Designed Cellulosic Nanostructures (DesignCell)

FINAL REPORT

Title of the research project	**Designed Cellulosic Nanostructures (DesignCell)**
Coordinator of the project	Mikael Ankerfors

BASIC PROJECT DATA

Project period	01.09.2007-28.02.2011
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URL of the project	-

FUNDING

Total budget in EUR	1330250
Public funding from WoodWisdom-Net Research Programme:	Total funding granted in EUR by source:
Finland Tekes - Finnish Funding Agency for Technology and Innovation	476000
Sweden Swedish Governmental Agency for Innovation Systems (VINNOVA)	330000
France Ministry of Agriculture, General Direction for Forest and Rural Affairs (DGPAAT)	75250
Other public funding:	None

Other funding:

Industrial funding	449000

PROJECT TEAM (main participants)

Mikael Ankerfors, MSc. Manager Paper Chemistry and Nanomaterials	M	Innventia	
Tom Lindström, Prof.. Senior Project Manager	M	Innventia	
Monika Österberg, Dr. Senior Scientist	F	Aalto University	
Janne Laine, Prof.	M	Aalto University	
Anna Olszewska Research Scientist	F	Aalto University	
Olli Ikkala, Prof.	M	Aalto University	
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Emelie Cranston, Dr. Post Doc.	F	KTH, Royal Institute of Technology	PhD from McGil University, Canada
Gero Decher, Prof. Professeur de chemie	M	University of Strasbourg CNRS Institut Charles Sadron (ICS)	

Gunnar Skoglund R&D Coordinator	M	Camfil
Christian Aulin, Dr. Senior Research Associate	M	Innventia (earlier at BIM Kemi and KTH, Royal Institute of Technology)

DEGREES
Degrees earned or to be earned within this project.

Year	Degree	Sex (M/F)	Name, year of birth and year of earning M.Sc.,	University	Supervisor of thesis, supervisor's organization
2008	D.Sc.	F	Susanna Ahola	TKK	Janne Laine, TKK
2012	D.Sc.	F	Anna Olszewska	Aalto University	Janne Laine, Aalto University
2009	D.Sc.	M	Christian Aulin	KTH	Lars Wågberg, KTH

ABSTRACT

The project “Designed Cellulosic Nanostructures” (DesignCell) was a research project within the WoodWisdom-NET programme. The over-all objective was to use nanofibrillated cellulose (NFC) to design new cellulosic nanostructures for new potential high-tech applications such as intelligent surfaces, templates for sensors, scaffold for biodevices, multilayer-based high flux non-fouling membranes, optically active/conductive devices for organic electronics and membranes.

1.1 Introduction

1.1.1 Background

Historically, nanocellulose was first produced at ITT by Turbak and co-workers (Turbak, A.F. et al. (1983). Journal of Applied Polymer Science: Applied Polymer Symposium (37): 815-827). Turbak et al. denoted the material Microfibrillated Cellulose (MFC) and typical dimensions of individual MFC-fibrils were 25-100 nm. The original process was based on delamination of pulp fibres using high-pressure homogenisers. The original process was never commercialised, because of its extensive energy use (30000 kWh/tonne) and clogging of the used homogenisers. The material has later been renamed to nanofibrillated cellulose (NFC) or nanocellulose to better describe the nanoscaled nature.

The project “Designed Cellulosic Nanostructures” (DesignCell) is a continuation of the previous WoodWisdom project “Nanostructrured Cellulose Products” (NanoCell). Among the accomplishments of the NanoCell project was the manufacture of nanocellulose in a commercially viable way. Development work carried out within the NanoCell project involved various pre-treatments of the pulp fibres in order to decrease the energy consumption and develop a viable process for the manufacture of nanocellulose. This project not only managed to decrease energy consumption an order of magnitude (approximately 3000 kWh/tonne), but also to make a completely different type of material.

Transparent films of nanocellulose was also shown to be the strongest paper-like material (“nanopaper”) ever produced by man. There are numerous uses of such materials from low-end products, such as: dry strength adjuvents, nanocoatings and surface strength applications in paper/board applications; bio-nanocomposite materials; rheology control applications (food, oil recovery, drilling muds); emulsion/dispersion applications; and hygiene/absorbent products; to high-end applications in cosmetics, medical/pharmaceutical; and electronic display applications.

Commercial production of nanocellulose is now possible for some targeted applications, but there is a need to develop the nanocellulose materials to applications in the high-end to speed up over-all developments in the sector.

1.1.2 Objectives

The over-all objective of DesignCell was to design new cellulosic nanostructures for new potential high-tech applications such as intelligent surfaces, templates for sensors, scaffold for biodevices, multilayer-based high flux non-fouling membranes, optically active/conductive devices for organic electronics and membranes. The project encompassed one project for the production of tailored nanocellulose (WP1), one project for fundamental understanding of

nanocellulose-polymer interactions (WP2), and three projects devoted to various high-tech products. The specific role of the partners are given in the specified workpackages.

Structural control (methodology) will be obtained by chemical modification allowing some degrees of self-assembly or by multilayering techniques. Commercialisation is helped by development of both low and high-end applications, though this project primarily aims at the high-end of the market (see background).

1.1.3 Partners

The working partners in the DesignCell have been Innventia (Coordinator), KTH Royal Institute of Technology, Aalto Univeristy, CNRS, BIM Kemi and Camfil. The project have also had the following funding parters: Kemira, Metso, UPM.

1.2 Results and discussion

WP1 - "Production of tailored nanocellulose"

WP1's responsibilities have been to manufacture low energy consuming nanofibrillated cellulose (NFC) of different versions and supply the research partners with these materials. A number of different versions have been prepered with different charge densities (both anionic and cationic), with different counter ion-forms, salt concentrations, and size distributions. All of these samples could be produced without any problems using low energy consumptions. WP1 has also investigated new fast characterisations tools for determining the degree of delamination and a method for this based on charge titrations has been developed. The performance of the different NFCs are described under the other WPs.

The industrial partner Camfil has tried using NFC in materials for filtration applications. The idea was to improve existent filtermedia with an environmently friendly product like NFC. The NFC was thought to improve the efficiency of the filtermedia by increasing the amount of very thin fibers into the existing filtermedia structure. Different methods to introduce the fibers into the structure were used like coating, impregnation by soaking and impregnation by filtration. The technical performance was bad for all samples. The NFC formed a dense surface on the filter medias which created very high differential pressures over the materials. So called aerogel-samples of pure NFC were also produced. The pure NFC-samples also show very high differential pressures in addition to a poor mechanical strength which made them very difficult to handle.

BIM Kemi AB prepared and characterized oil resistant cellulosic materials, ranging from model surfaces to papers and aerogels. The cellulosic materials were made oil resistant by chemical and topographic modifications, based on surface energy, surface roughness and barrier approaches. Detailed wetting studies of the prepared cellulosic materials were made using contact angle measurements and standardized penetration tests with different alkanes and oil mixtures.

Artificial structured cellulosic surfaces were prepared by a plasma etching process in combination with the adsorption of cellulose nanocrystals. These artificially intrinsic oleophilic cellulosic surfaces were made highly oleophobic when coated with a thin layer of fluorinated

silanes. It was demonstrated that the surface energy and the surface texture are essential factors preventing oil from spreading on the surface.

The use of NFC for surface coating on papers demonstrated very promising characteristics as packaging materials. Thin NFC layers reduced the sheet porosity, i.e. very dense structures were formed by the nanofibers resulting in superior oil barrier properties.
Finally, NFC aerogels were prepared by freeze-drying. The surface texture of the porous aerogels was carefully controlled by adjusting the concentration of the NFC dispersion used for the freeze-drying. The different scales of roughness of the NFC aerogels were utilized, together with the very low surface energy created by fluorination of the aerogel, to induce highly oleophobic properties.

WP2 - "Fundamental understanding of nanocellulose-polymer interactions for diverse applications"
Three different types of cellulose nanofibrils (NFC), their behaviour in different media and their interactions with polymers were investigated in detail. The studied NFCs were native, unmodified, highly anionic and highly cationic NFC. The charge of the fibrils affected water uptake and interaction with polymers.The adsorption of polymers onto the NFCs was studied using quartz crystal microballance (QCM-D). For this purpouse a procedure to coat the QCM-D crystals with NFC was developed. It was found that neutral or even anionic polyssaccarides adsorb onto cellulose and has dispersing effect on the fibrils. High charge cationic polyelectrolytes removes water from the swollen cellulose fibril film. Cationic block copolymers also adsorbed onto anionic NFC and the nature of the polymer affected the morphology of the adsorbed layer. The cationic fibrils were exceptionally thin as imaged for the first time in never dried state using AFM in water.

Anionic NFC significantly improved the wet and dry strength of paper sheets reinforced with poly(amideamine) epichlorohydrin. Using a small amount of NFC the amount of wet strength resin could be reduced. Recent findings show that this small amount of NFC well anchored to fibres do not deteorate drainage. The dispersion of fibrils on cellulose fibres is very important for paper strength, thus demonstrating the effect of polymer type on the dispersion of fibrils has large impact when optimising paper dry strength systems. A biomimetic approach of forming strong and light materials by adsorbing block-copolymers with a soft and dissipative block and a cationic anchoring block onto anionic NFC was demonstrated although it still needs optimization.

WP3 - “Self-assembly, networks and rheology of nanocellulose”
WP3 has implemented a new, simple and versatile platform concept to complex native nanofibrillated cellulose (NFC) with block copolymers via non-covalent interactions. We present a facile ionic self-assembly between fibrillar and spherical colloidal objects towards biomimetic nanocomposites with majority hard and minority soft domains based on anionic reinforcing native cellulose nanofibrils and amphiphilic block copolymer micelles with rubbery core.The cationic part of the block copolymer serves as a binder to NFC whereas the hydrophobic rubbery micellar cores are designed to facilitate energy dissipation and nanoscale lubrication between the NFC domains under deformation. This allows self-assembled biomimetic nanocomposites that contain a large fraction of NFC reinforcements separated by rubbery self-

assembled domains. The complexation between the colloidal nanofibrils and colloidal micellar spheres prevents macroscopic phase-separation and gives rise to composites with an alternating nanoscale hard/soft architecture. As a consequence of the improved mesoscale order, we identify a synergetic performance of the components beyond the simple rule of mixture. As the concept allows wide possibilities for tuning, the work suggests pathways for nanocellulose-based biomimetic self-assembled nanocomposites combining high toughness with stiffness and strength.

The effect of charges on the hydrogels were investigated systematically using anionically charged carboxymethylated nanofibrillated cellulose (NFC). The NFC was prepared at Innventia AB from a softwood sulfite-dissolving pulp. The dynamic rheology shows at high concentrations storage and loss moduli that are essentially indepenedent of the frequency, as in the neutral case, but drastically new behaviour is observed at low concentration. Whereas only a gel state was observed for the neutral NFC, in the anionic case the low concentration (0.1%-wt) rendered a more viscous fluid state. The increasing surface charge density along NFC has delicate effects. According to DLVO theory, at very long and at short distances van der Waals forces are expected to dominate and at short separations it is reasonable to expect hydrogen bonding to be dominant. At the intermediate distances, repulsive electrostatic double layer (EDL) interaction dominates, forming an energy barrier before the deep primary energy minimum close to the particle surface. The counter-ions of weakly dissociating groups of carboxymethylated NFC aqueous systems are expected to form the EDL layers, which will increase the low-shear viscosity of the dispersions. The EDL resists deformations and too close contacts make the dispersion behave in a more elastic manner. This could explain the higher modulus levels compared to unmodified NFC dispersions. Also, the smaller average fibril diameter of the carboxymethylated NFC results in higher surface area and better-defined hydrogen-bonded network structure. Previously, DLVO has been applied to a nanoscale cellulose. A complication exists, however, for concentrated dispersions, where each cellulose nanofibril will interact with several other fibrils and in different mutual orientations. It has been suggested that simultaneous collisions with multiple particles could lead to an open floc structure, i.e. entangled, hydrogen-bonded network, as some of the collisions lead to the collapse into the primary energy minimum.

WP4 - "Film formation of nanocellulose and polyelectrolytes"
The efforts in WP4 were initially focused on the preparation of free-standing films of NanoFibrillated Cellulose (NFC), charged polymers and other nanoparticles. The results showed that it was necessary to pretreat the silicon oxide surfaces used as templates for the LbL films in order to be able to remove the LbL films from the surface without harming the films. It was also found that the films had to be around 1 µm or thicker in order to be able to handle the films for further testing. The properties of the LbL films could be altered by selecting different polyelectrolytes and/or different nanoparticles.The second phase of the WP was focused around a mechanical testing of nanometer thick films of the prepared LbL films. Since the films could not be handled if they were thinner than 1 µm an alternative method was needed and it was decided to use the SIEBIMM (Strain-Induced Elastic Buckling Instability for Mechanical Measurements) technique. With this technique the LbL films are formed on an elastic backing material, with a Youngs modulus several orders of magnitude lower than the modulus of the film. When this sandwich-material is compressed a buckling pattern is formed to minimise the

energy stored in film and in the backing material. From the thickness of the LbL films, the eleastic properties of the backing material and the wavelength of the buckling pattern, it is then possible to calculate the Youngs modulus of the films. By using a small scale mechanical tester it was also possible to test the films either inside a Scanning Electron Microscope or in a laboratory environment to evaluate the importance of the relative humidity on the mechanical properties of the LbL films. The results show that films of NFC and PEI (polyethyleneimine) have a Youngs modulus around 2 GPa under ambient conditions and 17 GPa under absolute dry conditions. This is most probably due to the hydroscopic properties of both the NFC and the PEI and shows the large potential of this methodology to determine the influence of modificayions of the NFC on the properties of NFC films. Further experiments also show that the incorporation of nanosilica particles in the films could easily increase the Youngs modulus of the films with a factor of two.

WP5 - "Multilayer-based high flux non-fouling membranes"
WP5 worked on the preparation of a tailor made polymeric separation layer using NFC as well as conventional polyelectrolytes at the surface of commercially available high-flux membranes.

A polymeric separation layer attached directly to the surface of a porous support would partially block the pores and have an active area identical to the surface area of the pores in the absence of horizontal diffusion. This would lead to small flux and easy fouling. A multilayer of anionic and cationic NFC allows for horizontal diffusion between the polymeric separation layer and the supporting porous layer due to the interstitial space between the fibers. Despite of a tight separation layer, flux is expected to remain high.

Periodate/Chlorite Oxidation, the method that resulted in the best surface coverage of the membranes, was used to activate Regenerated Cellulose (RC) membranes. A homogeneous multilayer of anionic and cationic NFC was deposited on the activated RC membrane followed by a multilayer of polyelectrolytes like sodium poly(styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH). Flux measurements were then carried out.

We have studied a large number of different LbL-films assembled on different membrane types at different assembly conditions and characterized such functionalized membranes by various physico-chemical methods. The flux through these membranes varied as expected in the differently assembled hybrid membranes. The flux measurements of membranes constitute a proof of concept for the use of NFC nano-coatings as lateral diffusion layer.

In order for the membranes to be antifouling, we modified these commercial membranes containing NFC multilayers by grafting from them antifouling monomers like 2-hydroxyethylmethacrylate (HEMA) and ethyleneglycoldimethacrylate (EGDMA) using surface initiated atom transfer radical polymerization (ATRP) and creating block-copolymer grafts. These grafted block copolymers allow for antifouling. IR spectra and contact angle measurements showed the successful grafting of these membranes with antifouling brushes.

WP6 - "Coordination and Dissemination"
The coordination and dissemination has been coordinated by the Coordinator (Innventia) in accordance to the set up Consortium Agreement. The coordination activites have mainly be

carried out through scientist meetings (around 3 per year) and General Assembly meetings involving all partners (2-3 times per year). Dissemination has mainly been done through publications (see publication list, section 1.5).

1.3 Conclusions

WP1 - “Production of tailored nanocellulose”

- NFC of different charge densities (both anionic and cationic), with different counter ion-forms, salt concentrations, and size distributions can be produced using low energy consumption in order to delaminate the fibre cell walls.
- A charge titration method have been devloped for the determination of the degree of delamination.
- Existing filtermedia couldn’t be improved by NFC-impregnation or coating
- The NFC-solution created a dense surface on existing filtermedia
- Pure NFC-samples were very fragile and showed bad technical performance
- The use of the NFC for surface coating of paper/board resulted in superior oil barrier properties.
- Ultra light-weight NFC aerogels with tunable oleophobicity were fabricated by freeze-drying of NFC suspensions with different NFC concentrations
- The viscosity and surface tension of oils (unpolar liquids), as well as the dispersive surface energy of the cellulose surfaces, were found to be essential parameters governing the spreading kinetics of oils.

WP2 - "Fundamental understanding of nanocellulose-polymer interactions for diverse applications"

- A method to make reproducable NFC films from varous NFC types for fundamental QCM-D and AFM analysis was developed.
- The type of adsorbed polymer and solution conditions strongly affect the amount of water in the NFC film.
- Cationic NFC was imaged in never dried state using AFM and was found to be exceptionally thin due to the chemical modification prior to disintegration.

WP3 - “Self-assembly, networks and rheology of nanocellulose”

- The complexation between the colloidal nanofibrils and colloidal micellar spheres prevents macroscopic phase-separation and gives rise to composites with an alternating nanoscale hard/soft architecture.
- Improved mesoscale order, we identify a synergetic performance of the components beyond the simple rule of mixture.
- As the concept allows wide possibilities for tuning, the work suggests pathways for nanocellulose-based biomimetic self-assembled nanocomposites combining high toughness with stiffness and strength.
- The charges have substantial effect on the hydrogel properties, where a higher quality and more homogeneous hydrogel was obtained using carboxymethylated NFC than from the neutral NFC.The observation of both sol and gel states in anionic NFC hydrogels is interesting, as it allows routes for new applications.

- Higher strength gels, higher shear thinning, and sol-state were observed using carboxymethylated NFC.

WP4 - "Film formation of nanocellulose and polyelectrolytes"

- Free-standing films of polyelectrolytes and NanoFibrillated Cellulose (NFC) have been prepared.
- The SIEBIMM technique has been successfully adapted to thin films of NFC and polyelectrolytes. Elastic properties have been evaluated for films with thicknesses from 50 nm.
- Pure LbL films of cellulose can be prepared and tested by using anionic and cation NFC.
- It has been shown that the elastic properties can be significantly changed by components in the LbL films and by the relative humidity in the surrounding air.

WP5 - "Multilayer-based high flux non-fouling membranes"

- Commercial membranes like RC membranes were sucessfully modified by layer-by-layer deposition of NFC and other polyelectrolytes after membrane activation
- The flux of these membranes was measured and the presence of NFC multilayers and aerogels between commercial membranes and polymeric separation layers enhances the flux.
- RC membranes modified by LbL films of NFC were sucessfully ATRP grafted with antifouling polymer brushes while keeping a high flux.

1.4a Capabilities generated by the project

Not applicable. All progress has been published or is available as manuscript. See publication list (section 1.5).

1.4b Utilisation of results

Not applicable.

1.5 Publications and communication

1.5.1. Articles in international scientific journals with peer review

Aulin, C., Ahola, S, Josefsson, P., Nishino, T.,Hirose, Y., Österberg, M., Wågberg, L. (2009) “Nanoscale cellulose films with different crystallinity - Their surface properties and interaction with water” Langmuir 25(13) 7675-7685.

Aulin, C., Johansson, E., Wågberg, L. and Lindström, T. (2010) “Self-organized films from cellulose I nanofibrils using the layer-by-layer technique” Biomacromolecules 11(4) 872-882.

Aulin, C., Yun, S.H., Wågberg, L. and Lindström, T. (2009) “Design of highly oleophobic cellulose surfaces from structured silicon templates” ACS Applied Materials & Interfaces 1(11) 2443-2452.

Aulin, C., Gällstedt, M. and Lindström, T. (2010) “Oxygen and oil barrier properties of microfibrillated cellulose films and coatings” Cellulose 17, 559-574.

Aulin, C., Netrval, J., Wågberg, L. and Lindström, T. (2010) “Aerogels from nanofibrillated cellulose with tunable oleophobicity” Soft Matter 6, 3298-3305.

Salmi, J., Nypelö, T., Österberg, M. and Laine, J. (2009). Layer structures formed by silica nanoparticles and cellulose nanofibrils with cationic polyacrylamide (C-PAM) on cellulose surface and their influence on interactions. BioResources, 4 (2), 602-625

Ahola, S., Myllytie, P., Österberg, M., Teerinen, T., and Laine, J. (2008) “Effect of polymer adsorption on cellulose nanofibril waterbinding capacity and aggregation” BioResources 3, 315-1328.

Ahola, S. Turon, X., Österberg, M., Laine, J. and O. J. Rojas (2008) “Enzymatic hydrolysis of native cellulose nanofibril and other cellulose model films – Effect of surface structure” Langmuir, 24(20), 11592-11599

Ahola, S., Salmi, J., Johansson, L.-S., Laine, J. and Österberg, M. (2008) ”Model films from native cellulose nanofibrils. Preparation, swelling, and surface interactions”, Biomacromolecules 9, 1273-1282.

Ahola, S., Österberg, M. and Laine, J. (2008) “Cellulose nanofibrils - adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive" Cellulose 15, 303-314.

Olszewska, A., Johansson, L-S., Malho, J.-M., Ankerfors, M., Lindström, T., Ruokolainen, J., Laine, J., and Österberg, M. (2010) “Detailed characterization of cationic cellulose nanofibril films in aqueous environment”, Manuscript submitted to Langmuir.

Wang, M., Olszewska, A, Walther, A., Malho, J.-M., Schacher, F.H., Ruokolainen, J., Ankerfors, M., Österberg, M. Laine, L. Berglund, L., and Ikkala, O. (2010) ”Colloidal ionic self-assembly between anionic native cellulose nanofibrils and cationic block copolymer micelles into biomimetic nanocomposites for synergistic properties”, Manuscript to be submitted to Biomacromolecules.

Ikkala O., Ras R. H. A., Houbenov N., Ruokolainen J., Pääkkö M., Laine J., Leskelä M., Berglund L. A., Lindström T., ten Brinke G., Iatrou H., Hadjichristidis N. and Faul C. F. J., (2009) “Solid state nanofibers based on self-assemblies: from cleaving from self-assemblies to multilevel hierarchical constructs”, Faraday Discussions 143, 95-107.

Hiekkataipale, P., Järvinen, P., Wang, M., Pääkkö, M., Nykänen, A., Ruokolainen, J., Seppälä, J. V. Laine, J., Ankerfors, M., Lindström, T., Saarinen, T., and Ikkala, O. (2010). ”Dynamic Rheology in Carboxymethylated Cellulose Nanofiber Dispersions: The Elastic Gel and Viscous States”, Revised manuscript for Biomacromolecules.

Kettunen (née Pääkkö), M., Silvennoinen, R. J., Houbenov, N., Nykänen, A., Ruokolainen, J., Sainio, J., Pore, V., Kemell, M., Ankerfors, M., Lindström, T., Ritala, M., Ras, R. H. A., and

Ikkala, O. (2010). “Photoswitchable superabsorbency based on nanocellulose aerogels”, Advanced Functional Materials, published online: 6 December 2010 | DOI: 10.1002/adfm.201001431.

Granström, M., Kettunen (née Pääkkö), M., Jin, H., Kolehmainen, E., Kilpeläinen, I., Ikkala, O. (2010). ”Highly water repellent aerogels based on cellulose stearoyl esters”, Revised in Polymer Chemistry.

Eita, M., Granberg, H., Arwin, H. and Wågberg, L. (2010). ”Optically and mechanically enhanced nanofibrillated cellulose thin films for high-performance devices: a step toward sustainable multifunctional materials”. Manuscript ready for submission.

Cranston, E., Salajkova, M., Netrval, J., Jojhansson, E., and Eita, M., (2010). “Determination of the Young's modulus for nanofibrillated cellulose thin films using buckling mechanics”. Accepted for publication in Biomacromolecules.

1.5.2. Articles in international scientific compilation works and international scientific conference proceedings with peer review

Wågberg, L., Österberg, M. and Enarsson, J.-E., (2010) “Interactions at cellulose model surfaces” in Encyclopedia of Surface and Colloid Science 2nd ed, Vol.1, 1, Taylor & Francis, London, UK, pp.1-19

Ikkala O., Ras R. H. A., Houbenov N., Ruokolainen J., Pääkkö M., Laine J., Leskelä M., Berglund L. A., Lindström T., ten Brinke G., Iatrou H., Hadjichristidis N. and Faul C. F. J. (2009). “Solid state nanofibers based on self-assemblies: from cleaving from self-assemblies to multilevel hierarchical constructs”. Faraday Discussion 143: Soft Nanotechnology at the Royal Society in London, from 15-17 June 2009.

Pääkkö, M. Granström, M., Jin, H. Kolehmainen, E., Kilpeläinen I., Ikkala, O. (2009). Environmentally Sustainable Water Repellent Materials Based on Stearoyl Modified Cellulosic Networks. Polysaccharides as a Source of Advanced Materials September 21-24, 2009 Turku/Åbo, Finland by The European Polysaccharide Network of Excellence (EPNOE).

1.5.3. Articles in national scientific journals with peer review

Not applicable.

1.5.4. Articles in national scientific compilation works and national scientific conference proceedings with peer review

Not applicable.

1.5.5. Scientific monographs

Susanna Ahola, PhD thesis, Helsinki University of Technology, 2008.

Christian Aulin, PhD thesis, Royal Institute of Technology (KTH), 2009.

Anna Olszewska, PhD thesis, Aalto University, expected date 2012.

1.5.6. Other scientific publications, such as articles in scientific non-refereed journals and publications in university and institute series

Oral presentations at international scientific conferences:

Österberg, M., Eronen, P., Junkka, K., Olszewska A., and Laine J. "Cellulose nanofibrils - interactions with polymers and multilayer formation", Nordic Polymer Days, Helsinki, May 24.-26. 2010.

Olszewska, A.,, Wang, M., Walther, A., Ikkala, O., and Österberg, M. (2010) "QCM-D and AFM study on the interactions between nanofibrillated cellulose and bloc-co-polymer in biomimetic multilayers", Nordic Polymer Days, Helsinki, May 24.-26. 2010.

Olszewska, A., Ankerfors, M., Lindström, T, Laine, J., and Österberg, M. (2010) "Swelling behaviour of ultrathin cationic and anionic cellulose nanofibril films", 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010.

Österberg, M. (2009). "Present state of modelling wood polymer surfaces", 237th ACS National meeting, Salt Lake City, UT, United States, March 22-26, 2009.

Myllytie, P., Ahola, S., Teerinen, T., Österberg, M. and Laine, J. (2009) "Adsorption of polymers on cellulose nanofibril model surfaces: Effect on nanofibril water binding capacity and aggregation" 237th ACS National meeting, Salt Lake City, UT, United States, March 22-26, 2009.

Olszewska A., Eronen P., Ahola S., Österberg M., and Laine J. (2009). "Nanocellulose model films studied by Quartz Crystal Microbalance with Dissipation." Q-Sense Scientific meeting, Chalmers University of Technology, Gothenburg, Sweden, February 24-25 2009.

Laine, J., Österberg, M. (2008). "Surface interactions between polymers and nanofibrillated cellulose", Recent advances in fibrillar nanocellulose research – Characterisation and applications, Trondheim, Norway, November, 12-13, 2008.

Turon, X., Ahola, S. Österberg, M., and Rojas, O.J. (2008) "Enzymatic hydrolysis of cellulose thin film with different crystallinities and morphologies studied by QCM-D and AFM techniques" ACS National meeting, New Orleans, United States, April 6-10, 2008.

Ahola, S. Österberg, M. Salmi, J., and Laine, J. (2007). "Cellulose nanofibrils – A promising additive and a representative model for the pulp fibre surface", 2nd International Cellulose Conference, Tokyo, Japan, October 22-25, 2007.

Aulin, C., Wågberg, L., and Lindström, T. (2010). "Nanocellulose aerogels with tunable oleophobicity" 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010. Oral presentation.

Aulin, C., Johansson, E., Wågberg, L., and Lindstöm, T. (2009). ”Adsorption behaviour, structural and adhesive properties of microfibrillated cellulose-based multilayers” 13th IACIS International Conference on Surface and Colloid Science and the 83rd ACS Colloid &Surface Science Symposium, New York, United States, June 14-19, 2009.

Aulin, C., Wågberg, L, and Lindström, T. (2008). ”Preparation, characterisation and wetting of fluorinated cellulose surfaces”. 235th ACS National meeting, New Orleans, United StatesApril 6-10, 2008.

Eita, M., Wågberg, L. and Cranston, E. (2010). “Build-up and mechanical properties of microfibrillated cellulose-based thin films”, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010.

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1.6 National and international cooperation

The DesignCell project has not directly collaborated with other projects, but several of the partners (Innventia, KTH, Aalto University, CNRS) are also collaborating within the EU 7th framework programme SustainComp project (large-scale collaborative project). Within this project there are certain activities which have connections to the DesignCell project and the involved scientists are the same.