be distinguished: a) linking of the antibody, b) rinsing with buffer, c) unspecific adsorption of BSA, d) interaction with hIgG and e) washing with a glycine-HCl solution.

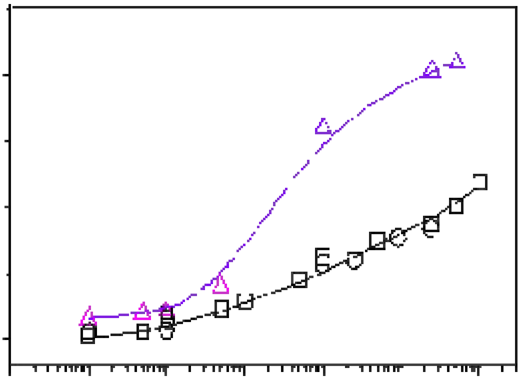
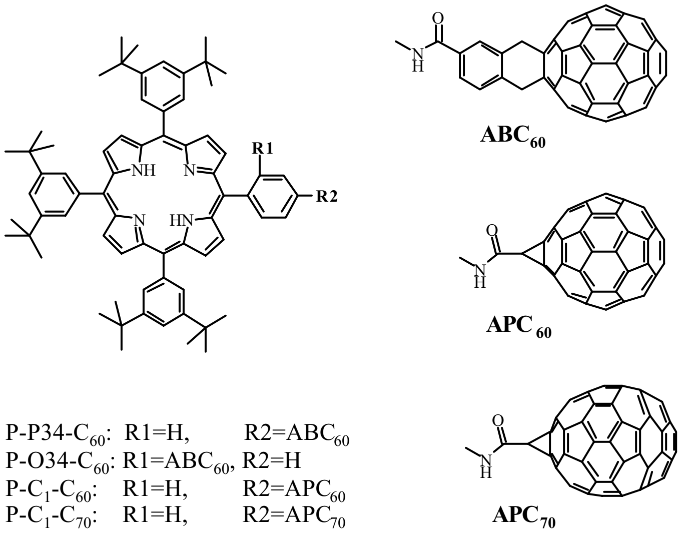


Fig. 12. The binding isotherm of hIgG to DOPC/DPPE-EMC/Fab′fragment and DPPC/DPPE-EMC/Fab′fragment layers.

3 International Aspects

Recently a group from Osaka University and **IMC** have joined their efforts in investigation of the porphyrin–fullerene DA systems and have obtained promising results. It was found that the close proximity of the por-phyrin and fullerene
results in formation of the light-emitting CT state [IMC 41]. The phenomenon has been observed for covalently linked porphyrin–fullerene macromolecules in solution (P-O34-C_{60}, Figure 13) and for intermolecular inter-action of the por-phyrin and fullerene in the solid state, e.g. LB films and micro-crystalline dry samp-les.



P-P34-C_{60}: R1=H, R2=ABC_{60}
P-O34-C_{60}: R1=ABC_{60}, R2=H
P-C_1-C_{60}: R1=H, R2=APC_{60}
P-C_1-C_{70}: R1=H, R2=APC_{70}

Fig. 13. Some of the compounds recently synthesised at Osaka University.

The Osaka group headed by Professors Yoshiteru Sakata, Shunichi Fukuzumi and Hiroshi Imahori is among world leading groups in synthesis and studies of molecular donor–acceptor systems in general and porphyrin–fullerene compounds in particular. The recent activities of the groups in the field can be summarised as followed:

a) Synthesis of porphyrin and fullerene related macro-molecular systems. This includes the first successful synthesis of the porphyrin–fullerene DA dyad, the following systematic studies of different arrangement of the dyads and synthesis of porphyrin–fullerene based triads, and pentads.

b) Photo-physical studies of donor-acceptor molecular systems, which is a key issue in research work of Japanese groups. Recently grate attention is paid to photophysics of the fullerene–containing DA systems [IMC 41].

c) Self-assembled monolayers of the DA compounds on gold. This is a relatively new research direction of the groups. However, recently a molecular system has been constructed, which has shown the highest quantum efficiency ever reported for the artificial self-assembled monolayer system. The cooperation with the Osaka group has increased the synthetic power of the IMC group and essentially improved its work.

The research performed at **IMC** is related to research activities of the group in the frame of following running international projects:

1) Project "Experimental and Modelling Aspects of Electron and Energy Transfer in Organised Molecular Materials", COST D14 (Functional Molecular Materials), and
2) Project "Redox Chemistry and Catalysis in the Microenvironment of Electrode Surfaces", COST D5 (Chemistry at Surfaces and Interfaces)

The following scientists from **ÅAP** have stayed longer than 4 weeks abroad: R. Österbacka, Dept. of Physics, Univ. of Utah (USA) for a total of 13 months and 3 weeks; H. Sandberg, Cavendish Laboratories, Univ. of Cambridge (UK) for a total of 3 months and 2 weeks (ongoing).

The following scientist have visited ÅAP for periods longer than 2 weeks: Dr. D. Bhattacharjee, CAT, Indore, (India) 3 months; Doc. A. Alexeev, General Physics Institute, Moscow State University (Russia), total of 10 months 3 weeks; Dr. A. Aleshin, A.F. Ioffe Physico-Technical Institute, Russian Academy of Science (Russia) 3 months; M.Sc. A. Chowdhury, IACS, Calcutta (India) 2 months 2 weeks; Prof. G. Juska, Dept. of Solid State Electronics, Univ. Vilnius (Lithuania) 2 weeks; Doc. K. Arlauskas, Dept. of Solid State Electronics, Univ. Vilnius (Lithuania) 2 weeks, M.Sc. K. Genevicius, Dept. of Solid State Electronics, Univ. Vilnius (Lithuania) 4 months.

The group is actively involved in cooperation with Dept. of Solid State Electronics, Univ. of Vilnius (Lithuania), Dept. of Physics, Univ. of Utah (USA), Indian Association for the Cultivation of Science, Calcutta (India), and CNR, Milano (Italy). The research of the group has been presented in numerous international conferences, including 2 invited papers and 15 oral presentations.

As an important dimension of the structure research, **ÅAPC** took part in the European Thematic Network "The calibration of SPMs" that was financed by the EU Standards, Measurements and Testing programme. The network consisted of altogether 13 partners representing industrial research laboratories and manufacturers, universities and national institutes. The aim of the network was to improve the current situation where users are uncertain about the metrological properties and achievable measurement uncertainties of SPMs (scanning probe microscope), effective calibration procedures, use of standards and re-calibration necessities. The partners jointly carried out several internal and external activities. The main ones were the completion of a "State-of-the-art review on metrological SPMs" and of a "Recommendation on the calibration of SPMs", the organization of comparison measurements of SPMs, and the organization of the "Quantitative Microscopy" seminar series. Further information is available in the network homepage: www.dfm.dtu.dk/SPMet.

The collaboration between **ÅAPC** and the General Physics Institute of the Russian Academy of Sciences has continued. Joined articles have been published on both experimental and theoretical studies on polymerization of diacetylene Langmuir films, and on aggregation properties of coumarin dye monolayers.

Dr. Janusz Sadowski at the group of Sensing Materials of **VTT** has coordinated an EU project "Biosensing devices based on biochips and tuning laser diodes"- a project closely related to this one. Within the project close collaboration has been establised with the group of L. Jullien at Département de Chimie CNRS in Paris and with the group of A. L. Laschewsky Département de Chimie, Université Catholique de Louvain in Belgium [VTT 9]. Postdoc students from both groups have spent time in the group performing measurements, which has been of benefit also for the MATRA project. Under the supervision of Martin Albers students from the Biotechnology department at Cranfield University, has spent about half a year in the group performing the experimental part of their master thesis [VTT 6].

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project.

Partner	Type of publication	1996	1997	1998	1999	2000	Total
TUT/IMC	Ref. Journal art.	9	10	6	9	21	55
	Ref. conf. papers	0	0	0	0	1	1
	Doctoral dissert.	0	1	0	0	2	3
	Licentiate degrees	1	1	1	1	1	5
	Master degrees	2	2	2	7	7	20
ÅAP	Ref. Journal art.	2	10	5	2	5	24
	Ref. conf. papers	3	4	4	5	7	23
	Doctoral dissert.	0	0	1	1	0	2
	Licentiate degrees	0	1	1	0	0	2
	Master degrees	2	0	2	1	0	5
ÅAPC	Ref. Journal art.	0	0	3	4	5	12
	Ref. conf. papers	0	0	1	0	0	1
	Doctoral dissert.	0	0	0	2	0	2
	Licentiate degrees	0	0	1	0	0	1
VTT	Ref. Journal art.	0	0	3	2	2	7
	Ref. conf. papers	0	0	1	0	0	1
	Doctoral dissert.	0	0	0	0	1	1
	Master degrees	0	0	0	0	2	2

5 Other Activities

The scientific work performed by the Tampere group in the field of photochemistry was internationally recognised by the photochemical society when the organizing of the XVIth IUPAC Symposium on Photochemistry 1996 was given to the Institute of Materials Chemistry. The symposium gathered altogether 533 participants from 40 different countries.

A symposium titled “Self-Assembly and Self-Organizing Systems” was organized in Turku in September 2000. The symposium was chaired by J. Peltonen and it was organized in collaboration by the hosting institute (ÅAU/PC) and the Finnish Surface and Colloid Society. The symposium turned out to be very useful for the project in bringing together experts on national level and bringing in new ideas given by the high-rank invited lecturers from abroad.

6 Publications

6.1 Refereed Journal Articles

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NOVEL PHOTOACTIVE MATRIALS

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Abstract

The conversion of solar energy into electricity has been studied by constructing photoelectrochemical cells. The primary goals of the project were design, synthesis and characterization of sensitizer dyes, study of the electron injection from the dye to the TiO_2 semiconductor, and the development of the redox system including the conducting glass electrodes.

A group of new ruthenium mono(bipyridine) compounds was synthesized and characterized during the course of the project. Ligand exchange reactions were used to modify the light absorption properties of the synthesized compounds. The study of the photophysics and femtosecond kinetics of the ligand exchange was initiated during the project.

The electron transfer from the dye to the TiO_2 was studied with the well known $Ru(dcbpy)_2(SCN)_2$ dye. Fundamental new findings were obtained of the electron injection mechanisms of the system down to 30 fs time resolution.

The preparation of conducting glass electrodes was done by a new electrodeposition technique. The reduction rate was found dependent on the Pt-layer on the electrode. Electrochemical preparation of organometallic photosensitive ruthenium mono(bipyridine) polymer film on the glass electrode was extensively studied during the project. The film growth was found to be photosensitive.

Theoretical methods were applied for modeling the light absorption properties of the dyes and for the attachment of the dyes to the carrier surface. The calculated spectra were in good agreement with the experimental values and theoretical results predicted clearly the effect of electron-withdrawing substituent on the bipyridine ring. The results demonstrate that modelling can be applied in the design of novel dye molecules.

A sensitized cell based on new ruthenium mono(bipyridine) dye was built and tested. The main advantage of the new dyes is that they allow modification of absorption properties of the compounds by simple ligand exchange reactions.

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1 Partners and Funding

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The research group consists of project leader professor Tapani Pakkanen, academy researcher Matti Haukka, docent Pipsa Hirva, Dr. Saija Luukkanen, Dr. Esa Eskelinen and technician Mirja Kallinen

1.2 Department of Chemistry, University of Jyväskylä

The research group consists of project leader professor Jouko Korppi-Tommola, M.Sc. Viivi Lehtovuori, M.Sc. Jani Kallioinen, Ph.D. student Pasi Myllyperkiö, and M.Sc. student Janne Savolainen

1.3 Laboratory of Inorganic Chemistry, Åbo Akademi

The research group consists of project leader docent Mikael Wasberg and Ph.D. student Sam Myllynen

1.4 Department of Physics, University of Joensuu

The research group consisted of project leader professor Timo Jääskeläinen, M.Sc. Hanna-Leena Onniselkä (20 months), and M.Sc. Mervi Pakarinen (8 months).

1.5 Funding

Table 1. Funding of the project in 1000 FIM in 1998-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1998	1999	2000	**Total**
JoY,Chem	JoY	100	100	100	**300**
	Academy	380	390	390	**1160**
JY, Chem	JY	100	100	150	**350**
	Academy	320	360	220	**900**
ÅA	ÅA			24	**24**
	Academy	180	190	166	**536**
JoY, Phys	JoY		20	20	**40**
	Academy		190	190	**380**
Total		**1080**	**1350**	**1260**	**3690**

2 Research Work

2.1 Objectives and Work Plan

The conversion of solar energy into electricity using photoelectrochemical cells has been studied extensively. Conventional solar cells are based on light induced charge transfer on a silicon semiconductor interface. The best conversion ratio is achieved in crystalline silicon cells, which are expensive due to the difficult manufacturing processes. More economical, but less active materials are sought from polycrystalline amorphous silicon technology. Most commercial solar cells are based on amorphous silicon.

Dye sensitised solar cells are considered as potential cost-efficient alternative to silicon based solar cells. In these devices the photoresponse of wide band gap semiconductors are extended to visible region by using chemically synthesised dye molecules as solar energy collectors on the surface of nanostructured semiconductor particles. Organometallic ruthenium compounds have been the most promising molecules in this respect and Grätzel *et al.* have demonstrated about 10% efficiency by using $Ru(dcbpy)_2(NCS)_2$ [dcbpy = 4,4'-dicarboxy-2,2'-bipyridine] on a thin nanocrystalline titanium dioxide (TiO_2) film in a chemical solar cell [1].

The general function of the chemical solar cell is relatively well understood. However, many fundamental physical and chemical phenomena crucial for the function of the cell are not so well understood. These include molecular mechanisms of electron injection from the dye to the nanocrystalline film, diffusion of the electron in the semiconductor film, transfer of electron from the counter electrode into the electrolyte and finally diffusion of the electron back to the ionised dye. Detailed understanding of these processes is important for the design and development of organic or organometallic dye cells of any kind.

Synthesis, spectroscopy and structural chemistry of known and some new active metal complexes was the focus of the present project. Photophysics of electron transfer processes in these compounds were studied. Synthesis of TiO_2 and Al_2O_3 nanoparticles, preparation of thin semiconductor films and construction of a few experimental cells were investigated as well. The research program for the basic studies on photoactive materials and solar cells was based on the combined expertise of the groups involved.

The synthesis team in Joensuu (Chemistry) developed a group of novel ruthenium bipyridine complexes with carbonyl, nitrosyl and thiocyanate ligands for new photoactive dye candidates. The spectroscopy group in Jyväskylä studied dye to semiconductor electron transfer processes, which are dependent on the structure of the photoactive complex at femtosecond time resolution. Electrochemical studies by the Åbo group was important in the characterization of the redox properties of the ruthenium bipyridine complexes and in preparation of the counter electrodes. The optoelectronics group at Joensuu (Physics) was responsible for testing optical components and carrying out efficiency measurements of the cells.

The primary goal of the project was to investigate photoactive materials based on novel ruthenium bipyridine complexes. The scientific aim was in the understanding of the structural and dynamic factors influencing the charge transfer processes.

2.2 Progress Report: Common Themes

The main research areas of the project were design, synthesis and characterization of the sensitizer dye, study of the electron injection from the dye to the TiO_2 semiconductor, and the development of the redox system including the conducting glass electrodes.

A group of new ruthenium mono(bipyridine) compounds was synthesized and characterized during the course of the project. Controlled thermal and photochemical methods were developed for the synthesis and modification of the ruthenium bipyridine compounds. The dyes were characterized by single crystal X-diffraction as well as spectroscopic and electrochemical methods.

Ligand exchange reactions were used to modify the light absorption properties of the synthesized compounds. The study of the photophysics and femtosecond kinetics of the ligand exchange was started during the project.

The electron transfer from the dye to the TiO_2 is one the key factors in the sensitised cell. This was studied with the well know $Ru(dcbpy)_2(SCN)_2$ dye. Fundamental new findings were obtained on the mechanisms of electron injection of the system down to 30 fs time resolution.

New methods were developed for the manipulation of the conducting glass electrodes. The electrodes were modified by new electrodeposition technique. The counter electrode is responsible for the reduction of the redox pair iodide/tri-iodide in the Grätzel type cells. The reduction rate is dependent on the Pt-layer on the electrode. Electrochemical preparation of organometallic photosensitive ruthenium mono(bipyridine) polymer film on the glass electrode was extensively studied during the project. The film growth was found to be photosensitive. This polymeric material was also found to be highly active in catalytic processes such as reduction of CO_2.

Theoretical methods were applied for modeling the light absorption properties of the dyes. The density functional methods were used for the geometry optimisation of the ruthenium bipyridine molecules. The optimised structures were then used for spectra calculations carried out using the ZINDO method. The calculated spectra were in good agreement with the experimental values and theoretical results predicted clearly the effect of electron-withdrawing substituent on the bipyridine ring. Similarly, the strong red-shift due to modification of the dye by ligand exchange was verified by computational methods. The results demonstrate that modelling can be applied in the design of novel dye molecules.

A sensitized cell based on new ruthenium mono(bipyridine) dye was built and tested. Although the effectivity of the novel cell was not as high as that of the commercial $Ru(dcbpy)_2(NSC)_2/TiO_2$ system, it showed that the new ruthenium mono(bipyridine) dyes can be utilized as sensitizers. The main advantage of the ruthenium mono(bipyridines) is that they allow modification of the absorption properties by simple ligand exchange reactions. On the long run this may offer a route for producing cells with specific light absorption range i.e. design of cells with specific colour.

2.3 Progress Report: Progress by the Department of Chemistry, University of Joensuu

Synthesis, structural characterization and modelling of photoactive complexes

The primary aim of this work was to tune the chemical and physical properties of the transition metal polypyridine complexes to achieve novel photoactive complexes. A group of new metal polypyridine complexes were synthesized and characterized during the course of the study.

The synthetic work was concentrated on ruthenium bipyridines because of their versatile photochemical and photophysical properties. The most important property of these complexes is the low metal-to-ligand charge transfer (MLCT) which can be influenced by modifying the ligand sphere of the ruthenium centre or by modifying the polypyridine ligand.

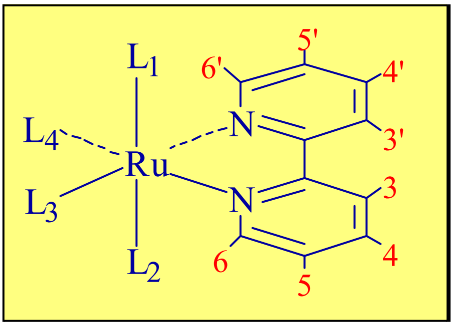

Fig.1. A schematic representation of a ruthenium mono(bipyridine) complex. Lx= ligands in the coordination sphere of ruthenium. Sites 3-6 are possible positions for peripheral substituents used in modification of bipyridine ligand.

Among ruthenium bipyridines ruthenium mono(bipyridines) were of particular interest. Unlike ruthenium tris(bipyridine) or bis(bipyridine) complexes ruthenium mono(bipyrides) have been much less studied in the context of photochemistry. The main reason for this is that these compounds have not been readily available until recent years. The mono(bipyridine) complexes allow diverse reactions in the coordination sphere of ruthenium.

The primary method for the characterization of new complexes in solid state was X-ray crystallography. The knowledge of the structural details, such as isomerism, is substantial in design and understanding of the functionality of photoactive materials. Basic spectroscopic methods, NMR, IR, UV-Vis, were used for characterization of the molecules in solution. Electrochemical characterization was carried out in collaboration with Åbo Akademi. Reactivity of the novel complexes was studied in catalysis tests using water-gas shift reaction as the probe reaction.

The theoretical work was focused on the structural analysis and reactivity of the new complexes and modelling of the attachment of the complexes on the semiconductor surface. The latter process is essential in the design of dye-sensitised solar cells.

Modification of the polypyridine ligands

The complexes were modified by adding different types of substituents on the polypyridine ring. Both electron donating and withdrawing groups were considered. Methyl group was the primary electron donating group. Carboxylic acid (-COOH), nitro (-NO_2) and phosphonic acid (-PO_3H_2) groups were used as electron withdrawing groups. Other polypyridine substituents such as halides were also tested.

The electronic effects of the peripheral substituents on the metal centre at the ground state were studied by cyclic voltammetry (CV). The studies showed that the electron donating substituents shifted the Ru(II)/Ru(III) oxidation to more positive values indicating lower oxidation tendency for these complexes at the ground state. Absorption spectra showed also systematic shift depending on the nature of the substituent. Electron withdrawing substituents caused slight shift to longer wavelengths and electron donating to shorter wavelengths.

The chemical reactivity of the complexes was tested in water-gas shift reaction. In the catalysis experiments the effect of the substituents was drastic: the activity was lowered with both types of substituents, indicating that the substituents influenced strongly on the chemical reactivity of the coordination sphere of the metal.

Only carboxylic acid and phosphonic acid could be used as attaching groups in anchoring the complexes on the TiO_2 semiconductor surface. Therefore, only these types of peripheral substituents could be used in the Grätzel-type dye-sensitised solar cells.

Ligand exchange reactions

Ligand exchange was proved to be effective method in modification of the photochemical properties of the ruthenium polypyridine complexes. The modification of the ligand sphere of ruthenium was carried out by using $Ru(bpy)(CO)_2Cl_2$ as a starting compound. Both thermal and photochemical reactions were used.
Halogen exchange had strong impact on both the physical and chemical properties of the transition metal complexes. The thermal halogen exchange involved chloride exchange to other halides or pseudohalides such as SCN. For example absorption/emission properties, studied by Jyväskylä group, and solubility were strongly affected by the halide. In addition to halides, also other groups such as nitrosyl, methoxycarbonyls and hydrides were used in the exchange reactions.

Thermal exchange reactions included also growth of the metal-metal chain of the ruthenium bipyridine complexes. The chain growth shifted effectively the visible light absorption towards longer wave lengths and increased absorption efficiency. The main problem in this method was the control of the chain growth and very poor solubility of the resulted polymers.

The chain growth also increased strongly the catalytic activity of the ruthenium bipyridines indicating strong impact of the chain, both electronic and steric, on the metal centre's coordination sphere. The chain growth can be carried out also by electrochemical method, developed by Deronzier's and Ziessel's group. Electrochemical polymerisation was studied in collaboration with the French group and with Åbo Akademi.

Molecular modelling

The modelling work, done in the University of Joensuu, was focused on optimisation of the ground state geometries of complexes, modelling the reaction mechanisms and modelling the attachment of the light absorbing dyes on the semiconductor surface. Modelling of the exited states was carried out by University of Jyväskylä exploiting the optimised geometries. Chemical reactivity of the complexes was studied by modelling the ligand exchange reactions.

The reaction studies confirmed the experimental observations of the active role of solvents, such as alcohols and water, in the reactions of carbonyl containing ruthenium bipyridines.

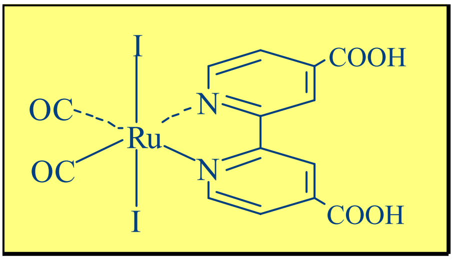

Fig. 2. Structure of trans(I)-Ru(dcbpy)$(CO)_2I_2$.

Trans(I)-Ru(dcbpy)$(CO)_2I_2$ was used as a probe molecule in studies of the interaction of ruthenium mono(bipyridines) with the TiO_2 surface. (Fig 2.) In this system the complex is attached to the surface via the peripheral carboxylate substituents of the bipyridine rings. A cluster model, derived from anatase 101 surface, were used as the model for TiO_2 surface.

According to the preliminary results the most probable bonding modes between the carboxylate containing Ru(dcbpy)$(CO)_2I_2$ and TiO_2 surface were bidentate bonding via single carboxylate group and two dentate bonding via two carboxylate groups (Fig 3).

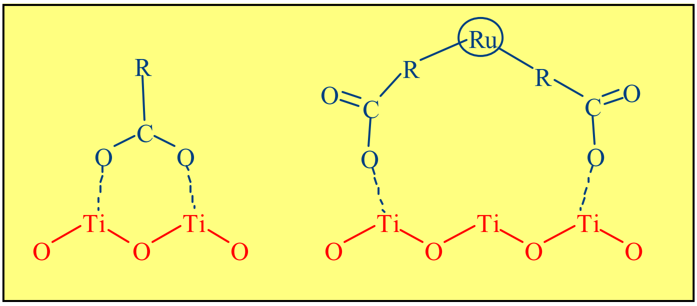

Fig. 3. The most probable bonding modes for Ru(4,4'-dicarboxy-2,2'-bipyridine)$(CO)_2Cl_2$ with anatase (TiO_2) 101 surface.

2.4 Progress Report: Progress by the Department of Chemistry, University of Jyväskylä

TiO_2 preparation and cell construction

The synthesis of nanocrystalline TiO_2 particles was carried out according to earlier published methods [2] by the hydrolysis of titanium isopropoxide. The nanocrystalline TiO_2 paste was used to prepare nanocrystalline TiO_2 electrodes both for the cells and for the femtosecond experiments. Also nanocrystalline Al_2O_3 films were made as high band gap reference films for femtosecond measurements. The average particle size of the nanocrystalline particle preparations was about 10 nm and the size distribution was fairly narrow (Fig. 4). The film thicknesses used varied form 3 to 5 µm.

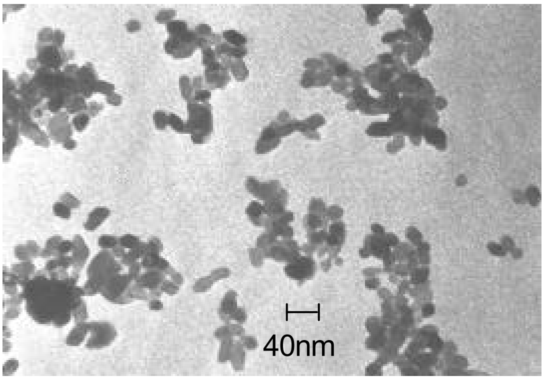

Fig. 4. Nanocrystalline TiO_2 particles.

The applicability of the synthesized dyes for use in solar cells was studied by measuring the UV-vis spectra of the dyes in solution and attached on the nanocrystalline Al_2O_3 and TiO_2 films. Special attention was put on the absorption widths and absorption efficiencies of the dyes. It was observed that bis(bipyridine) dyes have better absorption efficiencies than mono(bipyridine) dyes. Solvent ligand substitution of mono(bipyridines) increased absorption efficiency extending it towards red. The dimer and the polymer dyes showed the greatest absorption but the lack of attaching groups, solubility problems and the instability of the dyes on TiO_2 films inhibited testing them in cells.

The aim of the cell preparation was to test the performance of the new synthesized dyes in Gäetzel type cells and compare these to known dyes, such as Ru535. The cell construction proved to be more difficult than expected. The major problem was the sealing of the cells. Acetonitrile based electrolyte is very volatile and therefore the sealing had to become as impermeable as possible. Another problem with the sealing was that the most of the usual glues do not harden because of the presence of the iodine-containing electrolyte. After several attempts it was found that sodium silicate treated with glycerole works reasonably well in sealing. The performance of few trial cells were measured by the Joensuu physics group.

Photophysics of ligand exchange reactions

The change of carbonyl ligand of the monobipyridine compound to a solvent molecule increases remarkably its absorption efficiency. The reaction improves light collection efficiency of monobipyridyls in solar cells. Reaction takes place even after the reactant is attached to the TiO_2 film. The photophysics of the ligand exchange reaction was studied in order to characterise the electronic states involved in electron transfer and in the ligand exchange reaction.

The usual steady state spectroscopic methods were used to study the reaction. The temperature dependent luminescence indicates that the luminescent triplet state observable at liquid nitrogen temperatures thermally converts into a reactive state with an activation energy of 850 cm^{-1} in a narrow temperature range.

The ligand exchange reaction in itself is of fundamental interest because it is an unusual type of photon-induced reaction that contains bond formation instead of bond dissociation. Femtosecond excited state kinetics of the reactant and the product molecule revealed initial fast reaction steps identified as intramolecular and intersystem crossing processes as well as longer lived excited states. It is believed that these initially long-lived states are thermally activated and serve as reaction paths for the solvent ligand exchange reactions in halogenated monobipyridyls. The final goal of these unfinished experiments is to measure the kinetics of the solvent exchange reaction in real time.

Electron injection in the dye sensitised semiconductor thin films

Knowledge of the mechanism and rate of electron transfer from photo-excited states of transition metal complexes into nanostructured semiconductor thin films is of fundamental interest as well as important for development of solar cell devices and photocatalytic processes. Since the first demonstration of the $Ru(dcbpy)_2(NCS)_2$ sensitized titaniumdioxide (TiO_2) solar cell with ~10% total efficiency [1], several groups have studied the mechanism and related time constants of the electron transfer process of the cell. It is necessary for high solar energy to electrical conversion efficiency that a fast electron injection from the excited state of the sensitizer dye to the semiconductor is accompanied by much slower back electron transfer rate to the dye molecule [2,3].

Electron injection rates of $Ru(dcbpy)_2(NCS)_2$ dye on TiO_2, in the time window from a few tens of femtoseconds to hundreds of picoseconds, was studied. As reference measurements femtosecond kinetics of the dye in solution and on high band gap Al_2O_3 thin film were carried out. Kinetic measurements were made in the visible and near-IR region spectral regions. The kinetic results for $Ru(dcbpy)_2(NCS)_2$/ TiO_2 film indicated a reactant decay (excited state) and product formation (dye cation) depending on probe wavelength. It was shown that a considerable portion of electron injection takes place in picosecond time domain and the resolved components 1.1 ps, 12 ps and 100 ps are all related to electron injection from the excited states of the dye to the semiconductor

TiO_2 (Fig. 5). It was further shown that this part of electron injection takes place from thermalised triplet states. In addition to picosecond components the Ru(dcbpy)$_2$(NCS)$_2$/ TiO_2 system has also a significant electron transfer in sub 100 fs time scale.

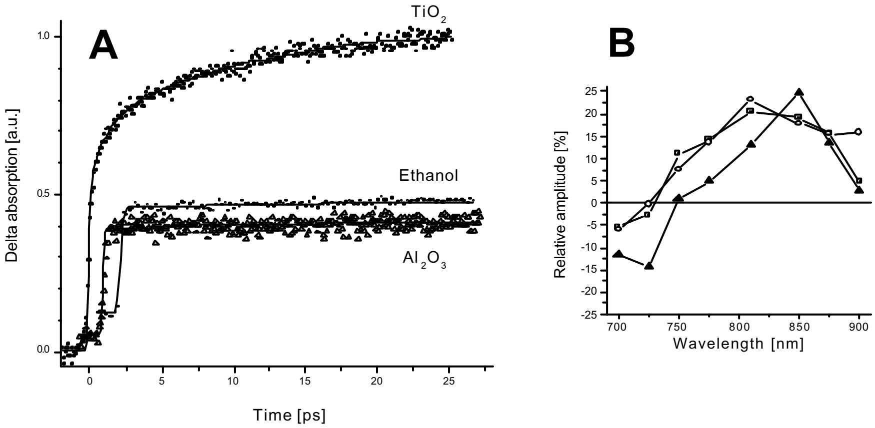

Fig. 5. Transient absorption measurements for Ru(dcbpy)$_2$(NCS)$_2$ dye: A) Comparison between electron injecting system (TiO_2) and non-injecting samples (Al_2O_3 and ethanol). For the dye on TiO_2 nanoparticles formation of the dye cation is observed. B) Globally fitted amplitude spectra of the dye on TiO_2 showed that all observed picosecond time components are related to the same process, electron injection.

Scientific co-operation with the University of Lund produced further insight to the fastest electron transfer process. It was concluded that a considerable part of electrons are injected directly from the excited singlet states before any thermalization takes place. This process takes place simultaneously with fast intersystem crossing to the triplet states. However, excitation energy is not lost in the process as electrons are subsequently injcted from the triplet state in the picosecond time scale. The measurements have brought the deepest understanding of the electron transfer processes in the Ru535/TiO_2 system so far available in the literature [24]. The results are positive news to the designers of dye sensitised chemical solar cells as extremely fast singlet and triplet electron transfer means that light energy is efficiently used to electron injection and not for heating of the dye during illumination.

Molecular modelling (ZINDO calculations)

A computational approach to study light absorption properties of the synthesized ruthenium(II) dyes was carried out. It was of interest of see how substitutions on the bipyridine-ring affect on spectral properties and molecular orbitals of the dye. The molecular geometries of the complexes were optimized at the University of Joensuu using DFT approach. The optimized structures were used as input geometry for semiempirical spectra calculation. Intermediate neglect of differential overlap method parametrized for spectroscopy at configuration interaction level of theory (ZINDO) was used for calculations [4].

Calculated transitions were blue-shifted as compared to experimental spectra, yet the lowest energy transitions have similar shape than the experimental spectra. Electron-withdrawing substitutions to the 4,4'-positions of the bipyridyl shifted the experimental absorption toward red and these shifts were reproduced well by the calculations. After addition of solvent molecules around the ruthenium complex the lowest electronic transitions were considerably red-shifted and better overlap with measured spectra was produced.

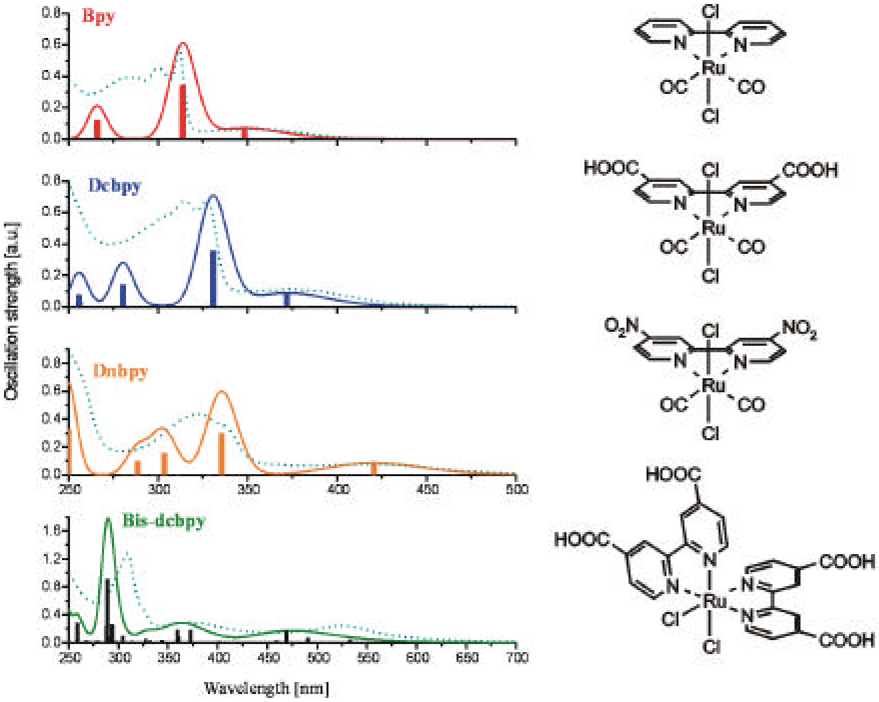

Fig. 6. Comparison between calculated stick-spectrum, convoluted spectrum (Gaussian function) and experimental spectrum of some studied complexes.

Calculations of spectral properties of the ruthenium complexes were based on former experience and on ongoing calculations of light absorption properties of natural light harvesting antenna of bacteria and plants. Red shift of the lowest energy absorption bands due to increasing size of the chromophore and red shift due to solvent (or protein) interaction observed for the ruthenuim complexes, turned out to be very similar effects than observed for chlorophyll and bacteriochlorophyll based systems and for which the computational approach used had been tested earlier in the group.

2.5 Progress Report: Progress by the Laboratory of Inorganic Chemistry, Åbo Akademi

The electrochemistry of transition metal organic ruthenium bipyridine complexes and derivatives has been evaluated. Electrochemical characterisation of Ru(bpy) complexes and properties of electrocatalytically and photocatalytically active polymer films prepared by electroreduction of these compounds has been the primary goal. Other areas of research have included the investigation of the counter reaction as well as the electrochemistry of titanium and titanium dioxide. Further, some work has also been carried out regarding the electrochemistry of the redox couple iodide/tri-iodide. Experimental methods such as the electrochemical quartz crystal microbalance (EQCM), quartz crystal impedance methods for determination of film viscoelasticity, hydrodynamic voltammetry for study of reaction kinetics and mechanisms, as well as spectrometric methods for studies of electrolysis products have been used in combination with other more basic electrochemical techniques.

Metal organic films made by electroreduction of Ru(bpy)-compounds

Polymer films made by electroreduction of ruthenium bipyridines possess properties such as the ability to reduce carbon monoxide to CO_2. The films may also be useful in photoelectrochemical cells if their stability can be improved. The EQCM was used as the primary method to establish the reaction mechanisms for trans(Cl)-$Ru(bpy)(CO)_2Cl_2$, trans(Cl)-$Ru(dmbpy)(CO)_2Cl_2$ (dmbpy = methyl substituted bipyridine), cis(Cl)-$Ru(bpy)(CO)_2Cl_2$, as well as the dimer forms of the first two. Further, trans(Cl)-$Ru(dcbpy)(CO)_2Cl_2$, (dcbpy = carboxylic acid substituted bipyridine) and trans(Cl)-$Ru(dcbpy)(CO)_2I_2$ were studied. Due to clearly lower film forming capabilities, less time was spent on the electrochemical characterization of the COOH substituted complexes.

Electron transfer is very rapid during reduction for all compounds. The current efficiency during film formation was estimated with hydrodynamic methods and was found to be high, above 97% for the monomers. This speaks for a direct attachment of reduced monomer to the film and a simple reaction mechanism. The two electron reduction with chloride emission was verified as well as the suggested polymer formation reaction (-$Ru(bpy)(CO)_2$-$Ru(bpy)(CO)_2$-). Deviations from the above mechanism were however found. The $Ru(dmbpy)(CO)_2Cl_2$-compound produced films with a rate almost double that of the corresponding unsubstituted compound due to the formation of anomalously heavy films during the initial stages of deposition. Crystal impedance measurements indicate that this is likely to be an effect of increased viscoelasticity and thus errors in the Sauerbrey estimation.

The electrical conductance of the films is high and the only indication of passivation in film formation at an active potential was found for the cis-form of the unsubstituted compound. At very negative potentials the polymer film formation completely ceases. The properties of the polymer film are dependent on reaction rate. During solution agitation a homogenous, rigid film is deposited while in static solution a film with higher viscoelasticity is formed, possibly as a result of CH_3CN solvent uptake. Clear indications of viscoelastic film behaviour were also found for thicker films formed during cyclic voltammetry.

The reaction rate is strongly dependent on type of solvent. The rate of film formation was clearly reduced in DMSO-based electrolytes and current efficiencies less than 80% was obtained for the methyl substituted compound. However, no evidence for incorporation of DMSO into films was found and the impedance measurements suggest rigid film behaviour.

When chloride is present in the solution the film formation process is inhibited, i.e. the chloride ion seems to affect the polymerisation process. Deposited polymer films are easily removed by electrooxidation and the mass/charge ratio shows that the film breaks up into larger fragments than monomers. The films were unstable under open circuit conditions and a constant, slow probably diffusion controlled chemical oxidation of the film by traces of oxygen was found.

Photosensitivity studies of polymeric $[Ru(bpy)(CO)_2]_n$ films was carried out in collaboration with the University of Joensuu. The reduction current and film growth was discovered to increase during illumination. When the light was switched off, the current returned to its original value, thus, indicating a reversible nature of the phenomenon.

The counter reaction

The counter reaction in Grätzel-cells is typically the reduction of iodine. This reaction is electrocatalytic and Pt must be present on the counter electrode glass to increase the rate. For this a method was developed for electrochemical manufacturing of Pt-layers on conducting counter electrodes in which the Pt was electrodeposited onto the ITO glass. The reduction rate dependence on Pt amount was studied with the redox pair iodide/tri-iodide and suitable amounts of Pt were determined.

Thin layer flow cell

A great deal of work was carried out in the construction of a reusable thin layer flow cell for *in situ* photo(electro)chemical studies. Rapid *in situ* modification of electrodes (dye attachment, electrochemical treatment, redox-electrolyte change etc.) is possible with this cell and once a certain electrode and cell composition has been prepared, spectroscopic characterization can be made, *in situ* or after closing of the cell and transport to another laboratory. The cell was mainly tested by cooperation partners at the University of Jyväskylä.

Electrolytic dissolution and deposition of Ti

The microscopic structure of the TiO_2 film has a direct influence on the photovoltaic efficiency. The porosity and the roughness factor of the films can be increased by further electrochemical treatment of baked, slurry-based films in electrolytes containing Ti-salts. For this reason electrochemical TiO_2 modification was investigated. Titanium metal is dissolved in CH_3CN based electrolyte if special precautions are taken. This was tested and the reduction and deposition of titanium on gold from the same solution was also attempted. The procedure was confirmed and deposition on gold plated quartz crystals was made.

2.6 Progress Report: Progress by the Department of Physics, University of Joensuu

In the very beginning of this project, our staff helped the researchers at the department of chemistry (JoY) in optical spectroscopy of the photoactive complexes. We have fabricated various thin films from organic materials for years. This knowledge was transferred to the department of chemistry (JY), where the samples for this project were fabricated. All prototypes of the fabricated cells were tested at our department. For comparison few crystalline silicon cells, amorphous silicon cells, and a commercial Grätzel cell were measured as well.

The following testing system was developed. A stable Argon ion laser was used as a light source at the wavelengths 488 nm and 514 nm. The beam was expanded and split into two plane waves. The other beam was used to monitor the input intensity and the other one illuminated the sample on the whole active area. To monitor the homogeneity of the solar cells we made point measurements, too. We measured the output current and voltage as a function of the input optical power for each wavelength and then calculated the conversion efficiency as a function of the input optical power. Maximum efficiency of the crystalline and amorphous silicon cells were 6.5 % and 8.5 %, respectively. High reflectivity limits the efficiency of the uncoated crystalline silicon cells to 10%, but using a proper surface coating the conversion efficiency might be more than 20%.

The above mentioned testing system was used for the chemical solar cells, too. The highest conversion efficiency for the commercial Grätzel type cell was about 7.5 % at 514 nm. The self-fabricated solar cells turned out to convert not more than 2.5 % of the optical power to electric power. The low conversion rate may be due the inhomogenity of the fabricated samples and the nonideal structure of the modified complexes for solar cell purposes. However, not all of the synthesized new potential dyes were tested within the project period. The construction of new cells of high optical quality turned out to be more time-consuming than planned.

3 International Aspects

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4. Eskelinen, E., Haukka, M., Luukkanen, S., Ahlgrén, M., and Pakkanen, T.A. “Department of Chemistry, University of Joensuu, P.O.Box 111, FIN-80101 JoensuuThe Photochemical and Redox Reactions of Ruthenium 4,4'-dicarboxylic acid-2,2'-bipyridine complexes” 34th International Conference on Coordination Chemistry, ICCC34, Edinburgh, Scotland, 2000.
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7. J. Kallioinen, J. Korppi-Tommola, V. Lehtovuori and P. Myllyperkiö, ‘Investigation on femtosecond dynamics of $Ru(dcbpy)_2(NCS)_2$ excited state and the dye cation on TiO_2 films’, 13th International Conference on Photochemical Conversion and Storage of Solar Energy, IPS2000, Snowmass, Colorado, USA, 2000.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, and theses in Section 6.2.

Partner	Type of publication	1998	1999	2000	**Total**	Publication numbers
JoY,Che	Ref. journal art.	2	4	9	**15**	1-15
	Doctoral dissert.			2	**2**	27,28
	Licentiate dissert.		1		**1**	26
JY, Che	Ref. journal art.	1	2	7	**10**	16-25
	Master degrees	1	1		**2**	30,31
ÅA	Ref. journal art.			2	**2**	7,13
JoY,Phy	Master degrees		1		**1**	29

5 Other Activities

A popular article ’On the possibilities of chemical solar cells’ has been written by one of the project leaders (JKT) in a national science journal **Tietoyhteys** 5/2000, pp. 26 – 27 published by CSC-Tieteellinen laskenta OY, Finland.

6 Publications

6.1 Refereed Journal Articles

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[2] Homanen, P., Haukka, M., Ahlgrén, M., Pakkanen, T.A., Baxter, P.N.W., Benfield, R.E. and Connor, J.A., “Ruthenium Bipyridine Complexes: Synthesis and Charaterization of $Ru(tmbpy)(CO)_2(Cl)_2$, Ru(dmbpy)(CO)2Cl2 and $[Ru(dmbpy)(CO)_2Cl]_2$” *J.Organomet.Chem.,* **552** (1998) 205-211

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6.2 Doctoral, Licentiate, and Master Theses

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[31] J. Kallioinen, 'Chemical solar cells and electron transfer reactions', Masters Thesis, University of Jyväskylä, 1998.

[32] S. Myllynen, `Electrochemical characterisation of conductive films formed by electroreduction of $Ru(L)(CO)_2Cl_2$ compounds´, Ph. Lic. dissertation, estimated to be completed by 2001.

[33] J. Kallioinen, 'Study of spectral and ultra fast electron transfer properties in dye sensitised solar cells', Ph.D. dissertation, estimated to be completed by 2002.

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7 Other References

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POLYELECTROLYTES AND ELECTROCHEMICALLY ACTIVE MEMBRANES: SYNTHESIS, CHARACTERISATION AND APPLICATIONS

Franciska Sundholm[1], Ritva Serimaa[2] and Göran Sundholm[3]

This report is dedicated to the memory of Jan H. Näsman who worked with us as subproject leader. Jan Näsman tragically died in September 2000.

Abstract

The aim of this project is to optimise structures of polymers for maximal conductivity, ion or electronic, and good mechanical strength to enable their use in polymer membranes for electrochemical cells and fuel cells, and in controlled release membranes. Both experimental and computational methods have been used in establishing structure-properties relationships in such complex polymer systems. Several types of electroactive membranes have been prepared. In the work on electronically conducting polymer membranes we have concentrated on derivatives of polypyrrole and polythiophen. The research on variable permeability membranes has concerned the study of polymerisation of pyrrole and the use of the formed membrane as an ion-gate for the controlled release of anionic drugs. Tosylate, salicylate, naproxen and nicoside anions were used as models. It was found that the first three of these anions could be released from the membrane in a controlled way by using simple electrochemical potential signals. The results show that polypyrrole can be used for drug release in special applications. This work is being continued.

Mapping of the electrochemical activity of electronically conducting polythiophens has been developed. Five thiophen derivatives have been electrochemically polymerised. Their properties have been studied with conventional electrochemical methods and *in situ* IR spectroscopy, in addition to two new electrochemical methods; *in situ* contact electric resistance, and contact electric impedance.

The major part of the project has been dedicated to the development and characterisation of ion conducting polymer membranes, with emphasis on proton conducting membranes for demanding uses, as in fuel cells. Proton conducting membranes have been made by pre-irradiation with electron beam, grafting of styrene on fluoropolymer matrices followed by sulfonation. The influence of the chemical nature of the matrix fluoropolymer on the

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preparation and the properties of the products was studied. It was found that the grafting kinetics vary, but that membranes with similar degreees of grafting and polystyrene graft distribution can easily be prepared. The main difference in the properties of the membranes with similar degrees of grafting is the water uptake from liquid water. This in turn affects the conductivity, the mechanical properties and the life time of the membrane in a fuel cell test. Good membranes must have low crystallinity and a flexible lamellar structure which allows the formation of ion aggreates necessary for high conductivity .

The characterisation of the membranes have revealed new features of polyelectrolytes and polyelectrolyte synthesis. Thus the preparation must guarantee an even distribution of sulfonic acid-water clusters in the matrix for optimal performance and stability. This work has also demonstrated the flexibility of the electron beam radiation grafting process and the advantages of this approach in preparing ion-exchange membranes. The irradiation, grafting and sulfonation conditions can easily be changed to obtain membranes of different ion exchange capacities, ion conductivities and other properties.Another approach to the preparation of proton conducting membranes is the direct sulfonation after heavy particle irradiation.

In fuel cell tests the membranes show promise for the development of cost-effective, highly conducting membranes. Further developments are possible as the membrane composition may be further optimised by varying the synthesis conditions.

Computational methods and atomistic modelling have been introduced to gain a better understanding of the mechanisms of ion and water transport in the conducting membranes. Force field parameters for the atomistic work have been optimised for the polymer systems. Good correlation between experimental and simulation work show that we have constructed models which may provide guidance in evaluating potential new ion conducting materials.

1 Partners and Funding

1.1 Laboratory of Polymer Chemistry, University of Helsinki, HUPol

The research group consists of the project coordinator, Professor Franciska Sundholm, and Professor Heikki Tenhu, Docent Sirkka Maunu, Docent Matti Elomaa (until May 2000), visiting senior scientist, Ph. D. Igor Neelov (part time), Lic. Phil. Satu Niemelä, graduates Jaana Ennari (Ph. D. March 2000), Sami Hietala (Ph. D. May 1999, until October 1999), Mikael Paronen (Ph. D. May 1999), Nadia Walsby, M. Sc. (Ph. D. Summer 2001), Tiina Launne Lic. Phil. (1997, until December 1999), Vladimir Aseyev (Ph. D. in August 2000). Four undergraduates have participated in the project over the years. Subcontractor group at Åbo Akademi University (1998-2000) lead by Professors Jan Näsman (until December 1999) and Carl-Eric Wilén.

1.2 Department of Physics, University of Helsinki, HUPhys

The research group consists of subproject leader, Docent Ritva Serimaa, and Docent Berit Mannfors, Doctor Veli Eteläniemi, Docent Sakari Vahvaselkä, Docent Eero

Rauhala, Ph. D. (1997) Milja Karjalainen, Ph. D. (2000) Mika Torkkeli, M. Sc., graduate student Kaija Jokela, M. Sc., graduate student, Johanna Blomqvist, M. Sc. graduate student, Virpi Korpelainen and undergraduate Teemu Ikonen.

1.3 Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, HUT

The research group consists of the subproject leader, Professor Göran Sundholm, and Docent Kyösti Kontturi, graduate student Tanja Kallio, M. Sc. (Lic. Tech. in 2001), Eeva Lankinen, D. Tech. (in 1999), Tero Lehtinen, D. Tech. (1999), Päivi Pentti, Lic. Tech. (1999), senior researcher (part time), Ph. D. Martin Bojinov, and undergraduate Matts Lundström.

1.4 Department of Polymer Technology, Åbo Akademi University, ÅA

The Department of Polymer Technology of the Åbo Akademi University got funding from the Academy of Finland only during the period ending in December 1997. The group then consisted of Professor Jan H. Näsman and graduate student Svante Holmberg (Lic. Tech. in 1996). Jan Näsman tragically died in September 2000. He left the Åbo Akademi University in the end of 1997. Svante Holmberg left the group in December 1996.

1.5 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
HUPolym	HU	420	570	570	570	**2 130**
	Academy	449	409	450	371	**1 679**
	NEFP*	173	177	317	39	**706**
	Ministry of Education**	152	409	480	506	**1547**
HUPhys	HU		114	360	386	**860**
	Academy		186	200	214	**600**
	Vilho, Yrjö ja Kalle Väisälä Foundation			40		**40**
HUT	HUT	100	85	85	90	**360**
	Academy	269	361	351	356	**1 337**
	Ministry of Education**	150	36	144		**330**
ÅA	Academy	258				**258**
Total		**1971**	**2347**	**2997**	**2532**	**9847**

* Nordic Energy Research Programme
** ESPOM graduate school

2 Research Work

2.1 Objectives and Work Plan

The main aims of this project were to prepare and characterise new conducting polymer membranes for applications as, on the one hand proton conducting membranes in electrochemical cells, ultimately in polymer electrolyte fuel cells, and on the other hand intrinsically conducting membranes in variable permeability membranes. The molecular and supramolecular structures of the new materials were to be analysed in great detail, and related to macroscopic properties such as order, crystallinity, mechanical and chemical stability, and electrochemical properties.

The work plan consists of several interactive subtasks, which are

- to prepare membranes by irradiation induced polymer grafting on various polymer films
- to functionalise the grafted membranes
- to prepare membranes by irradiation induced sulfonation of fluoropolymer films
- to study the structure of the membranes with spectroscopic, calorimetric and scattering methods to get information on ion transport, aggregation, mobility and order in the system
- to use molecular modelling to construct materials in which effects of free volume, chain dynamics and molecular association can be related to conduction mechanisms and mechanical properties
- to test and modify the PCFF force fields of polymers for molecular modelling
- to develop further the electrochemical characterisation methods used for measuring conductivity, transport numbers and electrode kinetic parameters related to proton conducting and variable permeability membranes, and to study the influence of humidity, water content of membranes and temperature on these parameters
- to study the suitability of proton conducting membranes for fuel cell use
- to electropolymerise functionalised thiophene monomers at electrodes and as free standing films at a liquid-liquid interface and to study the mechanism of electropolymerisation
- to study redox and transport processes of ions and solvent occurring during doping of an electronically conductive polymer film with the aim of exploring their applicability as variable permeability membranes
- to investigate the electropolymerisation of mesogenic thiophene monomers to give, hopefully, liquid crystalline, electronically conductive polymers.

2.2 Progress Report: Common Themes

Proton conducting polymer electrolyte membranes find use in a number of important fields, such as water purification and electrolysis, in the chlor-alkali industry, in sensors and in low temperature fuel cells. In this project new proton conducting polymer electrolyte membranes are developed primarily for fuel cell applications.

Proton conducting membranes have been prepared from several types of fluoropolymer films by electron beam radiation induced styrene grafting and subsequent functionalisation with sulfonic acid groups. In another approach proton conducting membranes have been prepared by radiation induced direct sulfonation of fluoropolymer films. In the first case electron beam irradiation was used, in the latter case also proton bombardment was used.

The structure and properties of the proton conducting membranes have been studied with thermal analysis, gas diffusion tests, thermochromatography-mass spectrometry, electron microscopy (SEM and TEM), atomic force microscopy (AFM), swelling tests, Raman spectroscopy with various techniques, liquid and solid state nuclear magnetic resonance (NMR) with various techniques, wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS), and by anomalous small angle scattering (ASAXS). Mechanical properties, ion exchange capacities, ion conductivities, the permeability to H_2 and O_2 by electrochemical methods (see Figure 1), and the kinetics of the O_2 reduction reaction (on platinum) have been determined [2-16, 19-21, 25, 26, 28-31, 36, 37, 43] and the membranes have been tested in fuel cells [35, 75]. Atomistic molecular modelling and statistical treatment of the results are included in the characterisation of the polymer electrolytes [1, 18, 22,-24, 27, 33, 34, 38, 43]. For this purpose adjustments of the forcefield parameters in the modelling software has been necessary [44 - 49].

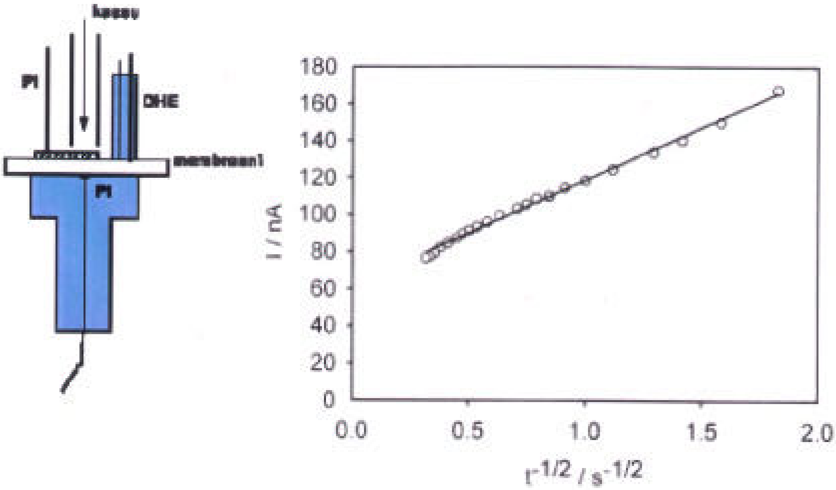

Figure 1. Schematic view of the microelectrode cell constructed [7] to measure the permeability of hydrogen and oxygen in a membrane with results of a chronoamperometric measurement on a PVDF-g-PSSA membrane in oxygen gas using the cell. The solubility and diffusion coefficient can be determined from the slope and intercept of the straight line.

It was found that even distribution of the grafts throughout the membrane is a prerequisite for efficient sulfonation and for effective incorporation of hydrated ion clusters, and thus good conductivity. A greater distribution of sizes of water clusters is found in our membranes than is generally assumed for *e. g.* Nafion®. The swelling (the water uptake) is slightly higher in our membranes than in Nafion®. Mechanical properties as well as proton and water transport properties improve as the crystallinity decreases.

The conductivity of the membrane depends strongly on the number of sulfonic acid groups, their distribution and the membrane water content. The crystallinity is clearly correlated with the conductivity [15, 26]. Water uptake and ion exchange capacity were also high for highly conducting membranes [6-8, 14, 31, 43, 71-79]. A tentative membrane structure is shown in Figure 2.

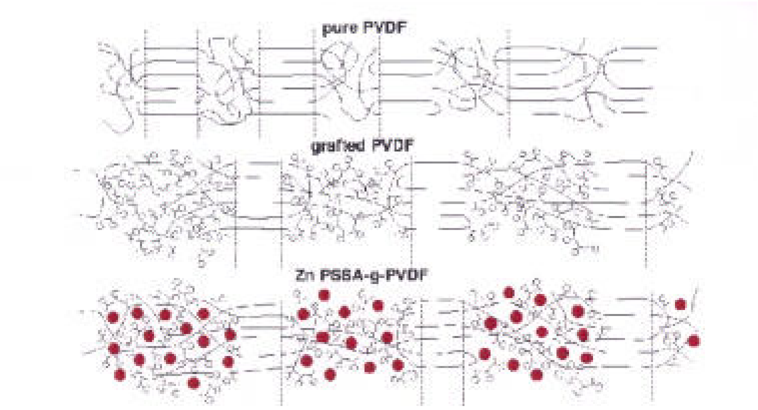

Figure 2. A schematic proposition for the membrane structure. Top: Pristine PVDF has alternating crystalline and amorphous layers. Middle: The film is grafted with styrene in the amorphous regions. Bottom: Cations penetrate the amorphous layers and form a weakly ordered system [31].

Several membranes have been tested in long term fuel cell runs in two laboratories, HUT and at the Norwegian University of Science and Technology in Norway [35]. We have found that our membranes are stable in the tests for periods up to 1000-1200 hrs, but that improvements have to be made in the preparation steps to achieve greater mechanical and chemical stability. In fuel cell runs so far we have used standard conditions defined for cells with Nafion® membranes, most probably adjustments of the running conditions can improve the membrane performance. We have found that incompatibility between membrane and electrodes causes great stress in the cell.

Thus the membranes produced in this work show promise for the development of cost-effective, highly conducting membranes for demanding uses. Further developments seem possible as the membrane composition may be further optimised by varying the synthesis conditions.

2.3 Progress Report: Laboratory of Polymer Chemistry, HUPol

1. Preparation and characterisation of proton conducting grafted and sulfonated poly(vinylidene fluoride) membranes, PVDF-g-PSSA membranes. PVDF-g-PSSA membranes were synthesised by pre-irradiation grafting of styrene into commercially available films of PVDF followed by sulfonation. This method overcomes the problem of processing the material into thin membranes. The conditions for the preparation have been studied in detail in order to optimise the synthesis. [8, 28, 36] The structure of and the phase separation and the crystallinity of the styrene grafted PVDF has been studied [20, 26]. The PVDF-g-PSSA membranes have been characterised by measuring their mechanical strength, ion exchange capacity [4, 16, 23, 31, 43], swelling and ion clustering [4, 6, 12, 15, 21, 23, 26, 29, 31, 43], phase separation [15, 20, 21, 23], ion conductivity [7, 16], thermal stability [9], crystallinity [3, 23, 31], morphology [19], surface structure [11, 19] and gas permeability [13].

It was found that the ion exchange capacities of the PVDF-g-PSSA membranes was of the same order of magnitude as available commercial membranes, their permeability to hydrogen is lower or equal to the reference materials. The PVDF-g-PSSA membranes are thermally stable in a strongly oxidising atmosphere to 220^0C, over which temperature they undergo multistep degradation by dehydration, desulfonation, degradation of the PSSA grafts, and finally, degradation of the matrix PVDF. The crystallinity of the PVDF decreases in the synthetic procedure. The grafting takes place in the amorphous regions of the PVDF, into which the polystyrene grafts form phase separated microdomains, from a few nm to 100 nm. The proton transport occurs through water clusters with a Bragg spacing of 2.5 nm. Water is included in the hydrophilic part of the structure in three different ways; water which is strongly bonded to the acidic sulfonate groups and evaporates only at temperatures exceeding 120^0C, water which is loosely associated with the sulfonate-water cluster and the polymer backbone, and free water. This is illustrated in Figure 3, from ref. [72].

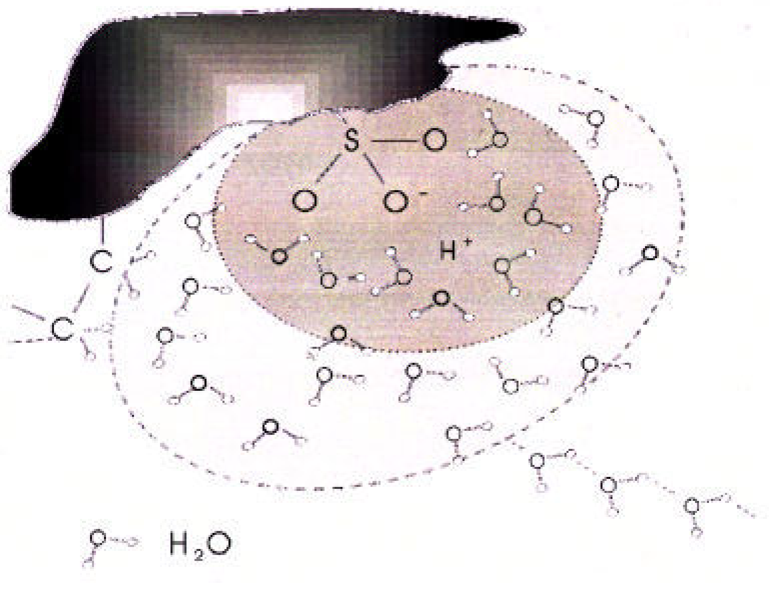

Figure 3. Different states of water in the PVDF-g-PSSA polymer belectrolyte membrane drawn schematically. Water in the dark grey area inside the dotted line (the primary hydration shell) are oriented due to the sulfonic acid group and can not crystallise on cooling. Water molecules inside the lighter grey area inside the dashed line are somewhat oriented due to the interaction with with the polymer backbone, the sulfonic acid group and the water molecules in the primary hydration shell, and therefore have properties different from liquid water. Water molecules outside the dashed line have structure and properties close to liquid water.

2. Grafted and sulfonated proton conducting membranes based on other fluoropolymers than PVDF. The investigation of the grafting and sulfonation reactions have shown that the reaction conditions used during the membrane preparation have a significant effect on the properties. With different fluoropolymers as matrix materials it is possible to get a vast variation in the properties of the polymer electrolyte membranes [30, 37, 77]. The kinetics of the grafting reaction vary according to the matrix material, cf. Figure 2, from ref. [77], but by changing the absorbed doses in the irradiation membranes with similar degrees of grafting and even polystyrene distribution can be prepared.

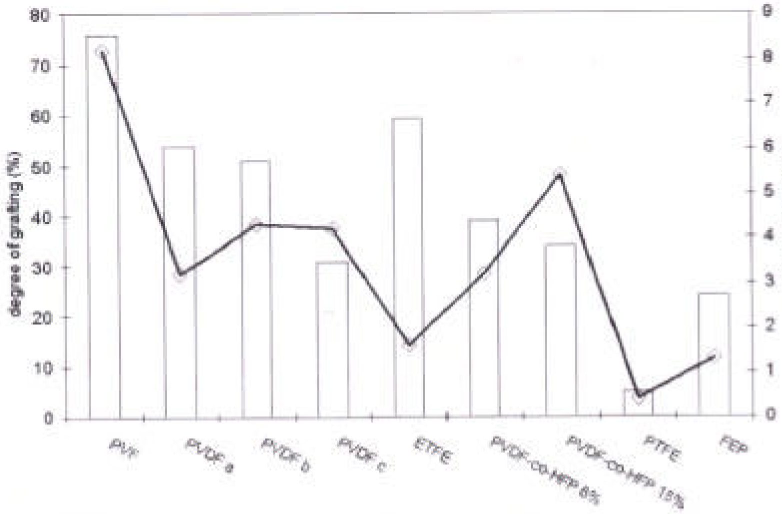

Figure 4. Degrees of grafting (columns) reached in various fluoropolymers after 2 hrs grafting in bulk styrene at 70^0C. Absorbed dose 10 kGy. Styrene uptake (line) of the initial films at 70^0C. PVDF a, b and c differ in thickness (a>b>c). PVF is poly(vinyl fluoride, ETFE is an alternating ethylene-tetrafluoroethylene copolymer, PTFE is teflon, FEP is a copolymer of tetrafluoroethylene and hexafluoropropene, and HEP is hexafluoropropene.

The same sulfonation conditions can be used for most of the styrene grafted fluoropolymers. Membranes based on different fluoropolymers differ most in their water uptake from liquid water, which varies with crystallinity. Calorimetric measurements show that higher water uptakes are accompanied by larger pores in the water swollen materials. The choice of matrix has an indirect effect on all the properties influenced by the water uptake; its role is one of restricting host to the PSSA grafts. The sulfonation of the grafted films with chlorosulfonic acid proceeds by a reaction front mechanism. High concentrations favour side reactions and lead to a loss of ion exchange capacity and conductivity, but also to an increase in the resistance to a hydrogen peroxide solution.

3. Preparation of proton conducting membranes by direct sulfonation. Direct sulfonation of the fluoropolymer films requires pre-treatmen. Electron irradiation produces a random distribution of reaction sites in the matrix which are not very efficient in the sulfonation reaction. Heavy charged particles like protons, on the other hand, form a mainly linear track with reactive structures through the polymer matrix. The reactive sites are radicals, the final concentration of which depends on the absorbed dose, storage temeprature and time. The irradiation increases the rate of sulfonation. The sulfonation takes place in these linear tracks thus producing sulfonated channels through the structure. With short sulfonation times the mechanical properties of the produced membranes remain good. As matrix materials in this part of the study we have used poly(vinyl fluoride) or ETFE (a copolymer of ethylene and tetrafluoroethylene). The membranes show ion conductivities similar to the ones measured for the grafted membranes, around 100 S cm^{-1}. The water uptake in these membranes is higher than in the grafted and sulfonated membranes [5, 12, 14]. The directly sulfonated membranes have been tested in fuel cell runs [35]. The most promising results were achieved with directly sulfonated ETFE mebranes, a test result is shown in Figure .

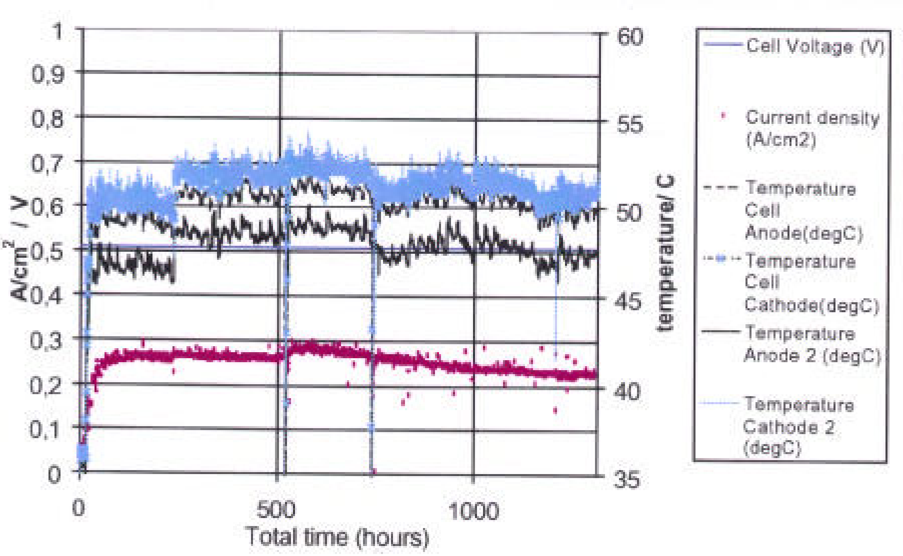

Figure 5. Fuel cell performance of a proton irradiated and sulfonated ETFE membrane. The electrodes were commercial Etek-Elat std electrodes with Pt loading 0.5 mg cm^{-2}. The electrodes were sprayed with a Nafion® solution. During the fuel cell test the potential was kept constant at 0.5 V [35].

4. Atomistic modelling of polyelectrolytes. Computational methods and atomistic modelling have been introduced to gain a better understanding of the molecular level processes governing the transport of water and charge in polymer electrolytes. The polymer modelling is highly dependent on the accuracy of the force field, which in many cases had to be adjusted [44 - 49]. In molecular dynamics simulations of polymer sulfonic acid anions in aqueous and in non-aqueous surroundings diffusion constants and conductivities corresponding to experimental results have been reached. At the same time it was possible to show that the hopping mechanism plays an important role in the transport. An important result of this work is the inclusion and treatment of charged particles in the polymer system, this has not been successful in previous attempts by other groups. The good correlation between the experimental and the simulated results shows that the model used may provide guidance in evaluating new proton conducting materials [1, 18, 22, 23, 24, 27, 33, 34, 38].

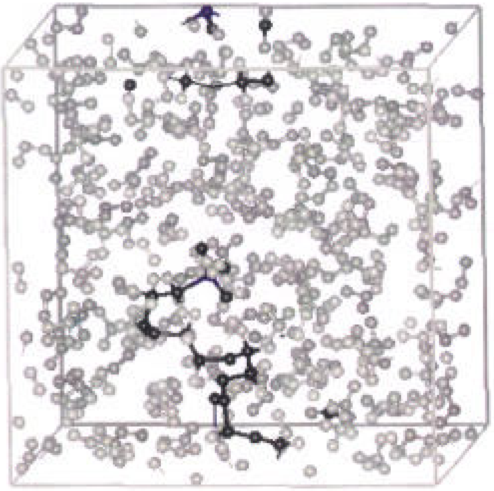

Figure 6. A snapshot from a molecular dynamics simulation of a 3D amorphous cell of the polymer electrolyte with boundary periodic conditions. The cell contains one PEO sulfonic acid dianion, one proton (a particle constructed in this work), one hydronium ion and 220 water molecules. The polymer backbone is drawn with a thick line.

2.4 Progress Report: Department of Physics, HUPhys

The work has been concentrated on the proton conducting membrane materials. Different matrix polymers were studied, all materials turned out to be lamellar semicrystalline polymers with a crystallinity in the range of 40 to 60 %. The PVDF-g-PSSA membranes have been of greatest interest within this project. The structure and properties of the membranes were analysed with scattering methods: wide angle scattering, WAXS, small angle scattering, SAXS, and anomalous small angle scattering, ASAXS. The ASAXS experiments were performed by synchrotron radiation at HASYLAB in Hamburg, Germany [31].

The complex structure of the membranes is understood on the basis of the WAXS, SAXS and ASAXS experiments. The matrix materials have a highly oriented semicrystalline lamellar structure. The sulfonated grafts are incorporated in theamorphous aprt of the semicrystalline polymer matrix. Grafting and sulfonation increase the lamellar period and slightly decrease the average size of the crystallites [15]. Interestingly, the preferred orientation of the lamellae decreases only slightly due to grafting and sulfonation [31]. In humid membranes ion aggregates are formed [31, 43].

The crystallinity of the grafted and sulfonated membrane is 20-30 %. The lamellar distnce is roughly 20 nm. The length of the crystalline lamella in the PVDF chain direction is about 6 nm and the width of the PVDF crystallites is 15 - 20 nm. The amorphous regions of a humid membrane contain ion aggregates whose average distance is 1.7 - 2.5 nm [15, 31, 23, 26, 30, 43].

Efficient analysis methods are presently developed within other projects for the determination of the absolute crystallinity of the membranes by WAXS, and the lamellar period frm the correlation function by SAXS , in which the intensity calculations of amorphous PVDF are based on molecular modelling.

The structure of the ion aggregates was studied and modelled. Changes in aggregate structure were followed as a function of temperature and humidity [26, 90].

A systematic study on the effect of the matrix material on the structure and properties of the fuel cell materials is in progress. The best conductivities are obtained for weakly crystalline materials, whose lamellar period increases considerably during sulfonation. This work is continued within other preojects (*e. g.* EMMA).

Another part of our work is concentrated on basic parameters for atomistic simulations of polymer systems. Force field parasmeters needed in PCFF for polymers have been optimised for esters [47-49, 91], and very recently for fluoropolymer repeat units within other projects (EMMA).

2.5 Progress Report: Laboratory of Physical Chemistry and Electrochemistry, HUT

The work of our laboratory has two main themes: 1) research on the electro- chemistry of conducting polymers based on thiophenes and pyrrole (as variable permeability or ion-gate membrane) and 2) the theme of electrochemical research on new proton conducting membranes mainly aimed at use in the polymer electrolyte fuel cell (PEFC). In addition we have developed electro- chemical and spectroscopic measurement methods for use in our work.

The research on variable permeability membranes, by which is meant membranes with controllable permeability to ions , started with a study of PVDF membranes irradiation grafted with acrylic acid. We showed that the permeability of such a cation exchange membrane could be controlled by changing the pH and ionic strength, temperature or dielectric constant. This work has continued with a the study of the electropolymerisation of polypyrrole with the aim of looking at its possible use as an ion-gate membrane for the controlled release of anionic drugs, since most drugs forming ions in solutions are in the form of anions. We started by studying the electropolymerisation conditions necessary to produce a poly- pyrrole film, which would be exchanging mainly anions with the solution [40]. We found that this required that the pH of the electrolyte solution should be neutral or acidic and the polymerisation potential should be above 900 mV (vs. SCE). As model anions for the drug release study itself we chose tosylate, salicylate, naproxen and nicoside, of which the three last mentioned have therapeutic effects.. Voltammetry in connection with an electrochemical quartz crystal microbalance, EQCM, was used to measure the weight changes of the polypyrrole film as a function of applied potential. It was found that the first three anions could, with suitable selection of experimental conditions, be released from the membrane in a controlled way and this could be achieved using simple electrochemical potential steps or staircase signals. Thus tailor made parts for iontophoretic devices can be manufactured. The releasable amount of drug, however, was small and therefore the applications will be limited to drugs with high therapeutic activity [41]. We thus were able to show that a polypyrrole membrane, which can be produced by polymerisation in aqueous solution works as an ion-gate membrane [83].

The research on conductive polymers has concerned five different poly- thiophenes: (poly(3-methyl thiophene), poly(thiophene-3-methanol), and three polythiophene acrylates synthetised in cooperation with our partner in this project, The Laboratory of Polymer Chemistry, HUPol [17]. These poly- thiophenes have been studied first using conventional electrochemical methods. The redox properties of the polymers in the presence of different anions in organic solvents has been elucidated. In addition to ordinary electrochemical methods we have used in particular *in situ* external reflexion IR spectroscopy to study the growth of the polymer film on electrodes. We have been able to show that the transport of IR-active anions (ClO and PF) can be followed using this spectroelectrochemical method. The same method was extended to the electropolymerisation of methyl thiophene in aqueous solutions, in which we could obtain IR spectra of much better resolution than has been presented in the literature so far [39]. The topography of these conductive polymer films has been studied using atomic force microscopy, AFM. It is known that several structures, connected with different stages of the deposition process can be observed on a platinum electrode and that they depend on the structure of the bare surface of the metal. This is demonstrated in the AFM images shown here.

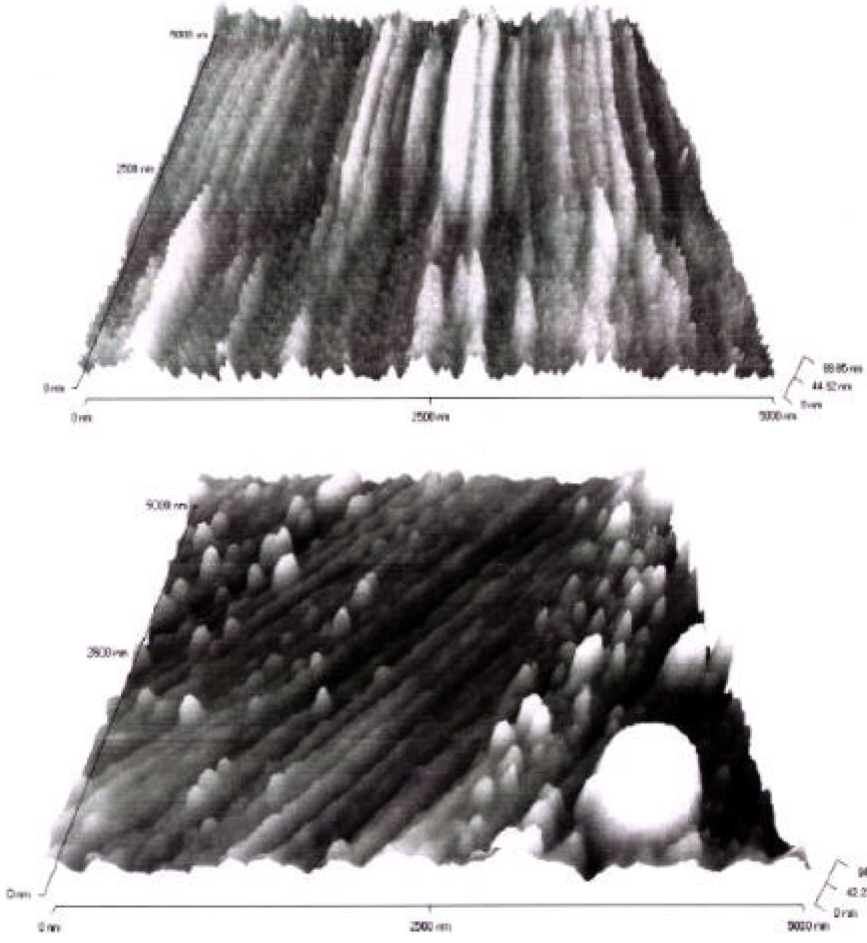

Figure 7. Top: AFM image of a bare platinum electrode surface. The parallel scratches are due to polishing with 0.05 µm Al_2O_3. Bottom: AFM image of a 20 nm thick poly((3-thienyl) methacrylate) film on the Pt electrode surface. Typically for polythiophenes the surface is partly covered with granules of various sizes.

In cooperation with VTT/Manufacturing technology we have extended the *in situ* contact electric resistance measurement method, CER, developed at VTT originally for the study of resistances or conductivities of anodic oxide films on metals, to the measurement of the film resistances during growth of conductive polymer films on electrodes [39]. This gives new information on the doping/ dedoping behaviour of these systems as we could measure the resistance of the films *in situ* .The conductivity values extracted were however rough estimates due to difficulties in determining the dimensions of the polymer film. It is worth noting that the conductivity behaviour of poly(3-thienyl methacrylate) was found to be one decade higher in aqueous than in nonaqueous solution and no over- oxidation was found for this polymer up to an anodic potential of 1.4 V (vs. SCE). In addition we found a conflict in the amount of charge carriers determined by IR spectroscopy and the conductivity of this polymer as a function of potential, which suggests that factors other than the amount and behaviour of (bi)polarons determine the conductivity in this material.

We have further shown that a combination of impedance measurements on the conductive polymer film in asymmetric, metal|film|solution, and symmetric, metal|film|metal, configuration (this latter measurement termed by VTT researchers the contact electric impedance method (CEI)) allows the determination of charge carrier concentrations as well as their diffusion coefficients in the film [42]. We report for the first time, to our knowledge, measurements on such electronically conducting polymers in the symmetric configuration. The homogenous film model proposed by Vorotyntsev was found to describe the impedance spectra for poly(3-methyl thiophene) in the asymmetrical configuration. The impedance spectra of the polythiophenes studied in the symmetrical configuration were found to be described by an extension of the homogenous film model for the metal|film|metal contact. On the basis of the calculated impedance parameters estimates of the diffusion coefficient and concentration of ionic and electronic charge carriers in the film as a function of potential were obtained. The information gained by the combination of impedance measurements in symmetric and asymmetric configuration parallel to the optical spectroscopic and dc resistance studies was found to give a comprehensive characterisation of a conducting polymer []. The same two techniques have been extensively used previously for the characterisation of anodic oxide films formed on Ni-Cr-Fe alloys, a project which has also been supported by the Academy of Finland (project n:o 44593).

2.6 Progress report: Progress by the Åbo Akademi University group, ÅA

It has not been possible to extract the results of the work done at Åbo Akademi University separately, for the tragic reason stated above. However, as can be seen from the list of published papers, this part of the project has been of great importance for the advancement of the preparation of the proton conducting membranes. The electron beam irradiation has been done at the Åbo Akademi University throughout the project, in practice Nadia Walsby from the Laboratory of Polymer Chemistry has spent a number of periods in Åbo doing the irradiation and grafting work. The supervision has been handled by Professors Bengt Stenlund and Carl-Eric Wilén, and D. Tech. Kenneth Ekman, SmopTech Ltd.

In the course of the present project we also developed several new ideas with the Åbo group of ion conducting membrane synthesis which are now in progress within other collaborative projects outside the MATRA funding.

3 International Aspects

The work of the group within this project has been made internationally visible in several ways. All our papers have been published in the leading international journals in the field, and thus have reached exactly the intended audience. *Macromolecules, J. Polym. Sci., Polymer, J. Mater. Chem. and Electrochim. Acta* have impact factors 1.5-3.5 which is high in the field of chemistry.

Visiting Scientists

One day meetings have been arranged in Helsinki, to which well known specialists from abroad have been invited to give talks, participate in Seminars and Discussion Meetings.

Professor Frans Maurer, previously at Chalmers University of Technology, presently at the Polymer Centre, Lund Technical University, Lund University, Lund, Sweden, is an expert on free volume studies in polymers, and visited the Laboratory in February1997, and was the external examiner of the Doctoral Thesis by Ritva Dammert in the Spring of 1997.

Dr. Günter Scherer from the Paul Scherrer Instititute, Zürich, Switzerland visited us in March 1997, he was later (May 1999) acting as external examiner to the Doctoral Thesis by Mikael Paronen.

Dr. Eivind Skou, Odense University, Denmark, highly involved in this project, visited the Laboratory of Polymer Chemistry in May 1999. Sami Hietala did part of the work for his Doctoral Thesis in the laboratory of Eivind Skou 1997-1998. Thus Eivind Skou partly supervised this work, and common papers resulted [9, 13]. Acting professor Per Jacobsson, Chalmers University of Technology, Göteborg, Sweden, was the external examiner of the Doctoral Thesis by Sami Hietala (May 1999).

Dr. Eivind Skou, University of Odense will be the external examiner of the Doctoral Thesis by Nadia Walsby in August 2001 [].

Dr. Igor Neelov, senior scientist from the Institute of Macromolecular Compounds of the Academy of Sciences in St. Petersburg, Russia, has been working in the Laboratory of Polymer Science full time in 1997-1999, and in 2000 in several periods for 5 months.

Professor Anatoly Darinskii from the same institute has visited our laboratory twice per year for two weeks. Each Autumn term Professor Darinskii has given a 24 h lecture course on polymer theory and statistical mechanics.

Research and Teaching Abroad

Mikael Paronen has spent a 4 month period (Autumn 2000) as post-doc at the Max Planck Institute for Polymer Research in Mainz, Germany, working on methods of preparation of ion conducting materials. Mikael Paronen has spent several shorter periods (1-2 weeks) in the Laboratory of Physical Chemistry of the Norwegian University of Science and Technology in Trondheim, Norway, working with fuel cell tests on membranes prepared in Helsinki.

Göran Sundholm is working as part time visiting professor at the Laboratory of Applied Electrochemistry at the Royal Institute of Technology, KTH, Stockholm, Sweden since the Autumn 1998.

The ASAXS measurements using synchrotron radiation were performed at HASYLAB, Hamburg, Germany in collaboration with Dr. G. Goerigk.

International collaboration

The project group is very strongly involved in a long term (since 1991) Nordic cooperation in the field of proton conducting polymer membranes funded by the Nordic Energy Research Programme (Nordisk Energiforskningsprogram, NEFP), which has been coordinated from the Laboratory of Polymer Chemistry.

The laboratories involved are the following: (common papers in brackets)

* The Laboratory of Material Physics, Chalmers University of Technology, Göteborg, Sweden, head until Autumn 1998 Professor Lena Torell, From the Autumn 1998 Acting Professor Per Jacobsson, senior reasearcher Denis Ostrovskii, Ph. D., Britta Mattsson, Ph. D., until December 1999, graduate student Hanna Ericson, [2, 4, 6, 10, 11, 12, 19, 25]
* The Laboratory of Applied Electrochemistry, Royal Institute of Technology (KTH), Stockholm, Sweden, head Acting Professor Göran Lindbergh, Professor Göran Sundholm (from this Consortium, part time since the Autumn 1998), graduate students Jari Ihonen and Peter Gode, [7]
* The Laboratory of Physical Chemistry, Norwegian University of Science and Technology, Trondheim, Norway, head Professor Signe Kjelstrup, Ph. D. Preben Vie, graduate student Monica Strømgård, [35]
* The Department of Chemistry, Odense University, Odense, Denmark, head of group Dr. Eivind Skou, [9, 13].

The project group is strongly involved in a programme called SUPERNET (1999-2003), funded by the European Science Foundation, Strasbourg, France. Franciska Sundholm is the SUPERNET coordinator and chairperson of the Steering Committee.

The laboratories involved are the following, for common papers the reader is refered to the half term report of the project [92]:

* Department of Physics and Astronomy, University of Leeds, IRC in Polymer Science and Technology, U. K., Dr. David Adolf,
* Physical Department, Deutsches Kunststoff-Institut, Darmstadt, Germany, Dr. Ingo Alig,
* Chemistry Department, UMIST, Manchester, U. K., Professor Julian Clarke,
* Centre for Experimental Mechanics, University of Ljubljana, Ljubljana, Slovenia, Professor Igor Emri,
* Department of Polymer Technology, Royal Institute of Technology, KTH, Stockholm, Sweden, Professor Ulf Gedde,
* Department of Organic Chemistry, University of Gent, Gent, Belgium, Professor Eric Goethals,
* Centre for Education and Research on Macromolecules, Université de Liège, Liège, Belgium, Dr. Jean-François Gohy,
* Danish Polymer Centre, Technical University of Denmark, Lyngby, Denmark, Professor Søren Hvilsted,
* Laboratoire de Recherche sur les Polymères, CNRS, Thais, France, Professor Françoise Lauprêtre,
* Condensed Matter Group, Johannes-Gutenberg-Universität, Mainz, Germany, Professor Kurt Binder.

An INTAS project, INTAS 99-01114 Dynamics of Novel Polymer Systems of Complex Topology Composed of Strongly Anisotropic Monomers. Theory and Computer Simulation (2000-2002) is coordinated by Franciska Sundholm.

The Laboratories involved are the following, for common papers the reader is refered to the first annual report [93]:

* Condensed Matter Group, Johannes-Gutenberg-Universität, Mainz, Germany, Professor Kurt Binder.
* H. H. Wills Laboratory of Physical Chemistry, University of Bristol, Bristol, U. K., Professor Mike Allen,
* Institute of Macromolecular Comopounds, Russian Academy opf Sciences, St. Petersburg, Russia, Professor Anatoly Darinskii,
* Institute of Mathematical Problems in Biology, Russian Academy of Sciences, Pushchino, Russia, Dr. Nikolai Balabaev.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
HUPol	Ref. journal art.	6	5	12	15	**39**	1-6, 7-11, 12-23, 24-31, 33-38, 43
	Ref. conf. papers	4	4	6	5	**19**	
	Monographs						
	Doctoral dissert.	1		2	1	**4**	
	Licentiate degrees						
	Master degrees	2		1	1	**4**	
HUPhys	Ref. journal art.	1	1	6	7	**15**	4, 14, 15, 23, 26, 30, 31, 43 - 49
	Ref. conf. papers						23, 26, 30
	Monographs						
	Doctoral dissert.			1	1	**2**	78, 79
	Licentiate degrees				1	**1**	84
	Master degrees		1		1	**2**	90, 91
HUT	Ref. journal art.	1	5	7	3	**16**	5, 7, 11, 14, 15, 16, 17, 21, 23, 30, 32, 37, 39-43
	Ref. conf. papers		2	4	3	**9**	
	Doctoral dissert.			2		**2**	
	Licentiate degrees	3	1			**4**	
	Masters degrees				1	**1**	
ÅA	Ref. journal art.	2	2	1		**5**	3, 4, 8, 11, 15

5 Other Activities

A joint two days meeting was arranged by Franciska Sundholm in Stockholm in February 1999 at the Royal Institute of Technology for participants from KTH, Chalmers, Odense University and the Norwegian University for Science and Technology. At the meeting around 15 short oral communications were presented by the young researchers in the groups, and further future plans for common research were made up.

The participants in the MATRA project have been efficiently participating in international and national meetings, which is manifested in the high rate of invited lectures and oral presentations at international conferences [50-70], as well as poster presentations [95-113], and presentations at national meetings [114-124]. Regular discussion meetings at least twice a year for all the participants have been arranged.

The attention is drawn to a video presentation, in English and in Finnish, done at the Laboratory of Polymer Chemistry, University of Helsinki, in collaboration with experts from the CSC Ltd (Centre of Scientific Computation, Espoo, Finland) which describes the atomistic modelling of polyelectrolyte systems [68]. The duration of the video presentation is around 20 min for each version, and is intended for students in their final years, graduates and researchers in the field. The video has been shown on several occasions at the Chemistry Department of the University of Helsinki and elsewhere.

The work on polymer electrolytes for low temperature fuel cells has been presented in full by Franciska Sundholm and Mikael Paronen at the Autumn meeting of the Swedish Academy of Engineering Sciences in Finland in December 1999. Mikael Paronen was awarded the first post-doc grant for work abroad, 100 000,- FIM, from the Academy. By this it was possible for Mikael Paronen to get acquainted with the work on fuel cell membranes in several laboratories in Germany, and the grant also made his stay at the Max-Planck-Institut in Mainz possible.

6 Publications

6.1 Refereed Journal Articles

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6.2 Refereed Conference Papers

International meetings, oral presentations

[50] *M. Paronen*, J. Juhanoja, F. Sundholm, Structural Investigation of Irradiated and Sulfonated Poly(Vinyl Fluoride), oral presentation at the Nordic Workshop on Experimental and Theoretical Methods in Fuel Cell Research, March 5-7 1997, Geilo, Norway.

[51] *F. Sundholm,* New Polyelectrolytes for Low Temperature Fuel Cells, invited lecture at the first Olle Lindström symposium, Stockholm, Sweden 1997.

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[58] I. Betova, M. Bojinov, E. Lankinen, *G. Sundholm*, Studies on the Conductivity Behaviour of some Polythiophene Derivatives in Symmetric and Asymmetric Configuration by Impedance Spectroscopy, oral presentation, 50th Annual meeting, International Society of Electrochemistry, Pavia, Italy, 1999.

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[117] *J. Ennari*, M. Elomaa, F. Sundholm), Modelling the structure and conductivity of polyelectrolytes containing PEO sulfonic acids, poster presentation at the jubilee seminar of the 40th Anniversary of the Society for Wood and Polymer Chemistry in Finland, Helsinki 1999, proceedings Polymers in the 21st Century, p. P8.

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[123] *F. Sundholm,* Nya polymermembran för bränsleceller i fordon med nollemission, invited presentation at the meeting of the Swedish Academy of Engineering Sciences in Finland, Helsinki 1999.

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PROPERTIES OF FIBROUS COMPOUNDS AND DISORDERED MATERIALS

Jussi Timonen[1], Mikko Alava[2], Risto Nieminen[2], Kimmo Kaski[3] and Tapio Ala-Nissilä[2,4]

Abstract

The main objective of the project was to bring together, from a statistical physics point of view, microscopic and macroscopic aspects of the structural and transport properties of disordered materials. Emphasis was on disordered fibrous structures such as paper, but many other disordered systems were also considered. The two main common themes of the consortium were the elasticity and fracture of disordered (fibrous) structures, and the dynamics of interfaces in disordered (fibrous) materials. On the first theme the main results include the formation of stiffness in these structures, the optimization of fracture paths, roughening of fracture surfaces, universal features in fragmentation and the properties of shear bands in granular packings. On the second theme the main results include the demonstration of Kardar-Parisi-Zhang scaling of slow combustion fronts in paper, the role of noise in their short scale behaviour, and the role of conservation laws in the behaviour of imbibition fronts. Applications were also successfully made to paper science and to the paper making processes in collaboration with industry, as evidenced by the many Master's theses completed during the project.

1 Partners and Funding

1.1 Department of Physics, University of Jyväskylä (JYFL)

The research group consists of subproject leader Professor J. Timonen, Professor M. Kataja, senior researchers Dr. J. Merikoski, Dr. J. Åström Dr. H. Häkkinen and Dr. A. Koponen, postgraduate students J. Hämäläinen, A. Jäsberg, P. Kekko, M. Kellomäki, M. Laajalahti, M. Latva-Kokko, J. Maunuksela, M. Myllys, J. Mäkinen, P. Raiskinmäki, M. Rasi, A. Shakib-Manesh and E. Viitala, and 18 students who finished their Master's Thesis during this project.

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1.2 Laboratory of Physics, Helsinki University of Technology (HUT/PHYS)

The research group consists of subproject leader Doc. M. Alava, Professor R.M. Nieminen, postgraduate students E. Hellen, V. Petäjä, L. Salminen and E. Seppälä, and students J. Rosti, P. Salmi and G. Szabo.

1.3 Laboratory of Computational Engineering, Helsinki University of Technology (HUT/CE)

The research group consists of subproject leader Professor K. Kaski, senior researcher Dr. P. Heino, postgraduate students M. Korteoja and A. Lukkarinen, and students M. Mäki-Jaskari, L. Nurminen, T. Peussa and P. Szelestey.

1.4 Helsinki Institute of Physics, University of Helsinki and Helsinki University of Technology (HIP)

The research group consists of subproject leader Professor T. Ala-Nissilä, senior researchers Dr. M. Dube, Dr. N. Provatas and Dr. M. Rost, postgraduate students M. Haataja, J. Heinonen, M. Kuittu, J. Lahtinen, R. Linna and S. Majaniemi, and students J. Asikainen and J. Vinnurva.

1.5 Funding

Table 1. Funding of the project in 1000 FIM in 1998-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1998	1999	2000	**Total**
JYFL	JYU	800	800	800	**2400**
	Academy	475	500	525	**1500**
	Tekes/VTT	700	800	700	**2200**
	Industry	600	600	500	**1700**
HUT/PHYS	HUT/PHYS	100	100	100	**300**
	Academy	320	330	330	**980**
	Tekes	300	300	300	**900**
HUT/CE	HUT/CE	140	170	170	**480**
	Academy	138	166	166	**470**
HIP	HIP	300	300	300	**900**
	HUT	150	150	150	**450**
	Academy	430	430	445	**1305**
Total		**4453**	**4646**	**4486**	**13585**

2 Research Work

2.1 Objectives and Work plan

The main objective of the project was to bring together microscopic, mesoscopic and macroscopic aspects of structual and transport properties of disordered elastic networks, both theoretically and experimentally. Emphasis was planned to be on the dynamic properties in particular.

Collaboration between the four groups of the consortium are important in several research topics, and are linked to the following areas of main expertise of these groups. Group at JYFL will pursue hydrodynamic and interface experiments, lattice-Boltzmann and fibre suspension hydrodynamics, and dynamical behaviour (fracture and fragmentation) of disordered networks of elastic beams and other similar systems.

Group at HUT/PHYS will pursue research on elastic, structual and quasi-static properties of random fibre networks, real paper and other related materials.

Group at HUT/CE will pursue research on viscoelastic and plastic behaviour of disordered lattices, real paper and complex fluids.

Group at HIP will concentrate on the theory of interface dynamics, deposition models and sedimentation.

Contacts of the consortium with industrial partners and the KCL Paper Science Centre will provide links to more application oriented research related to paper-like materials. New insight is projected to be achieved in the following topics.

Microscopic description of crack fracture and propagation: pinning effects, role of plastic deformations, branching properties, formation of crack patterns, viscoelastic effects and three dimensional behaviour.

Elastic behaviour and strength of disordered fibre networks and other similar structures: a proper effective medium theory, effects of ductility, and the nature of rigidity transition.

Fragmentation of brittle materials: mechanics and fragment size distribution under different impact conditions in three dimensions.

Detailed description of the dynamics of interfaces propagating in paper: slow combustion fronts and wetting front, kinetic roughening.

Microscopic description of flow in realistic three dimensional fibrous networks, in real paper sheets and in other porous materials: theoretical models, numerical simulations and experiments on paper samples, connection of porosity with macroscopic permeability, diffusive motion of tracers and mixtures of fluids.

Behaviour of suspension flows: fibre clustering in sedimentation and clustering and segregation in multicomponent suspensions under shear flow, application to paper coating, a detailed description of the formation of a lubrication layer in channel flows of dense fibre suspension, a general understanding of hydrodynamic interactions in fibre suspensions, and understanding of pressure loss in closed channel flows.

The projected results will improve our theoretical and experimental understanding of the basic structural and transport processes in fibrous materials. New achievements will also be the projected results for interconnections of microscopic and macroscopic features. Eventually these results will make an impact on application oriented research on paper and other similar materials. Notice however that these results will have important implications also for materials other than paper-like composites.

2.2 Progress Report: Common Themes

The two main common themes of the consortium were the dynamics of interfaces and fracture of disordered materials.

The work on interfaces was divided into slow combustion fronts in paper and the related theoretical efforts (JYFL, HUT/PHYS, HIP), and imbibition fronts in porous materials (HIP, HUT/PHYS). Extensive experimental work on slow combustion fronts was carried out at JYFL, and collaboration was crucial for good theoretical understanding of the problem and for the analysis of the experimental data. The main outcome of this work was the best experimental demonstration so far of the Kardar-Parisi-Zhang scaling of propagating interfaces. For slow combustion fronts this was realised for long time and length scales. For short scales the behaviour of fronts was dominated by the nature of noise, which in this case included both quenched and dynamic effects. Another main conclusion was thus the realisation that the observed crossover between short-scale and long-scale behaviour should be generic for all propagating interfaces. The work on the imbibition fronts produced as its main result the observation of the importance of conservation laws in the interface dynamics. Conservation laws introduce slowing down of the propagating interface, which must be taken into account when analysing its properties, and they thus also introduce a new length scale which controls many of the scaling properties of the interface.

The work on fracture of disordered materials was divided into several subtopics, and included many collaborative actions within the consortium. The quasistatic limit of crack propagation in a model disordered medium [11, 12, 47, 62] was considered by the group at HUT/PHYS, while the dynamical fracture [3, 27, 32, 34, 38, 59, 67] was considered by the group at JYFL, done alone as well as in collaboration with the group at HUT/PHYS. The main results from these studies include optimization of fracture path in quasistatic fracture, and roughening of the fracture surface, universality in the fragmentation process, and connections with catastrophic phenomena such as earth quakes in the case of dynamical fracture. Extension of this work to fracture of real paper was made in collaboration by the groups at HUT/PHYS and HUT/CE [9, 10], and between HUT/PHYS and JYFL [44], including the recent work on the acoustic emission during the fracture process [92, 115]. Ductile fracture was considered in the case of copper as a collaboration by the groups at HUT/CE and JYFL [17, 18, 28, 50].

In addition to these two main themes in the collaboration, a number of other common actions were undertaken by the groups, including e.g. the permeability of random fibre networks [1], which was later extended to the permeability of paper [81], and fibre deposition models [19, 54].

2.3 Progress Report: Progress by the Department of Physics, University of Jyväskylä

Elasticity and fracture of disordered materials. Various mechanical properties of materials that can be described as random networks of fibres were analysed in detail. A new effective medium theory for the elastic properties of these materials was developed, supported by simulation results for deposition modes of random (2D and 3D) fibre networks [35, 42, 124]. We also analysed low rigidity is formed in this kind of (2D) structures [60, 95, 100], and low elastic waves propagate in them [2, 95]. Fracture of random networks of elastic beams was analysed from different points of view including the properties of crack surfaces and roughening of planar crack fronts [3, 27, 38], and even an avalanche type of fracture [67]. Also the fragmentation caused by a rapid impulse of these and some other systems was shown to display universal features in analog with continuous phase transitions [34]. Recently these considerations were generalised to woven structures of fibres, this stage to their ground state geometrical structure in particular [68, 89]. An obvious application of the problem is to the design of fabrics used in the paper machines.

An extension of the work described above on the fracture of fibre networks, which was limited to brittle fracture, ductile fracture was considered on an atomistic level. As a first attempt in this direction, the behaviour of transition metals such as copper and nickel was considered because of their relative simplicity [17, 18, 37, 41, 103].

The work described above included collaboration with the groups in the Laboratory of Physics and in the Laboratory of Computational Engineering at Helsinki University of Technology.

Granular packings. As an extension of our work on random networks of elastic beams we also considered the formation and properties of the so-called shear bands in granular packings. From a methodological point of view these two problems are quite similar, and shear bands are also related to phenomena that appear in shear flows of pigment and fibre suspensions (see below). Apart from these interconnections, we also discovered that the dynamics of these shear bands very closely resemble those of tectonic fault zones [32, 59]. This work was carried out as an international collaboration with Professor Hans Herrmann (Stuttgart and Paris).

Kinetic roughening of slow combustion fronts in paper. The Jyväskylä part in this intraconsortium effort was to do the experimental work, and to collaborate with the other partners of the consortium on the theoretical aspects. The related work on the analogous imbibition processes was carried out collaboratively by the other partners of the consortium. The main achievement here was to show how slow combustion fronts in paper indeed display at long time and length scales the Kardar-Parisi-Zhang scaling with white noise [6, 25]. This appears to be the up to now best experimental verification of this universality class in kinetic roughening of interfaces. The other important achievement was to show in detail the role of short range correlations induced by both quenched and dynamical noise in the apparent scaling properties of slow combustion fronts at short time and length scales [33, 69]. The crossover from this short scale behaviour to that of KPZ with white noise appears to be a generic feature of rough interfaces. Theoretical considerations are so far reported only in two theses [105, 113].

Diffusivity and permeability of porous media. For measuring the diffusive and also the advective transport in porous media we have developed equipment based on the use of helium gas. With these equipment we analysed the porosity, diffusivity and permeability of mainly rock samples [8, 84, 85, 98, 126]. The main results of these studies include the structure dependent anisotropy in the transport properties, and the properties of disturbed zones near excavated surfaces. Experiments were also done with another equipment of own design on the permeability of paper samples under compression [81]. In this work the dependence of paper permeability on porosity, specific surface area and some furnish dependent factors was clarified.

Along with the measurements, numerical methods for simulating fluid flow in porous media based on the lattice-Boltzmann approach were developed [1, 5, 26, 94, 127]. With these methods we could determine e.g. how the permeability of generic porous media depends on their porosity [7, 94], and hoe these results should be extended to fibrous materials such as paper [1, 81, 94] and wood fibres [70]. The methods developed were also extended to the case of multiphase flows, and we could then analyse phenomena such as droplet spreading and absorption on a random porous substrate [36, 129]. This kind of problem appears for example in ink jet printing. Other multiphase problems that were considered include the rheological properties of pigment suspensions [39, 112], the boundary layer phenomena in pipe flow of fibre suspensions, which are responsible for a peculiar flow velocity dependence of pressure loss [40], and flocculation of fibres in these flows [82, 83, 109, 110, 120, 122].

This work included collaboration with the group in the Laboratory of Physics at HUT, international research groups (Amsterdam), and industry (including the research institutes KCL and VTT Energy).

Applications in paper technology. In addition to the applications already considered above, various problems of technological importance were considered in collaboration with industry. These problems include the strength of paper and glass fibre felts [111, 113, 119, 121, 123, 128], stress relaxation in paper [99, 117], curling [107] and formation [108] of paper, and water removal in impulse drying of paper [118].

2.4 Progress Report: Progress by the Laboratory of Physics, Helsinki University of Technology

The work can be divided into six main areas of emphasis as follows: statistical mechanics of fracture, disordered systems and combinatorial optimization, non-equilibrium phase transitions and self-organized criticality, paper physics, aggregation models and kinetic roughening.

These topics are discussed one-by-one in the following.

Fracture. We have concentrated both on dynamic and 'static' fracture. The main point is the role of disorder (quenched defects) in crack development. This has been addressed by fuse network simulations and by comparisons with scalar plasticity. Also, dynamical fracture has been studied in collaboration with the Jyväskylä group. This research has obvious connections to the other subtopics (optimization, paper physics, kinetic roughening). Publications [3], [9] - [12], [38], [47], [62] and [92]. The *main findings* concern optimization in slow fracture [11] and acoustic emission in 2D fracture experiments [92], [115].

Disordered systems and combinatorial optimization. In this field our work is of cutting-edge type when it comes to the application of computer science to disordered systems: groundstate solutions can be found efficiently and they are often of crucial relevance for the physics. Two invited talks at APS March meetings (1999, 2001), and a review in the series 'Phase Transitions and Critical Phenomena' (Academic Press, 2000) [93] are the main signs for the visibility of the research. Active collaborations are still continuing with Heiko Rieger (Saarbrücken), Cristian Moukarzel (Merida), and Phil Duxbury (Michigan State) and others are in the starting phase. The *main results* concern the energy landscapes of domain walls in random magnets ([46, 74]) and the physics of droplets in random field systems [73]. During the period, Finland joined the European Science Foundation Sphinx network on the statistical physics of glassy systems. Alava is the national coordinator of the network, which will run until 2004.

Non-equilibrium phase transitions and self-organized criticality. With Kent Lauritsen (formerly NBI/Copenhagen) we have discovered a way to map sandpiles models of SOC to driven interface depinning. This work was credited among others with an invited talk at the ICTP 2000 workshop on SOC, the most important conference in the field in the last few years. Various collaborations have started from this idea as evidenced by various publications [76]. *The main results* concern the nature of the possible universality classes in SOC ([63]) and the connection between interface depinning and absorbing state phase transitions.

Paper physics. The two main topics are the geometric structure of paper and the ensuing physical properties on one hand, and the behaviour of fiber networks on the other hand. This work has been done in collaboration with scientists from KCL, Jyväskylä and Lund University. The *main discovery* has been the fact that the PAKKA structure model of paper [130] yiels credible estimates for gas diffusion in fiber networks. Also, earlier joint work showed that creeping flow permeability, using the lattice Boltzmann method, is qualitatively at least well in agreement with experimental data [75].

Aggregation models. The studies of paper-like models have continued as a separate sub-topic. In particular cluster-cluster aggregation is under intensive study. ([19, 43, 49, 54]) *The main progress* concerns the scaling of cluster survival in diffusion limited cluster aggregation, a variant of 'persistence' (see also [49]).

Kinetic roughening. This topic was pursued in various collaborations involving often most other partners in the consortium. The two main projects concerned spontaneous imbibition and fronts in slow combustion of paper ([6, 25, 30, 33, 53, 55, 66, 69]). *Important results* were achieved in studying combustion fronts as a one-dimensional example of Kardar-Parisi-Zhang roughening ([33]) and in illuminating the role of a conservation law in a roughening process ([30, 53, 66]).

2.5 Progress Report: Progress by the Laboratory of Computational Engineering, Helsinki University of Technology

Electro- and Magnetorheological Fluids. Electrorheological (ER) fluids are suspensions consisting of base fluid and fine particles of size of the order of 0.1-100 µm. External electric field generates forces between suspension particles and, if these forces are strong enough, initially randomly placed particles form structures effectively modifying the properties of the suspension. ER fluids are not the only fluids being sensitive to the external field but there are also magnetic analogues called magneto-rheological (MR) fluids. The field induced structure formation modifies the effective physical properties of the fluid that are sensitive to the micro-structure of the suspension particles. These effective changes in the physical properties manifest themselves most clearly in the field generated increase in the viscosity of the suspension.

The properties of ER/MR fluids were studied numerically using a dynamic molecular dynamics like model. To summarize the results, point dipole model studies showed the mechanical properties of chains, grown, and organized lattice like structures to depend strongly on the direction of deformation of the system. It was seen that the systems were able to transmit clearly larger forces under compressive loading compared to the case of shear loading. Considering the periodically loaded systems it seems that under periodic compression elongation loading ER/MR systems are more sensitive to the oscillation frequency compared to the case of shear loading. In addition to the dynamic dipole model studies, the more accurate finite element method (FEM) was used to study the free energies of different lattice symmetries formed by suspension particles. The results of the FEM studies were in a very good agreement with the reference studies and showed that in all the studied cases the BCT symmetry should prevail in ER/MR systems. However, unlike in the reference studies, we studied also properties of systems consisting of two kinds of particles. The parameters of these particles were chosen such that the interaction between different kinds of particles could be described with a “reversed“ dipolar approximation. These studies suggested the minimum energy configuration to consist of phase separated particle columns each of which consisting of only one type of particles. However, such a phase separation was not seen in the dipole model studies. A plausible explanation for this is the surface energy that could not be included in FEM studies but that was, at the dipolar level, naturally included in the dynamic dipole model studies.

Paper physics. We also continued our studies in the statistical properties of paper strength [9,10] which included experimental work and numerical computer simulations. The studies showed the double-logarithmic probability distribution function to give results that were in good agreement with the experiments.

Ductile fracture in copper. We applied the recently introduced (JYFL) molecular dynamics model of copper, which included many-body effects in the interatomic potential, to the ductile fracture of this transition metal. Interesting results related to a kind of shear band formation were obtained [17, 18].

2.6 Progress Report: Progress by the Helsinki Institute of Physics

Dynamical processes in complex and structurally disordered systems. We have continued our work on the properties of disordered fibre networks and on the dynamics of fronts in such systems. In a more general setting, we study the dynamics of interfaces in complex, nonlinear systems using both continuum phase-field and discrete lattice models. We have carried out additional studies of a 2D deposition model where there is an effective repulsive interaction between the deposited particles (needles, fibers, and disks). One motivation for this work comes from trying to understand some of the unusual structural properties of paper sheets.

We have also carried out extensive studies of various deposition models of fibers. We have studied in detail percolation properties and spatial correlations within a number of simple models of 2D continuum deposition of fibers on a plane by computer simulations and analytic calculations. Another deposition model that we have studied describes the growth of flexible fibers in 3D. The important parameters in the model are the fiber length and flexibility. We have concentrated on the kinetic roughening exhibited by the model in the limit where the thickness of the deposit becomes large. By numerical simulations we have shown that the kinetic roughening is described by the Kardar-Parisi-Zhang (KPZ) equation.

A project closely related to the fibre deposition models concerns the diffusive dynamics of polymers, colloids and rodlike molecules on surfaces. We have continued the study of the dynamics and diffusion of colloidal particles (hard circles), rigid rods and grafted chains on smooth surfaces. Unlike in the case of flexible chains, for 2D hard circles and rods the collective diffusion coefficient is wholly determined by the thermodynamic factor which becomes very large upon approach to freezing. The tracer diffusion coefficient shows significant memory effects at larger densities and decays rapidly as a function of density.

We have previously derived a continuum phase field model to describe the dynamics and kinetic roughening of slow combustion fronts in disordered media. One of the main results of this study was to show that the kinetic roughening in this case follows the Kardar-Parisi-Zhang (KPZ) equation. We have extended this work to the case of circular geometry. We have also carried out extensive studies of the dynamics and kinetic roughening of fronts in simple lattice models of "forest fires". These types of models are used to study the spreading of epidemics, population dynamics, etc. On the experimental side, in collaboration with the group of J. Timonen (University of Jyväskylä) we have done an extensive amount of work to study slow combustion fronts in paper sheets. Experiments carried out in Jyväskylä have demonstrated that the long range and late time roughening of the fronts can be described the KPZ equation with white noise.

We have also developed a phase field model for the kinetics of imbibition (paper wetting). This situation is quite different from the paper burning, due to the conservation law associated with the fluid. An interface that is continuously slowing down is an important consequence of it. This also gives rise to a length scale that controls many dynamical scaling properties of the interface, such as the early time growth of the roughness. We have analysed the model in detail in the case of capillary driven wetting including also complications due to gravity or evaporation. We have also studied wetting front dynamics in the case of capillary rise between two plates containing disorder, and the diffusive spreading of droplets on surfaces.

Other projects in related problems include the following.

Fractal geometry of critical Potts clusters. The fractal geometry of the Fortuin-Kasteleyn clusters of 2D q-state Potts models at criticality have been studied via Swendsen-Wang simulations. The fractal dimensions of the cluster mass, hull, external perimeter, and singly connected bonds agree with the exact predictions. We also find new results for the number of large fjords on the cluster perimeter. Analytic results for the correction-to-scaling terms are obtained from the Coulomb gas representation and from Renormalization Group calculations.

Steady state dynamics under sedimentation. We have studied the steady state dynamics of sedimenting particles under gravity. A detailed analysis of the particle dynamics has revealed unusual intermediate time behaviour of the velocity autocorrelation function, similar to the case of strongly interacting particles diffusing on surfaces. This work is being extended to study anisotropic particles and the effects of box geometry (3D vs. 2D) to particle dynamics.

3 International Aspects

It is evident from the list of publications below that a lot of international collaboration was involved in the research reported here. Numerous visits abroad were made by many researchers and students in the research groups of the consortium, and these groups also received many visitors from abroad. Visibility of the research is also evidenced by the many invited talks by the members of the consortium, and their participation in the organization of international conferences. All groups in the consortium take part in European research programmes, including the European Science Foundation Sphinx network (HUT/PHYS) and the Visit project in the Esprit programme of the EU (JYFL).

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1998	1999	2000	2001	**Total**	Publication numbers
JYFL	Ref. journal art.	10	3	12	7	**32**	1-8, 17, 18, 25-27, 32-42, 44, 59-61, 67-70,
	Ref. conf. art.	1	5	1		**7**	80-85, 89
	Dr. dissert.	2	1		1	**4**	94, 95, 102, 124
	Lic. degrees		1	1	1	**3**	105, 116, 126
	MSc degrees	3	8	6	3	**20**	98-100, 107-114, 118-123, 127-129
HUT/PHYS	Ref. journal art.	10	2	13	12	**37**	1, 3, 6, 9-14, 19, 25, 30, 33, 35, 38, 43-49, 53-55, 62-64, 66, 69, 71-77
	Ref. conf. art.			1	1	**2**	90, 92
	Monographs			1		**1**	93
	Dr. dissert.				1	**1**	125
	MSc degrees	1	1			**2**	101, 115
HUT/CE	Ref. journal art.	6	2	3	1	**12**	9-10, 15-18, 28, 29, 50-52, 65
	Ref. conf. art.	2	3	1		**6**	79, 80, 86-88, 91
	Dr. dissert.	2				**2**	96, 97
	MSc degrees		1			**1**	115
HIP	Ref. journal art.	7	3	4	2	**20**	6, 19-25, 30, 31, 33, 53-58, 66, 69, 78
	Dr. dissert.		1			**1**	104
	Lic. degrees		1			**1**	106
	MSc degrees	2				**2**	101, 102

5 Other Activities

The consortium had an annual workshop meeting for all its members, students and visitors, and frequent meetings related to common research efforts. In addition, an international conference and a workshop were arranged by the consortium during the project. Members of the consortium were also involved in arranging other national and international meetings. Collaboration with industry developed favourably during the project so that many subprojects at the Master's thesis level were carried out. Also, application of the results in bone research lead to two US patents during the project.

Members of the consortium wrote a number of popular articles during the project [131-135], and took part in one science program (Tiedefoorumi) on the Finnish television.

6 Publications

6.1 Refereed Journal Articles

Publications 1998-2001

[1] A. Koponen, D. Kandhai, E. Hellen, M. Alava, A. Hoekstra, M. Kataja, K. Niskanen, P. Sloot and J. Timonen, Permeability of three-dimensional random fiber webs, Phys. Rev. Lett. 80 (1998) 716

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RESEARCH PROJECTS FUNDED BY TEKES

NANOMATERIALS AND THEIR MANUFACTURING METHODS

Jari Keskinen[1], Mikko Karttunen[2], Pekka Ruuskanen[1], Ville Pitkänen[3], Jorma Keskinen[3] and Simo-Pekka Hannula [4]

Abstract

The objectives of the project were to produce nanoparticles and nanostructured materials which can be applied as electrically conducting polymer composites, magnetic materials, hydrogen storage materials and electrodes in batteries. The aim was to develop techniques that can produce large amounts of materials compared with other nanomaterials production methods. In the case of electrically conducting polymer nanocomposites good electrical conductivity was achieved with remarkably lower filler particle concentration when compared with composites having fillers of larger particle size. Both flame sprayed and mechanically alloyed silver particles were used as fillers. The liquid flame spraying equipment designed and built in the project can be used to sample the silver particles produced by LFS-method, the number mean size of the particles being below 100 nm. Mechanical alloying was developed to produce silver particles of 20 - 300 nm depending on the process parameters. The magnetic nanocomposites were developed for high frequency applications. The high frequency properties were better than those measured for commercial ferrite material. The capacity of air-metal hydride battery was improved by 50 % and the power about 30 %. The manufacturing technology for the La_2Mg_{17} hydride material was developed. When mixed with $LaNi_5$ high hydrogen absorption capacity was reached at relatively low temperatures.

1 Partners and Funding

1.1 VTT Manufacturing technology

The research group consisted of subproject leader senior research scientist Jari Keskinen, research professor Simo-Pekka Hannula, group manager Pekka Ruuskanen, research scientist Mika Kolari and technician Kalevi Taskinen

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1.2 VTT Chemical technology

The research group consisted of subproject leader senior research scientist Mikko Karttunen, senior research scientist Jouni Enqvist, laboratory engineer Pekka Avellan, and technician Vuokko Rounioja.

1.3 Department of Physics, Tampere University of Technology

The research group consisted of subproject leaders research scientists Jukka Hautanen and Ville Pitkänen, professor Jorma Keskinen, and research scientist Markus Eerola.

1.4 Funding

Table 1. Funding of the project in 1000 FIM in 1997-1999.

Partner	Funding organisation	1997	1998	1999	**Total**
VTT Manuf.	TEKES	492	528	602	**1622**
	VTT	298	292	341	**931**
	Industry	30	60	60	**150**
VTT Chem.	TEKES	304	313	338	**955**
	VTT	193	179	205	**577**
	Industry	10	30	20	**60**
TUT Phys.	TEKES	567	609	488	**1664**
	TUT	68	37	55	**160**
Total		**1962**	**2048**	**2109**	**6119**

2 Research Work

2.1 Objectives and Work Plan

The aim of the research work was to develop methods for producing large quantities of nanoparticles and nanocrystalline materials for industrial applications.
The partial objectives were

1. Mechanical alloying was developed to produce the materials and nanoparticles needed in the applications of the project.
2. Nanoparticles needed in the applications were produced by flame spraying technique.

3. A novel real-time measurement of particle size distribution was applied in quality control.

The objectives in developing the material properties were
1. Hydride materials: nanocrystalline hydrides were developed. The hydrogen absorption and desorption properties are superior to the properties of conventional hydrides. This makes it easier to transfer hydrogen and on the other hand it improves the performance of batteries.
2. Polymeric nanocomposites were developed by adding mechanically alloyed or flame sprayed nanoparticles. Also commercially available magnetic particles were used as nanofillers. In this way electrical conductivity and magnetic properties were improved.

2.2 Progress Report: Common Themes

In this project the contribution of VTT Chemical technology formed the connection between the participants. VTT Chemical technology performed the mixing and processing of the nanoparticles developed by Tampere University of Technology and VTT Manufacturing technology.

Therefore this chapter describes the work made by VTT Chemical technology. Technically this work was divided to electrically conductive nanocomposites and magnetic materials.

2.2.1 Electrically conductive polymer nanocomposites

The aim of the research was to produce an electrically conductive thermoplastic polymer composite using the smallest possible amount of conductive filler. This way the composite maintains the best possible mechanical properties of its polymer matrix and processability by plastic processing methods. At the beginning of the work, volume resistivity of 0.01 ohmcm with a filler content of 20 vol% was set as the goal. Nanoscale Ag powders produced by mechanical alloying by VTT Manufacturing Technology, and by flame spraying by TUT, were used as electrically conductive fillers. The melt compounding method was selected for the production of nanocomposites which resulted in the most homogeneous material. Electrically conductive particles were for the most part mixed with thermoplastic elastomer.

According to the research, the volume resistivity of a nanocomposite is strongly affected by the degree of agglomeration of nanoparticles which, again, may be controlled at the particle production phase and during melt compounding. When particles are highly agglomerised, volume resistivity remains high even with a high filler content (over 20 vol%). Homogeneous powder produced by a liquid flame spraying can be turned into highly conductive nanocomposites (about $2x10^{-1}$ ohmcm) at a volume fraction of about 16 %. Volume resistivity of nanocomposites made of particles produced by mechanical alloying was at its lowest about $2x10^{-2}$ ohmcm at a 9.4 % volume fraction.

2.2.2 Magnetic nanocomposites

In this part of the project the nanoparticles were specified by VTT Manufacturing Technology. Their surface properties were optimised at VTT Chemical Technology. Also the mixing and compaction with polymers were made at VTT Chemical Technology.

Magnetic polymeric nanocomposites were developed for high frequency applications. Their properties were essentially better than those of ferrites. The table below shows the Q-values (the ratio between inductive and dissipation component) and permeabilities of these composites. It is typical for magnetic materials that the permeability increases and Q-value decreases when frequency increases. As can be seen from the table these values change less in the case of the developed materials than with commercially available ferrites. When the frequency
As a reference polymeric magnetic composites were manufactured also from iron powder having particle size of 10 - 50 µm. The permeability of this material is approximately the same as that of nanostructured iron. Instead the Q-value is a lot smaller than that of nanostructured iron. The reason is the growth of dissipation factor compared with smaller particles.

Table 1. Q-values and permeability of commercially available ferrite and polymeric magnetic composite measured at 8.2 MHz and 200 MHz.

	Commercial ferrite	polymer+ nano-Fe	polymer+ coated nano-Fe	oriented nano-Fe 2*2*20 (mm)	iron powder (d=10-50 µm)
Q (8.2 MHz)	400	140	175	100	25
µ (8.2 MHz)	100	12,5	11,1	<10	10
Q (200 MHz)	3	50	70	50	4
µ (200 MHz)	33	11	10	<10	10

2.3 Progress Report: Progress by VTT Manufacturing technology

2.3.1 Manufacturing of electrically conducting particles by mechanical alloying

Copper was produced in a ball mill by inducing the reaction between copper chloride and sodium. The result was copper and sodium chloride. Copper was in powder form. Sodium chloride was diluted by water and thus metallic copper powder was obtained.

The batch size was varied between 7 and 35 grams of copper. According to X-ray diffraction the product consisted of pure copper. Scanning electron microscopy revealed that the particle size varied depending on the batch size. At smallest the particle size was 20 – 50 nm. The biggest batches produced typically 100 – 300 nm particles.

Since copper particles oxidise too fast from the applications´ point of view, this sub-project mainly concentrated on the development of silver particle synthesis. The processing was first made in the same way as in the case of copper, except that silver chloride was used as raw material. The amount of elemental silver per batch varied between 13 and 65 grams. The particle size was typically below 200 nm. Especially in larger batches some bigger particle were formed. The reproducibility of the process was not adequate probably because of the high reaction rate between silver chloride and sodium.

Silver particles were also produced in ball mill by milling silver shots with graphite. Particles of 100 – 1000 nm were formed. When silver and sodium chloride were milled together, after dissolving sodium chloride silver particles of 200 – 500 nm were obtained.

2.3.2 Battery materials

Materials for air-metal hydride batteries were developed. Hydrides were processed by mechanical alloying as such or with various additives. The processing of the powder became a lot easier when ethanol was used as a process control agent. However, the best performance was obtained for a dry-milled powder. The mechanical strength of sintered hydride materials was improved by adding fibres to the powder.

The materials were compacted by cold isostatic pressing and sintering. The process pressure and temperature were optimized. In the electrochemical tests it was found that the sintered hydride material should be porous enough in order to give good performance. According to the results measured at Hydrocell Ltd it can be estimated that the capacity of air-metal hydride battery was improved by 50 % and the power about 30 %.

Preliminary experiments to produce Raney-nickel were done. Raney-Ni can be used to catalyse reactions on the hydrogen electrode. The experiments proved that mechanical alloying can be used to synthesise Ni catalysts.

2.3.3 Hydrogen storage materials

Hydrogen storage materials based on Mg_2Ni and La_2Mg_{17} were developed. Especially in the case of Mg_2Ni the properties were improved by producing nanostructured material. Palladium was used as a catalyst. The manufacturing technology of La_2Mg_{17}

compound was developed. To improve the hydriding properties of La_2Mg_{17} it was mechanically milled with $LaNi_5$.

Mg_2Ni was processed to nanocrystalline by mechanical alloying. The material absorbed hydrogen at room temperature up to 2,5 wt. %, when the surface of the powder was coated by a palladium coating made by atomic layer epitaxy. The properties of this particular material deteriorated rapidly during hydrogen absorption and desorption cycles. Several coating methods resulted in a hydrogen absorption of about 2 wt. %. Over 3 wt. % hydrogen absorption was achieved at 160 ^{o}C. The absorbed hydrogen was desorbed when the material was heated to about 200 ^{o}C in vacuum.

The developed manufacturing technology of La_2Mg_{17} is based on mechanical alloying and heat treatment. La_2Mg_{17} and $LaNi_5$ were mixed in a ball mill. The mixture absorbed 3.3 wt. % hydrogen at room temperature when the concentration of $LaNi_5$ was 30 wt. %. The total capacity was 4.4 wt. % hydrogen. At room temperature the absorption was relatively low but when the amount of $LaNi_5$ was added to 40 wt. %, the absorption time decreased to below 1 hour. When the hydrided material was heated in vacuum, it began to desorb hydrogen at about 230 ^{o}C.

2.4 Progress Report: Progress by VTT Chemical technology

The work at VTT Chemical technology is described in chapter 2.2.

2.5 Progress Report: Progress by Department of Physics

Liquid flame spray -method

In Liquid Flame Spray –method, one of the fuel gases is introduced coaxially around the precursor liquid inlet tube, and it nebulizes the slowly flowing precursor liquid, here silver nitrate, into small droplets which are sprayed into the hydrogen-oxygen flame. In the flame, both water and nitrogen oxides are evaporized and then also silver is evaporized. Furthermore, when the gas is cooling down after the flame, the silver vapour condenses back into small particles.

After the beginning part of the project, silver was chosen to be particle material under study, since other elements tested were seen to form oxides, and therefore the product was not as conductive as with silver compounds.

Most of the experiments were carried out with constant process parameters using silver nitrate in water as the precursor liquid. Here, concentration of 6.0 mol/dm^3 for $AgNO_3$ in water and liquid feed rate of 7.5 ml/min were used. The fuel gas volume flow rates in the experiments were 100 l/min for hydrogen and 50 l/min for oxygen.

Also other process parameters were tested, but with those other conditions we could not produce sufficient amounts of powder to be mixed with the polymer.

Efficient sampling of the particles turned out to be problematic and several practical sampling techniques were tested. Starting from simply spraying particles directly into the smelted plastic and finally ending up with a technique where the particles are sampled using their thermophoretic transport towards the cold walls of cylindrical chamber. The particles were afterwards brushed off from the wall to be mixed with the polymer.

When characterizing the particles, the XRD –analysis revealed that the particles consisted of almost pure silver. According to the SEM-graphs, the mean particle size was on the order of 100 nm, with several particles attached with each other to form agglomerates. Based on the aerosol number size distribution measurements, the geometric mean particle size was approximately 70 nm.

The equipment designed and built in the project can be used to sample the silver particles produced by LFS-method, the number mean size of the particles being below 100 nm. The generated mass yield of the particle was 0,85 g/min, corresponding to collection efficiency of approx. 37% of the generated total mass of silver.

3 International Aspects

In 1999 the project was connected to COST 523 Nanostructured Materials – cooperation. During the project one workshop was organised and a presentation was given there. Professor Simo-Pekka Hannula is a member of the management committee of this COST-action.

4 Publications and Academic Degrees

Table 1. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, theses in Section 6.3 and other publications in Section 6.4.

Partner	Type of publication	**Total**	Publication numbers
VTT	Ref. journal art.	**1**	1
	Ref. conf. papers	**2**	3, 4
	Other publications	**2**	6, 7
TUT Phys.	Ref. journal art.	**1**	2
	Licentiate degrees	**1**	5
	Other publications	**1**	8

5 Other Activities

The project has given a very good basis for the future research and product development work. Cooperation with the industrial partners has been continued also after the project.

A spin-off company Liekki Oy utilising LFS-technique in optical fibre manufacturing was founded.

Glass colouring tests have continued with Iittala Designor Oy

At TUT the project was followed by a Finnish Tekes –project focusing on Process parameters of LFS-technique.

6 Publications

6.1 Refereed Journal Articles

[1] Jari Keskinen, Pekka Ruuskanen, Mikko Karttunen, and Simo-Pekka Hannula: Synthesis of silver powder using a mechanochemical process, COST 523 Workshop, 20-22.10.1999, Frascati, Italy. *Applied Organometallic Chemistry* **15** (2001)393-395.

[2] Gross, K.A., Tikkanen, J., Keskinen, J., Pitkänen, V, Eerola, M. and Rajala M. (1999) Liquid Flame Spraying for Glass Colouring, *Journal of Thermal Spray Technology* **8**, 583-589.

6.2 Refereed Conference Papers

[3] Jari Keskinen and Pekka Ruuskanen: Mechanical Alloying and Characterisation of Nanocrystalline Mg_2Ni, Hydrogen Power, Theoretical and Engineering Solutions, Proc. of the Hypothesis II Symposium, 18.-22.8. 1997, Grimstad, Norway, 377 - 382.

[4] Jari Keskinen and Simo-Pekka Hannula: Synthesis of $La_2Mg_{17}/LaNi_5$ for hydrogen storage application by mechanical alloying, to be presented at EURO-PM2001, October 2001.

6.3 Doctoral, Licentiate, and Master Theses

[5] Ville Pitkänen: Nanokokoisten hiukkasten tuottaminen nesteliekkiruiskutus-menetelmällä, (Production of nanosized particles using liquid flame spray method), Lic.Phil, Thesis. Will be accepted August-September 2001.

6.4 Other publications

[6] Jari Keskinen and Pekka Ruuskanen: Hydride Processing for Battery and Hydrogen Storage Applications, 3rd Nordic Symposium on Hydrogen and Fuel Cells for Energy Storage, 25.-26.9.1997, Helsinki.

[7] Jari Keskinen, Pertti Kauranen, Pia Tuominen, Mika Kolari, and Pekka Ruuskanen: Powder metallurgically processed metal hydrides for energy storage applications. Joint Nordic Conference in Powder Technology, 5.-6.5.1999, Oslo, s. 54.

[8] Tikkanen, J., Pitkänen, V., Eerola, M and Keskinen, J. (1999) LFS Process; Effect of Particle Size on Glass Colouring in *Vapour Phase Synthesis of Materials III* July 18-23, 1999 Haikko, Finland, Book of Abstracts, Kauppinen, E.I., Okuyama, K. and Pratsinis, S. (Eds.), pp. 29-32.

ELECTROLUMINESCENCE IN Si/SiO$_2$ SUPERLATTICES

Heikki Ihantola [1] and Juha Sinkkonen[2]

Abstract

The project was the continuation of Electronics and Information Technology Laboratory superlattice studies, which had given very promising results of electroluminescence (EL) with all spectral colours. The Si/SiO$_2$ superlattices were grown in a low pressure, low temperature CVD-reactor, which is a part of the laboratory's self-made, patented multichamber semiconductor processor. It was very easy to change the number and thickness of the silicon and silicon dioxide nanometer scale layers. This method is very compatible with integrated circuits processing. The resulting superlattice structures were not very regular as shown by Atomic Force Microscopy (AFM) and in Transmission Electron Microscope (TEM) pictures. This disarray was one reason for the good electric conductivity of the oxide layers, and allowed at low voltages large current densities, essential to EL. The spectral distribution of the emitted light was measured changing the polarity and the current. The strongest light was in the area from green to red. Some samples exhibited very strong laser-type yellow light. This was, perhaps, the first observation of such a phenomenon in the world. The laboratory could quite conclusively show, too, that EL is possible only in structures where there is the interface of crystalline silicon and silicondioxide. The intensity and colour of the EL can be changed modifying the oxide composition. This project was realized in cooperation with a parallel project leaded by prof. J. Sinkkonen who is writing a separate report. Both projects had a common board of leaders with Tekes and industry representatives. In the biannual meeting the achieved scientific results were discussed extensively.

1 Partners and Funding

1.1 Laboratory of Electronics and Information Technology, Department of Applied Physics, University of Turku (UTU)

The research group consists of subproject leader professor H. Ihantola (vice-leader R. Punkkinen), senior researchers T. Kuusela and L. Heikkilä, postgraduate students H-P. Hedman and K. Jokinen (- mid 1999), and students N. Porjo and T. Suutari.

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1.2 Electron Physics, Helsinki University of Technology (HUT)

Project leader was professor J. Sinkkonen. He is preparing a separate progress report.

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
UTU	UTU	271	271	251	251	**1044**
	Academy	0	0	0	0	**0**
	Industry	10	10	10	10	**40**
	Tekes	0	516	556	626	**1698**
HUT	See their report					
Total		**281**	**797**	**817**	**887**	**2782**

2 Research Work

2.1 Objectives and Work Plan

The original objective was to create a large consortium comprising all Finnish parties relevant to study “luminescent silicon”. The groups applied for money either at the Academy or at Tekes. Tekes provided the funding for the above two groups. Important aspects like laser ablation to grow and anneal superlattices with strong characterization facilities (Oulu), TEM (Tampere), porous silicon, and energy band structure computations (Turku) were dropped out.

The main common target of the two remaining groups was to find out, what are the neccessary conditions for the silicon based superlattices to make them capable to create electrically controlled light i.e. electroluminescence, EL. The starting point of the research was the compilation of international papers on the subject. The two partners used different methods and equipment to build structures, and it was considered important to compare their benefits. UTU was using low pressure/low temperature chemical vapor deposition, CVD, and targeted from the beginning towards EL. HUT applied molecular beam epitaxy (MBE) , and made extensive PL measurements. During the project the targets were refined. UTU started to find out the light creation mechanism more thoroughly and HUT experimented with plasma enhanced CVD, ion implantation and Si nanopillars, and made EL measurements, too.

2.2 Progress Report: Common Themes

Both groups were able to obtain luminescent superlattices. The basic difference was that CVD grown lattices could be opereted at relatively low voltages (10…20 V) while MBE grown lattices needed 100-200 volts, but also the current densities were lower. It appeared too difficult to measure HUT samples at UTU and vice versa due to e.g. the different voltage/current requirements, so rigorous comparisons could not be made. Both parties received valuable information from the results of each other during the project.

Although the luminosities of the samples of both groups were encouraging, they were not yet satisfactory for practical applications – perhaps with the exception of the laser-like intense narrow-band phenomen observed by the UTU group. The latest HUT samples were also very good. During the research better understanding of luminescence was gained, and also the luminosities increased. To connect the light emitting devices or diodes (LED) to some other functional devices like transistors were not yet attempted, although it would have been a very interesting experiment. That will need a vehicle to change the vertical direction of the light lateral along the surface of the chip in a light conductor.

The most important applications of the EL devices should be the integrated displays of miniature electronic devices and the light transmitters across large integrated circuits to make the communication between different sections of the system faster.

2.3 Progress Report: Progress by the Laboratory of Electronics and Information Technology

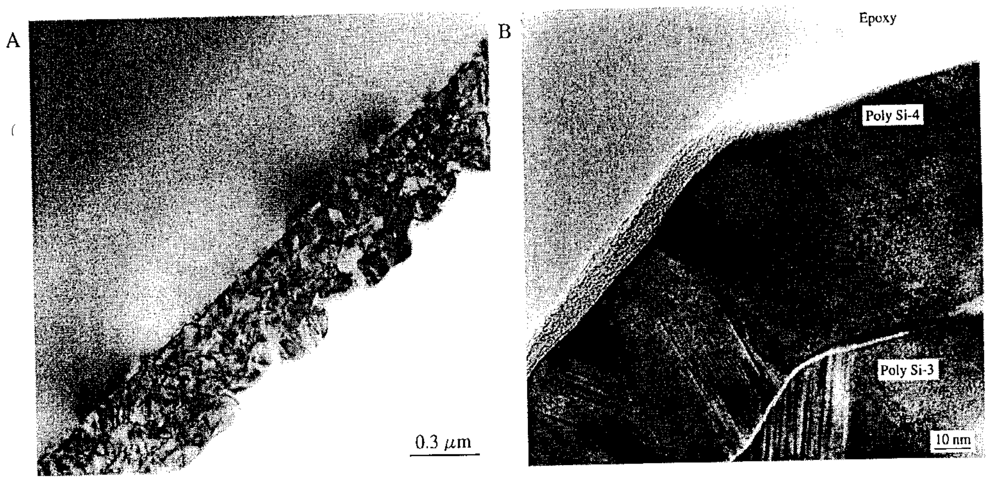

Fig. 1. A: TEM micrograph of a typical four layer pairs superlattice sample. Polysilicon grains are clearly seen. B: Magnified picture. Oxide layers are white.

To grow Si/SiO$_x$ ($x \leq 2$) low pressure/low temperature chemical vapour deposition (LPLTCVD) method was used. Typically the pressures were about 1 - 10 Pa and the temperatures 670-700 °C. The structure of superlattices was quite irregular, as seen in Fig. 1, which may have one reason for the early multi-coloured samples. Later the emission spectrum of the studied constructions was typically broad containing several details as explained below:

One of the clearest changes noticed in the visible spectrum (300 – 900 nm) is the change of the emitted colour, when **the polarity of the voltage is changed.** Typically the components work best with the positive potential on the p-type wafer and negative on the top gold electrode. The difference in spectra can be seen in Fig. 2. The pointed curve is obtained with normal polarity and the top is in the 600 – 700 nm area but with reversed polarity the top is flat and moved to 700 - 800 nm. Visually this was seen very clearly: with normal polarity the component appeared yellow and with reversed voltage it was red. Some samples worked well with both polarities some not. The reasons for this could not be explained. The change of the color was probably dependent on the different injection of charge carriers. The negative top electrode injected easily electrons and the positive bottom holes. It is possible, too, that the recombination took physically place at different depths depending on the polarity, and the move towards red could be explained with optical absorption.

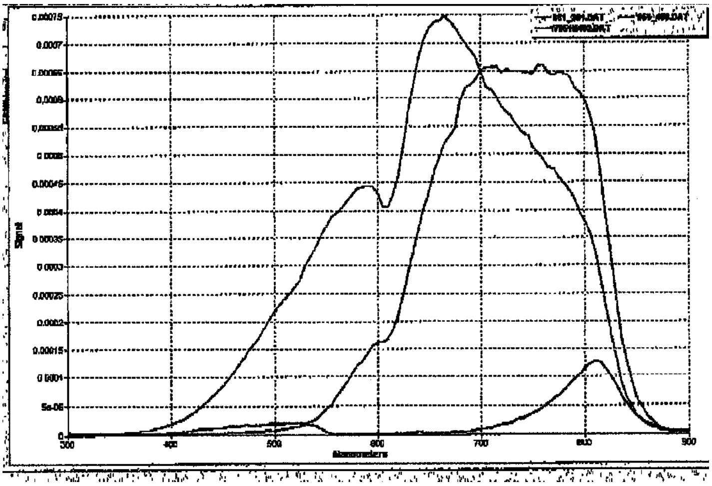

Fig. 2. EL-spectra of a superlattice sample with forward (pointed) and reverse current (flat top).

Some samples showed significant **laser-type emission spectrum narrowing.** Fig.3. shows, how a typically broad spectra are collapsing into a substantially narrow peaks, widths below 10 nm, when the current density is increased above some threshold value. Normally the intensity of the light is decreasing at the highest currents. It is noticable, too, that there seems to be a maximum in the normal spectrum about in the same place. The structure looks like favoring certain wavelength regions, but when the spectrum narrows only one top wavelength is left. This probably laser-type emission has been seen only at some samples, when the current density is increased above 100 mA/mm^2. Due to the high currents the samples were unfortunately very short-lived, and therefore scrutinizing them was difficult. [3]

In typical laser-diodes certain wavelength is selected placing the active area between reflecting mirrors. The total length of the here studied superlattice samples is 200 – 350 nm, which is about half of the wavelength of the observed peak, and it not sure that such a structure could function as an optical cavity. On the other hand the layered structure of the superlattice could operate like a certain Bragg reflector, which could lengthen the optical length of the component. Bragg reflector is composed typically of alternating layers whose refractive index is differing strongly. The alternating silicon and silicondioxide layers could in principle function in the same way. If the question is of the laser phenomenon, the multiple harmonics are so far away from the main peak that they cannot be seen in the measuring range of the spectrometer.

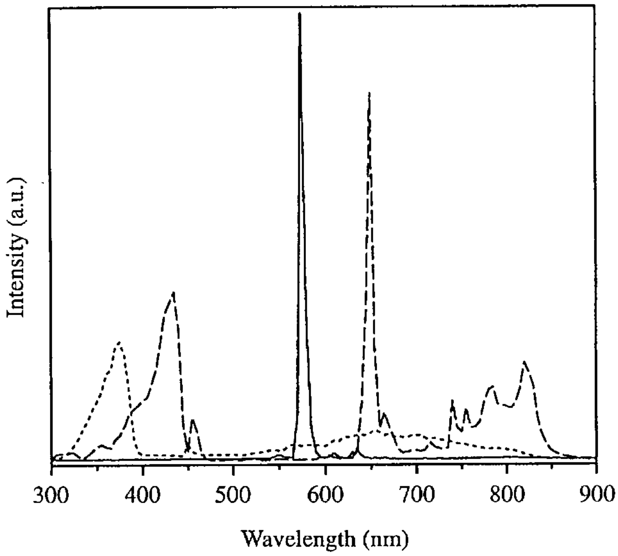

Fig. 3. Laser type of spectral narrowing for three different superlattice samples.

The research has shown that EL-phenomenon is possible also at a thin plain oxide layer grown on a base Si wafer. The spectra of native oxides are quite similar to them of thermally grown oxides. E.g. there is minimum at 600 nm with symmetric maxima at 550/650 nm. If a thin polysilicon layer is grown on the oxide there is little change of the intensity, but there is transition towards red at thicker layers. This gives a hint that important to EL phenomenon is the Si/SiO$_2$ junction and not the silicon layer alone.

When oxide and silicon layers are grown on a Si wafer using LPLTCVD method the layer has certain structure. The surface is composed of thin crystal platelets like scales, the vertical dimension being only a fraction of the horisontal. The orientation of the plates is the same across the whole wafer and independent of the crystal orientation of the bottom wafer. It is evident that the growing gas flows determine the orientation of the plates especially, when the growth is very slow.

The plates can be interlocked in relation to each others. More accurate atomic force microscopy (AMF) analyses show that between the plates there may exist few nanometers wide gaps where the quantum confinement could be important. These areas are some candidates to the creation of EL.

It has appeared that the emitted light is not distributed evenly across the whole area but concentrated in certain very small areas. The brightness of these spots is far stronger than in the average. The pictures taken by a CCD-camera show that between bright areas there are ones with no bright spots, although the spots seem to be statistically distributed. The density of the spots is lowest at thermally grown oxides (500 spots/mm^2) and highest at CVD grown oxides (2500 spots/mm^2). Si/SiO$_2$ layer couples are between. The photon production of a single spot is about 10000 photons/s.

When the fractal dimension was determined which showed that the most homogenous layer i.e. thermal oxide gave most random distribution of bright spots.Typically the dimension of a spot is smaller than 2 μm. The luminance and the surface structure did not seem to correlate in the comparison of careful brightness map and AFM or scanning tunneling microscope (STM) pictures.

A large series of different layer structure was measured in order to clarify the **mechanism of the luminescence.** The goal was to make a complete series of different combinations of silicon, silicon oxide, and gold films. Silicon structures were either the crystalline base wafer or grown CVD layers. Oxides were grown either with the CVD method or thermally. Except the base wafer layers were grown on a intermediate gold layer. The structures were divided to the illuminating and non-illuminating samples as shown in Fig. 4 (light is spelled wrongly).

The analys of the results reveals that the luminance is possible only in the cases where the structure contains the junction of silicon oxide – crystalline silicon. This result is important, because it explains previously observed results which seem contradictory. The result completely agrees with the illuminating results reported in the literature.

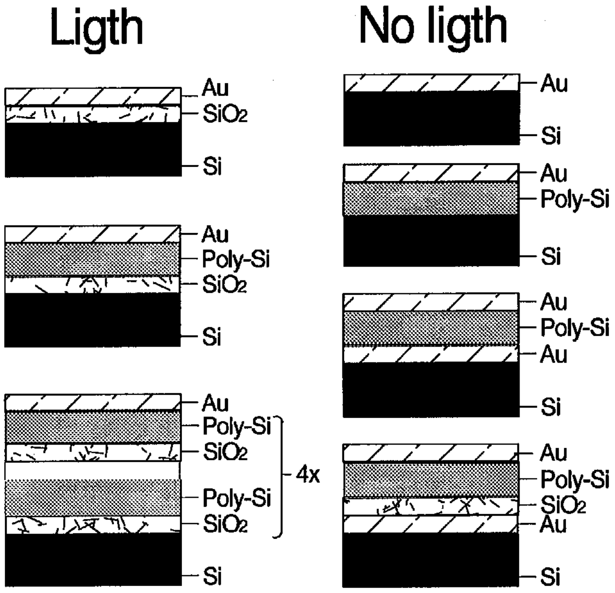

Fig. 4. Different combinations of studied layer stack structures. The left column structures emitted light the right column ones not.

2.4 Progress Report: Progress by the Electron Physics Laboratory, Helsinki University of Technology

The results of this subproject are being reported separately by Professor J. Sinkkonen.

3 International Aspects

The results have been reported in international refereed journals like Journal of Applied Physics, Applied Physics Letters, Solid State Phenomena, Applied Surface Science, and Superlattices and Microstructures. Several reprints have been sent to foreign research groups after the requests. In some cases the work of this group has been referred to. The low pressure, low temperature CVD growth has been of interest and the group has been invited to be a partner in a couple of EU program proposals. The reporting in international conferences and meetings has been regretably tiny.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
UTU	Ref. journal art.	1	1	1	3	**6**	1-6
	Ref. conf. papers	-	-	-	-	**1**	8
	Monographs	-	-	-	-	**-**	
	Doctoral dissert.	-	-	-	-	**-**	
	Licentiate degrees	-	-	-	-	**-**	
	Master degrees	-	-	-	1	**1**	7
HUT	Own report	-	-	-	-	**-**	

5 Other Activities

This project took place in cooperation with the Electron Physics Laboratory of the Helsinki University of Technology. A common board of leaders was following the progress of the two subprojects. The board had meetings three times in 1998 and two times annually in 1999 and 2000. The industry representatives were Mr. Heikki

Kuisma of VTI-Hamlin Oy making silicon microsensors, Mr. Markku Tilli (deputy Mr. Olli Anttila) of Okmetic Oyj making silicon wafers, and Mr. Reijo Tuovinen of Micro Analog Systems Oy (MAS) making integrated circuits. Tekes representive was initially Mr. Oiva Knuuttila, then Dr. Päivi Piironen, and finally Mr. Immo Seppänen. They attended meetings only twice. In the meetings the researchers represented their results quite extensively and in detail. It should be mentioned that the chairman of the board and the leader of Turku subproject Dr. Heikki Ihantola was retired in the beginning of the project. In spite of that he has been almost daily in contact by phone, e-mail or visiting the project persons.

6 Publications

6.1 Refereed Journal Articles

[1] L. Heikkilä, T. Kuusela, H.-P. Hedman, A. Pavlov, H. Ihantola, AFM and STM investigations of electroluminescence SiO_2/Si superlattices prepared by chemical vapour deposition, Diffusion and Defect Data. B: Solid State Phenomena 54 (1997) 13-20.

[2] L. Heikkilä, T. Kuusela, H.-P. Hedman, H. Ihantola, Electroluminescent SiO_2/Si superlattices prepared by chemical vapour deposition, Appl. Surf. Sci, 133 (1998) 84-88.

[3] L. Heikkilä, T. Kuusela, H.-P. Hedman, Laser type of spectral narrowing in electroluminescent SiO_2/Si superlattices prepared by chemical vapour deposition, Superlattices and Microstructures 26 (1999) 157-169.

[4] L. Heikkilä, T. Kuusela, H.-P. Hedman, Electroluminescence in SiO_2/Si superlattices, J. Appl. Phys. 89 (2001) 2179-2184.

[5) L. Khrianchtchev, L. Heikkilä, T. Kuusela, Red photoluminescence of gold island films, Appl. Phys. Lett. 78 (2001) 1994-1996.

[6] N. Porjo, T. Kuusela, L. Heikkilä, Characterization of fotonic dots in SiO_2/Si thin film structures, J. Appl. Phys. 89 (2001) 4902-4906.

6.2 Refereed Conference Papers

[7] N. Porjo, H.-P. Hedman, L. Heikkilä, T. Kuusela, Electroluminescence in Si/SiO_2 nanostructures prepared by low pressure CVD method, Tuorla Obs. Rep. Infnro 181, URSI XXIV Conv. on Radio Science in Turku, Finland, 1999, 76-77.

6.4 Doctoral, Licentiate, and Master Theses

[8] N. Porjo, The characterization of superlattice samples using CCD.camera (Finnish), Department of Applied Physics, University of Turku, 2000.

7 Other References

[9] T. Kuusela, Light emitting Si/SiO_2 superlattices, Nokia Research Center Tampere, Finland, 12.10.1998.

ULTRASONIC CHARACTERIZATION OF MATERIAL PROPERTIES OF ARTICULAR CARTILAGE

Jukka S. Jurvelin[1]

Abstract

Feasibility of high frequency (>10MHz) ultrasound for the characterization of material properties of articular cartilage and trabecular bone were investigated. Ultrasonic findings were related to microscopic and biomechanical results obtained for same cartilage samples in order to determine structure-function relationships and to judge diagnostic capabilities of different techniques. Experimental and theoretical techniques were developed to objectively determine acoustic parameters, i.e. sound velocity, attenuation coefficient, surface reflection coefficient and acoustic impedance of articular cartilage and to reveal their changes during enzymatic degradation of the tissue. Acoustic properties were found to sensitively reflect the status of articular cartilage. Surface reflection and acoustic impedance of cartilage were found to sensitively indicate condition of tissue collagen, proposing that the ultrasonic technique could provide a diagnostic method for characterization integrity of cartilage collagenous network, known to be impaired in osteoarthrosis. When the ultrasonic measurement was combined with the mechanical indentation measurement, cartilage degradation due to collagen disruption or proteoglycan (PG) depletion could be discerned. Based on these studies an acousto-mechanical method and instrument integrating ultrasound and indentation measurements was designed and validated. In the future, both theoretical and experimental frequency domain analyses of acoustic properties of articular cartilage, subchondral and trabecular bone will be conducted and applied to diagnostics of osteaoarthrosis and osteoporosis.

1 Partners and Funding

1.1 Department of Clinical Physiology and Nuclear Medicine, Kuopio University Hospital (KUH)

The Biophysics of Bone and Cartilage (BBC) research group consists of project leader Docent Jukka S. Jurvelin, Ph.D. and postgraduate students Juha Töyräs, Ph.D., Miika Nieminen, M. Sc and Rami Korhonen, M.Sc and physics students Mikko Laasanen and Heikki Nieminen. The important collaborator is Professor Heikki J. Helminen, MD and his research team, Department of Anatomy, University of Kuopio

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1.2 Funding

Table 1. Funding of the project in 1000 FIM in 1998-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1998	1999	2000	**Total**
KUH	KUH	200	200	200	**600**
	TEKES	372	220	220	**812**
	EU	50	50	50	**150**
	Industry	50	50	50	**150**
Total		**672**	**520**	**520**	**1712**

2 Research Work

2.1 Objectives and Work Plan

The objectives of the study were

- to develop sensitive techniques and instrumentation for the mechanical and acoustic measurements of articular cartilage
- to characterise interrelationships of structural, mechanical, acoustic and magnetic properties in normal articular cartilage
- to characterise interrelationships of structural, mechanical, acoustic and magnetic properties in enzymatically degraded articular cartilage
- to model theoretically propagation, backscatter and reflection of ultrasound in articular cartilage
- to design and apply an ultrasound technique and instrument for the in vivo measurement of articular cartilage

2.2 Progress Report:

Progress by the Biophysics of Bone and Cartilage group

High frequency ultrasound may provide a quantitative technique for the characterization structure and properties of articular cartilage [39,40]. In our approach the cartilage samples were studied using mechanical, acoustic, MRI and microscopic techniques. Both experimental and theoretical analysis techniques were utilized. The findings of these studies demonstrated that high frequency ultrasound measurements

[6,7,12,15,17,18,21,22,27,31,39], as well as high magnetic strength (9.4T) MRI studies [8,14,19,20,24,2526,36], provided diagnostically valuable information on the material properties of articular cartilage and bone. Especially, the structural changes typical to cartilage degeneration could be sensitively and specifically revealed by pulse-echo measurements. When integrated to mechanical indentation measurements the specific degradation of cartilage collagen and proteoglycans was differentiated from each other (Fig. 1) [6,27]. In cartilage, collagen fibrils seem to be the dominant backscatterers of sound. This can be highly important diagnostic finding while PG depletion may be still restored while cartilage collagen failure is known to be an irreversible phenomena. Based on the new information gathered in these studies, a novel instrument combining ultrasound and mechanical measurements was designed, a prototype was constructed and patent application submitted. A licensing procedure was initiated with a Finnish company.

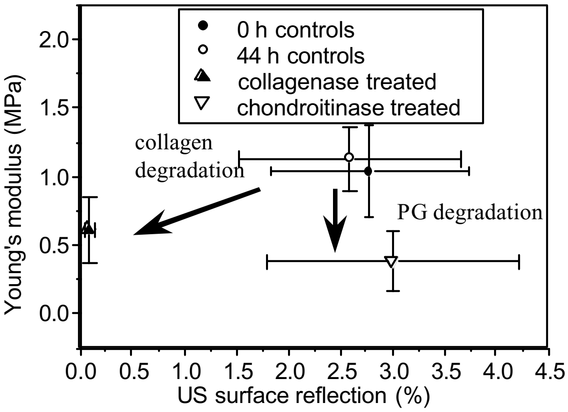

Fig. 1. Combined mechano-acoustic measurements (Mean±SD can differentiate proteoglycan and collagen degradation in articular cartilage. In both cases cartilage stiffness, i.e. Young´s modulus, is reduced (compared to control (0 or 44h) tissue), but only during collagen degradation ultrasound reflection (%) from cartilage surface diminishes.

3 International Aspects

During 1998-2000 an active international collaboration was established in the field of cartilage biomechanics. Especially, cartilage modelling studies were conducted with Prof. Ernst Hunziker and Dr. Marcy Wong, University of Bern, Bern, Switzerland [9, 10], Prof. Jun-Kyo Suh, Tulane University, New Orleans, USA [13] and Prof. Michael D. Buschmann, Ecole Polytechnique, University of Montreal, Montreal, Canada [1]. Also, BBC-group was an active partner in cartilage repair project, cordinated by Prof. Mats Paulsson, University of Cologne, Cologne, Germany, and funded by EU. Several scientific meetings in Europe and USA were attended 1998-2000.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4. [1]

Partner	Type of publication	1998	1999	2000	2001	**Total**	Publication numbers
KUH	Ref. journal art.	1	6	3	4	**14**	1-14
	Ref. conf. papers	2	4	5	6	**17**	15-31
	Monographs	-	1	1	-	**2**	32-33
	Doctoral dissert.	-	-	-	1	**1**	38
	Licentiate degrees	-	-	-	-	**-**	-
	Master degrees	1	2	-	1[2]	**4**	34-37

5 Other Activities

A Finnish patent application *Menetelmä ja laite kokoonpainuvan kudoksen tutkimiseksi* (JS Jurvelin, I Kiviranta, J Töyräs), desribing the method of ultrasound indentation of articular cartilage, was left 27.4.2001.

6 Publications

6.1 Refereed Journal Articles

[1] Buschmann MD, Soulhat J, Shirazi-Adl A, Jurvelin JS, Hunziker EB: Confined Compression of Articular Cartilage: Linearity in ramp and sinusoidal tests and the importance of interdigitation and incomplete confinement. J Biomechanics 31: 171-178, 1998.

[2] Lyyra T, Arokoski JP, Oksala N, Vihko A, Hyttinen M, Jurvelin JS, Kiviranta I Experimental validation of arthroscopic cartilage stiffness measurement using enzymatically degraded cartilage samples. Phys Med Biol 44:525-35, 1999.

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[1] In addition to listed publications, several manuscripts from the project has been submitted or are in preparation.

[2] B.Sc thesis (insinöörityö) from Pohjois-Savo Polytechnic

[3] Arokoski JP, Hyttinen MM, Helminen HJ, Jurvelin JS. Biomechanical and structural characteristics of canine femoral and tibial cartilage. J Biomed Mater Res 48: 99-107, 1999

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[10] Wong M, Ponticiello M, Kovanen V, Jurvelin JS. Volumetric changes of articular cartilage during stress relaxation in unconfined compression. J Biomechanics 33:1049-54, 2000

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[14] Nieminen MT, Rieppo J, Töyräs J, Hakumäki JM, Silvennoinen J, Hyttinen MM, Helminen HJ, Jurvelin JS: T2 relaxation reveals spatial collagen architecture in articular cartilage: a comparative quantitative MRI and polarized light microscopic study. Magn Reson Med, in press 2001.

6.2 Refereed Conference Papers

[15] Töyräs J, Valanta P and Jurvelin JS: Bone strength as estimated by mineral density, ultrasound attenuation and ultrasound velocity in vitro. Transact Orthop Res Soc 23: 23, 1998

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[18] Töyräs J, Kröger H, Jurvelin JS: Inconsistent Behaviour of Broadband Ultrasound Attenuation in Bone, Medical & Biological Engineering and Computing, 37, supplement 1: 424-425, 1999

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6.3 Monographs

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FLOTATION OF INDUSTRIAL MINERALS

Jaakko Leppinen[1], Kari Laajalehto[2] and Pipsa Hirva[3]

Abstract

The objective of this work was to increase fundamental understanding of structures and reactions on minerals surfaces essential for selective hydrophobisation of sparingly soluble calcium minerals apatite and calcite in flotation. The work, financed by the National technology Agency of Finland and the Technical Research Centre of Finland, was carried out by a consortium consisting of the research groups of flotation chemistry, material science and theoretical chemistry in 1997 to 1999. Several experimental and theoretical methods were used including ion chromatography, FTIR, XPS, AFM and molecular modelling. The results indicate that the hydrophobisation of calcium minerals takes place through surface reactions between the collector molecules, sodium oleate and oleoyl sarcosine, and mineral surfaces. The mechanism of this interaction involves ion exchange in which collector ions replace a stoichiometric amount of lattice constituent, phosphate and carbonate, ions from the mineral surface,. This interaction is not limited to monomolecular layer but may proceed to several molecular layers. Depending on solution conditions, calcium ion at the surface play an important role forming different reaction products: chemisorbed, surface precipitated and bulk precipitated species with the collector. The AFM studies revealed that the molecular layers are formed batchwise. The selectivity of collector adsorption between calcite and apatite can be explained by weaker interaction energies of binding of collectors on calcite. The most typical binding mode of sarcosine on apatite (001) surface is tridentate, while on calcite (001) surface the tridentate binding is not energetically favoured. Furthermore, the effect of the functional group in sarcosine molecule on calcite model varies from the apatite model, which may offer a way to control the selectivity of the collector. The results of the solution and surface chemistry are used in the selection of the parameters to be controlled in the flotation process especially in the development work of the optimisation of the conditioning stage. The methods of theoretical chemistry can be utilised in the development of new flotation reagents. In general, the experimental and theoretical methods developed in this work, can be utilised in many systems involving interactions between aqueous solution and solid surface.

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[2] Department of Applied Physics, University of Turku, Vesilinnantie 5, FIN-20014 Turku

[3] Department of Chemistry, University of Joensuu, P.O.Box 89, FIN-82300 Joensuu

1 Partners and Funding

1.1 VTT Chemical Technology, Mineral Processing

The research group focusing on flotation chemistry consists of subproject leader docent Jaakko Leppinen, researchers Pekka Stén and Mauno Miettinen.

1.2 Laboratory of Material Science, University of Turku

The research group focusing on surface analysis consists of subproject leader professor Kari Laajalehto, students Suvi Myrskyranta and Marianne Torhola and post graduate student Taina Laiho.

1.3 Department of Chemistry, University of Joensuu

The research group focusing on molecular modelling consists of subproject leader docent Pipsa Hirva, researcher Eini Puhakka and students Jari Gordeijev and Henna Ruuska.

1.4 Funding

Table 1. Funding of the project in 1000 FIM in 1997-1999.

Partner	Funding organisation	1997	1998	1999	**Total**
VTT	Tekes	202	214	210	**626**
	VTT	134	142	140	**416**
UTU	Tekes	300	288	227	**815**
UJO	Tekes	400	392	300	**1092**
Total		**1036**	**1036**	**877**	**2949**

2 Research Work

2.1 Objectives and Work Plan

The objective of this work was to increase fundamental understanding of structures and reactions on minerals surfaces essential for selective hydrophobisation of minerals in flotation. Several subfields of research were put together into a joint effort to determine and explain basic phenomena in the flotation of sparingly soluble calcium minerals, apatite, calcite and dolomite. The ultimate goal was to model the interactions between solution species, typical in flotation pulps, and the surfaces of minerals in order to master the hydrophobisation of minerals and consequently control the flotation process. Theoretical and experimental methods were combined to study the structures of organic layers and minerals surfaces themselves under various conditions in aqueous solutions. The structural data was also linked to the behaviour and properties of mineral slurries. An important goal for this program was to characterise the whole chain of phenomena in flotation from atomic level to separation of particles in the flotation cell.

An objective of the research plan presented in the following, was to strengthen the cooperation between Finnish research groups which are working in the field of surface chemistry of flotation. The expertise obtained through this consortium would be later applied also for other solid-liquid interactions in other processes. In order to ensure the high scientific standard of the research work it was also considered essential to create and maintain contacts to research partners outside Finland. During the research work, the objectives were adjusted in that the number of calcium minerals was reduced removing dolomite from the plan.

2.2 Progress Report: Common Themes

2.2.1 General

The collaboration between the three research groups has been illustrated in Fig. 1 showing that the surface analysis group at the University of Turku (Group B) acted as a link between the molecule modelling (Group C) and the flotation chemistry (Group A) groups. Significant direct interaction occurred also between all research groups. Particular common interests were found in the following subfields.

Groups A and B:	Combining of the information obtained from solution and solid surface.
Groups B and C:	Combining of the information of the binding mechanism between mineral and collector molecule.
Groups A and C:	Combining of the information of the effect of the interaction energy on the selectivity of the collector.

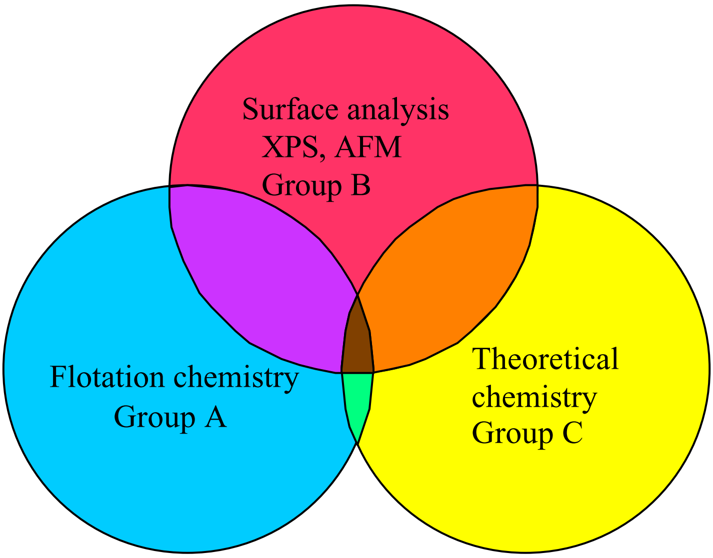

Fig. 1. Interaction between the research groups.

The results obtained using different methods provide new information about binding of the collector molecules on different calcium-bearing industrial minerals. The collaboration between the research groups has also increased the fundamental knowledge about the applicability of the research methods and techniques to investigation of the important reaction mechanisms in flotation.

By means of the solution analytical studies it has been possible to determine the reaction mechanisms between collector chemicals and mineral surfaces as well as the solution conditions affecting these interactions. These results give new opportunities for thermodynamic modelling of surface reactions in flotation processes.

It has been shown during the course of the project that direct surface analytical techniques such as XPS and AFM can also be applied to the flotation research of industrial minerals such as phosphates and carbonates. These investigations are complementary to the solution studies in order to verify the phenomena occurring at the surfaces.

The fundamental knowledge of the reactions and binding mechanisms helps to tailor the most suitable collector for each process. Consequently, the flotation selectivity between different calcium minerals can be improved. For example, varying the functional group in the sarcosine collector, affects clearly the interaction energy between the collector and mineral surface.

2.2.2 Interactions in the flotation of apatite and calcite

Background

Concentration of calcium minerals from ores is commonly carried out using flotation. Fatty acid and sarcosine derivatives are frequently used as the collectors in the flotation of sparingly-soluble calcium-bearing minerals. Flotation of the calcium minerals apatite and calcite is, however, complicated by the close similarities in their physicochemical properties, resulting from the presence of calcium ion as a lattice constituent ion [14]. Although the flotation of calcium minerals is usually successfully carried out on an industrial scale, the physicochemical basis for the selectivity achieved in practice is not fully understood and a lot of separation problems exist where no satisfactory solution has been developed.

There are indications that different products can be formed on apatite and calcite surfaces by the reactions with collectors. The mechanisms of the surface interactions of the collectors are not yet well defined although some early observations refer to an ion exchange mechanism where oleate ion replaces lattice constituent ions from the mineral surface [13]. On the other hand, because the calcium-bearing minerals are classified as semi-soluble materials, significant concentrations of various ions are dissolved from these minerals in contact with the aqueous phase. These ions are assumed to have an essential impact on the surface chemistry of apatite and calcite in the flotation pulp.

In this work the interaction between apatite and calcite surfaces and aqueous solution has been investigated using solution analysis, Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and the methods of theoretical chemistry.

Results and discussion

Ion chromatography used in the solution analysis revealed that phosphate and fluoride ions were released from the surface of apatite in the adsorption reaction with oleate [3]. Similar behaviour was observed for calcite, carbonate ions being released from the surface. For the minerals studied, the release of anions was stoichiometric with respect to the consumption of oleate ions taking into account that free calcium ions present in the solution were first precipitated as calcium oleate (Fig.3). Consequently, direct evidence for an ion exchange mechnism between oleate and calcium mineral surfaces was demonstrated. Similar mechanisms were observed for natural fluoroapatite and synthetic hydroxyapatite and no basic difference was observed between natural and synthetic calcite. The XPS studies confirmed the ion exchange reaction model showing lower intensities for lattice constituent elements after reaction between surface and collector.

The following principled reactions can be used to explain the inteaction between oleate ion and calcium-bearing minerals apatite and calcite. In the reactions surf denotes surface phase, aq aqueous phase and s solid phase.

PO_4^{3-} (surf) + 3 Ol^- (aq) = PO_4^{3-}(aq) + 3 Ol^-(surf) (1)
F^- (surf) + Ol^- (aq) = F^- (aq) + Ol^- (surf) (2)
CO_3^{2-} (surf) + 2 Ol^- (aq) = CO_3^{2-} (aq) + 2 Ol^- (surf) (3)
Ca^{2+}(aq) + 2 Ol^- (aq) = $CaOl_2$ (s) (4)

The analysis revealed that ion exchange is also involved in the interaction between oleoyl sarcosine and calcium minerals apatite and calcite [7]. On apatite, at low dosages of sarcosine the carbonate ion exchange is dominating while at high dosages the phosphate ion exchange is dominating.

The reaction between the calcium minerals and the collectors sodium oleate and oleoyl sarcosine were not limited to monomolecular amount of collector species but depending on pulp density, i.e. the ratio between mineral surface area to volume of solution, it may proceed up to several molecular layers. It was observed that the only part of the oleate, probably the chemisorbed species, can be removed in a reverse surface reaction by increasing the phosphate ion concentration in the solution. AFM studies indicated clearly that multilayer formation of oleoyl sarcosine took place as patches and not as evenly distributed layers (Fig. 5).

Calcium ion at the surface play an important role forming different reaction products: chemisorbed, surface precipitated and bulk precipitated species with the collector. It is notable that although the interaction energies of modified collectors with Ca^{2+} ion are larger than those of a small model of fluoroapatite (001) surface the relative difference between functional groups is similar. The result confirms that the calcium ion can be used to carry out preliminary studies involving comparison of the effectiveness of different collector molecules[2]. The most typical binding mode on apatite (001) surface is tridentate, while on calcite (001) surface the tridentate binding is not energetically favoured. Furthermore, the effect of the functional group in sarcosine molecule on calcite model varies from the apatite model, which may offer a way to control the selectivity of the collector.

In process conditions, the solution contains ions dissolved from carbonate minerals, e.g. carbonate, which may interact with the apatite surface [8]. In flotation pulps, the total carbonate ion concentration is typically in the range of several hundred milligrams per litre. In this study it was found that due to the high carbonate ion concentration in the aqueous phase, the outermost phosphate ions were replaced by carbonate ions making the apatite surface different from ordinary apatite. Ion chromatographic solution analysis showed that after exposing apatite to carbonate containing solution, the concentration of phosphate ions increases dramatically indicating an exchange between carbonate and phosphate groups (Fig 2). In distilled water the amount of phosphate ions released into solution is small being controlled by the solubility of apatite. This interaction can be described by the reaction principle presented in Eq. 5.

$$2\ PO_4^{3-}\ (surf) + 3\ CO_3^{2-}\ (aq) = 2\ PO_4^{3-}(aq) + 3\ CO_3^{2-}(surf) \qquad (5)$$

The interaction between sodium oleate and apatite preconditioned in carbonate solution was found to involve exchange between both surface carbonate ions and surface phosphate ions. When sodium oleate was added into a system where apatite was preconditioned with carbonate-containing water, a substantial decrease was observed in the phosphate ion exchange presented in reaction (1). Interestingly the effect was greater when apatite was added directly to carbonate solution compared to the case where apatite was conditioned in distilled water prior to the addition of sodium bicarbonate.

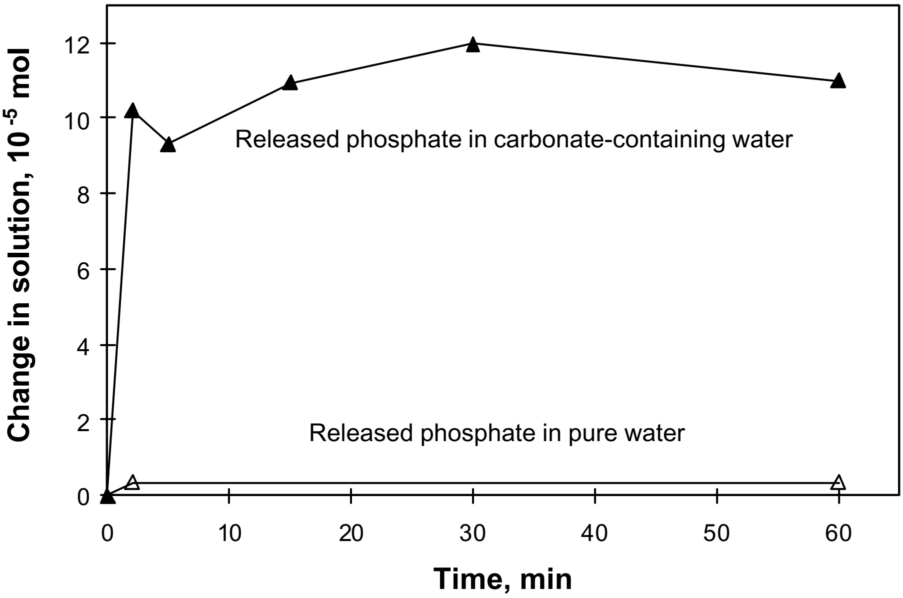

Fig. 2. Release of phosphate ions from apatite surface in distilled water and in the presence of carbonate ions ($NaHCO_3$ 500 mg/l) in solution at pH 10.

The surface modification of apatite by aqueous carbonate ions was verified by XPS studies where a C1s component typical for carbonate species at binding energy 289 eV was observed (Fig. 3a). At the same time, P/Ca ratio decreased from the value 0.76 obtained for the sample kept in water without carbonate addition, to the value 0.69 indicating dissolution of phosphate. On the surface of a sample treated additionally with sodium oleate, the carbonate signal almost completely disappeared (Fig. 3b) proposing further exchange of oleate with carbonate preadsorbed on the surface [8].

Interestingly, the adsorption of oleoyl sarcosine collector on apatite involved exchange predominantly with surface carbonate ions. As oleoyl sarcosine is considered a weaker collector than oleate it is evident that similar phosphate exchange than presented for oleate in reaction (1) does not take place with sarcosine. Apparently the adsorption of oleoyl sarcosine on apatite is favoured in the carbonate-containing process solution due to the carbonate-rich surface. This is likely to a reason for the success of sarcosine collector in industrial flotation processes. Consequently, for practical purposes, the adsorption and flotation studies should be conducted with carbonate-covered apatite rather than apatite it its normal aqueous environment. Also the kinetic and thermodynamic considerations should be addressed to the carbonate-modified apatite surfaces.

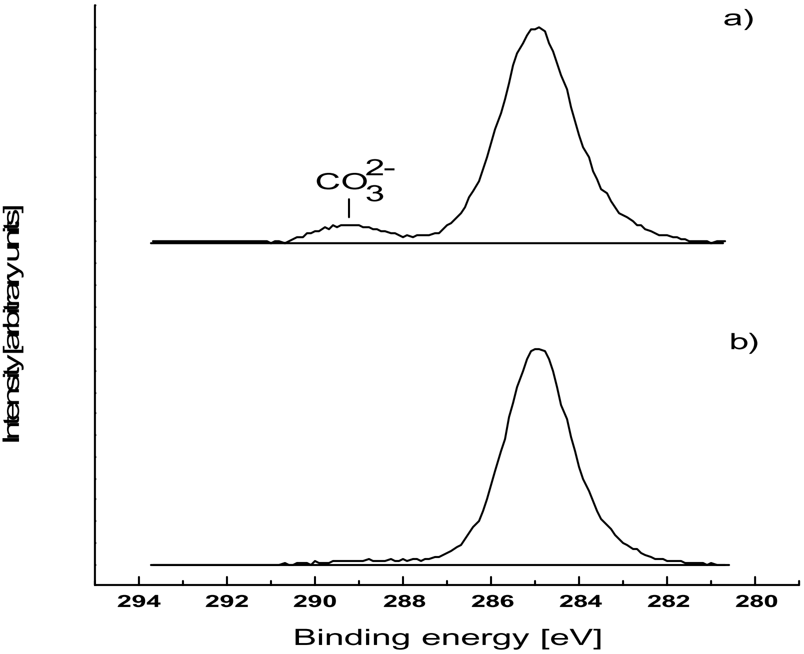

Fig. 3. Carbon 1s spectra of apatite samples after the following treatments: a) 30 min in 500 mg/l $KHCO_3$ solution, pH 10 and b) 30 min in 500 mg/l $KHCO_3$ solution + 15 min after addition of $5 \cdot 10^{-5}$ M Na-oleate, pH 10.

2.2.3 Industrial utilisation of the results

The results of the solution and surface chemistry are being used in the selection of the parameters to be controlled in the flotation process, especially in the optimisation of the conditioning stage. The methods of theoretical chemistry can be exploited in the development of new flotation reagents. In general, the experimental and theoretical methods developed in this work can also be used for investigation of other corresponding flotation systems as well as for other related surface chemistry applications.

The mining companies, Kemira Chemicals Oy and Partek Nordkalk Oyj Abp, processing industrial minerals, have been actively involved in the research project. The results concerning apatite has been of special interest of Kemira Chemicals' Siilinjärvi mine and the result of calcite Partek Nordkalk's Lappeenranta mine. The results from the experimental and theoretical studies have been transferred to the industry in several common meetings and also in separate mutual meetings held in both companies.

2.3 Progress Report: Progress by the Flotation Chemistry Group (VTT Chemical Technology, Mineral Processing)

The main aim of the mineral processing group was to find the factors affecting the floatability of calcium minerals, calcite and apatite, and define the major solution parameters affecting the flotation process. The main target in the experimental study was to investigate the reaction mechanisms between the collectors, sodium oleate and oleoyl sarcosine, and calcium mineral surfaces. This task was performed using various solution analytical techniques such as ion chromatography, ICP, ion selective electrodes and UV-VIS spectroscopy in addition to FTIR spectroscopy and microflotation tests.

2.3.1 Sodium oleate

It was observed in the solution studies that the interaction between oleate ions and the minerals calcite and apatite takes place through an ion exchange reaction mechanism where stoichiometric amounts of phosphate, fluoride and carbonate ions are liberated from the mineral surface in the reaction with oleate ions (Fig 4). This reaction is not limited to monomolecular amount of oleate but depending on pulp density, i.e. the ratio between mineral surface area to volume of solution, it may proceed up to amounts corresponding to several molecular oleate layers. The chemisorbed oleate can be removed in a reverse surface reaction by increasing the phosphate ion concentration in the solution. This explains the industrial findings that phosphate ions can be used to suppress the flotation of apatite [3, 6].

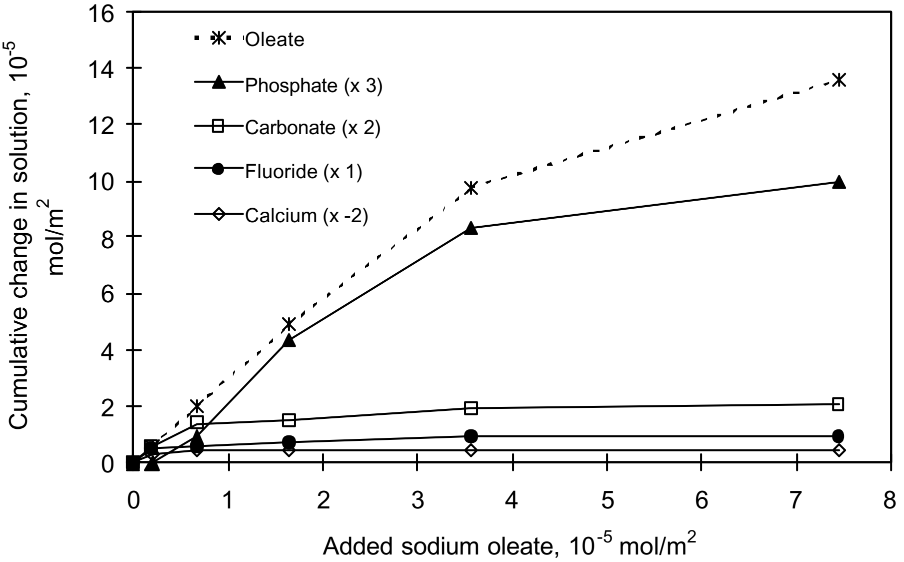

Fig. 4. Relationship between added sodium oleate and the amount of ions consumed and released from the surface. 5 g/l natural fluorapatite at pH 10.

Calcium ions dissolved from the mineral species to the solution phase are precipitated as bulk calcium oleate which forms separate crystallites but can also partly be adhered to the surface. At low pH, the concentration of calcium ions increases and calcium oleate precipitation is larger. The chemisorbed and precipitated oleate species are formed simultaneously but their ratio depends largely on pulp density. At high pulp density the main reaction product is chemisorbed oleate. Depending on pulp density, the surface of apatite becomes saturated by oleate that stops the oleate reactions with mineral surface. This saturation point occurs at oleate amount corresponding to 1 to 5 mono-molecular layers. On calcite the saturation of the surface does not occur even at oleate amount as high as 20 monolayers.

The maximum floatability of apatite was reached with oleate amount lower than the saturation point of the surface whereas at a higher amount of oleate the floatability decreased sharply. The decreasing floatability can be due to formation of a bilayer which is more hydrophilic due to inverse orientation of molecules. A decrease of floatability could not be observed with calcite, i.e. the bilayer formation did not occur at calcite surfaces.

Based on the experimental results, thermodynamic conditions for the formation of different oleate species on apatite and calcite can be defined. Correspondingly the important control parameters in the flotation process are concentrations of calcium and phosphate ions and pH. Unlike oleoyl sarcosine, the concentration of carbonate ions does not play an important role when oleate is used as the collector.

2.3.2 Oleoyl sarcosine

The solution analysis revealed that ion exchange is also involved in the interaction between oleoyl sarcosine and calcium minerals apatite and calcite. At low dosages of sarcosine the carbonate exchange is dominating while at high dosages the phosphate exchange is dominating. The reaction is not limited to monomolecular level but can end up to multilayers. Calcium and chemisorbed sarcosines can be formed simultaneously but independent of pulp density the surface sarcosine is formed first. Apatite surface becomes saturated by sarcosine but unlike oleate, similar saturation was also observed on calcite.

The maximum floatability of apatite and calcite occurred at oleoyl sarcosine consumption corresponding to monomolecular adsorption. At higher consumption than that of monolayer, the floatability of both apatite and calcite decreased sharply. In this sense, significant difference between sarcosine and oleate was observed.

In carbonate-containing process waters, the major reaction mechanism of oleoyl sarcosine with apatite is ion exchange with surface carbonate ions [8]. As a weaker collector than oleate, oleoyl sarcosine seems to be particularly suitable for the flotation of apatite the surface of which is modified by carbonate solution. Unlike oleate, the concentration of carbonate ions has an impact of the amount of sarcosine adsorbed on the surface of apatite.

2.4 Progress report: Progress by the Surface Analysis Group (Materials Science, University of Turku)

The main objectives of the group in this project were the following:

1. To develop practical methods for surface characterisation of calcium minerals using X-ray Photoelectron Spectroscopy (XPS, ESCA)

2. To apply Atomic Force Microscopy (AFM) for imaging calcium mineral surfaces under various conditions and after different treatments. Especially, the imaging of collector layers on mineral surfaces in the presence of aqueous phase was one of the main objectives.

The laboratory of Materials Science has a long experience in surface characterisation of sulfide minerals and reliable methods have been developed earlier for those materials. Calcium minerals (apatite and calcite) are, however, essentially more difficult to study. First of all, their low electrical conductivity causes great problems when using methods like XPS, where the surface will be positively charged during the analysis. Nevertheless, the information which can be obtained by using XPS, is so unique and essential for surface research that it was considered extremely important to be able to use that method to achieve the goals of the whole project. The other problem is that XPS measurements have to be carried out in ultra high vacuum whereas flotation takes place in aqueous environment. Therefore the whole sample treatment procedure has to be developed in such a way that no significant changes occur during sample handling and the measurement itself. On the basis of the work in this project, it is has become well defined, which are the best methods for preparing apatite and calcite samples for XPS. Proper treatment procedures for powder type samples were also examined in the project. This is an essential step towards investigation of real flotation systems where minerals are always in the form of powders. The main problem with XPS in this project was a very long measuring time (several hours per spectrum) needed to collect the spectra. This was, however, necessary because of the many elements to be analysed and to obtain statistically good quality spectra, where reliable resolving of the different chemical states of the elements was possible.

Identification of collector molecules directly on the surface is one of the best results, which can be obtained with XPS method. Therefore, the efficiency of collector adsorption and hence, flotation can be determined by analysing mineral surfaces prepared under different conditions. Two type of collectors, sodium oleate and oleoyl sarcosine, were used in this work. Oleate is quite problematic from the point of view of XPS, because the molecule can be identified only by using C and O atoms, which are always present in different forms on surfaces treated in aqueous solutions. However, we were able to determine the C and O signals which can be used for analysing chemisorbed oleate.

More emphasis was placed on studies with sarcosine-type collectors, which are used in phosphate mineral flotation on an industrial scale, but where only a few research results have been published. Sarcosine is more straightforward to be identified by XPS using the signal from N atom in the molecule structure. Even quite a small amounts (less than half a monolayer) of collector can be analysed.

It was clearly observed the different adsorption mechanisms between oleate and sarcosine. For calcite, the adsorption mechanism seems to the same for both collectors, whereas for apatite, there are clear differences [12]. Because one of the major problems in the flotation process is the selective separation of apatite and calcite, different adsorption mechanism of sarcosine may also explain its better selectivity. Furthermore, smaller collector concentrations (10^{-5} M) in the flotation pulp increase selectivity. We also studied the effect of changing the functional group in sarcosine molecule and found clear change in the adsorption mechanism. Here CH_3 group attached to nitrogen atom in sarcosine molecule was replaced by phenyl group. Phenyl sarcosine was synthesised in this project at the University of Turku (Dept. of Chemistry). The interesting observation was that CO_3^{2-} ions always present in flotation pulp have a strong influence particularly on sarcosine adsorption. When CO_3^{2-} concentration is high, sarcosine adsorption increases probably because of the favoured exchange reaction between pre-adsorbed CO_3^{2-} and the collector.

Mineral surface imaging with the AFM method formed an essential part of the project because the method is quite new and not much used for these applications before. Therefore, the work included a lot of basic studies of the system. Both apatite and calcite cleavage planes were studied in air and in collector solutions *in situ*. Calcite is a much easier system for AFM studies because it cleaves easily along well defined crystal planes. A lot of work were done to prepare good samples from apatite crystals As a highlight of the results obtained in this project, we were able to detect adsorbed sarcosine collector layers and structures on both apatite and calcite surfaces. As an example, an AFM image of apatite surface in sarcosine solution is presented in Figure 5. It is worth mentioning that the mineral is in liquid during the measurement and the image reflects the state of surface in real environment. The structures observed are about 80 nm in height and about 0,1-0,2 µm in diameter showing clearly that the growth of sarcosine layer takes place as patches and not as evenly distributed layers.

It was clearly demonstrated in this project that surface analytical and imaging techniques can be effectively used and they give essential and new information of the mineral surfaces treated in the flotation process. This conclusion is much more general and can be applied to many materials and technological processes.

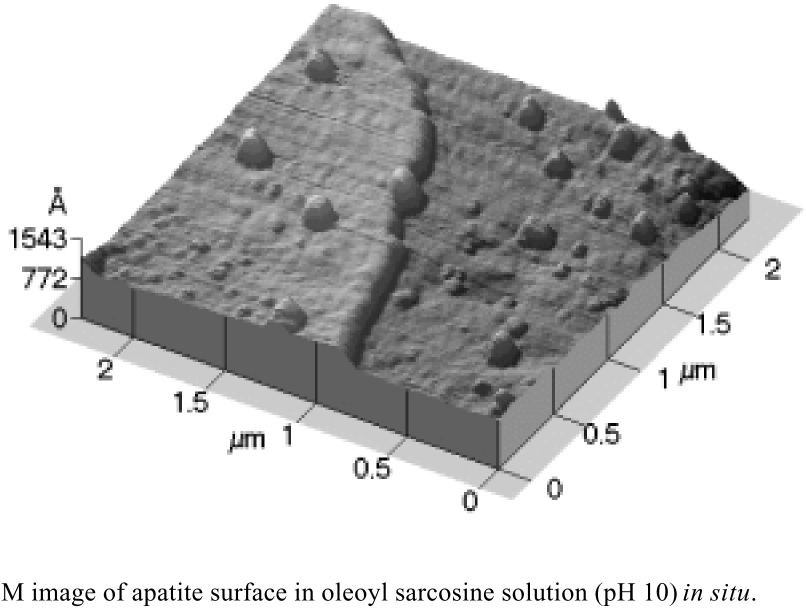

Fig 5. AFM image of apatite surface in oleoyl sarcosine solution (pH 10) *in situ*.

2.5 Progress Report: Progress by the Molecular Modelling Group (Department of Chemistry, University of Joensuu)

The main aim of the molecular modelling group was to study computationally the interactions of selected collector molecules with different surface sites on calcium minerals. In this work the basic properties of the interactions were studied in detail in order to explain the functionality of the collector molecules on the flotation process.

2.5.1 Surface structures

The structure of the surface sites plays an important role in the interaction of collector molecules with the surfaces. Therefore, the first step was to model structural characteristics of different calcium mineral surfaces. At this point, also a preliminary survey of the interacting molecules on the surfaces was performed with low-level methods. The study led to a selection of adsorption sites on typical cleavage planes of fluoroapatite and calcite.

2.5.2 Surface models

Different adsorption sites were modelled by cutting a cluster of atoms from the bulk structure of the minerals. This stage required thorough testing in order to establish the most suitable models for different minerals. Especially for semi-ionic calcite surfaces, the choice of the surface model was crucial because of the instability of small cluster models. Since the standard cluster termination techniques were not suitable for calcite surfaces, a new method was developed to increase the stability of the clusters [1]. In this method the cluster model was surrounded by water molecules which allowed the use of smaller models also for calcite surfaces. A further advantage of this method is the possibility to improve the model by taking into account some effects of the solvent. The method can also be exploited in embedding other types of surface models.

2.5.3 Interaction of collector molecules with the surface models

As an initial approximation, the basic properties of the interaction of collector molecules with calcium minerals were modelled using a single surface ion (Ca^{2+}). As the collectors we chose oleate and oleoyl sarcosine anions, which were also studied experimentally by the other groups of this project. In addition to a attaching polar group, the collectors have a long hydrocarbon “tail”. The flexibility of the carbon chain complicates further the theoretical study of the collector-surface system. Since the effect of the carbon chain on the surface interaction was found small, it was replaced with an ethyl group to make the calculations more feasible.

In this study we could find notable differences in the binding modes of different collector molecules. Whereas oleate anion can only exhibit mono- or bidentate binding, oleoyl sarcosine anion will tend to form a tridentate structure upon complexation (Fig. 6). The differences in the binding modes had a strong influence in the interaction energies of the collector molecules, thus the oleoyl sarcosine molecule was found to have the strongest interaction with a single calcium ion [2].

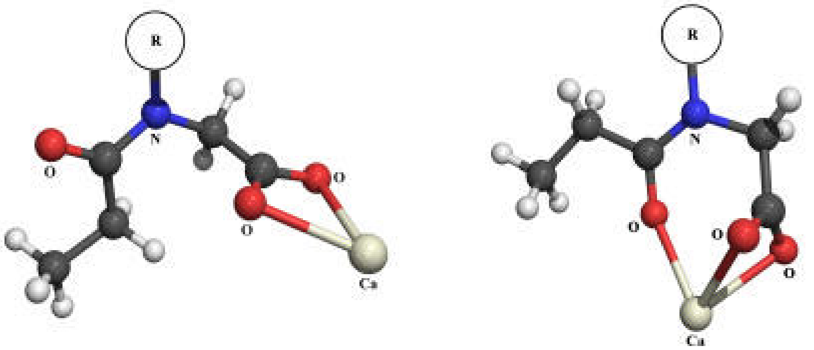

Figure 6. Bidentate and tridentate binding of the oleylsarcosine anion on a single surface calcium.

The effect of the functional group R (Figure 6) on the interaction energies was studied by replacing the methyl group in the oleoyl sarcosine with hydrogen atom, hydroxyl group, phenyl group and tertiary butyl group. Through the choice of different functional groups we aimed to study both electronic and steric effects on the interaction energies and charge distributions. This kind of information might help in explaining the properties of the interaction and eventually in designing the most effective collectors. Figure 7 shows the results for the interaction energies of modified collectors with Ca^{2+} ion and also with a small model of fluoroapatite (001) surface. It is notable, that although the interaction energies decrease with the larger surface model, the relative differences of functional groups are very similar. This result confirms that the calcium ion can be used to carry out preliminary studies involving comparison of the effectiveness of different collector molecules.[2]

We also compared the interaction energies of modified oleoyl sarcosine anions with small cluster models of calcite(001) and apatite(001). The results in Figure 8. show clear differences in the basic properties of the interaction, which is considerably stronger in the case of apatite. This result is in good agreement with experimental findings, and it is further emphasised with the differences in the binding structures of the collector on calcite or apatite models. The most typical binding mode on apatite (001) surface is tridentate, while on calcite (001) surface the tridentate binding is not energetically favoured. Furthermore, the effect of the functional group in sarcosine molecule on calcite model varies from the apatite model, which may offer a way to control the selectivity of the collector.

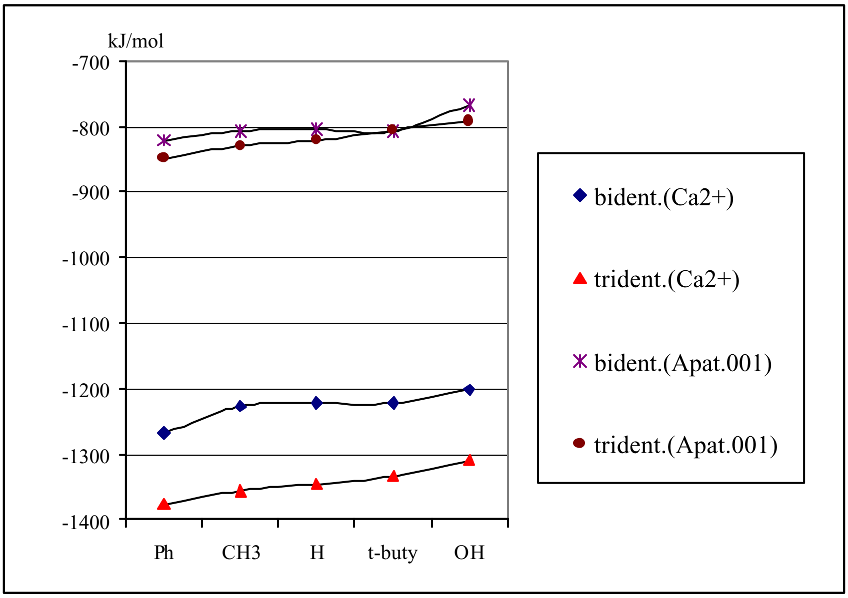

Figure 7. Interaction energies of bidentate and tridentate models of oleoyl sarcosine anion with Ca^{2+}ion and with the small cluster model of apatite(001) surface.

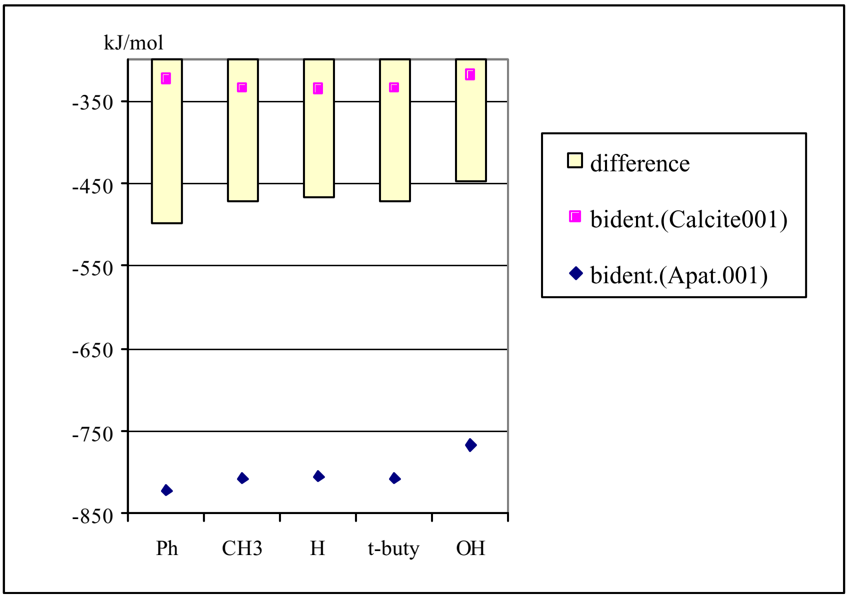

Figure 8. Interaction energies of modified oleoyl sarcosine molecules on apatite (001) and calcite (001) surface models.

2.5.4 Solvent effects in modelling the collector-surface interaction

Solvent effects of the aqueous solution can be very important in the flotation process. Therefore we tested some of the current computational solvation methods, which are used for small or medium sized molecules [11]. However, within surface adsorption studies, we found none of these to be very reliable and further studies will be necessary to effectively take into account the influence of the solvent molecules on the binding modes and the interaction energies. One possibility would be to explicitly include water molecules on the surface, as was done in stabilisation studies of the calcite surface models [1].

2.5.5 Summary of the results obtained by molecular modelling studies

The computational study on the interaction of collector molecules with calcium mineral surfaces has given information on the initial adsorption process during flotation:

1. Three possible types of binding were found for oleoyl sarcosine anion (mono, bi- and tridentate adsorption).
2. Generally, the tridentate adsorption is stronger than mono- or bidentate binding
3. The electrostatic properties of the functional groups in modified sarcosine molecules have major effect on the interaction energies.
4. The interaction of oleoyl sarcosine is weaker on the calcite(001) surface than on the apatite (001) surface. Furthermore, tridentate binding is not energet-ically favourable on calcite (001) surface
5. The interaction energies show, that it is possible to influence the selectivity of the oleoyl sarcosine molecule by modifying the attaching functional group. This will help in designing new, more effective collectors.

Additionally, we introduced a new method for stabilising small ionic or semi-ionic cluster models with surrounding water molecules [1]. The method can further be applied for other problems which include difficulties on the cluster embedding techniques.

3 International Aspects

The international visibility of this work has been predominantly maintained through presentations at international conferences. The most important meetings have been Minerals Engineering ‘98 in Edinburg, the Second European Conference on Computational Chemistry in Lissabon, the 8th European Conference on Applications on Surface and Interface analysis, in Sevilla and Flotation 2000 in Adelaide. There has not been direct international collaboration in this work but solid contacts to the universities and research institutes in Europe, USA and Australia have been used in during the course of the project, particularly in developing the experimental methods. These partners include University of Leipzig (Leipzig, Germany), Institute of Surface

Chemistry, Polish Academy of Sciences (Cracow, Poland), Virginia Polytechnic Institute (Blacksburg Virginia) and University of South Australia (Adelaide, Australia). This project has benefited from a Brite Eu Ram II project: Study of Surface Phenomena in Flotation, carried out parallel to this project at the University of Turku.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project.

Partner	Type of publication	1997	1998	1999	2000	2001	**Total**	Publication numbers
VTT	Ref. journal art.	-	-	-	1	0	**1**	3
	Ref. conf. papers	-	1	-	1	0	**2**	6, 8
UTU	Ref. journal art.	-	-	-	-	1	**1**	4
	Ref. conf. papers	-	-	1	1	-	**2**	7, 8
	Master degrees	-	-	1	-	-	**1**	12
UJOE	Ref. journal art.	-	-	2	-	-	**2**	1,2,
	Master degrees	1	1	-	-	-	**2**	9, 10
	Ref. conf. papers	1	-	-	-	-	**1**	5

5 Other Activities

Several joint meeting were held between the participating groups. Meetings were held also in the two industrial companies involved in the project. The results of this research have been presented in several national and international meetings. Special concentration of these presentations occurred at the IX National Symposium of Surface and Colloid Science organised by the Finnish Colloid and Interface Society in 1999, where all three groups presented a paper of their research work.

6 Publications

6.1 Refereed Journal Articles

[1] H. Ruuska, P. Hirva, and T.A. Pakkanen, Cluster Models for Calcite Surfaces: Ab Initio Quantum Chemical Studies, J. Phys. Chem. 103 (1999) 6734-6740.

[2] J. Gordeijev and P. Hirva, Theoretical Studies on the Interaction of Oleoyl Sarcosine with the Surface of Apatite, Surface Science 440 (1999) 321-326.

[3] J. Leppinen, M. Miettinen, Interaction between Sodium Oleate and Calcium Minerals. submitted to Int. J. Miner. Processing, February 2000.

[4] S. Myrskyranta and K. Laajalehto, XPS and AFM Studies of Interaction of Oleoyl Sarcosine on Fluoroapatite and Calcite Surfaces, Submitted to Surf. Interface Anal., February 2001.

6.2 Refereed Conference Papers

[5] Puhakka, E., Gordeijev, J. & Hirva, P. "Theoretical studies on flotation of industrial minerals: surface structures of fluorapatite, calcite and dolomite, and properties of collectors" The Second European Conference on Computational Chemistry, Lissabon, (1997).

[6] J. Leppinen, P. Stén and M. Miettinen, Interaction between Sodium Oleate and Calcium Minerals. Minerals Engineering '98, Edinburg, Scotland, September 14-16, 1998.

[7] K. Laajalehto, Adsorption of Oleoyl Sarcosine on Fluoroapatite and Calcite Surfaces,8th European Conference on Applications of Surface and Interface Analysis, Sevilla, Spain (1999).

[8]. J. Leppinen, M. Miettinen, P. Stén, S. Myrskyranta and K. Laajalehto, Role of Process Solution in the Flotation of Apatite. Flotation 2000, Adelaide, Australia, March 29-31, 2000.

6.3 Doctoral, Licentiate, and Master Theses

[9] J. Gordeijev, Kalsiummineraalien vaahdotus: Kokoojamolekyylien teoreettista tarkastelua (Flotation of Calcium Minerals: Theoretical Study of the Collector Molecules), Master Thesis, Department of Chemistry, University of Joensuu, 1997.

[10] H. Ruuska, Kalsiummineraalien vaahdotuksen teoreettista tutkimusta: Kalsiitin pintamallit (Theoretical Studies of the Flotation of Calcium Minerals: Surface Models of Calcite), Master Thesis, Department of Chemistry, University of Joensuu, 1998.

[11] J. Gordeijev, Kalsiummineraalien vaahdotus: Liuosvuorovaikutukset kokoojamolekyylien mallituksessa (Flotation of Calcium Minerals: Solvent Interactions in Modelling of Collector Molecule) Master Thesis in the Minor Subject, Department of Chemistry, University of Joensuu, 1998.

[12] S. Myrskyranta, Surface reactions of Apatite and Calcite with Anionic Collectors Under Conditions Relevant to Flotation, Master Theses, University of Turku, 1999.

7 Other References

[13] Bahr, A., Clement, M. and Surmatz, H., 1968. On the effect of inorganic and organic substances on the flotation of some non-sulfide minerals by using fatty-acid-type collectors, 8th International Mineral Processing Congress, Leningrad, paper S-11, 12 p.

[14] Finkelstein, N.P., 1989. Review of interaction in flotation of sparingly soluble calcium minerals with anionic collectors. Trans. Instn Min. Metall. (Sect. C: Mineral Process. Extr. Metall.), 98: C157-C177.

CONTENTS

COORDINATION COMPOUND CATALYSTS

Markku Leskelä [1]

Abstract

New transition metal complexes which are potential polymerization catalyst precursors have been synthesized in this project. Metallocenes of group 4 metals were in 80s a big invention in olefin polymerization catalyst technology. They facilitate polymerization with structurally known catalysts and tailoring of polymer structure by changing the metallocene ligand structure. The aim of the present work was to study early transition metal complexes which behave like metallocenes, i.e. are active and show single site behaviour. Several new complexes of group 4 metals having oxygen as donor atom were synthesised. Complexes containing didentate ligands showed best activity and high molecular weight polyethene could be produced.

The ability of late transition metal complexes to polymerize olefins was discovered at mid 90s. In this project the main emphasis has been given to different Ni, Pd, Co and Fe complexes, their syntheses, crystal structures and homo- and copolymerization properties. One important group of complexes involved symmetric and unsymmetric diimines but complexes containing other nitrogen donor ligands and other donor atoms like P, As, S have been studied as well. The catalytic properties of the complexes were studied in polymerization of ethene and different norbornenes.

Co-operation with University of Ulm and structural characterization of catalyst precursors prepared in Ulm formed one essential part of this project and numerous catalyst precursors were studied. The compounds include both metallocenes and late transition metal complexes..

1 Partners and Funding

1.1 Laboratory of Inorganic Chemistry, University of Helsinki

The research group consists of professor Markku Leskelä, senior researchers Martti Klinga (1997-99), Gerhard Jany (1.1. - 3.6. 1997), Jose Dobado (1.1. - 5.5. 1997; 1.8. - 15.9. 1998), Jaouad El-Bahraoui (1.4. - 31.8. 1998) and Adnan Abu-Surrah (15.5. - 31.12. 1999), postgraduate students Timo Laine (1997-99), Kirsi Hyvärinen (1.1. - 31.8. 1997), Erkki Aitola (1.1. 1998 - 30.6. 1999), and Markku Hämäläinen (1.4. 1998

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[1] Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki

- 31.3. 1999) and students Mika Kettunen (1.9. - 31.12. 1999) and Ulla Piironen (1.9.- 31.12. 1999).

1.2 Collaboration

This project was connected to the Molecules on Sale programme of Tekes and had common steering committee with the polymerization catalyst project of that programme. The synthetic work carried out in this project has been in very close connection to another MATRA-project "Design of novel polymeric materials of next generation" (Dr. B. Löfgren).

University of Ulm has been an important collaborating unit in this project. The collaboration has involved longer visits by post docs (Jany, Abu-Surrah), exchange of graduate students (3 persons/year) and experimental collaboration in synthesis and structural characterization of catalyst precursors and polymerization.

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1997-1999.

Partner	Funding Organisation	1997	1998	1999	**Total**
UH	UH	150	150	150	**450**
	Tekes	400	580	600	**1580**
	Borealis Polymers Oy	250	250	-	**500**
	Graduate school	150	150	150	**450**
Total		**950**	**1130**	**900**	**2980**

2 Research Work

2.1 Objectives and Work Plan

The goal of this research was to synthesise new coordination compounds and study their polymerization catalyst properties. The aim was to work with structurally fully characterised complexes in order to get information how the polymer structure and properties depend on the catalyst structure. The starting point of the research was to study single site catalysts which are not metallocenes. The metallocenes were the first structurally fully known polymerization catalysts and in metallocenes the relation between ligand structure and polymerization behaviour and polymer structure is rational.

The research work has been divided to the following topics: (i) coordination compounds of early transition metals, (ii) coordination compounds of late transition metals, and (iii) co-operation with University of Ulm

2.2 Progress Report

2.2.1 Coordination compounds of early transition metals

Earlier we had studied several Ti and Zr alkoxo, phenoxo and β-diketonato complexes [40]. Complexes with bidentate ligands show good activity in ethylene polymerization if activated with MAO (methylaluminumoxane) [40]. The resulting polyethene had often high molar mass but broad molecular weight distribution showing that several catalytic centers have been present in the polymerization. These complexes are not active in propene polymerization and results from ethylene polymerizations with ionic activation were only modest.

As a continuation to the alkoxide studies a few siloxo complexes of group 4 metals were studied. Best results were obtained with diphenylsilanediol as the ligand. The Ti complex could be crystallized as a dimer and when activated with MAO the complex showed reasonable activity in ethylene polymerization.

2.2.2 Late transition metal complexes

Late transition metal complexes have been known as olefin oligomerization catalysts for decades. In mid 90s it was discovered that late transition metal complexes can also polymerize olefins [41]. The great advantage of the late transition metal complexes compared to early transition metal complexes is their tolerance against polar comonomers.

In this project the aim was to prepare and characterize new pyridinylimine-based diimine complexes of Ni(II), Pd(II) and Co(II), and to investigate their catalytic behaviour. The steric and electronic effect introduced by various ligands utilized as well as the effect of changing metal center was studied [34]. Eleven new complexes (Figs. 1 and 2) which contained differently substituted pyridinylimine derivatives were synthesized and their structures were determined by X-ray crystallography.

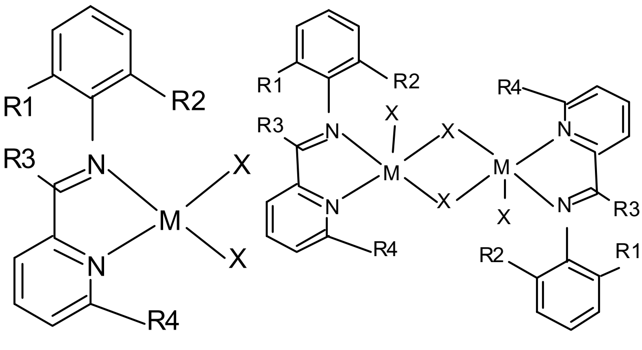

Fig. 1. Schematic drawing of the monomeric unsymmetric diimine complexes studied. M = Ni, Pd, or Co, R_{1-4} = alkyl groups which may be similar or different in one complex, X = halide. Depending on the metal and substituents R_{1-4} the complexes can crystallize as dimers.

The MAO activated Ni complexes polymerized ethene and produced polymer which was nearly linear or moderately branched with methyl branching predominating. Both the degree of branching and polymer chain length are highly dependent on reaction conditions and catalyst. Co complexes were able only to generate oligomeric oils. Pd complexes when activated with MAO were efficient in polymerization of norbornene (100 % conversion).

Palladium(II) complexes bearing ethylene-bridged didentate ligands containing donor atoms such as phosphorus, arsenic and sulfur were synthesised and studied as catalysts for strained cyclic olefins (Fig. 2). The active species were dicationic single component catalysts of type $[Pd(L\cap L)(NCCH_3)_2]$-$(BF_4)_2$.

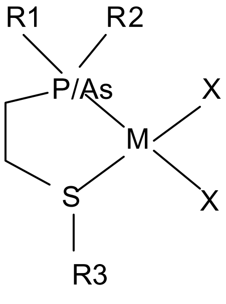

Fig. 2. Schematic structure of the Pd complexes with variable donor atoms.

Amorphous, high molecular mass polymers of norbornene and phenyl-norbornene (*endo/exo* ratio 80/20) could be produced by the dicationic Pd catalysts. With increasing the *trans*-influence of the donor atom in the ligands (P>As>S) the polymerization activity increases. Both molecular weight and thermal behaviour of the polymer can be tailored by using ethylene as chain transfer agent. The copolymerization of norbornene and carbon monoxide was possible and the glass transition temperature of polynorbornene could be lowered by introducing CO into the polymer chain [10,14].

New Fe(II) and Co(II) complexes of the general formula M(N∩N∩N)Cl_2 bearing 2,6-bis(imin)pyridyl ligands [A-N=C-Py-C=N-A] that carry bulky alkyl-free aromatic groups A (naphthyl, pyrenyl, benzyl, phenyl) or chiral cycloaliphatic moieties have also been synthesised. The Fe(II) complexes were very active in polymerization of ethylene in presence of MAO. Varying the steric bulkiness of the aromatic groups the activity, molecular weight and the microstructure of the polymer can be affected [19].

2.2.3 Co-operation with University of Ulm

During this project 35 different catalyst precursors have been examined. One important new metallocene type investigated unsymmetric substituted fluorenyl-indenyl zirconocenes which showed unique features in propene polymerization [3]. Their activity was high and the polymerization rate remained constant over hours. The complexes have two different coordination sites which lead to isotactic polypropenes with variable amounts of stereoerrors. The bulk properties of the polymer can be adjusted from flexible, semicrystalline thermoplastic to excellent thermoplastic elastic.

Several C_2-bridged palladium diphosphanes and diamines as well as unbridged palladium phosphanes were synthesised and studied (Fig. 3). When semi-fluorinated these complexes become electron-poor and they show superior polymerization properties in polymerization of 2-norbornene [13].

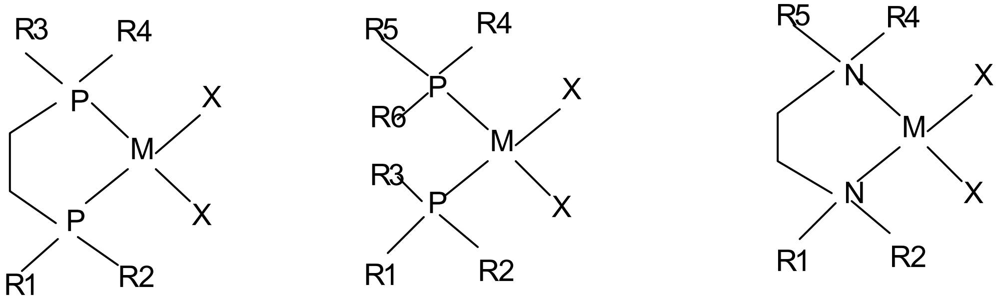

Fig. 3. Schematic pictures of diphoshane and diamine complexes. R_{1-6} are different aromatic groups which may be partially fluorinated. X represents halides.

Dicationic ruthenium(II) complexes containing bridged η^1: η^6 - diphosphino-arene ligands showed interesting ring-opening metathesis polymerization properties. The activation was made either by a diazo or ionic compound [11].

Four new substituted 1,4-diaza-2,3-dimethylbutadiene ligands were complexed with nickel and palladium (Fig. 4). The complexes represent C_2-symmetric diimines and they can be activated by MAO. Nickel complexes showed high activity in ethylene polymerization and the forming polymer was linear with high molecular weight and relative narrow molecular weight distribution [15].

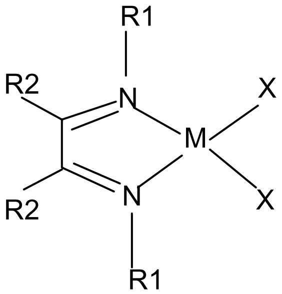

Fig. 4. Schematic presentation of Ni and Pd complexes bearing 2,6-diphenyl aniline moieties.

2.2.4 Co-operation with industry

Borealis Polymers Oy has supported this project both financially and materially. During the project several invention announcements have been sent to the company and out of them one patent was filed.

Collaboration was made also in investigating the use of UV-VIS spectroscopy in characterization of active species in catalysis. Metallocenes were suitable complexes for this type of studies and UV-VIS spectroscopy offers a fast and simple tool to study active metal center [16,17].

3 International Aspects

The most active collaboration has existed with University of Ulm and supported also by DAAD-Academy of Finland exchange programme. Every year 2-3 graduate students (1 month each) have visited the partner's laboratory. The visitors from Ulm have been: Ulf Dietrich, Wolfgang Huhn, Angela Mucke in 1997, Brigitte Lindner, Alexandra Abele in 1998 and Uwe Meier, Alexander Bauer and Jurgen Kukral in 1999.

The other institute with which we have had collaboration concerning also polymerization catalysts is University of Granada. Professor Molina visited for 1 month in 1997 and two post docs (Dobado and El-Bahraoui) have made longer visits in Helsinki.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
UH	Ref. journal art.	-	1	5	16	**22**	1-21
	Ref. conf. Papers	3	3	1	5	**12**	22-33
	Monographs	-	-	-	-	**-**	
	Doctoral dissert.	-	-	1	-	**1**	34
	Licentiate degrees	-	-	-	-	**-**	
	Master degrees	1	1	2	1	**4**	35-39
	Patents	-	1	-	-	**1**	40

5 Other Activities

Patents filed: T.V. Laine & M. Leskelä: A New Transition Metal Complex: Its Preparation, Its Intermediates and Their Preparation, Its Catalyst Systems and Their Use for Polymerization of Ethylenically Unsaturated Compounds. **Finn. Appl. 98 2090; PCT Int. Appl. WO 00 18 776.**

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CONTENTS

CONTROLLED GAS PHASE ROUTES TO NANO-STRUCTURED OXIDE AND METAL THIN FILMS AND POWDERS

Markku Leskelä[1], Esko Kauppinen[2], Jaan Aarik[3] and Suvi Haukka[4]

Abstract

This consortium consisted of two main projects carried out by Laboratory of Inorganic Chemistry at University of Helsinki (UH) and Aerosol Technology Group at VTT Chemical Technology. Two other partners, Institute of Materials Science at University of Tartu (UT) and ASM Microchemistry (ASMM), were associated to UH. The goal of the research was to study new synthetic routes for Al_2O_3, TiO_2, SiO_2, Cu, Pd and Mo thin films and powders by studying the reaction mechanisms *in situ* both on the surface of the substrates and in gas-phase when the particles are formed. The research was focused to two methods: Atomic Layer Deposition of thin films and gas-phase chemical routes to particle formation.

An important task of the work was to develop and construct equipment for *in situ* characterization of ALD processes. Quartz crystal microbalance (QCM) and quadrupole mass spectrometer (QMS) were the *in situ* methods selected since they can operate in the conditions met in the flow-type ALD reactors. The ALD-QCM-QMS instrument is unique in the world and it is working properly. The other aim of the ALD studies was preparation and characterization of thin films the focus being in oxides and besides those mentioned above other important oxides like those of Zr, Hf, Nb and Ta were studied as well. A third target in the studies was to investigate new precursors for thin films taking in account that they could possibly be used in powder syntheses, too.

Several oxide thin films were deposited and characterized. Most important innovation in these studies was the discovery of a so-called water-free oxide process where no separate oxygen precursor is used. Instead, oxygen is introduced as metal alkoxide which reacts with metal halide (or alkyl compound) and forms oxide film.

The focus in metal films was in Cu but deposition of all metal films by ALD is difficult. The key is to find an efficient reducing agent. Reducing agents are in a key role also in ALD deposition of transition metal nitride films. In the reducing agent studies the possible candidates were tested both in metal and nitride depositions. The nitride studies were successful and a few new processes could be developed.

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In the QCM measurements made in Tartu the focus was in real-time monitoring of different TiO_2 processes but Zr and Si oxides were studied as well. The investigations revealed the differences in adsorption of different Ti and Zr precursors on hydoxyl terminated surface. The comparison between chloride and iodide precursors showed that chloride forms more stable surface species than iodide. Hydrogen peroxide was compared with water as oxygen precursor. Especially at low temperatures the higher reactivity of H_2O_2 was beneficial compared to water. The use of molecular oxygen as oxygen precursor in connection with TiI_4 represents a totally new ALD process.

In ALD studies made on high surface area powders the adsorption mechanisms of several metal precursors were studied. The mechanistic studies made by *in situ* QCM and QMS measurements could be correlated with the experiments made on high surface area powders but the water-free processes studied on high surface area powder revealed the importance of the time scales in ALD processes.

In particle formation studies at VTT the aim was to improve the basic understanding of mechanisms in gas-phase and surface chemical reactions, particle growth via collision/coalescence, crystallite formation and growth of aerosol particles. Two primary materials were chosen to the studies: copper and titanium dioxide. A low temperature method of producing copper nanoparticles based on gas-phase reaction of metal-organic precursors was studied in ambient pressure (1 atm). A controlled synthesis and particle formation mechanisms of TiO_2 particles by aerosol decomposition method was studied. Two kinds of vertical laminar flow reactors have been designed and constructed during the project. It was shown that the size of primary particles could be varied in the range of 1 to 120 nm. The decomposition temperature and composition of the particles formed depended strongly on the atmosphere in the reactor.

In mechanistic studies of ultrafine TiO_2 aerosol particle crystallization the modelling of the aerosol reactors indicated that buoyant forces are important. The size change and crystallization of TiO_2 particles was studied by tandem differential mobility analyzer system and transmission electron microscopy. The formation of different phases at different temperatures was investigated. A schematic picture of the mechanisms during precursor droplet transformation to a single crystal TiO_2 particle was developed. Crystallisation of 20-40 nm diameter TiO_2 in an aerosol reactor starting from metal alkoxide precursor was studied. The most important finding was that the particles were single crystalline anatase at 600-1200 ºC. The high stability of the anatase phase was attributed to the defect-free particles, free of crystal-crystal attachment, and the faceted shape.

1 Partners and Funding

1.1 Laboratory of Inorganic Chemistry, Univeısity of Helsinki

The research group consists of subproject leader professor Markku Leskelä, senior researchers Mikko Ritala and Kaupo Kukli, postgraduate students Petra Alen, Marika Juppo, Raija Matero, and Matti Soininen. ASM Microchemistry and University of Tartu acted in this project as subcontractors to University of Helsinki. University of

Tartu was paid FIM 70 000 yearly by UH for the in situ growth studies. ASM Microchemistry gave the facilities to Matti Soininen for the growth studies on high surface area powders.

1.2 Aerosol Technology Group, VTT Chemical Technology

The research group consists of subproject leader, research professor Esko I. Kauppinen, senior researchers Dr Albert Nasibulin, Dr Unto Tapper, Dr Olivier Richard, Dr David P. Brown, Dr Jorma K. Jokiniemi, Dr Bertram Schleicher, and Dr Kari E. J. Lehtinen and postgraduate students Petri Ahonen, Jorma Joutsensaari and Anna Moisala.

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000.

Partner	Funding Organisation	1998	1999	2000	**Total**
UH	UH	150	150	150	**450**
	Tekes	630	630	630	**1890**
	Academy	150	200	200	**550**
	Graduate school	150	150	150	**450**
VTT	VTT	320	317	317	**954**
	Tekes	480	475	475	**1430**
Total		**1880**	**1922**	**1922**	**5724**

2 Research Work

2.1 Objectives and Work Plan

The objectives of this research were to study and develop synthetic routes for technologically important nanostructured films and powders of oxides and metals. More specifically, the research was focusing on two methods: Atomic Layer Epitaxy (or Atomic Layer Deposition, as called nowadays) of thin films and gas-phase chemical routes to particle formation. An important task in that work was a development and construction of the required equipments, especially the *in situ* characterization tool for ALE. Another part of the research involved preparation and characterization of thin films and powders the same precursors in both processes.The materials originally chosen to be examined were Al_2O_3, TiO_2, SiO_2, Cu, Pd and Mo which all find technical importance in various applications. However, in the course of the work this choice was not considered fixed but was on timely basis checked and revised and materials which were recognized to have become of an utmost importance, like new high-k dielectrics for CMOS transistor gate oxides, were investigated. Many of the changes led to siginificant inventions and patent applications. In thin film research the major revisions to the original plan include - moving some emphasis in the ALD research from metals to transition metal nitrides - extending the selection of oxide thin film materials examined to cover also ZrO_2 and other potential high-k gate oxides- focusing the research at Microchemistry (subsequently ASM-Microchemistry) more on reaction mechanisms instead of catalytic properties

In powder studies the aim was to improve the basic understanding of mechanisms in gas-phase and surface chemical reactions, particle growth via collision/coalescence as well as crystallite formation and growth of the product aerosol particles. During the course of the project, two primary materials were chosen. A low temperature powder synthesis method of producing copper nanoparticles based on gas-phase reaction of metal-organic precursors was studied in ambient pressure (1 atm). A controlled synthesis and particle formation mechanisms of TiO_2 particles by aerosol decomposition method was studied.

2.2 Progress Report: Common Themes

In the collaborative research synergy was looked for by examining the same kind of chemistries from different view angles (ALE on planar vs porous surfaces vs particle formation reactions) and from a shared use of characterization techniques. In ALE research the different approaches gave results which complemented and supported each other. The starting point for the particle formation processes, i.e. the chemical routes employed at VTT at the beginning of this project, was quite different from ALD chemistry but some closing took place. The key ideas in applying the ALE reactions in particle formation became well transferred and will form a topic of future research at VTT.

2.3 Progress Report: Progress by the Laboratory of Inorganic Chemistry, UH

2.3.1 *In situ* characterization of ALD chemistry

The objective of the *in situ* studies was to gain detailed understanding of the elementary ALD reactions. Important issues in this respect are the adsorption/reaction mechanism of each precursor, the rate with which the saturation is reached, and the contributions from undesired reactions like precursor decomposition or etching of the film by the precursor. For ensuring high relevancy the *in situ* studies should be carried out under conditions of the flow type ALD reactors which is the most common reactor.

Therefore, a vital part of the work was the construction of the *in situ* equipment in connection with the ALD reactor.

2.3.1.1 Equipment

Recognizing the special requirements arising from the flow type reactor conditions, i.e. about 1 mbar reactor pressure, relatively high operation temperature, fast changes during the ALD pulses and a relatively small amount of byproducts (about 10^{14} molecules per cm^s) formed during each step, a quadrupole mass spectrometer (QMS) and a quartz crystal microbalance (QCM) were chosen as the methods for analyzing the chemical species in the gas phase and on the surface, respectively.

The development of the *in situ* characterization equipment proceeded through two steps. The setup existing at the beginning of this project consisted of only a QMS which was a standard residual-gas-analyzer (mass range 1 - 300 amu, fixed ionization energy of 102 eV, Faraday cup detector) connected to the ALD reactor through a glass capillary and backed by a turbomolecular [1]. The reactor was further modified so that the total reactive surface area became enlarged to about 3500 cm^2 as needed to produce byproducts in amounts detectable by QMS.

The first version has some limitations complicating the data interpretation. Therefore, a second version was developed basing on a sophisticated triple filter QMS with a mass range of 1 - 510 amu, variable ionization energy of 0 - 150 eV, and dual Faraday/electron multiplier detector. Also the sampling was modified from a capillary to a 20 or 50 μm orifice. In addition, a QCM was added to this setup enabling simultaneous measurements of the surface layer weight and the gas phase composition in the ALD process (Fig. 1) [55].

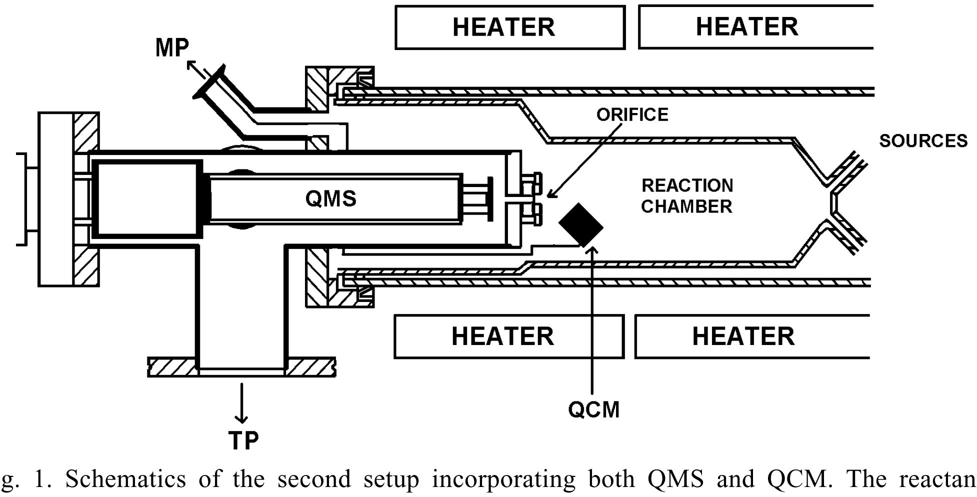

Fig. 1. Schematics of the second setup incorporating both QMS and QCM. The reactants transported by the carrier gas enter the reaction chamber from the right and are pumped by the mechanical pump (MP). A small part of the total flow is pumped by the turbo pump (TP) through the sampling capillary and the QMS chamber.

2.3.1.2 Results

The following ALD processes have been examined in the *in situ* studies:
$Al(CH_3)_3$ - H_2O; $Al(CH_3)_2Cl$ - H_2O; $TiCl_4$ - H_2O; $Ti(OCH(CH_3)_2)_4$ - H_2O; $M(OC_2H_5)_x$ - H_2O (M = Ti, Ta, Nb); $Sr(C_5{}^iPr_3H_2)_2$ - H_2O; $Ti(OCH(CH_3)_2)_4$ - H_2O - $Sr(C_5{}^iPr_3H_2)_2$ - H_2O; $ZrCl_4$ - H_2O; $ZrCl_4$ - $Ti(OCH(CH_3)_2)_4$; $NbCl_5$ - H_2O; $TiCl_4$ - NH_3 and $TiCl_4$ - $Al(CH_3)_3$ - NH_3.

In practise, D_2O and ND_3 were used instead of H_2O and NH_3 to better distinguish the reaction byprodcuts from the species directly formed from the metal precursors. Studies on the $Al(CH_3)_3$ - D_2O process [1-3] revealed that the reaction byproduct CH_3D was liberated during both $Al(CH_3)_3$ and D_2O pulses. In the first study, done with the first equipment and thus only with QMS, it was found that with increasing growth temperature the ratio of CH_3D liberated during the $Al(CH_3)_3$ pulse to that liberated during the D_2O pulse decreased. This means increasing dehydroxylation at elevated temperatures and it is in a good accordance with the reported thermal stability of hydroxyl groups on amorphous Al_2O_3 surface [2]. On the other hand, the surface may be hydroxylated by increasing the water dose or elongating the water pulse. The surface hydroxylation has another important consequence in that it opens a possibility to increase the oxide growth rate (see below).

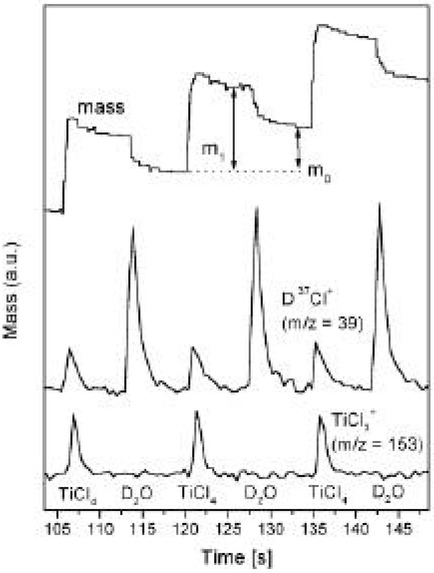

Fig. 2 Example of in situ characterization results obtained on a $TiCl_4$-D_2O process. The QMS data shows the time variation of the ions $TiCl_3^+$ (m/z = 153) and $D^{37}Cl^+$ (m/z = 39), the latter being the main reaction byproduct. Important features of the QCM data are m_1 and m_0 which denote the mass changes during the $TiCl_4$ pulse and during one completed ALD cycle, respectively, and are related to the intermediate surface species $-TiCl_x$ and TiO_2, respectively. In an agreement with each other, QMS and QCM results show that one -Cl ligand of $TiCl_4$ is released during the $TiCl_4$ pulse and the remaining three during the D_2O pulse.

$Al(CH_3)_2Cl$ - D_2O process [41] is interesting especially in that it allows an estimation of the relative reactivities of -Cl and $-CH_3$ ligands. According to QMS, methyl groups were released during both $Al(CH_3)_2Cl$ and D_2O pulses whereas chlorine was released mainly during the latter.

$TiCl_4$ - D_2O [7] *process* was also found to proceed at moderate temperatures through a mechanism where the adsorbing metal precursor loses some of its ligands in exchange reactions with surface hydroxyl groups (Figure 2). However, as the temperature exceeded 250 °C, approximately, in average less than one Cl per Ti was released during the $TiCl_4$ pulse, thus suggesting that part of $TiCl_4$ was adsorbing molecularly.

Studies on the $M(OC_2H_5)_x$ - D_2O (M = Ti, Ta, Nb) agreement with the QCM processes[1,4,67] revealed significantly different behavior as compared with the other oxide processes. The reaction byproduct C_2H_5OD was liberated almost exclusively during the D_2O pulse. However, the situation may be more complicated and a reaction with the hydroxyl groups, adsorption of C_2H_5OD and subsequent replacement of the adsorbed C_2H_5OD by D_2O may happen.The mechanism was recently verified for Nb_2O_5 in separate experiments where QCM indicated a mass increase when ethanol was dosed on freshly prepared Nb_2O_5 film [67]. Besides ethanol, $(C_2H_5)_2O$ was formed at high temperatures during the $M(OC_2H_5)_a$ pulses. In the case of $Ti(OC_2H_5)_4$, $(C_2H_5)_2O$ appeared to arise only from the decomposition of the titanium ethoxide but with $Nb(OC_2H_5)_5$ and $Ta(OC_2H_5)_5$ it was formed also in the exchange reactions.

$Ti(OCH(CH_3)_2)_4$ - D_2O process [5,6,55] was found to proceed at 150 - 250 °C through a mechanism where two isopropoxide ligands were released during each step. Above 250 °C $Ti(OCH(CH_3)_2)_4$ started to thermally decompose affecting the growth mechanism.

$Sr(C_5{}^iPr_3H_2)_2$ - H_2O process [5] was examined both separately and in combination with the $Ti(O^iC_3H_8)_4$ - D_2O process for the deposition of $SrTiO_3$. In the case of SrO no saturation of the mass increment was observed and this was attributed to $Sr(C_5{}^iPr_3H_2)_2$ decomposition and hydroxylation of SrO to $Sr(OH)_2$. When combined with the TiO_2 deposition, SrO was found to deposit more efficiently on top of TiO_2 layer than on top of itself.

$NbCl_5$ - D_2O process [67] was examined to elucidate the reason for the failure in employing this process in film growth in the early 90s. The suggestion made then on basis of thermodynamic calculations that $NbCl_5$ is etching Nb_2O_5 by forming volatile $NbOCl_3$ was now verified. Further, the results suggested that Nb_2O_5 could be deposited starting from $NbCl_5$ if that is first converted into $NbOCl_3$.

$ZrCl_4$ - $Ti(O^iC_3H_8)_4$ process [39] represents the new ALD oxide processes where no separate oxygen sources are used but metal alkoxides serve as both metal and oxygen sources (see 2.3.2.1). The *in situ* studies verified the suggested reaction mechanism where an alkyl halide is formed as a byproduct.

$TiCl_4$ - ND_3 and $TiCl_4$ - $Al(CH_3)_3$ - ND_3 processes [40] were the first nitride processes examined with the *in situ* QMS-QCM-ALD equipment. The results showed that -ND_x surface groups play an important role as surface intermediates similar to the -OD groups in the oxide processes. Therefore, the low growth rate obtained in transition metal nitride processes appear to be related to the low density of -NH_x groups. $Al(CH_3)_3$ was recently found to serve as an efficient reducing agent in ALD of transition metal nitrides (see 2.3.2.2). The in situ studies on the role of $Al(CH_3)_3$ in ALD of Ti(Al)N showed that the reaction mechanism was quite complicated.

2.3.2 Film growth experiments

2.3.2.1 Oxides

Water free processes of a type MCl_x - $M'(OR)_y$ opened up an entirely new chemical approach to ALD of binary or mixture oxide films. A patent application and a paper in Science [10] were written on these findings. The key aspect in this chemistry is that metal compounds themselves serve as oxygen precursors. Since no water or other separate oxygen compounds are needed, one may expect that the deposition process is less oxidizing for the substrate surface. This can have enormous impacts in silicon IC technology. A promising result of the new chemical approach is shown in Figure 3 where a cross sectional high resolution TEM image of the Al_2O_3-Si interface is shown with no distinguishable interface layer.

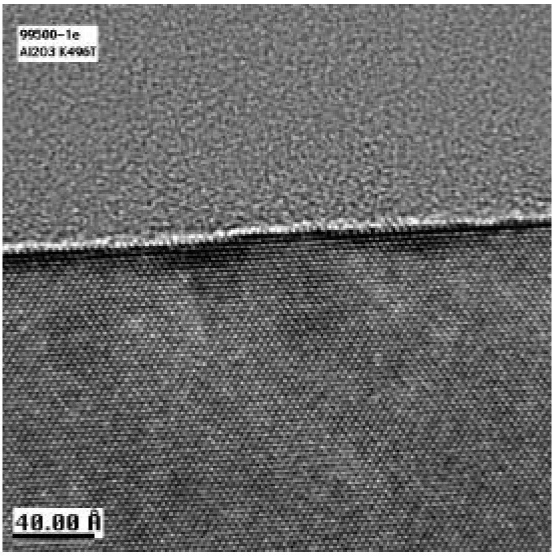

Fig. 3. A high resolution cross sectional transmission electron microscope image of an Al_2O_3 film on silicon.

This new chemical approach was also evidenced rather general as numerous precursor combinations gave good film growth rates [10]. Both binaries and mixtures have been obtained. One remarkable result of this new chemical approach is the incorporation of silicon into oxide mixtures. Until now, no facile chemistry has been found for depositing SiO_2 by ALD. With the present chemistry significant amounts of silicon were incorporated into Zr-Si-O mixtures, a material of a great potential for gate oxides.

Growth rate enhancement by using larger water doses [13] was another fundamental finding on ALD oxide processes. This effect was observed in all the processes examined and it was related to an increasing hydroxylation of the oxide surface after the water pulse (c.f. 2.3.1.1). The increase was in some cases, like with In_2O_3 and ITO, as much as 100 % [38] and may therefore have important consequences on the cost-effectiveness of these processes.

TiI_4 - H_2O_2 (H_2O) combinations were examined as new processes for TiO_2 [15] in research co-operation with the Uppsala University. The use of hydrogen peroxide was found important to avoid titanium suboxides. This TiO_2 deposition chemistry was examined also as a part of the process aimed for growing ferroelectric Bi-Ti-O films [17]. The TiI_4 - H_2O_2 process was also subjected to *in situ* QCM measurements in Tartu. Likewise, a ZrI_4 - H_2O_2 (H_2O) process was examined in co-operation with Uppsala and Tartu universities [33,34].

$TaCl_5$ - H_2O process [12,14] was examined in detail in a temperature range of 300 - 400 °C where the partial etching of Ta_2O_5 by $TaCl_5$ begins. Because of the competing effects of the etching, crystal growth and surface migration, quite peculiar behavior was observed in morphology, crystallinity and optical properties of the films.

The growth of ZrO_2 from alkoxide precursors was was studied, however, in a contrast with TiO_2, characteristic to the ZrO_2 ALD from $Zr(OEt)_4$, $Zr(O^iPr)_4$, and $Zr(O^tBu)_4$ was significant precursor decomposition. Only with $Zr(O^tBu)_4$ reasonably good films could be deposited [21], but even these were much lower in quality than those obtained from $ZrCl_4$. Mixed ligand metal alkoxide derivatives were examined as precursors for ZrO_2 and Nb_2O_5 using donor functionalized bidentate dimethylaminoalkoxide (-$OC_2H_4N(CH_3)_2$ = dmae) or β-diketonate ligands. ZrO_2 could be grown from $Zr(dmae)_4$, $Zr(O^iPr)_2(dmae)_2$ and $Zr(O^tBu)_2(dmae)_2$ but no true self-limiting growth could be achieved.

2.3.2.2 Metals and transition metal nitrides

A key issue in development of metal ALD processes for metals is finding effective reducing agents. Despite numerous trials, no major success was reached. The reducing agents are in a central role also in ALD of transition metal nitrides. First results indicated that the new reducing agents looked for metal depositions could make more progress in the nitride research and therefore some of the focus was shifted from the metals to the nitrides.

MCl_x - $Al(CH_3)_3$ - NH_3 [26] was recognized as a process enabling growth of transition metal nitrides with higher rates and at lower temperatures than possible with the conventional MCl_x - NH_3 chemistry. Relatively high aluminium and carbon residues were incorporated into the films. MCl_x - $H_2NN(CH_3)_2$ [22] is another process identified through the metal growth experiments. Also with this process the growth temperatures may be lowered far below those in the MCl_x - NH_3 processes. Allylamine and tert-butylamine [29] were identified as the most promising reductive nitrogen sources giving marked improvements in properties of TiN and TaN films deposited at 400 °C. A patent application has been made on these processes.

Metal growth studies focused nearly completely on copper because of its vast technological potential in IC metallizations. The copper compounds examined include the β-diketonates $Cu(hfac)_2xH_2O$ and $Cu(thd)_2$, halides CuCl and CuI, and a cyclopentadienyl $(Et_3P)CuCp$. Numerous reducing agents were tested, like H_2, Zn, NH_3, tert-butylamine, allylamine, dimethyl hydrazine, hydrazine hydrate, hydroquinone, triethylamine borane, $SnCl_2$, SnI_2, azo-tert-butane, $Al(CH_3)_3$. These were combined in various ways with the copper precursors but no good ALD growth was achieved.

2.3.3 Real-time Studies on Atomic Layer Growth of Oxide Thin Films

The kinetics of Atomic Layer Deposition was studied at University of Tartu in a hot-wall flow-type reactor using a QCM. The aim of the studies was to investigate the kinetics of ALD oxide processes in order to describe the mechanisms of the surface reactions and reveal (i) the temperature ranges suitable for growing oxide films and (ii) the mechanisms limiting the growth rate. In addition, microstructure and crystallization of the films were studied. The following processes were studied: titanium ethoxide ($Ti(OC_2H_5)_4$) and H_2O; titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$) and H_2O; titanium isopropoxide and H_2O_2; titanium chloride and H_2O (H_2O_2, O_2); titanium iodide and H_2O_2 (H_2O, O_2); zirconium chloride and H_2O (H_2O_2); zirconium iodide and H_2O_2 (H_2O); silicon iodide and H_2O_2, and silicon tetraethoxide (TEOS) and H_2O_2.

Amorphous films of high optical quality can be grown from $Ti(OC_2H_5)_4$ and water at 100-150 °C and nanocrystalline films are obtained at 180 °C and higher temperatures. According to the QCM data in average less than one hydroxyl group reacted with the absorbing titanium ethoxide molecule at substrate temperature of 200-270 °C. Thus, titanium ethoxide is partially absorbing molecularly and steric hindrance limits the growth rate to 0.6 Å/cycle at 100-270 °C [33].

The $Ti(OCH(CH_3)_2)_4$ and water process showed similar features as the ethoxide -water process. In adsorption on the -OH surface the ethoxide and isopropoxide behave differently. Isopropoxide looses two ligands in adsorption [34]. By changing water to hydrogen peroxide the growth rate could be doubled at low temperatures (100-150 °C). The benefits of hydrogen peroxide appear at low temperatures where high quality amorphous films can be grown at good growth rate (1.2 Å/cycle) [42,45].

TiI_4-H_2O_2 process studied showed that the adsorption of the iodide did not saturate completely and the growth rate increased also with the H_2O_2 dose. At lower temperatures and short pulse times 1-2 iodo ligands are released in adsorption while at higher temperatures/long pulse times 3 iodo ligands may release [16]. In the $TiCl_4$-H_2O process, on the other hand, the number of chloro ligands released is 1, 0 and 2 at temperatures of 100-150 °C, 200-350 °C, and above 400 °C, respectively [43]. The films made by the iodide process are polycrystalline (anatase) already at low temperatures and the rutile phase is appearing at substrate temperatures below 300 °C [49].

The use of molecular oxygen as the oxygen source was studied in connection with the titanium precursors. No oxide film was formed when chloride or isopropoxide were used as precursors but iodide did react with oxygen. The TiI_4-O_2 process showed similar unsaturative behaviour as the hydrogen peroxide process. Oxygen is less reactive than hydrogen peroxide and therefore slightly higher growth temperatures are needed [44].

ZrO_2 processes were also studied in Tartu and the chloride and iodide processes were compared. The results show that chloride saturates more completely in adsorption and forms more stable surface intermediates than iodide. Iodide tends to decompose and the growth rate obtained in the $ZrCl_4$ process is higher than that in the ZrI_4 process. $ZrCl_4$ allows growth of oxide films at lower temperatures than ZrI_4 [19,48].

The real-time measurements on SiI_4 - H_2O_2 and TEOS - H_2O_2 processes at 250-350 °C revealed that the reactions are very slow and no film growth is taking place during pulse times of tens of seconds. The main reason for this result is the insufficient sticking of silicon precursors on the surface.

2.3.4 Atomic Layer Deposition of Al_2O_3, TiO_2, ZrO_2 and SiO_2 on High Surface Area Powders

The aim of this work carried out at ASM Microchemistry was to use high surface area materials in an atomic level study of the ALD growth mechanisms of selected oxides. Because of the number of reactive sites on the substrate and the number of metal species bound in one atomic layer can be precisely determined using standard techniques known in analytical chemistry. The techniques employed included elemental analyses by a CHN-analyser for light elements and neutron activation analysis for metal elements, as well as different spectroscopic techniques (IR, Raman, NMR) for the species on the surface. Silica was mainly used as a substrate. Same experiments were also carried out on porous silicon made by electrochemical etching with HF:ethanol 1:1 as electrolytic solution.

The adsorption of the following complexes where studied: $Zr(OEt)_4$, $Zr(thd)_4$, $HfCl_4$, $Hf(OEt)_4$, $Hf(thd)_4$, $NbCl_5$, $Nb(OEt)_5$, $TaCl_5$, $Ta(OEt)_5$. The surface was saturated and next a water pulse was given. All reaction were made at seven different temperatures. The adsorption mechanism of these complexes could be deduced from the analytical data. The difference in adsorption of alkoxides and chlorides could be seen. These studies on high surface area powders gave a good basis for the *in situ* studies of thin film growth but the different time scales must be take in account and they play a significant role.

The water-free oxide process developed at UH was also studied on high surface area powders. The studies were focused to Ti-Zr-O system using $Ti(i\text{-}OPr)_4$, and $ZrCl_4$ as precursors. Carbon content was low in all samples but chlorine content depended on temperature and pulsing order used in the process. Best results were obtained at low temperatures (175 °C). Especially $Ti(i\text{-}OPr)_4$ begins easily to decompose on chlorine surface above 175 °C. When working with powder surfaces the proper combination of precursors plays a key role.

2.4 Progress Report: Progress by the Aerosol Technology Group, VTT Chemical Technology

2.4.1 Copper and copper oxide nanoparticles formation by chemical vapor nucleation from copper(II) acetylacetonate

Background. Copper and copper oxide particles are of significant interest. Applications for Cu powder include gas testing facilities, bronze bearings, electrical connections, conductive epoxys, metal-bonded abrasive wheels and cutting tools, and braking systems. Ultra-fine Cu particles may find new applications in metal injection molding, electronics, ceramics and thick/thin film applications. CuO_x may be applied in thin-film oxygen pressure sensors, as a binder in pastes for microelectronic circuits, and as a p-type semiconductor. In addition, copper and copper oxide particles may be applied as high surface area catalysts for different chemical processes.

Little work has been devoted to Cu and CuO_x particle formation by using chemical methods. The obvious advantage of these methods is the possibility to produce nanosized particles at relatively low temperatures and ambient pressure. The current work Cu and CuO_x particle formation has been examined by chemical vapor nucleation from copper (II) acetylacetonate ($Cu(acac)_2$), which has a suitable equilibrium vapor pressure and a relatively low decomposition temperature (t_{dec}=286 °C). The goals of the investigation are to produce nanoparticles at ambient pressure and at as low temperature as possible, to characterize the obtained nanoparticles synthesized with various reactor conditions, and to deduce the mechanisms of the precursor decomposition and nanoparticle formation.

Experimental methods. Two kinds of vertical laminar flow reactors have been designed and constructed. The equipment consist of a saturator, laminator and furnace. The flow of nitrogen carrier gas passes through heated $Cu(acac)_2$ powder and then the vapor-gas mixture enters to the furnace where the temperature is maintained higher than t_{dec}. The second setup was designed for the use of a suitable reagent (hydrogen and/or water vapor) to increase the decomposition rate of the precursor and to avoid the CuO_x formation. Nitrogen carrier gas saturated by $Cu(acac)_2$ vapor is mixed with reagent flow inside the furnace. The formation of supersaturated Cu or CuO_x vapors leads to the nucleation process and further growth of particles via condensation and agglomeration.

The aerosol number size distributions were measured by a differential mobility analyzer (DMA) system. The morphology, the primary particle size, and the crystallinity of the particles were investigated with a field emission TEM (Philips CM200 FEG) and SEM (Leo Gemini DSM982). An electrostatic precipitator was used to collect the aerosol particles on carbon coated copper grid. Electron (ED) and X-ray diffraction (XRD) were used for detection of the crystalline phase. Qualitative elemental analysis of particles was carried out with an energy dispersive X-ray spectrometer (EDS). The precursors and products were also analysed by thermogravimetry and infrared spectroscopy. A gas downstream of the furnace was collected into a retort and then analyzed using a gas chromatography mass spectrometer (JEOL SX-102).

$Cu(acac)_2$ decomposition in N_2 atmosphere. The experiments were performed in the precursor vapor pressure range from 0.06 to 44 Pa and at furnace temperatures of 432, 596, and 705°C. At the furnace temperatures of 432 and 596 °C only crystalline Cu particles were produced. At 705 °C the crystalline product depended on the precursor vapor pressure: Cu particles were formed at $P_{prec}>10$ Pa, Cu_2O at $P_{prec}=1$ Pa, and a mixture of the metal and oxide at intermediate vapor pressures.

The results could be explained by the kinetic restriction of Cu particle growth. The formation of Cu_2O particles occurs due to the surface reaction of the decomposition products of which CO_2 is the most important. A semiempirical phase diagram for the crystalline products made shows the boundary for the appearance of Cu_2O and is in agreement with the experimental results [42].

$Cu(acac)_2$ decomposition in the presence of O_2. Formation of nanometer-sized Cu_2O and CuO nanoparticle was studied by thermal decomposition of $Cu(acac)_2$ at three temperatures 432, 596 and 705 °C at precursor vapor pressure of 16 Pa. Two O_2/N_2 mixtures (0.5/99.5 and 10/90) have been used as carrier gas. Computational fluid dynamics simulations showed the existence of a recirculation region in the beginning of the reactor. The size of primary particles depended on the experimental conditions and varied from 10 to 200 nm. Introduction of oxygen in the carrier gas increased the decomposition rate and cleaned CuO_x particles [51].

The composition of the products depends on the oxygen content in the carrier gas: the higher the oxygen concentration the higher oxidation state of Cu. Higher temperatures favor the formation of the thermodynamically more stable phase CuO. A model taking into account the reaction mechanisms during the particle formation was created. The model allowed to build a phase diagram of the products formed. Fig. 4 shows the type of the diagram though presented in that figure for H_2O-N_2 system.

***Cu(acac)$_2$ vapor decomposition in the presence of hydrogen and/or water vapor*.** Cu and Cu_2O particle formation was studied in the presence of H_2 and H_2O vapor in N_2 carrier gas. The presence of hydrogen did not significantly affect the decomposition rate. The precursor decomposition was enhanced when water vapor was introduced into the system. The decomposition reaction pathway can be divided into three steps: formation of gaseous hydrate complex; a proton transition from the coordinated water to a ligand and release of gaseous acetylacetone; the partial destruction (oxidation) of the ligands and a reduction reaction of Cu^{2+} to Cu^0. The formation of copper particles initiates catalytic surface reactions where the organic decomposition products form low volatile long chain compounds containing ketone, alcohol, ester, and ether groups [52].

The effect of the experimental conditions on product compositions is presented in Fig. 4. It is worth to note that at the temperatures 432 °C and 596 °C the phase of the formed particles was changed from Cu to Cu_2O when the vapor precursor pressure was decreased. The formation of Cu_2O particles occurs due to the surface reaction of water vapor and copper dimers. Particle size distributions were studied in the presence of water and the size of the primary particles depended on the precursor vapor pressure.

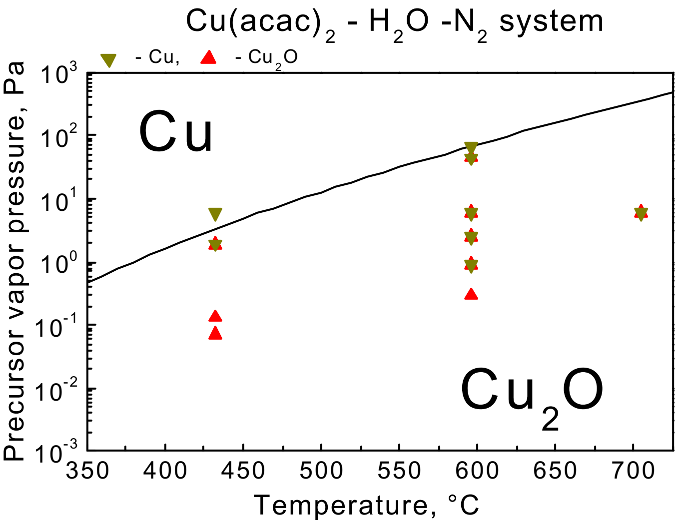

Fig. 4. The phase diagram of $Cu(acac)_2$ decomposition products in the presence of water vapor.

As conclusion, in decomposition of copper (II) acetylacetonate vapor and subsequent crystalline particle formation the most drastic effect is observed when oxygen and water vapor are introduced into the reactor. The temperature of complete decomposition decreases from 705 °C in nitrogen to 432 °C in water vapor. The mechanisms of copper and copper oxide particle formation during the precursor decomposition in the inert atmosphere and in the presence of the water or oxygen are proposed in Fig. 5.

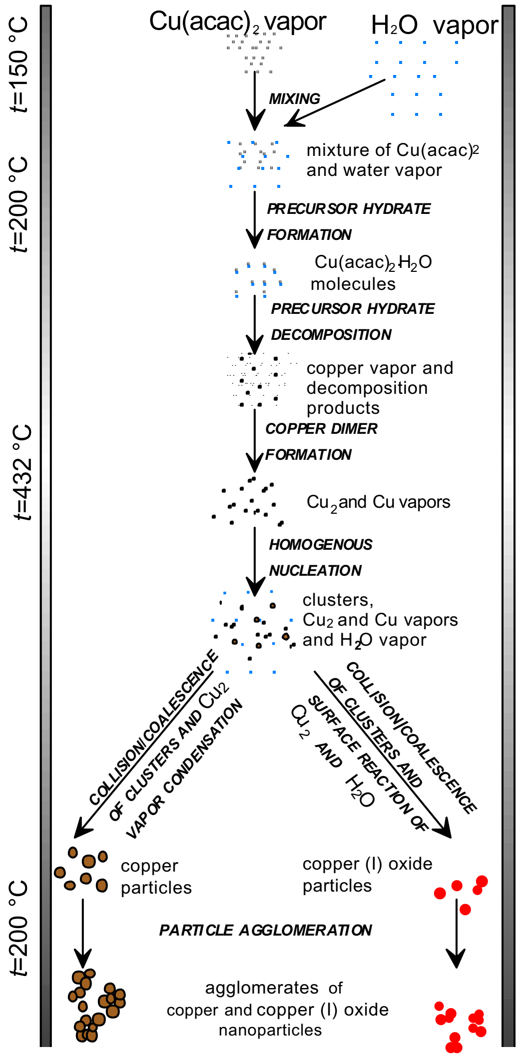

Fig. 5(a). The schematic presentation of copper and copper (I) oxide particle formation by the Cu(acac)$_2$ vapor decomposition in the presence of water vapor.

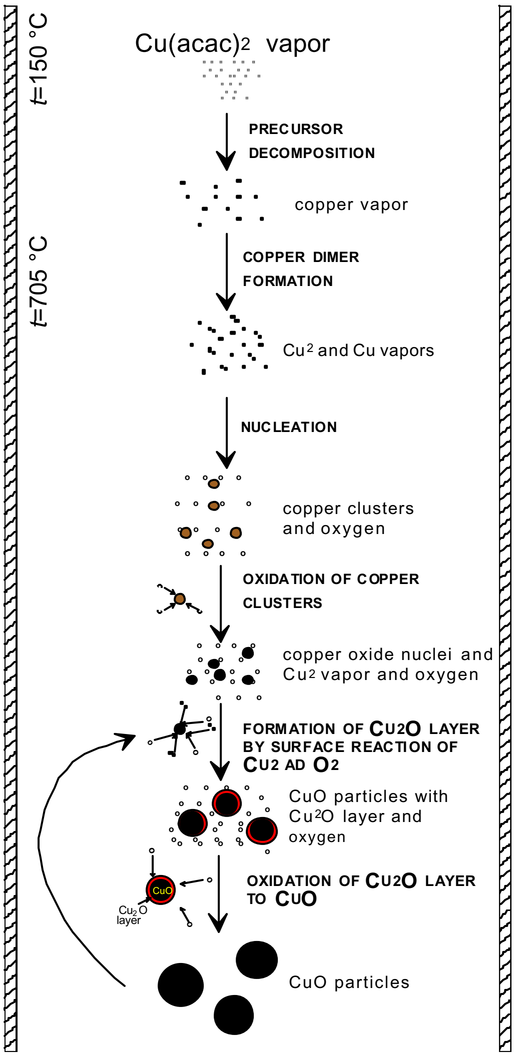

Fig. 5(b). The schematic presentation of copper (II) oxide particle formation by the Cu(acac)$_2$ vapor decomposition in the presence of oxygen.

2.4.2 Mechanistic studies on ultrafine TiO_2 aerosol particle crystallization

After the first results on the TiO_2 particle synthesis [53,54,66] the main objective was to study the mechanisms of TiO_2 crystallization. The modeling of the aerosol reactors indicated that the buoyant forces are important [67]. Also, the experiments on anatase crystallization showed way to a controlled experimental set-up [55]. The size change and crystallization of TiO_2 particles in an aerosol flow reactor was studied by tandem differential mobility analyzer system and TEM [56]. Computational fluid dynamics (CFD) was used to examine the effects of flow, heat transfer and buoyancy on particle trajectories through the reactor. Solid particles of hydrated TiO_x were prepared and size classified. A decrease in the particle size was observed up to 500 ºC due to combustion and dehydration. A further decrease was observed between 600 and 1000 ºC due to TiO_2 crystallization and the phase change from anatase to rutile. The increase of mobility diameters were observed above 1000 ºC for 60 nm particles and above 1200 ºC for 120 nm particles. At these temperatures the crystallite size reached the particle diameter and single crystal particles were formed. The increasing mobilities were due to the crystal habit formation that created faceted particles and an increased aerodynamic shape factor. Titanium dioxide particles consisted of nanocrystalline anatase at 600 ºC, a mixture of 20 nm anatase and rutile crystallites at 800 ºC, 50-60 nm crystallites of almost phase pure rutile at 1100 ºC, and single crystal rutile particles at 1300 and 1500 ºC. A schematic picture of the mechanisms during precursor droplet transformation to a single crystal TiO_2 particle in aerosol flow reactor was developed. Because the change of dynamic shape factor can be estimated from the change in mobility size distribution, TDMA can be used as a monitor for crystal habit formation. In production of TiO_2 particles with uniform size, shape and crystal structure the production can be thus monitored in real-time with DMA.

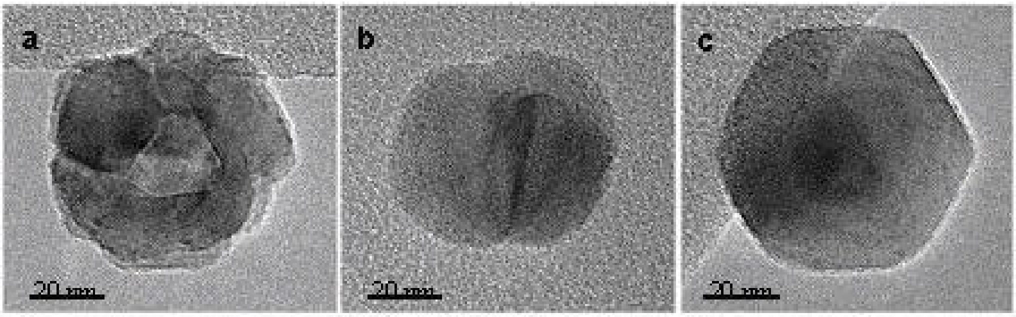

Fig. 6. Transmission electron microscope images of nanosized TiO_2 particles microstructure and morphology at different reactor temperatures of a) 800°C, b) 1000°C and c) 1300°C [56].

Furthermore, we studied the crystallisation of 20-40 nm diameter TiO_2 particles in an aerosol reactor starting from metal alkoxide precursor [57]. The particles were partly anatase at 500 ºC and single crystalline anatase at 600-1200 ºC. The high degree of stability of the anatase phase over a wide range of temperatures was attributed to the fact that the particles were defect-free, free of crystal-crystal attachment, and that the faceted shape promoted a higher activation energy to convert to the stable rutile polymorph. The synthesis method used inhibited the anatase to rutile phase transition that is normally expected well below 1200 ºC. The particle mobility size at different reactor temperatures showed that morphology of the particles changed from spherical at 700 ºC and above. Nanoparticle TiO_2 production is possible by the droplet-to-particle synthesis and, consequently, it is possible to study the properties of single, unagglomerated TiO_2 particles.

3 International Aspects

The research has been carried out in collaboration with the Institute of Materials Science at Tartu University. Two European Science Foundation funded networks, ESF-NANO (Vapor-Phase Synthesis and Processing of Nano-Particle Materials) and ESF-ALENET (Elementary Steps of Layered Growth in the Fabrication of Novel Materials by Atomic Layer Epitaxy) have been participated. The steering committees of the networks have been participated by E. Kauppinen (ESF-NANO) and M. Leskelä (ESF-ALENET). Research groups from both UH and VTT are members in European Consortium on Nanomaterials (ECNM) that was followed by the COST523 action on Nanostructured materials. Within the ECNM/COST activities Prof. Kauppinen has served as a steering committee member. The UH group participates the COST action 528 (Chemical Solution Deposition of Thin Films).

VTT group has made scientific co-operations under ESF action with for example University of Antwerp and Graz. In addition, the COST networking has conducted to co-operation with University of Madrid. VTT group is also collaborating with Mechanical Engineering Laboratory (MEL), AIST, MITI, Japan. In collaboration with Institute of Combustion & Advanced Technologies (Odessa National University) a model to build a semiempirical phase diagram of the precursor decomposition products will be made. This collaboration has already resulted in a few common papers in international journals and presentations in various conferences.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project.

Partner	Type of publication	1998	1999	2000	2001	**Total**	Publication numbers
UH	Ref. Journal art.	4	5	14	26	**49**	1-49
	Ref. conf. papers	-	-	3	-	**3**	63-65
	Monographs	-	-	-	1	**1**	69
	Master degrees	1	4	-	1	**6**	70-75
VTT	Ref. Journal art.	-	2	4	7	**13**	50-62
	Ref. conf. papers	3	-	-	-	**3**	66-68
	Doctoral dissert.	-	1	-	1	**2**	76-77

5 Other Activities

The following patent applications have been filed:

T. Hatanpää, T. Hänninen, M. Leskelä, M. Ritala, M. Vehkamäki: A method for grow oxide films containing strontium and barium. Finn Appl. 98 1959; PCT Int. Appl. WO 00 15 865.

M. Ritala, A. Rahtu, K. Kukli, M. Leskelä: Growth of oxide thin films by atomic layer epitaxy method using metal compounds as oxygen sources. Finn. Appl. 99 2223.

The following symposia have been organized at University of Helsinki: CERC3 Young Chemist Workshop on Chemical preparation of thin films, heterogeneous catalysts and related surface structures (1999) and NSF-ALENET Symposium (1999) M. Leskelä has participated the organizing committees of 5th and 6th International Display Phosphor Conferences held in San Diego (1999, 2000), 9th and 10th International Workshop on Electroluminescence held in Bend USA (1998) and Hamamatsu Japan (2000) and 12th International Conference on Thermal Analyses held in Copenhagen (2000).

Arranged meetings and conferences by the VTT group are: European Science Foundation (ESF) Workshop, High Temperature Sampling and In Situ Measurement of Nanoparticles, May 21 and 22, 1999, Karlsruhe, Germany. United Engineering Foundation (UEF) Conference, Vapor Phase Synthesis of Materials III, July 18-23, 1999, Porvoo, Finland. Conference Chair: Dr Esko Kauppinen (VTT). COST 523 Working Group Meeting, Nanomaterials Characterization, June 19–20, 2000, Helsinki.

6 Publications

6.1 Refereed Journal Articles

[1] M. Ritala, M. Juppo, K. Kukli, A. Rahtu, and Markku Leskelä, In Situ Characterization of Atomic Layer Deposition Processes by a Mass Spectrometer. J. Phys. IV **9** (1999) Pr8-1021.

[2] M. Juppo, A. Rahtu, M. Ritala, and M. Leskelä, In Situ Mass Spectrometry Study on Surface Reactions in Atomic Layer Deposition of Al_2O_3 Thin Films from Trimethylaluminium and Water, Langmuir **16** (2000) 4034.

[3] A. Rahtu, T. Alaranta, and M. Ritala, In Situ Quartz Crystal Microbalance and Quadrupole Mass Spectrometry Studies of Atomic Layer Deposition of Aluminum Oxide from Trimethylaluminum and Water, Langmuir **17** (2001) 6506.

[4] A. Rahtu, K. Kukli, and M. Ritala, In Situ Mass Spectrometry Study on Atomic Layer Deposition from Metal (Ti, Ta and Nb) Ethoxides and Water, Chem. Mater. **13** (2001) 817.

[5] A. Rahtu, T. Hänninen, and M. Ritala, In Situ Characterization of Atomic Layer Deposition of $SrTiO_3$, J. Phys. IV **11** (2001) Pr-923.

[6] A. Rahtu and M. Ritala, Reaction Mechanism Studies on Titanium Isopropoxide - Water Atomic Layer Deposition Process, Chem. Vap. Deposition in press.

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6.4 Doctoral, Licenciate, and Master Thesis

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CONTENTS

DEVELOPMENT OF NICKEL-TITANIUM COATINGS WITH GOOD CAVITATION, EROSION AND EROSION-CORROSION RESISTIVITY

Eero Haimi[1], Jari Koskinen[2] and Veikko Lindroos[1]

Abstract

The ultimate goal of the project was to realise NiTi coatings with pseudoelastic properties on conventional steel surfaces, since pseudoelasticity is related to high wear resistance of NiTi in various different wear modes. One of the principal challenges was how to achieve adequate adhesion between NiTi and substrate material. In the project hot isostatic pressing was applied to sinter a coating from austenitic NiTi powder onto AISI 316 stainless steel substrate. In the process metastable reactive diffusion takes place producing interfacial reaction layer, which consists mainly of titanium. The interfacial titanium rich layer promote relatively strong bonding between NiTi and AISI 316 steel. Pseudoelastic properties of the NiTi coatings were investigated utilising optical microscopy, chemical analysis, differential scanning calorimetry, hardness testing and nanointendation. The results showed, that the hot isostatically pressed NiTi coatings possessed pseudoelastic properties. Subsequently, cavitation, erosion and erosion-corrosion resistivity of the coatings were tested. The wear resistance of the NiTi coatings established to be excellent. As an alternative coating method, thermal spraying were investigated. After laser treatment also these coatings showed promising behaviour in cavitation tests. However, these results are only preliminary. As a conclusion, the results concerning hot isostatically pressed coatings opens new possibilities for technical utilization of NiTi coatings.

1 Partners and Funding

1.1 Laboratory of Physical Metallurgy and Materials Science, Helsinki University of Technology

The personnel who has participated to the project are project leader professor Veikko Lindroos, project manager Eero Haimi, senior researcher Ilkka Penttinen and students Petteri Kilpinen, Jani Ylänen, Mika Silander, Teppo Fält, Ari Hirvonen and Mirva Haikarainen.

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[2] Manufacturing Technology, VTT, P.O.Box 1703 , FIN-02044 VTT

1.2 Manufacturing Technology, VTT

At VTT the project leader was professor Simo-Pekka Hannula, the project manager Jari Koskinen, and researchers directly involved Tatu Muukkonen, Tom Gustafsson, Petri Jokinen, Jari Keskinen and Pekka Lintula.

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
HUT	Tekes	447	750	510	-	**1707**
VTT	VTT	277	160	137	-	**574**
	Tekes	415	406	370	-	**1191**
	Industry	-	110	110	-	**220**
Total		**1139**	**1426**	**1127**	**-**	**3692**

2 Research Work

2.1 Objectives and Work Plan

The basic motivation of the project was to generate solid scientific base for pseudoelastic NiTi coatings utilisation in Finnish industry. The ultimate goal was to realise NiTi coatings with pseudoelastic properties on conventional steel surfaces with sufficiently good adhesion.

2.2 Progress Report

One of the principal challenges in NiTi coating was how to achieve adequate adhesion between NiTi and substrate material. In the project hot isostatic pressing (HIPing) was applied to sinter a coating from austenitic NiTi powder onto AISI 316 stainless steel substrate. In the process metastable reactive diffusion takes place producing interfacial reaction layer, which consists mainly of titanium. The interfacial titanium rich layer promote relatively strong bonding between NiTi and AISI 316 steel.

Pseudoelastic properties of the NiTi coatings were investigated utilising optical microscopy, chemical analysis, differential scanning calorimetry, hardness testing and nanointendation. The results showed, that the hot isostatically pressed NiTi coatings possessed pseudoelastic properties. The accurate compositional and microstuctural control typical to HIPing is apparently adequate for sufficient A_f- and M_d-temperature reproducibility.

Cavitation resistivity of the coatings were tested using both ultrasonic cavitation-erosion tests and rotating disk type of tests. The coating showed excellent performance in the tests. Erosion and erosion-corrosion resistivity were tested with slurry pot type of experiment. The samples were rotated in a slurrytank that contained 100g/l of quartz sand in liquids of two types. In the neutral erosion tests the liquid was deionized water and in the corrosive test the liquid was 1N H_2SO_4- water solution. The wear resistance of the NiTi coatings established to be exceptionally good also in these tests.

As an alternative coating method, thermal spraying was investigated. After laser treatment also these coatings showed promising behaviour in cavitation tests. However, these results are only preliminary.

As a conclusion, the results concerning hot isostatically pressed coatings opens new possibilities for technical utilization of NiTi coatings. Patenting of the technology is in progress.

3 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 5.1 and theses in Section 5.2.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
HUT	Ref. journal art.	0	0	0	3	**3**	1-3
	Master degrees	0	0	0	1	**1**	5
VTT	Ref. journal art.	0	0	0	1	**1**	4

4 Other Activities

Dissemination of results in conferences and seminars:

1st annual meeting of HIP and powder metallurgy R&D net work, 11.2.1999, Tampere, talk.

Vuorimiesyhdistyksen Metallurgijaoston syyskokous, 19.11.1999, Tampere, talk.

ASM Finland, Powder Metallurgy Section Seminar, 27.1.2000, Tampere, talk.

Metalliteollisuuden keskusliitto, Materiaalitekniikan toimikunnan kokous, 12.4.2000, Helsinki, talk.

A Joint Nordic Conference in Powder Technology, 10-11.5.2000, Stockholm, poster.

ASM Finland, Funktionaaliset ja aktiiviset materiaalit seminaari, 13.9.2000, Helsinki, talk.

Patents and patent applications:

J. Koskinen, E. Haimi, Kavitaatiota, eroosota ja eroosiokorroosiota kestävän NITI-pinnoitteen valmistusmenetelmä ja tällä tavalla valmistettujen NITI-pinnoitteiden käyttö , Suomalainen patenttihakemus Nr. 981357, sekä (PCT/FI99/00519)

5 Publications

5.1 Refereed Journal Articles

[1] E. Haimi, J. Koskinen, and V.K.Lindroos, Successful Bonding of NiTi Intermetallic Compound to Stainless Steel by Hot Isostatic Pressing, submitted to Metallurgical and Materials Transactions

[2] E. Haimi, J. Koskinen, and V.K.Lindroos, Pseudoelastic Properties of NiTi Coatings Manufactured by Hot Isostatic Pressing, manuscript to be published

[3] E. Haimi, J. Koskinen, and V.K.Lindroos, Cavitation-erosion Resistance of NiTi Coatings Manufactured by Hot Isostatic Pressing, manuscript to be published

[4] J. Koskinen, E. Haimi, Arc Sprayed NiTi coatings, manuscript to be published

5.2 Master Theses

[5] M. Haikarainen, Characterization of Elastic Properties of Nickel-Titanium-Coating by Nanointendation. MSc thesis, Department of Materials Science and Rock Engineering, Helsinki University of Technology, 2000, 61 p.

FUNCTIONAL BIOMATERIALS SURFACES (FUMA)

Jukka Salonen[1], Antti Yli-Urpo[2], Bruno Lönnberg[3] and Risto Penttinen[4]

Abstract

Functional growth factor binding mineral surfaces were created on biomaterials (cellulose and polylactide-caprolactone) by biomimetic (BM) method using bioactive glass or its components. The apatite layer was characterized with SEM and infrared spectra and found to resemble natural hydroxyapatite of bone. The biomimetic coating method was developed to utilize purified chemicals instead of bioactive glass and applied to surface coating of cellulose and cell culture material. The BM celluloses bound connective tissue growth factors, especially TGF beta and bone morphogenic protein 2 (BMP-2) with a high affinity and stimulated the early growth of granulation tissue, even in bone. The effect was very significant during the first 10-14 days but persisted for one year in the non-degradable cellulose. The sponge material can be used to stimulate granulation tissue growth in clinical situations such as treatment of deep burns. Clinical studies have been started at the intensive care unit of the Töölö Hospital, in Helsinki. Biodegradable cellulose was developed.

Duration of the contract was 1998-2001 (three years).

1 Partners and Funding

1.1 The Turku Centre for Biomaterials (BMC)

The research group consisted of subproject leader docent Jukka Salonen and during his leave (1.1.1999-1.2.2001) professor Risto Penttinen, senior researchers M.Sc. Pia Ylhä, M.Sc. Kirsti Henriksson, postgraduate students M.Sc. Ari-Pekka Forsback, M.Sc. Mika Koskinen, and technicians Pasi Juntunen and Kirsi Suomi.

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[2] The Institute of Dentistry Biomaterials Project, University of Turku , Lemminkäisenkatu 2, FIN-20520 Turku

[3] The Laboratory of Pulping Technology, Åbo Akademi University, Porthansgatan 3, FIN-20500 Turku

[4] Department of Medical Biochemistry and Molecular Biology, University of Turku, Kiinamyllynkatu 10, FIN-20520 Turku

1.2 The Institute of Dentistry Biomaterials Project, University of Turku (TYHL)

The research group consisted of subproject leader professor Antti Yli-Urpo, M.Sc. Elena Kerimaa, (from 1.9.1999), M.Sci. Ari-Pekka Forsback (1.1.1999-31.3.2000) and technician Päivi Mäki.

1.3 The Laboratory of Pulping Technology, Åbo Akademi University (ÅAU)

The research group consisted of subproject leader professor Bruno Lönnberg, senior researchers professor Sorin Ciovica, M.Sc., M.Pharm. Ulf Södergård, postgraduate studend M.Sci. Tom Strandberg, and senior adviser, MD, docent Jouko Viljanto/ Cellomeda Ltd.

1.4 Department of Medical Biochemistry and Molecular Biology, University of Turku (LBK)

The research group consisted of subproject leader professor Risto Penttinen, postgraduate student M.Sci. Erika Ekholm (on maternity leave since 01.09.2000, M.Sc. Johanna Holmbom (since 01.09.2000), M.Sc. Virpi Ääritalo, graduate students B.Sc. Christa Finnberg, Stud. med. Miretta Liiho, M.Sc. Martin Nars.

1.5 Funding

Table 1. Funding of the project in 1000 FMK in 1998-2000. Internal funding consists of manpower costs and operational expenditures provided by the organization. The funding provided by the Turku Technology Center (TTC) is also indicated in the table.

Partner	Funding organization	1998	1999	2000	**Total**
BMC	TY				
	TEKES	405	410	404	**1.219**
	TTC	137	147	147	**431**
TYHL	TY				
	TEKES	410	406	376	**1.192**
	TTC				
LBK	TY				
	TEKES	391	400	421	**1.212**
ÅAU	TEKES	444	574	295	**1.313**
Total		***1.787***	***1.937***	***1.643***	***5.367***

2 Research Work

2.1 Objectives and Work Plan

The purpose of the FUMA project was to modify and develop different bioactive surfaces in order to obtain material properties that would be tissue friendly, and especially favor bone growth into the implanted material (implants). The final goal was to develop a new osteoconductive composite material from apatitized porous cellulose using a biomimetic method. This material could also contain BAG or silica gel. Another goal was to study the binding and possible enrichment of growth factors (TGF-β1, VEGF, PDGF, TNF-α and BMP-2) onto the porous activated surfaces of biomaterials. The aim was to combine the stimulatory effect of cellulose sponges to grow of granulation tissue and the osteoconductive properties of bioactive glass. This material should then be resorbed and leave new tissue ready for remodelling into normal bone. The third aim was to find out whether the apatite coating of cellulose sponges produced by the biomimetic method could increase the ostoeconductive or even osteoinductive properties of the cellulose sponges. The basic method (Kokubo et al. Japan) creates an apatite surface coating using bioactive glass granules in simulated body fluid (SBF) on surfaces that are in contact with the glass. In the present project the method was developed to form apatite on three-dimensional porous scaffolds (cellulose sponge).

Research on cellulose composite of bioactive glass and cellulose sponges has been carried out in another project "Effect of the combination of viscose cellulose sponge and biomaterials on bone formation“ (Tekes 40129/98, 40227/99, 40109/00). Thus this MATRA project was focused on the development of biodegradable cellulose and functionalization of cellulose sponges with apatite layer. The formation of apatite is a widespread biological phenomenon which is used in animal kingdom for making different supporting tissues such as bone and corals or shells, but is also involved in pathological calcifications like formation of kidney stones or atherosclerotic plaques.

One specific aim was to develop a new apatitization method using bioactive glass and other silica based chemicals and to understand the heterogenic nucleation of apatite at the molecular level.

2.2 Progress Report: Common Themes

Collaboration between the Åbo Academy University was necessary to develop cellulose matrices and functional surfaces on cellulose membranes and sponges. The expertise on biomineralization of the TYHL and BMC groups was necessary to create the biomimetic hydroxyapatite surface on the materials, cellulose and polylactide-caprolactone; the latter was used as reference material for cellulose. The protein and nucleic acid biochemistry of LBK was necessary to analyze the growth factors and protein expression in biomaterials. The work was carried out at the BMC, which has the routine analytical laboratory methods to estimate the bioactivity of glass and related materials and their cellular responses.

2.3 Progress Report: Progress by the BMC and Institute of Dentistry (TYHL)

Initial experiments failed to manufacture functionally active cellulose sponge implant by using the silica sol-gel process. The apatite formation on these materials was limited. Further investigations on sponge implants modified by the sol-gel process were also withdrawn because the pores of the sponges were effectively obstructed and this was considered a major drawback of the method.
Mineralisation of plastic surfaces, cellulose sponges and porous polylactide-caprolactone was achieved using the biomimetic method modified from the Kokubo method. The layer was characterized by infra-red spectra, electron microscopy and EDXA analyses and found to resemble the natural apatite of bone.

2.4 Progress Report: Progress by the Laboratory of Pulping Technology, Åbo Akademi University (ÅAU)

The aim of this subproject was to develop regenerated cellulose matrices with properties that allowed their functionalization and use for various medical or clinical purposes. Subsequently, the final matrix no matter whether in form of sponge, membrane or some other form, should be pure, hydrophilic, porous, stiff and above all biodegradable. The goals were achieved by modifications of the viscose cellulose process.

The highest cellulose content of the alkali cellulose after compressing to about 3:1 was obtained by 18 % NaOH, which is considered the “standard“ alkali concentration. These conditions also led to superior DP of the cellulose, and subsequently high density and tensile strength of the formed membrane.

Porosity of sponges or membranes and hydrophilicity contribute to similar matrix properties, such as water absorption capacity, which is important for certain applications. Porous membranes prepared according to a specially designed method were found to hold water about 3 times their own dry weight.

Regenerated cellulose is rather crystalline and thus inert, and hence good for certain applications in tissue. In many applications however biodegradability is required, and for this purpose cellulose was oxidised as to produce matrices useful for implants meant to function for a limited time only, whereafter the cellulose should “decompose“ and resorb. A combination of periodate and hydrogen peroxide oxidation of cellulose produced a variety of biodegradable matrices with resorption times from some days up to some weeks. These 2,3-dialdehyde or 2,3-dicarboxyl celluloses or combinations of them were biodegradable dependent on oxidation time, as indicated in Fig.1.

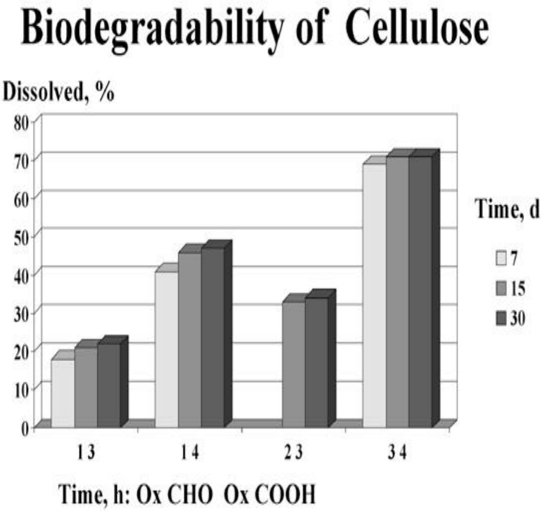

Fig. 1. Biodegradability in a simulated body fluid of cellulose membranes after sequential periodate and hydrogen peroxide oxidations.

It is seen that for example periodate oxidation for 3 h and a subsequent oxidation by hydrogen peroxide for 4 h would produce a sort of a biodegradable cellulose (columns to the right): 70 % dissolution in 7 days.

2.5 Progress Report: Progress by the LBK

Cellulose has been used to induce the growth of granulation tissue subcutaneously in experimental and clinical studies on wound healing for over 30 years. Recently, we have demonstrated that cellulose sponge also has bone growth promoting properties (Fig. 2).

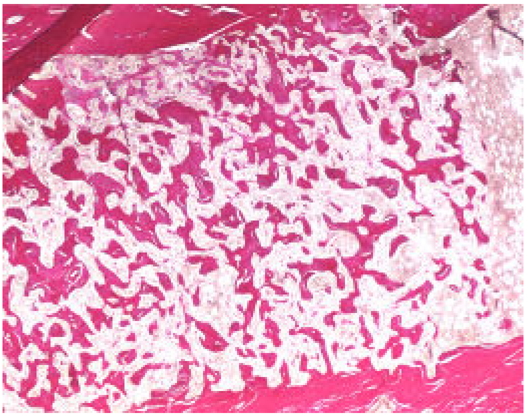

Fig. 2. Growth of bone into medical grade cellulose sponge implanted into rat femoral bone defect.

The good inductive capacity of cellulose sponges suggested us that the effect was due to attachment of growth factors, especially TGF beta 1 onto the sponge material.

In vitro binding studies demonstrated an active binding of TGF beta 1 and 2 to sponge material, already within minutes. Apatitization of the sponges increased the binding to over 90 % from added cytokine. This binding was nearly irreversible at neutral pH which was demonstrated by western analyses of the growth factor extracted from the sponges. Western analyses of growth factors in the Department of Medical Biochemistry were developed during this contract. BMP-2 was also detected to bind to the sponges, about one third was bound to the normal cellulose and almost 90 % or over to the BM cellulose. Enrichment of growth factors to apatite surfaces can explain the acute tissue response in subcutaneous sponge implants. This effect, however, limited bone growth into the implants. We interpret this as a result of a continuous inflammatory state induced by the non-degraded cellulose which is supported by a accumulation of foreign body giant cells in the implants maintaining high levels of inflammatory mediators (prostaglandins and interleukins) which hamper bone formation (Ekholm, thesis 2001).

The results pointed strongly to the importance of the biodegradability of cellulose scaffold to the bone formation. Recent results on chemically oxidized cellulose sponges implanted subcutaneously show that the treatment reduces dramatically the number of foreign body giant cells and the connective tissue response to the sponges. The analyses of bone forming capacity of biodegradable cellulose bone implants are in progress and will be reported later.

Northern analyses of connective tissue protein expression showed that the total RNA increased significantly (about 30%) in biomimetically treated sponges indicating cellular response. However, the relative amounts of specific RNAs for collagens I and III (the main fibrous proteins of soft connective tissue) were similar in BM and control sponges. This indicates that the new granulation tissue has no specific fibrotic tendency. In the biomimetically mineralized cellulose implanted in bone the collagen specific RNAs, and the amounts of hydroxyproline (as a measure of total collagen) were decreased in comparison with the normal sponge implants supporting the results on inhibitory effect of the non-degradable sponges.

Implants made of polylactide-caprolactone copolymer were used as controls and were mineralized like cellulose sponges. The subcutaneous implants showed a good granulation tissue response and BM treatment seemed to increase bone formation even though the increase was not larger than about 10 %. The result supports the idea that apatite coatings have a positive role in bone formation.

3 International aspects

Since 1998 the biomaterials research groups of The Institute of Dentistry (TYHL) and the University of Nijmegen, the Netherlands, (prof. J.A. Jansen) have had an active collaboration. During the last two years four visits longer than 2 weeks were made between Turku and Nijmegen. Prof. J.A. Jansen's research group is focused on studies with apatite coated titanium implants. Research groups have performed bone cell and animal experiments with the degradable thermoplastic composite of bioactive glass (S53P4) and caprolactone-polylactide co-polymer. Several national and international meetings have been organized, also during biomaterial congresses to strengthen the collaboration.

The binding of BMP-2 protein onto the surface of cellulose sponges has been studied with Dr Franz Weber, Universitätsspital, Klinik für Kiefer- und Gesichtschirurgie in Zurich, Switzerland, who has human recombinant protein. The biological response of haptotactic, cell attracting peptide grafted to cellulose sponges has been studied in collaboration with Dr Raphael Gorodetsky and HAPTO Biotech Ltd., Jerusalem, Israel.

4 Publications and Academic degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publication are given along with the reference numbers, List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in section 6.3 and thesis in section 6.4.

Partner	Type of publication	1998	1999	2000	2001	total	Publication numbers
BMC and TYHL	Ref. Journal art.	-	-	-	-	-	
	Ref. Conf. Papers	-	2	1	-	3	2, 3, 4
	Monographs	-	-	-	-	-	
	Master Degrees	-	-	-	-	-	
	Doctoral dissert.	-	-	-	1	1	10
ÅAU	Ref. Journal art.	-	1	-	-	1	1
	Ref. Conf. Papers	-	-	2	-	2	5, 6
	Monographs	-	-	1	-	1	7
	Master Degrees	-	1	1	-	2	8, 9
	Doctoral dissert.	-	-	-	-	-	-
LBK	Ref. Journal art.	-	-	-	-	-	
	Ref. Conf. Papers	-	1	1	2	-	3, 4
	Monographs	-	-	-	-	-	-
	Master Degrees	-	-	-	-	-	-
	Doctoral dissert.	-	-	-	1	1	10

5 Other Activities

The BMC arranged the scientific symposium of the Annual Meeting of the Medical Association Duodecim, “Biomaterials in Medicine“ Nov. 7th 2000 (program included) largely based on research activity granted by this contract. Biomaterials Research Program was chosen as one of the “high profile“ scientific programs representing frontiers of science in the University of Turku

6 Publications

6.1 Refereed Journal Articles

[1] S. Ciovica, B. Lönnberg, and K. Lönnqvist, Dissolving pulp by the IDE pulping process, Cellulose Chemistry and Technology **32** (1998) no. 3-4 279-290.

6.2 Refereed Conference Papers

[2] A.-P. Forsback, P. Ylhä, R. Penttinen, A. Yli-Urpo, and J. Salonen, Characterization of Ca/P layer produced on porous synthetic organic matrix by biomimetic method. Proceedings of the 12th International Symposium on Ceramics in Medicine, Nara, Japan, October 1999. Bioceramics 12, 1999.

[3] E. Ekholm, C. Finnberg, A.-P. Forsback, M. Liiho, J. Salonen, and R. Penttinen, Apatite coated viscose cellulose binds transforming growth factor beta 1 (TGF ß1). 15th European Conference 1999, Arcachon, France.

[4] M. Liiho M, E. Ekholm, C. Finnberg, A.-P. Forsback, J. Salonen, J. Viljanto, and R. Penttinen. Apatite coating increases connective tissue inducing capacity of cellulose matrix. Davos Tissue Engineering, 2000, Davos, Switzerland.

[5] S. Ciovica, B. Lönnberg, U. Södergård, T. Strandberg, and K. Lönnqvist, Cellulose – liquid interaction in regenerated medical cellulose, Proc. FiberMed, Tampere, Finland 2000, p. 87-98.

[6] U. Södergård, S. Ciovica and B. Lönnberg, Changes in crystallinity of regenerated cellulose, Proc. EWLP, Bordeaux, France 2000, p. 591-594.

6.3 Monographs

[7] S. Ciovica, B. Lönnberg and K. Lönnqvist, Cellulose composite materials as sorbents – sorption and rheological properties, Cellulosic pulps, fibres and materials, Woodhead Publishing Limited, Cambridge, UK, 2000, 305-317.

6.4 Doctoral, Licentiate and Master Degrees

[8] T. Strandberg, Undersökning av alkaliseringsbetingelserna vid framställning av cellulosamembraner (Study of alkaline conditions in the production of cellulose membranes), Master thesis, Laboratory of Pulping Technology, Åbo Akademi University, 1999

[9] U. Södergård, Degradation of regenerated celluloses in vitro, Master thesis, Department of Pharmacy, University of Helsinki and Laboratory of Pulping Technology, Åbo Akademi University, 2000.

[10] E. Ekholm, Bone repair. An experimental study on factors affecting the healing and the callus size. Ph.D. thesis, Ann. Univ.Turkuensis Ser. D 450, 1-82, 2001.

SURFACE STRUCTURE OF WOOD MICROFIBRILS: LOCATION OF CELLULOSE, HEMICELLULOSES AND LIGNIN IN NATIVE AND ENZYMATICALLY TREATED SAMPLES

Jaakko Pere[1], Jouko Peltonen[2], Raimo Alén[3] and Annikki Heikkurinen[4]

Abstract

The aim of the project was to study the surface composition of wood fibres and to correlate the morphological structure to the chemical characteristics by means microscopical (AFM, ESEM, CLSM) and microspectroscopical (FTIR) techniques. The model samples of lignin and hemicelluloses were studied in order to help the interpretation of data obtained on pulp samples for locating cellulose, hemicellulose and lignin on wood fibres. This worked very well in FTIR measurements which showed that the chemical characteristics of isolated model samples could be detected in pulps as well, and the multivariate data analysis further improved the interpretation. So called phase imaging technique of AFM gave promising results for distinguishing lignin patches from cellulose on fibre surfaces. Futhermore modification of AFM tip with CBD (cellulose binding domain) introduced as a novel method for characterisation of fibre surfaces chemically. Immunolabelling with the specific antibodies for different wood components potentiated chemical mapping of fibre surfaces.

The results of this project can be utilized when planning and carrying of new studies based on combination of techniques used within the project. The project was the first project carried out in Finland that applied AFM to a systematic surface characterization of wood fibres.

1 Partners and Funding

1.1 VTT Biotechnology

The research group of VTT Biotechnology (VTT) consisted of project leader senior researcher Jaakko Pere, professor Olle Teleman (project leader during years 1997 and

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[2] Åbo Akademi University, Department of Physical Chemistry, Porthaninkatu 3-5, FIN-20500 Turku

[3] University of Jyväskylä, Department of Chemistry, P.O.Box 35, FIN-40351 Jyväskylä

[4] The Pulp and Paper Research Institute of Finland, P.O.Box 70, FIN-02151 Espoo

1998), researchers Arja Paananen, Markus Linder and Andreas Heiner, and researcher Lauri Kuutti from VTT Chemical Technology.

1.2 Department of Physical Chemistry, Åbo Akademi University

The research group of the Åbo Akademi University (ÅA) consisted of subproject leader docent Jouko Peltonen, and postgraduate student Johanna Gustafsson.

1.3 Department of Chemistry, University of Jyväskylä

The research group of the University of Jyväskylä (JY) consisted of subproject leader professor Raimo Alén, and postgraduate students Anne Peltola, Jaakko Toivanen and Matti Ristolainen.

1.4 The Pulp and Paper Research Institute of Finland

The research group of the Pulp and Paper Research Institute of Finland (KCL) consisted of subproject leader senior scientist Annikki Heikkurinen, and senior researchers Hans Eklund, Bo Hortling, Patricia Moss and Hanna-Kaisa Hyvärinen.

1.5 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
VTT	VTT	385	350	373	-	**1108**
	Tekes	550	585	560	-	**1695**
ÅA	Academy	168	168	170	-	**506**
JY	Academy	155	144	145	-	**444**
KCL	KCL	145	91	159	-	**395**
	Tekes	145	91	159	-	**395**
Total		**1548**	**1429**	**1566**	**-**	**4543**

2 Research Work

2.1 Objectives and Work Plan

The objective of the project was to characterize and identify cellulose, hemicellulose and lignin in model and technical samples. The techniques used were atomic force microscopy (AFM) and FTIR in combination with ESEM and other microscopic techniques. Five aims were set for the project:

I. Identification of hemicelluloses and lignin based on suprastructures at the micrometer scale.

II. Direct identification of hemicelluloses and lignin based on molecular properties at the nanometer scale.

III. Use of 1 and 2 to locate cellulose, hemicelluloses and lignin in pulps.

IV. To study the effect on fibre, fibril and microfibril surfaces from enzymatic treatment *in aquo.*

V. Direct observation of bound enzymes, enzyme domains and chimeric proteins.

2.2 Progress Report: Common Themes

The most important constituents of wood are polymeric, i. e. cellulose, hemicelluloses and lignin, of which cellulose constitutes about half of both softwoods and hardwoods. Chemically, these polymers have been well characterized. Structurally, most research has focussed on cellulose, and, from electron diffraction experiments [7], the structure is known with fair precision both for triclinic and monoclinic cellulose I. In spite of this and in spite of the relevance for the pulp and paper industry, it has proven difficult to join structure and chemistry, i. e. to measure the interaction between the components of an individual fibre, of pulp or of paper. Mapping of different woody components on fibre surface has likewise not been possible, and it has particularly been difficult to discriminate hemicelluloses from cellulose. Cellulose does give the intrinsic stength for a fibre, but hemicelluloses has a crucial role in bonding ability between fibres.

The project used AFM and FTIR in combination with existing results from theory-supported studies of native cellulose surfaces [8, 9] to achieve a corresponding characterization and understanding of cellulose-hemicelluloses-lignin systems, integral cell walls and model pulps. It was also studied how enzymatic modification of hemicelluloses affects the fibre, fibril and microfibril surfaces. The project was the first project carried out in Finland that applied AFM to a systematic surface characterization of wood fibres [1].

Study of model and pulp samples

According to the initial plan, samples representing different stages of pulping and delignification were studied. These included conventional kraft pulp (KP), oxygen delignified KP (KPO), ECF-delignified KP (BKP), lignin isolated from KP (KPRL) and flow-through KP (FTRL), lignin isolated from wood (MWL) and finally hemicellulose (xylan).

The AFM measurements were started by using the contact mode imaging giving the 3D topographical image, together with simultaneous friction imaging [4]. The surface structure of KP turned out to be versatile, mainly non-fibrillar whereas for KPO and BKP samples also fibrillar areas and even individual microfibrils could be resolved. The same samples analysed by ESEM (environmental SEM), especially KP, also appeared granular, even if the resolution was not as high as with AFM. In contrast, the friction force microscopy did not give the expected result in resolving different material components, mainly because of large height fluctuations and soft samples. However, since the morphology of KPRL and FTRL also appeared to be granular we could conclude that the surface of the native wood fibre (KP) was dominated by lignin. The granularity of lignin correlated furthermore with the molar mass of the fractionated samples. The MWL samples were the most difficult to image, most probably because of the charged sample surface disturbing the tip-sample interaction during imaging.

The obtained AFM images were compared with the characterization data, and the kappa number data corresponding to the bulk lignin amount correlated to the relative surface concentration of the granular phase but absolute surface content was clearly higher than the bulk content. Also ESCA was used to determine the lignin content of the samples and the results correlated to the AFM results.

Because of the nonsensitivity of the friction images the vibrating tip imaging mode of AFM was tested next. The special feature of this technique is that simultaneously with topographical imaging the phase angle of the vibrating tip can be measured, giving valuable additional information about the mechanical and chemical properties of the studied samples. By using this mode of imaging the fibrillar and granular phases could be nicely localized on the sample surface. The ECF-delignification was found to dissolve lignin much more effectively than oxygen bleaching.

The chemometric analysis was used for the FTIR data in order to clarify how much the measured point of fiber contained cellulose, hemicelluloses, and lignin. With a PLS (projection to latent structure) method this relative amount could be measured if the spatial resolution was 400 µm x 80 µm or above. However, this kind of analysis was possible if the spatial resolution was lower, like 30 µm x 30 µm, but the roughness of the fiber surface was evidently affecting on the results. The PCA (principal component analysis) and MLPCA (maximum likelihood principal component analysis) methods were able to classify the spectral data into three categories: lignin, cellulose, and xylan. PCA is the most common method for this purpose, but this study also indicated that

MLPCA, which is commonly used for chemical data, was more suitable for the classification purposes especially because spectral data have a clear "offset"-problem. It was seen that the results were well correlated with the AFM results in the case of the fiber surface roughness of the unbleached and bleached pulps.

Study of xylanase treated birch kraft pulp fibres

Never dried samples of unbleached (KoSa) and bleached (KoSaO-ECF) kraft pulp fibres were treated with xylanases (2-48 h) in order to obtain pulps of varying xylan content (100-52% of original xylan) as compared with the untreated reference samples. Consequently, at maximum 42% and 48% of the original xylan was removed from the unbleached and bleached birch kraft pulps, respectively. The treatment was specific for xylan and no other carbohydrates were solubilized by the action of the xylanases. Although xylanases acted on accessible xylan everywhere on cell wall, one can suppose that xylan mainly from surface and sub-surface parts of cell walls was removed.

Thereafter surface structure of the xylanase treated samples was compared with those of the untreated samples in the ESEM. Prior to examination in ESEM the samples were air-dried and gold coated. No significant differences were detected between the samples. However, sample preparation, especially air-drying, might have influenced on the observed result by flattening or fading of fine surface structures as reported previously [10].

The same birch samples were also examined using a CLSM in a wet state when fibrillar material is supposedly more spread out than in dry state. In this case there was also little evidence of surface modification and no discernible differences were seen between the xylanase treated and untreated samples.

Wetting experiments were also undertaken using ESEM and CLSM. Changes in fibre width (i.e.swelling) and surface structures were investigated by observing the same never dried pulps after drying and rewetting. This work gave promising results. The reference samples showed no significant difference in lateral width of fibres during drying and rewetting procedures. On the other hand, fibre widths in the xylanase treated samples decreased upon drying and rewetting indicating of reduced tendency for swelling due to partial removal of xylan. The same phenomenon was visualized in CLSM by imaging fibres in z-direction. The reference fibres retained their cell width during drying and rewetting procedures, whereas the treated fibres did not. These results clearly demonstrated the important role of xylan in swelling ability of fibre cell wall. It is well known that cell wall swelling is essential for bonding ability of fibres.

In the AFM results, the enzymatic treatment by xylanase decreased the surface concentration of the granular phase, but also increased surface roughness. Xylan itself appeared both granular and linear but not as fibrillar as cellulose. The chemical contrast appeared as differences in the amphiphilicity within the granular phase. The same technique revealed how a CBD-protein attaches to the surface of the *Valonia* cellulose.

Immunomicroscopy

Chemical mapping of fibre surfaces can be performed using specific antibodies raised against different wood components. At VTT Biotechnology antibodies against lignin, hemicellulose (xylan, mannan and pectin) and extractives have been produced and applied in characterization of kraft and mechanical pulps using a CLSM. The method is based on recognition of the target component on fibre surface by the antibody, which thereafter is detected by a secondary antibody coupled to a fluorescent label.

Distribution of lignin on the surfaces of different mechanical pulp fibres (TMP, PGW) was studied. Immunolabelling of lignin was a sensitive method and it provided information about the distribution of lignin at a much finer structural level than could be obtained with other staining methods. The same technique was also used for localization of xylan on kraft pulps. An antibody specific for a xylo-oligosaccharide carrying the acidic side group (MeGlcA- Xyl) was used in the study [5, 6]. Distribution of xylan both on softwood and hardwood pulps could be visualized with the aid of this xylan specific antibody. Xylan removal by a xylanase prior to immunolabelling clearly decreased the intensity of label on the fibres, which indicated of decrease of xylan from fibre surfaces. Using the same technique and a mannan specific antibody glucomannan could be localized on softwood fibres.

2.3 Progress Report: Progress by VTT

The tasks of the research group at VTT was also to provide polysaccharide samples, enzymes and enzyme treatments, and preparation of two-component model samples (cellulose-hemicellulose). The results are reported in Section 2.2.

Cellulose-hemicellulose model samples were prepared by adsorbing xylan on cellophane membranes. The model samples were prepared for checking the surface composition and location of different polymeric components on the surface by AFM in a well-defined sample consisting of only two components. This information could then be used for interpreting AFM images of fibre surfaces. The sample preparation turned out to be very difficult, and the adsorption of xylan on cellulose could not be proved with the techniques used within the project.

In addition, a technique using modified AFM tip was developed in order to locate cellulose on fibre surfaces. The cellulose binding domains (CBD) of cellobiohydrolase I were coupled to the tip surface, and the tips were used as in basic force curve measurements. The modification of the tip surface was successful, the control measurements on atomically flat surfaces showed a clear difference between the CBD-tip and the untreated tip. When applying the technique to the model cellulose sample, i.e. an ultramicrotomed cross-section of bleached cotton cellulose, the interpretation of force curves was hampered by the characteristics of the sample. For unambiguous data analysis, the roughness of the sample, and hence, the contact area between interacting surfaces should be better controlled.

2.4 Progress Report: Progress by ÅA

The task of the research group at ÅA was to study the morphological structure of wood fibres and their smallest structural units like microfibrils, and to correlate the morphological structure to the chemical characteristics by means of AFM. The results are reported in Section 2.2.

In addition, the group investigated the phase contrast imaging technique and its applicability to characterise wood fibre surfaces, and developed a method for analysing AFM image data [2].

2.5 Progress Report: Progress by JY

The task of the research group at JY was to study the chemical composition of wood fibres by means of FTIR microscopy. The samples were model samples, technical pulps, and enzymatically treated pulps. The results are reported in Section 2.2.

The group at JY developed a method for analyzing the surface of wood fibre by FTIR spectrometry combined with multivariate data analysis [3]. Of existing FTIR techniques so called DRIFT was found to be more suitable for the bulk measurement of pulps, although it could not be applied to the chemical characterization of individual fibers. FTIR microspectroscopy, in turn, can be applied to the chemical analysis of the fiber and the smallest theoretical spatial resolution is 10 µm x 10 µm, which turned out to be very difficult to reach in practice. In studies of preparing good samples for FTIR microspectroscopy the method using stainless steel plate technique was found to be the best option. The roughness of the fiber surface had a clear effect on the measurements, which could not be avoided by grinding the sample before measurement, as with the model substances. The crystallinity of the samples, as well as the chemical structure, had a clear effect on the IR spectrum.

2.6 Progress Report: Progress by KCL

The task of the research group at KCL was to provide model and technical pulps, which were conventional (KP), oxygen delignified (KPO), bleached (BKP) and flow-through (FT) kraft pulp, as well as residual lignin samples (KPRL and FTRL) as such and further fractionated by preparative GPC according to molecular size. The KCL group performed basic characterization to the samples, i.e. kappa, viscosity, brightness and yield determinations for pulps, and molar mass distributions of hemicelluloses and celluloses delivered by VTT.

In addition, ESEM was used to study the morphological structure of wood fibres, including technical pulps and enzymatically treated pulps. The results are reported in Section 2.2.

3 International Aspects

The results of the project have been presented in several international and national conferences and symposia (see Section 5). The project benefited from a collaboration with an EU-project, "The strength of wood fibers: Association between hemicellulose and cellulose at the molecular level" (FAIR CT96-1624), the results of which were directly exploitable within the national project. The collaboration with the SPM group at the University of Bristol, especially Dr. Andy Baker and professor Mervyn Miles, helped the development of the method for preparing model surfaces and the technique for tip modification. Many important international relations, including the collaboration with the Bristol group, were formed during a post-graduate course entitled "EMBO Practical Course on Scanning Probe Microscopy", which was held on 8th-14th August 1997 in Basel, Switzerland.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
VTT	Ref. journal art.	-	1	-	1	**2**	1, 3
	Ref. conf. papers	-	1	1	-	**2**	4, 5
ÅA	Ref. journal art.	-	1	-	1	**2**	1, 2
	Ref. conf. papers	-	1	-	-	**1**	4
JY	Ref. journal art.	-	-	-	1	**1**	3
KCL	Ref. conf. papers	-	1	-	1	**2**	4, 6

5 Other Activities

The results of the project were presented at the final seminar “Wood Fiber Surfaces: Structure and Chemistry”, in Espoo, Finland, 2000, which was arranged together with an EU-project, The strength of wood fibers: Association between hemicellulose and cellulose at the molecular level (FAIR CT96-1624). The oral presentations were:

1. Spectroscopic Data and Multivariate Data Analysis, Petteri Malkavaara, University of Jyväskylä
2. Microscopic Techniques for Investigating the Effects of Partial Removal of Xylan on Fibre Properties**,** Patricia Moss, KCL
3. Analysis of Fibre Surfaces by Immunomicroscopy, Jaakko Pere, VTT
4. Properties and structures of fibre surface material in situ and after isolation from the pulp, Bo Hortling, KCL
5. Scanning Probe Microscopy of Wood Fibres: Granular Lignin, Damage on the Microfibril Level, and Inhomogeneous Surface Energy and Elasticity, Jouko Peltonen, Åbo Akademi

The results of the project were also presented in following conferences:

1. O. Teleman, A.P. Heiner, L. Kuutti, J. Peltonen, and J. Pere, The Interface between Cellulose and Water, an oral presentation at the TRICEL 97, 1997, Ghent, Belgium.
2. O. Teleman, A. Paananen, J. Simola, J. Peltonen, L. Kuutti, H.-K. Hyvärinen, P. Moss, J. Pere, and B. Hortling, Surface Structure of Wood Microfibrils, a poster presentation at the International Pulp Bleaching Conference, 1998, Helsinki, Finland.
3. J. Peltonen, Some Selected Applications of Scanning Probe Microscopy in Surface Characterisation, An oral presentation at the VIII National Symposium on Surface and Colloid Science, 1998, Espoo, Finland.
4. M. Österberg, A. Paananen, O. Teleman, and P. Stenius, AFM Studies of Cellulose, Lignin and Wood Resin, a poster presentation at the AFM and Polymers Workshop, 1998, Bristol, England.
5. O. Teleman, A.P. Heiner, A. Paananen, J. Simola, J. Peltonen, and J. Pere, The Interfaces of Cellulose, an oral presentation at the SXM3, the 3rd Conference on Development and Technological Application of Scanning Probe Methods, 1998, Basel, Switzerland.
6. J. Simola, J. Peltonen, R. Koljonen, P. Malkavaara, H.-K. Hyvärinen and B. Hortling, Study of Morphological and Mechanical Properties of Wood Fibers by SPM, A poster presentation at the Cellucon ‘98, 1998, Turku, Finland.
7. B. Hortlig, T. Jousimaa, K. Holopainen, and H-K. Hyvärinen, Investigations of spruce pulp fibers by swelling experiments, light-microscopy and FTIR-microscopy, a poster presentation at the Cellucon '98, 1998, Turku, Finland.
8. J. Peltonen, J. Simola, and J. Pere, Factors Affecting SPM Phase Imaging of Kraft Pulp Fibres, an oral presentation at the Microscopy as a Tool in Pulp and Paper Research and Development, 1999, STFI, Stockholm, Sweden.

9. J. Simola, A. Paananen, J. Pere, B. Hortling, and J. Peltonen, Morphology of Cellulose, Lignin and Hemicellulose as Studied by Scanning Probe Microscopy, a poster presentation at the Microscopy as a Tool in Pulp and Paper Research and Development, 1999, STFI, Stockholm, Sweden.
10. J. Pere, A. Lappalainen, and M. Tenkanen, Immunochemical Methods for Chemical Mapping of Pulp Fibres, an oral presentation at the Microscopy as a Tool in Pulp and Paper Research and Development, 1999, STFI, Stockholm, Sweden.
11. J. Peltonen, Phase Contrast Imaging of Tapping Mode SPM; The Contributions from the Solid-Liquid and Solid-Solid Interactions, an oral presentation at the IX National Symposium on Surface and Colloid Science, 1999, Espoo, Finland.
12. J. Simola and J. Peltonen, Scanning Probe Microscopy Study of Morphological and Mechanical Properties of Wood Fibres, an oral presentation at the 9th European Student Conference in Colloid and Polymer Chemistry, ESC'99", 1999, Nagu, Finland.
13. J. Peltonen and J. Simola, Scanning Probe Microscopy of Thermochemically Treated Kraft Pulp Fibers: Morphology and Wetting Characteristics, an oral presentation at the 219th ACS National Meeting, 2000, San Francisco, USA.
14. J. Peltonen and J. Simola, Studies on morphology, mechanical properties and wetting characteristics of kraft pulp fibres by scanning probe microscopy, an oral presentation at the COST E20 Workshop: Wood Fibre Cell Wall Structure, 2000, Athens, Greece.
15. P.A. Moss, Techniques for Detecting Lignin on the Surfaces of Mechanical Pulp Fibres, an oral presentation at the COST Action E11 Characterisation Methods for Fibres and Paper, 2000, CTP, Grenoble, France.

Project meetings were organised 3-4 times per year, except 1 meeting during year 2000.

6 Publications

6.1 Refereed Journal Articles

[1] J. Peltonen and L. Kuutti, Atomivoimamikroskopian Uudet Ulottuvuudet, Kemia-Kemi, **25** (1998) 771-775.

[2] J. Simola, B. Hortling and J. Peltonen, Scanning Probe Microscopy and Enhanced Data Analysis on Lignin and ECF- or O_2-delignified Pine Kraft Pulp. Colloid and Polymer Science, submitted, 2000.

[3] M. Ristolainen, R. Alen, P. Malkavaara, and J. Pere, Effect of Xylan Removal on Unbleached and Bleached Birch Kraft Pulps, Holzforschung, submitted, 2000.

6.2 Refereed Conference Papers

[4] O. Teleman, A. Paananen, J. Simola, J. Peltonen, L. Kuutti, H.-K. Hyvärinen, P. Moss, J. Pere, and B. Hortling, Surface Structure of Wood Microfibrils, International Pulp Bleaching Conference, Helsinki, Finland, 1998, 591-593.

[5] J. Pere, A. Lappalainen, and M. Tenkanen, Immunochemical Methods for Chemical Mapping of Pulp Fibres, Microscopy as a Tool in Pulp and Paper Research and Development, STFI, Stockholm, Sweden, 1999.

[6] P.A. Moss, Techniques for Detecting Lignin on the Surfaces of Mechanical Pulp Fibres, COST Action E11 Characterisation Methods for Fibres and Paper, CTP, Grenoble, France, 2000, 1-12.

7 Other References

[7] J. Sugiyama, R. Vuong, and H. Chanzy, Electron diffraction study of two crystalline phases occuring in native cellulose from an algal cell wall, Macromolecules **24** (1991) 4168-4175.

[8] L. Kuutti, J. Peltonen, J. Pere, and O. Teleman, Identification and surface structure of crystalline celllose studied by atomic force microscopy, J. Microscopy, **178** (1995) 1-6.

[9] A.P. Heiner, J. Sugiyama, and O. Teleman, Crystalline cellulose Iα and Iβ studied by molecular dynamics simulation, **273** (1995) 207-223.

[10] Duchesne, I. & Daniel, G., The ultrastructure of wood fibre surfaces as shown by a variety of microscopical methods - a review. Nordic Pulp and Paper Research Journal **14** (1999) 62-72.

TARGETED WOOD PROTECTION

Tuija Vihavainen[1], Anne-Christine Ritschkoff[1], Riitta Mahlberg[1], Liisa Viikari[2] and Marjaana Rättö[2]

Abstract

The wood preservation in Europe is currently under pressure for change. The use of conventional wood preservatives has been restricted or even banned recently. Therefore, new solutions in the field of wood preservation are needed. A new approach for the improvement of the durability of wood is presented here. The objective of the study was to evaluate the applicability and performance of hydrophobic treatments and biomodification of wood as a new method to protect wood against moisture and biological attack. A wide range of commercially available hydrophobic compounds deriving from paper, textile or masonry industry was under study. The most promising results in terms of dimensional stability and resistance against wood decaying fungi were obtained with some siloxane water emulsions. In addition, the siloxanes studied prevent the growth of mould and blue stain on the treated wood material in high solution concentrations. These compounds decreased considerably also the equilibrium moisture content of wood. Secondly, the potential of using phenolic compounds, occurring in naturally durable wood species, for wood protection was under investigation. Efforts to decrease the leachability of these compounds were made by enzymatic polymerization of the compounds. Biopolymerization of phenolic compounds such as tannin and vanillin in wood made the wood more resistant to some decay fungi compared to the original efficacy of the compounds. In addition, the fundamental aspects on the decaying mechanisms of brown rot fungi were studied in this project. In the enzymatic hydrolyzing of treated wood, it was shown that most of the new treatments, such as acetylation, inhibited the enzymatic hydrolysis of wood.

1 Partners and Funding

1.1 VTT (VTT Building and Transport, VTT Biotechnology)

The research group consisted of the project leader in charge professor Tuija Vihavainen, research manager Liisa Viikari, senior research scientist Anne-Christine Ritschkoff (project leader), senior research scientist Marjaana Rättö and research scientist Riitta Mahlberg.

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[1] VTT Building and Transport, P.O.Box 1806, FIN-02044 VTT
[2] VTT Biotechnology, P.O.Box 1500, FIN-02044 VTT

1.2 Funding

Funding for the project is presented in Table 1 without allocation between the two units of VTT (VTT Building and Transport, VTT Biotechnology).

Table 1. Funding of the project in 1000 FIM in 1997-2000.

Partner	Funding organisation	1997	1998	1999	2000	**Total**
VTT	VTT	128	144	260	122	**654**
	Tekes	151	677	450	206	**1484**
	Industry	126	1	100	-	**227**
Total		**405**	**822**	**810**	**302**	**2365**

2 Research Work

2.1 Objectives and Work Plan

The objective of the study was to evaluate the applicability and performance of hydrophobic treatments and biomodification as the new generation's methods to protect wood against moisture and biological attack. Knowledge on decaying mechanisms of fungi and on preventing effects of the wood protecting agents gained in previous studies at VTT were utilized and further studied in this project.

The project was carried out in co-operation with VTT Building and Transport and VTT Biotechnology during the time period of 1997-2000. The project was composed of the following three tasks:

1. Enzymatic reactions of brown rot fungi and control of the reactions
2. Hydrophobization of wood cell wall
3. Utilization of enzymes with polymerizing capability in wood modification.

2.2 Progress Report: Common Themes

1. Enzymatic reactions of brown rot fungi and control of the reactions

The methods developed for improvement of the biological resistance and dimensional stability of wood modify the chemical structure of wood but the mechanisms of their function are unknown. By studying enzymes which have the ability to hydrolyze the components of wood, it is possible to gain knowledge on how the treatments have changed the enzyme hydrolysis of cellulose and hemicellulose. The knowledge gained can be used in the development work of new wood protection methods.

The fundamental aspects on the decaying mechanisms of brown rot fungi achieved in the previous projects at VTT were further studied during this project. In the enzymatic hydrolysization of treated wood, it was shown that most of the new treatments (such as acetylation) not based on general toxicity inhibited the enzymatic hydrolysis of wood. The effect was directed both to cellulose and hemicellulose.

2. *Hydrophobization of wood cell wall*

Background

When water penetrates the wood cell wall structure, water molecules form bonds with the cell wall components and swelling of the wood takes place. Penetration of water to wood structure can be reduced by treating wood with water repellents. Furthermore, additional swelling of the wood due to moisture is limited or even prevented by bulking the wood cell wall with the water repellent. In addition to increased dimensional stability, the decrease in the moisture content of wood makes wood also less susceptible to biological degradation (attack by fungi).

Materials and Methods

In this part of the project, the effect of commercially available hydrophobic compounds and products deriving from paper, textile or masonry industry on biological resistance of wood was studied. These model compounds and products were chosen on the basis of their chemical structure and nature as well as of their predicted reactivity with wood. Products supplied as water dispersions or emulsions were favoured for the treatments. The products included perfluoroacrylic, alkylsuccinicanhydride, alkylketene dimer based compounds and silane/siloxane emulsions. Predominately, the concentrations of the treatment solutions varied from 5 to 20 percent. Pine sapwood (*Pinus sylvestris*) was used as the wood material. The treatment solutions were applied to wood by vacuum impregnation.

The effect of the model compounds on the wetting properties of wood was determined by using contact angle measurements. The effect of the treatments on the water uptake and dimensional stability of wood was evaluated by means of repeated water soaking/drying cycles. In addition, changes in the dry volume of the wood specimens after and prior to the treatments were measured. An increase in the dry volume of wood specimens due to the treatments indicates that the compounds not only fill or cover the cell lumens but have also ability to penetrate the wood cell wall. Likewise, an increase in the dimensional stability of wood due to a treatment is an indication of the bulking effect of the compound in the wood structure. In order to find out the ability of the compounds to react with the wood cell wall components, chemical analyses (nuclear magnetic resonance spectroscopy i.e. NMR) of the treated wood were carried out. The impact of the treatments on the biological resistance of wood against decay, mould and bluestain fungi was studied by means of biological tests based on EN standards. The attack of wood by decay fungi causes weight losses in the wood due to the degradation processes taking place in the wood components. The extent of mould and bluestain growth on the wood specimens was evaluated visually or by means of a light microscope using a scale from 0 to 5.

Results

In the screening phase of the study, a few compounds/products stood out in terms of their efficacy against wood decaying fungi, blue stain and/or mould. The potential of the compounds seemed to be related to their ability to get into contact with the cell wall components (increase in the dry volume of the specimens due to the treatments).

Treatment of wood with fluoropolymers (more commonly known as Teflon polymers) resulted in extremely hydrophobic wood surfaces (high water contact angles), however, the effect of some of these polymers on the decay resistance of wood was negligible. There were also fluoropolymers which showed adequate protecting effect against decay fungi when used in large quantities filling mainly the cell lumens in wood. The consumption of the protective agents should be within profitable limits and taking into account the price of the fluoropolymers, these compounds can not be considered as potential alternatives for protective impregnation treatments of wood.

Impregnation of wood with a derivative of succinicanhydride (SAND) commonly used for paper applications protected wood rather effectively from decay damages. In addition, the dimensional stability of wood due to the treatment was increased. The determination of the changes in the dry volume of the wood specimens indicated also that penetration of the chemical into the wood cell structure had taken place. The results of these treatments were encouraging to that extent that the effect of SAND on the durability of wood was studied in more detail. The disadvantage of SAND for wood applications is that the best results were obtained with acetone-based treatment solutions which makes SAND less feasible when the cost and safety aspects are considered.

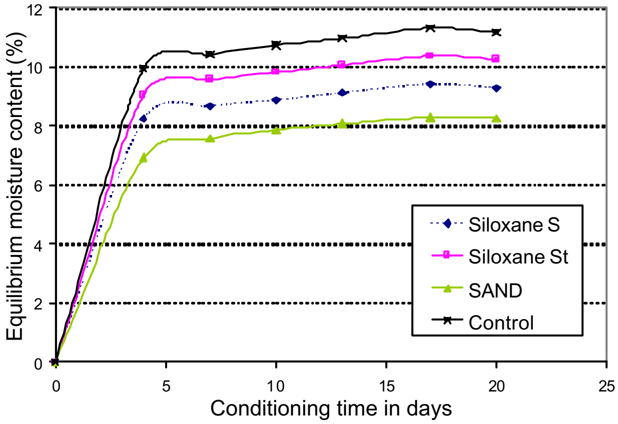

Fig. 1. Effect of hydrophobic treatments on the equilibrium moisture content (EMC) of pine sapwood (*Pinus sylvestris*) at 65 relative humidity (RH). The concentration of the solutions/emulsions was 20 % (w/v).

A wide range of silane/siloxane products was under investigation. Generally without exceptions, the siloxane treatments of wood made the wood surface highly hydrophobic, increased the dimensional stability and decreased the equilibrium moisture content (Fig. 1) of the samples. Furthermore, the results indicate that siloxane water repellents of a certain kind have efficacy against wood decaying fungi (Fig. 2). Leaching do not affect the efficacy of the treatments which is an indication of fixation of the compounds in the wood structure. Fixation ability (formation of chemical bonds with the wood components) of the most promising siloxanes were recorded also in the NMR analyses. In addition, some of the compounds studied prevent the growth of mould fungi and blue stain on the treated wood material and were even more effective than some of the traditional wood preservation agents (Fig. 3 and Table 2).

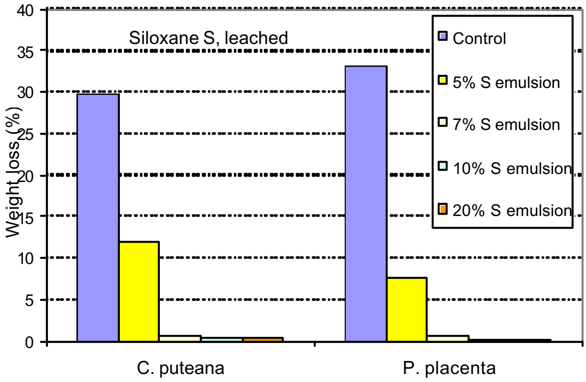

Fig. 2. The effect of siloxane hydrophobic treatments of wood on the weight loss caused by the brown-rot fungi *Coniophora puteana* (*Cp*) and *Poria placenta* (*Prp*). Pine sapwood (*Pinus sylvestris* L.) samples were treated with treatment solutions of different concentrations.

Table 2. The prevention efficacy of SAND and siloxane treatments against the growth of mould and bluestain fungi on pine sapwood during the outdoor exposure of 3 months.

Treatment	Mould and bluestain growth (scale 0-5)
Control	5
Preservative 1	0
Preservative 2	1
SAND	4
Model siloxane S (10 %)	0

0 = no stain or mould present on block surface (microscope)
1 = small amounts of stain or mould on surface (microscope)
2 = <10 % coverage of stain or mould on surface (microscope)
3 = 10-30 % coverage of stain or mould on surface (visual)
4 = 30-70 % coverage of stain or mould on surface (visual)
5 = > 70 % coverage of stain or mould on surface (visual)

By making wood surfaces hydrophobic, the wetting process of the wood by water-born adhesives is impaired. More research and development work on the adhesion between hydrophobic surfaces and surface treatment agents/adhesives are needed to solve the compatibility problems.

3. *Utilization of enzymes with polymerizing capability in wood modification*

Background

There is a great variation in the natural decay resistance between wood species. The decay resistance of naturally durable wood species is considered to derive from the nature and quantity of extractives, especially polyphenols, terpenoids and tannins. However, small molecular aromatic compounds are leachable and can not be used as such for wood protection. In this work, the potential of enzymatically polymerized phenolic compounds as non-leachable wood protecting agents is studied.

Materials and Methods

Enzymatic polymerization of vanillin and tannic acid was carried out by means of laccase enzyme from *Trametes hirsuta.* The enzyme was added to the vanillin and tannin acid solutions after which the blocks were impregnated with the solutions and incubated over night. The biological durability of the test blocks was evaluated by exposing the samples to decay fungi according the EN standards. The changes in the molecular mass due to the enzyme treatments were determined by means of gel permeation chromatography (GPC).

Results

The GPC results indicated that vanillin and tannin were polymerized by the enzyme treatments. The biological tests showed that vanillin and tannin increase the decay resistance of pine sapwood. However, the effect of vanillin and tannin was enhanced by enzymatic polymerization (Fig. 3.). The polymerization of the phenolic compounds decreases the leachability of the compounds. [1]

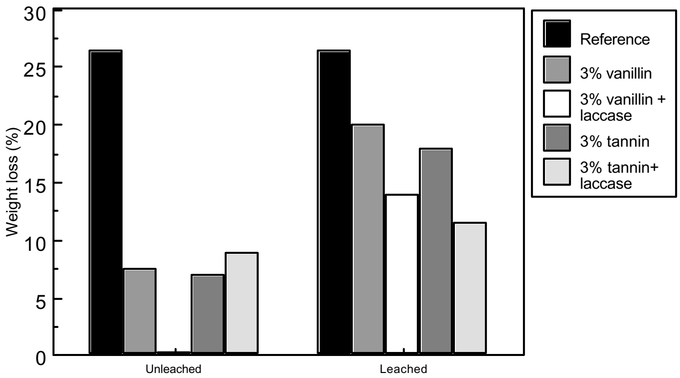

Figure 3. Weight losses caused by *C. puteana* in unleached and leached pine sapwood samples impregnated with non-polymerized and enzymatically polymerized vanillin and tannin (laccase dosage 3000 nkat/g substrate). [1]

In the impregnation of wood with laccase and a polymerizable substrate, a correct enzyme dosage is essential. Thorough development work in this field is still needed but based on the results gained in this project, wood preservation by means of biopolymerization can be considered as a potential alternative for future wood preservation.

3 International Aspects

International contacts with some chemical suppliers were established in order to market the new concept of wood preservation.

4 Publications and Academic Degrees

Table 3. Publications produced within the duration of the project.

Partner	Type of publication	1997	1998	1999	2000	**Total**	Publication numbers
VTT	Ref. journal art.						
	Ref. conf. papers						
	Monographs						
	Doctoral dissert.						
	Licentiate degrees						
	Master degrees						
	Other publications				4	**4**	1-4

5 Other Activities

The inventions achieved during the project are in the process of being protected by a patent (Patent application PCT/FI00/00850). A seminar for the dissemination of the results to the Finnish wood processing industry was organised. Marketing letters and flyers were prepared and disseminated to the wood industry.

6 Publications

6.1 Refereed Journal Articles

Under preparation (see chapter 7)

6.2 Refereed Conference Papers

(see chapter 7)

7 Other References

[1] Rättö, M.; Viikari, L. & Ritschkoff, A.-Ch. Enzymatically polymerized fenolics as wood preservatives (manuscript)

[2] Ritschkoff, A.-Ch.; Mahlberg, R. & Viikari, L. Improvement of moisture behaviour and durability of wood by siloxane treatments (manuscript)

[3] Patent application: PCT/FI00/00850

[4] Mahlberg, R., Ritschkoff, A.-Ch. & Viikari, L. Improvement of durability and moisture properties of wood, The Second Woodcoatings Congress, The Hague, October 23-25, 2000. (poster presentation)

NEW TECHNOLOGY FOR STRUCTURAL STUDIES OF MEDICINALLY IMPORTANT PROTEINS: THE STRUCTURE DETERMINATION OF TESTOSTERONE BINDING FAB FRAGMENTS

Juha Rouvinen[1]

Abstract

The Fab-fragments of Immunoglobulin gamma are potential proteins to be used in human diagnostics. The properties of Fab-fragments can be imporved by using mutagenesis. In this project we have detemined crystal structures of wild type and mutant testosterone-binding Fab-fragments. The results clearly show how testosterone binds to Fab-protein. In addition, significant conformational changes occur in antibody during ligand binding. When comparing mutant and wild type Fab structures it was found that increased affinity and selectivity of mutant Fab is based on small structural changes which allow more compact packing of testosterone against protein binding site. These results can be used further to design new mutants to improve the properties of Fab-fragments.

1 Partners and Funding

1.1 Department of Chemistry, University of Joensuu

The research group consists of project leader docent Dr Juha Rouvinen, researcher PhLic Jarkko Valjakka and laboratory technician Reetta Kallio-Ratilainen.

1.2 VTT Biotechnology

The research group consists of project leader docent, Dr Kristiina Takkinen, researcher Kaija Alfthan. The VTT group has had a separete application in the programme and their work and funding has not been described here.

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[1] Department of Chemistry, University of Joensuu, PO BOX 111, FIN-80101 Joensuu

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1998-2000. In addition, University of Joensuu has provided research infrastructure and some work of laboratory technician.

Partner	Funding organisation	1998	1999	2000	**Total**
JoY	TEKES	310	305	305	**920**
Total		**310**	**305**	**305**	**920**

2 Research Work

2.1 Objectives and Work Plan

In human diagnostics it is important to measure levels of hormones with high accuracy. One possibility is to use specific antibodies which bind to these hormones. If recombinant antibodies are available their specificity and selectivity can be improved by using site directed mutagenesis or evolutionary methods. In this work the goal was to determine structures of wild type Fab-fragments of Immunoglobulin gamma antibody which is cabable to bind testosterone and to investigate how testosterone bind to protein and identify the amino acid residues which interact with the ligand. In addition, the goal was to determine structures of mutant Fab-fragments which have been developed by using evolutionary methods. These mutant Fab's have improved affinity and selectivity concerning testosterone binding. The mutant Fab-structures would thus help us to understand the molecular basis of improved properties.

2.2 Progress Report: Common Themes

The wild type (WT) testosterone binding Fab-fragment as well as two different mutant Fab-fragments (A60 and F77) were produced and purified at VTT.

2.3 Progress Report: Progress by the Department of Chemistry

We were able to get crystals from all three different proteins with and without ligands (testosterone and other steroid hormones which have lower affinity). Many of the crystal forms diffracted only weakly. However, we were able to determine four high resolution (2.1-2.7 Å) structures (1) WT without ligand, 2) WT with testosterone, 3) F77 without ligand, 4) F77 with testosterone) and one low resolution (3.1 Å) structure (A60 with testosterone).

The most important scientific results are 1) the improved crystallization method for Fab-fragments[1]. 2) identification of testosterone binding mode and the amino acid residues which form the binding pocket. 3) the binding mode and interacting residues and their position in the amino acid sequence I similar to other steroid-binding Fab-fragments. 4) there are significant conformational changes in the Fab-fragment during testoterone binding [2, 3]. 5) there exist similar conformational changes in the mutant Fab. 6) improved specificity and selectivity of mutant Fab is based on many small structural changes of Fab which allow more compact packing of testosterone against protein atoms [4]. 7) new mutations for Fab be suggested in order to further improve selectivity and specificity of protein against testosterone. The results can be directly used to design new modifications for Fab-proteins in order to improve their use in human dignostics.

3 International Aspects

The results of the project will be published in international scientific journals and presented in international conferences.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 5.1and theses in Section 5.2.

Partner	Type of publication	1998	1999	2000	2001	**Total**	Publication numbers
JoY	Ref. journal art.			1	3(exp)	**4**	1-4
	Doctoral dissert.				1(exp)	**1**	5

5 Publications

5.1 Refereed Journal Articles

[1] Valjakka J, Hemminki A, Teerinen T, Takkinen K & Rouvinen J: X-ray studies of recombinant anti-testosterone Fab-fragments: the use of PEG 3350 in crystallization. *Acta Cryst. D* 56 (2000) 218-221.

[2] Valjakka J, Takkinen K, Söderlund H & Rouvinen J: Structural insights to steroid hormone binding: crystal structure of a recombinant anti-testosterone Fab fragment in free and testosterone-bound form. Submitted.

[3] Valjakka J, Kyngäs J & Takkinen K: The structure-function analysis of the X-ray structures of the antibody Fab fragments: The Comparative analysis between the hapten and the peptide binding CDR-loops. Manuscript.

[4] Valjakka J, Takkinen K, Söderlund H & Rouvinen J: Improvement of properties of anti-testosterone Fab fragments by directed evolution: A protein crystallographic study. Manuscript.

5.2 Doctoral, Licentiate, and Master Theses

[5] J. Valjakka: The crystal structures of recombinant antitestosterone Fab fragments: insights for antibody engineering, manuscript.

USAGE OF DNA TRANSPOSITION COMPLEXES IN GENE TECHNOLOGY

Harri Savilahti[1]

Abstract

DNA transposition is a phenomenon in which a mobile element moves from one location into another in its host genome. The reaction series proceeds within protein-DNA complexes that can be assembled *in vitro* using purifid reaction components. The objective of this study was to develop DNA transposition complexes of phage Mu into general tools for modern gene technology. An efficient *in vitro* system was established that now can be used in a variety of ways in molecular biology. We have used the system already in DNA sequencing, insertional mutagenesis, functional analysis of DNA regions, and protein engineering. The developed technology is expected to expand into new areas of biotechnology in the near future.

1 Partners and Funding

1.1 Recombination Group, Institute of Biotechnology, University of Helsinki

The research group consisted of project leader (i) Harri Savilahti, Ph.D. (ii) post doctoral researchers: Suvi Taira, Ph. D., Arja Lamberg, Ph.D. (iii) postgraduate students: Saija Haapa, M. Sc., Anna Helena Mykkänen, M. Acric. Sci., Eini Heikkinen, M. Sc. (iv) undergraduate students: Juha-Matti Aalto, Anna Kassinen, Heikki Vilen (v) technicians: Sari Nieminen, Pirjo Rahkola, Auli Saarinen.

1.2 Transposition Team in the Finnzymes OY, collaborators[2]

The research team consisted of the research director Tuomas Tenkanen (Dipl. Engin.), postgraduate researcher Ville Tieaho (M.Sc.), technician Kirsi Multanen.

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[1] Institute of Biotechnology, University of Helsinki, Viikinkaari 9, FIN-00014 University of Helsinki

[2] Finnzymes OY, Riihitontuntie 14 B, FIN-02200 Espoo

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1997-1999. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1997	1998	1999	**Total**
UH	Tekes	920	1050	1059	**3029**
	Academy	109	99	40	**248**
	Biocentrum Helsinki UH)	150			**150**
	Instit. Biotechnology (UH)	45	55	50	**150**
Total		**1224**	**1204**	**1149**	**7200**

2 Research Work

2.1 Objectives and Work plan

The objective was to develop a functioning *in vitro* system for generation of Mu transposition complexes and strategies for their novel uses in gene technology. The strategies with corresponding transposon constructions were intended to form a basis for commercial product family involving the established core technology.

2.2 Progress Report: Common Themes

Most importantly, we have proven that the proposed Mu *in vitro* transposition technology is functional and can be utilized in many ways in gene technology [1-3]. What is more, the system now works robustly and therefore is amenable to commercialization as kits [9,10] .

2.3 Progress Report: Progress by the Recombination Group

During the years 1997-1999 we were able to establish requirements for Mu transposition technology [1, 2] . This included optimization of reaction conditions and purification protocolls for the components required as well as characterization of reaction products and functionality of different types of reaction substrates. We utilized the system successfully in DNA sequencing [1], insertion mutagenesis and functional analysis of genomic regions [2, 7] , protein research using pentapeptide scanning mutagenesis approach [3] and later for the construction of gene-targeting vectors for transgenic animals [8] .

2.4 Progress report: Progress by the Finnzymes Group

The transposon team in Finnzymes OY successfully manufactured as kits two of the developed gene manipulation systems for the global market in a relatively short time frame. The “Template Generation System“ [9] was launched in 1999 and “Mutation Generation System“ [10] in 2000. For our collaborative effort we received two innovation awards (see below).

3 International Aspects

Internationally the project has been visible in two ways: (i) through the published papers [1-4, 7, 8] and (ii) through the products that now can be used everywhere in the laboratories wordwide [9, 10].

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1 and theses in Section 6.2.

Partner	Type of publication	1997	1998	1999	**Total**	Publication numbers
UH	Ref. journal art.			4	**4**	1-4
	Master degrees			2	**2**	5-6

5 Other Activities

5.1 Practical course

Our group arranged a course [ref. 11]: In vitro transposition technology 29.11.-20.12.1999. This may have been the first of its kind globally.

5.2 Patents

Finnish patent #103809, In vitro-menetelmä sekvensointitemplaattien tuottamiseksi (Finland, filed 14.7.1997, granted 30.9.1999)
Inventors: Tenkanen Tuomas, Soininen Timo, Savilahti Harri, Multanen Kirsi

Patent application:
PCT/FI98/00586, In vitro method for providing templates for DNA sequencing (International patent pending, filed 10.7.1998)
Inventors: Tenkanen Tuomas, Soininen Timo, Savilahti Harri, Multanen Kirsi

5.3 Awards

17.11.1999:	The Chemical Industry Prize for Innovation in Recognition of an Outstanding Innovation in the Field of Chemistry Awarded to the Research Team of Dr. Harri Savilahti and Finnzymes Ltd. The Chemical Industry Federation of Finland and the Scientific Advisory Board of the Chemical Industry
3.4.2000:	The Finnish New Technology Foundation Innovation Award Awarded to the Research Team of Dr. Harri Savilahti and Finnzymes Ltd. The Finnish New Technology Foundation

6 Publications

6.1 Refereed Journal Articles (1997-1999)

[1] Haapa, S., Suomalainen, S., Eerikäinen, S., Airaksinen, M., Paulin, L. and Savilahti, H., An efficient DNA sequencing strategy based on the bacteriophage Mu in vitro DNA transposition reaction, Genome Res. **9** (1999a) 308-315.

[2] Haapa, S., Taira, S., Heikkinen, E. and Savilahti H., An efficient and accurate integration of mini-Mu transposons in vitro: a general methodology for functional genetic analysis and molecular biology applications, Nucleic Acids Res. **27** (1999b) 2777-2784.

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6.2 Master Theses

[5] Anna Kassinen, PRD1-faagin insertiomutageneesi Mu-transpositiolla *in vitro*. Master thesis, Department of Applied Chemistry and Microbiology, University of Helsinki 1999.

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7 Other References

[7] Laurent, L. C., Olsen, M. N., Crowley, R. A., Savilahti H and Brown, P.O. **2000**: Functional characterization of the human immunodeficiency virus type 1 genome by genetic footprinting. **J. Virol.** 74: 2760-2769.

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FUNCTIONAL OLEFIN COPOLYMERS

Jukka Seppälä[1]

Abstract

Functionalization via the precise tailoring of polymer structure gives polymers new properties. Very accurate structural tailoring of polyolefins has become possible after the discovery of highly active metallocene catalysts. The aim of this project was to increase understanding of the copolymerization properties of metallocene catalysts and to develop new polymer properties via copolymerization techniques. ‘Catalyst structure – polymer property’ relationships were developed with novel siloxy-substituted and conventional metallocenes. This information was successfully employed in polymerization research in which ethene/diene and novel ethene/silane copolymers and long-chain branched (LCB) polyethene were produced. With LCB in polyethene, the rheological properties were dramatically modified. Moreover, oxygen and nitrogen functionalized ethene copolymers were successfully employed in the compatibilization of polyethene/polyamide blends resulting in the improved mechanical properties.

1 Partners and Funding

1.1 Laboratory of Polymer Technology, Helsinki University of Technology

The research group worked independently in the MATRA program. The group had intense collaboration with the Polymer Science Centre (PSC) and Åbo Akademi University. Cooperation with the PSC included polymerization research work and the testing of polymer properties. The studies using novel siloxy-substituted metallocene complexes – developed [25] in Åbo Akademi University – resulted in several coauthored publications.

The research group consisted of project leader professor Jukka Seppälä, graduate students Ulla Anttila (7/1998-12/1999), Outi Härkki (4/1997-6/1998), Esa Kokko, Petri Lehmus (funded by Neste Foundation), Sami Lipponen and Pirjo Pietikäinen (funded by HUT). The research group also employed students as summer trainees and part-time research assistants.

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1.2 Funding

Table 1. Funding of the project in 1000 FIM in 4/1997-3/2000. Internal funding consists of manpower costs and operational expenditures provided by the organization.[a]

Partner	Funding organisation	1997	1998	1999	2000	**Total**
HUT	HUT	215	215	215	54	**699**
	Neste Foundation	80	85	85		**250**
	Tekes	525	832	894	215	**2466**
Total		**820**	**1132**	**1194**	**269**	**3415**

[a] Industry funding on parallel projects enabled the purchasing of modern analysis equipment and their utilization in this project.

2 Research Work

2.1 Objectives and Work Plan

The aim of this research project was to prepare new functional olefin copolymers with novel properties. The research goals were: 1) understanding 'catalyst structure – polymer property' relationships to investigate homo and copolymerization properties of siloxy substituted bis(indenyl) metallocene catalysts, 2) understanding monomer structure – monomer polymerizability relationships and the development of new olefin copolymers containing amino, amido, ester, and silane groups, 3) to develop long-chain branched (LCB) polyethene grades, 4) to develop new stereospecific homopolymers from novel monomers, and 5) to improve polarity, adhesion, printability, compatibility, recyclability, and the controlling of crosslinkability and rheological properties.

2.2 Progress Report: Laboratory of Polymer Technology

Catalyst structure – polymer property relationships. The ligand structure of a metallocene catalyst has a crucial importance in tailoring polymer properties. The primary goal of this research project was to study the effect of ligand substitution on the polymerization behavior of methylaluminoxane activated catalysts. Comonomer response, polymerization activity, and termination mechanisms were studied. Fig. 1 shows the studied catalysts, which included commercial metallocene complexes (**1**-**4**,**6**), novel siloxy-substituted complexes **5**, **7**-**10**, and a silyl substituted complex **11**.

Ethene–1-olefin copolymerization. Comonomer response depended on the interannular bridge, ligand structure, and siloxy-substitution as summarized in Table 2.

Compared to commercial catalysts, siloxy-substitution in 3-position (**7**,**10**) improved copolymerization properties whereas siloxy-substitution in 2-position (**5**) did not. The best comonomer response was obtained with *meso*-complexes **8** and **9**. The importance of siloxy-substitution can be seen from poor comonomer response of the silyl-substituted complex **11**.

Polymerization activity. Complex **5** had about 5-fold higher polymerization activity compared to the non-substituted analogue **3**. Moreover, polymerization activity was extremely high at unusually low Al/Zr ratios and decreased with increasing MAO concentration. This behavior was very pronounced with 3-siloxy-substituted complexes **7** and **10**. Furthermore, the activity increased when part of methylaluminoxane was replaced with triisobutylaluminum. [4]

Table 2. α-Olefin response of the studied metallocene complexes. Lower reactivity ratio value (r_{ethene}) indicates better comonomer response. [4,10,13,14,16]

Complex	1	2	3	4	5	6	7	8	9	10	11
r_{ethene} (40°C)	-	-	32	-	36	-	14	11	10	15	64
r_{ethene} (80°C)	112	160	48	26	55	71	30	-	-	19	100

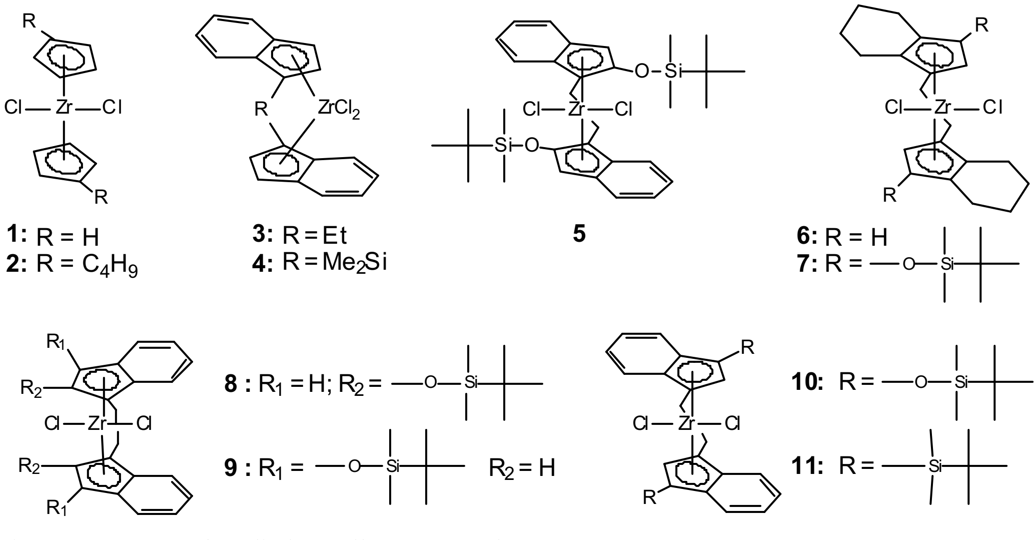

Fig. 1. Structures of studied metallocene complexes.

Chain transfer mechanisms. The chain transfer mechanism determines the molecular weight dependency and the end-group structure of a polymer. Two main chain transfer mechanisms were found to dominate. β-H elimination to metal took place with non-bridged **1** and **2**, tetrahydroindenyl ligand substituted **6** and **7**, and silyl substituted complex **11**. The chain transfer to the monomer dominated with the indenyl ligand substituted complexes **3**-**5**, **8**-**10**. Chain transfer to MAO had a minor role with some catalysts. The chain transfer mechanism appeared to have a major impact on the end-group types. In addition to vinyl unsaturations, the polymers contained small amounts of *trans*-vinylenes. Vinyl selectivity was substantially higher when chain transfer to the monomer dominated [4,10,13,14,16] and this information was utilized for production of LCB polyethene.

Long-chain branched polyethene. The narrow molecular weight distribution of metallocene based polyethenes – compared to the conventional polyethene grades – makes the processing of new materials more difficult. It is well known that the introduction of long side chains into polymer main chain alters the polymer processing properties. It was assumed that LCB can be introduced into metallocene catalyzed homopolyethene by copolymerizing ethene with vinyl terminated polyethene chains.

The ability of different metallocene complexes to produce LCB structures in ethene homopolymerization was studied with complexes **1-6**,**8-10** (Fig. 1). The catalysts with good comonomer response and high vinyl end-group selectivity were able to produce polyethene with significantly modified melt rheological properties. Melt rheological behavior of the prepared homopolyethenes depended heavily on the used catalyst and polymerization conditions. Based on ^{13}C NMR spectroscopic measurements it was estimated that the prepared polymers contained less than 0.2 LCB/1000 C atoms. This was sufficient to significantly alter the rhelogical behavior. [3,10,13,16]

Ethene copolymerization with nonconjugated dienes. In this research work rich molecular architecture was produced in a controlled way and, thus, it was possible to tailor the properties of polyethene copolymers. [6,7,11,15] Fig. 2 shows the obtained structural variations of ethene/diene copolymers. With long side chains it is possible to alter rheological behavior whereas unsaturations in the side chains improve printability and adhesion. Furthermore, polyethenes with small amounts of unsaturations can be used as intermediates for post-reactor functionalization.

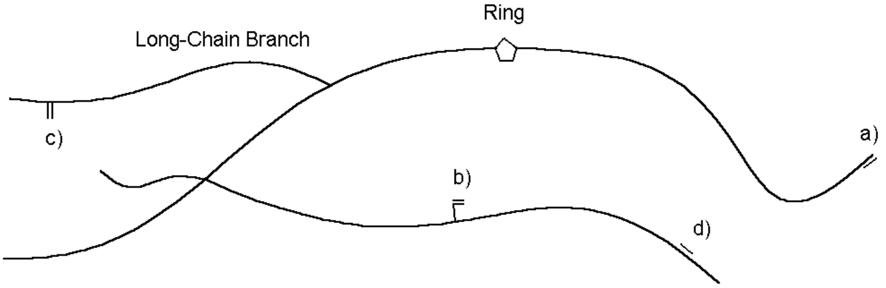

Fig. 2. Possible structures obtained in ethene/diene copolymerization. In addition to rings and long branches, copolymer may contain a) vinyl terminations at the end of a chain, b) vinyl terminations c) vinylidene or d) vinylene unsaturations.

Copolymerization with novel silane comonomers. The copolymerization of oxygen or nitrogen containing comonomers with group 4 metallocenes results in rapid decline in the polymerization activity. In this work novel weakly interacting silane monomers were synthesized and copolymerized with ethene using $Et(Ind)_2ZrCl_2/MAO$ catalyst system. The effect of different silane groups (Fig. 3) on the polymerization activity and comonomer incorporation tendency was examined. Also, the feasibility of an alternative route for producing oxygen-functionalized copolymers was studied.

In copolymerization with ethene, silane comonomers **4** and **5** behaved like 1-octene or 1-decene. However, the use of shorter monomers **1** and **2** resulted in lower activity and pronounced decrease in the M_w. Based on these results a new method was developed to bring siloxane functionality into the polyolefin chain via post-reactor treatment. First, **6** was synthesized and copolymerized with ethene. Copolymer **7** containing methoxysilane groups was obtained when the product was treated first with hydroboric acid, and then with methanol and sodiummethoxide. [26]

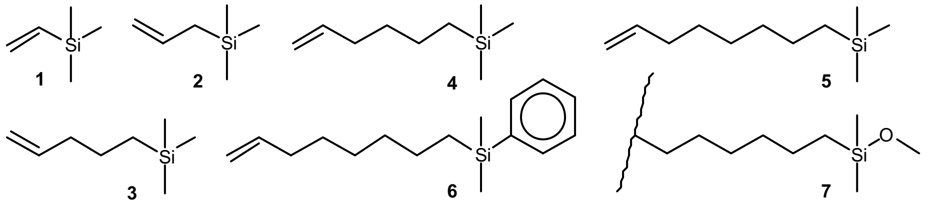

Fig. 3. The used silane comonomers. **1** and **2** were obtained commercially, **3**-**6** synthesized in the laboratory. **7** was obtained via post-reactor treatment of the copolymer of ethene and **6**.

Functionalized polyethenes as compatibilizers in PE/PA6 blends. Blending polyolefins with engineering thermoplastics, such as polyesters or polyamides, offers an interesting route to new combinations of polymer properties. These polymers are, however, immiscible, and a compatibilizer is needed. The compatibilizer is supposed to be miscible with both blend components and hence improve the compatibility. Typical compatibilizers are produced by grafting polyolefins or elastomers with functional monomers.

In this study metallocene catalyst technology was utilized to prepare functionalized polyethylenes, which were then used as compatibilizers in polyethylene/polyamide 6 (40/60) blends. Functionalized polyethylenes were prepared in cooperation with the PSC. The copolymers were used as compatibilizers in polyethylene/polyamide 6 (40/60) blends. Adding 10 wt-% of functional polyethylene to the blends increased considerably the toughness. Surprisingly, the stiffness of the blend was also slightly improved. Morphology became much more uniform with an addition of compatibilizer, and crystallization and melting behavior changed. [9]

3 International Aspects

The group has published the results of research work in highly ranked international journals and presented the work actively in international conferences. These include three invited lectures; Europolymer Conference Polyolefins (Italy, June 1998), BASF Conference on Insertion Polymerisation (Germany, October 2000), and 221st National ACS Meeting (USA, March 2001); two other oral, and seven poster presentations in 11 conferences have been given. The presentations have been listed in World Wide Web. [27]

Petri Lehmus studied metallocene catalyzed propene polymerization in University of Ulm (Germany) from July 1998 to September 1999. Esa Kokko started a research period in McMaster University (Canada) in March 2000.

4 Other Activities

The results have been presented for industrial cooperation partners in regular meetings. The collaboration with the Marketing Molecules program was also notable as the research project had a joint steering group.

A paper dealing with functional polyolefins was published in Kemia-Kemi with the PSC. [28]

5 Publications and Academic Degrees

Table 3. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 5.1, refereed conference papers in Section 5.2, monographs in Section 5.3, and theses in Section 5.4.

Partner	Type of publication	1997	1998	1999	2000	2001	**Total**	Publication numbers
HUT	Ref. journal art.	-	3	6	4	1	**14**	1-14
	Ref. conf. Papers	-	-	1	-	2	**3**	15-17
	Monographs	-	-	-	1	-	**1**	18
	Doctoral dissert.[a]	-	-	-	-	1	**1**	19
	Licentiate degrees	-	2	1	1	-	**4**	20-23
	Master degrees	1	-	-	-	-	**1**	24

[a] Two dissertations based on this project will be finished in 2001 and 2002.

5.1 Refereed Journal Articles

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[9] U. Anttila, K. Hakala, T. Helaja, B. Löfgren, and J. Seppälä, Compatibilization of polyethene/polyamide 6 blends with functionalized polyethenes prepared with metallocene catalyst, *J. Polym. Sci. Part A: Polym.Chem.* **37** (1999) 3099.

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[12] P. Lehmus, E. Kokko, R. Leino, H. Luttikhedde, B. Rieger, and J. Seppälä, Chain End Isomerization as a Side Reaction in Metallocene Catalyzed Ethene and Propene Polymerizations, *Macromolecules* **33** (2000) 8534-8540.

[13] E. Kokko, P. Lehmus, R. Leino, H. Luttikhedde, P. Ekholm, J. Näsman, and J. Seppälä, *meso-* and *rac*-Diastereomers of 1- and 2-tert-Butyldimethylsiloxy Substituted Ethylenebis(indenyl)zirconium Dichlorides for Formation of Short- and Long-Chain Branched Polyethene, *Macromolecules* **33** (2000) 9200-9204.

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5.2 Refereed Conference Papers

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5.3 Monographs

[18] B. Löfgren and J. Seppälä, New Functionalized Olefin Copolymers Synthesized by Metallocenes and Novel Organometallic Catalysts, in *Metallocene-based Polyolefins, Preparation, Properties and Technology*, J. Scheirs and W. Kaminsky (Eds.), John Wiley & Sons, Chichester, 2000, Volume II, p. 143-157.

5.4 Doctoral, Licentiate, and Master Theses

[19] P. Lehmus, Structure-property relations of some highly active *ansa*-metallocene catalysts in olefin polymerization – a polymerization study, Dissertation, Department of Chemical Technology, Helsinki University of Technology, 2001.

[20] O. Härkki, Studies on the effects of the structure of some metallocene catalysts on ethylene homo- and copolymerizaition. Licentiate's Thesis, Department of Chemical Technology, Helsinki University of Technology, 1998.

[21] P. Pietikäinen, Copolymerization of ethylene and non-conjugated dienes with metallocene catalyst Cp_2ZrCl_2, Licentiate's Thesis, Department of Chemical Technology, Helsinki University of Technology, 1998.

[22] P. Lehmus, Structure-property relation of some highly active *ansa*-metallocenes in ethene homo- and copolymerizations, Licentiate's Thesis, Department of Chemical Technology, Helsinki University of Technology, 1999.

[23] E. Kokko, Metallocene-catalyzed ethylene polymerization: long-chain branched polyethylene Licentiate's Thesis, Department of Chemical Technology, Helsinki University of Technology, 2000.

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6 Other References

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[26] S. Lipponen and J. Seppälä, Functionalization of polyethylene by using silane comonomers, *Organometallic Catalysts and Olefin Polymerization, New Millenium International Conference*, Oslo, Norway, June 18-22, 2000, Poster presentation.

[27] B. Löfgren and J. Seppälä, Funktionaalisia polymeereja metalloseenikatalyyteilla. Kemia-Kemi, **24** (1997) 288-291.

[28] Anon., Laboratory of Polymer Technology; Publication Search Engine, http://pt.hut.fi/pote/english/research/publicat.html, 19.6.2001

LIGHT EMITTING SILICON BASED SUPERLATTICES

J. Sinkkonen[1]

Abstract

Light emission from silicon based materials system is studied. Si/SiO_2-superlattices are grown by MBE and PECVD. Compositional SiO_x-superlattices and homogeneous layers are also made by MBE. Samples exhibit rather broad emission spectrum in near-infrared and visible range. The position of the spectrum depends on the silicon layer thickness. However, the dependence is weaker than predicted by the quantum confinement model. Annealing at high temperatures leads to formation of silicon nanocrystals in superlattices and also in homogeneous SiO_x-samples. Nanocrystallites influence both the spectral position and intensity of emission. Usually a large enhancement of intensity takes place. Nanocrystalline samples are also made by implanting silicon ions into SiO_2. Strong light emission is obtained after annealing. Phosporous doping of nanocrystals enhances the light intensity. Manganese ions are introduced into SiO_2 by knock-on-implantation. The samples show additional yellow peak associated with Mn. Light emitting devices (LED), where various nanostructured Si/SiO_2-systems are used as active layer, are fabricated. Also nanopillar-LEDs are made. Best external quantum efficiencies exceed 10^{-3}. A model based on oxygen related defects is presented for the light emission mechanism.

1 Partners and Funding

1.1 Electron Physics Laboratory, Helsinki University of Technology

The research group consists of project leader professor Juha Sinkkonen, senior researchers PhD Sergei Novikov, PhD Alexei Malinin, PhD Victor Ovchinnikov, and PhD Vadim Sokolov, postgraduate students Lic.Sc. Tero Majamaa, M.Sc. Olli Kilpelä, and M.Sc. Xia Chuan, and students Sanna Yliniemi and Timo Saloniemi. Dr Novikov is MBE-specialist. He has been responsible for MBE-growth of samples. In addition he has had a major role in planning and performing of various annealing procedures, in fabrication of LED samples and in their characterization. Dr Novikov has been supervising Olli Kilpelä and Timo Saloniemi in MBE-technology. Dr Malinin has been involved in PECVD-growth of samples, processing of LED-structures and their characterization. Especially he has been developing nanopillar-based LEDs utilizing dry etching and electron beam lithography. He has been supervising Xia Chuan in his licentiate work. Dr Ovchinnikov has taken part in PECVD-growth, dry etching and

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especially in fabrication of ion implanted LEDs in last part of the project. Dr Sokolov has specialized in optical measurements. He has been supervising Sanna Yliniemi in her diploma work. Tero Majamaa has been concentrating in ultra thin oxide study utilizing MBE-growth and MOS-type characterization. He completed his doctors thesis work in early part of the project. The total volume of the project is 176 person-months. Table 1 shows the distribution of manpower according to the funding source.

Table 1. Distribution of manpower during 1998 – 2000 in person-months.

Researcher	Tekes	HUT	Academy	Total
S. Novikov		36		**36**
A. Malinin				**30**
V. Ovchinnikov	30	18		**18**
V. Sokolov	12			**12**
T. Majamaa	3		5 *	**8**
O. Kilpelä	30		6 *	**36**
X. Chuan	14	5		**19**
S. Yliniemi			12	**12**
T. Saloniemi		5		**5**
Total	**89**	**64**	**23**	**176**

*Graduate School

1.2 Funding

Table 2. Funding of the project in 1000 FIM in 1998 - 2000.

	Funding organisation	1998	1999	2000	**Total**
	HUT	505	483	608	**1596**
	Academy	269		103	**372**
	Tekes	833	861	751	**2445**
Total		**1607**	**1344**	**1462**	**4413**

2 Research Work

2.1 Objectives and Work Plan

In 1990's it became evident that light emission from silicon is possible whenever nanoscale structures are involved. In the pioneering work of Canham [30] porous silicon was used. It consists of nanoscale Si-columns covered by SiO_2 layer. Since Canham's work, light emitting samples have been made by a great variety of methods including evaporation, sputtering, laser ablation, ion implantation, chemical vapor deposition, molecular beam deposition, etc. The origin of light emission is still unclear. It seems that there are several competing mechanisms whose strength is dependent on the fabrication method and subsequent annealing treatments. The most frequently cited emission mechanisms are: (1) Quantum confinement, where the light is generated by the radiative transitions inside nanoscale silicon particle. Owing to spatial confinement the band gap of nanocrystalline silicon is shifted to visible range and the oscillator strength is increased. (2) Oxygen related defects in silicon rich SiO_x ($x \leq 2$) layer covering the nanocrystalline silicon particle. (3) Impurity states in SiO_2 associated with other chemical elements such as hydrogen, which may be unintentionally introduced during sample processing. Intentional doping of SiO_2 by active centers can also be utilized. (4) Hot carrier recombination in silicon substrate. Emission efficiency is still weak compared with III-Vs. Best reported quantum efficiencies are around 10^{-2} for porous silicon, defect related mechanism yield $\eta \cong 10^{-3}$ and the weakest mechanisms, hot carrier recombination, has the limit $\eta \cong 10^{-6}$.

The original research plan was made in 1997. Actually a consortium of five university laboratories was created. Funding was applied both from Academy of Finland and Tekes. Only Tekes made positive funding decision and two projects could be started. The other project, adjoint to the present one, is "Electroluminescence in Si/SiO_2 superlattices" lead by professor Heikki Ihantola from Laboratory of Electronics and Information Technology, University of Turku. A stearing group, common for the two projects, was formed.The group members were: a representative of Tekes (O. Knuuttila, P. Piiroinen, or I. Seppänen), representatives of Finnish semiconductor industry (M. Tilli or O. Anttila from Okmetic Ltd, H. Kuisma from VTI Hamlin Ltd, and R. Tuovinen from Micro Analog Systems Oy) and project leaders H. Ihantola and J. Sinkkonen. The stearing group had seven meetings during the project period. All aspects regarding the project i.e. progress, targets, staff, costs, etc. were handled in the meetings.

The following tasks were put forward in the original research plan: (1) Making light emitting superlattices by the means available at the laboratory, (2) attempt to identify and intensify the emission mechanism by processing means, and (3) making various kinds of light emitting device demonstrations. In addition to the superlattices the other nanostructured samples i.e. nanopillar- and nanocrystalline samples were included during the course of the project.

In Electron Physics Laboratory silicon MBE-equipment together with *in situ* oxidation option was available. This allows a good control of layer thicknesses. This is essential in order to test the quantum confinement model. PECVD-growth was also available to EPL due to the Microelectronics Center (MEC) of HUT. The processing facilities of MEC were developing during the course of the project. For thermal treatments of the samples furnace annealing and RTA became available in 1999. Ion implantation was possible first time in 2000. PL-spectroscopy and TEM-analysis were the main characterization methods to be used. In the beginning they were obtained as external service from University of Helsinki, Tampere University of Technology and Ioffe Institute (Russia). Since the defect characterization project (EMMA-program, Academy of Finland) was started in 1999 the PL- and TEM-services were obtained from project partners.

2.2 Progress Report: Progress by the Electron Physics Laboratory

MBE-growth of Si/SiO_2-superlattices has continued through the whole project period. The spectral position of light emission depends on the silicon layer thickness. However, the dependence is clearly weaker than predicted by the quantum confinement model. When SiO_2-growth was done in the presence of hydrogen a strong increase of emission was observed. Compositional SiO_x-superlattices were also made by MBE. They exhibit similar emission spectra as Si/SiO_2-superlattices. Annealing at higher temperatures leads to the formation of silicon nanocrystallites. The observed red shift of spectrum in red and near infrared part together with the increase of intensity can be connected with the nanocrystallites. On the other hand, the short wavelenght part in blue region, which shows no shift by annealing can be associated with oxygen related defects in SiO_2. Nanocrystalline structures are also made by implanting silicon ions into SiO_2 and performing then proper annealing. The implanted samples show typically stronger light emission than the superlattice samples. Phosphorus doping of Si-implanted samples enhances the intensity. For comparison Mn-doped SiO_2 samples were also made. An additional yellow peak, associated with manganese, was seen in the spectrum. LEDs with various kinds of nanostructured Si/SiO_2 as active layer were made. In addition nanopillar-LEDs were fabricated. Highest external quantum efficiencies exceeding 10^{-3} were measured from P-doped Si-implanted and Mn-doped SiO_2 samples. Light emission from Si/SiO_2-system can be understood by an oxygen defect related model [25, 31].

A comprehensive report of the obtained results is given in Ref. [25]. In electrical form the report is also available at http://www.hut.fi/Yksikot/Elfys/Publictions2001.htm

3 International Aspects

Co-operation in sample characterization with various laboratories of A.F. Ioffe Institute, St. Petersburg, Russia, helped the progress of the project. In particular, PL-measurements of PhD S. Gastev, TEM-analysis of PhD A. Sitnikova and cathodoluminescence measurements of PhD M. Zamoryanskaya are gratefully acknowledged.

4 Publications and Academic Degrees

Table 3. Publications and academic degrees produced in the project.

Type of publication	1998	1999	2000	**Total**	Publication numbers
Ref. journal art.	2	5	6	**13**	1-13
Ref. conf. papers	3	3	3	**9**	14-23
Monographs	1		1(2001)	**1+1**	24, 25
Doctoral dissert.			1	**1**	28
Licentiate degrees		1	1(2001)	**1+1**	27, 29
Master degrees		1		**1**	26

5 Other Activities

A postgraduate course dealing with light emission from silicon was arranged in 1998 [24]. Eleven students participated in the course.

6 Publications

6.1 Refereed Journal Articles

[1] J. Keränen, T. Lepistö, L. Ryen, S. Novikov and E. Olsson, Transmission electron energy-loss spectroscopy measurements of the dielectric function of Si/SiO_2 multilayers, J. Appl. Phys. **84** (1998) 6827-6831.

[2] A. Malinin, T. Majamaa and A. Hovinen, Anisotropic Si Reactive Ion Etching in Fluorinated Plasma, Microelectronic Engineering 43-44 (1998) 641-645.

[3] V. Ovchinnikov, A. Malinin, S. Novikov and C. Tuovinen, Silicon Nanopillars Formed by Reactive Ion Etching Using Self-Organized Gold Mask, Physica Scripta **T79** (1999) 263-265.

[4] O. Kilpelä, M. Karpinen, S. Novikov, V. Sokolov and S. Yliniemi, Absorption in a-Si/SiO_2 superlattices, Physica Scripta **T79** (1999) 95-98.

[5] S. Novikov and J. Sinkkonen, Fabrication of SiO_2/c-Si/SiO_2 double barrier structure using lateral solid phase epitaxy, Physica Scripta **T79** (1999) 213-215.

[6] V. Ovchinnikov, A. Malinin, S. Novikov and C. Tuovinen, Silicon nanopillars formed by reactive ion etching using self-organized gold mask, Physica Scripta **T79** (1999) 263-265.

[7] L. Khriachtchev, M. Räsänen, S. Novikov, O. Kilpelä and J. Sinkkonen, Raman scattering from very thin Si layers of $SiSiO_2$ superlattices: Experimental evidence of structural modification in the 0.8-3.5 nm thichness region, J. Appl. Phys. **86** (10) (1999) 5601-5608.

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[12] A. Malinin, V. Ovchinnikov, S. Novikov, C. Tuovinen, A. Hovinen, Fabrication of a silicon based electroluminescent device, Materials Science & Engineering B **74** (2000) 32-35.

[13] V. Ovchinnikov, A. Malinin, V. Sokolov, O. Kilpelä and J. Sinkkonen, Photo- and Electroluminescence from PECVD Grown a-Si:H/SiO_2 Multilayers, accepted for publication in Optical Materials, 2001.

6.2 Refereed Conference Papers

[14] V. Ovchinnikov, A. Malinin and C. Tuovinen, Fabrication of Silicon Nanopillars by Reactive Ion Etching Self-Organized Gold Mask. Abstracts of the 18th Nordic Semiconductor Meeting, Linköping, Sweden, 7-10 June 1998, 75.

[15] O. Kilpelä, M. Karpinen, S. Novikov, V. Sokolov and S. Yliniemi, Absorption in a-Si/SiO_2 superlattices. Abstracts of the 18th Nordic Semiconductor Meeting, Linköping, Sweden, 7-10 June 1998, 51.

[16] S. Novikov and J. Sinkkonen, Fabrication of SiO_2/c-Si/SiO_2 double barrier structure using lateral solid phase epitaxy. Abstracts of the 18th Nordic Semiconductor Meeting,Linköping, Sweden, 7-10 June 1998, 108.

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[20] A. Malinin, V. Ovchinnikov, S. Novikov, O. Kilpelä and J. Sinkkonen, Photo- and Electroluminescence from a-Si/SiO_xN_y Multilayers. E-MRS 2000 Spring Meeting, Strasbourg, France, May 30-June 2, 2000, 11.

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6.3 Monographs

[24] J. Sinkkonen (ed.), Light Emission from Silicon – Porous Silicon, Reports in Electron Physics 18, Electron Physics Laboratory, Helsinki University of Technology, Otaniemi, 230 pp. (1998).

[25] A. Malinin, S. Novikov, V. Ovchinnikov, V. Sokolov, O. Kilpelä, T. Saloniemi and J. Sinkkonen: Light Emission from Silicon-based Materials. Reports in Electron Physics 25, Electron Physics Laboratory, Helsinki University of Technology, Otaniemi, 41 pp., (2001).

6.4 Doctoral, Licentiate, and Master Theses

[26] Sanna Yliniemi, "Optical properties of multilayers", master's thesis, 1999.

[27] Xia Chuan, "Electron beam lithography", licentiate thesis, 1999.

[28] Tero Majamaa, "Ultrahigh vacuum plasma oxidation in the fabrication of ultrathin silicon dioxide films", doctorate thesis, 2000.

[29] Olli Kilpelä, "Growth, processing and characterization of MBD-grown Si/SiO_2 superlattices", licentiate thesis, 2001 (expected).

7 Other References

[30] L.T.Canham, Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers, Appl.Phys.Lett. **57** (1990) 1046

[31] M.V. Wolkin, J. Jorne, and P.M. Fauchet, Phys. Rev. Lett., 82, (1999) 197.

NEW TECHNOLOGY FOR STRUCTURAL STUDIES OF PHARMACEUTICALLY IMPORTANT PROTEINS:

Development of membrane protein binding antibodies (collaboration between VTT Biotechnology and Orion Pharma)

Structure determination of testosterone binding Fab fragments (collaboration between University of Joensuu and VTT Biotechnology)

Kristiina Takkinen[1]

Abstract

In the collaboration project between VTT Biotechnology and the Drug Design Group of Orion Pharma the goal was to develop antibodies for the purification and crystallization of two pharmaceutically important membrane proteins. Both hybridoma technology and phage display technology were applied for the antibody production, but in spite of using many different selection and screening strategies no specific antibodies were found for the first target antigen. As a deviation of the original research plan the resources of VTT Biotechnology were used to optimize the production and purification of the second antigen during the last eight months. The screening of antibodies for the second antigen was not finished due to this change in the research plan. In the collaboration project between VTT Biotechnology and University of Joensuu the goal was to determine the three-dimensional structures of recombinant Fab-fragments binding testosterone with high affinity and specificity. These Fab-fragments having commercial potential as diagnostic reagents had been developed at VTT Biotechnology during an earlier Tekes project. Four high resolution crystal structures of Fab-fragments were determined at the University of Joensuu giving excellent tools for further refinement of the Fab fragments for diagnostic applications.

1 Partners and Funding

1.1 VTT Biotechnology

The research group consisted of project leader docent Dr Kristiina Takkinen, researcher PhLic Kaija Alfthan and technician Pirkko Veijola-Bailey.

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[1] VTT Biotechnology, P.O.Box 1500, FIN-02044 VTT

1.2 Department of Chemistry, University of Joensuu

The research group consisted of project leader docent Dr Juha Rouvinen, researcher PhLic Jarkko Valjakka and laboratory technician Reetta Kallio-Ratilainen. The group of docent J. Rouvinen had a separate project budget and their funding is not described here.

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1998-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1998	1999	2000	**Total**
VTT	VTT	198	268	197	663
	Tekes	475	580	474	1529
	Orion Pharma	119	119	119	357
Total		**792**	**967**	**790**	**2549**

2 Research Work

2.1 Objectives and Work Plan

The rational drug design is based on the three dimensional structure information of the drug binding proteins, which often are complex membrane proteins. Both the purification and crystallization of membrane proteins is usually a demanding task and many different technical procedures are evaluated in this context. In recent publications antibody assisted membrane protein purification and crystallization experiments have been described [5,6,7]. In the collaboration project between VTT Biotechnology and Orion Pharma the goal was to develop antibodies binding to two pharmaceutically interesting membrane proteins. The antibodies were intended to use in the purification and crystallization of these target antigens.

2.2 Progress Report: Common Themes

In the collaboration project with the University of Joensuu the goal of VTT Biotechnology was the large-scale production and purification of recombinant anti-testosterone Fab fragments for the crystallization experiments. These high affinity and specificity anti-testosterone Fab-fragments having commercial potential as diagnostic reagents had been developed at VTT Biotechnology during an earlier Tekes project [7,8]. A high cell density *E.coli* bioreactor production system was applied for the Fab fragments and a two step chromatographic purification protocol was used for the purification. Purification yields of the active Fab fragments varied between 50 - 100 mg/l of culture supernatant. The purity of the Fab fragments was high enough to obtain protein crystals [1]. Three different anti-testosterone Fab-fragments were produced and purified: the wild type (wt) testosterone binding Fab-fragment as well as two different high affinity and specificity variants of the wt Fab-fragment (mutants A60 and 77).

The high-resolution three-dimensional structures of the Fab fragments with and without the ligand can be used to identify the ligand binding mode and interacting residues [2, 3]. Improved specificity and selectivity of the mutant Fab fragments are based on many small structural changes that allow more compact packing of the testosterone ligand against the protein atoms [4]. Based on the structures new site specific mutations leading to further improvement in the binding properties of these antibody fragments can be deduced.

2.3 Progress Report: Progress by VTT Biotechnology

Both hybridoma technology and phage display technology were applied for the antibody production, but in spite of using many different selection and screening strategies no specific antibodies were found for the first target antigen. As a deviation of the original research plan the resources of VTT Biotechnology were used to optimize the production and purification systems of the second antigen during the last eight months. In the original research plan the production and purification of the target antigens needed for the antibody development were planed to be the tasks of Orion Pharma. The screening of antibodies for the second antigen was not finished due to this change in the research plan. Due to the confidentiality of the research results a more detailed description of the project progress is not possible.

3 International Aspects

The results, which do not have industrial / commercial interest, will be published in international scientific journals and presented in international conferences.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles is given in Section 5.1.

Partner	Type of publication	1998	1999	2000	2001	**Total**	Publication numbers
VTT	Ref. journal art.	-	-	1	3 (exp)	**4**	1-4

5 Publications

5.1 Refereed Journal Articles

[1] J. Valjakka, A. Hemminki, T. Teerinen, K. Takkinen and J. Rouvinen. X-ray studies of recombinant anti-testosterone Fab-fragments: the use of PEG 3350 in crystallization. *Acta Cryst. D* **56** (2000) 218-221.

[2] J. Valjakka, K. Takkinen, T. Teerinen, H. Söderlund and J. Rouvinen. Structural insights to steroid hormone binding: crystal structure of a recombinant anti-testosterone Fab fragment in free and testosterone-bound form. Submitted.

[3] J. Valjakka, J. Kyngäs and K. Takkinen. A structure-function analysis of the X-ray structures of antibody Fab fragments: A comparative analysis between the hapten and the peptide binding CDR-loops. Manuscript.

[4] J. Valjakka, K. Takkinen, H. Söderlund and J. Rouvinen. Improvement of properties of anti-testosterone Fab fragments by directed evolution: A protein crystallographic study. Manuscript.

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[5] G.Kleymann, C.Ostermeier, B.Ludwig, A.Skerra and H.Michel. Engineered Fv fragments as a tool for the one-step purification of integral multisubunit membrane protein complexes. Bio/Technol. **13** (1995) 155.

[6] S.Iwata, C.Ostermeier, B.Ludwig and H.Michel. Structure at 2.8 Å resolution of cytochrome c oxidase from *Paracoccus denitrificans.* Nature **376** (1995) 660.

[7] A.Hemminki, S.Niemi, A.-M.Hoffren, L.Hakalahti, H.Söderlund and K.Takkinen. Specificity improvement of a recombinant anti-testosterone Fab fragment by CDRIII mutagenesis and phage display selection. Protein Eng. **11** (1998) 311.

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ADVANCES PROPERTIES OF COPPER ALLOWS

Tuomo Tiainen[1], Pentti Karjalainen[2] and Antti Korhonen[3]

Abstract

The aim of the project was to develop new dilute copper alloys free of harmful alloying elements for applications where good electrical conductivity and high strength are required simultaneously. The second aim was to outline industrially viable processes for producing the alloys as semifinished products and for optimizing their properties. The alloy development was based on precipitation hardening with intermetallic compounds as precipitating phases in order to enhance the thermal stability of the properties of the alloys. For the processing a route utilizing thermomechanical treatments for enhancing both the strength and conductivity was aimed for in the work. Based on both theoretical evaluations and earlier work the alloys CuCrP, CuZrSi, CuCoSi and CuNiSi (Corson bronze) were selected as studied alloys. The alloys were produced by using both conventional casting plus hot extrusion and by novel upcasting techniques and their microstructures and precipitation behaviour were characterized. The influence of prior, simultaneous and postprecipitation deformation on the strength, hardness and electrical conductivity of the alloys were characterized by both laboratory experiments and physical Gleeble- simulations and the consequent microstructures were characterized by optical and TEM microscopy. The results showed that the aimed strength and conductivity combinations could be obtained in the studied alloys by proper thermomechanical treatments and that the thermal stability of the obtained properties was adequate for the practical use of the alloys. Industrial processes for the production of the alloys as semifinished products and for optimizing their properties were outlined on the basis of obtained results.

1 Partners and Funding

1.1 Institute of Materials Science, Tampere University of Technology

The research group consisted of the project coordinator and subproject leader professor Tuomo Tiainen, senior researchers Nan Gao and Elina Huttunen-Saarivirta and (for a part of the project time) postgraduate students Yu Ji and Mari Tanttari.

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[1] Institute of Materials Science, Tampere University of Technology (IMS/TUT), Korkeakoulunkatu 2, FIN-33720 Tampere

[2] Materials Engineering Laboratory, University of Oulu (MEL/UO), Linnanmaa, FIN-90570 Oulu

[3] Laboratory of Processing and Heat Treatment of Materials, Helsinki University of Technology (LPHTM/HUT), Vuorimiehentie 2, FIN-02150 Espoo

1.2 Materials Engineering Laboratory , Department of Mechanical Engineering, University of Oulu

The research group consisted of the subproject leader prof. Pentti Karjalainen, senior scientist Dr Mahesh Somani and (for a part of the project time) postgraduate students Mikko Hemmilä and Pekka Kantanen.

1.3 Laboratory of Processing and Heat Treatment of Materials, Helsinki University of Technology

The research group consisted of the subproject leader prof. Antti Korhonen, senior scientist, prof. emeritus Martti Sulonen, postgraduate student Ahti Viljamaa and (for a part of the project time) student Mirva Heinonen.

1.4 Funding

Table 1. Funding of the project in 1000 FIM in 1998-2000. Besides the internal funding of the partners the project was funded by Tekes and industry.

Partner	Funding organisation	1998	1999	2000	**Total**
TUT	TUT	97	104	76	**277**
	Tekes	444	440	375	**1259**
	Industry	0	51	33	**84**
UO	UO	65	65	65	**195**
	Tekes	193	313	285	**791**
	Industry	0	30	33	**63**
HUT	HUT	32	32	32	**96**
	Tekes	201	275	240	**716**
	Industry	0	29	33	**62**
Total		**1032**	**1339**	**1172**	**3543**

The funding presented in Table 1 is based on the actual expenditures and the annual decisions of Tekes and distributed to the three project years according to the decisions. Actually some parts of the project were allocated continuation time over the end of the year, but that has not been taken into account in Table 1. The project ended officially after the completion of the last continuation time 30.04.2001.

2 Research Work

2.1 Objectives and Work Plan

The aim of the project consortium was to develop new dilute copper alloys free of harmful alloying elements (such as beryllium or cadmium) for applications where both good electrical conductivity and high hardness are needed simultaneously. The strength of the developed alloys was aimed to be based on precipitation hardening with intermetallic compounds as precipitating phases in order to obtain better thermal stability for the properties of the studied alloys. The precipitation phenomena and the consequent strength properties were to be enhanced by thermomechanical treatments, which have not been systematically studied for copper alloys in earlier research. One of the aims was also to outline the industrial processes by which the studied alloys can be produced as semifinished products and their properties can be optimized. These goals were aimed for by using theoretical studies on alloy development, physical simulation of thermomechanical treatments with Gleeble- simulator and by characterizing the mechanical properties of processed alloys by tensile hand hardness testing. The microstructures of the studied alloys were to be characterized by utilizing analytical transmission electron microscopy (TEM) technique. The original goals remained unchanged for the whole course of the project.

2.2 Progress Report: Common Themes

In the following the research themes common to all partners in the project are outlined and the most important results will be reviewed.

2.2.1 Selection of the studied alloys

The theoretical studies to form the basis for studied alloy development were carried out by IMS/TUT. The alloying element selection was based on finding the proper alloying elements for forming the desired intermetallic compounds by precipitation processes. The alloying element contents were selected by aiming for a situation where all the alloying elements could be precipitated ou from the matrix in order to leave a clean matrix for good electrical conductivity. On the basis of this work the following alloy types and alloying element concentrations were selected for the study (contents are given in weight per cents:

CuCrP alloy: Cu + 0.6 % Cr + 0.07 % P
CuZrSi alloy: Cu + 0.2 % Zr + 0.04 % Si
CuCoSi alloy: Cu + 0.6 % Co + 0.32 % Si
CuNiSi alloy: Cu + 1.85 % Ni + 0.6 % Si

The last (CuNiSi) alloy was mainly studied by LPHTM/HUT and MEL/UO whereas the other three alloys were studied by IMS/TUT together with MEL/UO.

2.2.2 Experimental research

The materials were produced by the industrial partner Outokumpu Copper Products Oy R&D- unit. Their microstructures and precipitation behaviour were characterized by IMS/TUT and LPHTM/HUT (CuNiSi alloy) in order to find optimum parameters for the consequent thermomechanical treatmens. The existence of eventual dynamic recrystallization (DRX) and dynamic precipitation (DP) during the hot deformation of the studied materials was studied by MEL/UO by using the Gleeble 1500- simulator of the laboratory.

Different thermomechanical treatments were studied in laboratory scale experiments by IMS/TUT in order to find the optimum parameters for the consequent thermomechanical processing procedures for the studied alloys. The resulting hardness and conductivity values as well as microstructures were characterized. Simultaneously similar physical simulation experiments were carried out by MEL/UO on Gleeble-simulator. These experiments were aimed for clarifying the influence of simultaneous high temperature deformation on the precipitation behaviour whereas the experiments carried out by IMS/TUT studied the effect of either prior or post deformation on the precipitation behaviour. On the basis of the results of these experiments an outline for the suggested industrial fabrication processes for these alloys as semifinished products with optimum properties was agreed to form the basis of the final stage of the project.

The alloys and semifinished products were prepared according to the agreed processing stages by Outokumpu Copper Products Oy. They were delivered to the partners for further studies. As the deformations applied in the industrial processing stages were different from the earlier experimental studies, the precipitation annealing temperatures and times included in the industrial processing sequence were optimized for these materials by IMS/TUT.

In the industrial production experiments the materials were prepared as semifinished product wires with the diameter of 2 mm (CuCrP- and CuCoSi- alloys) or 11.5 mm (CuZrSi- alloy). The fabrication steps of these wires included solution annealing, cold deformation with true strain of 1.5 to 1.7, aging at temperatures optimized for each alloy and consequent cold deformation into final product diameter. For the final diameter of 2 mm the last cold deformation was carried out in two steps the first having a true strain of 1.0 and the second of 1.8. For the final diameter of 11.5 mm the last cold deformation was carried out in one step with the true strain of 0.5. Samples were taken at each fabrication step in order to characterize the properties of obtained alloys and to compare them with those obtained in laboratory and simulation experiments. The hardness and electrical conductivity values of these industrially produced materials at each fabrication step were characterized by MEL/UO.

2.2.3 Main results of the project

The main results of the work showed that the developed alloys were capable of strong precipitation hardening and that the thermomechanical treatments were capable of enhancing the precipitation behaviour. The sizes of the precipitates in the maximum hardness stage were too small for exact structural and compositional analyses, but in strongly overaged specimens the precipitating phases turned out to be of the desired character.

a) Conventional precipitation characteristics of the studied alloys

The hardness/conductivity combinations obtained by following the optimized conventional solution annealing + aging treatments in the studied CuCrP-, CuCoSi- and CuZrSi-alloys are shown in Fig. 1 [6]. If the hardness of the CuZrSi-alloy would have been allowed to drop by 5 HV5- units by aging at a slightly higher temperature, the conductivity of that alloy would have been of the order of 90 % IACS. With the CuNiSi- alloy the maximum hardness obtained by the conventional precipitation treatment was 194 HV and the electrical conductivity at that stage was 38 % IACS [8].

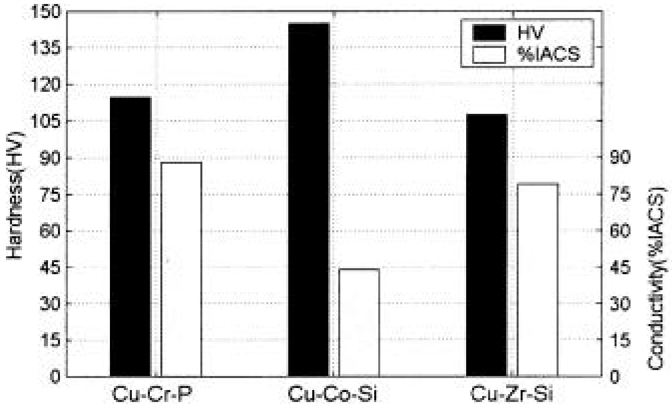


Fig.1. The optimized hardness/conductivity combinations obtained in the present study by conventional solution annealing and aging treatments for three of the studied alloys [5], [6].

b) The influence of thermomechanical treatments on the hardness/conduct- ivity combinations of the studied alloys

By applying different thermomechanical treatments the hardness/conductivity combinations of the studied alloys could be improved. The combination of solution treatment-deformation (compression by 30%)-aging was able to increase the maximum hardness by about 30 HV5-units in the CuCrP- and CuZrSi- alloys and 20 HV5-units in the CuCoSi- alloy as compared to the conventional solution annealing + aging treatments while the conductivity was dropped by about 5 % IACS [6]. By applying an extra aging treatment after solution annealing and before compression the conductivity could be recovered to the level existing after conventional solution annealing + aging treatment without loosing the hardness. Then, the best conductivity/hardness combinations obtained by the thermomechanical treatments in IMS/TUT were 135HV5/89%, 160HV5/45% and 139HV5/78% for the CuCrP-, CuCoSi- and CuZrSi- alloys, respectively. In practice, the CuCrP- and CuZrSi- alloys were in this respect almost identical (see the remark in the previous paragraph). Interestingly, it was noted that the deformation of the hot extruded material prior to the solution annealing-deformation-aging treatments did not give any benefits; it actually led to similar or even lower final strength values as compared to the conventional solution annealing and aging treament. Thus, the idea of enhancing the efficiency of solution annealing treatment by prior deformation did not work in the studied alloys.

For the CuNiSi- alloy the best hardness/conductivity combination obtained by thermomechanical treatment (solution annealing- deformation by 80 % compression-aging) was 210HV5/43% [8]. The values are better than those obtained with the CuCoSi- alloy, which may partly due to the higher alloying element content and consequently more efficient precipitation behaviour of the CuNiSi-alloy.

The thermomechanical treatment experiments and their results carried out by MEL/UO are presented in Table 2 [7]. The selected thermomechanical treatment procedure was solution annealing- deformation-aging-deformation. As shown in Table 1, this procedure yielded maximal hardness values, if the true strain applied in both the prior and post-aging deformation was of the order of 0.5.The obtained maximum hardness values for the studied alloys were higher than those measured by IMS/TUT, which was most probably due to the efficient hardening during the deformation of the aged structures.

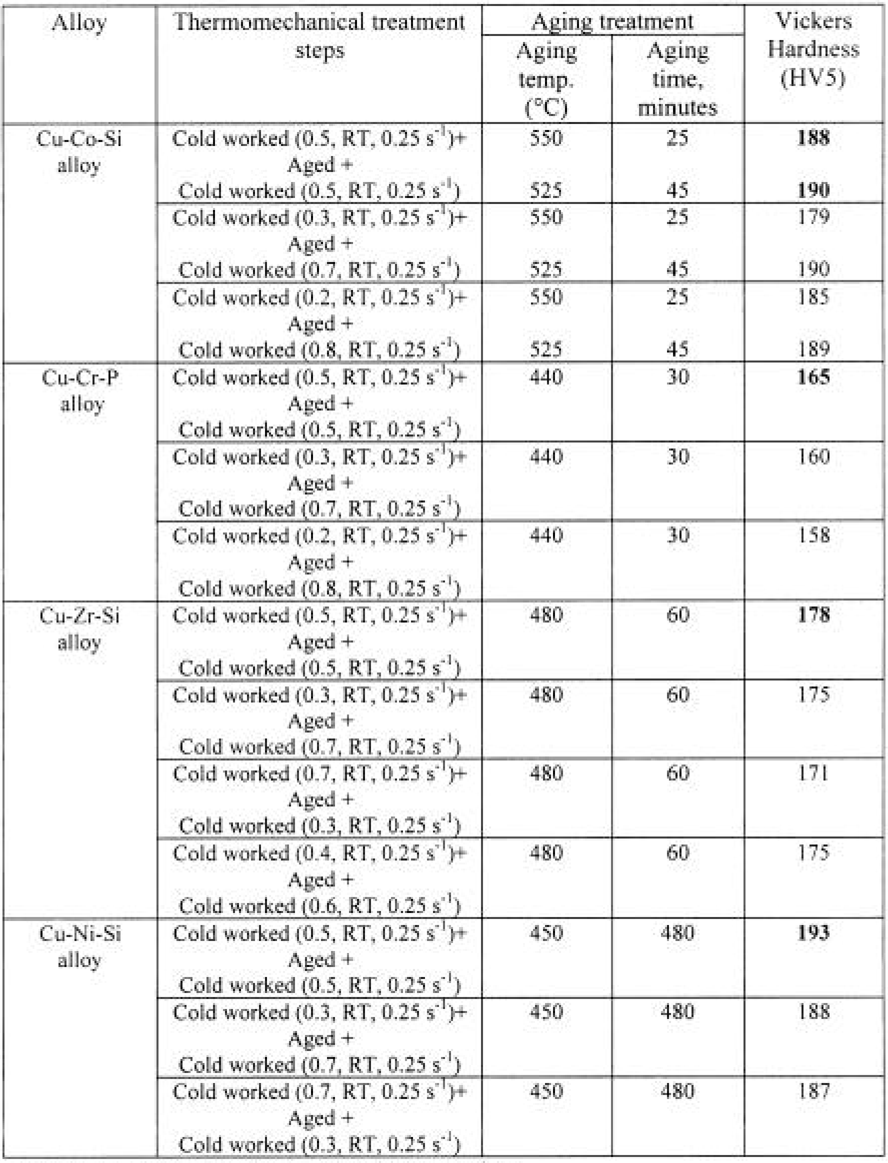
It was noted in the experiments of MEL/UO that the hot deformation prior to the deformation-aging-deformation procedure improved significantly the final conductivity and reduced somewhat the hardness of the CuZrSi- alloy (Tables 2 and 3) [4], [6]. In the CuCrP- alloy the corresponding prior hot deformation resulted in a slight decrease of hardness and almost no influence on conductivity whereas no significant influences were noted in the CuCoSi- alloy. This observation is most probably due to the grain refinement obtained in the CuZrSi- alloy as a consequence of the prior hot deformation.

For the CuZrSi- alloy a special thermomechanical treatment was developed by MEL/UO. It included hot deformation (true strain of 0.5) at 450 ^{o}C before the aging and consequent cold deformation. The consequent aging and cold deformation yielded a significantly higher hardness than that obtained by cold deformation-aging- cold deformation sequences (190 HV5 vs 178 HV5, respectively). This behaviour is most probably due to the dynamic precipitation assisted by the high density of dislocations, which leads to a more dense distribution of precipitates in the consequent aging treatment [4].

c) *The properties of materials obtained in industrial production experiments*

The results showed that the general properties of the materials produced by the industrial processes corresponded to those obtained in laboratory and simulation experiments, if the processing routes were approximately equal. Especially the hardness and conductivity results obtained after the industrial deformation-

Table 2. The different thermomechanical procedures and resulting maximum hardness values for the studied alloys in physical simulation experiments [4], [7]

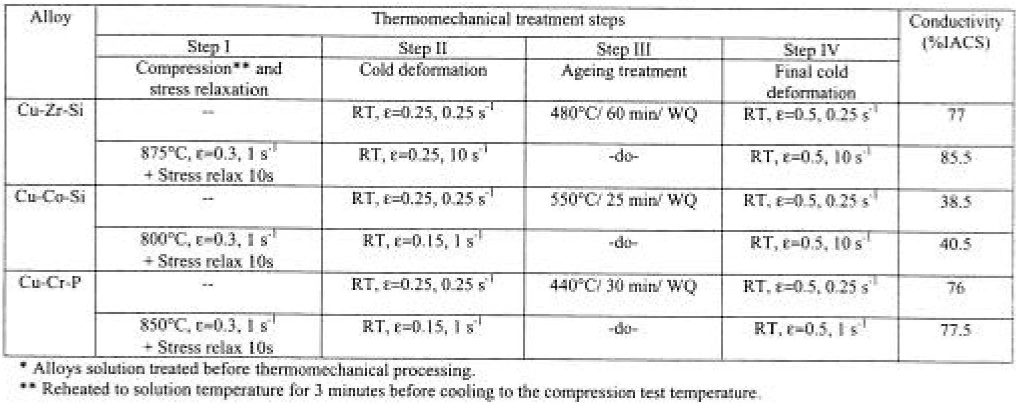


Alloy	Thermomechanical treatment steps	Aging treatment		Vickers Hardness (HV5)
		Aging temp. (°C)	Aging time, minutes	
Cu-Co-Si alloy	Cold worked (0.5, RT, 0.25 s^{-1})+ Aged + Cold worked (0.5, RT, 0.25 s^{-1})	550 525	25 45	**188** **190**
	Cold worked (0.3, RT, 0.25 s^{-1})+ Aged + Cold worked (0.7, RT, 0.25 s^{-1})	550 525	25 45	179 190
	Cold worked (0.2, RT, 0.25 s^{-1})+ Aged + Cold worked (0.8, RT, 0.25 s^{-1})	550 525	25 45	185 189
Cu-Cr-P alloy	Cold worked (0.5, RT, 0.25 s^{-1})+ Aged + Cold worked (0.5, RT, 0.25 s^{-1})	440	30	**165**
	Cold worked (0.3, RT, 0.25 s^{-1})+ Aged + Cold worked (0.7, RT, 0.25 s^{-1})	440	30	160
	Cold worked (0.2, RT, 0.25 s^{-1})+ Aged + Cold worked (0.8, RT, 0.25 s^{-1})	440	30	158
Cu-Zr-Si alloy	Cold worked (0.5, RT, 0.25 s^{-1})+ Aged + Cold worked (0.5, RT, 0.25 s^{-1})	480	60	**178**
	Cold worked (0.3, RT, 0.25 s^{-1})+ Aged + Cold worked (0.7, RT, 0.25 s^{-1})	480	60	175
	Cold worked (0.7, RT, 0.25 s^{-1})+ Aged + Cold worked (0.3, RT, 0.25 s^{-1})	480	60	171
	Cold worked (0.4, RT, 0.25 s^{-1})+ Aged + Cold worked (0.6, RT, 0.25 s^{-1})	480	60	175
Cu-Ni-Si alloy	Cold worked (0.5, RT, 0.25 s^{-1})+ Aged + Cold worked (0.5, RT, 0.25 s^{-1})	450	480	**193**
	Cold worked (0.3, RT, 0.25 s^{-1})+ Aged + Cold worked (0.7, RT, 0.25 s^{-1})	450	480	188
	Cold worked (0.7, RT, 0.25 s^{-1})+ Aged + Cold worked (0.3, RT, 0.25 s^{-1})	450	480	187

* Solution treated before thermomechanical processing.

aging- first deformation step- procedure were in good agreement with the results obtained in the physical simulation experiments using the optimized deformation-aging-deformation procedure [6], [7]. The conductivity values of the CuCrP- and CuCoSi- alloys in this processing stage were close to those presented above for IMS/TUT experiments, but the hardness values of all studied alloys were approximately 30 HV5- units higher.

Table 3. The influence of prior hot deformation on the conductivity values of the studied allloys [4].



Alloy	Thermomechanical treatment steps				Conductivity (%IACS)
	Step I Compression** and stress relaxation	Step II Cold deformation	Step III Ageing treatment	Step IV Final cold deformation	
Cu-Zr-Si	--	RT, ε=0.25, 0.25 s^{-1}	480°C/ 60 min/ WQ	RT, ε=0.5, 0.25 s^{-1}	77
	875°C, ε=0.3, 1 s^{-1} + Stress relax 10s	RT, ε=0.25, 10 s^{-1}	-do-	RT, ε=0.5, 10 s^{-1}	85.5
Cu-Co-Si	--	RT, ε=0.25, 0.25 s^{-1}	550°C/ 25 min/ WQ	RT, ε=0.5, 0.25 s^{-1}	38.5
	800°C, ε=0.3, 1 s^{-1} + Stress relax 10s	RT, ε=0.15, 1 s^{-1}	-do-	RT, ε=0.5, 10 s^{-1}	40.5
Cu-Cr-P	--	RT, ε=0.25, 0.25 s^{-1}	440°C/ 30 min/ WQ	RT, ε=0.5, 0.25 s^{-1}	76
	850°C, ε=0.3, 1 s^{-1} + Stress relax 10s	RT, ε=0.15, 1 s^{-1}	-do-	RT, ε=0.5, 1 s^{-1}	77.5

* Alloys solution treated before thermomechanical processing.

** Reheated to solution temperature for 3 minutes before cooling to the compression test temperature.

An interesting and unexpected feature of the results was that in the production sequence including the second deformation step (2 mm wires) this second deformation step reduced the hardness of the material and decreased markedly the conductivity values. This feature is most probably due to the heavy deformation, which leads to an extensive shearing of precipitates and distributes the alloying element atoms from the precipitates back into the matrix.

d) Summary of the main results

The main results of the project show that the combination of precipitation hardening and thermomechanical treatments (consequent deformation and heat treatment sequences as combined in an appropriate way) form an efficient way of improving simultaneously the conductivity and strength properties of dilute copper alloys. Figure 2 presents a comparison of the strength/conductivity combinations obtained in the present work to the values obtained in earlier studies [5]. The results of the present study show better strength-conductivity combinations than those obtained in previous studies. When remembering that the CuCrP- and CuZrSi- alloys were approximately equal and by taking into account that a slight reduction in alloy hardness from the maximum stage can improve the conductivity by 10 % IACS (see section 2.2.3 a), Fig. 2 shows that the idea of introducing intermetallic compound precipitation via ternary alloying elements really works and can improve significantly the properties of dilute CuZrX- alloys

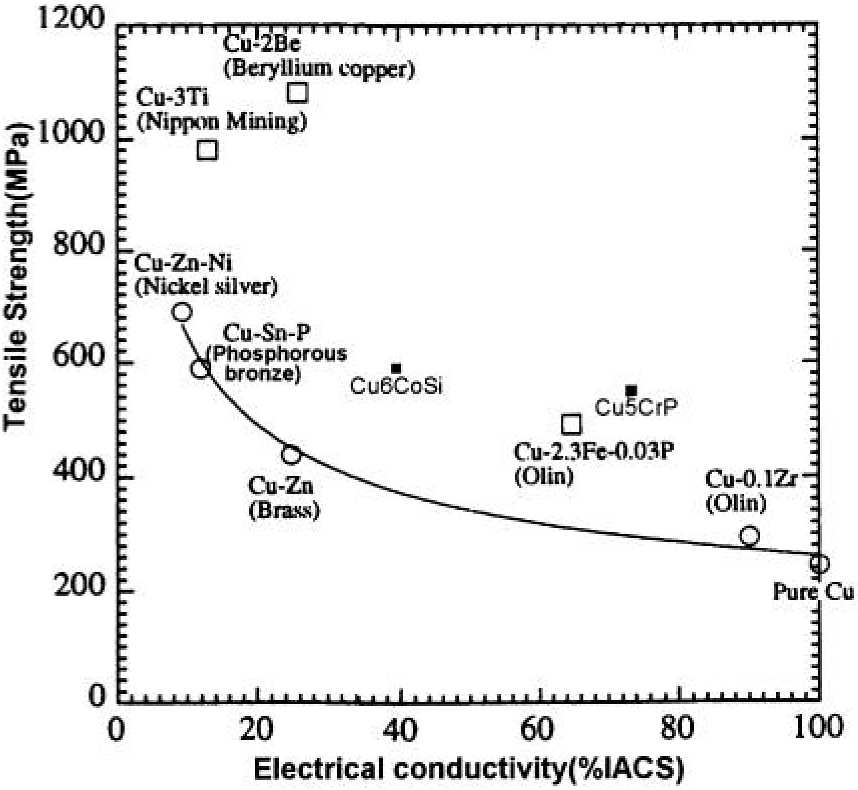


Fig. 2. The tensile strength vs conductivity combinations obtained in the present study for the CuCoSi and CuCrP alloys. CuCr5P is a version of the CuCrP alloy with slightly lower Cr content and lower hardness/conductivity combination than the actual CuCrP alloy studied here [5].

Another important result of the project is that the physical simulations can be used for optimizing the thermomechanical production routes for novel copper-based alloys. If the simulated processes contain similar sequences, same deformation types and same orders of magnitude of true strains in each sequence as the actual industrial processes, the correspondence between simulations and real processes can be rather good. This gives good possibilities for tailoring novel alloys and processes for better and better material properties.

2.3 Progress Report: Progress by the Institute of Materials Science, Tampere University of Technology

Besides carrying out alloy selection studies and laboratory experiments for characterizing the responses of the studied alloys to conventional precipitation and novel thermomechanical treatments, IMS/TUT carried out TEM microscopy studies for characterizing the microstructures resulting from different processing procedures. Fig. 3 gives examples of the results obtained on different alloys in conventional precipitation treatments [6]. Even if (as stated above) the details of the microstructure were too small for an exact and reliable characterization the results show that the formed precipitates are of the desired type and that the basic differences between different alloys are clearly visible also in the microstructures.

The TEM studies of thermomechanically treated alloys are even more demanding due to the high density of dislocations in severely deformed structures. However, the TEM microscopy can reveal the changes in general dislocation structures and the interaction between dislocations and precipitates during the course of aging, as shown in Fig 4. [6]

2.4 Progress Report: Progress by the Materials Engineering Laboratory of University of Oulu

The Materials Engineering Laboratory of University of Oulu carried out comprehensive physical simulation studies in order to study the influence of eventual dynamic recrystallization (DRX) and dynamic precipitation (DP) occurring during the deformation on the deformation response of the studied alloys at elevated temperatures. The main results can be summarized as follows [7]:

In the temperature range of 300-700 ^{o}C none of the studied alloys showed any signs of DRX. Most probably the precipitation processes and their influence on dislocation mobility prevent the occurrence of DRX in this temperature regime. At 800 ^{o}C the CuCoSi-, CuNiSi- and CuCrP- alloys showed the presence of DRX, while the alloy CuZrSi showed no signs of that. DP was observed in all studied alloys in the temperature range of 300-700 ^{o}C. The stress relaxation technique used in the Gleeble simulator proved to be an efficient method especially for revealing the offset of the DP process at higher temperatures.

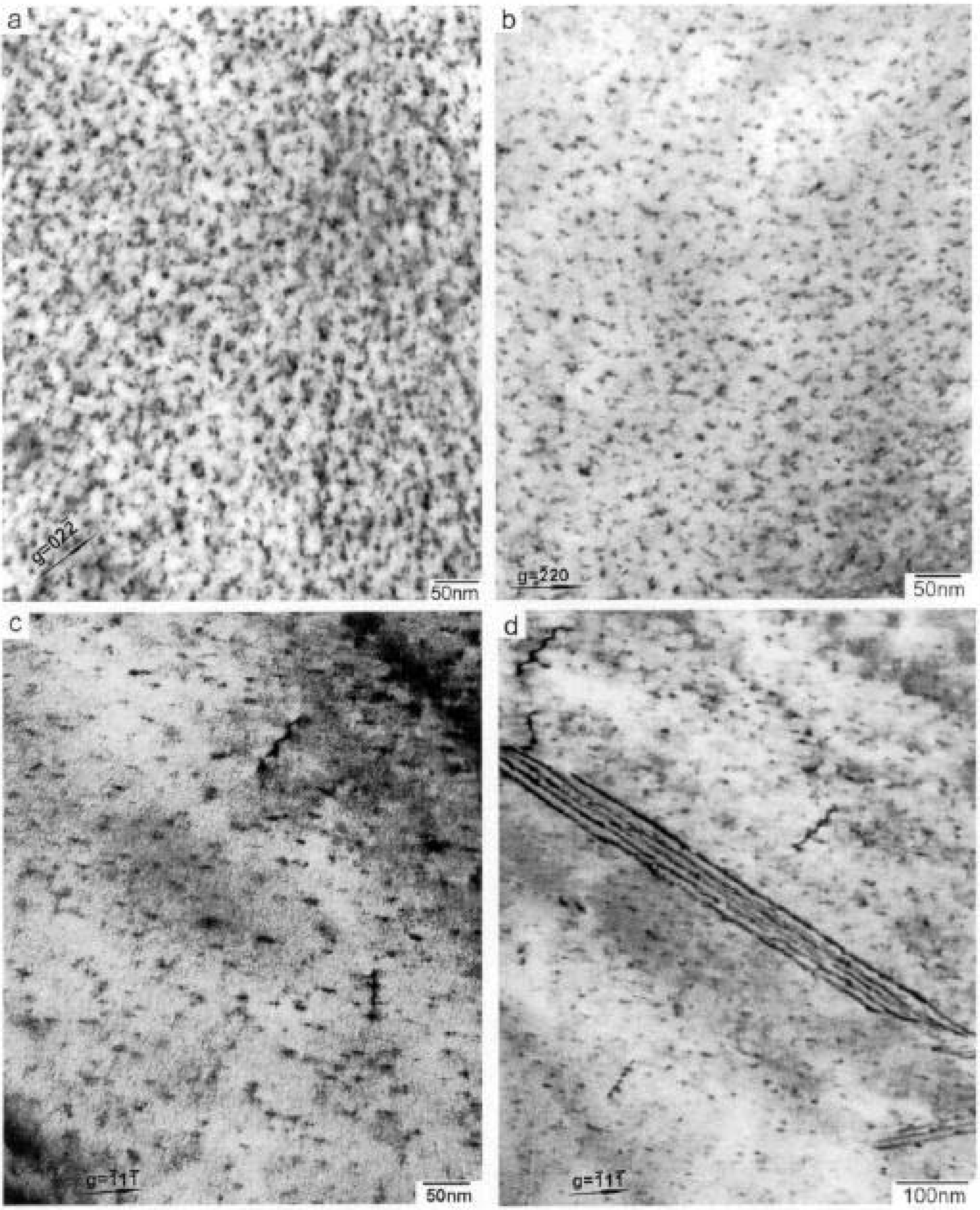


Fig.3. TEM micrographs showing the precipitate distributions in three of the studied alloys: a) CuCoSi alloy aged at 550 °C, b) CuCrP alloy aged at 510 °C, c) and d) different magnifications of the CuZrSi alloy aged at 480 °C ([4].

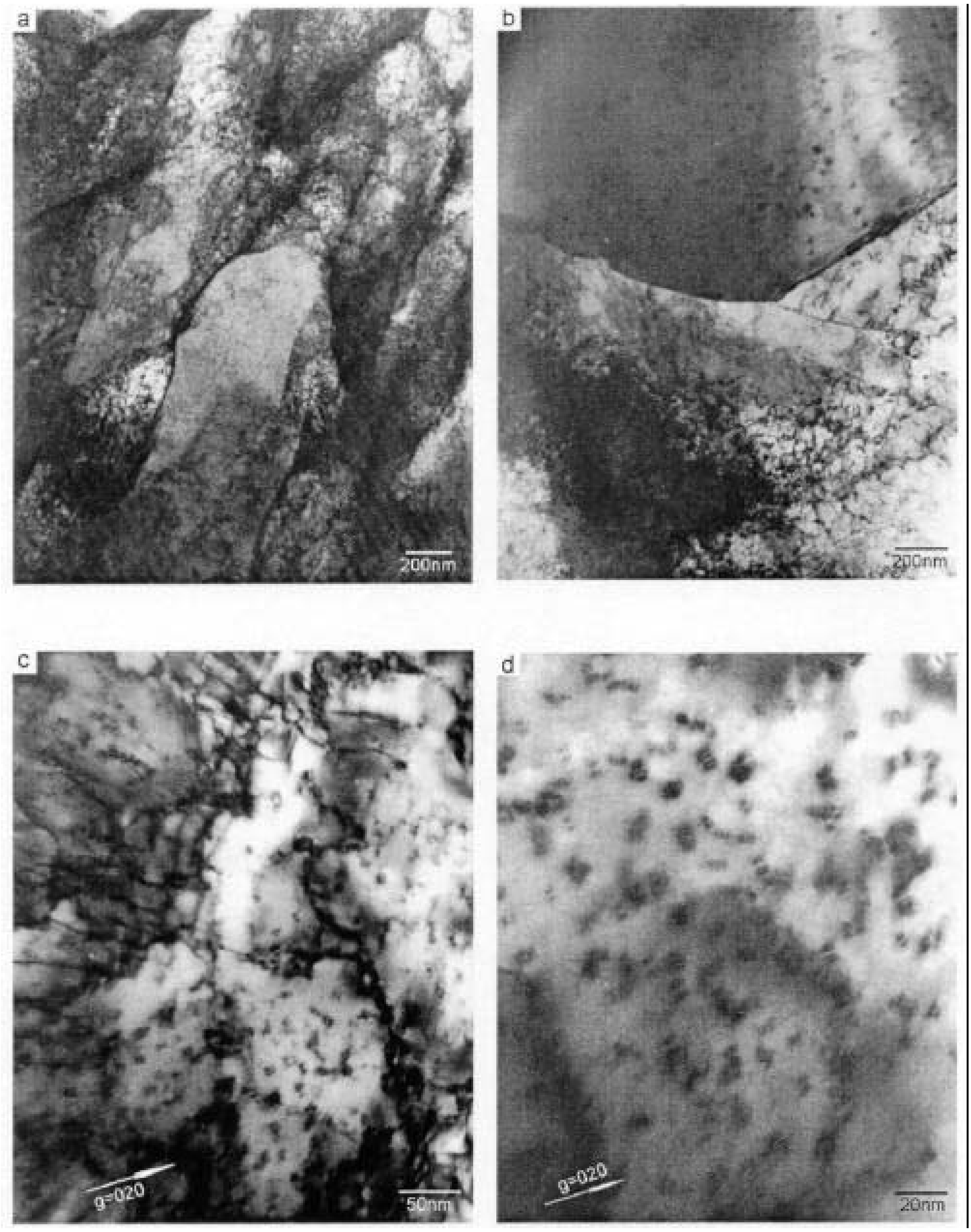


Fig.4. TEM micrographs showing the microstructure in the CuCrP alloy predeformed by the true strain of 0.9 and then aged for 60 min at the temperature of 510 °C: a) planar dislocation cell structure, b) a recrystallized grain containing precipitates (upper part of the figure), c) interaction of precipitates with dislocations, d) a close-up of c) showing the coherency of precipitates [5].

2.5 Progress Report: Progress by the Laboratory of Processing and Heat Treatment of Materials, Helsinki Universtiy of Technology

During the course of the project LPHTM/HUT carried out Atomic Force Microscopy (AFM) studies in order to explore the possibilities for characterizing the precipitation phenomena in the studied CuNiSi alloys. The technique was capable of revealing the precipitation phenomena from the polished surface of the sample, but the resolution was not sufficient for a more detailed characterization of the precipitates [8].

3 International Aspects

The project work in IMS/TUT and in MEL/UO was carried out mainly by foreign researchers (Chinese postgraduate students in IMS/TUT and Dr Mahesh Somani from India in MEL/UO). MEL/UO has significant collaboration with international universities and research institutes in the area of physical simulations and it can utilize the project results in subsequent collaboration. Besides the participation of the project researcher Nan Gao of IMS/TUT in the Junior Euromat- conference in Lausanne, Switzerland in August 2000 the project had little international collaboration.

4 Publications and Academic Degrees

Table 4. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1998	1999	2000	2001	**Total**	Publication numbers
TUT	Ref. journal art.	-	-	1	1	**2**	1-2
	Ref. conf. papers	-	-	1	-	**1**	3
	Doctoral dissert.	-	-	-	1	**1**	5
TUT	Non-ref. interim reports	5	7	3	1	**16**	6
	Monographs	-	-	-	1	**1**	4
	Non-ref. interim reports	1	6	4		**11**	7
HUT	Non-ref. interim reports	-	5	2	1	**8**	8
	Seminar reports	-	1	-	-	**1**	9

5 Other Activities

The project arranged an opening seminar "Advances in Copper Alloy Research: New Production Methods, Alloys and their Research and Modelling Techniques" for the project participants and the representatives of industry on 29.03.1998. LPHTM/HUT was the main organizer of the seminar, which yielded a report containing the presentations (altogether 11 presentations). The report is publication N:o [9] in the list of publications presented below.

The project arranged three common meetings of project researchers and representatives of industry during the course of the project, on 17.02.1999, 21.10.1999 and on 11.02.2000. The project also arranged a workshop for the representatives of industry on 17.11.1999. In these meetings and workshop the obtained results were reviewed and the continuation plans for the research work were outlined. The project will arrange the closing seminar for the project reseachers and the industrial representatives on the 17th of August of 2001.

The steering group of the project consisted of the representatives of the partnering research institutes, industry and the Technology Develoment Center (Tekes, the financer). The steering group has had altogether 12 meetings during the course of the project. In these meetings the performed project work and the obtained results have been reviewed by the project researchers and the future research work in each laboratory has been decided. The last steering group meeting will be held in relation to the closing seminar on 17.8.2001.

6 Publications

6.1 Refereed Journal Articles

[1] N. Gao, T. Tiainen, Y. Ji and L. Laakso: Control of Microstructures and Properties of a Phosphorus-Containing Cu-0.6wt%Cr Alloy, Journal of Materials Engineering and Performance 99(6) (2000) 623-629.

[2] N. Gao, T. Tiainen and Y.Ji: Influence of Prior Deformation on Age Hardening in a Phosphorus-Containing Cu-0.6wt%Cr Alloy (manuscript). To be submitted to the Journal of Engineering Materials and Performance, 2001.

6.2 Refereed Conference Papers

[3] N. Gao, T. Tiainen, M. Hemmilä and Y. Ji, Strain Age Hardening in a Phosphorus-Containing Cu-0.6wt%Cr Alloy, Proc of the Int. Conf. "Junior Euromat", 28.08.-01.09.2000, Lausanne, Switzerland.

6.3 Monographs

[4] M. Somani and L.P. Karjalainen: Simulation of Thermomechanical Processing of High-Strength, High-Conductivity Copper Alloys, University of Oulu, Department of Mechanical Engineering. Materials Engineering Laboratory, Research Report xx/2001 (in print).

6.4 Doctoral, Licentiate, and Master Theses

[5] N. Gao, Studies on Age-Hardenable Dilute Cu-Cr-P Alloys: Compositional Design, Characterization and Comparison to other Dilute Copper Alloys (manuscript), Tampere University of Technology, Institute of Materials Science, Dr.Tech Thesis 2001.

6.5 Non- Refereed Interim Reports

[6] TUT/IMS produced altogether 16 non-refereed interim reports for the steering group meetings, researcher meetings and workshops during the course of the project. The reports were written by N. Gao and M. Tanttari.

[7] MEL/UO produced altogether 11 non-refereed interim reports for the steering group meetings, researcher meetings and workshops during the course of the project. The reports were written by M. Somani, M. Hemmilä and P. Kantanen.

[8] LPHTM/HUT produced altogether 8 non-refereed interim reports for the steering group meetings, researcher meetings and workshops during the course of the project. The reports were written by A. Viljamaa and M. Heinonen.

7 Other References

[9] Advances in Copper Alloy Research: New Production Methods, Alloys and their Research and Modelling Techniques, Helsinki University of Technology, Laboratory of Processing and Heat Treatment of Materials, Report N:o TTKK-MML 1/99, Espoo 1999

The National Programme on Materials and Structure Research (MATRA) was launched in 1993 to promote re-industrialisation. The programme was pioneering cooperation between the Academy of Finland and the National Technology Agency, Tekes. A total of 48 consortia were funded by EUR 31 million during 1994-2000.

The first progress report of the Programme was published in 1996. It consisted of reports of the consortia accepted in the first and second rounds of application. The second progress report gives an overall picture of the work of the consortia funded in the later stages of the programme: in the third and fourth rounds of application. It also includes reports of the projects funded by Tekes. The progress reports, in addition to other material, were used for the evaluation of the whole research programme. This report gives an overall view on the advancement and level of materials and structure research in Finland.

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ISBN 951-715-402-X (print)
ISBN 951-715-403-8 (pdf)

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