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Research highlights in
industrial biomaterials 2009–2012

VTT RESEARCH HIGHLIGHTS 5

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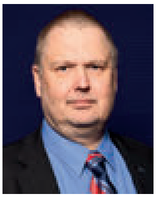
Preface: Industrial renewal with the aid of bio-platform chemicals



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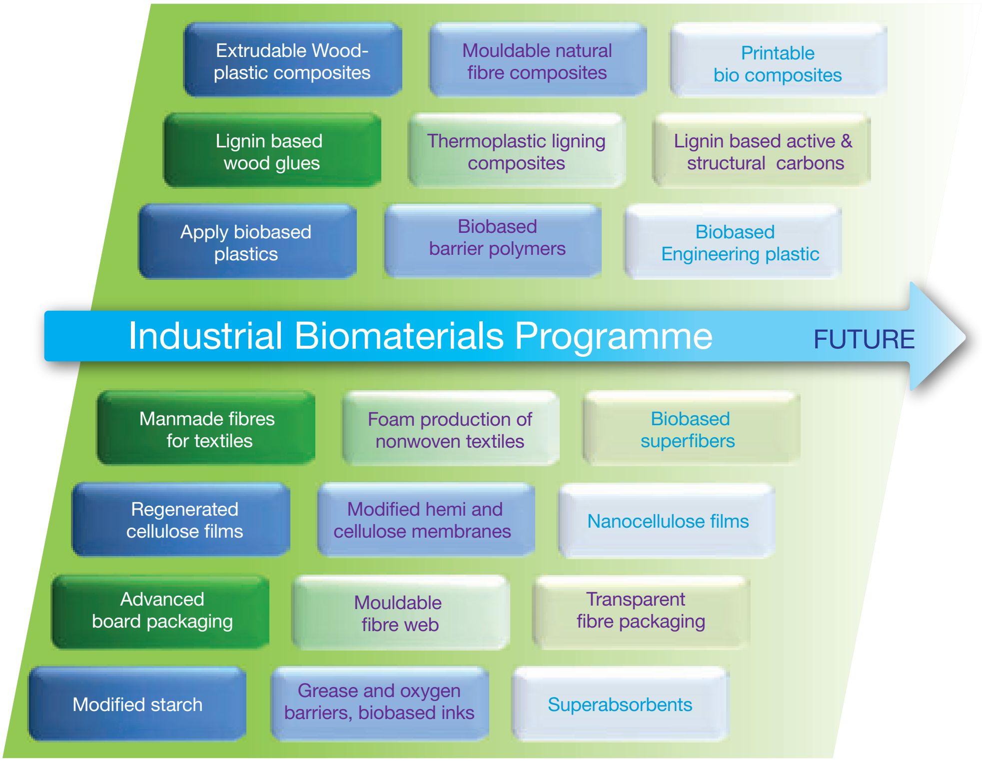
In the field of bio-economy, the Industrial Biomaterial Spearhead Programme 2009–2012 focused on renewing industry by means of emerging technologies of materials and chemicals based on non-food biomass, including food side streams, agricultural leftovers and natural material waste fractions. The programme invested a total of 96 million euro in application-driven focus on winning value chains in packaging and extending these to appliances and construction materials.

The scientific areas of global excellence in biomass conversion into materials include fractionation, metabolic engineering, biochemical and chemical conversion, nanotechnologies, chemical engineering and modelling, as well as design and converting sustainable materials into customer solutions. Technologies were developed in mouldable and translucent fibre webs, bio-based plastics, glues and adhesives, foams, latexes, and barrier and hybrid materials including nanocellulose applications and thin film barriers. We have also developed the next generation of fibre plastic compounds for mouldable furniture.

Oil-based general purpose polymers are cost-competitive as well-performing materials, but increased consideration for the carbon footprint, the cost effects of oil peak expectations and environmental issues support alternative raw materials. The first generation of synthetic biopolymers was developed to improve the performance of modified starch biopolymers. However, these are based on agricultural streams, which may compete with food or feed. The concept of biodegradable polymers and the missing concept of recycling simultaneously emphasise waste creation and increased waste management.

In the development of the second-generation synthetic biopolymers, renewable non-food raw materials should be applied. The use of the existing industrial infrastructure is also of great importance. Marked solutions may be found in the benefiting industrial side streams and by looking at the forest industry. Bio-based polyethylene has recently started to be produced (again) from overproduced fuel ethanol in Brazil. VTT has developed alternative routes for alcohols, e.g. ethanol from recycled pulp and methanol from gasified organic waste which can be applied for olefins. Other alternatives are beneficiating Fisher-Tropsch and hydrodeoxygenated bio-oils.

Beverage producers have launched a rally towards bio-based tereftalic acid used in polyethylene tereftalic acid PET, especially plastic bottles, and in film packaging as well as textiles. Behind this, there may be greater economic concern on feasible shale gas condensate, which reduces the production of aromates including tereftalic acid, used for PRT



production. VTT applies metabolic engineering and catalytic chemistry to create alternative routes for the aromates based on industrial side streams. Beyond valuable polymers, this will also affect structural carbon production.

VTT also develops novel, modified natural polymers based on agricultural and forest industrial side streams like lignin derivates, replacing phenolic glues and styrenic coatings. Other extracted natural polymers like modified hemicellulose from dissolving pulp production can also be applied to various applications including oxygen and grease barriers. The polymers can be applied to many products, but they do not fully remove the need for easily processable thermoplastic materials.

One example of a superior performance biopolymer is polyglycolic acid (PGA), which is very similar to polylactic acid but with a markedly higher oxygen barrier and mechanical strength properties. As a barrier, PGA is better than ethyl vinyl alcohol (EVOH), the most commonly used oxygen barrier polymer in the packaging industry. VTT has developed its own metabolic production method for glycolic acid and improved the polymerisation thereof. The novel polymerisation methods enable rapid and efficient production of high performance polymers while the biotechnical production method provides pure monomers for demanding applications.

Glycolic acid belongs to hydroxy acids and is found in quantities in black liquor. In the pulp mill's side stream, glycolic acid is found as a mixture with lactic acid and 3-hydroxy propionic acid. VTT has shown that it is possible to polymerise the hydroxy acids from black liquor. As a result, polymers with properties for sealing and hot melts have been made. VTT has also developed new technologies to produce latexes of hydroxy acid by means of polymerising the monomers.

The anticipated technological and scientific benefits achieved were in applying the novel technologies to the renewing industry and emerging customer-oriented value chains in the selected high-performing biomass-based materials and products thereof. The emerging technologies were aimed particularly at renewing forest industry and creating completely new bio-economy businesses. The main customers of the programme are B2B industries based on material bio-refineries and sustainable consumer brand owners.

The beneficiation and commercialisation of the research project outcome have focused on 100% bio-packaging materials with brand owners and manufacturing companies. The next accelerated offerings were in the field of appliances and construction, e.g. fibre composites and textiles. IndBioMat has supported VTT's internationalisation plans in the USA, Canada, Brazil and Australia through contract work with selected customers and co-operation in joint research with local institutes. The strong presence in the EU research community has continued.

Bio-based raw materials have been developed in the Industrial Biomaterials Spearhead Programme to a novel level for production technologies. The benefiting agricultural and forest industrial side streams enable new polymers with superior performance and materials thereof.

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1 Success stories of cellulose

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This chapter summarises the main highlights related to nanocellulose and cellulose-based materials in public research projects of the Industrial Biomaterials Research Programme during the years 2010–2012.

Nanocellulose has been shown to have potential in a number of technical applications. The key to understanding how nanocellulose will behave in different applications is to have a thorough understanding of how the structure and interactions of nanocellulose affect its function and hence its suitability for different applications.

The research performed at VTT relates to the whole production chain of nanocellulose – from the selection of raw materials to the development of production processes and modification of nanocellulose material according to the needs of various applications, as shown in Figure 1.

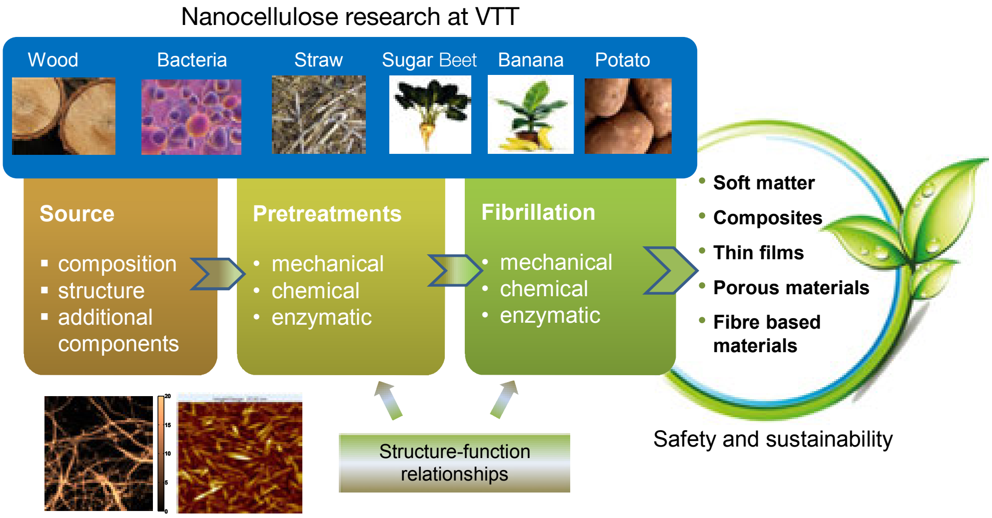

Figure 1. Flow of material and steps during nanocellulose processing. A strong link to understanding the whole chain, especially how the starting points affect applications, provides versatile and competitive expertise for developing applications and technology.

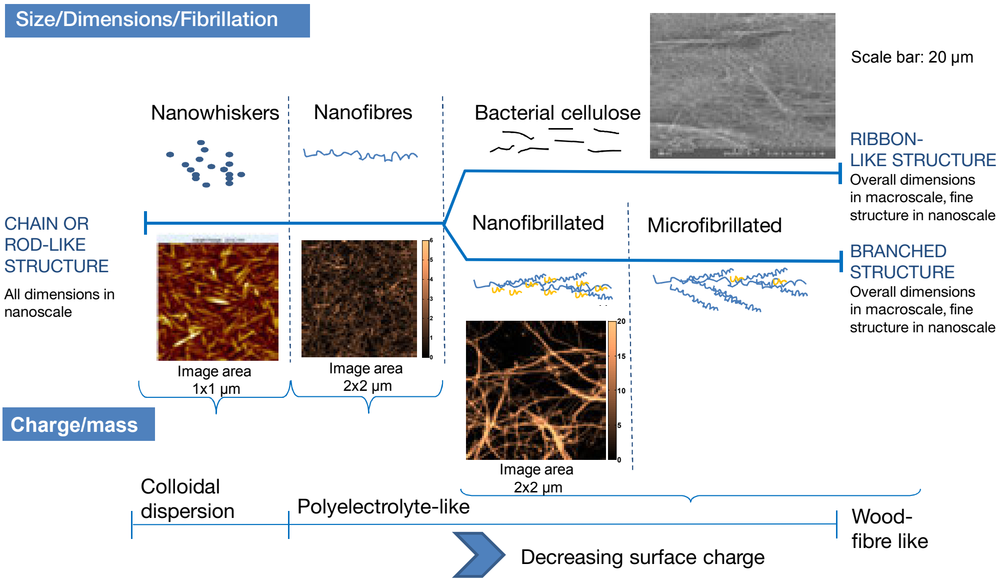

Figure 2. A classification scheme for micro- and nanocelluloses.

In this chapter, special characterisation techniques developed, and the most interesting applications developed as well as some observations about upscaling and sustainability are discussed.

1.1 Development of characterisation methods

VTT has actively developed various characterisation methods to assess the properties of micro- and nanocelluloses from production to their use during processing and in the final products. The methods can be used to address issues from nanocellulose properties (fibril dimensions and distribution, branching degree, surface charge, visual appearance, specific surface area etc.) to process characteristics (viscosity, pumping and mixing characteristics, dispersion stability, preservability) to final product properties (strength, structure, etc.) and aspects important from the safety point of view (amount of nanomaterial, exposure levels). The most relevant properties of nanocelluloses, a suggestion for their trading characteristics and the associated characterisation methods have been identified together with industrial partners and communicated internationally. One of the basic measurements is viscosity. The method has been tuned for fibrillated material, and Stora Enso, Kemira, UPM and VTT have already unified their viscosity measurements. This unification is an important step towards international standardisation of measurement methods, which is needed for reliable comparison of different nanocellulosic products.

VTT, together with Finnish Forestcluster's EffNet[1] programme partners, has been developing a proposal for the classification of micro- and celluloses based on the physical and chemical characteristics of fibrils. The main implication of the classification is that different characterisation methods are needed for different classes; see Figure 2. The first criterion for the classification of nanocelluloses is a combination of: 1) size (length), 2) number of dimensions on the nano-scale and 3) branching degree. The second classification criterion is charge/mass of nanocellulose.

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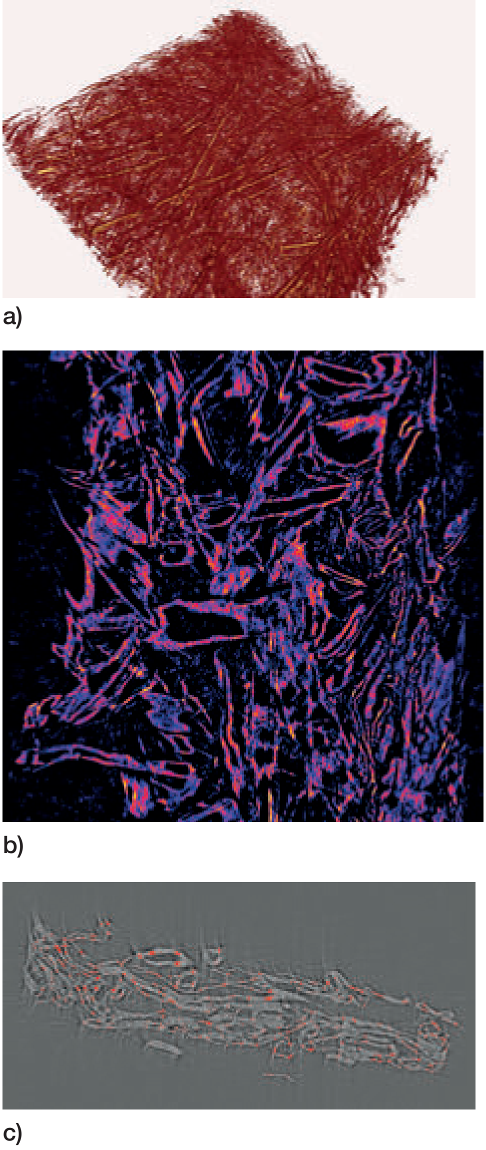
[1] ForestCluster EffNet programme: Efficient Networking towards Novel Products and Processes (2010–2013)

VTT Technical Research Centre of Finland and Aalto University have developed a pilot-scale method to manufacture nanofibrillated cellulose film. The method enables industrial-scale roll-to-roll production of the film, which is suitable for specific packaging applications and can be used in several added-value applications of printed electronics and diagnostics.

Nanocelluloses are typically characterised using simple analysing methods based on Optical Microscopy, Scanning Electron Microscopy and viscosity measurement. These methods can be used for the classification of different grades of nanocelluloses. However, these measurements are not able to relate the measurement to the actual nano fibrillar cellulose (NFC) dimensions like the size of the aggregates, or the average length or thickness of the fibrils. Novel methods were developed and commercial devices were tested for the classification of different grades of nanocelluloses. The mechanical fractionator at VTT is now ready to characterise nanocelluloses in terms of particle size (Figure 3). The fractionation stage with a membrane could screen out almost all particles, though the permeate suspension contained some dissolved substances. Reproducibility is at a good level. This method is recommended for comprehensive characterisation of nano and micro fibrillar celluloses (NFC and MFC). The NanoSight optical nanoparticle analyser and dynamic light scattering measurements can be used for nanocellulose analysis

Figure 3. Novel mechanical fractionator at VTT.


a)

b)

c)

Figure 4. Images of a hand sheet sample containing labelled NFC: a) Tomography picture, dense areas are lighter, b) reconstruction picture, dense areas are yellow, c) thresholded picture, dense areas are red.

if the size of the fibrils really is in nano-scale. This means that the size distribution of cellulose nanocrystals (CNC) and nano fibrils produced with strong oxidised pre-treatments can be analysed with these instruments.

VTT, together with industrial partners, has been active in forming a national group for the standardisation of micro- and nanocelluloses, organising an international workshop on standards for nanocelluloses and making a roadmap for their standardisation that will be taken onwards within the TC-229 nanotechnologies. One of the latest methods is NFC labelling, which aims to find the NFC distribution in the z-direction and measure NFC retention directly. Figure 4 illustrates the NFC distribution in a paper sample.

1.2 NFC product demonstrators – translucent NFC film

The NFC films are translucent, showing no shrinkage or defects. The high smoothness of the surfaces provides excellent printing quality, and the densely packed structure results in a material with outstanding oxygen barrier properties. Based on their properties, the potential applications for these films are numerous: high performance packaging, flexible displays and printable electronics, and low-cost diagnostics.

Nanofibrillated cellulose typically binds high amounts of water and forms gels with only a few per cent dry matter content. In the manufacture of the films, removal of water and drying are challenging, so this characteristic is one bottleneck for industrial-scale manufacturing. In most cases, fibril cellulose films are manufactured through pressurised filtering, but the gel-like nature of the material makes this route difficult. In addition, the wires and membranes used for filtering may leave a so-called 'fabric marking' on the film, which has a negative impact on the evenness of the surface. Surface topography determination suggests that the bottom side surface of the NFC film is almost an exact copy of the base substrate.

Nanofibrillated cellulose films are manufactured by evenly coating fibril cellulose on plastic films so that the spreading and adhesion on the surface of the plastic can be controlled. The films are dried in a controlled manner using a range of existing techniques. Due to the management of spreading, adhesion and

Figure 5. The SutCo surface treatment and coating line at VTT.

drying, the films do not shrink and are completely even. The more fibrillated the cellulose material used, the more transparent the films that can be manufactured.

Several metres of fibril cellulose film have been manufactured with VTT's pilot-scale device in Espoo; see Figure 5. All the phases in the method can be transferred to industrial production processes. The films can be manufactured using devices that already exist in the industry, without the need for any major additional investment.

Even though these films look like plastic, their affinity to water molecules (liquid and vapour) through hydrogen bonding is still considerable, thus the dimensional stability of the film can be affected when exposed to highly humid environmental conditions. This particular behaviour may be considered a drawback in terms of certain applications, like in the case of packaging. In order to increase the hydrophobicity of the films, chemical modification through, for instance, silylation chemistry can be performed directly on the surface of the densely packed NFC film.

As expected, after such modification, the wettability of the film surface is drastically modified, becoming much more hydrophobic. The contact angle values of unmodified NFC film are between 15 and 30 degrees, correlating with previously reported contact angle values of NFC films. On the other hand, these values go up to 70 degrees after modification, indicating a clear hydrophobisation of the film surface through silylation chemistry; see Figure 6. Furthermore, the improvement in the hydrophobicity of the film does not only occur on the surface but is extended through the whole film, as verified by its significantly higher dimensional stability when submerged in water.

It is well known that due to the tightly packed structure of films made from nanocellulose, enhanced by its crystalline structure, their rate of gas diffusion is very low, meeting the required values for packaging. Nevertheless, this behaviour is affected slightly when certain environmental conditions, such as relative humidity, are changed. Figure 7 shows oxygen transmission rate (OTR) values as a function of relative humidity for NFC film manufactured by a conventional filtration method (referred to as the NFC film reference) compared with the plastic-like film obtained by our method, both before and after surface modification. The oxygen transmission rate of our unmodified plastic-like films observed at high humidity values is one order of magnitude lower than the reported OTR of the NFC film reference.

The behaviour can be explained in terms of the short times needed by the NFC suspension to be fully dried in the case of our method. Fast drying of the NFC is presumed to yield a much denser film structure, with a more enhanced packed hydrogen-bond network, providing fewer possibilities for the fibrils to interact with water molecules. Moreover, OTR is also low in the case of the chemically modified NFC films, which was expected due to their more hydrophobic nature.

VTT and Aalto University are applying for a patent for the production technology of NFC film. Trial runs and the related development work are performed at VTT. The invention was implemented in the Naseva – Tailoring of Nanocellulose Structures for Industrial Applications – project by the Finnish Funding Agency for Technology and Innovation (Tekes), which is part of the Finnish Centre for Nanocellulosic Technologies project entity formed by UPM, VTT and Aalto University. The nanofibrillated cellulose grade used was UPM Biofibrils supplied by UPM.

1.3 New product opportunities – substrate for printed electronics

Filler-nanocellulose structures have been shown to offer a cost-effective substrate for printed electronics applications with a superior temperature tolerance that only very special plastic films can withstand nowadays; see Figures 8 and 9. Furthermore, the properties of these substrates can be varied within a relatively large range by the selection of raw materials and their relative proportions.

The substrates performed well in printing tests. The conductivity values of the patterns were similar to those printed on PET film (Mylar A). The best conductivity was obtained for silver nanoparticle patterns printed on kaolin-based sheets. Most interestingly, curing temperatures as high as 220 °C could be used without causing any damage to the sheets. The thermogravimetric analysis (TGA) showed that the substrates can tolerate short exposure to temperatures up to 270°C and over 12 h exposure to 230°C. These temperatures are much higher than the current substrates that printed electronics can tolerate, thus making them an attractive alternative once their production is upscaled.

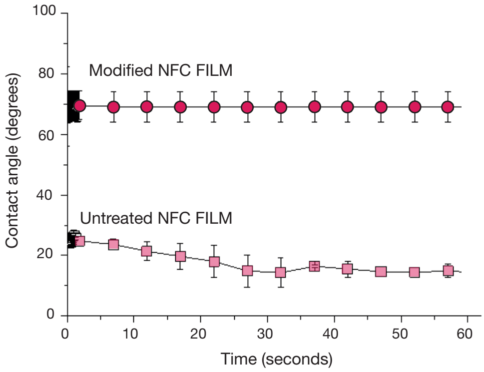


Figure 6. Contact angle values versus time for unmodified NFC film compared with the modified one.

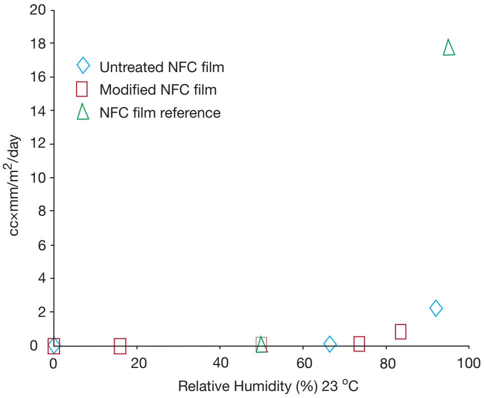


Figure 7. Oxygen transmission rate of NFC film at different relative humidity values.

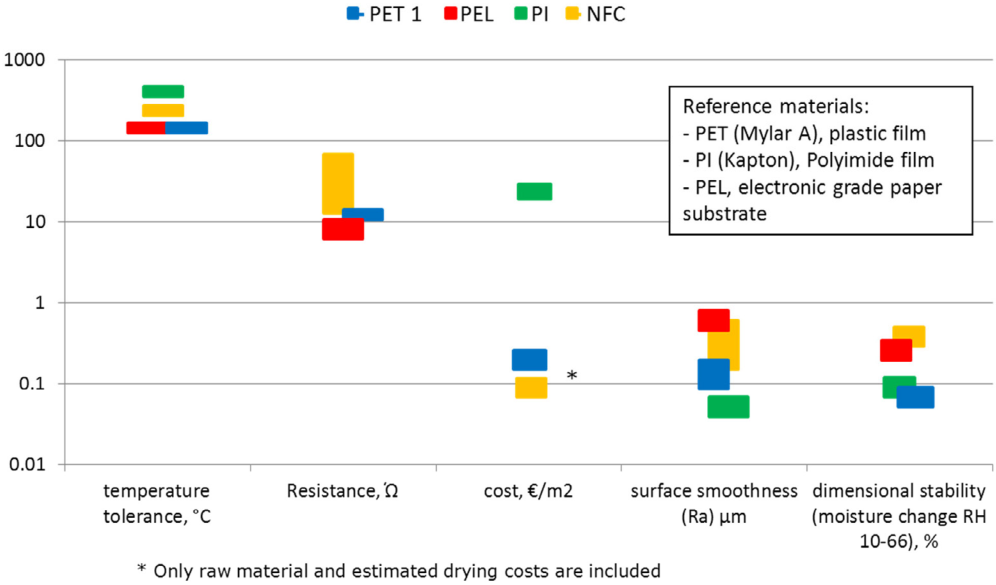


Figure 8. Filler-nanocellulose composites (yellow) offer a cost-effective substrate for printed electronics applications with a superior temperature tolerance with which only special plastics can compete. Plastic film mylar A (PET), electronic grade paper substrate (PEL) and polyimide Kapton film (PI).

1.4 High filler content paper

For some paper grades, one of the most effective ways to reduce energy consumption in papermaking is to increase filler content. Here we tested the effect of increasing the filler content of SC paper from 24% to 48% by simultaneous adding NFC using a standard laboratory sheet former. The main findings (see Table 1) were that 2–4% of NFC is sufficient for the wet strength, the optical properties are clearly better than for the reference case and the dry strength drops by approximately 40%. Interestingly, the limiting factor seems to be the dry and not the wet strength. We also estimated that the carbon footprint would be approximately 15% lower for the high filler case.

1.5 Special applications with foam coating

The high viscosity at low solid content and insufficient bonding between cellulose nano fibrils and pigment particles are big challenges in traditional pigment coating. This is true, especially in products in which high surface strength is needed. The use of NFC in traditional pigment-coated products, partly due to

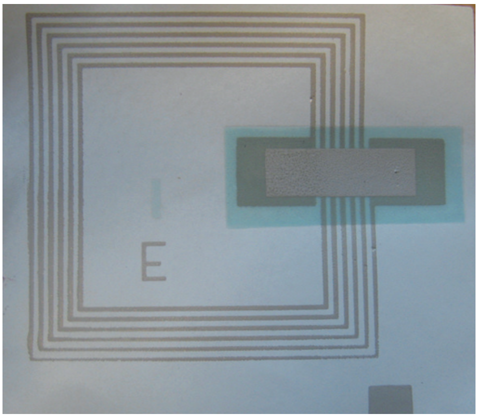


Figure 9. Example of an LC resonator printed on a filler-nanocellulose substrate.

Table 1. Differences between high filler content and reference SC papers.

	Tensile index (Nm/g)	Strain at break %	Brightness, calandered	Rightness, uncalandered	Opacity calandered	Opacity uncalandered	Drainage time (s)	Air permeance	Spec formation
Reference SC	28.6	2.0	68.6	71.7	93.9	95.1	120	81.8	0.77
48% filler and 3% NFC	15.7	1.9	72.8	75.4	95.4	96.1	130	76.8	0.88

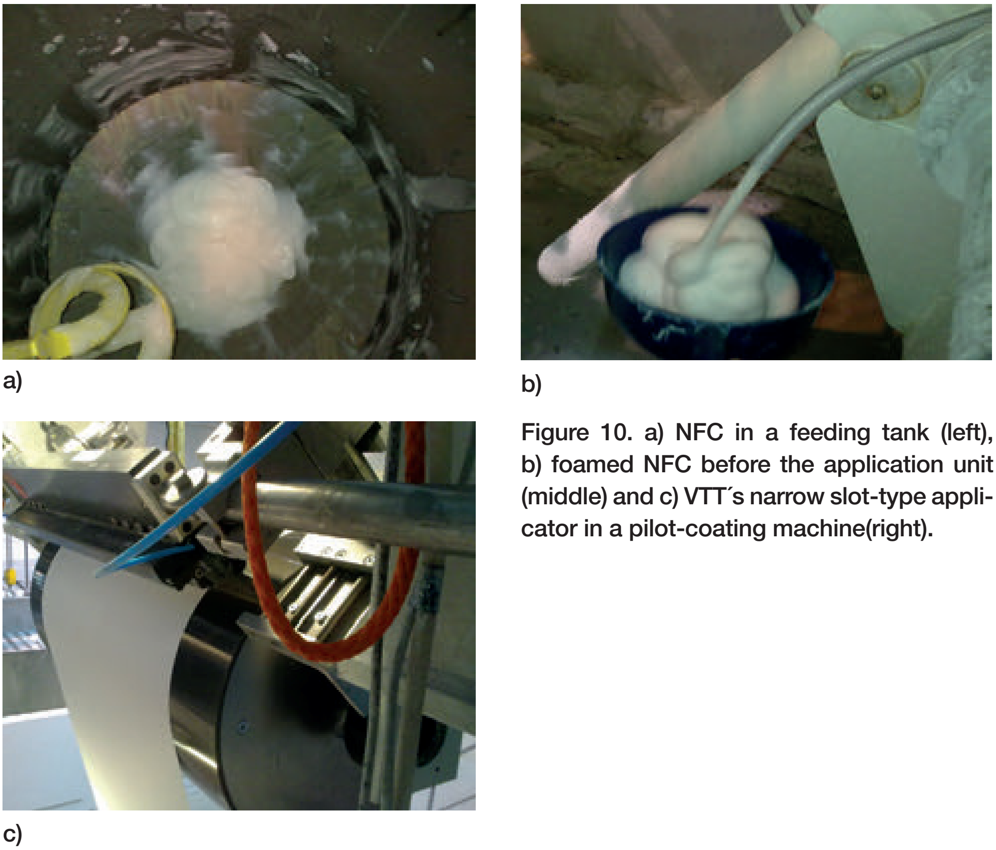

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Figure 10. a) NFC in a feeding tank (left), b) foamed NFC before the application unit (middle) and c) VTT´s narrow slot-type applicator in a pilot-coating machine(right).

the low solids content, does not give any real benefits in quality or costs. The use of NFC only seems to be favourable in a small number of special cases such as a rheology modifier or as an additive in applications in which novel functionalities, like antimicrobiological properties and photo activity, are targeted, e.g. with inorganic nanoparticles. Very high antibacterial activity of papers could be achieved with thin layers of NFC-TiO_2 and/or ZnO (the TiO_2 contents were approximately 0.3% and the ZnO contents even lower). NFC-TiO_2 has significant activity for the oxidation of NO and NO_x, also in low coat weights (e.g. in a coat weight of 0.9 g/m^2 and the amount of TiO_2 on paper was 0.2%).Thin layers of cellulose nano fibrils can be applied to the surface using a novel foam-coating applicator. Using air instead of water makes the application of viscous cellulose nano fibril solutions possible (Figure 10). The

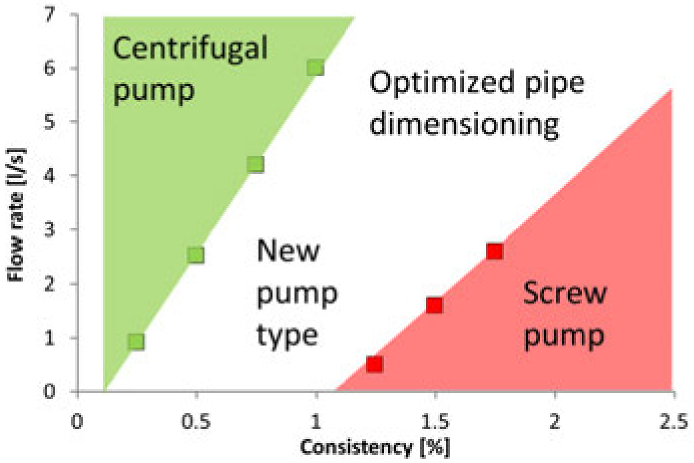

Figure 11. Pumping of nanocellulose suspensions.

applied amounts are smaller than in traditional coating. VTT now has this technology available for paper- and board-coating studies on a pilot scale. It can also be used for the application of other novel materials giving special functionality to the products.

1.6 Towards mill-scale processing

Studies on pumping, mixing and preservability of nanocelluloses have shown that handling these materials on a mill scale requires changes to the current papermaking processes. Pumping experiments carried out with centrifugal and screw pumps indicated that the flow behaviour is sensitive both to the consistency and the nanocellulose type. For low consistencies and at high flow rates, an ordinary centrifugal pump works well and for higher consistencies a screw pump can be used. However, there is a consistency region in which neither of the pumps operates well. The operating limits depend on the nanocellulose type. Similarly, mixing of nanocellulose has to be done with care, as there is a risk – especially for high nanocellulose concentrations – that good enough mixing only takes place in the fluidised cavity formed around the impeller. For low consistencies and at high flow rates, an ordinary centrifugal pump works well and for higher consistencies a screw pump can be used see Figure 11.

1.7 Sustainability

The sustainability of NFC production and its use in different applications in printing paper, technical paper and packaging board value chains have also been studied at VTT. The assessment was based on the data collected from the chosen mill cases and from the pilot-scale studies carried out in the project. The production of NFC was carried out in different ways. From the environmental perspective, the main differences between the NFC production options can be found in the electricity consumption, raw material efficiency and water consumption. Enzymatically pre-treated NFC production is an energy-intensive process, however, with high yield and low water consumption, while chemically pre-treated NFC consumes less energy, but more water is required for the process and it is behind in yield. The application of NFC makes the same quality level with a lower material amount possible and reduces the need for raw materials as demonstrated in, e.g., the wet-laid nonwoven application and

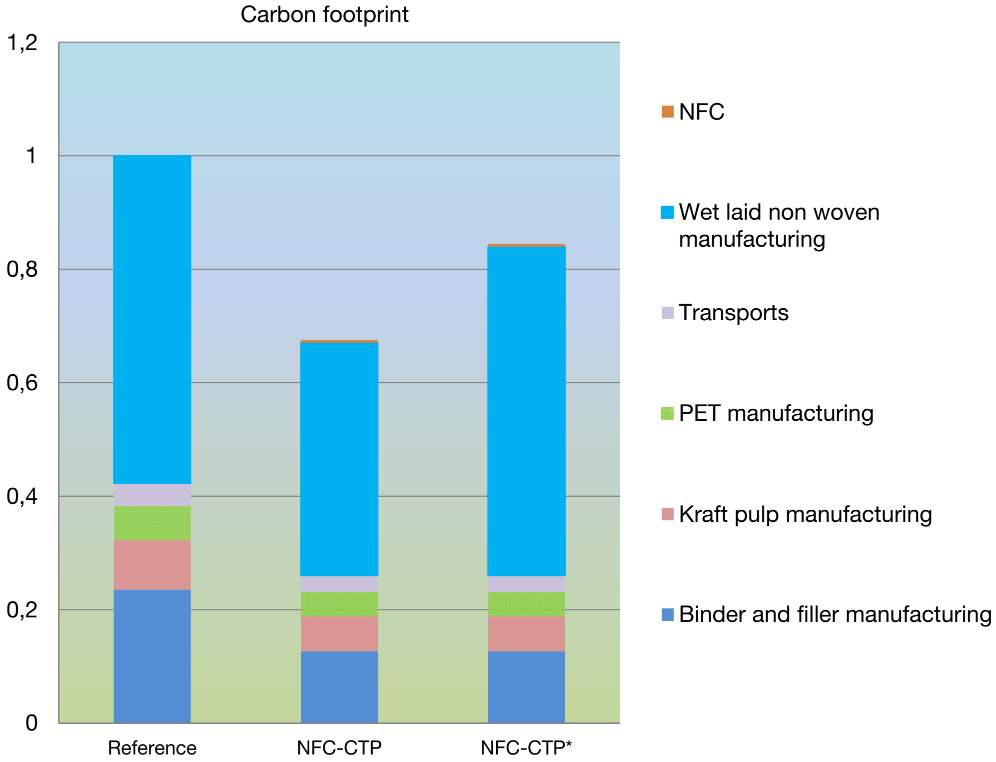

Figure 12. Carbon footprint of the wet laid nonwoven.

enables lower environmental impacts calculated as carbon footprint (Figure 12). Similar results can also be expected in other products (e.g. board applications) in which long and not extensively fibrillated fibres are used. With the lower weight and less raw materials, all the environmental burdens are significantly lower. NFC can also be applied to coatings to reduce the need for binders. This was demonstrated in Solid Bleached Sulphate (SBS) board coating. However, the amounts of NFC represented less than 1% of the total product and the environmental effects were not detectable.

Risk assessment is a demanding process in product development based on novel materials. The hazard assessment should follow the development steps, and exposure profiles cannot be preciously defined. The exposure assessment was based on the gathered information and expert's judgement of possible exposure scenarios. The two common control banding models were tested in the risk assessment of NFC. They indicated that higher risks than in full production will probably be the outcome due to the limited information or limitations in the simple models. More advanced tools for organic nanomaterials are therefore needed in which the analysed results of the hazard assessment are also taken into account. When pre-commercial and commercial productions are started, real exposure measurements can be carried out and the measured exposure levels used in the next risk assessments.

Risk assessments should be carried out at all stages of the value chain. Besides occupational exposure in the production of the nanomaterial and final end-use product application, more information about consumer exposure and end-of-life exposure are needed in the risk assessment.

1.8 National co-operation with Finnish industry

Strong industrial partnership

VTT has been working as a partner with The Finnish Centre of Nanocellulosic Technologies since February 2008. The centre was established to focus on the development of industrial mass-production processes of nanocellulosic materials and enhancement of the markets of cellulose-based materials. It is a virtual co-operation centre of VTT, Aalto University and UPM. The work is realised in a huge project portfolio – a combination of public and private funding – with a volume of 40 person years or 5 million euro annually. The impressiveness of VTT's work can be seen in the publishing of the UPM's press release on November 15, 2011 of the pre-commercial production of fibril cellulose and also in the number of scientific publications and conference presentations in the field of nanocellulosic technologies.

Outside this co-operation, VTT has participated in Stora Enso's development work in the area of production of microfibrillated cellulose. Stora Enso published news of building a trial production site of MFC to Imatra in south-eastern Finland at the end of June 2011.

Activating national and international co-operation for sustainable use of nanocelluloses

With Forestcluster's EffNet programme, and the large-scale Integrating Project SUNPAP in the European Community's 7th Framework Programme, VTT has been activating discussions on sustainable and safe use of nanocelluloses. The co-operation has led to a fruitful discussion between scientists, industry representatives and administrators on the topical and open issues related to occupational and product safety, environmental efficiency and regulation issues related to nanocelluloses. As a conclusion, relevant indicator and measurement methods are needed to address NFCs in final products, together with their migration and toxicity properties, and exposure during production. Furthermore, efficient communication channels between customers, authorities and consumers need to be created. A manual on nanocelluloses has been written in co-operation with the Nanotechnology and Forest Industry Future Centre and the expertise programmes of Jyväskylä Innovation Ltd. The manual is specially aimed at small and medium enterprises in Finland to accelerate the implementation of nanocelluloses by SMEs and help their application development.

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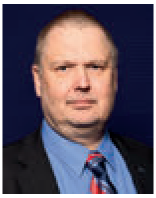
2 Novel hardwood hemicellulose applications



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The growth of 'added-value' celluloses, such as dissolving pulp and nanocellulose, will lead to a potential increase in the availability of hemicelluloses. High molar weight xylan is therefore a well-motivated option for added-value applications. A pure white xylan was isolated from bleached birch kraft pulp. Water-soluble xylan ether derivatives were produced successfully either from the extracted non-dried xylan or from the birch pulp by reactive extraction. At VTT, the applications of xylan ethers were demonstrated for inks, barrier coatings, pigment coatings, hot-melt adhesives and films.

2.1 Background

The development of materials from natural polymers for different applications has been of great interest for several years due to the increasing prices of petrochemicals and growing environmental concerns.

Starch-derived chemicals have been developed for decades but, recently, attention has been drawn to their conflict as part of the food supply chain. Abundant non-food polysaccharides, such as cellulose and hemicelluloses, therefore have great potential for material applications. Hemicelluloses are the second most abundant plant material in nature. Nevertheless, high molar mass hemicelluloses are not produced in significant amounts, though production is expected to expand. For example, one interesting option for producing polymeric xylan in large quantities will be available if, for instance, beech, birch or eucalyptus wood can be sourced and used for the production of high-alpha cellulose-dissolving pulp. In this process, the hemicelluloses will have to be removed.

The global annual growth of wood and other bio raw materials provides an annual maximum availability of hemicellulosic raw materials of approximately 35–70 billion tons, thus representing practically unlimited resources. Xylans are the main hemicelluloses in hardwood. Hemicelluloses have been reported for use as additives in papermaking, e.g. as such or modified for barrier applications, food additives, thickeners, hydrogel, emulsifiers, a coating colour component and as cancer protective agents (Ebringerová et al. 1994, Ebringerová & Heinze 2000, Gatenholm et al. 2004, Gröndahl et al. 2004, Kataja-aho et al. 2012, Laine et al. 2008, Pohjanlehto et al. 2011, Söderqvist Lindblad et al. 2004, Talja et al. 2011).

Hemicelluloses and, in particular, xylan can be produced from different kinds of wood or agro-based materials using different kinds of extraction methods (Ebringerová & Heinze 2000, Glasser et al. 1995). The extraction of xylan from wood and agro-based material can be performed rather easily in alkaline condi-

Figure 1. Bright white suspension of purified (desalted) xylan(left) and barrier coating on precoated board (right).

tions after lignin removal. Bleaching before the extraction is optional depending on the desired properties, e.g. whiteness. Alkaline extraction and purification of white and pure xylan from hardwood pulps, like bleached birch kraft pulp, enable the production of high adsorption and high crystalline pulp. The same is also possible for softwood, but then a mixture of xylan and galactoglucomannan is obtained. In recent years, the demand for dissolving pulp has increased. A further increase in production from 4.1 million metric tons in 2008 to 6.3 million metric tons has been forecasted by Pöyry. In addition, future production of nanocellulose opens new possibilities for hemicellulose production, as hemicellulose will be at least partly removed prior to nanocellulose production.

Various possibilities for chemical modification of hemicelluloses have been reported in the literature. Typical modifications are esterification and etherification (e.g. alkoxylation, cationisation or carboxymethylation), and methacrylation (Jain et al. 2001, Volkert et al. 2010, Fang et al. 2000, Fanta et al. 1982). These methods can be used separately or subsequently. Rather broad and industrially relevant assortments of derivatisation chemicals are available for both methods. Selected properties such as hydrophobicity-hydrophilicity balance, solubility, thermoplasticity, film-forming properties, to name a few, can be adjusted with these methods.

2.2 Production of xylan from bleached birch kraft pulp

A production process for pure and essentially linear xylan has been developed and upscaled at Keskuslaboratorio (KCL), Finland and VTT Technical Research Centre of Finland. The process includes alkaline extraction of bleached birch pulp and purification by, e.g., ultrafiltration, precipitation or a combination of the methods (Laine et al. 2012). The xylan extract is very pure (i.e. free from other hemicellulose components) with only 1–2% of total sugars other than xylose.

After extraction, the pH of the xylan extract is about 12—13. Precipitation with acids and CO_2 can be applied yielding xylan as a finely dispersed milky white liquid or a wet paste; see Figure 1. Salts can be removed by dialysis. Xylan, with an average molecular weight (Mw) of 25,600 Da (before dialysis) and 26,750 Da (after dialysis) have been isolated, showing a minor (4–5%) increase in Mw during dialysis.

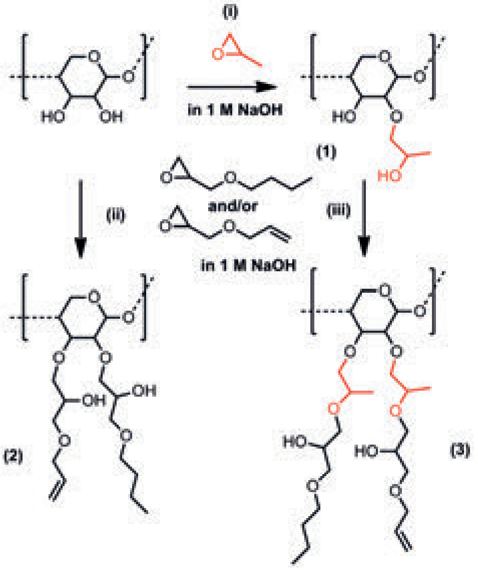
The studied xylan from bleached birch kraft pulp has low solubility, and alkaline conditions have to be applied to dissolve it. Once dried, this xylan becomes almost insoluble even in strong alkaline due to the deacetylation of xylan in pulping and bleaching.

Xylan production was scaled up to obtain several kg of xylan using alkaline extraction followed by ultrafiltration with membranes of a nominal cut-off of 10 000 Da.

2.3 Modification of xylan

It is necessary to adjust xylan properties, such as the hydrophobicity-hydrophilicity balance, solubility, thermoplasticity and film-forming properties, for many applications. The xylan extracted from birch kraft pulp as such is amorphous and insoluble in water. Internal plasticisation was performed to obtain film-forming and thermoplastic compounds. By choosing hydroxyalkylation at a suitable substitution level, these compounds are also water soluble and have suitable reactivity for further modifications. Xylan was therefore modified into xylan ethers using propylene oxide or glycidyl ether reagents. The modifications were performed for isolated non-dried xylan or in a so-called reactive extraction (Pohjanlehto et al. 2011, Laine et al. 2012). The reaction routes are shown in Scheme 1.

Derivatisation of xylan in the extraction phase without previous separation from the pulp dispersion – the so-called ‘reactive extraction’ – is an attractive alternative to save tedious and expensive intermediate separation and concentration steps. Another major benefit of the process is the enhanced reactivity of the xylan in the extraction liquor without intermediate separation and, especially, drying. This technique was applied to produce hydroxypropylated xylan and butyl-allyl derivatives of xylan.



Scheme 1. Major reaction routes: (1) hydroxypropylated xylan (HPX), (2) butyl-allylated xylan (X-BA), and (3) hydroxypropylated and butyl-allylated (HPX-BA). In addition, either of the allyl or butyl substituents can be introduced alone.

2.4 Bio-based binder solutions from wood hemicellulose

Many ink manufacturers already have eco-friendly (EF) ink in their product portfolio (Casatelli 2009, Smyth 2010). EF inks are typically partly based on raw materials from renewable sources, like soy and pine rosin. Solvent is often partly based on water. Ink requirements are set by printing technique and end usage (Leach 1999). In addition, storing and recyclability need to be taking into account.

Printing inks usually contain many different ingredients to fulfil all demands. The main ink components are pigment (colourant), resin (binder), solvent and additives. In EF inks, the binder is typically bio-based. At VTT, the scope of bio-based ink binder development is to find

Figure 2. UV-curable flexo inks printed on liquid packaging board, coated BCTMP board, coated BCTMP board, liquid packaging board and PP top white laminate (from left to right).

the least modified polysaccharide from wood that fulfils the needs of a printing ink in flexo and inkjet printing methods for different end uses (Ilmonen & Kela 2011). Additional benefits are potential non-toxicity, work safety issues (VOC-free) and non-food origin of the raw material. At VTT, we have also noticed that pine resins, tall oils and natural and starch-based pigments have the potential to be used in printing inks, thus increasing the portion of materials from renewable resources in final ink.

At VTT, water-based and UV-curable flexo inks have been developed that contain different hemicelluloses and their modifications, e.g. xylan ether derivatives (Scheme 1)(Ilmonen & Kela 2011). For example, water repellency can be improved by modifications. Hemicelluloses can also be modified in UV-curing applications.

The developed flexo inks were tested with an IGT F1 test printer. Inks were printed on kraft sack paper, coated board, liquid packaging board and PP top white laminate. The inks adhered to all the surfaces and the print quality was good, as can be seen in Figure 2. In addition, inkjet inks were tested with Fujifilm Dimatix Materials Printer DMP-2831.

Further development is planned together with the different partners involved in the production value chain of eco-friendly ink. Potential partners in the value chain could be raw material, binder and ink manufacturers, pigment companies, converters, substrate manufacturers and brand owners.

2.5 Pigment-coating binder for offset grade printing grades

The coating binders in the pigment-coating of paper are currently mainly synthetic latexes (dispersions) and soluble starches. The potential of xylan ethers as a replacement for latexes and starch such as in binders in coating colours for offset grade printing papers has been studied (Laine et al. 2012).

Coating colours were prepared using 70% calcium carbonate and 30% kaolin in formulations, and xylan derivates were added at levels of 5 or 10 ppm. Styrene-butadiene latex or starch was used for reference coatings. The viscosity of the coating colours was lowest for the synthetic latex coating colour at constant solids, while it was at a level of up to 2700 mPas at 100 rpm and 425 mPas at 2000 rpm with the colours of the xylan-derivative binders, especially at the 10 pph level. This is a drawback of the xylan-derivative binders tested here, mostly due to the high to medium solubility. Modified xylans also increased the water retention remarkably. The effect of these xylan derivatives on the latex coating colour was even higher than that of starch. The result is emphasised due to the fact that the coating colours containing xylan derivative binders had a lower solid content than the pure latex or latex and starch coating colours.

For the coated papers, the air permeance was slightly higher with xylan-derivative binder components in the coating than with latex at 10 pph. The addition of xylan derivatives to the coating colour gave a rougher surface compared with the latex colour. The effect of xylan derivatives on opacity and brightness of coated and calendered papers was insignificant even though the xylan derivatives slightly increased the brightness. The opacities of the calendered samples ranged from 92.3 to 93.2% and the brightness from 80.3 to 82.2%.

Good surface strength of the coated paper was demonstrated with some of the xylan ether derivatives as binders in the coating colour, and it performed almost as well in the tests as the reference latex.

2.6 Barrier coatings on board

The new xylan ethers were evaluated as barrier coating materials in packaging (Laine et al. 2012). The properties related to grease, water vapour and oxygen permeability were of specific interest. Chemically cross-linked water-soluble xylan derivatives showed the best overall barrier properties on precoated board. The key to success lies in the water solubility and particle dimension as well as the structure of the board substrate. Barrier analyses were carried out on biobarrier board coatings of coat weights between 7 and 12 g/m^2. The xylan ethers are internally plasticised compared with the xylan itself. This improves the film formation. The unmodified xylan as such was not film forming and thus no barrier analyses were performed.

Cross-linking was used as a technique to further improve the barrier properties of the xylan ethers and their coatings. Cross-linking should increase the effective molecular weight of the biopolymers as well as rigidify their network and that way decrease intruding or exuding agents such as oxygen, water vapour or aroma. Chemical cross-linking via citric acid (CA) was effective for each derivative group, especially when observing the water vapour permeability values. UV cross-linking did not improve the permeability values as much as the chemical cross-linking route in these specific cases, most probably due to an insufficient concentration of cross-linkable double bonds with respect to these barrier applications.

The best oxygen permeability (OP) with 15±1 cm^{3}µm/d,m^2,kPa at 23 °C and 0% RH was exhibited by cross-linked hydroxypropylated xylan with citric acid. The OP value was three times better than that of the best reference (PET-coated board). Internal plasticisation was most effective when xylan was hydroxypropylated. The combination of multiple modifications may cause steric hindrance and a decrease in free hydroxyl groups. The incorporation of, e.g., allyl groups decreases the number of hydroxyl groups present and thus the possibilities of the hydrogen bonding needed for continuous film formation.

In water vapour, the transmission rate (WVTR) measurements at 23 °C and 0% RH, cross-linked hydroxyl propylated xylan and butylated allylated xylan performed equally well and exhibited water vapour permeability (WVP) values of 6±1 gµm/m^2,d,kPa. These values were three times as high as those for the PET-coated reference board. WVP is generally an issue with bio-based materials, but improvement is seen compared with a commercial board with biobarrier. Internal plasticisation of butylated allylated xylan slightly increased the WVP values. The incorporation of external plasticisers (glycerol and sorbitol) into the xylan derivates also leads to higher WVPs. Oil and grease resistance was good to excellent for all the tested coated samples. Apart from the standard barrier measurements, mineral oil migration was also analysed. In this case, the migration of mineral oil from printing ink was detected through the whole structure of a backside-biobarrier-coated board. Cross-linked hydroxypropylated xylan showed a value of only 0.2 mg/kg, clearly meeting the requirements of JECFA (Joint FAO/WHO Expert Committee on Food Additives).

Table 1. Example of composition and compounding conditions of the hot-melt adhesive.

Oxidised cellulose acetate	20% = 1 g
Hydroxypropylated xylan	35% = 1.75 g
Triethylcitrate (TEC)	45% = 2.25 g
Compounding T (°C)	150
Compounding t (min)	40

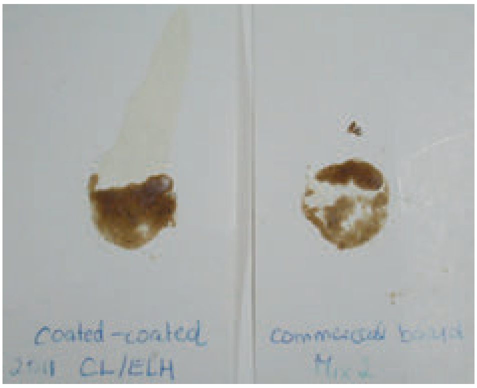


Figure 3. Samples after tear testing by hand.

2.7 Xylan-based adhesives

Current polymers in hot melt and pressure-sensitive adhesives are most commonly synthetic polymers. The market for bio-based adhesives is increasing steadily due to environmental concerns and the increasing prices of polymers based on petrochemicals. Starches and their derivatives are major components and have been developed for a long time. Protein is also a traditional source of bioadhesives. Due to the competition with food, there are ethical aspects that make non-food component such as hemicelluloses attractive as raw material also for hot-melt adhesives. The use of the hot-melt adhesives includes, e.g., bookbinding, packaging and the textile industry. The Pressure-sensitive adhesives are used in labelling applications of food, household, pharmaceutical and industrial products. Cope (2005) has defined hot-melt adhesives and pressure-sensitive adhesives (PSA) as follows: ‘The main constituent of hot melts is a thermoplastic polymer that may be blended with thermoplastic modifiers and extenders and inert fillers to create a system that is a load-bearing solid at the service temperature but a mobile liquid at the higher application temperature.’ and ‘PSA are those that may be applied as dispersions, solutions or hot melts and that convert to a rubbery, tacky film of relatively low adhesive strength and rather higher cohesive strength. They may be used to produce bonds that are permanent, but not creep resistant, and also temporary or serial temporary bonds. Such materials are often used supported on flexible substrates.’ VTT has a background in hot-melt adhesives based on cellulose acetate that consists of a component to provide cohesive strength, a low molar mass component (diluent, regulating viscosity, tack) and a softener (Mikkonen et al. 2011).

Hydroxypropylated xylan was synthesised from xylan extracted from birch kraft pulp as outlined in Scheme 1, page 27. The derivative was a thermoplastic polymer. The degree of substitution and molar mass of the hydroxypropyl xylan was analysed by NMR and SEC techniques and the thermal properties were investigated by TGA and DSC analysis.

The molar mass of the hydroxypropyl xylan was roughly on the same level as the starting xylan with 25 and 22 kDa, respectively. The molar mass thus increased slightly in the hydroxypropylation. The degree of substitution of the hydroxypropylated xylans with hydroxypropyl was between 0.5 and 1.3 as determined by 13C-NMR. Even the low degree of substitution is high enough to result in an internally plasticised xylan polymer that has thermoplastic properties. The glass transition temperature of the modified xylan was reduced to 60 °C from 171 °C of the pure xylan (Talja et al. 2010) extracted from birch kraft pulp. The thermal degradation property of the hydroxypropylated xylan was determined to define suitable temperatures in the compounding process. The analysis showed that compounding can be carried out at 150 °C, which is far from the modified xylan's degradation temperature ($T_{10\%}$) of 265°C.

The modified xylan was blended under elevated temperature in the compounder with oxidised cellulose acetate (CA ox) and triethyl citrate (TEC) (Table 1). The components were compounded, successfully producing a tacky blend in a melted form. The tackiness remained in the blend after cooling down. This hot-melt adhesive formulation based on modified xylan reinforced with CA ox was spread and molten between two card boards by heat activation under pressure. The card boards adhered well to each other. The adhesion was tested by tearing the card boards by hand slowly and fast. The slow tearing test showed a tacky seam and no fibre damage was observed whereas the fast tearing resulted in fibre rupture (Figure 3).

The advantage of this hot-melt adhesive is that the molecular weight of the xylan extracted from bleached hardwood pulp is suitable as such and simple derivatisation by, e.g., hydroxypropylation delivers a suitable adhesive component while, e.g., the molecular weight of cellulose or starch has to be adjusted in addition to derivatisation.

2.8 Hemicellulose films

Allyl/butyl derivatives of xylan show good properties for film formation. A film with a thickness of 0.2 mm prepared from butylated and allylated xylan (X-BA) derivative was mechanically the strongest one within a series of xylan derivatives: the tensile strength was 44 MPa (highest value), elongation at break 22% (highest value) and Young's Modulus 524 MPa (moderate). The transparent and flexible film can be further modified into thermo-formable films (Figure 4), which can be used in packaging applications (see also Towards 100% bio-based packaging by Vähä-Nissi in this publication).

Xylan derivatives with degrees of substitution (DS allylation and DS butylation) of 0.4 and 2.1, respectively, were fully soluble in water up to 15–20 wt%. The high DS in the butylation value indicates that approximately all of the hydroxyl groups in the xylan chain were derivatised with the substituent B. Additionally, it seems that the hydroxyl group of the substituent B can be further substituted. When a hydroxyl group of an anhydroxylose unit reacts with an epoxy group of allyl or butyl glycidyl ether, it generates a new hydroxyl group due to the ring-opening of the epoxy group. This new hydroxyl group can react again with an epoxy reagent and, thus, the degree of substitution can be higher than two.

Figure 4. A transparent and flexible film obtained from a butylated and allylated xylan (left). Thermo-formable film produced thereof (right).

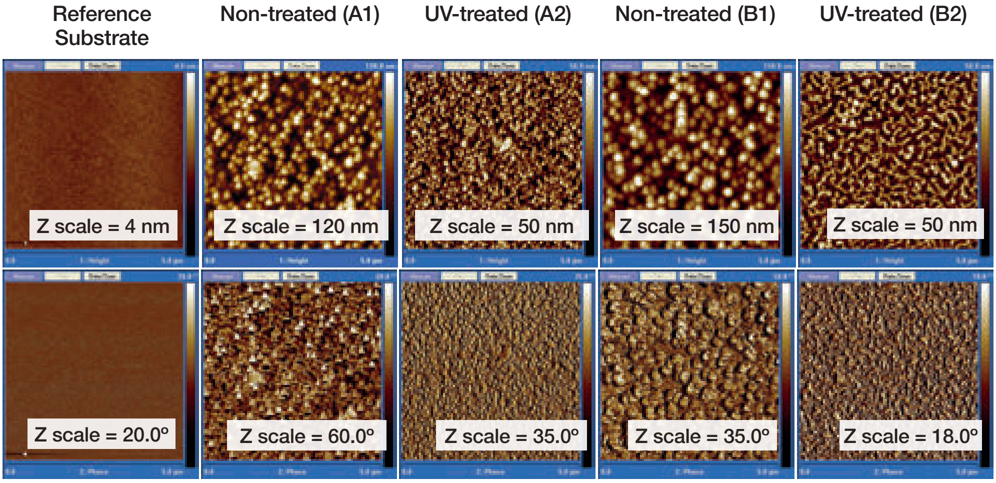


Figure 5. AFM topography images (top) and phase contrast images (bottom) for silica surface (reference substrate) and allylated as well as butylated xylans on silica before (A1, B1) and after UV-radical treatment (A2, B2). The image size is 5 x 5 µm.

Water-soluble allylated and butylated xylan derivatives formed smooth and thin model films, and these model films facilitated the investigations of water interactions and water sensitivity using surface-sensitive methods such as QCM-D, AFM (Figure 5) and contact angle measurements. Significant structural changes were observed after treating the films with mild heat treatment and UV-radical initiated cross-linking, and these treatments lead to dramatic changes in the wettability and water vapour uptake behaviour of the xylan derivatives in question (Peresin et al. 2012).

Experimental evidence suggests that the effect of film post-treatments depends on whether or not cross-linking and/or molecular reassembly take place within the film structure. In the case of hydrophilic allylated xylan, UV-radical initiated cross-linking between the double bonds of allyl groups present in the xylan backbone was taking place, leading to alternated behaviour with respect to wettability and water vapour interactions. The allylated xylan film became more hydrophilic after the UV-radical initiated cross-linking. However, cross-linked films were able to uptake 80% less water vapour when compared with the films, which were only heat-treated in mild conditions.

Butylated xylans, being somewhat more hydrophobic, showed lower sensitivity to humidity even prior to any post-treatments. After the UV-radical treatment and mild heat treatment, the ability of this derivative to uptake water vapour was further reduced by approximately 50%. Since the butyl groups are not expected to perform any cross-linking reactions, it can be concluded that the changes with respect to water sensitivity and wetting behaviour are solely due to the heat-induced reassembly of xylan-derivative molecules. The re-orientation of the hydrophobic groups towards the film surface leads to more hydrophobic surfaces resulting in a lower ability to uptake water molecules.

2.9 Conclusions

The availability of hemicellulose will depend on the process solution when investing in added-value celluloses, such as dissolving pulp or nanocellulose. In the future, xylan will also be isolated from sources other than bleached birch kraft pulp, with VTT being active in finding new fractionation and recovery methods. VTT has now developed applications of xylan ethers and demonstrated them for inks, barrier coatings, pigment coatings, hot-melt adhesives and films. The materials justify strategies to produce more added-value celluloses because of the improved material efficiency and more added-value products. Furthermore, the xylan ethers are a versatile group of derivates that enables a broad spectrum of novel materials and applications thereof.

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3 Lignin – new openings for applications

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VTT´s long experience and strong competence in chemical pulping, lignin chemistry, analytics and synthesis chemistry provides a solid basis for the development of lignin-based products. Lignins from different processes are suitable as such or after chemical and enzymatic modifications for different lignin applications. VTT has developed new thermoplastic lignin materials suitable for, e.g., composites and barrier materials in fibre-based packages, replacing oil-based coatings. New hydrophilic sulphur-free lignins perform like good adsorbents. The development of new products is directed by sustainability assessment.

3.1 Lignin availability and current use

Lignin (Figure 1) is one of the most abundant natural polymers, together with cellulose and hemicelluloses. During the annual production of 130 million tons of chemical pulp (Forest industries 2012), approximately 60 million tons of kraft lignin is annually produced and approximately 4 million tonnes of lignosulphonates. However, only a small amount (approximately 1–2%) of the lignin is isolated from spent pulping liquors and used for chemicals and material applications. The rest of the lignin serves as fuel as it has a high energy value that is exploited in kraft mills by burning it in the recovery boiler.

MeadWestvaco in the US is the only industrial producer of kraft lignin and its derivatives for chemical use, with an estimated annual production of approximately 50 000 tons. Metso has, however, started sales of commercial

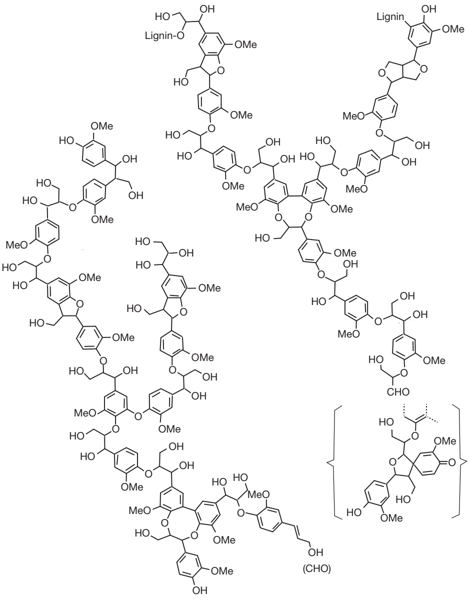


Figure 1. Structure of lignin (Syrjänen, Brunow et al. 1998).

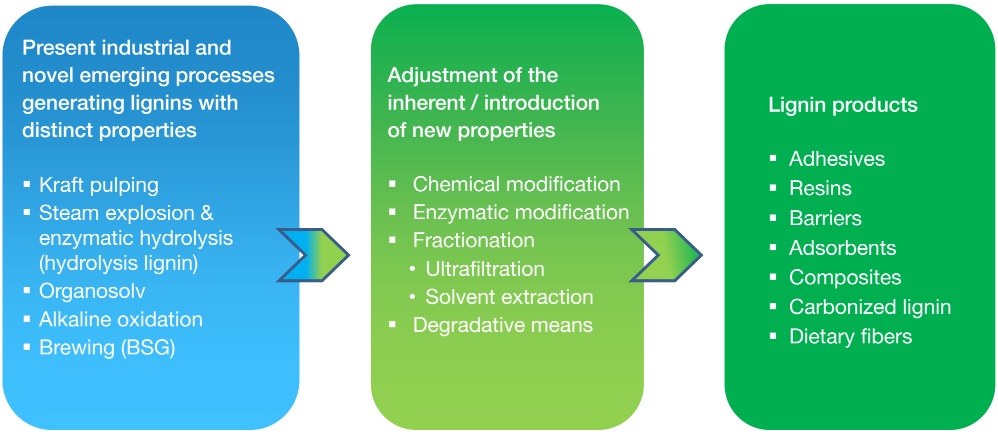


Figure 2. Development of lignin products at VTT.

LignoBoost isolation plants (Wallmo & Theliander 2007). Most kraft lignin that is used industrially is converted before various uses into water-soluble products, e.g. sulphonated lignins.

Borregaard is the major producer of lignosulphonates. Some major products from lignosulphonates on the market are listed below (Ek 2005):

- Concrete admixtures (volume: large)
  - Dispersing agent to reduce the amount of water needed to form a plastic workable mixture
  - One of the most desirable markets for lignosulphonate producers
- Animal feed (volume: large)
  - Binding the pellets and lubricating the pelletising equipment
- Dust control (volume: large)
  - Dust control and stabilisation of the road base
- Dye and Pigment Dispersant (volume: medium)
- Gypsum wallboard dispersant (volume: medium)
- Oil well drilling mud additive (volume: medium to small)
- Other uses of lignin
  - Vanillin manufacture, leather tanning, emulsifier, etc.

3.2 Development of lignin products at VTT

VTT´s long experience and strong competence in chemical pulping, lignin chemistry, and analytics and polymer modifications provides a solid basis for the development of lignin-based products. Besides kraft pulping, which produces sulphur-containing lignin, sulphur-free lignins from different organosolv and other processes are suitable as such or after chemical and enzymatic modifications for different lignin products (Figure 2). Recently, our focus has been on lignin as barrier coatings, e.g. in fibre-based packages and composites.

3.3 Introducing novel properties by lignin modification

Ultrafiltration

The wide molar mass distribution of dissolved lignin in kraft black liquor offers an opportunity to use membrane technology to separate fractions for different uses. The conventional way of precipitating lignin by reducing pH is relatively unselective and does not provide an opportunity to isolate a desired fraction of lignin with a specific molar mass. An additional advantage of membrane filtration is that it provides a tool for controlling the metal content using diafiltration. It also offers an easy way of recycling the filtrate of the process.

Solvent fractionation

A sequential extraction method with organic solvents has been developed at VTT for softwood and hardwood kraft lignins to give lignin fractions with new properties (Ropponen et al. 2011). The lignins isolated from the main soluble fractions are rather homogeneous with narrow molar mass distributions. Moreover, they are more hydrophilic and have significantly lower glass transition temperatures (Tg) than the original lignin, which gives them potential for material applications that require thermoplastic properties.

Lignin esterifications

In general, technical lignins do not have good thermoplastic properties and film-forming ability, which is a prerequisite for many applications. Chemical functionalisation of lignin with fatty acids is a potential route to lower the glass transition point of lignin and thus increase its thermoplasticity. Both hardwood and softwood lignins have been esterified, with fatty acids having different carbon chain lengths. The fatty acids used were palmitic acid (C16), lauric acid (C12) (Hult et al. 2011) and tall oil fatty acid fraction (TOFA) (Tamminen et al. 2011a, Tamminen et al. 2012). TOFA contained 3.5% saturated fatty acids and 86.3% unsaturated fatty acids. Depending on the dosage of fatty acid (chloride) used, the degree of lignin esterification can be adjusted according to the demands of the end use. Moreover, the introduced unsaturated function provides active reaction sites for further chemical modifications.

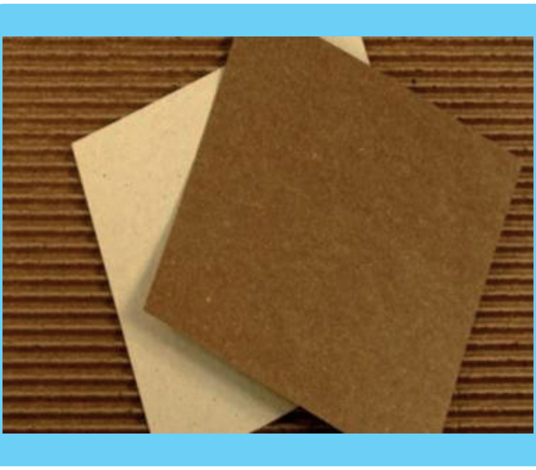
Enzymatic oxidation and polymerisation

The Volatile Organic Compounds (VOC) present in lignin as such and also formed during thermoplastic processing cause unwanted odour to lignin-based composites (Kalliola et al. 2012). Laccases (from *Thielavia arenaria and Melanocarpus albomyces*) showed potential in reducing lignin odours by polymerising the volatile low-molar mass lignin fragments. The same effect was also obtained without enzymes by oxidising lignin with oxygen at alkaline pH at room temperature. However, oxygen treatment increased the glass transition temperature of lignin, not favouring the thermoplastic processing.

3.4 The use of lignin enables development of new products

LignoBond technology – strength and water resistance

The LignoBond technology for reinforcement of packaging materials was invented in the late 1980s (Forss et al. 1988). At VTT, we have recently successfully widened the lignin raw material basis in LignoBond application.



LignoBond is a smart and simple technology to give strength and water-resistance to fibre-based packages by lignin precipitation.

LignoBond reinforced recycled pulp.

Unmodified and unfractionated as well as fractionated softwood and hardwood kraft lignins and VTT organosolv lignin (20% calculated as dry/dry fibres) have been added to recycled fibres (i.e. 50% magazine and 50% newsprint). After the addition of lignin, the pH was adjusted to pH 4 with sulphuric acid in order to precipitate the lignin on the fibres. The retention was further improved by adding alum and a retention agent. All the lignins increased the paper sheet´s strength by 20—50% and water resistance by 90%. The remarkable increase in air resistance (ca. 300%) indicates that the addition of lignin has created barrier properties on the sheet. A prerequisite is that the lignin is converted into a soluble form before adding it to the pulp slurry. With the lignin addition, the brightness decreased however. The LignoBond process is thus a simple process to reduce the water absorption and improve the compression strength of corrugated and fibre board, i.e. to increase the strength of recycling fibres to the level of virgin kraft fibres in corrugated board or to lower the need for kraft fibres.

Lignin adhesives

In the Karatex process, either sulphite lignin or kraft lignin was copolymerised with phenol formaldehyde resins to give adhesives for particle boards (Forss & Fuhrmann 1978). One reason for the industrial use of Karatex was that lignin was able to bind the released harmful formaldehyde and thus improve the environmental performance of the adhesive. In research on thermoset adhesives based on lignin, the focus is on the replacement of phenol- and urea formaldehyde resins using lignin as the main component in the manufacturing of building boards such as plywood, water board, oriented strand board and particle board. In the efforts to replace phenol-formaldehyde adhesives by environmentally-friendly substitutes, efficient cross-linkers have been looked for. Cross-linking of lignin with other aldehydes than formaldehyde has shown to be promising. Instead of using formaldehyde as the main cross-linking agent in adhesives for wood-based gluing such as plywood, the kraft lignin fractions or sulphur-free organosolv lignins were reacted with other cross-linking agents, i.e. glutar aldehyde, furfuryl alcohol and polyethylene glycol diglycidyl ether.

The formation of an adhesive joint of formulations containing lignin and an extender with or without the use of a cross-linker was successful. The best-performing formulations with respect to the strength properties contained a cross-linker. The advantages obtained with lignin adhesives are competitive pressing time and comparable strength properties to those of commercially available adhesives.

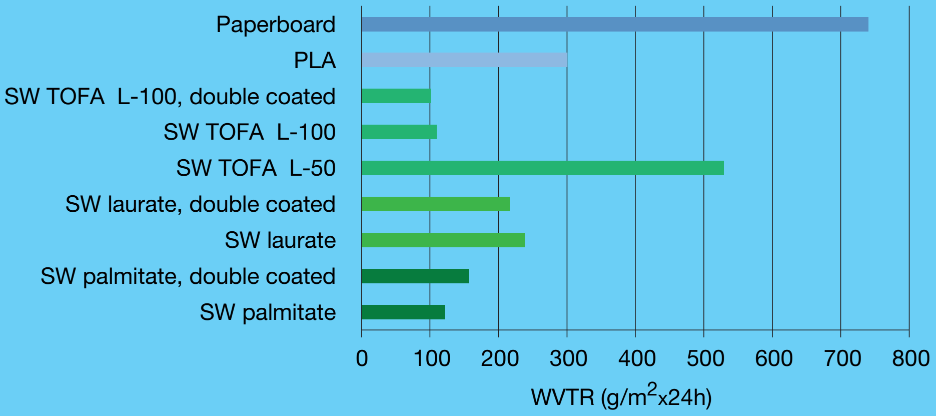
Lignin fatty acid esters as coating and barrier materials

Lignins esterified with fatty acids (lactic acid, palmitic acid, tall oil fatty acid fraction, i.e. TOFA) formed films without any external plasticisers, with a high and stable contact angle on paperboard (Hult et al. 2011, Tamminen et al. 2011b). In contrast to external plasticisers, internal plasticisers do not migrate out of the product, which is a great advantage. Lignins esterified with fatty acids are potential materials for coatings of fibre-based packaging materials, significantly reducing water vapour and oxygen transmission rates (Poppius-Levlin et al. 2012, Tamminen et al. 2012). The barrier properties against water vapour are as good as or better than those of commercial polylactic acid (PLA) and they act as medium barriers against aromas. The main impacts of the results come from the replacement of oil-based barrier materials by completely bio-based lignin derivatives. Both lignin and fatty acids are potential side streams of the pulp mill.

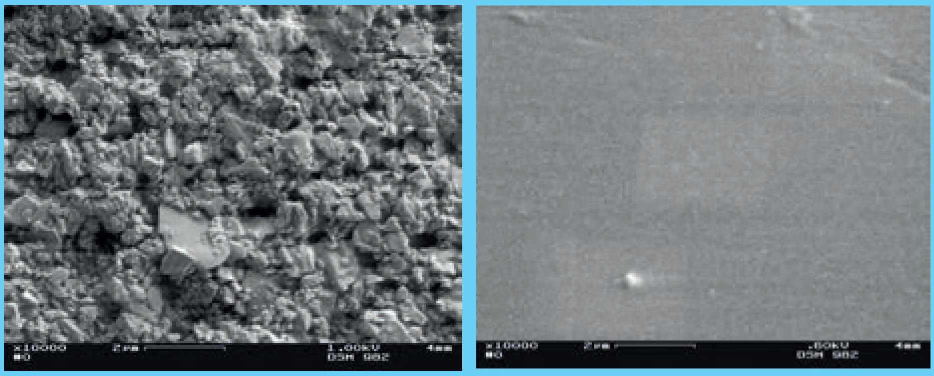
Composites of thermoplastic lignin

Lignin is typically used as an adhesion promoter between aliphatic polymers and natural fibres or as a component in blends with an aliphatic polymer or modified starch. In order to improve its plasticity, lignin is often chemically modified by esterification or alkylation. Besides the internal, covalent plasticisation, external plasticisers

Lignin fatty acid esters are potential novel bio-barrier materials for fibre-based packages.



Water Vapour Transmission Rates (WVTR) of paperboard coated with softwood (SW) lignin esters (normalised to coat weight 10 g/m2) (L-100: all hydroxyl groups esterified; L-50: 50% esterified).



FE-SEM images of paperboard (left) and the softwood kraft lignin palmitate coated paperboard (right).

Figure 3. Process chain for thermoplastic lignin composite.

such as polyvinyl alcohol (PVA), polyethylene glycol (PEG) and polyethylene oxide (PEO) have been used. The purpose of plasticisation is to improve the processability and performance of the material.

At VTT, the use of PEG plasticised kraft lignin as a matrix material in the composites together with TMP and bleached cellulose fibres was targeted (Figure 3).

A processing temperature range of 170 to 200°C is optimal as no thermal degradation of wood-based fibres occurs below 200°C.

The performance of plasticised lignin composites is moderately good in terms of the tensile properties compared with reference materials such as cellulose-reinforced PP and PLA (Figure 4). Improvement, however, is needed in ductility, environmental stability (moisture, water) and release of odours.

Polymer foams with lignin

Solid synthetic polymer foams are currently used in various end-uses such as packaging, construction and insulation materials. In our work to promote the transfer from synthetic to bio-based materials in solid foam applications, the addition of VTT organosolv lignin (Mikkonen 2008) to both fibre-based foams and synthetic foams was found to be beneficial. The texture of the wet fibre foam was improved by the addition of lignin particles, resulting in solid foam with increased compression strength. We were also able to produce solid polystyrene foam structures with lignin using a batch process with supercritical CO_2. The compression strength with samples containing 5–10% lignin, and produced with the best processing parameters, was higher than that of commercial extruded polystyrene (XPS) samples. In addition, lignin was found to have the potential to bring functionality to the polymer foams, e.g. to boost thermal insulation through its physical and chemical structure. The attractive visual appearance with silver gloss of the lignin-containing polystyrene foam material is a surplus exploitable for certain applications.

3.5 Sustainability assessment of the new lignin-based packages

Our aims are to direct the research of new products in a sustainable direction through environmental evaluation using life cycle assessment (LCA) as well as an economic and social feasibility study and SWOT analysis (Hohenthal et al. 2011, Tamminen et al 2011b). The sustainability evaluation was carried out for two reference products: 1) a corrugated cardboard box and 2) an FBB cereal package with a plastic bag inside, and for the corresponding new lignin-containing products.

Fossil greenhouse gases (CO_2, CH_4 and N_2O) are included in the carbon footprint and expressed as carbon dioxide equivalents (CO_2 eq.). The carbon footprint was calculated from

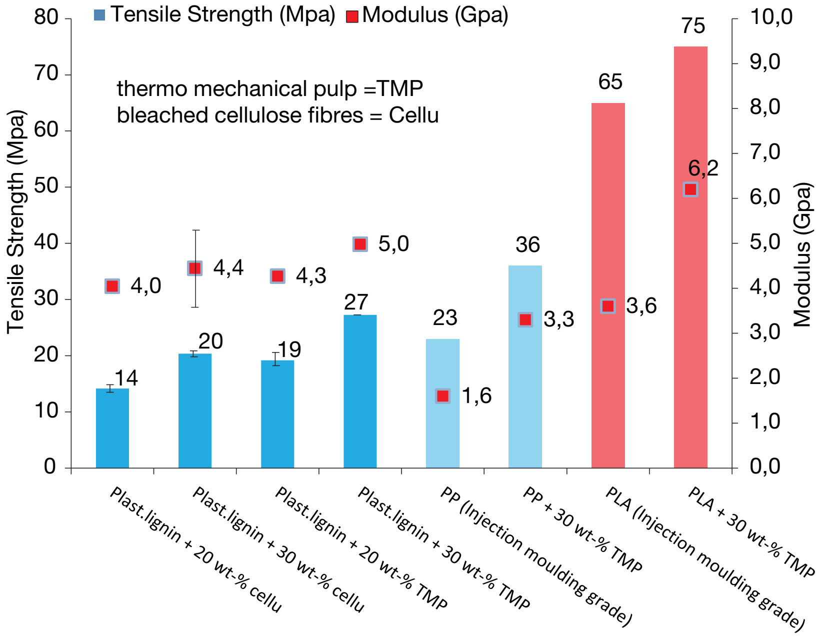


Figure 4. Performance of the plasticised lignin composites compared with reinforced PP and PLA reference materials.

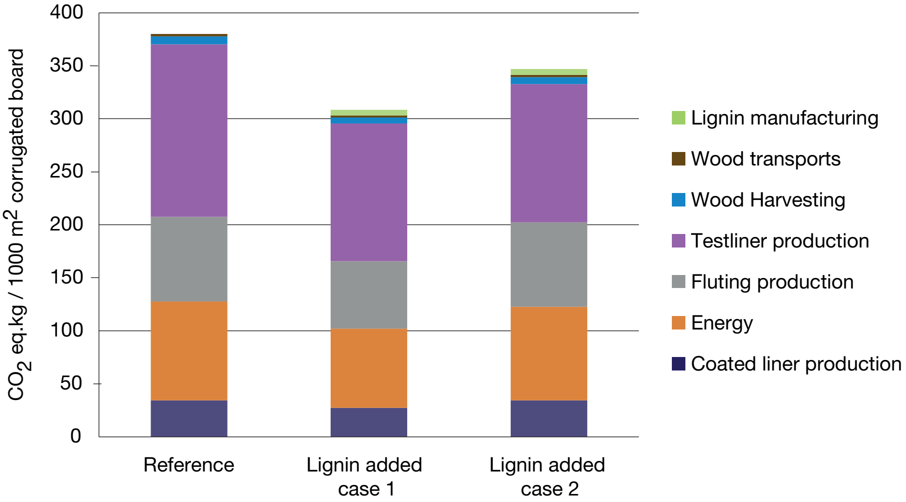


Figure 5. Carbon footprint of the corrugated cardboard and of the corresponding new lignin-containing product.

cradle to gate (corrugated board manufacturing), so the end of life was not included. In this calculation, it was assumed that lignin was extracted from black liquor with carbon dioxide. The lignin was then assumed to be added to the whole corrugated board in case 1, compensating for fresh fibre 1:1. The amount of lignin DS/fibre DS added was 20%. However, the amount could also be higher. The increased strength and thereby lower weight of

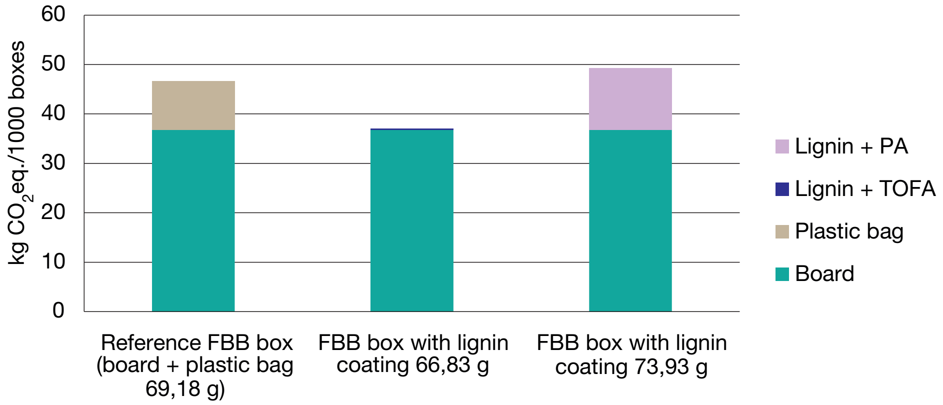


Figure 6. Carbon footprint of the folding board box, e.g. the cereal package with a plastic bag inside and the corresponding new lignin-containing product.

the corrugated board in this case is assumed to be 20%. So the reference board was 442 g/m^2 while the board with added lignin was 353 g/m^2. The carbon footprint for the new lignin-based product is 20% lower than that for the reference product. In case 2, the lignin was only added to the test liner, reducing the test liner weight by 20% and the total weight reduction of the corrugated board was thus 10% (Figure 5, page 41).

The LCA calculations in the cereal package case were performed with TOFA lignin and lignin palmitate (PA). The carbon footprint of the cereal package is 20% lower when TOFA lignin is used as a barrier material instead of a plastic bag (HDPE). The carbon footprint is slightly higher with lignin palmitate than with the reference case however (Figure 6). Kraft lignin and lignosulphonates have both gained FDA approval for safe use in manufacturing and in a wide variety of food-grade applications (Holladay et al. 2007).

The water footprint results depend on which methodology was used for the assessment. The result of the water stress impact depends on the local availability of fresh water, giving, for example, products manufactured in Finland and New Zealand better results than products manufactured in Spain.

With regard to the product end of life, lignin has a high calorific value and is suitable for incineration. It may also be used as landfill. However, the recyclability of the material is uncertain because neither lignin-based corrugated board nor lignin-based coatings have been tested for recycling. The potential economic impacts are difficult to evaluate due to the lack of data. Estimations about the costs and prices of lignin manufacturing vary greatly.

The results of the sustainability assessment point out the potential strengths, weaknesses, opportunities and threats related to the use of lignin in packaging. The results are promising as lignin can, to some extent, replace virgin fibre and oil-based products and have lower environmental impacts.

The two new lignin-based products look promising from the carbon footprint point of view, and the products have a light weight and are thus ecological.

3.6 The future of lignin research and development

Sulphur-free lignins

At VTT, our future focus will be on new lignin sources: side-stream lignins from different biorefinery processes using different biomasses as raw materials. New fractionation technologies are being looked for. Sulphur-free lignins from organosolv pulping processes and other sulphur-free processes will provide new opportunities for lignin applications. Being sulphur-free, they provide further modification and functionalisation possibilities, e.g. with different catalysts, which often cannot withstand sulphur. Depending on the organosolv process used, the lignins have various reactive functionalities. The lignins from the LGF (Lignofibre) process developed at VTT contain phosphorous, which gives the lignin unique properties (Mikkonen 2008). The hydrolysis residue from the bioethanol process also provides an interesting sulphur-free lignin for future applications.

The pretreatment of lignocellulosic biomass by alkaline oxidation with or without a catalyst produces highly charged lignin-containing side-streams (Blomberg & Kalliola 2011). As they are rich in carboxylic acid groups, these lignins have been shown to be better adsorbents, e.g. for calcium ions present in different processes and municipal waters, than the conventionally used complex forming agent EDTA (Figure 7). By using 0.5 kg of the lignin material per 1m^3 with a calcium ion concentration of 100 ppm, the free calcium ion concentration is reduced by almost 50% to 58 ppm. These values can be considered to withstand high calcium removal and indicate respective results also with other metal ions. Lignin can also be a good adsorbent for, e.g., heavy metals, dyes, pesticides, etc. This area is likely to grow as waste and effluent regulations continue to increase.

Carbonised lignin

Hydrothermal carbonisation (HTC) is a well-established technique for biomass carbonisation and a potential process to obtain various products (Hu et al. 2010). HTC is performed in an aqueous phase under autogenous pressure and relatively low temperatures (180–350°C), compared with dry pyrolysis (400–600°C) or gasification (800°C). The HTC

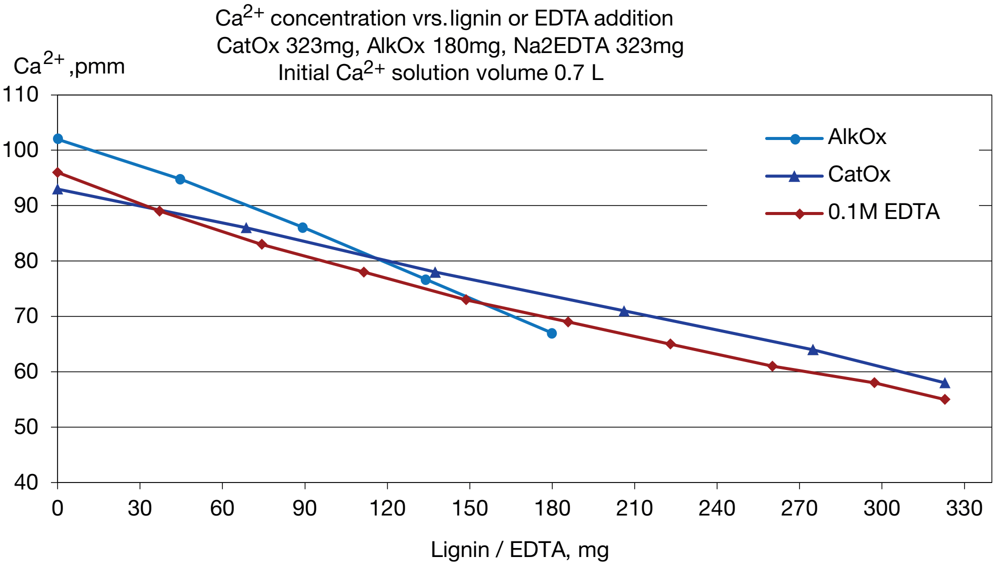


Figure 7. Calcium ion adsorption by CatOx and AlkOx lignins compared with EDTA.

process can be applied to a wide range of organic materials, and it is especially attractive for wet biomass. The process has been applied to a wide variety of feedstock, including wood leaves, cellulose, animal manure, municipal waste and microalgae. However, HTC technology has not been widely applied to lignin. At VTT we have started research on HTC carbon from fractionated lignins to obtain materials with varying ratios of carbon to oxygen. One of our future aims is to use HTC carbon in several novel applications.

Dietary fibre

One interesting potential application of lignin is as dietary fibre. Inspired by the beneficial properties of lignin (e.g. antioxidant and radical scavenging properties, ability to adsorb carcinogenic compounds), VTT has started to investigate the effects of high lignin dietary fibre in diet (Niemi et al. 2011). The results have showed that the cereal fractions with high lignin content have not caused any inhibition to microbial or enzymatic activities. Several phenolic metabolites were detected during the fermentation, and it is possible that they were lignin fragments cleaved by the microbes. However, the role of lignin in diet still needs more research to confirm the health effects observed previously.

3.7 Conclusions

VTT has long experience and strong competence in chemical pulping, lignin chemistry and analytics, providing a solid basis for the development of lignin-based products. During the IndBioMat programme, we have developed lignin esterification and solvent fractionation technologies to introduce new properties and functionalities to lignin and prepare thermoplastic lignin for various applications. Our focus has been on sustainable barriers, adhesives and composites.

Lignin fatty acid esters are potential biobarrier coating materials for fibre-based packaging materials, significantly reducing the water vapour and oxygen transmission rates. The barrier properties against water vapour are even better than those of commercial polylactic acid (PLA). The new lignin-based products look promising from the carbon footprint point of view. Lignin-based sustainable adhesives can replace phenol-aldehyde adhesives.

The development of value-added materials from kraft lignin will continue. However, in our research, we will focus on sulphur-free lignins from different fractionation processes and their use in applications. The promising start to replacing fossil carbon by hydrothermal carbon from lignin in several novel applications will also continue.

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4 Expanding the performance of bio-based hybrid materials

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Here, hybrid materials refer to the chemical or physical (mechanical) combination of two or more distinct components with the aim of producing a product with significantly improved performance. The targeted properties may be, e.g., durability, barrier performance, surface tension or topography, mechanical stability, or tensile or ductile performance. Such materials are typically used in structural composites and packaging. At VTT, the focus of the research has been on hybrid materials used for composites.

When introducing new biopolymer-based materials and applying existing ones to an increasingly challenging environment, it has become apparent that there is a need to improve or modify their performance. A typical approach is to incorporate reinforcement into the polymer structure, hence creating a composite benefiting from both the stiffness of the added fibres and the elasticity of the polymer matrix. In the biopolymer field, the use of natural fibres as reinforcement is the obvious choice to maintain the bio-based composition and biodegradability and to gain better compatibility (Nättinen et al. 2010). VTT has been working with the biocomposites from the early 90s. The latest major development in the field of biocomposites is indisputably the use of nano-size cellulosic reinforcement, microfibrillar cellulose (MFC) and cellulose nanowhiskers (CNW). Due to the tendency for agglomeration, the material is typically delivered as 1% aqueous dispersion. This and the different surface energies of the unmodified nanocellulose and the polymeric matrix create a challenge that requires a combined effort of process and material development.

Other recent developments are related to the use of wood components in the production of novel materials through plastics processing. Interesting results have been obtained using lignin and hemicellulose as matrix materials in these composites. The results of the thermoplastic lignin are described in more detail in the chapter Lignin – new openings for application by Poppius-Levlin in this edition.

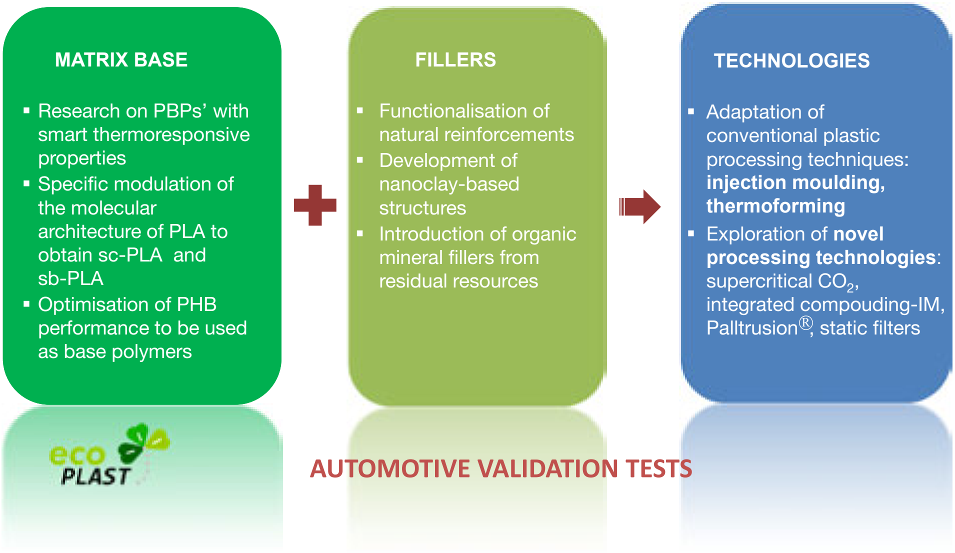

Figure 1. Material development concept with the VTT contribution in bold (EU project ECOPLAST)[1].

4.1 Advanced thermoplastic biocomposites for the automotive industry

New biomass-based composites from renewable resources with improved properties for vehicle parts moulding were developed in the EC-funded project EcoPlast, along with 13 partners. The overall concept of the project is presented in Figure 1. The aim was to bring the performance of thermoplastic biocomposites to the specifications of the automotive industry.

The following specific properties of the biocomposite materials were selected as improvement targets:

1) Compatibility between fibres and the polymer matrix (PLA, PHB)
2) Dimensional stability (against moisture, temperature)
3) Processability of fibres (homogeneity of mixing, length of fibres).

The mechano-chemical cellulose fibre modification method – a flexible, high output, ultra-high consistency modification method based on high shear physical compaction of fibres through a sieve matrix, developed by VTT – was applied to several types of wood-based cellulosic materials. The effect of the chemical fibre modification on the tensile and impact performance of PLA compounds reinforced with lignin-free cellulose fibres is shown in Figure 2 and Figure 3. The simultaneous impact strength and tensile strength improvements indicate the presence of cross-linking and improved fibre dispersion in the polymer matrix – the strength of the fibre was more homogeneously and effectively transferred to the matrix, improving the overall performance.

In addition to thermoplastic (melt-processable) composite fibre modification, methods for the production of modified fibres for thermoset, 'epoxy-type' compositions, were

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[1] 'ECOPLAST': FP7-NMP-2009-SME Collaborative Project. Funding from the European Commission is gratefully acknowledged.

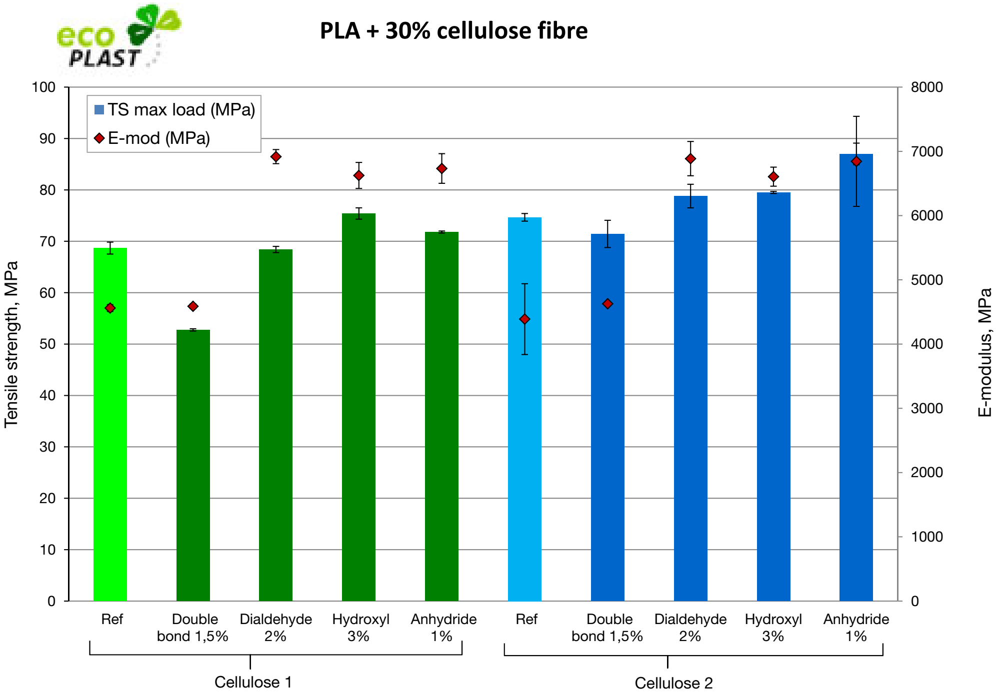

Figure 2. Tensile strength and stiffness for composites with lignin-free cellulose fibres treated with additives with different functionalities.

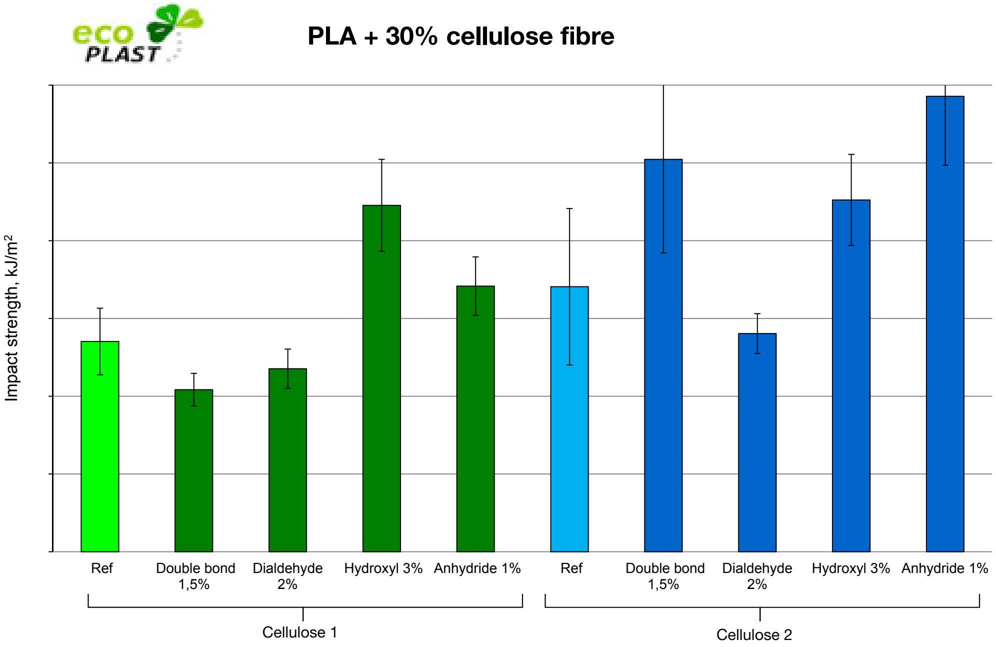

Figure 3. Impact strength for composites with lignin-free cellulose fibres treated with additives with different functionalities.

Figure 4. Untreated and APS-treated fibre mats used for thermoset composite reinforcement.

developed in the ECOSHELL EU project[2]. An example of treated and untreated fibre mats is shown in Figure 4.

The water uptake and swelling of composite samples were significantly reduced by several treatment methods; see Figure 5. This improved the environmental stability of the materials and helped to bring new biocomposite products to the automotive market with demanding specifications. Target applications in the automotive industry include indoor panels and covers.

4.2 Nanocellulose-reinforced rubber composites

Surface modification and non-aqueous carrier media of cellulosic materials (fibrillated and crystalline) may enhance their compatibility with lower surface energy polymers and compounding systems. For rubber composites, the partial replacement of the inorganic reinforcing fillers with cellulosics has been approached by developing oil-dispersible nanofibrillated and microcrystalline celluloses in order to improve the hydrophobicity and coupling functionality.

On the way, the particle dispersion was changed from water to organic solvent for chemical modification and subsequent blending, e.g. with rapeseed oil. For hydrophobation, acetone-exchanged nanofibrillated cellulose was modified using hexamethyldisilazane, producing trimethylsilylated NFC (TMS-NFC) at a DS of 0.3. Additional functionalisation onto nanofibrils and microcrystalline cellulose (MCC) was obtained using (3-chloropropyl)trimethoxysilane as the reagent, producing modificates (CPTMS-NFC and CPTMS-MCC) at a DS of 0.2. Solvent evaporation resulted in oil-based dispersions at around 2/10 wt-% solids (Figure 6), the fluid thickening effect limiting the loading.

Natural rubber-based compounds with the preset dosage of oil and thus loadings of 0.2 phr of TMS-NFC and CPTMS-NFC were compared with an unloaded reference. ShoreA hardness of the rubber was unaffected by adding NFCs, but the functionalised fibrils (CPTMS-NFC) imparted higher stiffness and reduced the elongation and damping effect on the compounds (Figure 7). For rubber applications, the targeted solids content and non-fibril-

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[2] 'ECOSHELL': Collaborative Project, FP7-SST-2010-RTD-1. Funding from the European Commission is gratefully acknowledged.

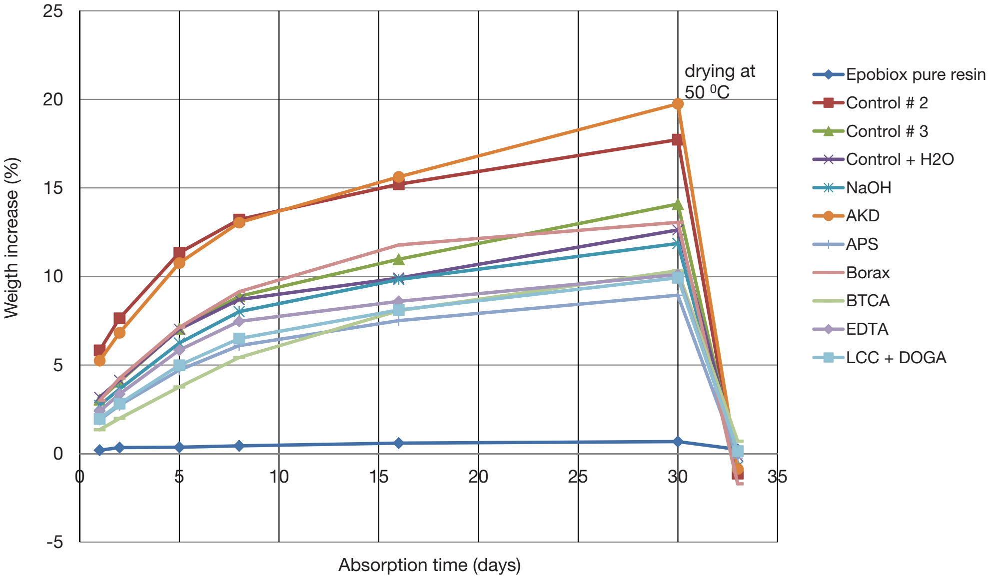

Figure 5. Water absorption of composite samples with fibres treated with various methods. The water absorbance was halved by the surface treatment.

lar morphology directed the interest towards crystalline cellulose grades.

4.3 100% wood-based thermoset composites

An increasing amount of hemicellulose raw materials such as xylans is derived from bio refineries, and efficient use of these polysaccharides will be one of the challenges of resource efficiency in the future. Hemicelluloses are the second most abundant plant polysaccharides after cellulose. Hemicelluloses consisting of several different sugar units, owing to an outstanding degree of chain branching and a ten to one hundred times higher degree of polymerisation than that of cellulose, are not yet used as efficiently as cellulose or starch (Bledzki & Gassan 1999).

Novel 100% wood-based thermosets were prepared in order to use hemicellulose raw materials as an alternative to replacing current non-renewable, hard-to-recycle materials based on glass and carbon fibre-reinforced thermosets. The low density of cellulosic reinforcement is an additional benefit that is becoming increasingly important due to the demands to reduce energy consumption in the transport sector.

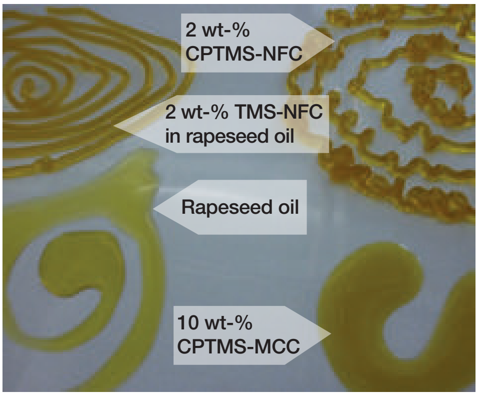

Figure 6. Rapeseed oil with 2 wt-% nanofibrillated silylated cellulose (upper cases) and with 10 wt-% microcrystalline silylated cellulose (lower right).

Thermoset composite was produced by solution impregnation of water-soluble and curable xylan-based pre-polymer into the foam

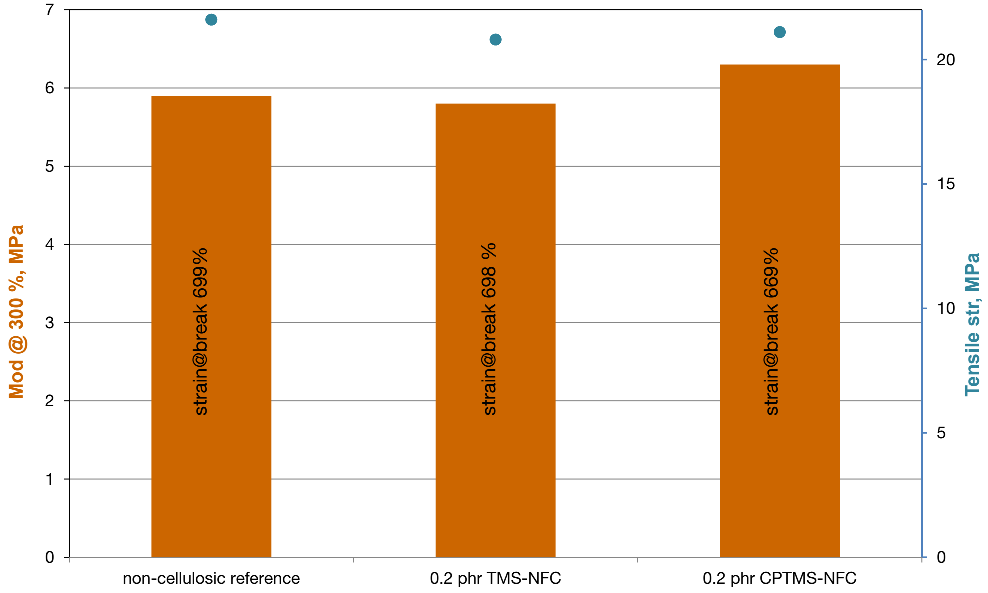

Figure 7. Mechanical properties of natural rubber compounds containing 0 and 0.2 phr modified nanofibrillated cellulose.

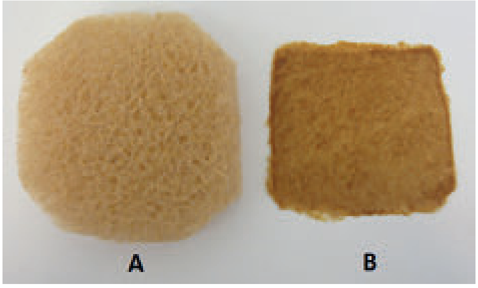

Figure 8. Foam sheet-formed fibre mat (A) and compression moulded hemicellulose-based thermoset composite (B).

sheet-formed fibre mats (Figure 8A) thus avoiding the use of organic solvents and improving penetration compared with particle dispersions. Low viscosity polymer solutions were used in order to improve interaction between polymer and reinforced fabrics. The impregnated mats were oven-dried and compression moulded into thin sheets; see Figure 8B.

The influence of the cross-linker agent amount (maleic anhydride MAH) and the effect of the different polymer-reinforced fibre ratios on the thermal behaviour of the compression moulded composite sheets were analysed with Dynamic Mechanical Thermal Analysis (DMTA) and a Differential Scanning Calorimeter (DSC). The room temperature flexural modulus (E', tensile storage modulus) of the composites with different MAH contents ranged from approximately 2 GPa to 7–8 GPa. Above 100 oC, modulus values of approximately 1–2 GPa were attained. The results showed that a higher xylan content and higher MAH proportion gave higher rigidity. The rather large variation between parallel samples can be attributed to the varying homogeneity of the fibre-reinforced thermoset structures.

In conclusion, lightweight and thin 100% wood-based thermosets were successfully prepared. The developed cross-linking system is suitable for a wide range of bio-based components to form composites. In addition, the relatively low degree and simple type of derivation is adequate for the developed system. For industrial applications, the cross-linking level and process would be optimised to further improve the tensile and, particularly, ductile

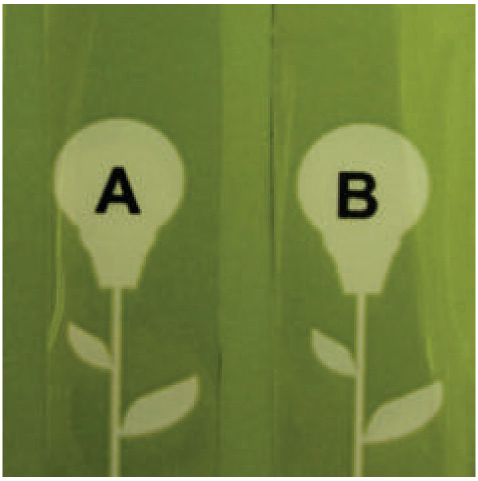

Figure 9. Pure PVA (A) and modified NFC-PVA composite film (B).

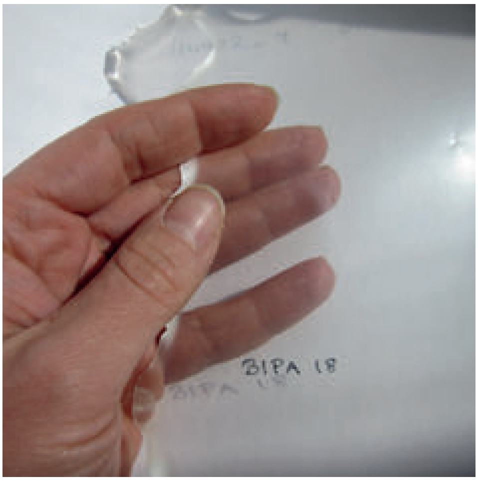

Figure 10. Transparency of the oriented PLA/nanoclay-composite film.

properties, which were not analysed due to the small scale of the synthetics.

4.4 Modified nanofibrillated cellulose (NFC) – polyvinyl alcohol composites

Nanofibrillated cellulose can be used as a building block, offering further means for biopolymer modification and interesting new qualities, such as a highly reactive surface and the opportunity to make lighter, strong materials with greater durability – properties that have not previously been achieved simultaneously (Hubbe et al. 2008). Polyvinyl alcohol (PVA) is a synthetic, water-soluble and fully biodegradable polymer with outstanding chemical resistance, and optical and physical properties. Due to its PVA properties, it can be used in a wide range of applications including filtration materials, membranes and packaging materials (Alexy et al. 2002, Jipa et al. 2012, Bochek et al. 2010, Bin et al. 2006).

Surface functionalisation of nanofibrillated cellulose was used to produce NFC-based polyvinyl alcohol composites with improved mechanical properties. Composites were prepared by the film casting method in an aqueous medium. Fully transparent films with different modified NFC loadings were prepared; see Figure 9. Chemically modified NFC showed favourable results and improved the mechanical properties of PVA. As a result of the addition of modified NFC reinforcement to the PVA, the tensile strength and E-modulus of PVA were improved by 230 and 370%, respectively.

4.5 Biaxially oriented PLA-montmorillonite-nanocomposite for barrier film applications

As the global packaging market is huge, there is a well-defined call for sustainable solutions to packaging materials. The development of green polymeric materials that do not use toxic or noxious components in their manufacture and allow degradation via a natural composting process is needed. These materials would still need to fulfil the requirements set for food and/or pharmaceutical packages however.

Processing of PLA/layered silicate nanocomposite and some properties of biaxially oriented films for food packaging are studied and developed at VTT. The aim is to manufacture a PLA/nanoclay composite with reduced oxygen and moisture permeability and, at the same time, maintain the processability and optical transparency of the PLA film; see Figure 10.

Figure 11. PLA films in sandwich packages as an option, among other bio-based package covers.

PLA/nanoclay composites were manufactured using three different clay contents: 3 w-%, 5 w-% and 8 w-%, and six different compatibilisers were tested to improve the dispersion of nanoclay in the PLA matrix. Biaxially oriented films made of PLA-Montmorillonite nanocomposites were prepared successfully. The transparency of the oriented films was satisfactory for food and pharmaceutical packaging; see Figure 11. The barrier properties of PLA were improved remarkably by a nanoclay loading of 5 w-%, the oxygen permeability was reduced to less than half the value of pure PLA and the moisture permeability was reduced to 50% of the numerical value of pure PLA.

4.6 Biocomposite kitchen furniture components

In collaboration with the Finnish furniture and plastics industry, VTT has developed a composition for use in kitchen furniture components. The use of natural fibre-reinforced polymer composite reduces the weight of the skeleton of the kitchen by 25–30 w-% compared with plywood while simultaneously reducing the carbon footprint. The kitchen components were made using common plastics processing methods, enabling the production of injection moulded parts within strict dimensional requirements and no further need for machining. The result of the process is a cost-effective composite product with high performance and a visually appealing appearance.

4.7 Conclusion

The hybrid materials development at VTT has already helped to commercialise bio-based materials by improving the performance and cost-efficiency of the compositions. The work will be continued together with leading European institutes and industrial operators to enable a more sustainable future with green high-performance materials.

Injection moulded bio-based composite frame for kitchen components.

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5 New bio-based man-made fibres and textiles

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Textiles are widely used in everyday life. They are also used in many technical applications in which their presence may not be as apparent. There are many application areas such as clothing and home textiles in which textiles cannot be substituted by other materials. Advanced materials such as high-tech fibres and processing technologies including surface treatments can improve the properties even further, making it possible to create new application areas for textiles in the future. VTT has research activities in the areas of fibres, and nonwoven and technical applications of textiles.

5.1 Markets and trends

The Finnish and European clothing and textile industry has undergone fundamental change in the last decades. While many companies have their headquarters in Finland or Europe, the actual manufacturing has been shipped to low-wage countries. This has created new challenges, including how to manage and ensure preferred product quality and how to handle logistics. Regardless of the structural change in the textile sector, the textile and clothing industry is still is one of Europe's major industrial sectors with an annual turnover of over 200 billion euro and a workforce of 2.3 million in 2005. The competitive advantage of the Finnish and European textile industry lies in high scientific knowledge and expertise, fashion and creativity as well as innovations. There are 170,000 textile companies in Europe, 96% of which are SMEs. Textile production has been divided into clothing, home and technical textile areas of approximately 41%, 33% and 26%, respectively (Euratex 2004).

The growth rate for technical textile products and new applications is higher than the growth rate for the traditional clothing and home textile sector. The global production of textiles and the market value of textile products are expected to grow in the foreseeable future. The major trends in Europe include focusing on more specific products, new application areas for textiles and a move towards increased customisation. Examples of new application areas include construction materials in the automotive industry, aircraft, aeronautics, machinery, electronics, electrotechnical and medical devices, and many other smaller application areas. The growing world population needs its basic needs met. Textiles can also be used in agriculture, horticulture, fishing, land reclamation, health care and protection, in which they can help to provide clean water, food, energy and other basic needs for the growing human population (Euratex 2006, Euratex 2004).

Other major topics in the textile industry in the Western World are corporate responsibility and increased environmental awareness. In

Table 1. Processing stretch ratio, fibre titre and mechanical properties of recycled fibres and reference fibres.

Pulp grade	Stretch ratio %	Titre (dtex)	Tenacity (cN/dtex)	Stretch %
Fine paper	60	2.42	1.93	21
	80	2.31	2.02	20
	100	1.97	2.00	17
	120	1.86	2.07	16
Cardboard	60	2.55	1.72	22
	80	2.40	1.83	20
	100	2.06	1.91	18
	140	1.99	1.97	16
Ref commercial dissolving pulp	60	2.58	1.98	21
	80	2.10	2.01	18
	100	1.97	2.14	15
Ref viscose		1.9	2.1	

the Western World there is a need to develop new more environmentally friendly production processes to meet the tight environmental regulations. This step is demanding for the Western textile industry as, using the current production infrastructure, the developing countries are benefiting from lower production costs. However, the change will eventually reach the rest of the world, which will follow and apply the more stringent requirements for production processes and waste management. Green technologies may include, for example, the use of bio-based and recycled raw materials, and enzymes (Frost & Sullivan 2007). Other interesting possibilities for the future of the textile industry include nanotechnology (Forrest 1995), smart textiles (Lymberis & Paradiso, 2008) and functional materials for protective clothing such as laminates, moisture wicking materials and technical fibres (Frost & Sullivan 1998).

5.2 Bio-based man-made textile fibres

The textile sector uses approximately 80 million tons of fibres per year and demand is expected to increase by 4–5%. The share of natural fibres (cotton, wool, silk, flax, etc.) is approximately 40% while 60% are man-made fibres. Man-made fibres are mainly produced from non-renewable fossil sources.

Natural fibres are renewable, but an increase in their production has some constraints. For example, the production of cotton consumes a large amount of water (Chapagaina et al. 2006) and chemicals that lead to environmental and societal problems. Due to the large water footprint and other environmental issues, cotton production is no longer on a sustainable base, and the increasing demand for cellulosic fibres most certainly cannot be covered by it.

Textile fibres from new dissolving pulp raw material

Industrial biotechnology has opened new opportunities for the textile industry. Cellulose, which is the structural element of cotton, is the most abundant polymer in nature. The use of this raw material base is therefore interesting for the textile industry. In textile fibre manufacturing, cellulose is used in the form of dissolving pulp. There has been a long history of producing viscose textile fibres from wood-based cellulose. The viscose process, however, requires chemicals such as carbon disulphide that are toxic and pose an environmental risk. Alternative more environmentally friendly processes for producing fibres from dissolving pulp have been developed in recent decades. These include the Lyocell (Tencel) process, which is already commercial. Processes such as BioCellSol, using enzymatic and CarbaCell, including the use of urea, are also promising though not yet commercial processes.

VTT has been involved in the development of the CarbaCell process, which has more environmentally friendly chemistry than the viscose process. Another advantage is that it has a stabile intermediate product that can be transported and stored in dry form. The dissolving is carried out in two steps, first in mildly alkaline and second in cold and highly alkaline conditions. It is possible to prepare solutions of high quality and have a high dry matter content in a mixing time of just a few minutes (Valta & Sivonen 2010, Valta et al. 2011). Nowadays, the average strength of carbamate fibres fulfils the nonwoven fibre requirements and, occasionally, also those for textile production.

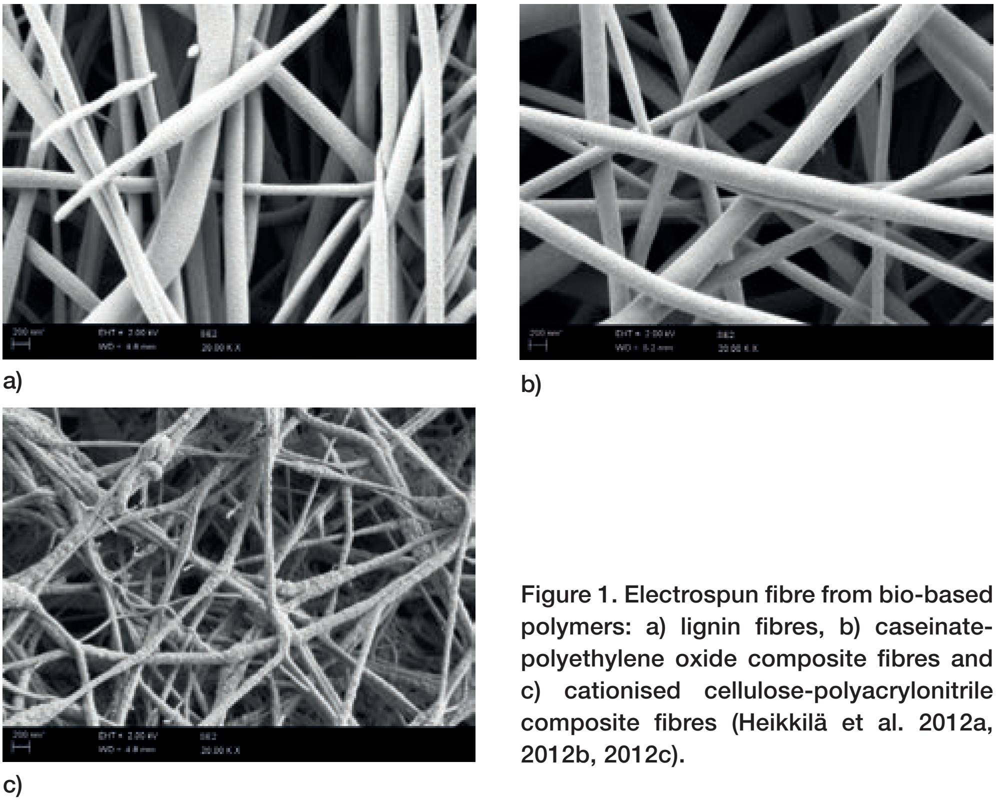
Wood-based cellulose has been used in textile fibre production for a long time. Nowadays, the price of wood (SW) raw material in the production of dissolving pulp using the prehydrolysis kraft process makes up over 65% of the production costs in the Nordic countries (RISI 2009). Alternative and cheaper raw materials are needed and one possibility is to use recycled fibres such as deinked fine paper and fluting clips (cardboard). Due to the origin of fibre composition, these materials contain lignin, hemicelluloses, extractives and inorganic impurities – unwanted components in dissolving pulp. In order to meet the quality parameters of commercial dissolving pulps, recycled fibres should be conducted through a purification process with several stages.

Fibres produced from recycled cardboard.

Dissolving pulps with alkali resistance (R18), cellulose content of over 90% and reactivity of 63-81% measured using the Fock method (Fock 1959) can be prepared at VTT. These kinds of prepared dissolving pulps were tested using the carbamate method and wet spinning. The fibres had very good mechanical properties. The tenacity of the fibres was the same as for native dissolved reference cellulose made from commercial dissolving pulp and the same as for existing commercial viscose nonwoven fibres (Table 1).

Nanofibres by electrospinning

Electrospinning is a method that can be used in the production of polymeric sub-micron and nanofibres. The small fibre diameter, small pore size and high surface area of the nanofibre web are advantageous properties, especially for filtration applications (Barhate & Ramakrishna 2007). This is also one targeted application area at VTT since the dramatic increase in filtration efficiency can be observed with a very small amount of fibres (Heikkilä 2008, Heikkilä et al. 2008). Our measuring capabilities for aerosol filtration studies include filtration efficiency



a)

b)

c)

Figure 1. Electrospun fibre from bio-based polymers: a) lignin fibres, b) caseinate-polyethylene oxide composite fibres and c) cationised cellulose-polyacrylonitrile composite fibres (Heikkilä et al. 2012a, 2012b, 2012c).

for different particle sizes, pressure drop, loading tests for capacity/lifetime measurements and flame retardancy tests. Other potential application fields of electrospun fibres include protection, composite reinforcement, sensoring, energy and catalyst applications. VTT has been involved with electrospinning in various projects, and the materials developed include carbon nanofibres for catalyst carriers[1], TiO_2 fibres for photocatalysts[2] and polymeric fibres for use in fibrous membranes[3].

The polymer solution is drawn into nano-sized fibres using an electric field. Electrical forces initiate the jetting and cause instabilities and stretching, while the viscoelasticity of the polymer solution stabilises the jet. Fibre diameters smaller than those achieved using conventional fibre drawing methods are possible because the mutual charge repulsion caused by the electric force overcomes the surface tension. In conventional fibre-forming methods, surface tension restricts the surface area of the fibre and, thus, limits the drawing ratio. Electrospun fibres are typically collected as a coating layer but can also be used in the formation of a self-sustaining nonwoven web. In addition to neat polymers, solutions containing additives and fillers can be used to functionalise fibres and prepare composite fibres for use in specific applications. Specialty fibres can also be prepared by combining electrospinning with heat treatments. Metal-containing nanofibres, for example, can be pyrolysed into ceramic nanofibres, and organic nanofibres graphitised into carbon nanofibres. Examples of electrospun fibres made from bio-based materials are presented in Figure 1.

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[1] Marapoke project, Tekes joint research project (research institutes and companies).

[2] PhotoCaMat project, 2011, VTT basic funding.

[3] Fubio JR2 project, TEKES and FIBIC joint research project (research institutes and companies).

5.3 Technical textiles

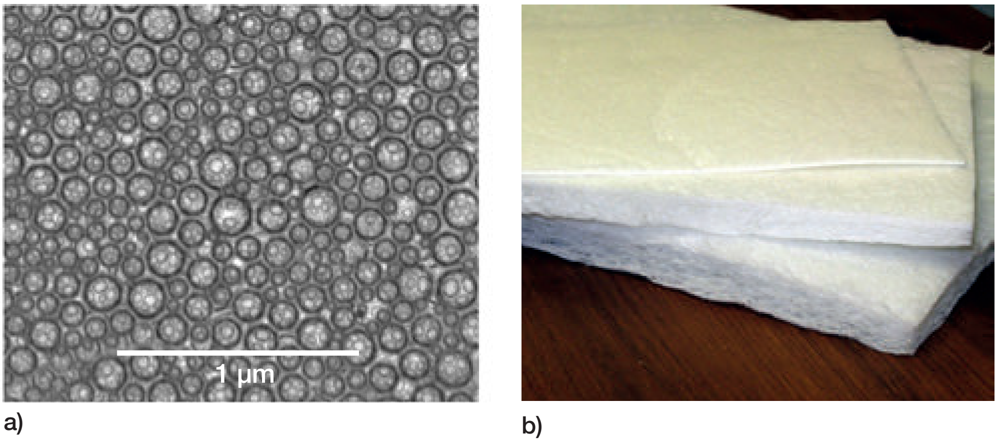
While the manufacturing of clothing has been moved to countries with low labour costs, the production of technical textiles has been able to maintain a stronger foothold in the Western World. Technical textiles are typically divided into twelve classes (Horrocks & Anand 2000), including agrotech, buildtech, clothtech, geotech, hometech, indutech, medtech, modiltech, oekotech, packtech, protech and sporttech.

Nonwoven products are an important sector of technical textiles. Advanced properties such as improved chemical, mechanical and thermal resistances, stain and water repellency, and protective properties are often needed in applications. These properties can be obtained using specialty fibres, advanced textile structures as well as various treatments including for surfaces and coatings. Currently, only one-fifth of the raw materials used in nonwoven fabric are bio-based, mainly viscose, wood pulp and natural fibres. The increasing use of bio-based materials has certain advantages since they use sustainable, renewable materials including wood-based by-products and biowastes and enable preparation of biodegradable products (Heikkilä 2012).

Nonwoven materials and their functionalisation have been studied in the NeoWeb[4] project and advanced properties of technical textiles in the Flexifunbar project . The NeoWeb project has combined VTT's raw material, foam-forming and surface treatment knowledge to improve nonwoven materials. The aim of the Flexifunbar initiative was to develop an innovative generation of hybrid multi-barrier-effective textile materials based on multi-layer complex structures and the functionalisation of micro- and nanostructures. It included re-thinking the production of multi-barrier-effects based on nano-scale technologies to ensure high performances. New characterisation methods and industrial concepts were required in order to control the nanostructure and microstructure. The development of such materials covered a wide range of textile applications.

Nonwoven and foam-forming

Nonwoven production methods can be classified into dry-, wet- and direct laying methods. In direct methods such as melt spinning, melt blowing, electrospinning, flash spinning and film fibrillation, a nonwoven structure is formed directly from the polymer melt or polymer solution. Dry- and wet-laying methods are suitable for readymade staple fibres such as cellulosic fibres. Dry-laying includes a carding process (similar to the process step used in yarn forma-



a)

b)

Figure 2. a) Appearance of foam and b) bulky materials obtained by foam forming.

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[4] NeoWeb project, Novel Emerging of Fibre Web Products, 2012–2013, VTT basic funding.

Figure 3. Working procedure of the foam-laid hand sheets. The size of the sheets is 38.5 cm x 26.5 cm (left). Production of the foam and fibre mixture (centre), fibre foam is decanted into the hand sheet mould (right), and fibre foam is filtered using a vacuum chamber and the suction table.

tion), air-laying and preparation of dry paper. Wet-laying is similar to paper formation since fibres are dispersed into a large amount of water. New technology based on foam can be included as a second method into the wet laying class.

The foam-laying technique was first applied to the paper industry in the 1970s. Foam is a suitable carrier phase for various materials, and it has been used in both web formation and web-coating processes, e.g. the Radfoam and the Wolvercoat concepts (Radvan & Gatward 1972, Smith et al. 1974, Punton 1975). In the Radform process, fibres were delivered to the wire in suspension (3–5%) in aqueous foam with an air content of 60–70%. The paper formed had high bulk and low strength characteristics in an unpressed state compared with a comparable water-laid paper, but the strength could be regained by beating or pressing. Pressing raised the strength to the water-laid level whilst correspondingly reducing the bulk.

The foam allows the use of longer textile fibres up to 200 mm. Bulky materials (Figure 2b) can be obtained when fibres are located in ‘bubble pockets’ (vertex) and the structure can be formed or ‘frozen’ in its dispersed state, providing excellent formation, high bulk and excellent layer purity. The benefits of foam forming include energy savings in pumping, drying, refining, reduced water consumption, the possibility of using bio-based foam chemistry, excellent formation regardless of fibre length and production speeds higher than those of common nonwoven technologies (up to 1000m/min).

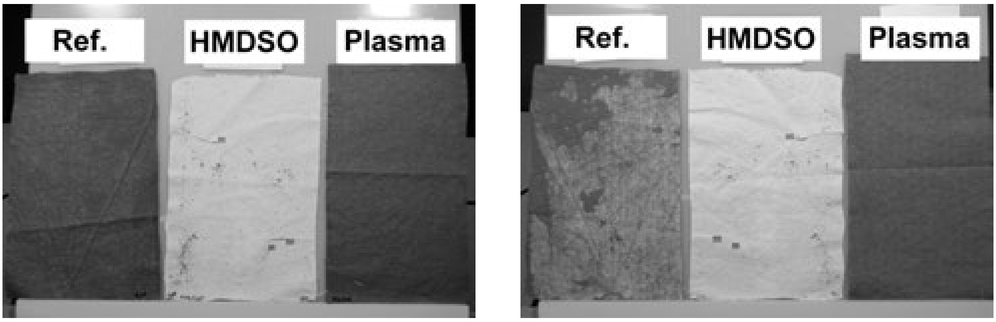
VTT has foam-forming facilities ranging from laboratory to pilot scale; see Figures 3–4. Foam-laid hand sheets can be made using a method and equipment set-up adopted from the glass fibre industry; see Figure 5.

Surface treatments and coating technologies

The functional properties needed for technical textile products can be obtained using various surface treatments and coating methods including plasma, foam coating, atomic layer deposition (ALD) and various printing methods.

Plasma technology can be used in surface treatment and deposition applications. Surface treatments can be combined with other processes such as pre- and post-treatment and enable partial surface chemistry control. New technologies enable continuous atmospheric operation. There are also commercial systems available for plasma deposition. An example of the effects of plasma treatments on the wetting of cotton fabric in the dyeability test is presented in Figure 5. The untreated reference sample was fully dyed from the contact side and partly through the structure. Plasma activation increases hydrophilicity and the plasma-activated sample was therefore fully coloured through the fabric. When fabric was coated with hydrophobic hexamethyldisiloxane (HMDSO), most of it remained unwetted and uncoloured.

Figure 4. Foam-forming hand sheet mould and equipment set-up.



a)

b)

Figure 5. Untreated (Ref), HMDSO-coated and plasma-activated cotton fabric samples after the dyeability test: a) the side in contact with the dye bath, b) the other side (Nättinen et al. 2011).

In foam-coating, foam is used as a carrier phase to transfer the coating material onto the substrate. On the surface, the bubbles collapse due to absorption, leaving the coating material on it. The advantages of foam include that it is a non-contact application and allows very thin coatings, e.g. 0.5 g/m^2. Foam contains 90% air, so instead of a 1 µm layer, a 10 µm layer is applied. Foam also has a tendency to migrate into the substrate compared with liquid and enables the application of gel-like material, such as nanofibrillated cellulose. Foam coating is a versatile method and is compatible with a wide range of materials.

ALD on the other hand can be used in the preparation of thin coating layers of the nanometre range. The method is based on self-terminating gas-solid reactions and a surface-controlled layer-by-layer process. Coating materials typically include ceramic and metallic coatings. Coatings are conformal, pinhole free and have fixed thickness, even inside porous structures and they are typically used as protective and barrier layers. A wide variety of substrates, including polymeric fibres, can be coated, for example, ceramics, metals, hybrids and polymers. VTT has actively studied the use in ALD coatings of papers (Hirvikorpi et al. 2010, 2011a) and biopolymer films (Hirvikorpi et al. 2011b).

Printing techniques are widely used in the decoration of clothing materials. Different printing methods also enable local functionalisation of the printed surface. VTT has long experience in paper printing applications, but many of the printing methods such as inkjet printing can

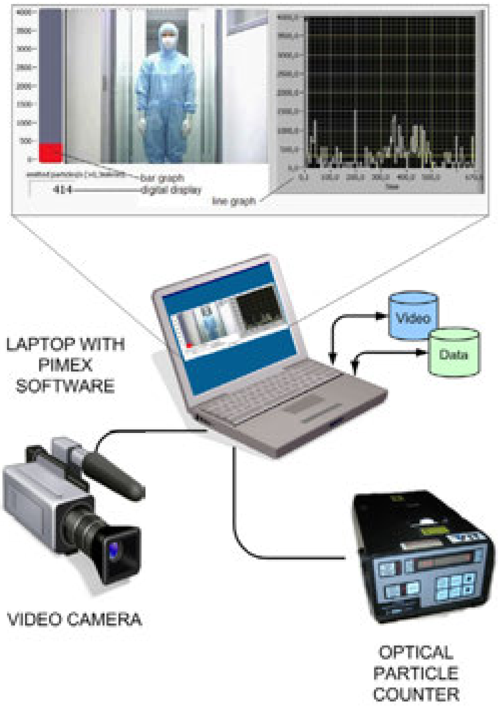


Figure 6. Video exposure monitoring system (VEM).

also be used in the decoration of the functionalisation of textiles. Application areas include personalised products, traceability and protection applications. VTT's core competences include development of functional and bio-based inks, improving printability by optimising ink-substrate interactions, carrying out process optimisation and enhancing the understanding of printing processes.

Applications in work clothing and textiles for specific environments

Work and protective clothing vary widely depending on the intended environment. Work and protective clothing are used in demanding surroundings such as hospitals, food, electronics, energy, ICT and the construction industry as well as protection occupations. The required properties vary from antibacterial, antistatic and anti-linting properties to mechanical protection and fire-proofing. In addition to these functional properties such clothing should be light-weight, comfortable by controlling the heat and moisture, and durable in use and maintenance. Biodegradability or recyclability is also considered an advantage. Research work has been active, for example, in the areas of hospital and clean room textiles (Nurmi et al. 2002, 2003, 2006; Lintukorpi & Nurmi 2006; Salmela et al. 2012), static control clothing (Nurmi et al. 2007, Nurmi et al. 2001, Maijala & Nurmi 2001, Tappura et al. 2002, Paasi 2004), EMC shielding (Nurmi et al. 2007) and improved fire-retardancy (Mielicka et al. 2007).

Hospital textiles have been studied in the High-Tech Hospital Project[5]. The aim of the project was to develop comprehensive concepts for managing high-level hygiene in hospitals. The study made use of the best practices of the high-tech industry (such as the pharmaceutical and electronics industries) to benchmark and adapt new operation models for the health care sector (Enbom et al. 2012, Salmela et al. 2012). The project assessed potential risks in the hygiene value chains and generated tentative proposals for improvement. The project focused on the following work packages: state-of-the-art, high hygiene zones, protective clothing and drapes, cleaning, service and maintenance, hospital logistics, management, reporting and exploitation. High hygiene protective clothing for operating units and operating rooms was developed, including the value chains of textiles and footwear. The video exposure monitoring (VEM) method was exploited for monitoring airborne contaminants of protective clothing (Figure 6). The measurement instruments for environmental or other factors are connected to the VEM equipment. Concurrently with the measurement, the work or other event under investigation is filmed. Signals from the video camera and the measurement instrument are mixed to provide information on the current level of the measured variable. The continuous signal from the measuring instrument is converted into a bar graph and displayed at the edge of the

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[5] High-Tech Hospital – the concepts of high-level hygiene control in hospitals.

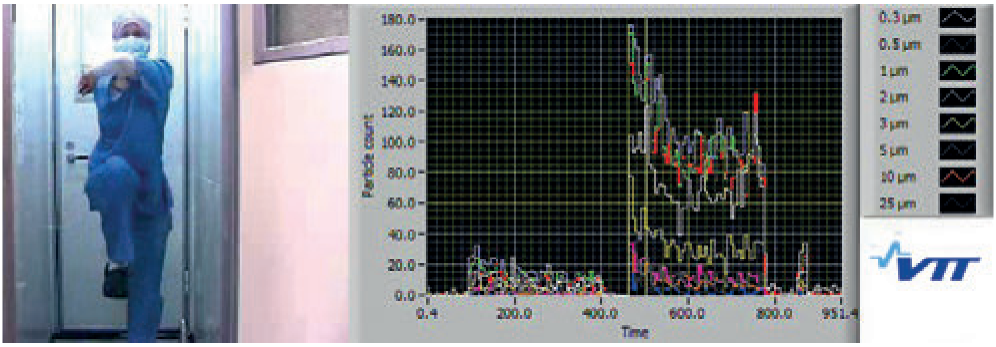

Figure 7. Body-box test system measures particle emissions and cleanliness of hospital textiles.

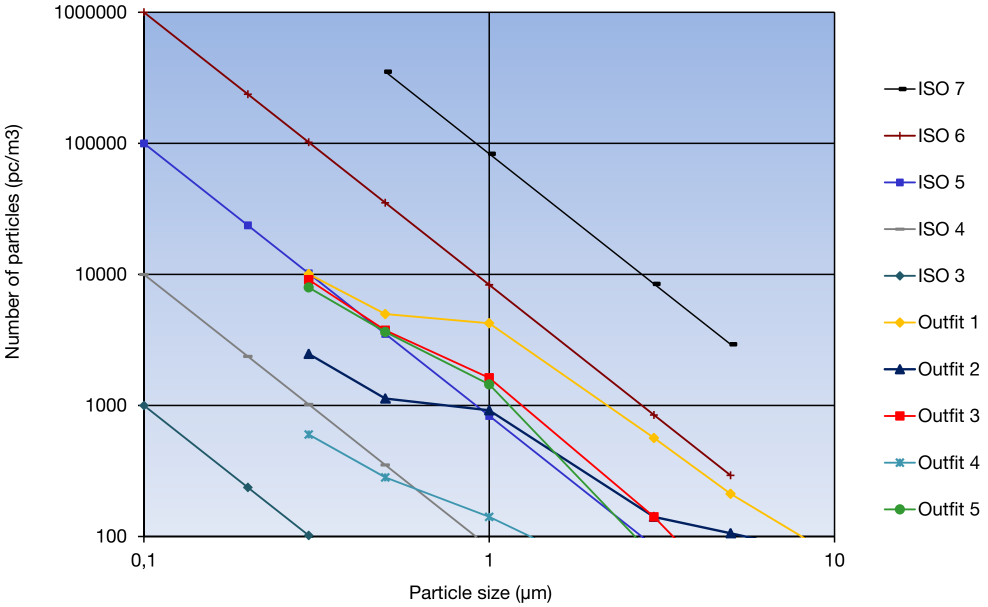

Figure 8. Particle emission results of clothing integrated into clean room classes.

video screen. The height of the bar is proportional to the measured signal.

A person dressed in protective clothing moves in a test clean room (body-box) for eleven minutes; see Figure 7. All released particles (living and non-living) are calculated by size and number. Garments should be designed to envelop personnel and prevent the dispersion of contamination. The body-box system analysing method was developed to help design low-linting and well-protective clothing to enhance clean and hygiene work environments. The microbiological purity can also be examined.

Large amounts of contamination are dispersed from the people to the clean environments. It is very important try to minimise the particles dispersed from textiles and working personnel in order to keep the environment clean and microbe safe. VTT has researched activities in the membrane area including material development and membrane testing facilities. The Eureka projects (Batex, Mulfunc, Mango) developed multifunctional textiles (woven, knits, nonwoven) and garments for demanding environments (EPA, GMP, clean room, hygiene, explosive). VTT researched activities in low-linting and electrostatic testing facilities and developed a method to integrate particle emission measurement results for clean room classes; see Figure 8.

5.4 Conclusion

Fibres, textiles and nonwovens are important materials in many fields of life. Originally, the materials used in this sector were natural, but in the last century they have been replaced by synthetic materials. New and improved bio-based materials offer new possibilities for the future, as the increased use of cotton is no longer a viable option, due to the scarcity of water. On the other hand, raw material for oil-based synthetic fibres is not sustainable either. New fibre materials use bio-based raw materials in a sustainable way. The new processes are more environmentally friendly than the existing ones. The functionalisation of fibres and textiles provides new properties that correspond to the needs of various current and new application areas for these materials.

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6 Towards 100% bio-based packaging

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VTT has responded to the need for more sustainable packaging materials from so far poorly used renewable resources and industrial side or waste streams. VTT has developed novel fibre-webs with properties close to those of plastics, enabling thermoforming and translucency. Likewise, VTT has looked into wood-based polymers, other polysaccharides and hydroxyl acid polymers to create new packaging materials using the unique competence on chemical modification. These materials can also be upgraded to meet more stringent packaging requirements.

6.1 Markets and trends

The global packaging container business has been estimated as having reached close to 600 million USD in 2009 (WPO/PIRA 2008). The primary functions of packaging are to contain a specific amount of product, to protect this from various hazards and to enable both economically and technically feasible logistics. Although packaging clearly contributes to sustainability by limiting food waste and product loss, and supporting the well-being and safety of consumers, it still requires consumption of natural resources and has a direct impact on the environment (Matilainen et al. 2012). It is important to consider how packaging should be designed to fulfil its functions listed above feasibly in the most sustainable way. Environmental awareness is increasing and preferences among consumers are changing (GMA & Deloitte 2009). Governments and multinational organisations are setting new regulatory requirements for the amount, type and recovery of packaging waste. The motivation for developing and adopting more sustainable solutions along the packaging value chain has changed from mere cost saving to, e.g., investments that also enable short-term differentiation and long-term business growth (Accenture 2012).

Sustainable packaging has been estimated to comprise 32% of the total market, although in 2010 only 3% of product launches included an environmental statement about packaging (Chambers 2011). The hierarchy for managing packaging waste has evolved during the last decades from Reduction, Reuse and Recycling to also include Recovery, Renewal, Reimagine and Redesign. These seven Rs are reflected in the current environmentally oriented packaging material trends, such as overall material, energy and operational efficiency, light-weighting, continuous competition between packaging materials, and the introduction of bio-based materials based on renewable resources and poorly exploited industrial streams. The purpose of the following research examples is to demonstrate the steps taken towards 100% bio-based packag-

VTT's barrier and packaging technologies have been demonstrated at various venues by, e.g., roll-to-roll coating of biohybrid materials and manufacturing packaging prototypes. These demonstrators combine several of VTT's technologies to provide concrete examples of possible packaging applications.

ing materials within the Industrial Biomaterials Spearhead Programme.

6.2 New fibre-based substrates

Fibre-based materials made from cellulosic fibre networks, such as paper and board, form the largest packaging material segment owing mainly to secondary and bulk packaging. Plastics have gained a market share in primary packaging, although paper and board are manufactured from a renewable resource and used in sustainable packaging formats (Barnett 2010). Paper and board also have excellent stiffness vs weight ratio and enable high-quality printing and special effects, recycling and composting.

Unlike many plastics, paper and board are not typically transparent or even translucent, yet they are not adequate light barriers for many packaging applications. Due to their limited barrier properties, moisture resistance and optical properties, paper and board are often coated with polymers or applied with a separately attached plastic window, which, in itself, creates problems and costs. In addition, the design flexibility of paper and board is limited compared with the plastics found in the most innovative shapes today. The relatively rigid network of cellulosic fibres typically leads to poor elasticity and low strain at break for the board, thus limiting the possible shapes. In order to replace plastics, mouldability of fibre-based webs has to be improved significantly.

VTT has developed a novel mouldable and translucent bio-based web for packaging and composite applications. This technology is based on foam-formed webs and polymer impregnation. The potential of novel fibre webs was also demonstrated by manufacturing thermoformed products and benchmarking developed materials to commercial ones.

High elongation was achieved by combining the foam-forming, long fibres and high portion of chemical pulp fines. The key for maximising the strain of the fibre-based web was to use long and intact fibres to form a porous and elastic web structure and fines with a high bonding potential to achieve sufficient strength for this web. The elasticity was further improved by the in-plane compression process leading to additional micro compressions to the web. The elongation was also enhanced by impregnating elastic polymer into the fibre-based web. This contributed to sliding between individual fibres during loading. For example, alginate treatment led to a fivefold improvement in the strain at break value for wet samples. For dry samples, this value was still tripled when using proper thermoplastic polymer. However, the fibre-based web has to be thoroughly impregnated to achieve good mouldability.

Translucent features can be created by impregnating cellulose or starch acetate into the fibre-based web (Mikkonen et al. 2009, Mikkonen et al. 2010, Peltonen et al. 2005). Impregnation can be carried out with aqueous dispersions or as polymer-melt impregnation. In order to meet the challenge related to webs with a higher basis weight, a new solution based on a layered structure was developed. The idea was to produce a high basis weight translucent paper by attaching lower basis weight translucent sheets together by pressing. This worked well for sheets based on chemical pulp. These layered materials were also feasible for moulding.

A fibre-based package from VTT demonstrating dramatically improved thermoforming properties together with a fibre-based lidding material with a built-in translucent window, i.e. features typically linked to plastic packaging materials.

6.3 Polymers from renewable resources

Plastic packaging forms the fastest growing market, especially when it comes to rigid plastics, driven by an increasing demand for PET bottles and ready-meals and, in general, by substitution of other packaging materials. Plastics are transparent, have good barrier properties and can be thermoformed into complex shapes.

Fluctuating oil prices, legislation and limitations on landfill, and consumer demand are examples of the driving forces for replacing oil-based non-renewable polymers and other packaging materials with biomass-based alternatives. Bioplastics therefore constitute a fast-growing market, although the consumption was a mere 100,000 tonnes in 2009 compared with the total of 100 million tonnes of plastics made into packaging (Anon. 2009). Bioplastics must also meet the requirements set by the product and preferably by several packaging waste recovery techniques. However, sustainability does not justify underperformance in other areas of material performance.

Some bioplastics are facing concerns today, as their raw materials also form part of the food or animal feed supply. The main philosophy at VTT has therefore been to concentrate on abundant polymers available from non-food sources and the process side and waste streams. A major contribution has been in specific on wood-based cellulose, hemicellulose and lignin derivatives, agro- and crustacean-based polysaccharides, such as pectin and chitosan, and various hydroxy acid polymers. Work with starch, VTT’s strong competence area, has led to hot melts with a low melting temperature and aqueous adhesives developed by chemically modifying starch and starch derivatives. In the packaging field, the various biopolymers can serve as films, coatings, ink components, and adhesives in lamination and box gluing. Cost-wise these materials can be competitive with the current commercial alternatives.

Polymers from natural sources, such as polysaccharides, tend to be excellent gas and grease/oil barriers owing to the high number of hydrogen bonds, but brittle and non-thermoplastic without a significant amount of additives. However, it has been demonstrated at VTT during, e.g., the EU Flexpakrenew project that xylan extracted from birch pulp, for example, can be chemically modified not only to improve moisture resistance and hydrophobicity but also to provide heat-sealing and thermoforming properties (Laine et al. 2008, Laine

As a result of the research work performed at VTT, wood-based xylan can be tailored into novel thermoplastic packaging materials, such as heat-sealable barrier coatings for fibre-based substrates or transparent films for thermoformed plastic cups and blister packs.

et al. 2012, Talja et al. 2010, Talja et al. 2013, Vähä-Nissi et al. 2012a). As presented in the chapter Novel hardwood hemicellulose applications by Harlin, xylan derivatives showed better barrier properties than PLA and reached the level of PET coatings. Likewise, xylan coatings can provide an excellent barrier against the migration of mineral oils from recycled board or printed surfaces.

Lignin, another major component of wood, was found to increase both the mechanical strength and hydrophobicity of fibre-based materials when added to fibre furnish. This helps to develop lightweight fibre-based materials or aim for more demanding high humidity applications. VTT has also developed kraft lignins modified with bio-based fatty acids as internal plasticisers (Tamminen et al. 2011). These modified lignins can be used as oxygen and water vapour barrier coatings on fibre-based materials thus providing an alternative to other biopolymers, such as PLA, or eventually oil-based polyolefins. See the chapter Lignin – New openings for applications for more details.

Poly(α-hydroxy acid)s are an interesting group of polymers – not least because hydroxy acids can be found both in nature and in process side and waste streams. The exploitation of the acids found in industrial waste or side streams has gained scattered interest despite some currently having well-established uses, in particular lactic acid. VTT, for example, has successfully synthesised novel polyesters based on mixtures of the three smallest α-hydroxy acids found in kraft pulping spent liquor (Mehtiö et al. 2011, 2012, Ropponen 2012). This suggests that a separation step of the monomers is not required. These copolymers may be used as hot-melt adhesives and heat sealable coating materials for fibre-based materials. Related materials based on lactic acid and functional precursors that are able to undergo cross-linking reactions have been developed. Such thermosets have been shown to exhibit improved properties, e.g. as a barrier layer in packaging applications. In addition, aqueous, optionally cross-linkable, dispersions based on such lactic acid polyesters have been developed and tested for easier and more sustainable application in paper and board manufacturing (Rämö et al. 2012).

α-Hydroxy acids have the potential to be produced by fermentation as they exist in the metabolic pathways of micro organisms. VTT has recently developed biotechnical production methods for glycolic acid (GA) from sugars. The emphasis has been on the use of yeast as production organisms due to their low pH tolerance compared with bacteria. These developments enable industrial exploitation of a bio-based GA for polymers. The focus of the research efforts at VTT has been on developing cost-efficient production and application methods to produce polyglycolic acid (PGA). In addition to being biodegradable, PGA has several outstanding properties such as very high barrier properties, good mechanical properties and high chemical resistance. VTT has developed proprietary production slurry polymerisation technology in which organic bases yield high molecular weight PGA with very short reaction times (Shan et al. 2011). The efforts to find new sustainable and cost-efficient production methods for PGA are on-going.

6.4 Upgrading biopolymers

Another challenge is to overcome the limited barrier properties of several bioplastics. This would enable either more demanding packaging applications or film down gauging. Natural polymers are hydrophilic by nature, and films produced from these materials are usually hygroscopic, resulting in a partial loss of their barrier properties at high humidity. Besides strong competence in the chemical modification of natural polymers, VTT has demonstrated other means to upgrade these materials. Expanded bioplastics are also an interesting option not dealt with in detail here, similar to nanocellulose-based materials, for used as, e.g., additives in films or to seal the surfaces of fibre-based substrates (work done in the EU project Sunpap). Cellulose solutions are presented in the chapter Success stories of cellulose by Qvintus in this publication.

A frequently applied method to enhance the strength, stability and barrier characteristics of plastics is to blend in a small amount

VTT has developed biotechnical production methods for glycolic acid currently produced from fossil resources. Its polymer, poly(glycolic acid), has outstanding properties. Its good gas barrier property, in particular, makes bio-PGA useful in various packaging applications as a barrier layer. The research emphasis is on technologies that enable cost reductions and deliver a competitive bio-PGA polymer to the market.

of inorganic nanoclays. Regardless of the polymer type or aqueous or melt processing used for film-making, proper dispersing and homogenisation is needed to ensure a sufficiently defoliated and nanosized structure. Biaxially oriented PLA films consisting of a small amount of montmorillonite were prepared (Härkki et al. 2011). Likewise, nanoclays were added to sugar beet pectin and chitosan (Vartiainen et al. 2010a, 2010b, 2010c). In the EU Flexpakrenew project, xylan was reinforced with nanoclays. The barrier properties were improved without sacrificing the other important properties. See the chapter Expanding the performance of bio-based hybrid materials by Nättinen for further details.

Cross-linking of chitosan-nanoclay and hemicellulose films was also studied (Laine et al. 2012, Vartiainen & Harlin 2011, Vähä-Nissi et al. 2012a). The moisture sensitivity of the films decreased as a result of cross-linking, leading to improved barrier properties against water vapour and oxygen. Cross-linking may thus be used as an effective tool to formulate hydrophilic biopolymer coatings for packaging applications.

VTT also looked into thin film deposition techniques, especially atomic/molecular layer (ALD/MLD) and atmospheric plasma deposition, as a way to improve the barrier properties of bioplastics. Packaging applications for thin metal oxide coatings have included lidstock, stand-up pouches, juice cartons, polymeric bottles, pharmaceutical and medical products, detergent powders and chocolates. The ALD/MLD is suited to producing high-performance, dense and pinhole-free thin films. The advantages over currently used deposition techniques also include low impurity content and mild deposition conditions in terms of temperature and pressure. The barrier properties of various plastics can be dramatically improved with a thin inorganic layer applied with ALD/MLD (Hirvikorpi et al. 2010a, Hirvikorpi et al. 2010b, Hirvikorpi et al. 2011a, Hirvikorpi et al. 2011b, Vähä-Nissi et al 2012b, Vähä-Nissi et al. 2012c). More recently, we used ALD/MLD to adjust the wetting and adhesion properties of different substrates. The atmospheric pressure plasma deposition, for example, was used to apply hydrophobic SiOx coatings to polyethylene-coated paper (Nättinen et al. 2011). The EU PlasmaNice project was one forum for developing VTT's plasma competence.

6.5 Conclusions

Sustainable packaging not only meets the changing demands of more environmentally aware consumers and more stringent requirements set by legislation but also enables, e.g., long-term business growth. Although sustainability as such has rarely been used as the main selling argument, the underlying thinking has changed dramatically in the last decades. One of the resulting packaging material trends has been the work towards bio-based materials based on renewable resources.

At VTT, new technology for producing bio-based webs with features typical of plastics was developed. The potential of these webs was demonstrated by the manufacturing of thermoformed products. In the area of biopolymers, VTT has worked with, e.g., wood-based cellulose, hemicellulose and lignin derivatives, agro- and crustacean-based polysaccharides, and hydroxy acid polymers to create films, coatings, ink components and adhesives. VTT also has tools to take the performance of these materials to a new level, such as fillers, chemical modifications and thin films.

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7 Research facilities

7.1 ALD technology: Ultrathin recyclable barrier coatings for packaging materials

VTT has developed an ALD-technology-based (Atomic Layer Deposition) method for the packaging industry to produce barrier materials that are thinner and lighter than traditional paper, polymer and foil laminates. Thin film formed on bio-based substrate using atomic layer deposition can offer a solution for replacing aluminium foil in packaging. Completely bio-based and recyclable barrier materials can be produced. The process does not require high temperature treatment. An ALD coating has been demonstrated to reduce the oxygen transmission rate and water vapour transmission rate of packaging materials.

VTT has a Picosun batch SUNALE^{TM} ALD reactor in a semi-clean room environment (as well as several ALD reactors in a clean room). The operating temperature of the reactor can be adjusted between 50 °C and 500 °C depending on the application. The ALD technique can be used to produce inorganic as well as organic coatings. Typical coating materials include Al_2O_2, TiO_2, SiO_2 and ZnO, and these can be formed on various packaging materials. The method has been demonstrated to function at unusually low temperatures of 80—100 °C and on various fibre-based and polymeric substrates. Conformal and precise coatings can be produced.

For more information on the ALD technique, possible research co-operation and trial services, please, contact:

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The ALD technique is based on sequential self-terminating gas-solid surface reactions. It can be used to form nanometre scale inorganic, organic and hybrid films from, for example, oxides, nitrides and sulphides. It is suited to producing high-performance coatings as it allows preparation of dense and pinhole-free inorganic films that are uniform in thickness following the topography and accessible pore structure. Current applications for the ALD cover catalysts to electroluminescent displays to microelectronics and beyond.

VTT has an ALD reactor suitable for versatile substrates and precursor materials beyond the usual because it is not limited to clean room conditions. In addition to barrier studies, it enables research on, e.g., flexible antimicrobial, conductive or contamination-free surfaces or non-flammable materials.

7.2 Biocomposite development and processing

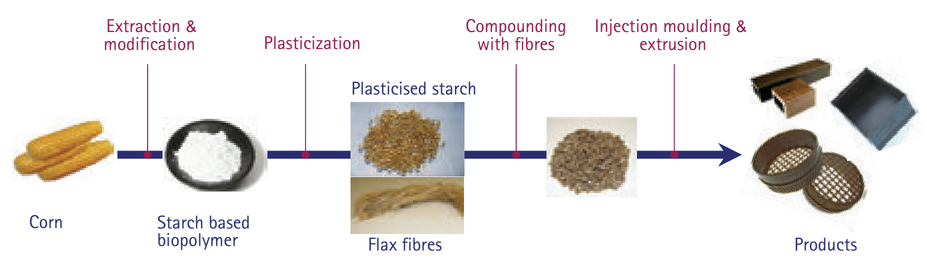
High-performance natural fibre composites have been developed at VTT for over a decade. The biocomposite research focuses on the development of material combinations of wood or versatile natural fibres together with oil and bio-based polymers as well as the development of new processing technologies suitable for these materials. The whole process chain from the preparation of biopolymer matrix materials, additives and coupling agents, to the fibre modification and, finally, to the processing of biocomposites is covered. VTT offers pilot-scale facilities for the processing of biocomposite materials.

Composite material development and processing facilities at VTT include:

- Polymerisation and modification of polymers and oligomers
- Fibre modification (physical, chemical, enzymatic)
- Batch mixing and pelletising
- Compounding from micro (6 g) to pilot scale (20–50 kg/h)
- Injection moulding
- Extrusion
- Compression moulding
- Foaming.

The processing development of biocomposites has brought improvements in plasticisation, compounding, injection moulding, extrusion moulding, multilayer structures and foaming technologies. Bionanocomposite formulation and processing technologies are also covered. Various characterising and analysing methods for biocomposite materials are also available at VTT.

The pilot-scale composite material processing facilities at VTT are comprehensive. There are three co-rotating twin-screw compounders, injection moulders and extruders for making films, coatings and profiles. The available pre- and post-processing methods include drying, milling, reactive compacting, orientation (MD-stretching and biaxial orientation), AC-corona film treatment and atmospheric plasma treatment.



Process chain example starting from corn starch raw material to final biocomposite products.

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7.3 Biomass fractionation and biopolymer modification

VTT has been profiled as a leading research and scale-up provider for the development of biomass-based chemicals and materials. The laboratory and pilot infrastructure specialises in process chemistry, fermentation and bio-processes to offer versatile equipment for biopolymer modification, pre- and post-treatment. Together with advanced analytical expertise, VTT has an excellent environment for the development of novel biomass fractionation and biopolymer modification technologies.

The fractionation facilities for forest and agro biomass include methods such as:

- Physical breakdown of complex biomass structures (chipping, grinding and ultrafine milling)
- Liquid-liquid and solid-liquid extractions
- Membrane separations
- Dry fractionation methods.

Added to these techniques, VTT has special expertise in the field of biomass fractionation in the use of supercritical fluids, preparative chiral chromatography, biomass treatment under pressure and catalytic reaction technology. The application areas vary from the biorefinery concept to the paper and pulp industry, as well as the food and beverage industry.

In many cases, the natural polymers or other components obtained from biomass are not applicable as such, but the properties have to be modified to meet the requirements of the target applications. VTT's expertise in laboratory and pilot-scale modification of natural polymers covers physical modification of natural fibre as well as versatile chemical and enzymatic derivatisations of polysaccharides (starch, cellulose, hemicelluloses) and lignin. VTT has also developed methods to use biogenic monomers in polymerisations targeting the bio-replacement of oil-based monomers in existing applications. In addition to the biopolymer modification, VTT has gained expertise in bio-based product formulations such as biopolymer water dispersions and organic pigment preparation technologies. These new technologies are based on 20 years of experience in biopolymer research and scale-up by VTT.

Pilot-scale processing facilities for biomass raw materials include:

- Multi-purpose reactor systems, 1–1800 dm^3, 10mbar–60 bar, -50–250 °C
- Special reactors for high consistency processing, 5–250 dm^3
- Separation units: decanter centrifuge, separators
- Filters: rotary vacuum filters, ultra and micro filters, Seitz filter
- Dryers: vacuum contact and spray dryers
- Falling film evaporators
- Extruders for plastic processing and reactive compounding
- Pilot fermenters 30–1200 dm^3

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7.4 Lignin analytics

Lignin analytics at VTT

VTT has first-class analytical facilities for the characterisation of the lignin structure and its material properties. Added to the strong competence and long history in the lignin chemistry, VTT provides an excellent environment for lignin research and the development of new lignin-based products.

Analytical methods for the structural characterisation of lignin include for example:

- Analytical pyrolysis (Py-GC/MC)
- Nuclear magnetic resonance (NMR) spectroscopy in liquid and solid state
- Size exclusion chromatography (SEC)

Pyrolysis-GC/MS is a valuable method for the structural analysis of lignin. It provides information about the substitution pattern of the aromatic subunits (H/G/S) and, to some extent, also about the lignin side chain structures. In addition to lignin samples, it is applicable to any biomass as such without the laborious lignin isolation. Insoluble lignin fractions, e.g. hydrolysis residue from bioethanol production, can also be investigated and some additional information on protein and carbohydrate residues obtained at the same time. As an additional benefit, only a very small amount (10 µg) of the sample is required.

For a more detailed structural analysis of lignin, VTT has five NMR instruments applicable to solid and solution state analysis (up to 600 MHz frequency). The 31P-NMR after sample derivatisation can be applied to quantitatively determine the lignin functionalities, i.e. the amount of aliphatic and phenolic hydroxyl groups and carboxylic acids, affecting lignin reactivity and solubility. In addition to the traditional 1D 1H-NMR, 13C-NMR spectroscopy, various 2D techniques can provide detailed information about the individual inter-unit linkages. Solid-state NMR also provides means to evaluate the structural features of insoluble lignins.

The molar mass of lignin can be evaluated by size exclusion chromatography (SEC) relative to external standards. Several methods and column systems (aqueous, organic) are available.

Techniques for the characterisation of the material properties of lignin include:

- Differential scanning calorimeter (DSC) equipped with an autosampler to analyse melting and crystallisation enthalpies and glass transition temperatures
- Thermal gravimetry (TGA) to evaluate the degradation properties
- Laser light scattering to analyse particle size distribution (wet and dry modules)
- Potentiometric titration method for lignin charge determination
- Zeta sizer equipped with titrator unit to analyse the net charge of colloidal particles
- Rheometer (StressTech) to measure, e.g., viscosity as a function of shear rate
- Light and confocal microscopical techniques with specific staining techniques to investigate the microstructure.

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7.5 Functionality with plasma treatment and coating

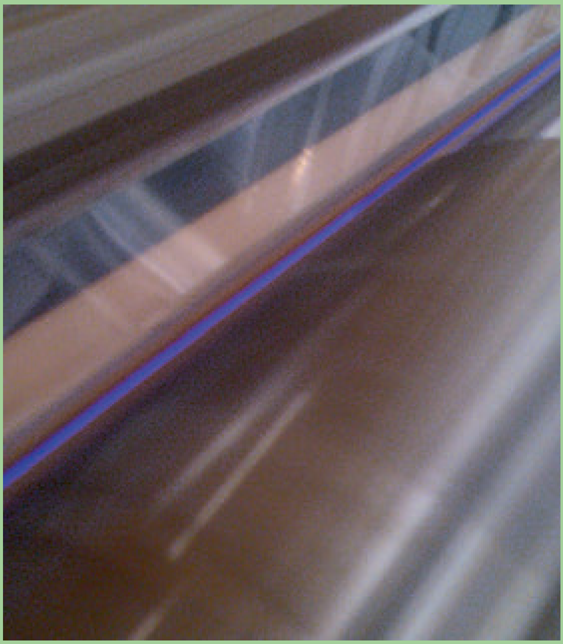
Atmospheric plasma technology at VTT

VTT has successfully developed atmospheric plasma technology for use with biopolymer films in order to improve barrier performance as well as film adhesion in coating applications. The available systems allow both experimental and pilot-scale treatment and deposition in inline conditions. Treatment of both sheets and R2R materials is possible. The method allows controlled tailoring of the surface chemistry and surface energy.

The atmospheric plasma technique is well suited to treating fibre-based materials as there is virtually no fibre melting. It can be used in-line and upscaled to high line speeds and web widths. The running costs of plasma treatment are low and there are no break downs.

In plasma treatment, a substrate surface is physically activated to tailor its hydrophilicity. It is used as a pretreatment method for painting, gluing and coating to improve adhesion between the different materials.

In plasma-coating, a substrate is coated with an aerosol of vaporised coating material. By this method, adhesion between hard-to-joint materials such as plastics and metals can be obtained. The application areas include high barrier coatings for packaging and moisture-sensitive products, hydrophobic coatings and corrosion protection of metals.



Atmospheric plasma station integrated into SUTCO pilot line offers a powerful tool for surface engineering.

For more information on plasma treatment and coating, possible research co-operation, and trial services, please contact:

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7.6 Surface treatment concept for fibre-based materials and plastics

VTT has created a roll-to-roll surface treatment concept (SUTCO) that can be used for coating and surface treatment of fibre-based webs and plastics. The concept includes several coating methods, pre-treatments and curing options. SUTCO line discards the idea of a fixed process.

The SUTCO pilot line consists of 16 individual components that can be connected as desired and the line set up according to research needs. It offers a possibility to trial new surface treatments for special applications with small material demands for fibre-based as well as plastic materials.

The main benefits of the surface treatment concept are low cost, low coating material demand and testing for a broad base of materials including all plastics, paper and carton board. The sealable coating unit followed by exhaust air removal during drying makes it possible to test coatings containing harmful volatile substances. Coating methods include flexo-type roll coating, soft bar coating, curtain coating and spray coating. All three of the first-mentioned methods can be followed be spray coating to make wet-on-wet coatings. Surface treatments can be cured using cold or hot air drying, IR drying or UV curing.

Operational units available for the SUTCO line:
- Corona
- Plasma
- Flexo-type roll coating
- Soft bar coating
- Curtain coating
- Spray coating
- Air dryer 5 pc
- IR dryer
- UV unit
- Winder
- Offline calendar.

Common features:
- Speed 3–90 m/min
- Web width 550 mm
- Roll diameter 500 mm
- Online coating, moisture and temperature monitoring
- Web material, either fibre- or plastic-based.

For further information on surface treatment co-operation possibilities in research and trial services, please contact:

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Title	Research highlights in **industrial biomaterials 2009–2012**
Author(s)	Harlin, A., Qvintus, P., Poppius-Levlin, K., Nättinen, K., Heikkilä, P. and Vähä-Nissi, M.
Abstract	Industrial biomaterials 2009—2012 summarises the key findings and inventions developed during the VTT's Industrial biomaterials spearhead programme. In the field of bio-economy, the Industrial biomaterial spearhead programme focused on renewing industry by means of emerging technologies of materials and chemicals based on non-food biomass, including food side streams, agricultural left-overs and natural material waste fractions. This publication focuses on the development of novel biopolymers and production technologies based on lignocellulosics, such as hydrolysed sugars, cellulose, hemicelluloses, and lignin. The spearhead programme's main achievements include the development of nanocellulose products, new packaging films and barriers from nanocellulose, hemicellulose and lignin, new production methods for hydroxyacids and their polymers like high performance bio-barrier PGA, the development of novel biocomposites for kitchen furniture, and textile fibres from recycled pulp.
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