



# Industrial Biomaterials

Research highlights

**2009** 2010 2011 2012 2013 2014

Editor: Minna Vikman  
Graphic design: Tuija Soininen

Copyright: © VTT Technical Research Centre of Finland 2010

## Foreword – Industrial biomaterials – year 2009

VTT's Industrial Biomaterials spearhead programme 2009–2013 develops technologies and competencies utilising basic skills in chemistry, biotechnology, process technology, material science, modelling and analytics. The technologies and competencies developed in the spearhead programme are steered to generate value chains stretching from forest biomass to selected high-volume consumer products, without disputing the fragile value chains of the food sector. Some example results are presented below.

### IndBioMat programme focus and impact

The spearhead programme focuses on the development of materials and production technologies based on fibres and nanocellulose, as well as biomass-based monomers and polymers. The aim is to integrate these new value chains into existing biorefineries (e.g. pulp mills, biofuel producers, breweries, and cereal sidestreams).

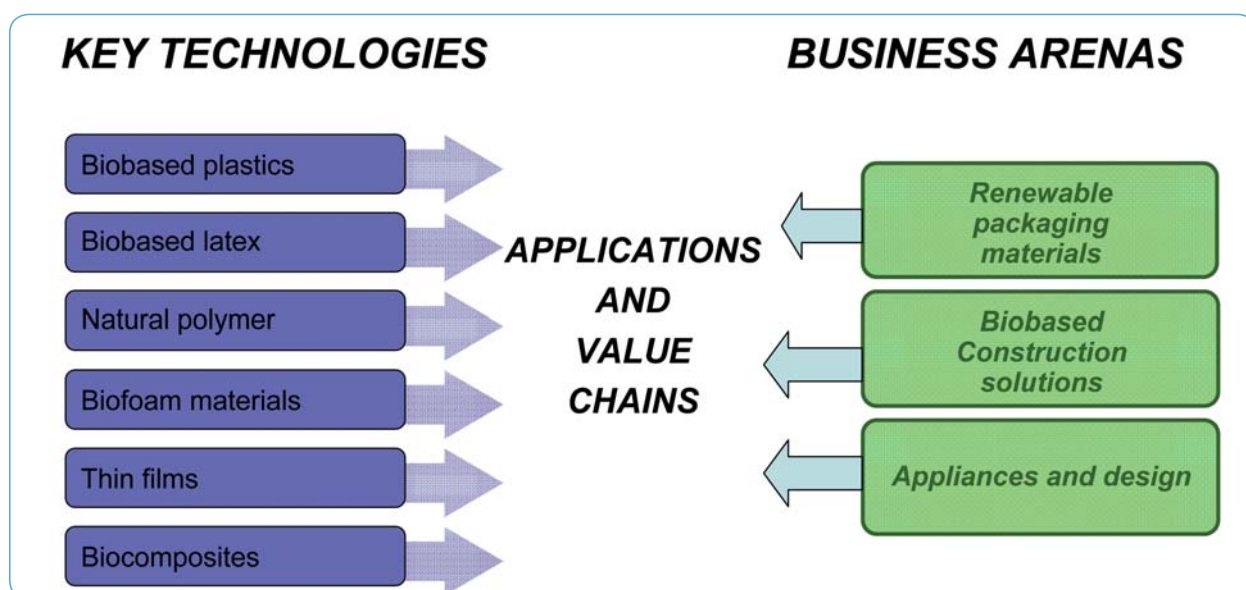
The IndBioMat spearhead programme's total budget for 2009 was EUR 14.8 million, of which 58% comprised

jointly funded, 31% contract research, and 11.5% basic funded research. The main sources of financing were private funding (MEUR 4.3), the Finnish Funding Agency for Technology and Innovation (Tekes) (MEUR 2.8) and the EU (MEUR 1.3).

Public research carried out under the Industrial Biomaterials spearhead programme involved cooperation with 14 research institutions, 22 universities and 43 enterprises. Within VTT, 25 multi-skilled research consortia were formed, comprising 29 research teams mainly from three separate research clusters. During 2009, a total of 12 EU projects and 11 academy projects with significant international connections were implemented. From international connections 58% were research institutions and 27% enterprises, in addition the participating Finnish enterprises had significant activities abroad.

### Research activities

Basic research has been made in the field of white biochemistry and green chemicals. Synthesis of non-commercial black liquor hydroxyl acids was carried out to provide reference material for isolation studies. Reasonable separations have been demonstrated, but further chro-



matographic resin tailoring is required. Catalytic decomposition of wood was found to be analogous with non-catalysed oxidation, leading to dissolution of lignin rich in carboxylic acid groups. Conversion of lignocellulosic sugars to novel products was focused on finding optimal dehydrogenases for converting pentose sugars. Biotechnological production of sugar acids was focused on generating and characterising strains where aldaric acids have been successfully esterified. Xyloglucan modification of wood fibre surfaces and methods thereof were also studied. Capsulation techniques based on amphiphilic polymers, i.e. star-like block copolymers, was also researched.

Nanocellulose is an emerging component of future biocomposites. Novel modification technologies have been developed for nanocellulose materials, with the focus on developing new applications outside the paper industry. Main contribution is in the areas of biochemical and chemical modification and new drying methods for nanocellulose materials. Application assessment is focused on composites, industrial additives and filters.

The main tools used in nanofibrillated cellulose (NFC) material characterization have included different microscopic techniques (AFM, SEM and TEM), giving valuable information, e.g. on the fine structure and re-dispersibility of the materials. To obtain strength properties, the NFC must be well dispersed in the matrix and adequate adhesion to the matrix must be achieved. The routes investigated for dispersing NFC in the matrix have given promising results.

New cellulose types and special fibres are also being applied to biocomposites. The mechanical properties of biocomposites have been improved by using bio-based material as a compatibilizer. Pelletized wood fibres with specific surface additives meet the criteria for maximum fibre length and good feeding and dispersion in compounding. The maximum cellulose content applied to pilot-scale reactive extrusion was 70%, where also on-line extrusion modification was performed.

A variety of different natural polymers were studied. For example, methods of modifying lignin and other aromatic process side-stream components into materials applicable in composites, coating adhesives and barriers were studied. Spruce bark was pre-treated using steam explosion. The cross-linking ability of birch bark suberin was improved with biopolymers and cellulose. Structural characterisation tools were developed for industrial biomaterial analysis applications. As a material source, selected samples of, e.g., lignin, polysaccharides and hemicellulose were used.

Bio-based materials are also being developed for packaging applications. The barrier properties of packaging board were improved using inorganic nanomaterials together with a biomaterial-based polymer. In another example, over 80% reduction in oxygen transmission was obtained with pectin films containing 30 wt% of nanoclay measured in 80% humidity. In another project, new functional solid foam materials were developed from natural polymers and biomass for several industrial application fields. The target of the project is to replace synthetic foam components with natural polymers and compounds sourced from wood or agro-materials.

## Main achievements

VTT has developed, with its partners and co-operators, several technologies suitable for developing biomass-based material solutions aimed at replacing non-renewable materials in terms of performance and product life-cycle, and which do not compete with food production.

- Efficient fractionation and hydrolysis of wood and agricultural biomass sugars enables bioconversion of novel chemicals and polymer precursors. Bio-based latex and glue polymers, in particular, are a key development focus.
- Modified hemicelluloses and lignin polymers are developed by combining fractionation and reactive steps targeted at cellulose and natural fibre compounds.
- Modification technologies have been developed for nanocellulose materials aimed at new applications

outside the paper industry. Main contribution is in the areas of biochemical and chemical modification and conversion of nanocellulose materials and application assessment.

- Plasma deposition for roll-to-roll materials was developed and demonstrated for the hydrophobisation capacity of equipment for paper, polyolefines, and non-wovens. Enhancement of packaging board barrier properties using inorganic nanomaterials together with biomaterial-based polymers.
- Development of new functional solid foam materials were developed from natural polymers and biomass for several fields of industrial application, with the aim of replacing synthetic foam components with natural polymers and compounds sourced from wood or agro-materials.

## Exploitation of results

The results will be exploited by actors in the chemical, process technology and material sectors, both domestic and global. Target sectors of special interest include the plastics, process, forest and energy industries, as well as packaging and construction. The spearhead programme will cooperate closely with the Finnish Strategic Centres for Science, Technology and Innovation, particularly Forestcluster Ltd.

The Industrial Biomaterials spearhead programme has a marked influence on reorienting forest cluster business activity through innovative solutions based on value-added wood- and other biomass-based products. Additionally, the programme targets sustainable technologies that enable the export of products and expertise for emerging processes and fields of industry.



**ALI HARLIN**

Professor, Biomass based materials

[ali.harlin@vtt.fi](mailto:ali.harlin@vtt.fi)

+358 20 722 6386

# Contents

Foreword – Industrial biomaterials – year 2009 .....	2
Future Biorefinery (FuBio) program .....	6
CoE White Biotechnology – Green Chemistry (CoE WB-GC) .....	7
Advanced wood-based composites – wood fibre selection and processing .....	8
Hydrophobic films by atmospheric in-line plasma deposition .....	12
Sustainability impact assessment of the forestry-wood chain (EFORWOOD) .....	15
Nanomaterials in coating applications, NANOCOAT .....	18
Biohybrid packaging materials from pectin and nanoclay .....	21
Biomass-derived novel functional foamy materials – BIO-FOAM .....	24
Tailoring of the nanocellulosic materials for industrial applications .....	27

## Future Biorefinery (FuBio) program

“Future Biorefinery” (FuBio), the second research program of Forestcluster Ltd., was officially started on March 1, 2009. The program is planned to last for five years. The effective financing decisions, which add up to app. 18.7 M€, cover the first two years. The main funding for the initial two-year period comes from Tekes (50%) and the industrial owners of Forestcluster Ltd. (40%). The final 10% is financed directly by the four owner universities and the two owner research organizations (University of Jyväskylä, Lappeenranta University of Technology, Helsinki University of Technology (TKK) and Åbo Akademi University, Metla and VTT).

The main objective of the FuBio research program is to build a strong knowledge platform in the field of wood biorefinery R&D in Finland. The platform will comprise a variety of R&D competences (people), new processing technologies including new propriety technologies as well as state-of-the-art pre-industrial processing equipment, novel business ideas and coarse tools to evaluate the business potential.

The actual generation of new business, utilizing the attributes of the FuBio platform, is up to the companies (alone or in cooperative consortia). Hence, the establishment of actual new value chains is mainly achieved in separate, industry-led projects.

The specific areas of interest for the FuBio program are specified by the content of so-called Themes. Currently, FuBio comprises five Themes focusing on wet laboratory work, of which four are active. The active ones include Fractionation technologies, Cellulose for material applications, Hemicelluloses for materials and hydroxy acids, and Biochemicals for the protection of products and health. A Theme focusing on management activities within FuBio is also active.

The main results in 2009 were as follows:

- The modelling toolkit developed by the FuBio “Modelling Team” (i.e. GloCell, Pöyry and VTT).

- A pressurized hot-water extraction reactor has been taken into operation at Metla.
- New ionic liquids, suitable for wood processing, have been synthesized and tested. These include a completely new class of ionic liquids.
- Novel hemicellulose fractions have been produced applying pressurized hot water extraction. The fractions are tested for further upgrading. Polymers have also been produced chemically from a specific hydroxy acid.
- Cellulose modification methods by mechanical action and chemical methods have been set up, enabling production of functional, e.g., hydrophobic fibres.
- Biotesting of hemicellulose preparates and polyphenol-rich wood extracts has been initiated.

VTT is a key performer in the FuBio research program. These activities are also included in the Industrial Biomaterial Spearhead Programme.



**NIKLAS VON WEYMARN**

Programme Manager  
 niklas.weymarn@vtt.fi  
 +358 20 722 7138

# CoE White Biotechnology – Green Chemistry (CoE WB-GC)

The Finnish Centre of Excellence in White Biotechnology – Green Chemistry Research is a status given to VTT by the Academy of Finland for the years 2008-2013. The CoE is committed to developing new biotechnological and chemistry methods for the efficient production of chemicals and materials from renewable natural resources. “White” or industrial biotechnology combined with “green chemistry” has a vital role to play in developing sustainable production processes that can help save energy and the environment. A considerable improvement is needed in the efficiency of bioprocesses before they can be considered a serious alternative to petrochemical industrial processes. One of the challenges is how to get microbes to convert the sugars contained in biomass into the required compounds as effectively as possible. The CoE brings together the relevant expertise available at VTT in the fields of biotechnology (molecular biology, enzymology, bioprocess technology), chemistry (synthetics, polymer chemistry), systems biology (bioinformatics, mathematical modelling) and engineering sciences (micromechanics, measurement technology, nanotechnology).

The CoE’s aim is to develop new technologies for production new biomaterials. Microbial cells are engineered to produce useful new compounds out of plant biomass sugars. Sugar acids and their derivatives are produced by applying the tools of genetic technology to engineer the metabolism of microbes. These compounds have many industrial applications, for instance as precursor molecules in the production of new bioplastics. The produced molecules are then further modified chemically and used in material applications or polymerised to new biopolymers. The CoE also has two important supporting activities. One is to develop sensitive measurement techniques, e.g. new measuring devices based on micro and nanotechnologies that can be used to measure and control the productivity of microbes in bioreactors during production. Another is to use genome-wide methodology and bioinformatics to understand cell function, and mathematical modelling to generate (predictive) mathematical models of the production organisms.

The Enzymology team has searched suitable enzymes for a metabolic route to convert D-galacturonic acid, D-xylose, rhamnose and L-arabinose to the corresponding mono and dicarboxylic acids. Novel enzyme activities have been selected based on genome data bases and the activity of the enzymes studied in detail by first cloning of the corresponding genes, then expressing them in bacteria or yeast, followed by purification and analysis of kinetic properties and substrate and cofactor specificities. Dehydrogenases, lactonases and dehydratases (for conversion of the acids to keto-deoxy forms) have been analysed. The most suitable enzymes have been then expressed in yeast and filamentous fungi by the Metabolic engineering team to analyse the best host organism for production of each acid. Until now the CoE has been successful in showing the feasibility of production in gram quantities of xylonate, galactonate, arabinonic acid, keto-deoxy-L-galactonate, keto-deoxy-arabinonic acid, best titers so far obtained with xylonite 20-30g/l. Gram quantities of keto-deoxy-L-galactonate have been provided to Chemistry team. The Chemistry team has generated model reactions and model compounds for sugar acid derivatisation. Mucic acid has been chemically converted to monomers as tetra-O-acetyl, tetra-O-alkyl mucic acid, galactar-2,3,4,5-tetra-O-acetyl-bis-[(2-hydroxyethyl)amide], and to allyl amides and epoxides with various degree of O- substitution. Acetylation could be made in heterogeneous reaction medium without common solvents as pyridine or DMF. Conversion to amide worked without catalyst yielding desired dihydroxy functional amide of mucic acid with high yield and purity. In addition, chemical conversion of mucic acid to industrially important polyester monomers such as 2,5-furandicarboxylic acid has been initiated. The Measurement tool team developed a CE-based method for analysis of 17 different acids, including those produced in the CoE.



**MERJA PENTTILÄ**

Research Professor  
merja.penttila@vtt.fi  
+358 20 722 4504

## Advanced wood-based composites – wood fibre selection and processing

*Elina Laatikainen, Heidi Peltola, Petri Jetsu, Mika Härkönen*

**Wood Plastic Composites (WPCs) are typically compounds of thermoplastic polymers and wood-based reinforcement or fillers. The most common polymer used is polypropylene (PP) and, if biodegradability is needed, polylactide (PLA) is often used. Reinforcing or filler material typically consists of sawdust/sawdust powder or wood fibres. Despite much research in the field of WPCs, commercial applications in Europe are limited. The principal drawbacks of conventional WPC technology are low impact strength and brittleness, inconsistent material properties due to different fibre qualities, low temperature resistance, strong smell and high emission levels, and instability in humid conditions.**

Many features affect the mechanical and thermal properties of WPC materials. These are generally related to material selection or the technology used in the manufacturing and processing of WPC materials.

- Material properties: matrix plastic, fibre strength, fibre length and diameter, fibre to matrix interaction (compatibilisation), polymer additives (plasticizers, impact modifiers, etc.)
- Processing properties: dispersion of fibres, fibre orientation, fibre length preservation, fibre and matrix polymer degradation

The main aim of the EU-FP7 project BioStruct ([www.biostructproject.eu](http://www.biostructproject.eu)) is to overcome the barriers to success in the WPC material market by developing the next generation of the material, so-called enhanced Wood Plastic Composites (eWPCs). The project has objectives both for material and processing development, but the main focus of the work described here is on advanced and optimised wood fibres for eWPC materials. This work includes the selection, processing and modification of wood-based reinforcing fibres.

### Materials and methods

The bleached pulps selected for the processing and compounding tests were as follows: pine kraft pulp, eucalypt-

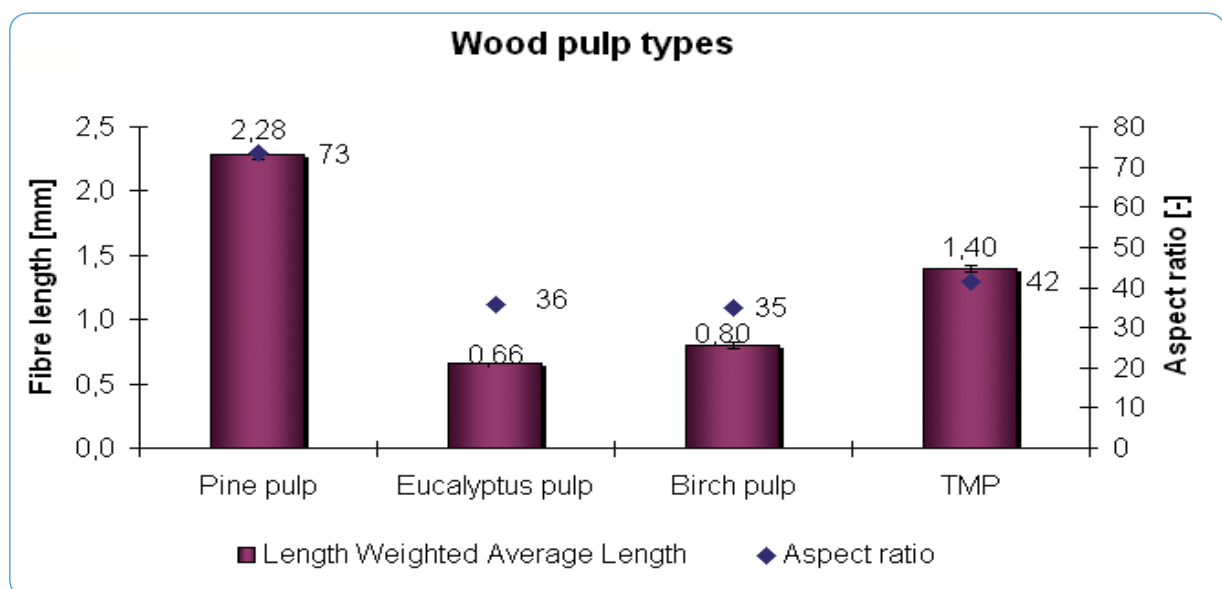


Figure 1. Fibre length and aspect ratio of different wood pulp types. The fibre analyses were performed on dried and reslushed pellets.

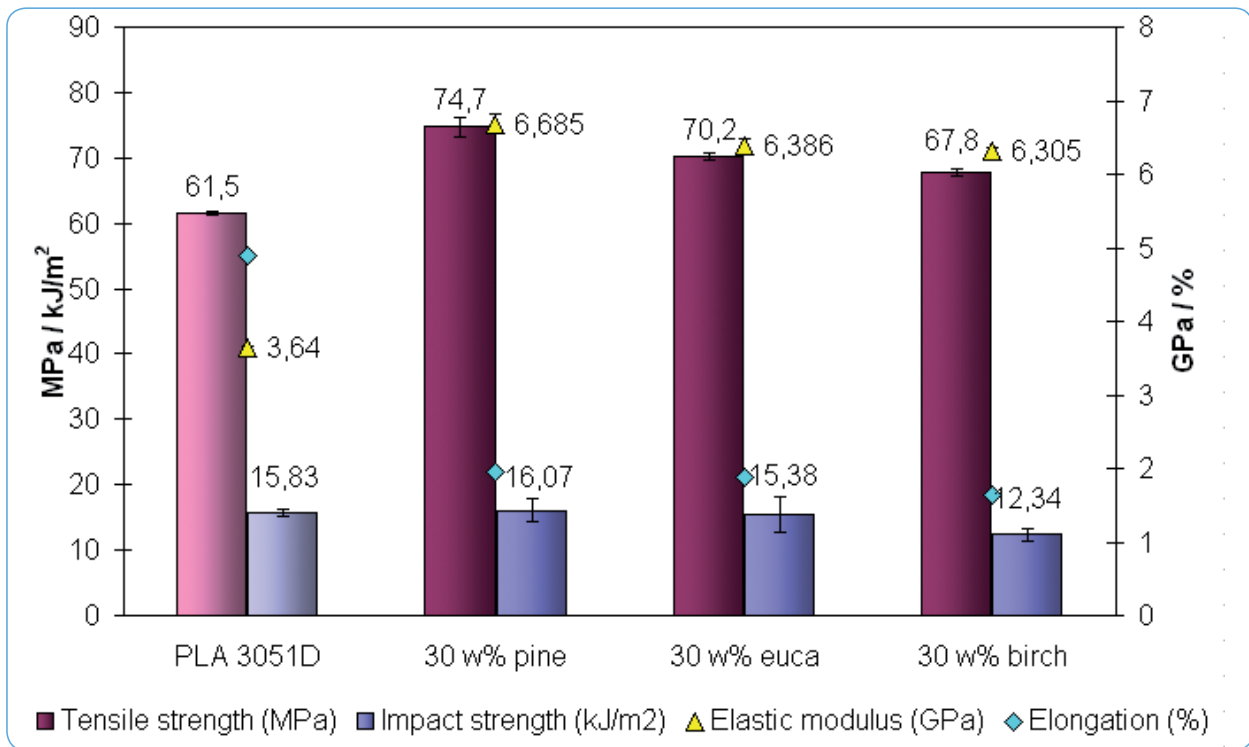


Figure 2. Mechanical properties of PLA 3051D composites with 30 wt% of various wood pulp types: pine, eucalyptus and birch.

tus pulp, birch pulp and TMP pulp. All the pulp samples were supplied by UPM Kymmene.

The fibre length distributions of the pulps and the injection moulded specimens were measured using the L&W STFI FiberMaster device. Fractionation of the TMP pulp was performed using the Metso FS-03 laboratory sorter. The fibres were pelletised with a planar matrix pelletising machine before compounding, except for the TMP fractions, which were made into thick sheets and then shredded.

The main test for wood-fibre-based composites was based on the compounding of fibres and the PLA matrix with a co-rotating twin-screw extruder (Berstorff ZE 25x33D). The compounds were then injection moulded with an injection-moulding machine (Engel ES 200/50 HL) into tensile test specimens, and this was followed by normal mechanical testing of the specimens (ISO-527, ISO-179).

## Results and discussion

### Comparison of wood pulp types

Figure 1 presents the average fibre length and aspect ratio of the pulps after pelletising. It is a known fact that pine

pulp has the longest fibre length and eucalyptus pulp the shortest. Pine fibres also have the highest aspect ratio (length-width ratio).

The mechanical properties of PLA 3051D composites with 30 wt% of various wood pulp types can be seen from Figure 2. Composites containing pine pulp give the highest tensile strength, impact strength, elastic modulus and elongation.

The pine pulp fibres are initially longer and have a higher aspect ratio than eucalyptus and birch fibres, and therefore pine pulp as a PLA composite reinforcement gives the best mechanical properties. However, the differences between the mechanical properties of composites containing various pulp types are not as significant as it could have been expected from the initial fibre length data (Figure 1). One reason for this is that the higher fibre length of the pine pulp fibres is lost in the processing step. Fibre-length analyses after compounding with PLA and injection moulding have shown an extensive decrease in pine fibre length: from an initial 2.2 mm down to 0.5 mm.

### Fractionation

Fractionation of fibres offers a great opportunity to affect the fibre material uniformity and strength properties

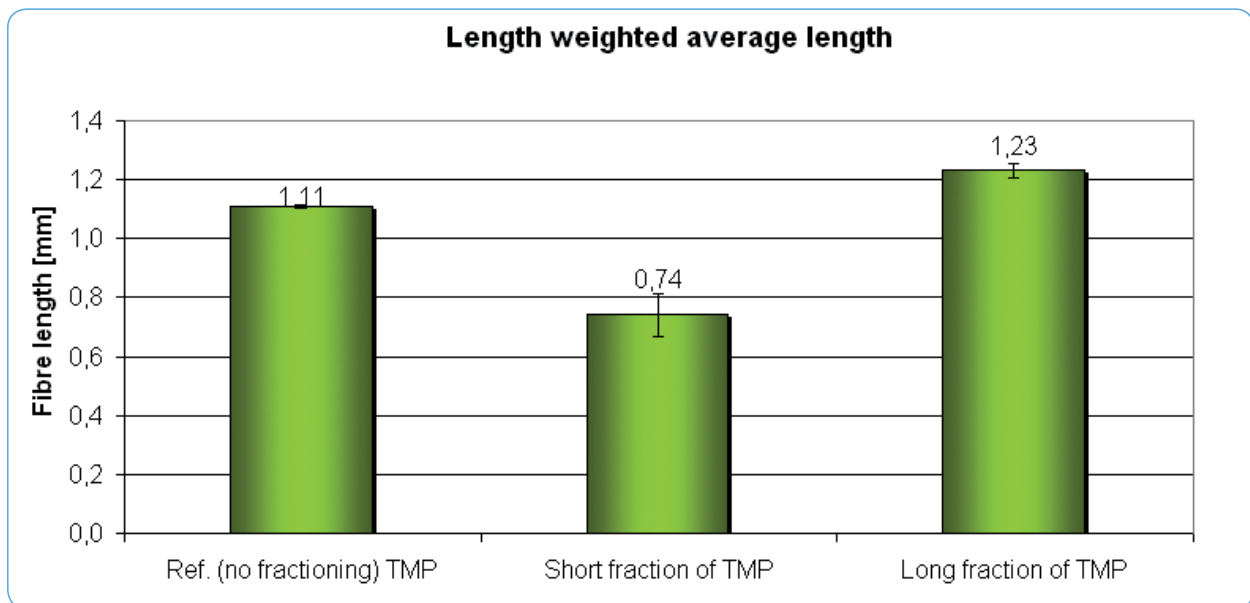


Figure 3. Fibre length of different fractions of TMP before compounding.

of WPCs. The TMP pulp was fractionated by fibre length, and the effect of the fractions on the strength properties of WPCs was studied. Figure 3 shows clear differences in fibre length of TMP fractions before compounding.

The mechanical properties of PLA 3001D composites with 30 wt% of reference (no fractioning) and fractioned TMP fibres can be seen from Figure 4. Compared with pure PLA, the addition of TMP fibres increases the tensile

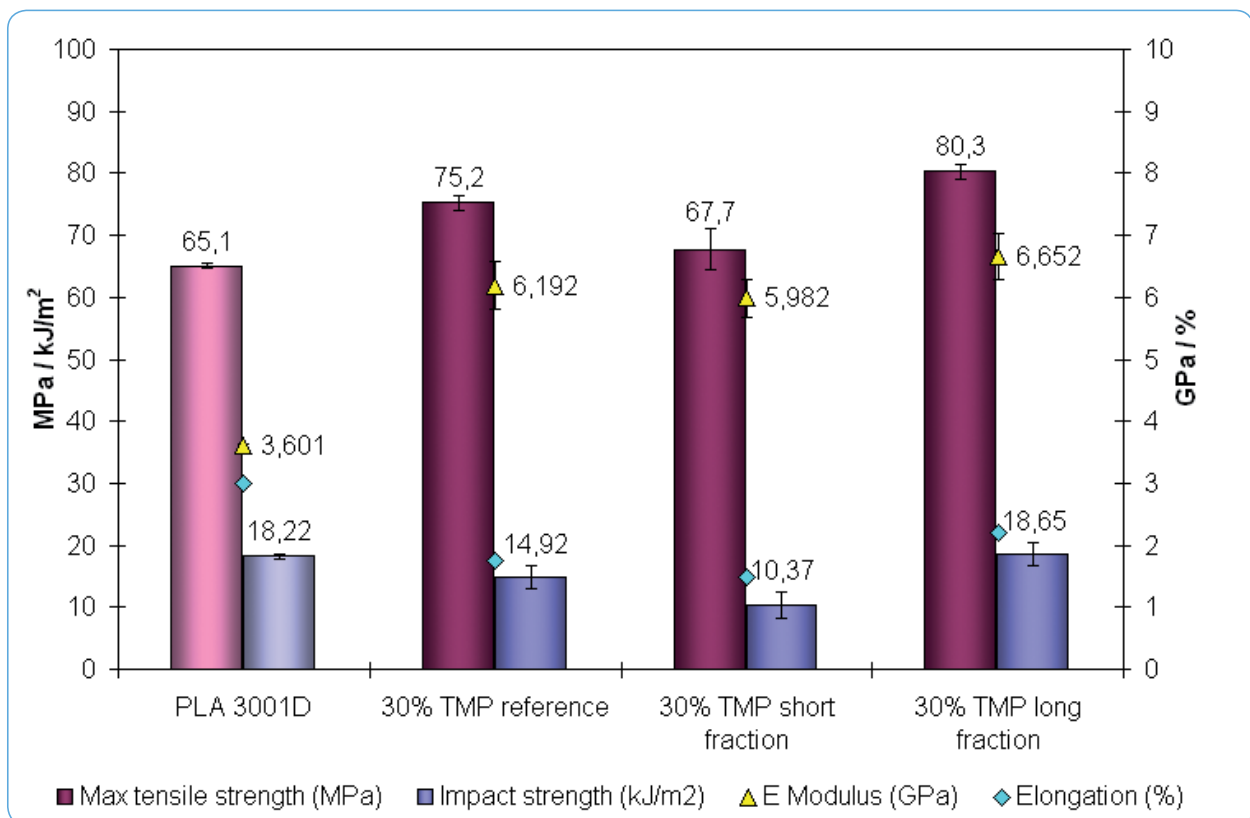


Figure 4. Mechanical properties of PLA 3001D composites with 30 wt% of TMP reference, short fraction and long fraction fibres.

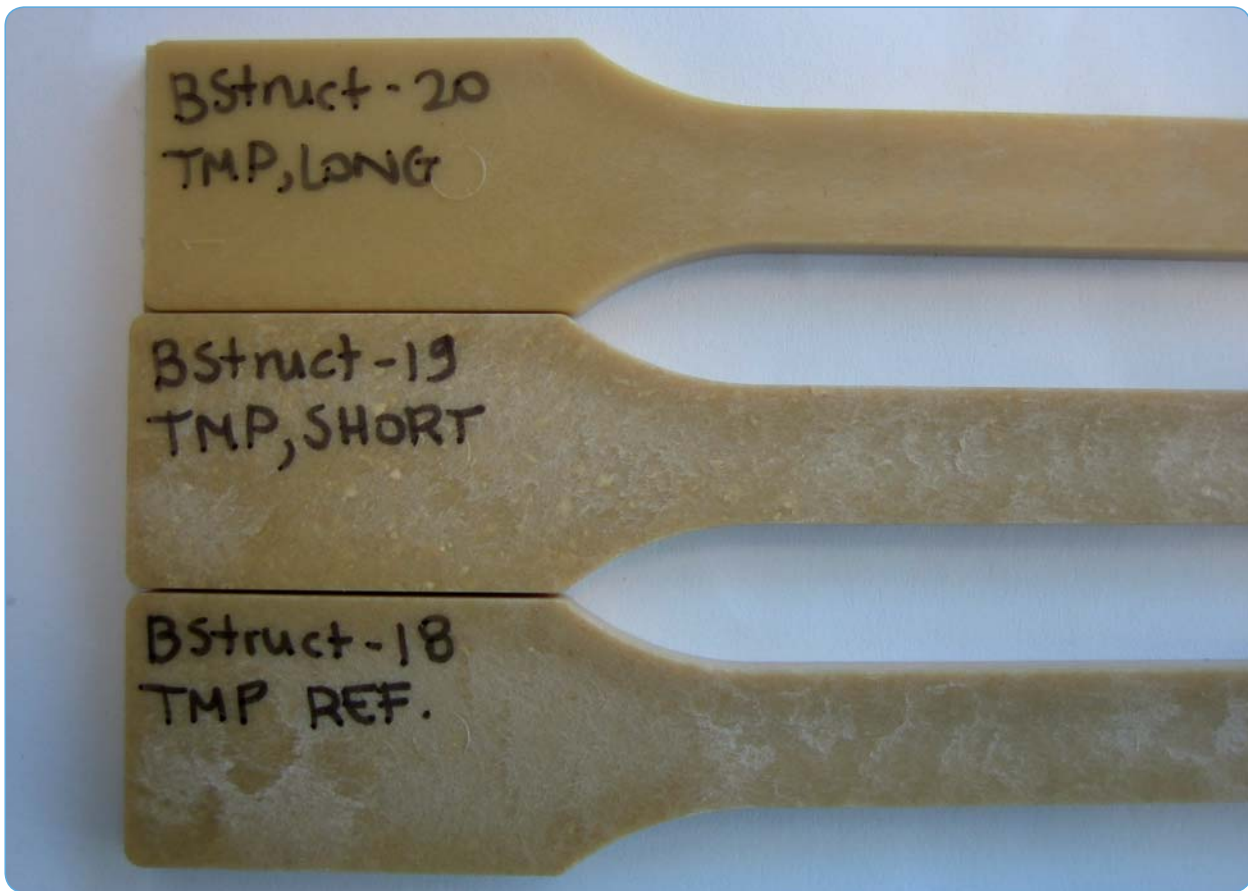


Figure 5. PLA composites with 30 wt% of TMP fibres.

strength and elastic modulus, regardless of the fraction level. The strain at break and impact strength decrease however. The only exception is the composite containing TMP long fraction fibres: the impact strength appears to remain at the same level as with the pure PLA. Compared with the non-fractioned reference fibres, the short fraction fibres decrease all the mechanical properties and the long fraction fibres increase them.

## Conclusion

Of the chemically bleached fibres, the pine pulp, as a composite reinforcement, gives the best mechanical properties for PLA-based WPC materials. The pine pulp fibres are also initially longer and have a higher aspect ratio than eucalyptus and birch fibres.

TMP fibres perform very well as a fibre reinforcement for PLA, and the long TMP fibre fraction provides the best WPC mechanical properties of the tested wood fibres. Compared with the reference and short fraction, the long fraction has the highest average fibre length and the fibres seem to be well distributed (Figure 5).



**ELINA LAATIKAINEN**

Research Scientist (fibre processing)  
elina.laatikainen@vtt.fi  
Tel. +358 20 722 2554



**HEIDI PELTOLA**

Research Scientist (composites)  
heidi.peltola@vtt.fi  
Tel. +358 20 722 3019

## Hydrophobic films by atmospheric in-line plasma deposition

Kalle Nättinen, Juha Nikkola, Juha Mannila, Mikko Tuominen, Juho Lavonen, Pirjo Heikkilä

Functional coatings on paper, paperboard and plastic film are used for special and enhanced properties in the field of paper converting as well as in fibre material applications. Besides modifying the surface energy of the substrate, the possibility of applying chemical coatings by plasma deposition has also recently been investigated. Hexamethyldisiloxane (HMDSO) was used as the precursor for the atmospheric pressure plasma deposition of hydrophobic  $\text{SiO}_x$  coatings on PE-coated paper. In order to produce high-barrier films, in-line sol-gel-coated paper was used as a base material for further plasma deposition.

### Introduction

Plasma deposition or plasma-enhanced chemical vapour deposition is typically based on dielectric barrier discharge plasma. The two general types of PECVD deposition methods are direct (glow) and remote (afterglow). In the direct method, the plasma gas together with the precursor compound is introduced into the discharge area, resulting in complete decomposition of the precursor. In the remote mode, only the carrier gas is fed through the discharge, resulting in "secondary" activation of the pre-

cursor, which is fed downstream from the discharge. The remote mode does not decompose the precursor completely, allowing deposition of larger molecules and molecular fragments. Due to the greater distance of substrate from the discharge, the remote method enables the treatment of heat-sensitive materials such as polymers and polymer-coated materials.

In principle, all materials can be deposited when a suitable precursor exists<sup>1</sup>. The exact composition of the deposited films is very difficult to predict. Besides the precursor, it depends on the carrier gas and the process conditions: the system, power, geometry, distance from the discharge to the substrate, etc. Models have been developed in an attempt to predict the results<sup>2,3</sup>, but, in principle, mixtures of compounds will be obtained. A positive effect has been observed regarding the desorption of impurities from the surface when using  $\text{H}_2$  carrier gas and heating the substrate<sup>4</sup>. During the last ten years there has been general interest in studying the potential of inorganic-organic hybrid sol-gel thin films. The sol-gel process involves the evolution of nanoscale networks in a continuous liquid phase through the formation of a colloidal suspension and the subsequent gelation of the sol<sup>5</sup>. Controlled hydrolysis and condensation reactions are the keys

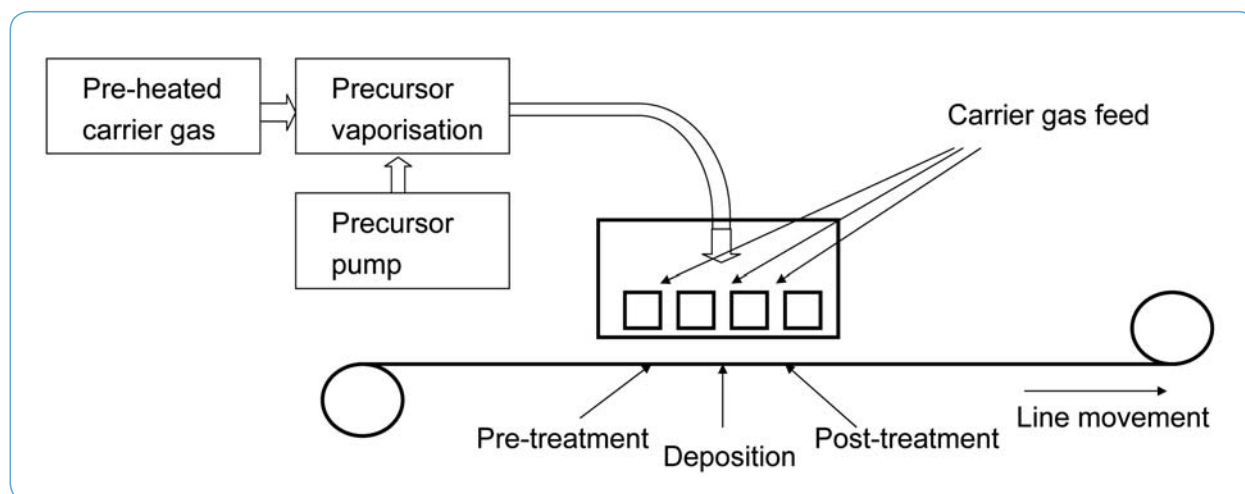


Figure 1. Atmospheric plasma deposition unit configuration developed in the project.

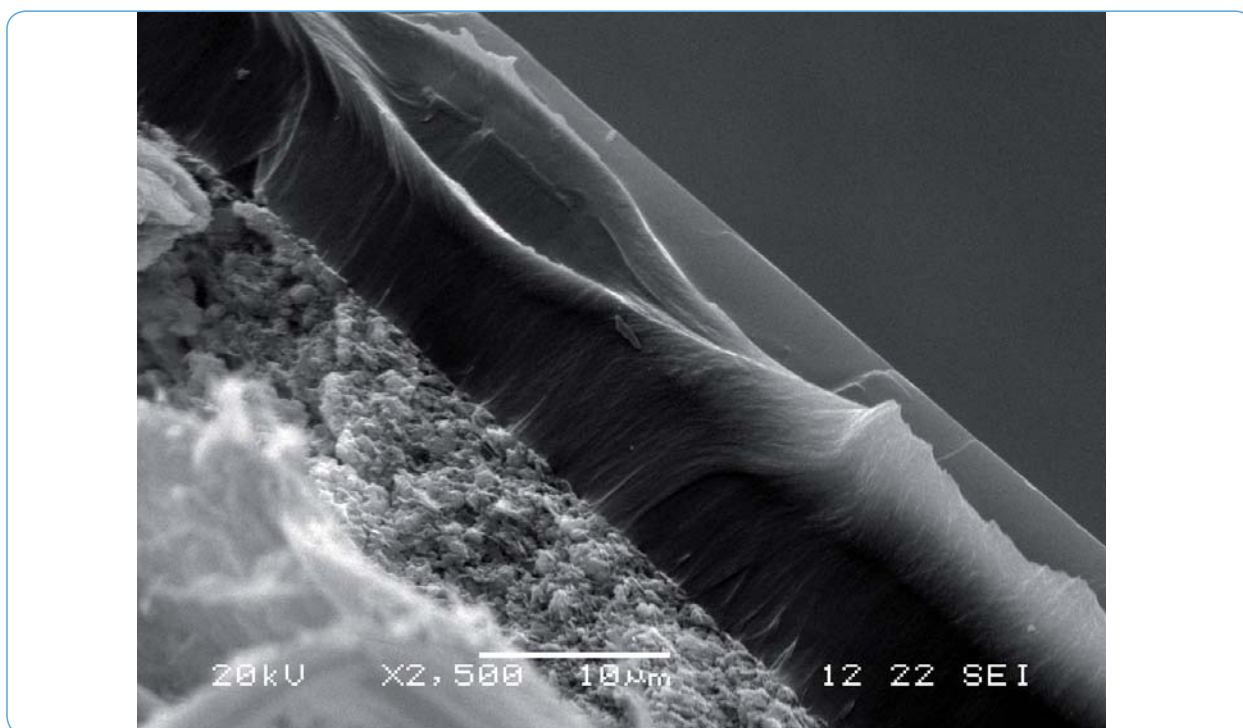


Figure 2. Plasma-deposited  $\text{SiO}_x$  film on PE-coated paper.

to the formation of the sol-gel matrix. Due to these reactions, the sol-gel technique offers a great opportunity to produce functional and premium transparent thin films. Hydrolysis acts as a rapid initial reaction in the sol-gel process, in which reactive alkoxide groups react with water molecules to form hydroxyl groups. The sol-gel technique with atmospheric plasma pre-treatment has proved to be a potential method to produce functional sol-gel thin films on roll-to-roll products<sup>6</sup>. Paulussen *et al.*<sup>7</sup> have studied the use of atmospheric pressure plasma to obtain hybrid inorganic-organic barrier coatings on polyethylene terephthalate (PET) films. They suggested that atmospheric plasma-enhanced coatings could be an effective and environmentally friendly alternative for traditional barrier coatings like polyvinylidene chloride (PVdC) lacquers. Durable hydrophilisation of PET, PP and PE films has also been studied by Dubreuil *et al.*<sup>8</sup>. They used acetic acid and ethyl acetate as a precursor to deposit a hydrophilic layer on polymer surfaces with DBD atmospheric pressure plasma. Based on the experiments, the atmospheric plasma-induced coatings can be used to produce durable hydrophilisation of polymer surfaces.

## Method

The pilot extrusion coating line located at TUT was equipped with an atmospheric plasma-deposition unit

developed at VTT, with the aim of obtaining high-barrier structures of PE-coated paper applied with different surface treatments and coatings. Plasma-enhanced sol-gel coatings were applied to a PE-coated paper, and, in comparison, HMDSO was used as a precursor for atmospheric pressure plasma deposition of  $\text{SiO}_x$  coatings on the same substrate. A plasma-deposited  $\text{SiO}_x$  coating was also applied to the plasma-enhanced sol-gel-coated base substrate for reduced moisture dependency barrier performance.

## Experimental

The plasma-deposition unit developed in the project is described in Figure 1. It consists of three carrier gas feeds, in which, for example, helium or argon gases can be used. Precursors are vaporised in pre-heated carrier gas prior to the deposition. The plasma deposition is performed in three continuous steps between the four electrodes of the cassette: pre-treatment, deposition and post-treatment. The power of the plasma-deposition unit may be varied between 0.5-2.0 kW.

## Results and discussions

The coating formation was observed with SEM. A cross-section image of a plasma-deposited  $\text{SiO}_x$  coating is shown in Figure 2. The  $\text{SiO}_x$  film was seen to decrease the topography variation of the PE-coating layer on paper.

It was also observed that the processing marks of the PE-coating were smoothed by the deposition step. The film formation was inhomogeneous however. The film thickness varied from 0.3 to 3  $\mu\text{m}$ .

The deposited  $\text{SiO}_x$  coating is expected to have an effect on the surface chemistry of surfaces. Water-contact angle measurements were performed to compare the surface energies and the composition of the surfaces after plasma activation and deposition. With the atmospheric plasma *activation*, the contact angle value of all the treated substrates (paper, LDPE-coated paper and cotton fabric) was decreased. With plasma deposition using HMDSO as the precursor, the contact angle values of paper and cotton fabric were increased, whereas the already initially high contact angle of LDPE-coated paper remained at the same level. Heat sealability measurements were carried out to also confirm the formation of a coating on the LDPE-coated paper. The significantly elevated minimum heat-sealing temperatures proved that a coating of significant thickness had been obtained. It was observed that the  $\text{SiO}_x$  thin film could be coated onto the low surface energy LDPE surface by plasma deposition even at a line speed of 50 m/min. The  $\text{SiO}_x$  film deposited on the sol-gel-coated polyethylene surface led to a decrease in oxygen transmission at relative humidity contents 0 and 50 RH% respectively.

## Conclusions

A plasma deposition unit for a roll-to-roll process was developed and demonstrated.  $\text{SiO}_x$  film was successfully plasma-deposited onto paper, PE-coated paper and textiles in the roll-to-roll process, with line speeds from 5 to 50 m/min. An atmospheric plasma-enhanced sol-gel coating was applied to PE-coated paper in laboratory scale and pilot scale. The sol-gel-coated substrate showed improved oxygen-barrier properties compared with uncoated substrate. The hybrid barrier structure of the sol-gel coating and plasma-deposited  $\text{SiO}_x$  film was also produced using the in-line roll-to-roll process. The combination of the plasma deposition and sol-gel coating offers a promising combination of surface treatments for applications in which tailoring of permeability and surface properties is needed.

## Acknowledgements

Plastek and Plastek 2 Surface modification with plasma and corona techniques 1.9.2005 - 28.2.2010.  
Project funded by Tekes (Finnish Funding Agency for Technology and Innovation) and a project consortium

- Research partners: VTT, Tampere University of Technology and Åbo Akademi
- Industrial partners: Stora Enso, UPM Kymmene, Vephone, Omya, Sun Chemicals, Millidyne and KWH Plast
- Team working with plasma activation and deposition: Kalle Nättinen, Juha Nikkola, Juha Mannila and co-workers (VTT), Mikko Tuominen, Juho Lavonen, Pirjo Heikkilä and co-workers (TUT)

## References

1. C. Tendero, C. Tixier, P. Tristant, J. Desmaison, P. Leprince, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2006, 61, 2-30.
2. S.E. Babayan, J. Jeong, A. Schütze, V.J. Tu, M. Moravej, G.S. Selwyn and R.F. Hicks, *Plasma Sources Sci. Technol.* 2001, 10, 573-578.
3. R. Foest, F. Adler, F. Sigeneger and M. Schmidt, *Surf. Coat. Technol.* 2003, 163-164 323-330.
4. K. Inomata, H. Ha, K.A. Chaudhary and H. Koinuma, *Appl. Phys. Lett.* 1994, 64, 46-48.
5. C.J. Brinker and G. W. Scherer. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press, Inc., 1990.
6. J. Nikkola, K. Nättinen, J. Vartiainen, J. Mannila, M. Kallio, E. Hurme, J. Kuusipalo, M. Tuominen, K. Lahtinen and J. Lahti. *NETCOAT Annual Seminar 2006*. Tampere, Finland, 24 Oct. 2006.
7. S. Paulussen, R. Rego, O. Goossens, D. Vangeugden and K. Rose. *Surf. coat. Technol.* 2005, 200, 672-675.
8. M.F. Dubreuil and E.M. Bongaers. *Surf. coat. Technol.* 2008, 202, 5036-5042



**KALLE NÄTTINEN**

Senior Research Scientist  
+358 20 722 3498  
kalle.nattinen@vtt.fi

# Sustainability impact assessment of the forestry-wood chain (EFORWOOD)

Arto Usenius

Sustainable development of the forest sector is being increasingly emphasised by political and industrial decision makers both at the European level and globally. In order to implement this thinking in practice, there is a need to define measures and indicators of sustainability as well as procedures and methods of evaluation. EFORWOOD offers tools (ToSIA) for sustainability impact assessment of the forestry – wood chain at the national, regional and European level. The tools can also be used for company and mill level assessments.

## Sustainability indicators for the forest sector

For each of the three pillars of sustainability – economic, environmental and social – the following indicators were defined for the forest sector:

**Economic:** gross value added; production costs; resource/material use; total production; investment and research & development.

**Environmental:** Energy generation and use; greenhouse gas emissions and carbon stocks; transport distance and freight; water use; soil, water and air pollution; waste generation; forest biodiversity; forest resources.

**Social:** Employment; wages and salaries; occupational safety and health; education and training

## Tool for Sustainability Impact Assessment (ToSia)

The forestry–wood chain (FWC) spans continuously from seed to tree, through to end product and consumer. The FWC can be broken into the following main components: forest resource management; forest to industry interaction; processing and manufacturing; industry to consumer interaction. The material flow chain comprises a series of processes, such as timber harvesting, log sorting, sawing, drying, secondary conversion, transportation, storage, etc. In the ToSIA calculations, sustainability indicator values are linked to all production processes based on defined material flows. ToSia then aggregates the indicator results throughout the FWC. In order to achieve effective coverage at regionalwise, national or European level, a “ToSIA-network” of forestry–wood chains is established. Interaction between chains may also exist, since, for example, solid wood chains provide wood chips for pulp and paper chains. Forestry–wood chain networks can also be established for individual forest companies.

## Model mills for describing production

The solid wood value chains are presented in Figure 2. Five main product groups can be identified: sawn timber, wood-based panels, building components, furniture, and packaging products. European production was described country- and region-specifically with using sets of Model Mills specific to the industrial structure of the production area. Each Model Mill is described

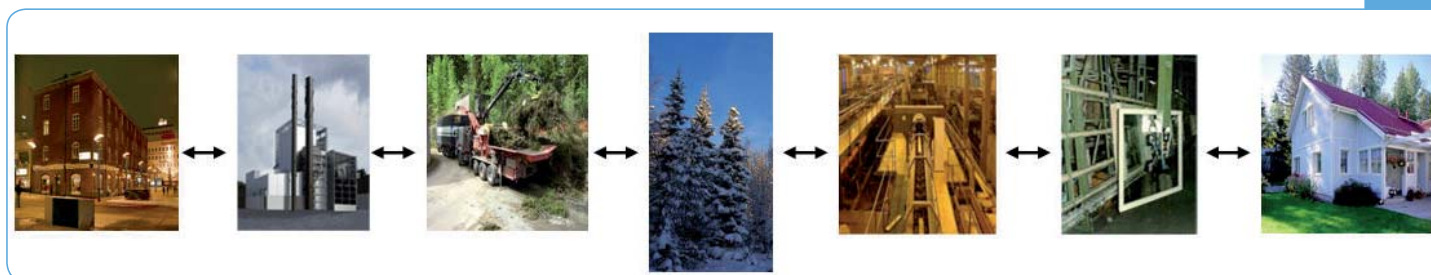


Figure 1. All value chain phases – from wood raw material to end products – are interrelated. VTT participated in value chain research for the solid wood and bioenergy sectors.

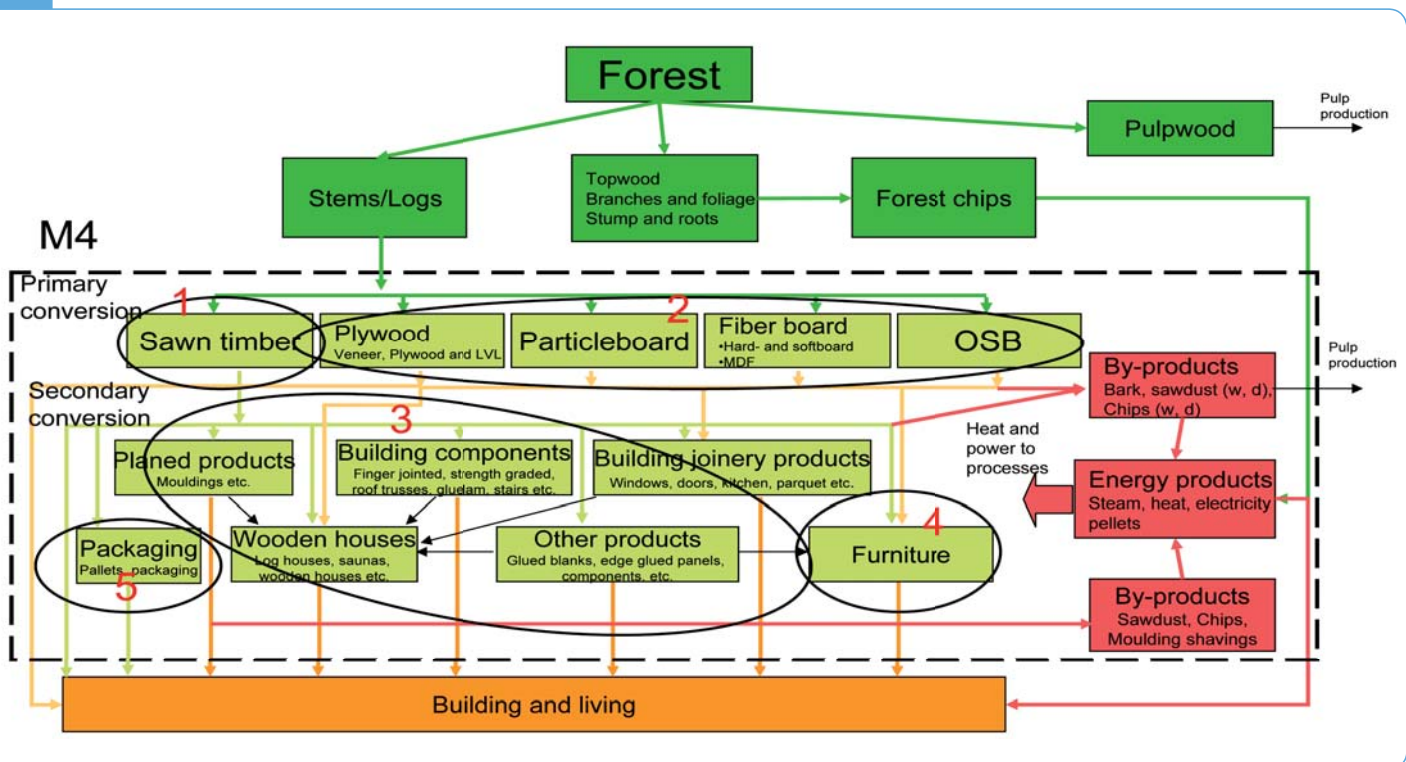


Figure 2. Model Mills describing material flows and wood-based product manufacture.

in terms of capacity, technology and human resources. Sawn timber production in Finland is represented by three Model Mills. The mill capacities are 50,000 m<sup>3</sup>, 150,000 m<sup>3</sup> and 300,000 m<sup>3</sup>. Material flows and indicator values are determined for each Model Mill.

### Data collection for material flows and sustainability indicator values

VTT was strongly involved in the data collection regarding the wood material flows and sustainability indicator values of solid wood products and bioenergy production in Finland and the Nordic countries. The data sources included official statistics, literature and VTT's internal databases. VTT was also involved in data evaluation using the WoodCIM® system for the evaluation of wood chain optimisation models. One of the key results of the project was the creation of a comprehensive database covering the European forest sector. The database serves as a useful resource for future research.

### Scenarios for mirroring future production

Scenarios for 2015 and 2025 were created to estimate improvements in manufacturing systems for solid wood products in the short and long term. Finland is at the leading edge of ICT implementation in the wood industry worldwide. However, wood raw material and product

scanning technology, flexible and self-learning systems, and advanced process control systems offer room within the wood industry for radical future improvements in profitability, value yield, and customer orientation, reduced energy consumption, and waste reduction. A key area of potential is precise early-stage detection of wood properties for optimal allocation and processing of wood raw materials. X-ray scanning of logs (Figure 3) is a step in that direction. A value chain shift from bulk production towards value-added components is also needed. Implementation of new business and processing concepts has the potential to increase value yield by 30 percent.

### Conclusion

The multidisciplinary EFORWOOD project has established strong new networks with institutions and researchers. The project's European-level database and sustainability assessment tools and indicators provide useful resources for future forest sector analyses to support policy decision-making and the needs of industry. The project's technology scenario analyses showed that considerable potential exists to improve the profitability of wood products companies.

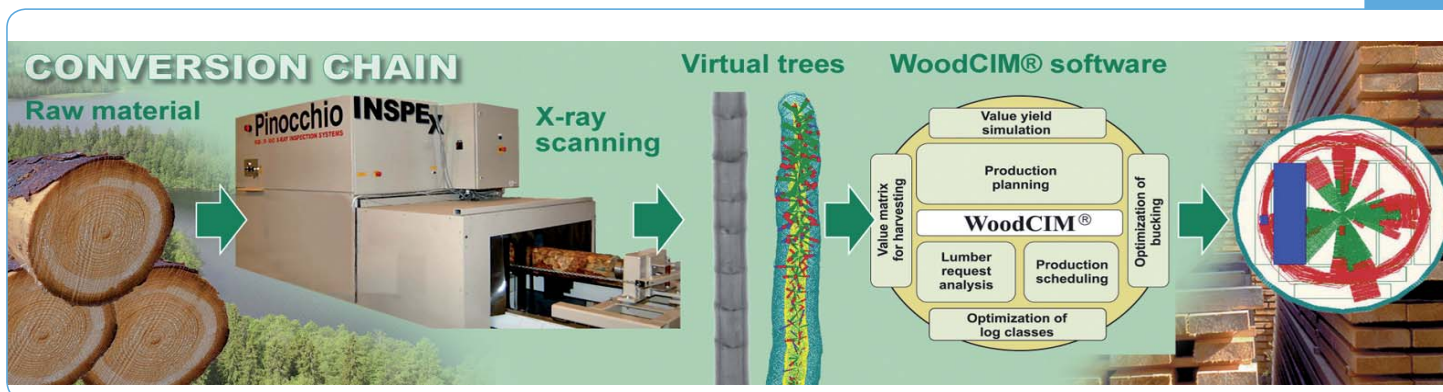


Figure 3. New technologies as tools for business enhancement.

## Acknowledgements

The IP project EFORWOOD was implemented during the period 1 Nov. 2005 – 31 Oct. 2009

- Financed by the EU and partner organisations. Total budget: EUR 20 million.
- 38 partners from 21 countries involved in the project. Co-ordinated by professor Kaj Rosen of Skogforsk, Sweden.
- VTT involved in solid wood and bioenergy aspects of the project. Team working with solid Wood: Arto Usenius, Antti Heikkilä, Jorma Fröblom and Tiecheng Song. Team working with bioenergy: Margareta Wihersaari and Markku Kallio.

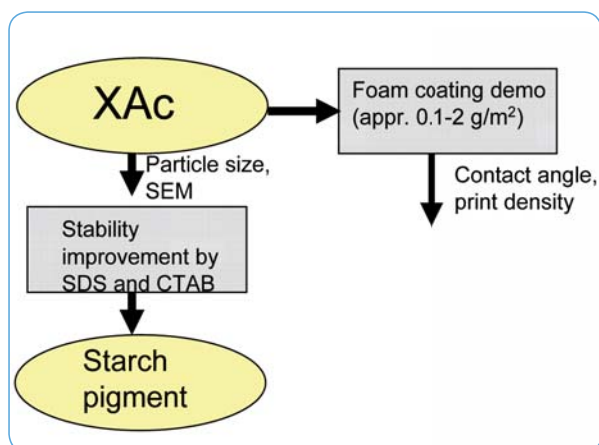


**ARTO USENIUS**  
 Professor  
 +358 20 722 5540  
 arto.usenius@vtt.fi

## Nanomaterials in coating applications, NANOCOAT

Tekla Tammelin, Annaleena Kokko

The aim of the project was to modify and use xylan-based nanomaterials in foam coating on paper and board substrates. As a background to the project, it can be noted that birch xylan and xylan-based colloidal dispersions and polymeric solutions have been extensively investigated in joint projects at KCL and VTT. In addition, nanoparticles are successfully used in pilot-scale coating applications at KCL. After these projects, it was considered very important to explore the potential of these new nanoscale materials as pigments and other paper and board surface modification components. VTT's goal was to produce stable xylan acetate pigment dispersions as well as to modify xylan (for example by cross-linking) in order to produce xylan with special functions. KCL's part in the project was to apply these nanoscale pigments and polymeric materials as foam on the board surface and characterize the achieved properties. The aim of the strategic initiative is to identify in which direction the xylan modification should be taken in a future large-scale project. The project objective was to create novel coating innovations using value-added, mainly wood-derived chemicals and technologies developed in KCL and VTT projects.



The plan was that the project should study the possibility of small xylan acetate particles with a high softening temperature functioning as nanoscale pigments and clarifying if the xylan-based cross-linking binders and, for example, xylan-based particles have an ability to form thin polymeric films. Furthermore, the project plan was also to explore the potential of thin coatings to improve interactions between ink-jet dyes and paper and board surfaces.

The project was divided into the following tasks:

- Task 1. Preparation and testing of xylan cross-linkers
- Task 2. Preparation of stable xylan acetate dispersion
- Task 3. Surface interactions and film/layer preparation + activation
- Task 4. Coating of the board surface and evaluation of the functionality of the xylan-based layers
- Task 5. Printability evaluation

The project plan with xylan acetates is shown in Figure 1, and for xylan cross-linkers in Figure 2.

### Experimental

Experiments to improve the stability of the anionic xylan acetate dispersions were conducted using anionic surfactant (SDS) and cationic surfactant (CTAB) as stabilizers. The particle size of the dispersions was determined based on dynamic light scattering.

The cross-linking functionality of the pure films of xylan cross-linkers before and after UV-treatment was evaluated by FTIR and UV-Raman.

*Figure 1. Xylan acetate route in the project. Starch pigment was used in the foam-coating experiments when the functionality of the xylan cross-linker was tested due to the still inadequate stability of the xylan acetate dispersions.*

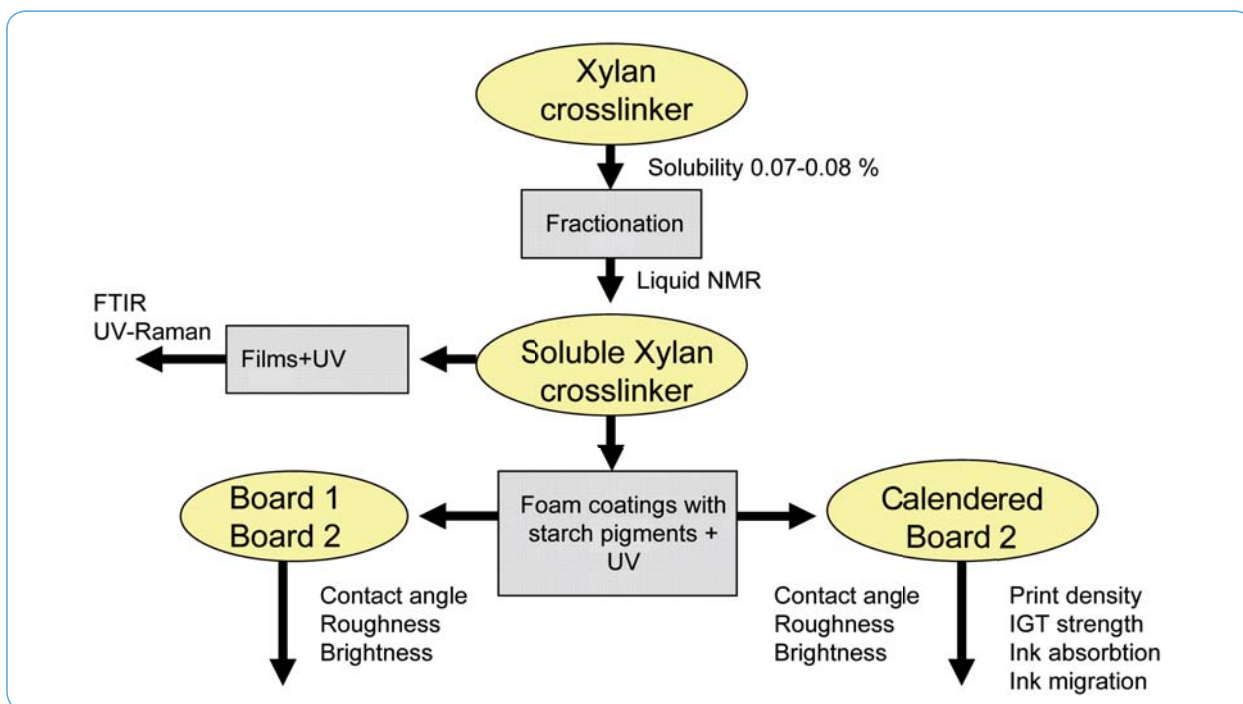


Figure 2. Xylan cross-linker route in the project.

Foam coatings were performed in laboratory-scale, and the coated commercial board sheets 1 and 2, were UV or air/heat dried. Surfactant ensuring good foaming (dodecyl ethyl dimethyl ammonium bromide) was used in all laboratory tests. As shown by Figures 1 and 2, several board surface properties were explored.

## Results

The particle size of the moderately stable xylan acetate dispersions was approximately 200 nm. The addition of SDS improves the dispersion stability – no agglomeration of the xylan acetate particles was detected over night. The ionic strength of the dispersions needs to be controlled, as the use of milliQ water clearly improves stability – electrostatic interactions seem to dominate the dispersion properties.

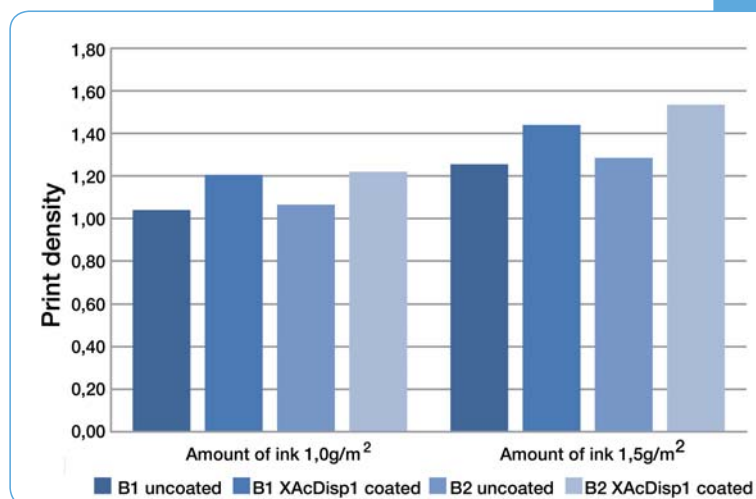
The UV-Raman technique appears to be sufficiently sensitive to detect the disappearance of C=C bonds when the xylan cross-linker is exposed to UV-light. The cross-linking ability and its detection still need further research efforts however.

Figure 3. Print density of the xylan acetate foam-coated boards.

With regard to the coated surface and its properties, the following can be concluded: it was possible to foam-coat with all of the studied dispersions (xylan acetate, starch acetate, starch acetate + soluble xylan cross-linker and pure soluble xylan cross-linker).

Foam coatings with xylan acetate dispersions resulted in a clear (>15%) improvement in measured ink densities, see Figure 3.

For uncalendered boards, the foam coatings that used starch pigment and the xylan cross-linker did not roughen the surface. On the contrary, minor smoothing was



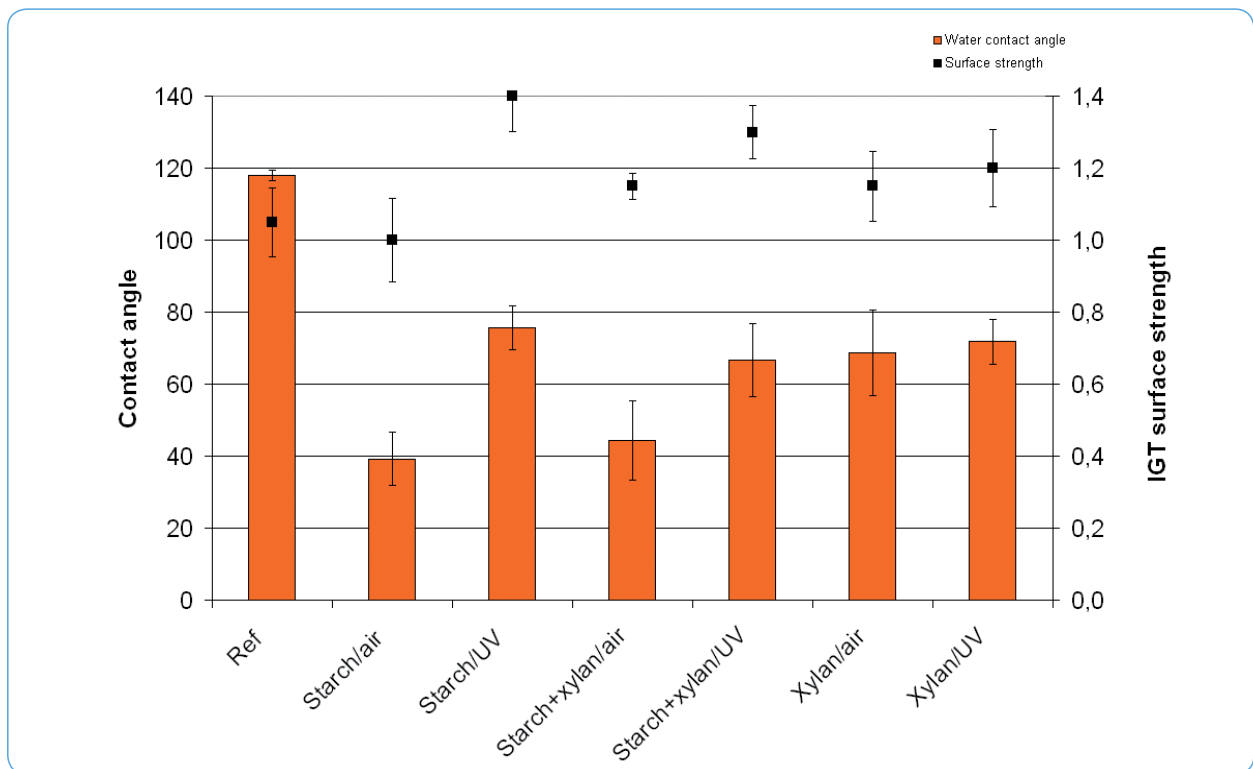


Figure 4. Water contact angle and IGT surface strength of the foam-coated pre-calendered boards.

detected. However, a pre-calendered baseboard re-roughened in the foam coating and was seen clearly as a higher final PPS roughness.

UV-treatment of the pre-calendered and foam-coated samples using starch pigment gave interesting result. UV-treated starch coating seems to improve the board surface strength although the surface becomes rougher, see Figure 4. The explanation for the achieved result is unclear.

Thin xylan film seems to cover the board surface, as can be seen indirectly from the contact angle results (the water contact angle after the pure xylan cross-linker foam coating is independent of the UV treatment and higher than the air-dried, starch-containing coatings), see Figure 4. The surface strength is also slightly improved compared with the untreated reference.

The effect of the cross-linking functionality of xylan on paper surface properties and printability was small, probably due to the low coat weights applied (due to the low solubility of the xylan derivative). Cross-linking was observed, however, for pure xylan films, and higher applied amounts thus need to be studied further.

## Acknowledgements

NANOCOAT project group: Harri Setälä, Sari Hyvärinen, Katriina Matilainen, Mika Härkönen, John Kettle and Ali Harlin



### TEKLA TAMMELIN

Senior Research Scientist  
tekla.tammelin@vtt.fi  
Tel. +358 20 722 4632



### ANNALEENA KOKKO

Senior Research Scientist  
annaleena.kokko@vtt.fi  
Tel. +358 20 722 7444

# Biohybrid packaging materials from pectin and nanoclay

Jari Vartiainen, Tekla Tammelin, Jaakko Pere, Unto Tapper, Ali Harlin

**There is growing interest in utilizing by-products from agriculture and the food industry to develop biodegradable materials to also replace petroleum-based polymers in packaging applications. In addition, nanotechnology in food packaging is expected to grow strongly over the next five years as increased globalization places demands for shelf-life-enhancing packaging. In recent years, much effort has been aimed at developing new biobased polymer-containing films and nanocomposites which can act as, for example, barriers in packaging materials.**

Unlike plastics, in dry conditions, the films of natural polymers exhibit good barrier properties against oxygen and grease due to the high number of hydrogen bonds in their structure. Natural polymers are hydrophilic in nature, however, and films produced from these materials are often hygroscopic, resulting in a partial loss of their barrier properties at high humidity. A major challenge for pack-

aging developers is therefore to overcome the inherent hydrophilic behaviour of biomaterials.

A frequently applied method to improve the strength, water resistance and barrier properties of natural polymers is to blend them with inorganic fillers. These hybrid organic-inorganic systems, especially those in which the inorganic material is dispersed in a polymeric matrix at a nanometric level, have been reported to possess enhanced strength, stability and barrier characteristics. Due to the platelike structure and high aspect ratio of nanoclays, they can effectively increase the tortuosity of the diffusion path of the diffusing molecules. Significant improvements in barrier properties can therefore be achieved with the addition of relatively small amounts of clays.

Sugar beet pectin films have previously been shown to act as an efficient oxygen barrier (the project "Tailored nanostabilisers for biocomponent interfaces", partially funded by Tekes through the FinNano Technology Program).

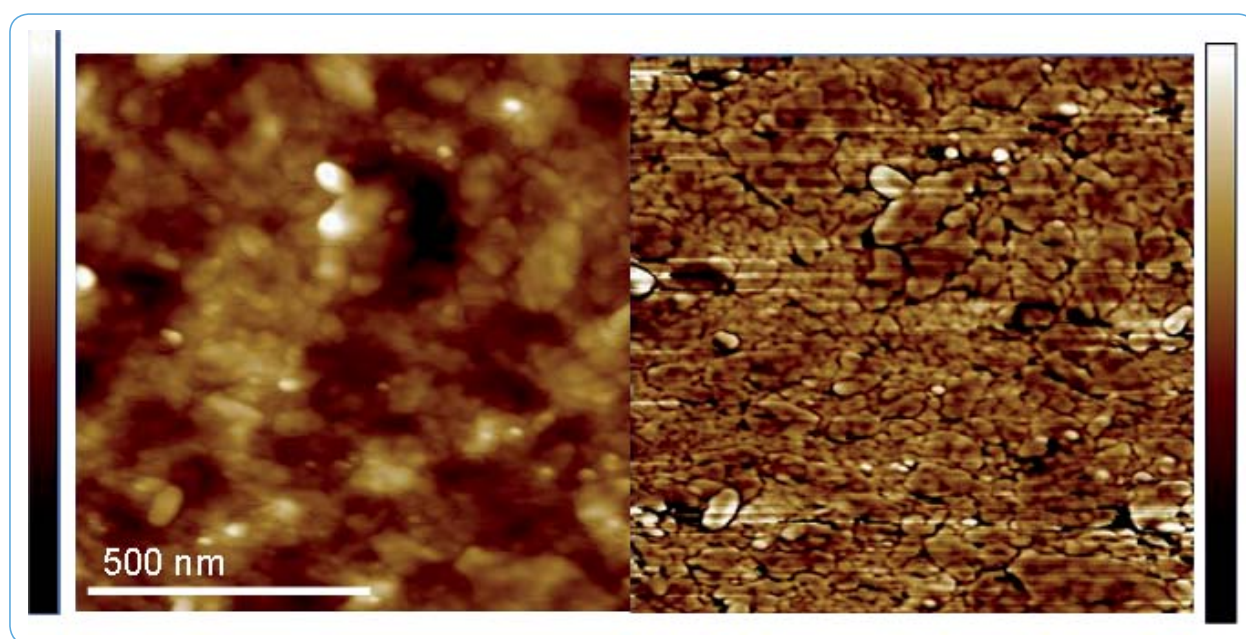


Figure 1. Atomic Force Microscopy (AFM) topography image (left) and phase contrast image (right) of spin-coated nanoclay platelets after high-pressure fluidizer treatment. The Z-range scale bars are 20 nm and 45 degrees, respectively.

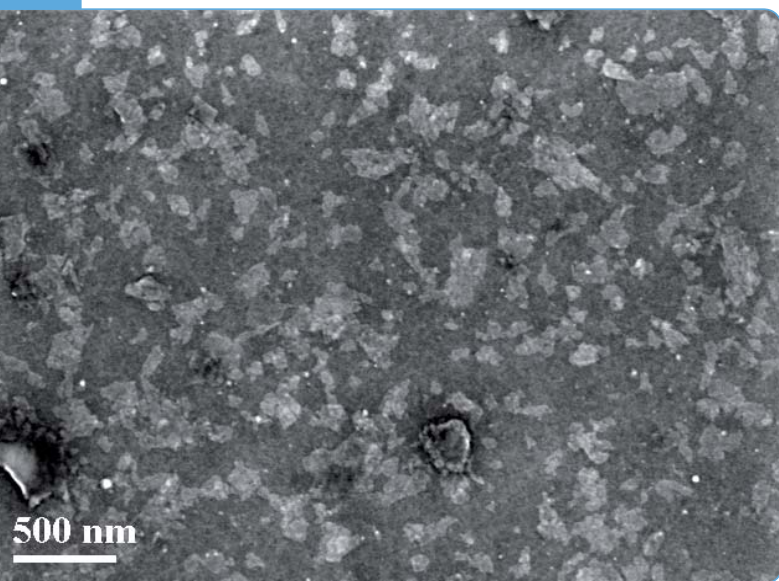


Figure 2. Scanning Electron Microscope (SEM) image of the spin-coated pectin/nanoclay thin film after treatment in the fluidizer.

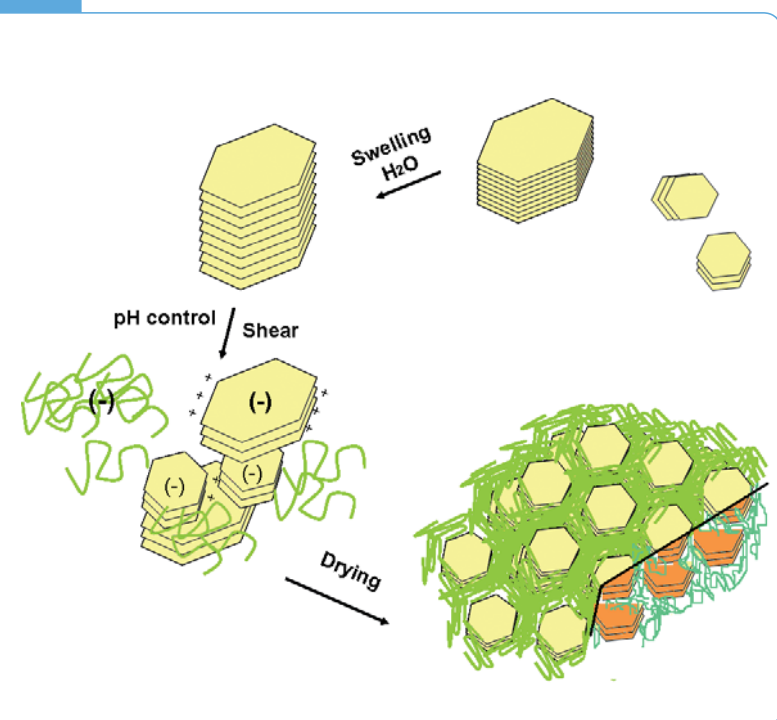


Figure 3. Schematic illustration of the structural features of the sufficiently defoliated nanoclay platelets dispersed in a continuous pectin matrix. Due to the high shear, the nanoclay platelets disintegrate into stacks consisting of approximately 15 individual nanoclay platelets. Pectin matrix glues stack into laterally organized films and also prevent the stacks from agglomerating at low pH.

Insoluble and hydrophobized pectin films, which possessed improved barrier properties in humid conditions compared with untreated pectin films, were obtained by means of enzymatic modification. The main aim of this work was to study the effects of nanosized montmorillonite on the barrier properties of unmodified sugar beet pectin films as a function of relative humidity.

## Materials and methods

Sugar beet pulp pectin was used as a continuous natural polymeric matrix in which an inorganic nanosized material, montmorillonite, was dispersed. The high-pressure and high-shear fluidizer was used for homogenization of pectin-nanoclay dispersions to ensure a sufficiently defoliated and nanosized structure of the nanoclay platelets. Films of pectin and fluidized mixtures of pectin and nanoclay were prepared by solvent casting. Water vapour transmission rates, oxygen transmission rates and grease resistance of the hybrid barrier films were determined. In addition, the model surface approach (high-shear spin coating of the dispersions on the solid surface) was used to further explain the structure of the hybrid material.

## Results and discussion

After the fluidizator treatment, the nanoclay forms stacks consisting of approximately 15 individual nanoclay layers (the thickness of one layer is ~1 nm) as can be determined from the AFM topography image, Figure 1. The AFM phase contrast image suggests the formation of a uniform and laterally oriented nanoclay surface. The nanoclay platelets were ripped off by high-pressure fluidization and uniformly distributed within the pectin matrix as shown in Figure 2. Figure 3 illustrates the structural features of the hybrid film.

The addition of nanoclay clearly improved the oxygen barrier properties of the pectin film in high humidity conditions (Figure 4). The oxygen transmission rate was reduced by 80% with pectin films containing 30 wt% of nanoclay compared with the pectin film without nanoclay. The oxygen barrier properties of nanoclay-containing pectin films were significantly better in humid conditions compared with the commercial polyolefin films of the same thickness. The water vapour transmission results also indicated improved barrier properties (results not shown). The water-soluble pectin lacked the ability to fully prevent the transmission of water vapour, however, and thus the total barrier effect of the films with ~30 wt% nanoclay was not more than 23%. The actual pectin formed an excellent barrier property against

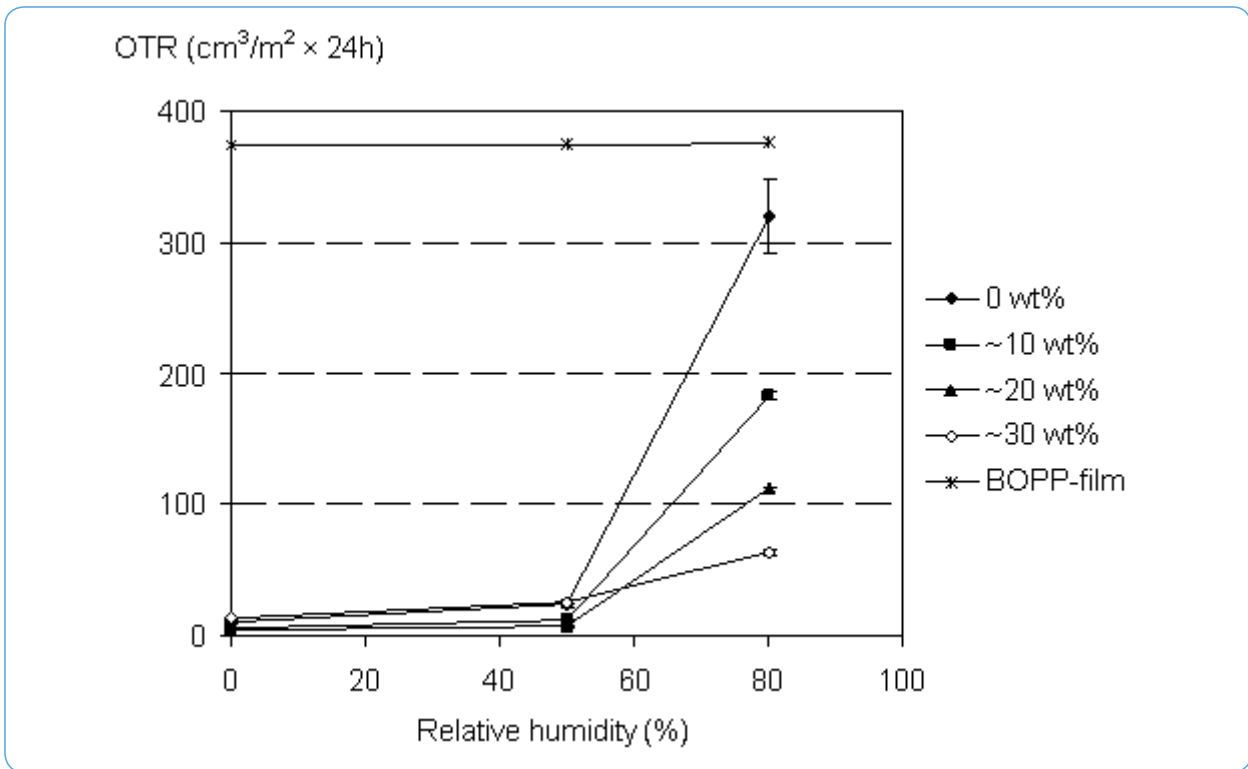


Figure 4. Oxygen transmission rates (OTR) of solvent-cast hybrid films of pectin films with different amounts of nanoclay. The BOPP film is a commercial biaxially-oriented polypropylene film. The OTR of the BOPP film is normalized to a film thickness of 100  $\mu\text{m}$ .

grease, and the nanoclay addition did not improve this barrier property in any way. All the films were completely impermeable to grease under the conditions tested.

Barrier improvements are explained using a tortuous path theory which relates to the alignment of the nanoclay platelets. As a result of sufficient defoliation, the effective path length for molecular diffusion increases, and the path to reduce the effect of gas transmission through the film becomes highly tortuous. In high humidity conditions, water molecules penetrate pectin films and destroy the hydrogen-bonded structure and weaken the barrier properties. Nanoclay amounts up to

30 wt% effectively prevented the transmission of oxygen in 80% relative humidity.

## Conclusions

Nanoclay was successfully dispersed in an aqueous pectin solution using a high-pressure fluidizator. Nanocomposite films made of pectin and montmorillonite showed improved barrier properties against oxygen and water vapour. The films were completely impermeable to grease. The developed biohybrid material can potentially be exploited as a safe and environmentally sound alternative to synthetic barrier packaging materials.



**JARI VARTIAINEN**  
Research Scientist  
jari.vartiainen@vtt.fi  
Tel. +358 20 722 6188



**JAAKKO PERE**  
Senior Research Scientist  
jaakko.pere@vtt.fi  
Tel. +358 40 5257 420

# Biomass-derived novel functional foamy materials – BIO-FOAM

Anna Suurnäkki, Anne Savolainen

**There is currently great interest in replacing synthetic materials with biomaterials in lightweight products. Porous and foamy products are light and can be applied in various end-uses such as foods and packaging, construction and insulation materials, and printing and coating of paper products.**

## Introduction

The objective of BIO-FOAM is to develop novel functional solid foamy materials from natural polymers and biomass for a number of industrial applications, e.g., food snacks, construction materials (insulation and concrete) and explosives. The aim of the project is to replace synthetic foam components with natural polymers originating from wood or agromaterials. To retain the important lightness and technical behaviour of foamy materials, the properties of natural polymers are tailored by targeted enzymatic and chemical methods. A basic understanding of the formation of biofoams by chemical and mechanical processing methods is also generated. Project consortia including VTT, Åbo Akademi and the University of Helsinki as research partners and industri-

al partners from the whole biomaterials to foamy material applications provide the best scientific, technical and application knowledge in the field of biomaterials and their end-use applications.

## Methods

The aim of polymer engineering is to modify the properties of biomaterials by chemical and/or enzymatic methods to meet the requirements of fundamental physico-chemical studies of polymer systems and foam formation, stabilization and properties. Na-caseinate is a surface-active protein and known foaming agent for food and other applications. As tailoring of caseinate foaming properties is of interest from an application point of view, different chemical cross-linking modificates of Na-caseinate have been prepared. Galactoglucomannan, acetylated to different degrees, has also been prepared for fundamental physico-chemical studies in Åbo Akademi.

One of the main objectives is to prepare and characterise the basic properties of various solid foams. So far, three different model foam systems have been studied: synthetic polymer foam dispersions, food foams (snacks) prepared by extrusion, and foamy concrete. In the study of synthetic polymer foam dispersions, the preparation of solid model foams from polymer dispersion in laboratory scale has been demonstrated. Furthermore, the way properties of solid foams alter when synthetic polymer dispersion is partly substituted by a biopolymer such as lignin that can be enzymatically cross-linked has been investigated. There have been two approaches in food foam preparation: to investigate how healthy snacks can be produced by adding protein and fibre ingredients to barley flour, and to gain a better understanding of expansion mechanisms of ce-

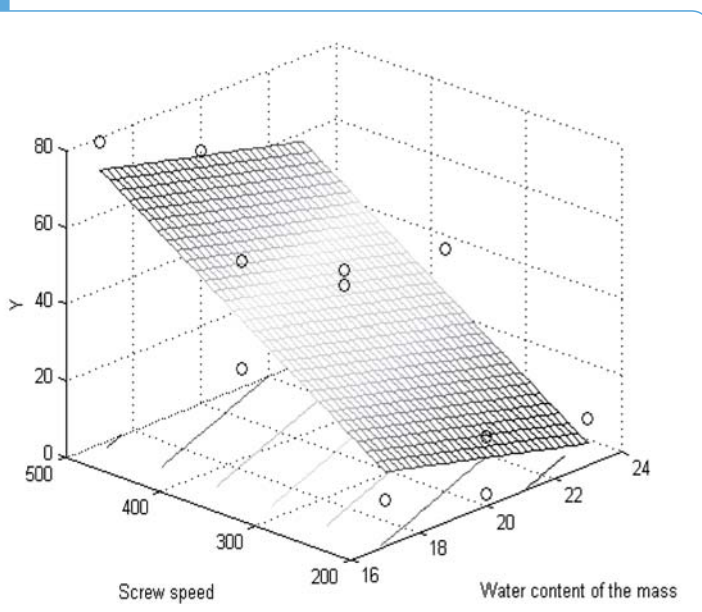


Figure 1. Response surface plot of the expansion (Y) of barley flour+polydextrose plotted against the screw speed and water content of the mass.

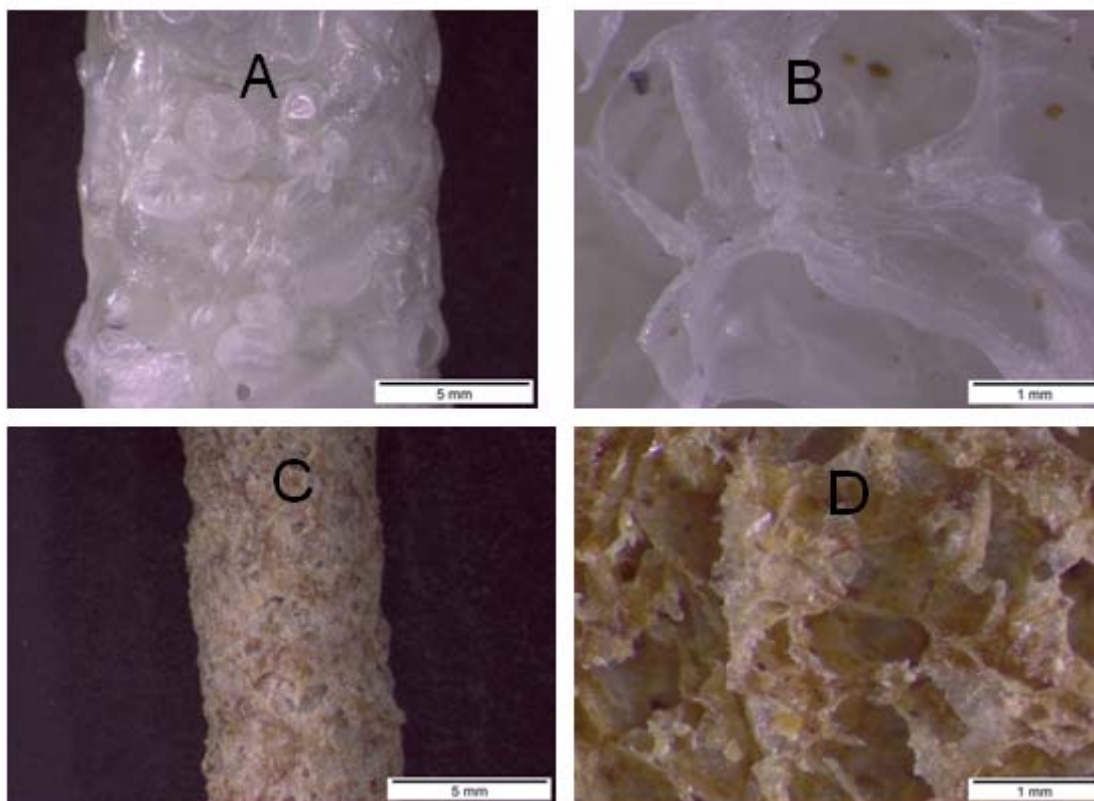


Figure 2. The outlook and cross-section of the extrudates visualised by stereomicroscopy. A and B are 100% barley starch; C and D are 100% rye bran.

reals by investigating a starch-bran model system. In the study of foam concrete application, reference foam concrete has been produced using a synthetic, commercial foaming agent, and its performance has been compared with that of foam concretes containing additional biomaterials.

## Conclusions

In model solid polymer foams, the properties of foam can be altered by changing the biopolymer content and using biomaterial as an additive in the system. Of the biomaterials tested in synthetic polymer system replacement and enforcement, wood pulp fibres were found to greatly affect foam formation. When modified with an oxidative enzyme, lignin further improves the properties of these foams.

The crucial role of the processing parameters and the fibre and protein content on expansion was demonstrated in the work related to extruded food snacks. The expansion and structure of barley flour extrudate could be altered with the addition of biomaterials and a change of process variables (Figure 1). The expansion decreased

from 280% to 120% as the system was changed from barley starch to rye bran (Figure 2). Based on the extrusion studies with the barley starch-rye bran mixture, it was suggested that the expansion of biomaterial in extrusion depends greatly on its film formation ability at the die.

The results of the concrete work indicated that biomaterials affect the processing and properties of foam concrete.

## Acknowledgements

Biomass-derived novel functional foamy materials - BIO-FOAM 1.9.2008-31.8.2010.

- Project funded by Tekes (Finnish Funding Agency for Technology and Innovation) and a project consortium
- Research partners: VTT, Åbo Akademi and the University of Helsinki. Industrial partners: Consolis Technology, Danisco Sweeteners, Finnfoam, Laihian Mallas, Forcit, Weekend Snacks, Taivalkosken mylly, Termex Eriste, UPM-Kymmene

### List of publications and reports

Forssell, P., Partanen, R., Myllymäki, O., Lille, M., Paananen, A., Flander, L., Linder, M., Lantto, R., Suurnäkki, A. & Buchert, J. Enzyme tools for bulk and interfacial engineering to create better food foams, BIOFOAMS 2009, Niagara Falls, Canada.

Kirjoranta, S., Hyvönen, L., Helén, H., Tenkanen, M. & Jouppila, K. The effect of whey protein isolate on the properties of barley snack products made by extrusion, BIOFOAMS 2009, Niagara Falls, Canada.



**ANNA SUURNÄKKI**  
Chief Research Scientist  
anna.suurnakki@vtt.fi  
Tel. +358 20 722 7071



**ANNE SAVOLAINEN**  
Trainee Research Scientist  
anne.savolainen@vtt.fi  
Tel. +358 20 722 4979

# Tailoring of the nanocellulosic materials for industrial applications

Mika Härkönen, Sauli Vuoti, Lisa Wikström

The forest industry is looking for new technological solutions and products. One very interesting opportunity is the production and utilisation of cellulose nanofibres for new types of materials and novel applications. Nanocellulosic materials are expected to have their first application areas within paper industry products. One of the aims, however, is also to create new application and product openings outside the paper sector that require the creation of novel, gross-disciplinary scientific knowledge of the fundamental material characteristics as well as of chemical and biotechnical modification of nanocellulose fibres. These are the main aims of a public cross-disciplinary project called Tailoring of the Nanocellulosic Materials for Industrial Applications (Naseva) jointly run by TKK, VTT and nine industrial partners.

The work in the project can be divided into three main areas: a) to modify the surface of nanocellulose by different means with the aim of enhancing the applicability of nanocellulose materials in new products, b) to understand the interactions between modified nanocellulose and other substances on a molecular level and c) to evaluate the suitability of the modified nanocellulose in various applications such as composites, nanomaterial additives and porous materials. This paper will present chemical hydrophobisation and the application of nanocellulose in thermoplastic composites as examples of VTT's research topics in the project.

## Hydrophobisation of nanocellulose

Modification of the surface of cellulose microfibrils to make them compatible with non-polar polymers has been attempted by, for example, introducing hydrophobicity into the fibre<sup>1-3</sup>. The adhesion of hydrophilic cellulose to hydrophobic polymer matrices has been increased by the use of hydrophobic coupling reagents such as silylating agents, ether or ester derivatives.

## Surface silylation

In our work, the fibre surface was hydrophobized using either silyl or ester groups. The degree of substitution for the trimethylsilyl groups ranged from 0.1 up to 2.7. It is therefore possible to approach complete silylation of the fibre. The fibre can be modified either from the surface or inside the fibrils depending on the requirements. The contact angles measured for the silylated samples show a steep increase when a degree of substitution above 0.1 is reached. When the degree of substitution starts to approach 1.0, the fibre also tends to become slightly soluble in organic solvents such as toluene or chloroform.

## Surface esterification

Seven different cellulose esters have been prepared for the study of the hydrophobizing effect of various ester substituents, which include aromatic and alkyl groups of several lengths and forms. In our studies, the highest contact angle and therefore highest hydrophobicity was achieved using the palmitine and stearine esters.

## Thermoplastic nanocellulose composites

Applications of cellulose-fibre-reinforced polymeric composites are found in, for example, the construction and automotive industry. The surface area of nanomaterials is large, which often makes nano-scale materials effective modifiers. The objectives of the composite work package in the Naseva project have focused on preparing nanocellulose-reinforced composites using biopolymers and demonstrating the benefits of the nanocellulose additive.

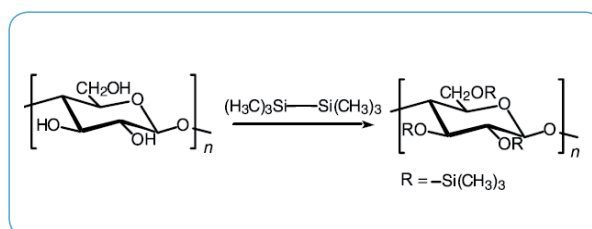


Figure 1. Preparation of trimethylsilylcellulose.

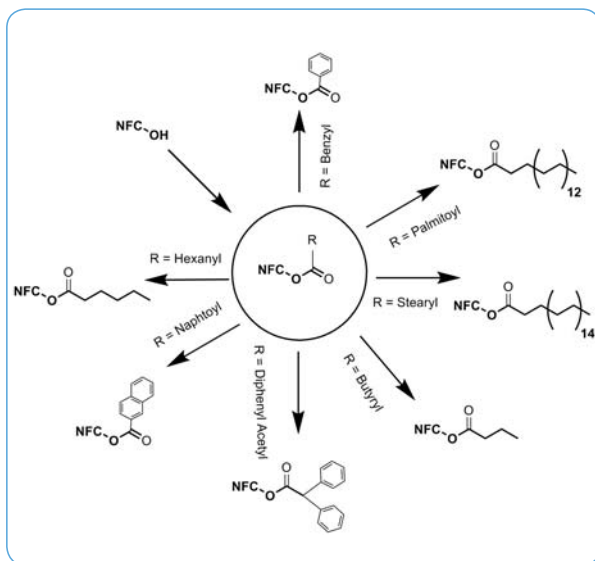


Figure 2. Various cellulose esters prepared in our studies.



Figure 3. Optical micrograph of NFC composite made by conventional melt compounding.

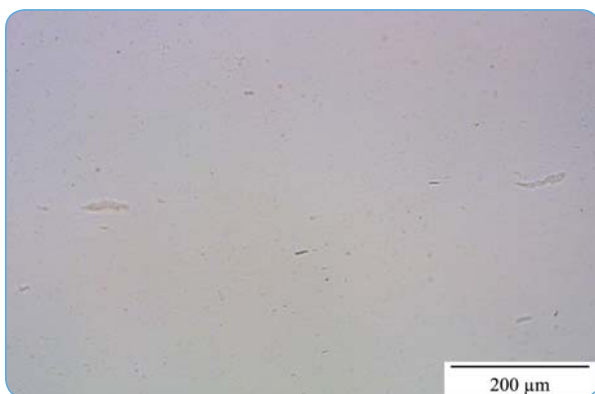


Figure 4. Optical micrograph of NFC composite made by solvent blending followed by melt compounding.

Fibre-reinforced plastics are conventionally made by melt compounding the dried fibre with the polymer. When dealing with nanofibres, the major challenge is to achieve good nanodispersion of the fibres in the polymer. Adhesion between the nanofibres and the matrix is also needed for positive effects. In this project, good dispersion has been achieved by different process methods, chemical modifications of nanocellulose (NFC) and/or with additives. The modification of the NFC aims for good compatibility as well as adhesion between the NFC and the matrix polymer.

Melt compounding of thermoplastic biocomposites with dried NFC has not led to good dispersion of the NFC in the polymer matrix. Good dispersion can be achieved by, for example, solvent blending of the NFC and the polymer<sup>4, 5</sup>. In this project, solvent blending has also been found to be a proper small-scale method test to compare the benefits of differently modified NFCs in the polymer matrix. After solvent blending, the NFC-polymer mixture was dried and melt compounded, and the test samples were moulded. Figures 3 and 4 compare the dispersion of the conventionally melt-compounded nanofibre cellulose composite and the nanofibre cellulose composite of the modified NFC made by solvent blending followed by melt compounding. Conventional melt compounding causes clear nanofibre agglomerates in the composite, but solvent-blended NFC and cellulose acetate propionate copolymer (CAP) show very good dispersion of NFC.

Tensile tests also indicate good dispersion and positive effects of nanofibre reinforcement of the solvent-blended samples. As an example, Figure 5 shows that 10 w-% NFC solution has already blended in CAP, notably enhancing the tensile test results of the NFC-CAP composite: the modulus increases by 70%. Tensile stress also increases notably, which is typically an indication of good dispersion of reinforcing fibre.

## Acknowledgements

Naseva Project funded by Tekes (Finnish Funding Agency for Technology and Innovation) and a project consortium:

- Research partners: TKK and VTT
- Industrial partners: UPM, Ahlstrom, Carlsberg, Dynea, Elastopoli, Glykos, Kareline, Nokia, Teknos

Team working with chemical modifications and composites at VTT:

- Mika Härkönen, Hannu Mikkonen, Kaisa Putkisto, Harri Setälä, Tekla Tammelin, Sauli Vuoti, Lisa Wikström and co-workers

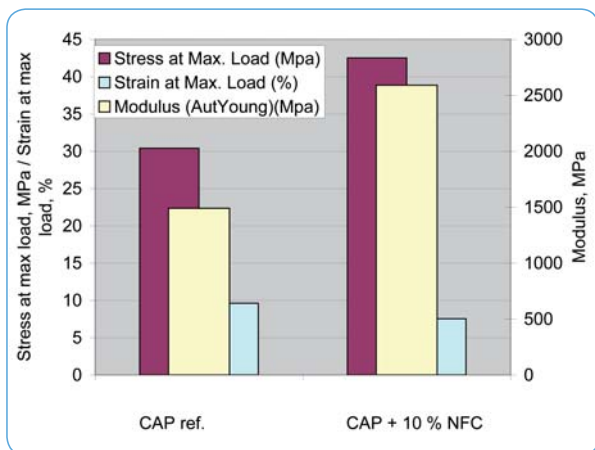


Figure 5. Tensile test results of CAP and NFC – CAP composite.

## References

1. Dalvag H, Klason C, Strömvall H. Int. J. Polym. Mater. (1985) 11, 9-38.
2. Maldas D, Kokta B, Daneault C. J. Appl. Polym. Sci. (1989) 37, 751-75.
3. Felix J, Gatenholm P. J. Appl. Polym. Sci. (1991) 42, 609-20.
4. Iwatake, A., Nogi, M., Yano, H., Composites Science and Technology 68 (2008) 2103-2106
5. Sanchez-Garcia, M.D., Gimenez, E., Lagaron, J.M., Carbohydrate Polymers 71 (2008) 235-24



**MIKA HÄRKÖNEN**

Senior Research Scientist

mika.harkonen@vtt.fi

+358 20 722 2942



**SAULI VUOTI**

Research Scientist

sauli.vuoti@vtt.fi

+358 20 722 2945



**LISA WIKSTRÖM**

Research Scientist

lisa.wikstrom@vtt.fi

+358 20 722 3560



VTT Technical Research Centre of Finland is the largest multitechnological applied research organisation in Northern Europe. VTT provides high-end technology solutions and innovation services. From its wide knowledge base, VTT can combine different technologies, create new innovations and a substantial range of world class technologies and applied research services thus improving its clients' competitiveness and competence. Through its international scientific and technology network, VTT can produce information, upgrade technology knowledge, create business intelligence and value added to its stakeholders. VTT is a non-profit-making research organisation.



**VTT TECHNICAL RESEARCH CENTRE OF FINLAND**

Vuorimiehentie 5, Espoo

P.O.Box 1000, FI-02044 VTT

Tel. +358 20 722 111, Fax +358 20 722 7001

[www.vtt.fi](http://www.vtt.fi)