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Research highlights in
industrial biomaterials

VTT RESEARCH HIGHLIGHTS 2

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industrial biomaterials

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Contents

Industrial biomaterials as an emerging business 4
CoE White Biotechnology – Green Chemistry (CoE WB-GC) 7
Future Biorefinery (FuBio) Programmes 9
Nanocellulose research at VTT 10
Towards sustainable packaging 13

Bio-based mono-, di- and polymers

Sugar acids – Building blocks for a bio-based future 16
Inversed esterification – Reactivity of aliphatic diacids with aromatic diols 21
Polyesters based on hydroxy acids obtainable from black liquor 25

Modification and analysis of hemicellulose and cellulose

Hemicellulose and cellulose modifications 31
Hemicellulose on PVA 35
Superadsorbents and hydrogels 37
Surface analysis and water interactions of biomaterials using QCM-D 46

Barriers and ALD-technique

Packaging barriers from renewable sources 52
Biaxially oriented PLA-montmorillonite-nanocomposite for barrier film applications 59
Atomic layer deposited thin-layers for upgrading bio-based materials 63
Nanotubes and nano-coral by the fibre template method 69

Bio-based latexes and adhesives

Development of bio-based latexes for paper coating applications 76
Bio-based adhesives 79

Demonstrators

Packaging demonstrators 83

Industrial biomaterials as an emerging business

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Bio-economics is defined as the means to create sustainable prosperity by applying renewable raw materials. The original Brundtland Agenda combines environmental, economic and social aspects, and it was approved as a United Nations agenda in the mid-80s. Recently, and much later, the OECD has improved the agenda by adding more tangibles and a framework. The political debate is gradually turning into concrete targets and pathways leading us towards restricted availability of oil and, especially, water.

The main drivers of the bio-economy are increasing consumption and population combined in a way that will avoidably lead to some crises when the limits of the volumetric growth are met. The issues are broader than just energy, carbon dioxide and global warming. The problems lie in the availability of food or the land area to produce it, quality of water, and future sources of housing and clothing. The long-term concerns are also becoming of interest to people in different ways, such as worries over food quality, plastic waste and sustainable living environments, and we are also increasingly seeing conflicts based on control of still productive land areas.

The scale of influence is still restricted, but none of the growing problems is declining. Natural resources are already hitting all-time highs and economic depression is the only thing temporarily reducing the need to find new raw material sources. The issue is no longer only about one sector of the economy, the lack of a renewable raw material base is penetrating all industry and influencing the economic growth and prosperity of nations.

The availability of raw materials is currently controlled by applying easily convertible reserves like oil and ferrite. Raw materials are used more than biosphere is able to produce and further much of it is wasted. Put simply, the consumption of raw materials is at an unstable and unsustainable level in the long term. There are thus simply not enough bio-materials to easily replace the current use of materials. This will lead to adaptive measures in consumption patterns and hopefully also efficiency of energy and material usage. This means that we will not enter a bio-economy straight away but through a metamorphosis in the industries that may take a few decades.

Business concepts for the bio-economy transition period come either from ideas, replacements or renewals with alternative products. Replacement is simply an attempt to produce existing products from new raw materials such as biomass. Several technical routes are available, but the question is predominantly one of cost, while the products are well known. In the longer term, certain valuable goods will have to be produced through a replacement route. A renewal route would require the development of new consumption habits and be more demanding but enable broader development of business.

Behind both concepts there are still the solid laws of the consumption society and of measuring the value of the good, applying mainly material as a cost-carrier. Later, it will also become obvious that novel products will require additional elements such as services, maintenance and second-hand retailing. Furthermore, the functions and use of the products will also have to develop to meet upcoming requirements, such as a long service life.

The added value of the products does not come from their materials but their function. If the wrong material is used, the consequences may be markedly greater than the original benefits gained from the material selection. Examples range from wasted food when packaging has failed to moisture-damaged housing, not to mention related human losses such as health. In the design and selection of the materials, the actual use and requirements always come first.

The feasibility of applying bio-based materials is related to access to the fractions, especially where the biomass is collected together in sufficient quantity and of high enough quality to be fractioned by reasonable techno-economic methods. The issues lie in the complication of converting the fractions into industrially viable materials and the variation and sensibility of the biomaterials. Conversion and selectivity limitations can both be partially solved by means of energizing the residuals, like black liquor being burned in chemical pulping. This leads us to the development of completely new processes but also in search of added-value products for which the biomass has a real benefit.

The time to market is becoming shorter all the time. Consumer preferences for sustainable goods have been recognized by brand owners and retailers. New products are seen everywhere and business is developing from experiments to sales. Development has been fast in fields such as renewable packaging, and there is interest in applying bio-based materials to designer goods ranging from furniture to automobiles. New products based on available materials are coming onto the market rapidly.

Customers are differentiated into several groups, from green consumers through the preferred LOHAS (Lifestyles of Health and Sustainability) segment to consumers who are less interested or even reject considerations of adopting bio-based solutions. It is notable, however, that the more positively positioned customers are young and less settled. In these circumstances the development can be either accelerated or restricted based on the availability of and publicity given to the renewable material option. This communication also requires a high level of expertise and transparency because the target customer groups are highly intelligent and knowledgeable of the facts and background. New designs and creativity are also required to provide visibility of the renewed offering.

The technical concepts that are developed focus on access to raw materials that solve the issues of collection and fractionation of precursor molecules and polymers suitable for application to the added-value materials. There is also focus on attempts and developments to try to understand the products that could be manufactured in a highly sustainable way that can be valorized. The main challenges lie in the issues of integrating the new technologies into existing industrial and business ecosystems and trying to reach the level at which both the required operational cost and investments can enable renewal of the business.

One example of the issues is the way the distance to the raw material sources is solved because of the low content of the added value component, which does not typically support ideas of being transported long distances. Here, distributed harvesting and fractionation in which the value-added materials are sent further and residuals are applied locally, for example, energy and fertilizers, are motivated. Another concept is to use large volumes ad hoc where they are available, such as in side-streams of pulp and paper or food production. Here, recycling is also of great importance.

All the achievements in real economics are possible, however, through solutions that provide customers with the desired and valuable function they really need. In our programme we focus on new material solutions. We look forward to new applications for high-performing materials that cannot only replace but also solve bottlenecks and limitations, whatever they may be in the current products. This publication provides some examples of the technical solutions developed for the purposes. We are fascinated by the possibilities the bio-economy will open to national offerings to solve global demands.

Keywords: non-food biomass, biomaterials, packaging, nanocellulose

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

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The Finnish Centre of Excellence in White Biotechnology – Green Chemistry Research is a status that has been given to VTT by the Academy of Finland for the years 2008-2013. The CoE is committed to developing new biotechnological and chemistry methods for the efficient production of chemicals and materials from renewable natural resources. 'White' or industrial biotechnology combined with 'green chemistry' has a vital role to play in developing sustainable production processes that can help save energy and the environment.

A considerable improvement is needed in the efficiency of bioprocesses before they can be considered a serious alternative to petrochemical industrial processes. One of the challenges is to get microbes, i.e. the production organisms used in bioprocesses, to convert the sugars contained in biomass into the required compounds as effectively as possible. This development effort requires a wide range of skills and knowledge from biosciences to engineering. The CoE brings together the relevant expertise available at VTT in the fields of biotechnology (molecular biology, enzymology, bioprocess technology), chemistry (synthetics, polymer chemistry), systems biology (bioinformatics, mathematical modelling) and engineering sciences (micromechanics, measurement technology, nanotechnology).

The aim of the CoE is to develop new technologies for the production of new biomaterials. Microbial cells are engineered to produce useful new compounds from plant biomass sugars. Sugar acids and their derivatives (e.g. xylonic, arabonic, galactonic, 2 keto-3 deoxy galactonic and galactaric acids) are produced by applying the tools of genetic technology to engineering the metabolism of microbes. These compounds have many industrial applications, for instance, as precursor molecules in the production of new bioplastics. The produced molecules are then further modified chemically and used in material applications (e.g. cross-linkers in absorbent applications) or polymerized into new biopolymers. The CoE also has two important supporting activities. One is to develop sensitive measurement techniques, e.g. new measuring devices based on micro and nanotechnologies that can be used to measure and control the productivity of microbes in bioreactors during production. Another is to use genome-wide methodology and bioinformatics to understand cell function and mathematical modelling to generate (predictive) mathematical models of the production organisms.

The CoE activities were evaluated in June 2010 by international Scientific Advisory Board members. The Academy of Finland granted a three-year continuation period for the CoE for the years 2011–2013.

Some of the key CoE achievements during 2011 include:

- Sugar acid production using various yeast and filamentous fungal species has been addressed. Due to the intrinsic differences in acid tolerance and other physiological traits, clear differences in acid productivity were observed. Species with superior titres and production rates will generally be well suited to the development of industrial processes for organic acid production.

- Glycolic acid production with yeast has been demonstrated. Glycolic acid is a valuable monomer for bioplastics production. Yeasts have been genetically engineered to improve their metabolism towards increased glycolic acid production. Yeasts provide potential hosts for low pH production, which is expected to provide significant downstream processing benefits.
- Polymerization processes for glycolide, the cyclic dimer of glycolic acid, have been investigated in detail. A ring-opening polymerization that proceeds rapidly in ambient conditions has been developed and provides a cost-efficient route to polyglycolide (PGA). The PGA polymer has been processed and its beneficial properties confirmed.
- Together with the newly established VTT/MSI Institute for Bioengineering (Berkeley, USA), single cell monitoring tools have been used to address intracellular pH, productivity and cell death in cultures producing organic acids. This work aims to control acid production at individual cell level in order to obtain the highest overall productivity in a process.

Future Biorefinery (FuBio) Programmes

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Forestcluster Ltd, one of the six Strategic Centres for Science, Technology and Innovation in Finland, was established in 2007. This private-public partnership plays an important role in implementing the National Research Strategy of the Finnish forest sector. Forestcluster Ltd is owned by nine companies from the forest industry, VTT, the Finnish Forest Research Institute Metla and eight universities.

Future Biorefinery (FuBio) is one of the major research directions of Forestcluster Ltd. The main objective of the five-year FuBio entity is to establish globally competitive knowledge platforms, in Finland, in the area of bio-based economy, for the renewal of the existing forest industry and the creation of new business. More specifically, FuBio is developing competences and technologies that will form the basis of new value chains in which wood components are refined into new products for substantial global markets. Some of the potential markets are well known to the forest industry (e.g. fibre-based packaging), but most are essentially new to it (e.g. textiles, nonwovens, polymers, resins and thermoformable composites). Hence, FuBio is looking, in particular, at novel bio-materials and bio-chemicals.

The research work within FuBio was started in March 2009, when the first two-year research programme ('FuBio JR 1') was initiated. It had a total volume of app. 19 million euros. The main financers of FuBio JR 1 were Tekes (BioRefine programme) and the industrial owners of Forestcluster Ltd. In June 2011, two, three-year follow-up programmes were started. FuBio JR2 is the larger one, taking forward opportunities linked to, for instance, bio-plastics, bio-barriers and extractives with health benefits. The FuBio Cellulose programme is focused at value chains, in which cellulose is dissolved, regenerated and then uses as textiles, chemicals or nonwovens.

VTT plays an important role in the execution of FuBio, both in the research and development as well as in the management of the programmes. The input by VTT in FuBio is part of the VTT Industrial Biomaterials spearhead programme. Examples of VTT-related research topics in FuBio are lignin/fibre composites, biomass-derived barrier materials, mouldable and translucent fibre webs, novel bio-polymers and process/factory modelling.

Some of the main achievements of FuBio, so far, have been compiled into a public programme report that is available at www.forestcluster.fi (see under 'Publications').

Nanocellulose research at VTT

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Nanocellulose has been shown to have the potential to be very useful for a number of technical applications in the future. 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 the production process and the modification of nanocellulose material according to the needs of various applications.

The successful use of nanocellulose in different applications requires a profound understanding of the structural and molecular properties of nanocellulose. The most important properties can be grouped as follows:

- Aspect ratio. The diameter and length of the fibrils.
- Range of polydispersity. The preparations are usually mixtures of fibrils with different size distributions.
- Surface chemistry. How the surface has been modified by adding chemical functionalities, such as charge, hydrophobic groups, etc.
- Presence of impurities and other polymers. Nanocellulose rarely consists only of cellulose; the presence of other compounds may have a major impact on the properties of the preparation.
- Currently, nanocellulose research at VTT can be divided in four main research areas (Figure 1):
- soft matter – emulsions, encapsulation, stabilization of dispersions, hydrogels
- condensed matter – composites
- porous matter – filters, adsorbents, scaffolds
- thin films – barriers, supports, adhesive layers.

Raw materials
In principle, it is possible to use any type of material containing cellulose as a source of nanocellulose. Currently, wood and pulp-based methods receive most focus and are the approach selected by industry. Other possible raw materials include annual plants (grass, cotton, bast fibres and leaves), fruits and vegetables, marine sources, bacterial sources and biomass side-streams.

Processing
One large cost of producing nanocellulose comes from the energy input required for defibrillation of the starting materials. The processing energetics come from understanding the fundamental thermodynamics of the system as well as the most energy-efficient route towards it. The surface properties of nanocellulose affect its processability and the efficiency of production. Different types of modifications may prove efficient for facilitating production and resulting in surface-functionalized nanocellulose that may be advantageous in different applications.

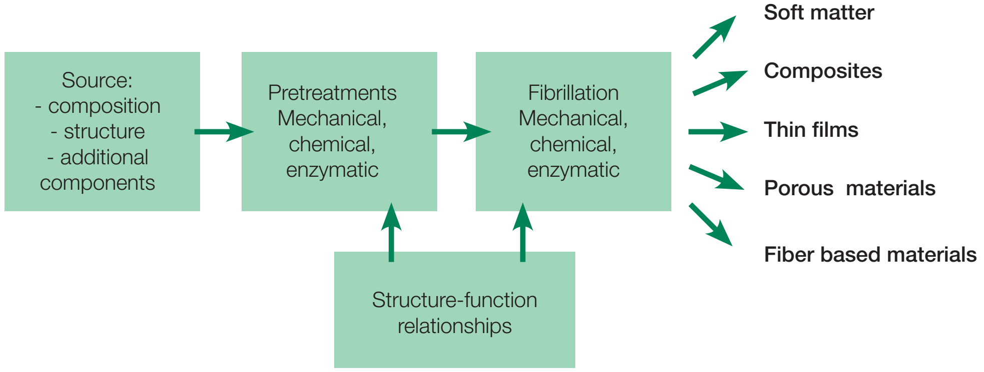

Figure 1: Flow of material and steps during nanocellulose processing. A strong link in understanding the whole chain, especially how the starting points affect applications, gives versatile and competitive expertise for developing applications and technology.

Characterization

One cornerstone of nanocellulose research is a well-functioning set of analytical techniques to characterize the nanocellulose during its production and as part of the final products. Skilled personnel and state-of-the-art equipment are required, especially for the techniques of electron microscopy, atomic force microscopy, rheological behaviour and surface properties.

Safety

Safe handling and use of all nanomaterials are an essential part of the research in this field. Although nanocellulose is a natural material and part of our biological environment, responsible use requires all potential aspects of safety to be addressed.

Standardization

The expanded use of nanocellulose will lead to a demand for materials that have predefined and predictable properties. Standardization may also become a necessity due to the requirements to demonstrate safety.

Recent achievements of NFC product demonstrators

In January 2012, VTT published a press release related to the production of transparent plastic-like packaging material from birch fibril pulp. The NFC films were on a pilot scale. VTT Technical Research Centre 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, e.g., food packaging to protect products from spoilage.

Nanofibrillated cellulose typically binds high amounts of water and forms gels with a dry matter content of only a few per cent. In the manufacture of the films, the 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 pressurized 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 ‘mark’ on the film that has a negative impact on the evenness of the surface.

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. Thanks to the management of the spreading, adhesion and 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. 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.

VTT and Aalto University are applying for a patent for the production technology of NFC film. The 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 included in the Finnish Centre for Nanocellulosic Technologies project entity formed by UPM, VTT and Aalto University. The nanofibrillated cellulose grade used was UPM Fibril Cellulose supplied by UPM.

Strong industrial partnership

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

Towards sustainable packaging

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Packaging has become an integral part of everyday life in modern society. The way a society does or does not use different packaging reflects the degree of general advancement in the society. A common sight in today's Western culture is the busy commuter having a mobile breakfast on the go, while the less developed cultures of the globe are still struggling with the issues surrounding health and hygiene of food and drink, which were some of the early drivers of the packaging industry.

As a result, the increase in the volume of packaging used today is due to the growth in developing countries, while in the Western World the growth of the packaging industry comes only from developing better quality properties and added value. Furthermore, the requirements for quality have been increasing, especially in relation to the usability, environmental friendliness and safety properties of packaging.

Sustainable packaging should ideally be designed together with the product to fulfil its performance requirements during its life cycle with minimal environmental and social impact. The most important functions of sustainable packaging are preserving, protecting and delivering the product, thus minimizing food waste and product loss.

From the consumer's point of view, packaging is typically considered to have only a secondary and a temporary function to protect the contained product until the right time and place of consumption. After the consumption, the packaging becomes redundant, which has led to litter-related issues and consequently to new packaging waste management concepts in several countries.

VTT has consistently kept the emphasis on sustainable packaging material development towards renewable and fibre-based packaging components in order to make the waste management efforts easier and simultaneously give material sourcing an alternative alongside the synthetic petrochemical-based polymers.

VTT is active in barrier development with its fibre-based barrier protection concepts, developing several variants of renewable barrier materials, with different properties for different applications. VTT's strength lies in the width of experience and multitude of scientific initiatives, which can give several possible solutions to any given theme simultaneously. This enables selective use of VTT's expertise and IPR in various markets without ending up with conflicts of interest, and the benefit of this has indeed been demonstrated in the field of commercial barrier developments.

In 2012 and beyond, VTT will enhance its approach to the packaging value chain by taking an increasingly customer-driven path to the future. This will involve a dual concept of searching for an ideal way to combine the needs of the packaging value chain and VTT's technology offering with an optimal outcome.

By definition this means that we will need to re-evaluate and add features to VTT's current packaging technology offering and, at the same time, be selective with regard to the fields of packaging research in which we want to be present. VTT needs to become increasingly international in its approach so that we obtain maximum exposure for the international packaging value chains.

In order to drive pragmatic changes in the packaging converting industry, VTT will enhance its networking with the manufacturers of converting machines and with the converters themselves. Until now, plastic packaging converting and fibre material converting have been completely separate technologies in the industry, each with its own type of converting machines. This will change with VTT's approach of searching for hybrid materials, with fibre-based materials coming closer to the behaviour of synthetic polymers even in terms of converting. This will most probably lead to partial merging of converting technologies, with, for example, fibres being both extruded and injection moulded.

Various initiatives for mechanical strength and stiffness of corrugated boards, cardboard and possible new hybrid concepts will be pursued for standard and extreme atmospheric conditions using the multiple scientific initiatives that are filtered through VTT's scientific platform.

VTT's development of renewable packaging materials has advanced promisingly during 2011. The development, which includes novel bio-based barriers and adhesives, has given a strong scientific platform for the Industrial Biomaterial programme. The basic science has created initiatives that have led to innovative applied research projects, which have now largely moved towards commercialization programmes.

Bio-based mono-, di- and polymers

Sugar acids – Building blocks for a bio-based future

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In 2004, the Department of Energy (U.S.A.) published a report listing chemicals that could potentially be derived from plant biomass and further defined those that would be most useful as building block chemicals, i.e. molecules that can easily be transformed into a variety of other useful molecules, including but not limited to polymers. Of the top 30 potential candidate molecules, 16 were organic acids, with 10 included in the 15 chemicals with the most potential[1]. VTT has been studying and developing the production of several acids derived from the sugars of plant biomass hydrolysates. Among these are D-xylonic[2-4] and L-arabonic[5] acids derived from the 5-carbon sugars D-xylose and L-arabinose, and galactaric[6], L-galactonic and 2-keto-3-deoxy-L-galactonic[7] acids derived from the 6-carbon sugar D-galacturonic acid found in plants with a high pectin content.

The bio-based production of sugar acids requires enhancement of production via existing biosynthetic pathways, the reduction in carbon loss to alternative by-products and/or the addition of new biosynthetic routes to suitable production hosts. Environmental conditions for high production levels are also considered and optimized.

D-Xylonic Acid

D-Xylonic acid is derived from D-xylose by oxidation (Figure 1). Although D-xylonic acid could be used as a buffer or chelator, e.g. as a substitute for glucose-derived gluconic acid[8], it is not yet produced in bulk. D-xylonate has also been shown to be useful in the production of copolyamides[9] and as a precursor of 1,2,4-butanetriol[10].

VTT has developed various production hosts for the production of D-xylonic acid from pure D-xylose and from plant biomass hydrolysates with high D-xylose content.

Gluconobacter oxydans (Figure 2) is one of the best-known producers of D-xylonate. VTT has also developed various yeast (Figure 2) as alternative hosts for its production. Yeast have better tolerance to plant biomass hydro-

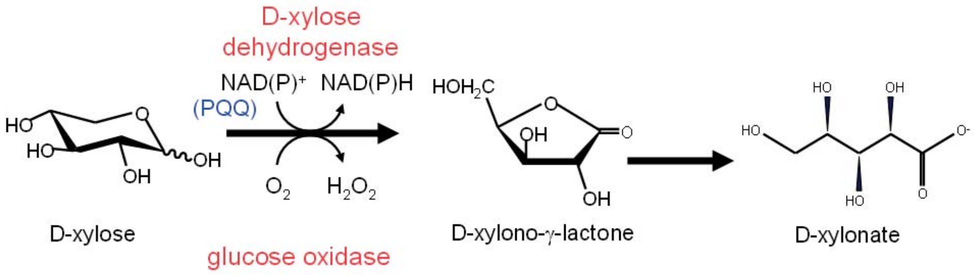

Figure 1. Synthesis of D-xylonate by enzymatic oxidation of D-xylose.

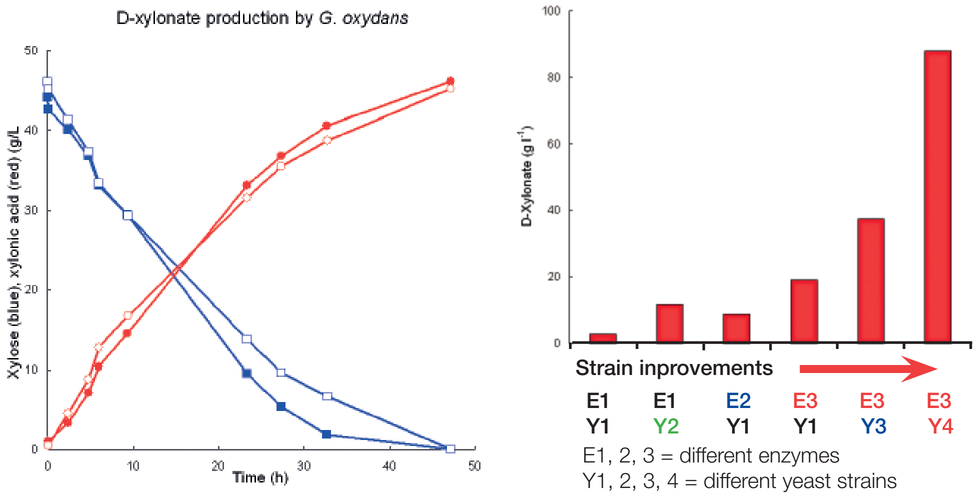

Figure 2. Production of D-xylonic acid by Gluconobacter oxydans (left) and yeast (right) from D-xylose l^{-1} at pH 5.5.

lysates than *G. oxydans* and produce fewer acid by-products, although some D-xylose may be converted into xylitol. In order to produce D-xylonic acid, the ability to produce the enzyme D-xylose dehydrogenase (Figure 1) is introduced to a suitable yeast host. By expressing the right enzyme in the best host, yeast strains have been constructed that produce D-xylonic acid at titres and rates comparable to those obtained with *G. oxydans*. By also studying and understanding the physiology of D-xylonic acid production, further improvements in the production process can be achieved.

Galactaric acid

The current industrial production of galactaric acid involves oxidation of D-galactose with nitric acid, an expensive process generating toxic waste material, or electrolytic oxidation of D-galacturonate. Galactaric acid can also be microbially produced by enzymatic oxidation of D-galacturonate (Figure 3). Galactaric acid is used as a chelator and dispersant, e.g. in skincare products, and has potential applications in polymer synthesis[11].

Galactaric acid has been produced from D-galacturonic acid by *Hypocrea jecorina* (alternative name, *Trichoderma reesei*) by intro-

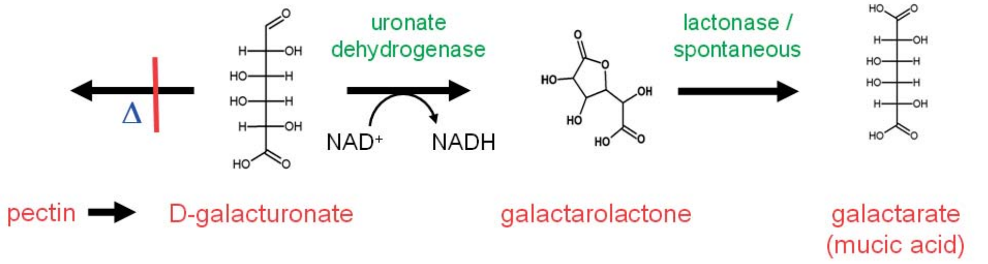

Figure 3. Biosynthetic pathway for galactaric acid production. In some organisms, a native pathway for D-galacturonate metabolism must first be disrupted (Δ). The substrate may be D-galacturonic acid or the pectin from which D-galacturonic acid is derived.

Figure 4. Galactaric acid produced from D-galacturonic acid by Hypocrea jecorina, purified by acid precipitation[6].

ducing a uronate dehydrogenase gene into a strain from which the native D-galacturonate reductase had been deleted[6]. Concentrations of 7 to 10 g galactaric acid l^{-1} have been produced. Galactaric acid presents an interesting challenge for biological production because of its low solubility. This low solubility, however, makes it possible to readily recover galactaric acid of high purity, suitable for further chemical reactions (Figure 4).

2-Keto-3-deoxy-L-galactonic acid

D-Galacturonic acid also serves as a substrate for the production of 2-keto-3-deoxy-L-galactonic acid, another chemical with potential use as a chelator, clarifier, preservative or plastic precursor. Keto-deoxy sugars are also useful precursors for further derivatives, e.g. in the synthesis of medicinal and other compounds. Keto-deoxy-L-galactonate is a natural intermediate in the fungal D-galacturonate metabolic pathway (Figure 5), and thus keto-deoxy-L-galactonate can be produced in a simple biological conversion.

2-Keto-3-deoxy-L-galactonic acid accumulates extracellularly in cultures of *Aspergillus niger* and *Trichoderma reesei* in which the native keto-deoxy-L-galactonate aldolase has been disrupted when it is grown or incubated in the presence of D-galacturonate (Figure 6). *A. niger* is more efficient in the production of 2-keto-3-deoxy-L-galactonic acid than *T. reesei* and is also able to produce it directly from the cheaper substrates pectin and polygalacturonic acid. 2-Keto-3-deoxy-L-galactonic acid has been purified by ion exchange chromatography.

Conclusion

A limited number of organic acids (e.g. acetic, citric and lactic acids) have a long history of industrial-scale microbial production. The past decade has seen a significant increase in the range of organic acids that can be produced at substantial titres. Some, such as D-xylonic acid, are now being produced at titres and rates relevant to industrial exploitation. There is also increasing awareness that different host strains offer unique benefits for the production of specific acids. *A. niger* has a long history of use in the production of citric and gluconic acids and has been shown to be a good choice for the production of 2-keto-3-deoxy-L-galactonic acid production. It is

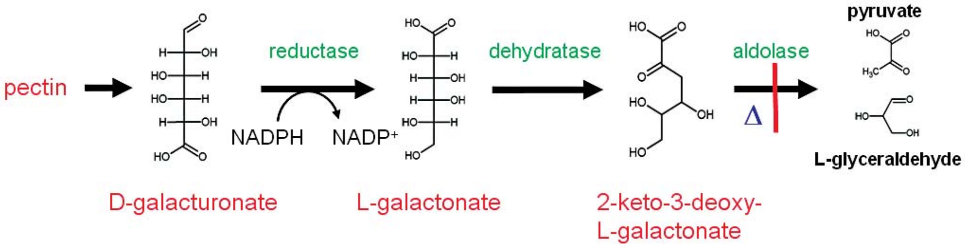

Figure 5. Biosynthetic pathway for 2-keto-3-deoxy-L-galactonic acid production in filamentous fungi[12].

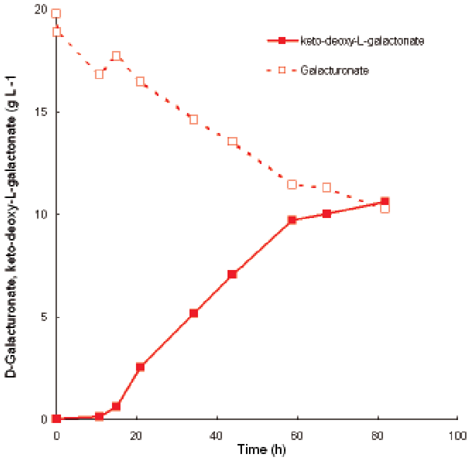

Figure 6. Conversion of D-galacturonic acid into 2-keto-3-deoxy-L-galactonic acid by A. niger[7].

also suitable for consolidated processes. *T. reesei*, although not known as an acid producer, has been found to be a good source of galactaric acid. Several yeast strains with high tolerance to plant biomass hydrolysate inhibitors are being developed for the production of D-xylonic and L-arabonic acids. With acids such as these now being produced in quantities of ten to one hundred grams per litre, the development of novel applications, particularly in the area of polymer chemistry, becomes feasible and will lead to novel bio-derived compounds from plant biomass.

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Inversed esterification – Reactivity of aliphatic diacids with aromatic diols

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Aromatic polyesters constructed from aliphatic diacids and aromatic diols are studied less extensively than the corresponding polyesters of aromatic diacids and aliphatic diols, such as polyethyleneterephtalate. Polyphenyl esters of this type have been produced from bisphenols or aromatic alcohols together with diacids[1-8]. A series of oligoesters with a poly(arylene-co-alkylene dicarboxylate) structure were prepared from aliphatic diacids of chain lengths from two to eight carbon atoms together with hydroquinone. The polymerization reactions were carried out by interfacial polycondensation and for poly(p-phenylene adipate) also by melt polycondensation. The polyesters formed were analysed by NMR, DSC, TGA and FT-IR. This study is aimed at demonstrating a platform for further studies with six carbon sugar diacids.

Materials and methods

Hydroquinone (99%), diethyl oxalate (99%), adipoly chloride (98%), glutaryl chloride (97%), pimeloyl chloride (98%), succinyl chloride (95%) and suberoyl chloride (97%) were purchased from Sigma-Aldrich and used as such. Hydroquinone diacetate was synthesized from hydroquinone with acetic anhydride in pyridine according to Drewitt [4].

^1H and ^{13}C NMR spectra were detected with a Varian 300 spectrometer in DMSO-d and in HFIP-d. FT-IR spectra were recorded with a Bruker Equinox 55 and an IR-microscope IRScope II. The thermal properties were analysed with a Mettler Toledo DSC820. The glass transition temperatures were analysed from the second heating curve between -45 and 200°C at a heating/cooling rate of 10oC/min. Decomposition temperatures were analysed from a heating curve of 20.0–550.0°C at the rate 20°C/min. A thermogravimetric analysis, including temperatures of 10 wt% decomposition ($T_{dec10\%}$), was conducted with a Seiko TG/DTA320 Instrument.

Polyesterification procedures

Poly(phenylene succhinate) (PFS), poly (phenylene glutarate) (PFG), poly(phenylene adipate) (PFA), poly(phenylene pimelate) (PFPim) and poly(phenylene suberate) (PFSub) were prepared by interfacial polycondensation[3] without surface active agent, e.g. 4.0 g NaOH and 5.5 g hydroquinone were dissolved in 300 ml distilled water, and 7.75 g succinyl chloride (or equimolar amount of another diacid chloride) was dissolved in 150 ml chloroform. Solutions were rapidly combined and mixed for 10 min at ambient temperature under N_2 flow. A white precipitate formed immediately. Chloroform was evaporated under reduced pressure to ensure coagulation of the polymer. Polymer precipitate was filtered off, washed twice with distilled water and dried in a vacuum at RT for 12 h.

Poly(phenylene adipate) 2 (PFA2) was prepared by interfacial polycondensation including a surfactant[9], and 4.0 g NaOH and 5.5 g hydroquinone were dissolved in 300 ml distilled water under N^2 flow together with 3.0 g of sodium lauryl sulphate. Adipoyl chloride

(9,145 g) was dissolved in chloroform (150 ml) under N^2 atmosphere. The solutions were mixed together quickly and stirred for 15 min. Chloroform was evaporated under reduced pressure, and the product was filtered and washed several times with water to remove monomers and surfactant. The purification was tedious due to the foam introduced by the surfactant. The product was dried in a vacuum oven at RT for 12 h.

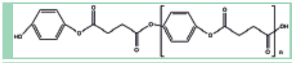
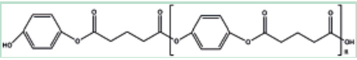
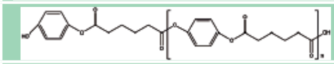
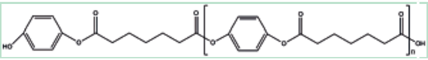
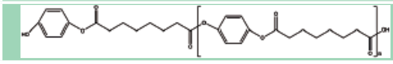
Poly(phenylene adipate) 3 (PFA3) was prepared by melt condensation to compare the effect of the polymerization method on molecular weight. Equimolar amounts of hydroquinone diacetate and adipic acid were mixed in a glass flask and heated in an oil bath at 220°C under N^2 flow for 2 h after which pressure was reduced to 250 mbar for 2 h. Brown solid material was obtained and purified in a vacuum at 150°C for 2.5 h to evaporate unreacted monomer and acetic acid.

Results and discussion

The structures and properties of poly(phenylene alkylene dicarboxylates) prepared by interfacial polycondensation are shown in Table 1. The yield was best for poly(phenylene adipate) consisting of six carbon diacid chloride. The other polymers with an even number of carbons in the aliphatic diacid units (PFS, PFSub) also gave better yields than those with an uneven number of carbons. Youk et al. have reported that polymers with an even number of carbon atoms in the aliphatic unit lead to higher heats of fusion and thus higher melting temperatures and faster crystallization[10]. The thermal resistance seemed to be in accordance with this finding: an even number of carbons in aliphatic diacid generally led to a higher peak decomposition temperature. Poly(phenylene glutarate) did not follow this trend, however, it started to decompose at lower temperatures compared with PFS and PFA, when comparing the T_{dec}10 % temperatures. The products were insoluble in chloroform and tetrahydrofuran. Thus, size exclusion chromatography (SEC) could not be used to verify the molecular weight.

The ^1H and ^{13}C NMR spectra (Figure 1) showed that the molecular weights obtained were low, only oligomeric products were gained, judging from the extent of the non-esterified end group signals. These oligomers were, however, considered sufficient to determine the polymerizability, ester bond structure and thermal resistance of the polymers. The preparation of longer chains would require optimization of the polymerization conditions in terms of monomer purity, additives, solvents and reaction time.

Table 1. Properties of poly(phenylene alkylene dicarboxylates). T_{dec}10 % is measured by thermogravimetric analysis. Glass transition temperatures T_g are given as the peak values measured by differential scanning calorimetry (DSC).

Name	Sturcture	Yield [%]	Chain lenght	Tg10% [°C]	Tdec [°C]
PFS		80.6	oligomeric	225.8	230
PFG		60.2	oligomeric	202.5	400
PFA		86.7	oligomeric	246.4	340
PFPim		29.0	oligomeric	271.8	449
PFSub		55.2	oligomeric	244.7	458

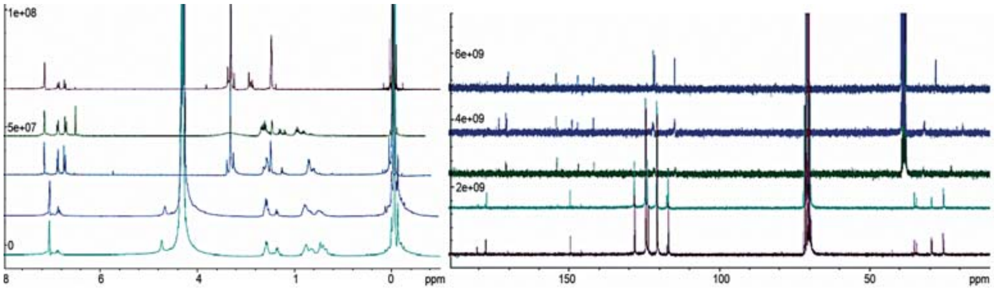


Figure 1. 1H NMR (left) and 13C NMR (right) spectra of poly(phenylene dicarboxylates) prepared by the interfacial polycondensation method from the top: PFS in DMSO, PFG in DMSO, PFA in DMSO, PFPim in HFIP and PFSub in HFIP.

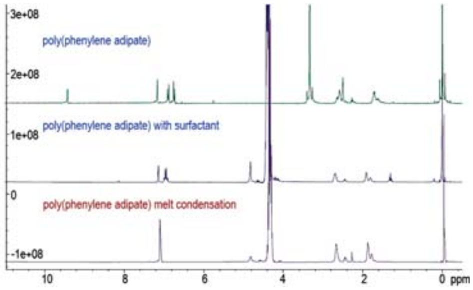


Figure 2. 1H NMR spectra of PFA prepared by interfacial polycondensation (above) recorded in DMSO by interfacial polycondensation with the addition of a surface-active agent (PFA2) (middle) and by melt condensation (PFA3) (below) recorded in HFIP.

Poly(phenylene adipate) was prepared by three different methods. The highest molecular weight was achieved by melt polycondensation, as seen from the NMR spectrum in Figure 2. In this case, no end group signal was seen in the aromatic region. The use of a surface-active agent did not have as significant an effect on the molecular weight.

The results of the DSC measurement are shown in Table 2. The aliphatic sequence length had a clear impact on the crystallization behaviour in this homological series of polymers. The secondary arrangement processes should be studied in more detail by means of polymer morphology and crystallography. In particular, it was observed that PFS was amorphous while PFG, PFA and PFPim were semicrystalline and PFSub a crystalline polymer. It is probable that in these polymerizations the crystallinity potential of the polymers was only partly achieved.

The FT-IR studies were performed to study the mobility of the ester groups in the polyesters. In poly(ethyleneterephtalate), the C=O stretching is shifted to 1715 cm^{-1} as the carbonyl group is conjugated to the aryl group[2]. For these oligoesters, the ester group C=O stretching signals were above 1750 cm^{-1} in all cases. This was due to the activation by the single bonded oxygen. This difference implies that the chain is more rigid in the case of the polymers with -O- between the aromatic ring and the C=O unit, and the bond rotation is more hindered.

Conclusions

The prepared poly(phenylene succhinate), poly(phenylene glutarate), poly(phenylene adipate), poly(phenylene pimelate) and poly(phenylene suberate) polymers clearly indicated the importance of an even carbon number in diacid monomers in terms of improved reactivity. The polyesters had a crystalline structure and high thermal stability. With this series of polymers, it was demonstrated that the crystallinity increased as the diacid unit became longer and more olefinic in

Table 2. Melting temperatures (Tm), glass transition temperatures (Tg), crystallization temperatures (Tc), crystallininities and enthalpies of the poly(alkylene-co-arylene) dicarboxylates as detected by differential scanning calorymetry measurements. In the calculation, the total enthalpy was estimated at 65 J/g.

Polymer	Tm [ºC]	Tg [ºC]	Tc [ºC]	Tc´ [ºC]	Tc´´ [ºC]	Cryst %	dH J/g	Type
PFS	182.19	na	168.4	na	na	2.4	1.57	Amorphous
PFG	120.04	na	114.45	81.77	na	37.7	24.5	Semicrystalline
PFA	114.55	na	96.59	75.77	na	18.6	11.93	Semicrystalline
PFPim	119.94	77.5	104.04	51.82	na	44.8	29.1	Semicrystalline
PFSub	127.28	71.53	145.89	90.73	59.13	83.68	54.39	Crystalline

nature. The shorter chain length of the diacid component was seen to promote a higher melting temperature. Moreover, at higher diacid chain lengths the ester bond rotation was seen to become more restricted. Only oligomeric products were gained when using the interfacial polycondensation. The six carbon aliphatic diacid proved to be the most reactive monomer to polymerize with hydroquinone.

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Polyesters based on hydroxy acids obtainable from black liquor

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Black liquor consists of numerous degradation products of polysaccharides, including significant amounts of organic acids. These acids include glycolic acid (GA), racemic lactic acid (LA) and racemic 2-hydroxybutyric acid (2HBA) that could be used as monomers for polymeric products. The composition of the hydroxy acids in black liquor depends on the pulping process and raw material source. In this study, a series of copolymers of GA, LA and 2HBA were prepared via melt condensation polymerization. The monomer composition was varied to investigate its effect on the copolymerization reaction and the properties of the copolymer products, including molecular weights and thermal properties. Preliminary application trials were carried out to explore potential applications for the obtained materials.

One major side-stream in the paper industry is cooking liquor, or black liquor, from the kraft pulp process. Black liquor consists of numerous degradation products of polysaccharides, depending on the raw material and pulping conditions[1]. Among other compounds, up to 29 wt% of black liquor dry content consists of a broad range of different organic acids, mainly hydroxy acids. However, the majority of the black liquor hydroxy acids has a very low heat value when considering their value as a source of energy. Hence, it may be advantageous to separate and isolate them from the black liquor for use as starting materials for polymeric products[2]. Isolation of the three smallest α-hydroxy acids: GA, LA and 2HBA, from black liquor as pure compounds is challenging due to their similar physical properties (Figure 1). The possibility of utilizing the mixture of these three components with varying compositions without further separation steps would significantly improve their applicability and, on the other hand, reduce pressure from challenging fractionation technology development.

GA and particularly LA are commonly used as monomers in the preparation of biodegradable polyesters[3]. On the other hand, the utilization of 2HBA as a monomer in corresponding systems has not been reported previously. Copolymerization with GA and LA would therefore open the utilization potential for 2HBA as a monomeric compound. Currently, the use of 2HBA as a polymer precursor may be limited due to its demanding synthetic strategies and commercial unavailability in high volumes. Thus, the aim of the study was to investigate how its presence affects the copolymerization reactions and the properties of the copolymer products. 2HBA homopoly-

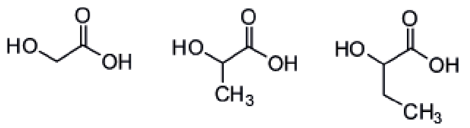
1 2 3

Figure 1. Chemical structures of glycolic acid (1), D,L-lactic acid (2) and D,L-2-hydroxybutyric acid (3).

mer and polymers with a high 2HBA content were also studied.

Materials and methods

The copolymers were synthesized by melt condensation polymerization. Monomers in predetermined ratios were placed in a three neck flask equipped with a magnetic stirrer and a distillation apparatus. Sn(II)oct catalyst (0.5 wt%) was added to the vigorously stirred monomer solution. The flask was immersed into an oil bath at room temperature, and the temperature was gradually increased to 165ºC within 1 h. Shortly thereafter, the pressure was reduced in a stepwise manner to 250 mbar. The obtained polymer was purified by precipitation into methanol and dried to a constant weight. A water-based dispersion was prepared from the polymer dissolved in organic solvent by a previously described method[4].

^{1}H NMR and ^{13}C NMR measurements were conducted with a Bruker 500 MHz spectrometer in deuterated chloroform ($CDCl_3$). The molecular weights and their distributions were determined with SEC on a system consisting of Waters Styragel columns and Waters 2414 Refractive Index Detector. The results were calculated with respect to polystyrene standards. DSC measurements were conducted using a Mettler Toledo DSC820 STAR^e SW 9.20 instrument. Samples were heated under a nitrogen atmosphere twice from -10°C to 200°C at a rate of 10°C/min. Temperatures of 10 wt% decomposition ($T_{dec10\%}$) were evaluated using a Seiko TG/DTA320 instrument.

Results and discussion

A series of copolymers of GA, LA and 2HBA were prepared via melt condensation polymerization, similarly to procedures commonly utilized for the preparation of copolymers of GA and LA.[5,6] The polymers, their compositions and main properties are presented in Table 1.

The aim of the polymer series was to:

- Prepare relevant reference materials without 2HBA
- Observe the effect of the 2HBA monomer on polymer properties
- Test polymers based on literature values for hydroxy acid compositions in softwood (sample PLGHA-SW) and birch hardwood (sample PLGHA-HW) black liquors[1]

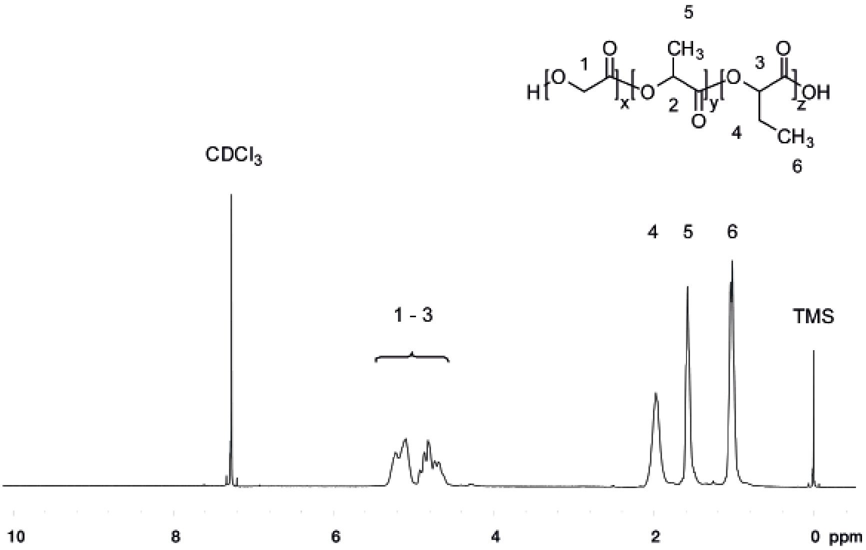

Figure 2. The 1H NMR spectrum of PLGHA-HW.

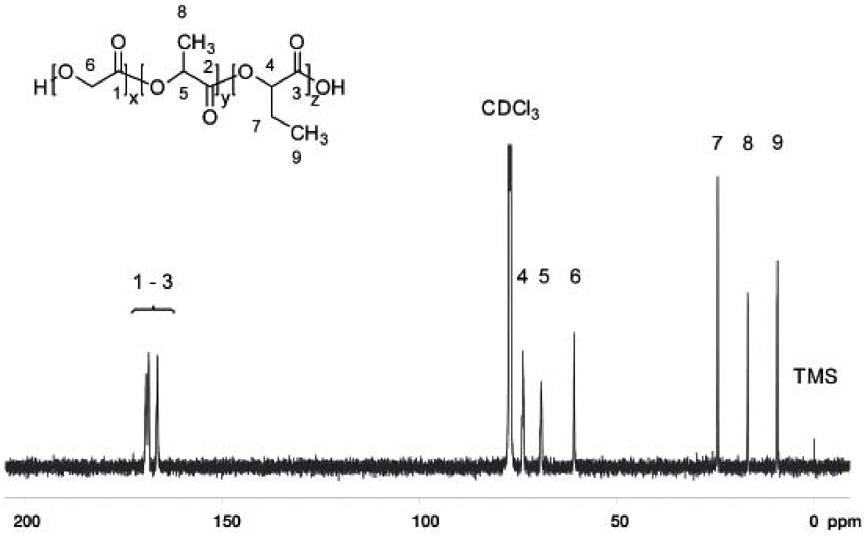

Figure 3. The 13C NMR spectrum of PLGHA-HW.

Table 1. The conducted polymerizations and the monomer compositions, size exclusion chromatography (SEC) results and thermal properties of the obtained polymers. Glass transition temperatures (T*g*) are measured by differential scanning calorimetry (DSC). T*dec*10 % is measured by thermogravimetric analysis (TGA).

	Composition in feed (mol%)			Composition in polymer (mol%) (^{13}C NMR)			SEC (g/mol)			DSC (ºC)	TGA (ºC)
	GA	LA	2HBA	GA	LA	2HBA	Mw	Mn	M_w/M_n	T_g	$T_{dec10\%}$
PLGA1	33.3	66.6	0.0	42	58	0	6570	5090	1.29	22	228
PLGA2	66.6	33.3	0.0	72	28	0	insoluble in THF			26	230
PLGA3	50.0	50.0	0.0	58	42	0	9000	4200	2.12	21	224
PLGHA1	47.5	47.5	5.0	49	46	5	5900	3700	1.61	20	230
PLGHA2	45.0	45.0	10.0	47	44	9	9300	5800	1.60	23	235
PLGHA3	20.0	20.0	60.0	22	21	57	6200	4300	1.45	7	240
PLGHA4	10.0	10.0	80.0	11	10	79	3400	2700	1.26	-1	237
PHBA	0.0	0.0	100.0	0	0	100	2800	2300	1.18	-3	244
PLGHA-SW	34.6	48.6	16.8	38	46	16	10100	6800	1.50	28	243
PLGHA-HW	24.4	30.9	44.6	29	30	41	7500	4500	1.66	22	236

The chemical structures of the prepared polymers were analysed with ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR and ^{13}C NMR spectra of sample PLGHA-HW are presented in Figures 2 and 3 respectively. The ^{13}C NMR spectra were used to calculate the monomer compositions of the polymers. The results of the NMR analysis show that the monomer compositions in the copolymers are close to the monomer compositions in the feed.

The number of GA units in the polymer was consistently slightly higher than the feed. This is due to the higher reactivity of the primary hydroxyl groups of GA over the secondary hydroxyl groups of LA and 2HBA. This is in agreement with previously reported work[5]. In copolymerizations, the reactivity of 2HBA was considered similar to that of LA.

The molecular weights of the synthesized polymers varied in the range M_n = 2000–6000 g/mol and are typical of those prepared by polycondensation of α-hydroxy acids[5,6]. It is difficult to exceed molecular weights above 15 000 g/mol by polycondensation. Various methods have therefore been developed to obtain higher molecular weights[5,7-9]. The monomer composition did not have a significant effect on the molecular weight. A decrease in molecular weight was only observed when the 2HBA content in the monomer feed exceeded 60 %.

Thermal analysis indicated that all polymers were amorphous as no endotherms due to melting were observed. This is expected based on the statistical distribution of monomers in the prepared copolymers as well as the use of racemic mixtures of LA and 2HBA, which prevents crystal formation of the short GA segments.

The use of racemic 2HBA also explains the amorphous nature of the 2HBA homopolymer. Thus, 2HBA may follow a similar behaviour to that reported for the poly(lactic acid) homopolymer[9]. GA segments in copolymers with LA have been reported to be able to crystallize when the LA content is below 10%[5].

Application testing

Water dispersions of selected materials were applied on board and tested as potential barrier coatings. The materials were found to be heat sealable. This is in direct contrast with bio-based barrier materials derived from naturally occurring polysaccharides, which typically cannot be heat sealed due to high T_gs and poor heat deflection temperatures. The high strength of the seams suggests that the copolymers may also be suitable for hot-melt applications (Table 2). The barrier properties are currently being studied.

Conclusions

A series of novel polyesters based on GA, LA and 2HBA has been synthesized and characterized. In most cases the properties of synthesized copolymers were very close to each other. The amount of 2HBA in feed had to exceed 60% before significant changes in molecular weight or thermal properties were observed. Furthermore, the thermal properties

Table 2. Results from heat-sealing tests.

Sample vs		Sealing strength (N/m)			Fibre tear (%)		
		110 °C	150 °C	190 °C	110 °C	150 °C	190 °C
PLGA2	PLGA2	296	334	269	58	68	88
PLGA1	PLGA1	250	237	N.A.	95	100	N.A.
PLGA1	Fibre	224	244	N.A.	30	95	N.A.
PLGA1	Pigment	230	217	N.A.	100	100	N.A.
PE	PE	328	N.A.	N.A.	N.A.	N.A.	N.A.

of copolymers mimicking literature compositions of softwood and hardwood black liquors were relatively close to each other. Based on this, the polymer exhibits some internal tolerance for variation in the monomer composition. Thus, the wood source in the pulping process should not greatly affect the resultant polymer properties. The successful polymerization of the monomer mixtures suggests that a separation step of the monomers is not required. Preliminary results suggest that the polymers, depending on their composition, may be used as hot melt glues, coating materials for paper and board, and plasticizers.

Publications

Mehtiö, T., Rämö, V., Harlin, A. and Ropponen, J. Polyesters based on hydroxy acids obtained from black liquor. Poster presentation, NWBC2011-Nordic Wood Biorefinery Conference, Stockholm 22–24 March 2011.

Mehtiö, T., Nurmi, L., Rämö, V., Harlin, A., Ropponen, J., Copolymerization of glycolic, D,L-lactic and D,L-2-hydroxybutyric acid mixtures present in kraft black liquors. European Polymer Journal 48 (2012) 774-778.

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Modification and analysis of hemicellulose and cellulose

Hemicellulose and cellulose modifications

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Hemicelluloses and celluloses are the most abundant of the natural polymers, and their availability practically outranges the current volumes of plastic production. This paper demonstrates opportunities of xylan and cellulose derivatives in material applications as developed for wood-based xylan and cellulose. Routes to chemicals and materials useful for coating and packaging – including films, barrier materials and coating binders – were demonstrated for white and pure xylan from bleached birch kraft pulp as well as extracted pulp. The polysaccharides were modified with novel chemistry and conversion technologies. Materials with improved plasticization, processability and barrier properties were achieved. The large platform, tailoring of chemicals and materials enable further development for specific applications.

Materials and methods

Bleached birch kraft pulp was alkaline-extracted yielding a xylan-rich extract and hemicellulose-poor pulp. The xylan was concentrated by ultrafiltration and partly used as a non-dried suspension.

Etherifications and esterifications were performed using propylene oxide and analogues as well as acetic anhydride and analogues by modifications and adjustments of published methods[1,2]. Benzyl ethers were prepared as described earlier[3]. Esterification of cellulose was performed in dimethylacetamide/lithium chloride (DMAc/LiCl) using acid chlorides[4].

Xylan ether derivatives have also been prepared by reactive extraction from bleached birch kraft pulp. The bleached birch kraft was dispersed in a mixture of t-butanol and aqueous alkaline solution, and the etherification reagent was added. After the reaction, the mixture was neutralized, filtrated and the xylan derivative precipitated from the filtrate.

Results and discussion

Modification methods for the abundant natural polymers cellulose and xylan have been developed after pulp extraction and concentration of xylan. This xylan is white in color and very pure compared to e.g. xylan extracted from wood.

Modification methods for the abundant natural polymers cellulose and xylan have been developed after pulp extraction and concentration of xylan.

A selection of prepared neutral xylan ethers from the Future Biorefinery project of Forestcluster Ltd. is presented in Figure 1 and some characterization is shown in Table 1.

Films could be prepared from all derivatives. As an example, a film prepared from X-BA2 is shown in Figure 1.

A coating of cross-linked hydroxypropylated xylan (HPX2 with citric acid) on precoated board demonstrated a good grease barrier and low oxygen transmission rates with 234 $cm^3/(m^2 \times bar \times d)$ at 50% relative humidity.

Fatty acid esters of hemicelluloses and cellulose were coated successfully on paper and cupboard respectively. Pinhole- and

Table 1. The prepared xylan ether derivatives. HP = hydroxypropyl; A = allyl; and B = butyl substituents; and some basic properties of xylan ethers.

Sample code	Preparation method and starting material	DS (HP)	DS (A)	DS (B)	DS (cat)	Film-forming properties	Solubility (w/w)*	Tg (oC)
HPX 1	Alkaline reactive extraction from birch pulp	1	No	no	No	Transparent film	20% in water	Nm
HPX 2	From extracted non-dried xylan X	1.5	No	no	No	Transparent flexible film	20% in water (66%)	66
X-BA1	Alkaline reactive extraction from birch pulp	No	0.4	0.8	No	Transparent flexible film	20% in water	61
X-BA2	From extracted non-dried xylan X	No	0.3	0.5	No	Transparent flexible film	20% in water (96%)	58
HPX-BA1	From hydroxy-propylated HPX2	0.6	0.2	0.3	No	Slightly opaque film	18% in water	64

* The minimum solubility.

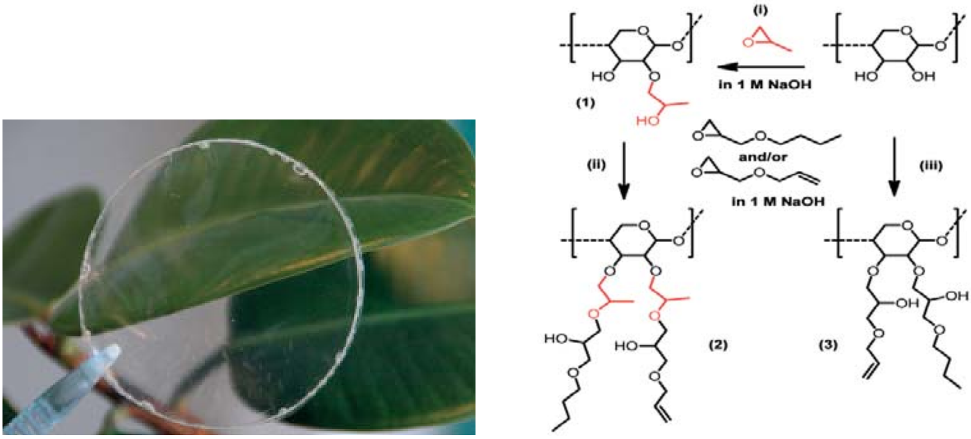

Figure 1. A transparent and flexible film obtained from a butylated and allylated xylan (left). Etherification routes using epoxy reagents in alkaline conditions(right): (i) xylan is first hydroxypropylated using propylene oxide and then (ii) further etherified using butyl and/or allyl glycidyl ethers; (iii) xylan is only etherified using butyl and/or allyl glycidyl ethers. (1) Hydroxypropylated (HPX); (2) hydroxypropylated and butyl-allylated (HPX-BA), and (3) butyl-allylated (X-BA) xylans.

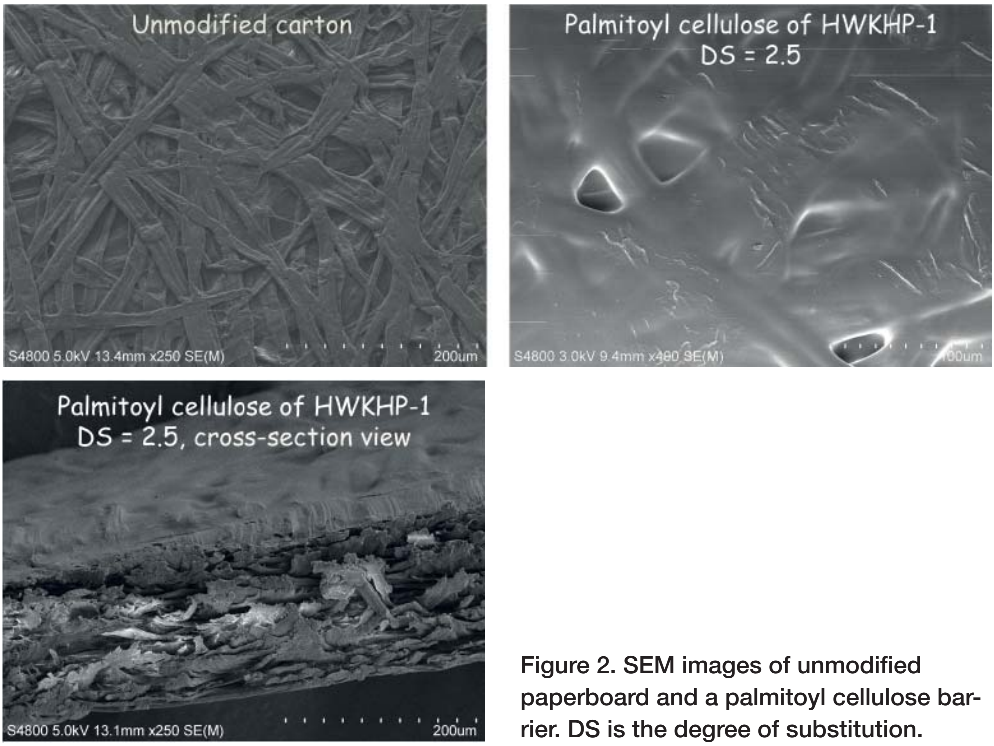

Figure 2. SEM images of unmodified paperboard and a palmitoyl cellulose barrier. DS is the degree of substitution.

crack-free coatings show high hydrophobicity and stability in the same range as commercial PLA-coated standards (Figure 2). Cellulose fatty acid esters provided a good grease, water and water vapour barrier, while the best hemicellulose derivatives were equally good grease and water vapour barriers. The best water and water vapour barrier was achieved with the cellulose derivatives esterified with the longest fatty acid. Barrier applications are also discussed in *Packaging barriers from renewable sources* by Hartman et al. (page 49 in this publication).

Benzyl ether derivatives of birch xylan with varying degrees of substitutions were prepared, to name another example of hydrophobic derivatives. These derivatives are hydrophobic and thermoplastic polymers capable of forming free-standing film from organic solvent[3].

Xylan derivatives were also tested as binders in pigment-coating applications for offset grade papers. Good surface strength of coated paper could be demonstrated with butylated and allylated xylan (X-BA2), and it performed almost as well in the tests as the reference latex (Figure 3). The performance of hydroxypropylated xylan (HPX2) was not as good as that of X-BA2. Some development is needed as, e.g., shear viscosities of the coating colours with xylan derivative binders were generally considerably higher than those of the latex colour.

Some more xylan derivatives are described in *Hemicellulose on PVA* by Anghelescu-Hakala et al. (page 33 in this publication) and *Superadsorbents and hydrogels* by Setälä et al. (page 36 in this publication).

Conclusions

Xylan provides a good starting polymer for modification of potential chemicals in film, coating and barrier applications. By further optimization and tailoring, even better properties are expected. Currently, there is no industrial production of hemicelluloses for

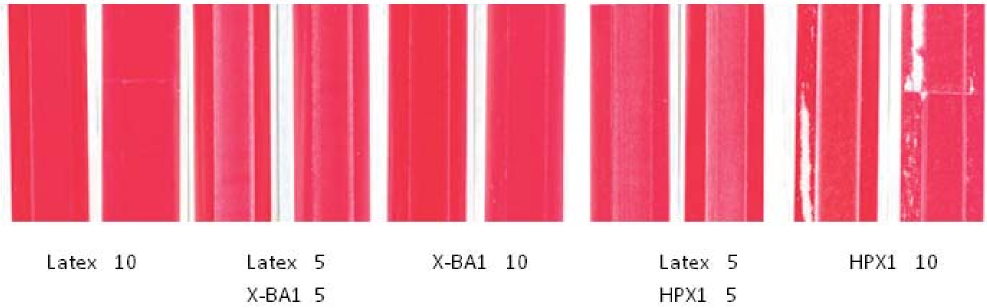

Figure 3. Coated paper samples after the Prüfbau wet pick test, second coating series. The labels describe the binder type and the binder amount (pph) in the coating colours. Mixtures of binders were also tested.

product development. However, xylan and other hemicelluloses may become readily available in case the production of dissolving pulp increases significantly. This would be the case if the demand to use wood-based fibres to replace, e.g., synthetic textile and cotton fibres would grow significantly. In addition, the developed modification routes can be applied and adjusted for new sources of polysaccharides in agricultural or marine biorefineries.

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Hemicellulose on PVA

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The current trend of using environmentally friendly products has resulted in extensive use of new materials derived from natural resources. Xylan is one of the main components of wood-based hemicellulose and commonly found in birch[1]. Xylan is studied as a replacement for traditional products, e.g. paper chemicals, barriers in packages, binders in coatings, etc. Various possibilities for chemical modification of xylan have been reported in literature, such as: esterification, cationization, methacrylation and carboxymethylation[2]. By appropriate modification, the properties of xylan can be tuned to various applications. The chemical modification strategy was also applied to cationized xylan. In this work, the functionalized xylan derivatives were tested as retention chemicals used on the paper machine wet end for their applications as fixatives.

Materials and methods

The starting material for the chemical modification was alkali-extracted xylan from birch kraft pulp. (see also Laine et al., page 29 in this publication). The structure of synthesized xylan derivatives was characterized by FTIR, NMR spectroscopy and size exclusion chromatography (SEC). Solubility tests were performed and thermal properties investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis.

The fixative experiments were carried out for TMP pulp, which was hot-disintegrated to a consistency of 1.5%. Disintegrated pulp was further diluted to a consistency of 1% and mixed at a temperature of 60°C for 3 hours in order to dissolve anionic trash. After that, the studied fixatives were added and the pulp was mixed for 10 min. Finally, the pulp was centrifuged with 520 g (1700 rpm) for 15 min and the filtrate was taken for further analysis. The principal measurements for characterizing the xylan derivatives were turbidity, charge density and conductivity.

Results and discussions

The chemical modification of xylan and cationized xylan (Figure 1) consisted of two steps:

1. Reaction with maleic anhydride with formation of xylan maleate and cationized xylan maleate precursors;
2. Functionalization of xylan maleate and cationized xylan maleate precursors by covalent linkage with poly(vinyl alcohol).

The modifications of xylan and cationized xylan were confirmed by the presence of the ester linkage seen in the FTIR spectra. After esterification, the presence of a new peak at 1714 cm^{-1} was observed due to the carbonyl groups linked to xylan.

With our strategy, xylan maleates and cationized xylan maleates were successfully synthesized in mild conditions. Appropriate conditions to avoid the degradation of xylan were found (Figure 2 and Table 1). Different degrees of substitution can be achieved depending on reaction conditions[3].

For the preparation of functionalized xylan with PVA, the amount of PVA linked to xylan

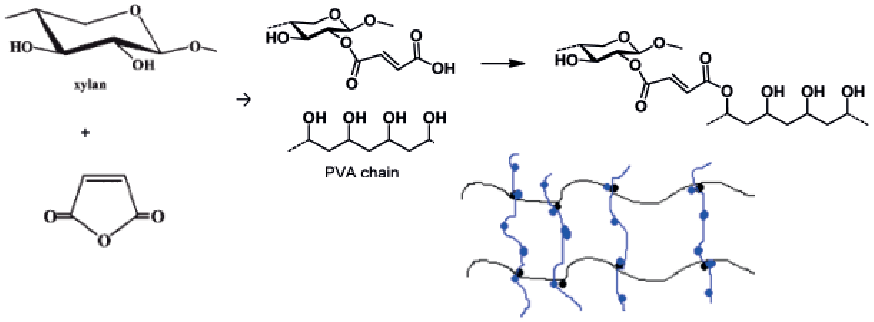

Figure 1. Functionalization of xylan by covalent linkage of PVA

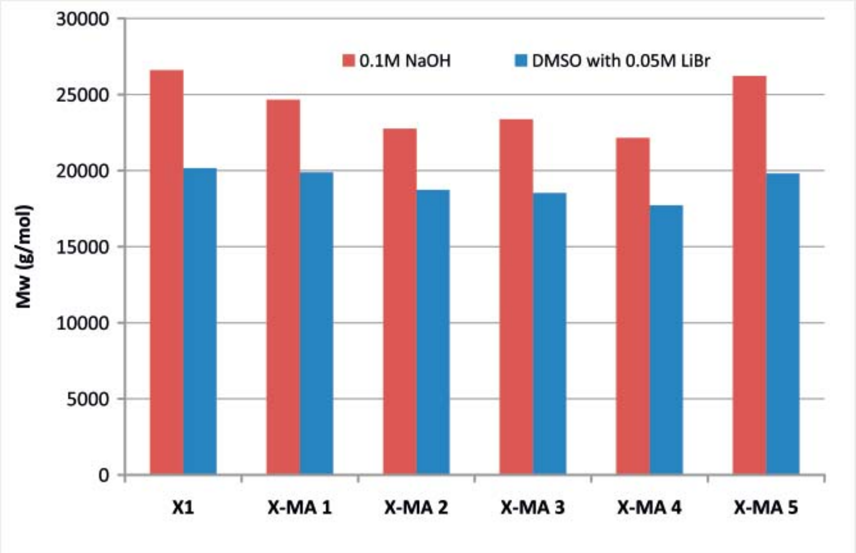

Figure 2. SEC characterization of xylan (X1) and xylan maleates in different eluent systems.

Table 1. Molar masses of starting xylan, xylan maleates, cationized xylan maleates and their corresponding funtionalized derivatives with PVA. PDI refers to the polydispersity index and is calculated by dividing Mw with Mn.

Sample	M_n	M_w	PDI
Xylan	23 870	28 120	1.17
X-MA	18 380	20 900	1.13
PVA	88 600	112 910	1.27
X.MA-PVA	112 660	144 940	1.28
CatX	26 770	29 730	1.11
CatX-MA	24 720	28 430	1.15
CatX-MA-PVA	103 480	138 280	1.33

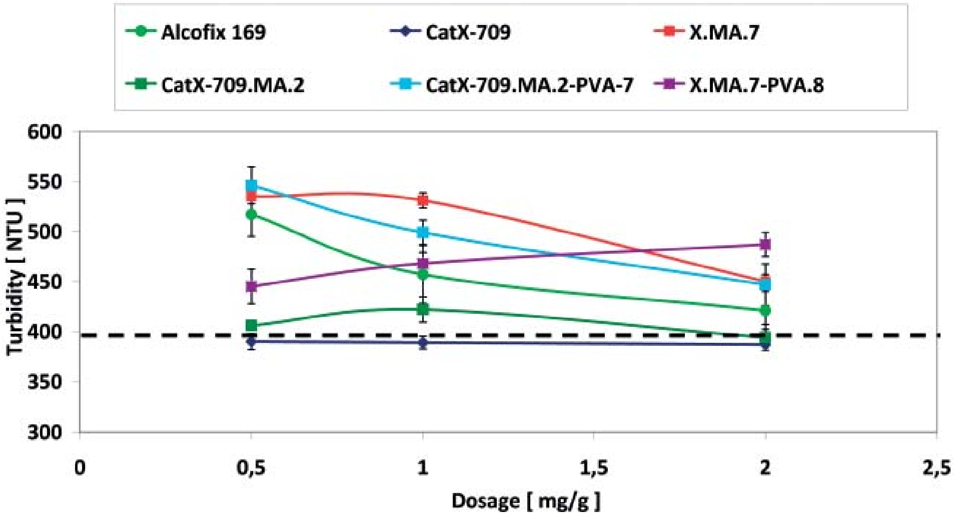

Figure 3. Turbidity values measured from filtrates of the studied samples

can be adjusted both by the degree of substitution of xylan maleate precursors and the molar mass of PVA.

Fixative tests of xylan derivatives

Turbidity values decrease with increasing dosage of xylan maleate (X.MA.7 sample) and cationized xylan maleate functionalized with PVA (CatX-709.MA.2-PVA-7 sample) (Figure 3). The decrease is similar to Alcofix 169 (commercial product)[4].

Conclusions

Xylan maleates and cationized xylan maleates were successfully synthesized in mild conditions. Appropriate conditions to avoid the degradation of xylan were found. After their functionalization with PVA, xylan derivatives with increased molar masses were obtained.

Similar behaviour in turbidity measurements with a reference fixative, Alcofix 169, was observed for xylan maleate and cationized xylan maleate functionalized with PVA. The preliminary investigations show that some of the synthesized xylan derivatives have potential applications such as fixative chemicals.

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Superadsorbents and hydrogels

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Superadsorbent hydrogels are chemically or physically cross-linked networks that are water-insoluble but capable of absorbing large amounts of water, saline or physiological solutions compared with general absorbing materials. They can be made from synthetic or natural starting materials, though commercial hydrogels have traditionally been prepared mainly from acrylates and acrylamides. Hydrogels based on naturally occurring products are of interest not only for their renewable character and nontoxic nature but also because they may offer biocompatibility and biodegradability[1-3]. Superadsorbent and hydrogels possess a degree of flexibility due to their significant water uptake properties (up to 20-400 g of water/g of an adsorbent material)[4] and they are potential material candidates, for example, in tissue engineering[1], controlled drug release[5] and hygiene products[6].

Carbohydrates are a class of natural products widely available in nature. They have a wide range of functionalities and are very hydrophilic, which makes them good candidates for superadsorbent and hydrogel preparation. Cellulose and hemicelluloses, such as xylan, have hydroxyl groups in each repeating unit that can be chemically derivatized to new reacting groups. When compared with cellulose and starch[3,7,8], hemicelluloses have been somewhat neglected in research and they are normally disposed of as organic waste from the forest industry side-streams. However, recent research has begun to find new applications also for hemicelluloses, and examples of hydrogels prepared from modified hemicelluloses can be found[9-12]. Some reviews of cellulose-based superadsorbents and hydrogels have also been published, for example, by Chang et al.[13]

Smart, intelligent, stimuli-sensitive or -responsive, environmentally sensitive, functional materials react to stimuli such as temperature, pH, solvent content, ions and light by yielding a response that is usually reversible, e.g. a phase transition, collapsion-swelling, colour change, conductivity change. Poly(alkylacrylamides) such as poly(*N*-isopropylacrylamide) (PNIPAM) are one very intensively studied group of these materials. They have a so-called lower critical solution temperature (LCST, 32–35°C), which means that below the LCST, they are hydrophilic and in a swollen stage and above the LCST they collapse throwing water out and are hydrophobized at the same time. It is possible to measure the LCST and ΔH (enthalpy) using a differential scanning calorimeter (DSC). Cellulose and hemicellulose-based stimuli-responsive materials for adsorbent or hydrogel applications have been studied increasingly in recent years. For example, cellulose-based materials such as lyocell fibres[14], hydroxypropylcellulose[15], dextrane[16] and cellulose powder have been grafted with PNIPAM[17]. Some hemicelluloses-based stimuli-responsive materials have also been synthetized, for example, xylan grafted with acrylic acid yielding a pH-sensitive material[18].

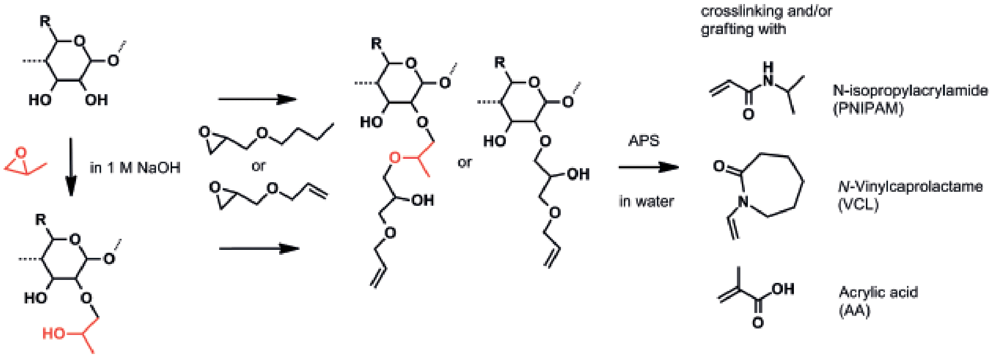


Figure 1. The derivatization of polysaccharides and further cross-linking/grafting reaction options yielding hydrogels and/or superadsorbents.

Chemical cross-linking is a highly versatile method to create hydrogels with good mechanical stability. The amount and type of a cross-linker also impacts other properties such as hydrophilicity, water uptake or biodegradability[2,19].

Materials and Methods

Preparation of starting materials

Several different polysaccharide-based materials can be used for the preparation of adsorbents and hydrogels. The bleached birch pulp was used for the preparation of starting materials and polysaccharide derivatives. The starting materials for adsorbent preparations were prepared at VTT. The main reaction routes are presented in Figure 1. The basic properties of polysaccharide derivatives were determined before the use in the adsorbent preparations. Some novel cross-linkers were also prepared based on modified aldaric acids[12].

Preparation of birch xylan: bleached birch kraft pulp was extracted with alkaline yielding *a birch xylan* (X).) (see also Laine et al., page 29 in this publication).

Preparation of cellulose fibres: bleached birch kraft pulp was extracted using a so-called reactive extraction method in which cellulose fibres were first pre-modified in alkaline conditions with glycidyl butyl ether (B) followed by a mechanical treatment that produced more homogeneous *microfibrillated fibres with butyl substituents (MFC-B)*. During the reactive extraction, approximately 40% of the xylan was removed from the birch pulp, yielding a xylan-poor pre-modified birch pulp (MFC-B). The degree of substation (DS_B) was rather low, approx. 0.01.

Preparation of allylated cellulose fibres: The pre-modified and microfibrillated cellulose fibres were further solvent-exchanged from water into acetone to decrease the amount of water in a reaction mixture. The fibres were then modified in alkaline conditions with glycidyl allyl ether (A), yielding the end product MFC-A to be used as a starting material for adsorbent materials. The DS_A was approx. 0.06.

Preparation of allylated xylan derivatives: The birch xylan was modified using propylene oxide and/or butyl glycidyl ether and/or allyl glycidyl ether in alkaline conditions yielding several etherified xylan derivatives with hydroxypropyl (HP), 1-butoxy-2-hydroxypropyl (B) and/or 1-allyloxy-2-hydroxypropyl (A) substituents presented in Table 2. The more detailed reaction conditions and results are published by Pohjanlehto et al.[12].

The preparation of aldaric-acid-based cross-linkers is reported in the article by Pohjanlehto et al.[12]. These cross-linkers

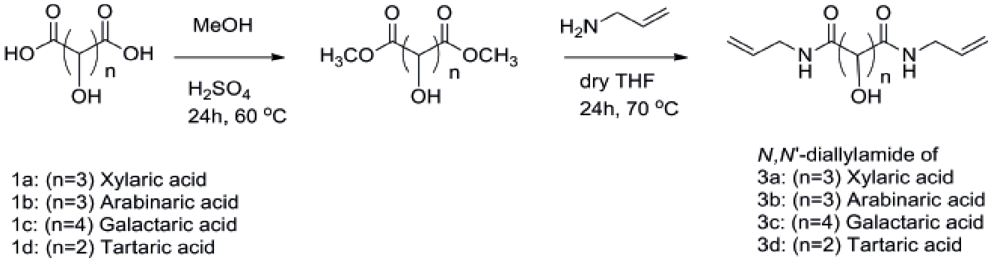


Figure 2. Aldaric-acid-based cross-linkers and their preparation.

and their synthesis are presented in Figure 2. The commercially available cross-linker (+)-*N,N'*-diallyltartardiamide (DAT) was also used.

Preparation of adsorbents and hydrogels

The preparation of xylan-based hydrogels is illustrated very well in the article by Pohjanlehto et al.[12]. The cellulose-fibre-based hydrogels were prepared in a similar way.

General procedure for stimuli-responsive hydrogel-like membrane preparations: 20 g of allylated cellulose fibres as a 5 wt% suspension in 20% aqueous ethanol (1 g of MFC-A) was mixed with 63 ml of water, 0.5 g of NIPAM or VCL in 10 ml of water, 2 ml of a macromolecular cross-linker (commercial hydroxypropyl cellulose that is butulated and allylated) in ethanol (0.2 g of HPC-BA, 10 wt% solution in ethanol) and 0.1 g of APS in 5 ml of water. The total volume was 100 ml. A reaction mixture was poured onto a Petri dish (diameter 18 cm, glass, sealed) and kept for three hours at 60°C. A Petri dish was opened and left to dry over night at 60°C. Prepared membranes were wetted with 5 ml of APS solution (0.1 g APS in water) and exposed for 3 x 20 sec to UV light. 50 ml of water was added to swell and unfasten the membranes. The membranes started to come off from a Petri dish during this process. The membranes were then washed several times in turn with hot and cold water, and finally with 20% aqueous ethanol.

Some xylan-*grafted*-PNIPAM hydrogels were also prepared and demonstrated. A reaction mixture of 1 g of xylan and 1 g of NIPAM with 0.1 g of APS in 20 ml of water was used. Otherwise, the procedure was very similar to the published one by Pohjanlehto et al.[12], Figure 5. The swelling ratios (water uptake) for most of the products were determinated.

Results and Discussion

Reactivity of allylated polysaccharide derivatives

Before the preparation of hydrogels, the cross-linking and grafting efficiencies of polysaccharide derivatives were tested; see Tables 1 and 2. The cross-linking efficiency of MFC-A was determined by performing the reaction without any monomers. The result 64.4% indicates a very high reactivity of allylic double bonds with each other's. The value 84.4% of reacted allyl groups includes both cross-linking and grafting reactions occurring at the same time. Only 15.6% of the allylic double bonds were not reacted using VCL as a monomer in these reaction conditions; see Table 1. The cross-linking efficiencies of xylan derivatives were also presented in Table 2. The allylic double bonds can be used for the cross-linking of the xylan molecules themselves or at the same time or separately for grafting reactions; see Figure 1.

Xylan-based hydrogels

A typical example of a xylan-based hydrogel is presented in Figure 3. This rather solid gel-

Table 1. Degree of substitution, DSA and the reaction efficiencies of allylic double bonds, calculated from the bromine analysis: for the starting materials (MFC and MFC-A), for the cross-linked MFC-A and the cross-linked and grafted MFC-A with a vinylcaprolactame monomer (VCL).

MFC sample	Br content wt%	DSA	Amount of reacted allyl groups (%)	Other
MFC	0.06	0.001	0	starting material
MFC-A	5	0.056	0	allylated MFC
MFC-A cross-linked	1.9	0.020	64.4	Cross-linking efficiency
MFC-A grafted	0.78	0.008	84.4	+ grafting efficiency

Table 2. Xylan derivatives and the cross-linking efficiency of allylic double bonds calculated from the amounts of bromine found with the instrumental neutron-activation method. Degrees of substitution determined by the bromination and 1H NMR methods are also presented.

Sample	Br-content (wt%)	DSA (Br)	DSA (^{1}H NMR)	DSB (^{1}H NMR)	DSHP (^{1}H NMR)
Xylan	0.04	0	0	0	0
HPX-A	13.7	0.20	0.36	0	0
HPX-A cross-linked	11.3				
HPX-BA	6.5	0.10	0.17	0.34	0.63
HPX-BA cross-linked	4.4				
X-BA	10.9	0.20	0.38	0.75	0
X-BA cross-linked	5.4				

Figure 3. A hydrogel prepared from the allylated hydroxypropyl xylan (HPX-A) using 5 wt% of diallylarabinardiamide (DAD) straight after cross-linking in a UV oven.

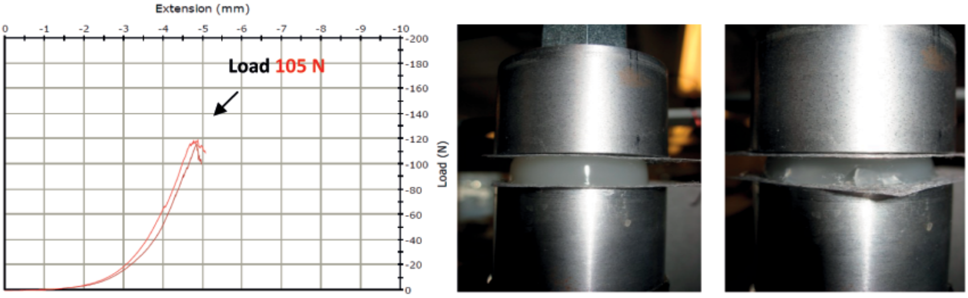
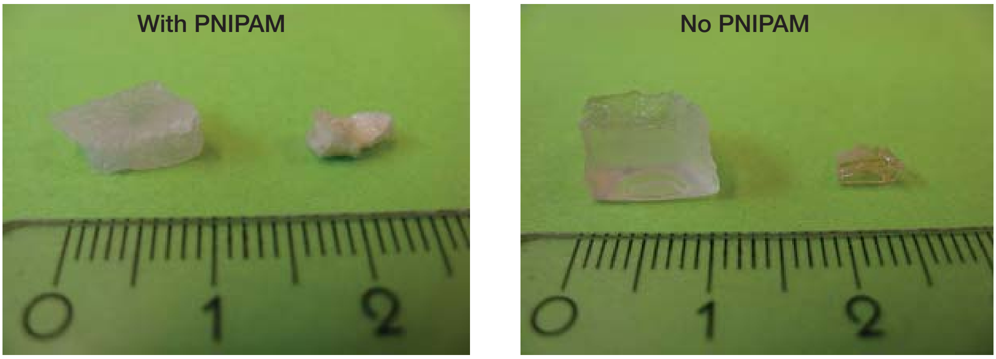


Figure 4. Mechanical strength of the HPX-A with 5 wt% of the DAD cross-linker.



570%

1000%

Figure 5. Degree of swelling of allylated xylan-based hydrogels with or without stimuli-responsive polymers: poly(N-isopropylacrylamide) PNIPAM. The hydrogels are in dry (right one) and swollen states (left one).

like structure is formed when water-soluble starting materials are cross-linked with a three-dimensional network. The mechanical strength of some hydrogels was also determinated and one example is presented in Figure 4.

The degree of swelling was determinated for all hydrogels prepared from the xylan derivatives. The most important correlation was observed between the cross-linking efficiency of the allylic double bonds and the water absorbency. The water absorbency (up to 350%) was highest for hydrogels prepared from HPX-A with the lowest cross-linking efficiency at 18%. Contrarily, the lowest water absorbency (about 100%) was observed for hydrogels prepared from X-BA, with the highest cross-linking efficiency at 50%. When the cross-linking efficiency of the allylic double bonds of xylan derivatives increases, the incorporation of an additional DA cross-linker into the hydrogel network decreases. However, the amount of DA cross-linkers had only a small influence on the water absorbencies. The use of DA cross-linkers in the preparation of hydrogels had an influence on the pore structure, making it more uniform. The effect of HP and B substituents to water absorbency was not as clear[12]. The highest value for the degree of swelling in some experiments (unpublished results) was 1000%, which means that the material is able to absorb water at ten times its dry weight; see Figure 5.

Some pictures of the washing processes and membranes are presented in Figures 6–7.

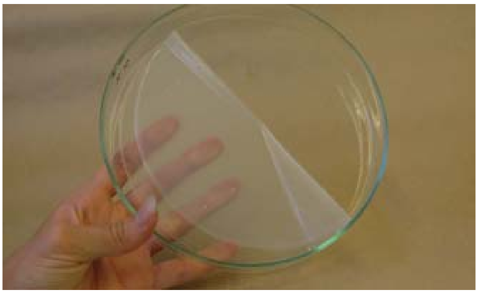


Figure 6. Allylated cellulose fibres cross-linked to a soft hydrogel-like membrane without any additional cross-linker or without grafting.

Some cross-linking and grafting efficiencies of the starting materials and allylated MFCs are presented in Table 2.

The xylan-based stimuli-responsive hydrogels were also demonstrated. One example of these demonstrations is presented in Figure 5. The non-grafted hydrogel appears able to absorb more water than the xylan-*graft*-PNIPAM hydrogel.

Cellulose-based hydrogels and membranes

Allylated cellulose fibres formed hydrogel-like membranes; see Figure 6. The MFC-A was also grafted with PNIPAM, producing a stimuli-responsive material on a glass plate (d = 18 cm). The stimuli-responsive behaviour was clearly observed when the dry membrane was treated with water. The membrane starts to come off from a Petri dish during a wetting step indicating some kind of 'self-organizing' or stimuli-responsive behaviour (Figure 7). The thermo-responsive cellulose membrane also becomes slightly white at 40°C indicating the same behaviour. The washing and purification of the thermoresponsive hydrogel-like membrane was very effective when hot and cold water was used in turns.

Conclusions

It was demonstrated that carbohydrate-based materials such as hydrogels and membranes can be prepared from polysaccharides such as cellulose fibres and xylan. New monosaccharide-based derivatives can be used as additional cross-linkers:

- Novel monosaccharide-based *N,N'*-diallylaldardiamide cross-linkers were prepared from galactose, xylose and arabinose.
- The basic properties of polysaccharides, such as solubility and/or hydrophilicity-hydrophobicity balance, molecular weight, or compatibility with other polymers/plastics or other biomaterials, can be modified and adjusted with substituents such as alkyl side-chains.
- Novel reactive polysaccharide derivatives with allyl substituents were prepared for use in cross-linking and grafting reactions.
- Polysaccharide-based materials such as hydrogels or stimuli-responsive materials have been developed by changing the polysaccharide starting materials and/or by modifying polysaccharides with different kinds of substituents and/or by grafting with suitable monomers or cross-linkers.
- The cross-linking and grafting efficiencies of activated polysaccharides and cross-linkers were determinated and observed to be rather high.
- The swelling ratios of hydrogels were quite high, up to 1000% (10 g of water/g of hydrogel).
- The mechanical properties of hydrogels were moderate.
- The stimuli-responsive properties were demonstrated and determinated tentatively.

Publications

Pohjanlehto, H., Setälä, H., Kammiovirta, K. and Harlin, A. 2011. The use of N,N'-diallylaldardiamides as cross-linkers in xylan derivatives-based hydrogels. Carbohydr. Res. 346(17), 2736–2745.

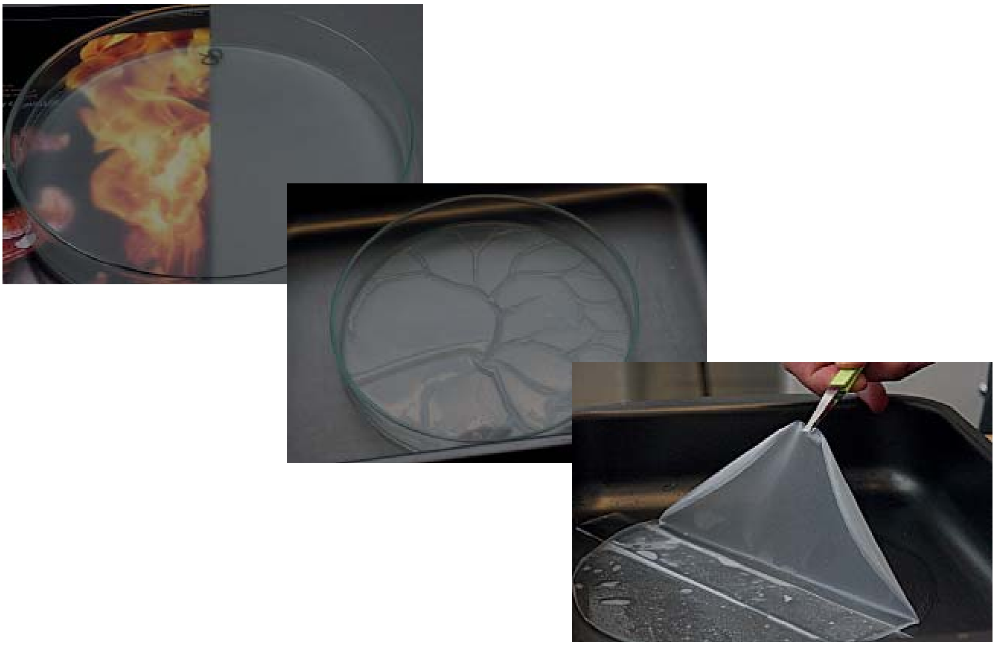


Figure 7. A stimuli-responsive membrane prepared from allylated cellulose fibres grafted with PNIPAM.

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Surface analysis and water interactions of biomaterials using QCM-D

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Sophisticated, effective and reliable methods are needed to investigate systematically interfacial phenomena present in, e.g., thin films, foams, emulsions, dispersions and aerogels. The quartz crystal microbalance with dissipation monitoring, the QCM-D instrument, measures mass changes due to, e.g., adsorption and desorption with nanosensitivity. In addition, information about structural behaviour, water vapour uptake and viscoelastic properties of the materials can be attained.

This paper gives an example of how the changes in the water vapour uptake of the xylan derivatives can be studied using the model film approach and QCM-D. Model films were prepared using the xylan derivative containing cross-linking groups. The water vapour uptake of the thin xylan model films was monitored using the QCM-D humidity module, and the mass uptake due to the water vapour binding was defined. Simultaneously, the changes in the viscoelastic properties of the xylan derivative when subjected to different relative humidity conditions were determined. Clear changes in the water uptake ability took place before and after the cross-linking of the films.

In surface science, the model surfaces of small amounts of chemically defined compounds are deposited on a flat surface by means of, e.g. spincoating technique. The model surface approach enables investigations of direct surface interactions on the molecular level since it enables efficient and well-established use of the surface-analytical techniques.

The QCM-D method enables the use of an approach that links the material behaviour at interfaces to macroscale physical properties. For example, the following investigations can be carried out:

- Affinity and interaction studies – the stabilization of particles, controlled compatibility and film formation are essential parameters when considering dispersions stability (e.g. bio-based inks) or strength enhancement of bio-inspired (nano)composites.
- Degradation and dissolution studies – these enable, e.g., determination of the optimal usability of (modified) biopolymers (e.g., choice of solvents and other solvent parameters for example pH and ionic strength).
- Changes in material properties – Physical changes in biomaterial-based films and coatings due to heat, UV or enzymatic treatments can be studied systematically. Essential information can be achieved when considering thin (nanoscale) surface treatments to introduce additional functionalities, e.g. smooth, cured surfaces for printed intelligence.
- Swelling and water vapour uptake studies enable investigations related to the barrier films and water interactions using the specific QCM-D humidity module.

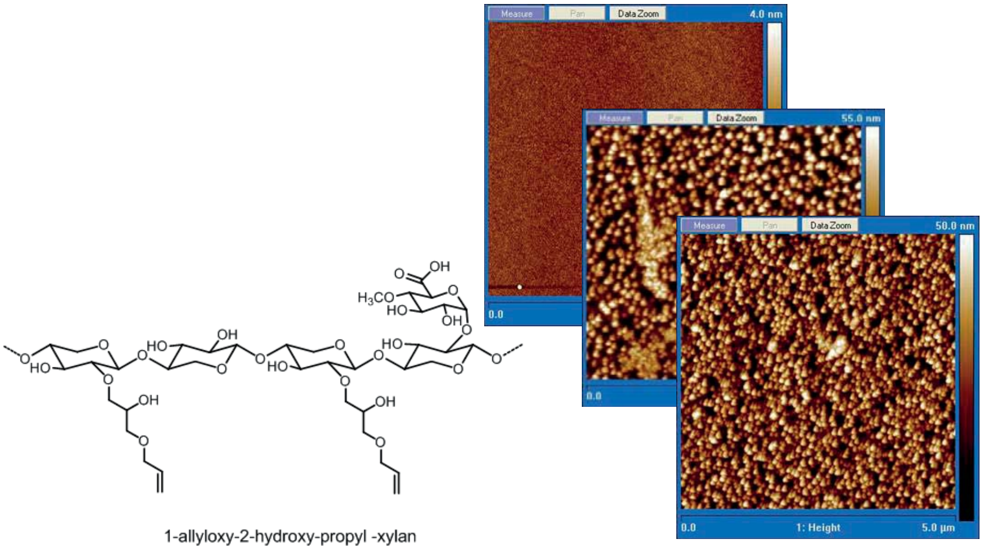

Figure 1. Chemical structure of allylated xylan (left) and AFM topography images (right) of a pure silica surface (model surface substrate), as well as allylated xylan thin film before and after UV-radical treatment.

Materials and methods

Birch xylan was allylated similarly as described in Pohjanlehto et al.[1]. In brief, unmodified xylans were reacted in alkaline conditions with allyl glycidyl ether, and 1-allyloxy-2-hydroxy-propyl groups were directly attached to the xylan backbones. Thus, the xylan derivative contains a cross-linkable site for further reactions.

Model films of the allylated xylan were prepared using a spincoating technique and then further cross-linked with the following procedure: an equivalent amount of H_2O_2 in a mixture of acetonitrile and water was added as the evaporable radical initiator for the cross-linking reaction on allylated xylan. The reaction was activated in a UV oven, and the cross-linked samples were finally heat treated at 60 °C for 1 hour to evaporate the remaining water. Figure 1 shows the AFM topography images of the pure silica substrate on which the xylan derivative was spincoated, and allylated xylan films before and after the cross-linking procedure.

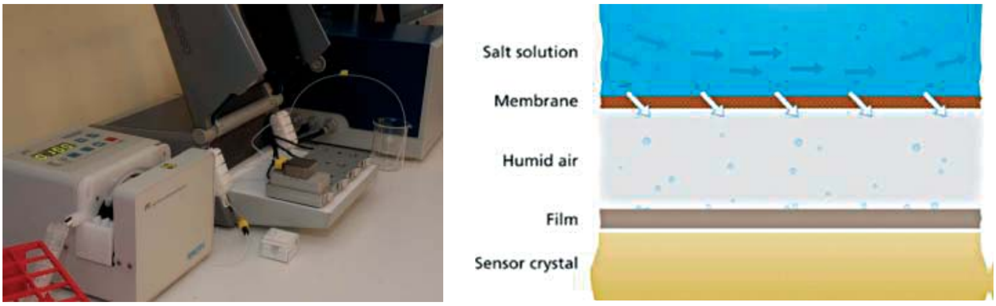

Figure 2. QCM-D instrument equipped with the humidity module (left) and a schematic drawing of the principle of the humidity chamber (right).

The water vapour uptake of the allylated xylan films before and after cross-linking was studied using a quartz crystal microbalance with dissipation monitoring QCM-D E4® (Q-Sense AB, Göteborg, Sweden)[2-3] coupled with a QHM 401 humidity module; see Figure 2.

The mass uptake of the thin films due to water vapour was monitored via changes in frequency, as a result of their exposure to different relative humidity conditions. For that purpose, saturated solutions of different salts were circulated through the humidity chamber as shown schematically in Figure 2. The different saturated salt solutions used are listed in Table 1.

Table 1. Different saturated salt solutions and respective relative humidity used in water vapour uptake monitored with QCM-D [4].

Salt solution	Relative Humidity (%)
LiCl	11
$MgCl_2$	33
$Mg(NO_3)_2$	53
NaCl	75
K_2SO_4	97
pure milliQ H_2O	100

Results and discussion

The resistance to humidity, the swelling behaviour and the ability to uptake water vapour are features that are strongly related to the behaviour of wood and agro-derived polymers in different applications such as in barrier films and membranes. These features also have a direct link to the mechanical and thermal properties and therefore need to be fully understood and controlled when the aim is to prepare bio-based materials that also function effectively at higher humidities.

Changes in water vapour uptake were monitored with QCM-D, and the behaviour of the different xylan derivatives was studied against increasing relative humidity. Figure 3 summarizes the data obtained for allylated xylan before and after UV-radical treatment.

The major changes in water vapour uptake are observed when the relative humidity (RH) exceeds 90%. The untreated allylated xylan film (-■-) seems to release some water at an RH level of approximately 10%, and stabilization of the film starts at approximately 50% RH. The positive change in frequency indicates that the film may release water until reaching the equilibrium with the surrounding environment. Negligible changes in dissipation (-□-) indicate that the allylated xylan film is rigid and well adhered on the underlying silica surface.

When the allylated xylan-derivative film is exposed to the relative humidity conditions of 97%, the film starts to uptake significant water vapour, attaining a negative change in frequency of 105 MHz. The higher changes in dissipation indicate softening of the film due to the presence of water molecules. It is worth noting that the uptake of water vapour was even more pronounced when pure water vapour (RH = 100%) was run through the chamber, but due to condensation issues, it was not possible to measure this step for longer periods of time.

After the UV-radical treatment (-●-), the behaviour of allylated xylan clearly changes. The equilibrium state of the film with the environment was reached from the very beginning of the experiment at low relative humidity conditions. UV-treated allylated xylan shows 80% less uptake of water vapour than the corresponding untreated allylxylan at the relative humidity of 97%. This can be explained by the cross-linking taking place between the allyl groups present in the xylan structure. Conformational changes also seem to take place, which indicates swelling of the film at high relative humidity conditions, seen as the increase in the dissipation signal (-○-).

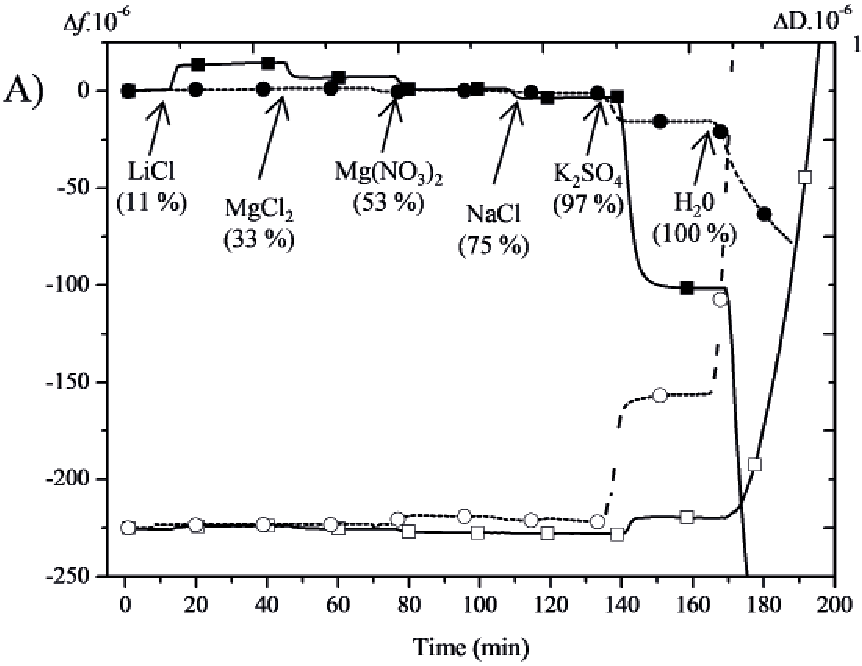

Figure 3. Water uptake monitored with the QCM-D of allylated xylans before (-■-/-□-) and after (-●-/-○-) UV-radical treatment at different relative humidity. The filled symbols correspond to changes in frequency (a negative change in frequency indicates a positive mass change of the xylan-derivative-coated QCM-D crystal due to the water vapour uptake of the xylan film). The empty symbols represent changes in dissipation due to the viscoelastic changes of the allylated xylan film.

Conclusions

The QCM-D method with the humidity module is a relatively simple method to detect changes in water vapour uptake of modified biomaterials. Cross-linking of allylated xylan seems to reduce the water vapour uptake ability of the material.

Publications

Kammiovirta, K., Peresin, M.S., Setälä, H. and Tammelin, T. 2011. Changes in water vapour uptake ability of xylan derivatives monitored by QCM-D humidity module. Poster presented in the 2nd EPNOE Polysaccharide Conference 'Polysaccharides as source of advanced and sustainable products', Wageningen, Netherlands, August 28-September 2, 2011.

Kammiovirta, K., Peresin, M.S., Setälä, H. and Tammelin, T. 2011. Model surface study on water vapour uptake behavior of xylan derivatives. Poster presented in the 19th BioEnvironmental Polymer Society (BEPS) Annual Meeting, Vienna, Austria, September 27–30, 2011.

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Barriers and ALD-technique

Packaging barriers from renewable sources

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VTT will enhance its approach to the whole packaging value chain by augmenting the investigation of processing, converting and design as well as by continuing research within isolation, extraction, modification and application of bio-based materials. This will give us the edge we want within the targeted market sectors, including corrugated board. With recent investments, we can simulate larger scale production and converting processes better than before using our pilot-scale equipment and packaging cutting and creasing table. Wood- and agro-derived barrier materials have been coated and studied on a pilot-scale, achieving good barrier properties.

VTT has long-term research experience in the area of isolation, extraction, modification and application of bio-based materials. Traditionally, synthetic polymer coatings have been used on paper and board to increase the barrier against water, water vapour, oxygen, aroma and grease. The demand for fibre-based packaging is estimated to rise from 145 to 210 billion Euros globally by 2012[1]. Simultaneously, there is a clear trend to shift from fossil oil-based package coating materials to bio-based ones. This opens opportunities for fully biomass-based packaging. VTT's bio-barrier portfolio includes polylactic acid (PLA), starch, xylan, pectin and lignin as raw materials. For example, hemicelluloses constitute a scarcely used but extensive forest-based biomass resource. Xylan, a hemicellulose abundant in hardwoods, is obtained from, e.g., the initial stages of kraft pulping (developed at VTT) or through extraction from bleached pulp or wood[2,3]. Hemicelluloses have been reported to be effective oxygen barriers, though their water vapour barrier properties still need improvement[4]. By chemical derivatization of xylan, or any other of our biomass-derived raw material for that matter, branching or internal plasticization can be introduced to avoid processability and migratory issues brought on by external plasticization. Enhanced thermoplasticity and hydrophobicity are two of the main criteria required for packaging applications and versatile barrier properties, which have been under scrutiny through either esterification or etherification or both. We have studied various phenomena through both lab-scale and pilot-scale coating trials, since larger online coaters have a marked influence on layer formation. The improvement in primary barrier properties, including aroma gas resistance, varies from moderate to significant.

As a whole, our bio-based barrier coatings show excellent grease, good oxygen and moderate to good water vapour resistance. VTT's barrier technologies have been demonstrated by manufacturing packaging prototypes (see also article by Kunnari, page 79). Below is a short depiction of a few recent VTT IndBioMat biobarrier projects.

BioPack: Up-scaling bio-hybrid barrier coating to pilot coater

In the Biopack project, various biohybrid coating dispersions were applied on a com-

Figure 1. VTT's lab-scale coater (left) and our pilot-scale coater (right).

mercial board grade using the lab-scale kiss coating and the pilot-scale roll to roll equipment (Figure 1).

The target dry coating amount was 10 g/m^2. The coating dispersions applied contained agro-derived pectin with and without the addition of nanoclay[5], various starch grades and wood-derived xylan. A styrene-butadiene-latex dispersion with talc was used as a synthetic non-renewable reference. While the lab-scale coatings were relatively easy to run, the pilot-scale coatings were more demanding, requiring optimization of the solids contents and viscosities of the coating dispersions. Some bio-based dispersions were hydrophobized, which made the dispersion adhesion on the board substrate more challenging. To improve adhesion, the board was plasma-treated before coating. A solids content of over 40% was preferable during kiss coating on a pilot scale, not to be restricted too much by the transfer of a coating amount and drying capacity.

The oxygen transmission rates (OTR) of pectin, hydrophobic starch I and xylan dispersions were at the same or lower (better) level compared with the reference. The water vapour transmission rates (WVTR) were also

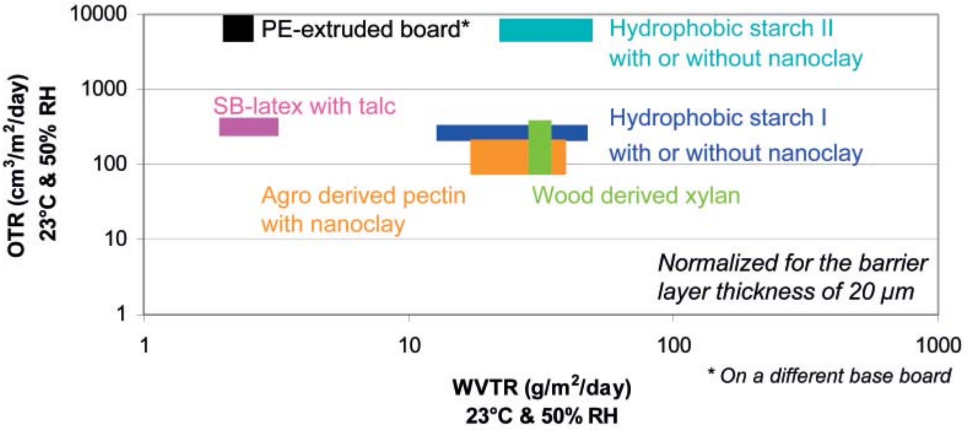

Figure 2. A Normalized (to 20 µm) oxygen transmission rate (OTR, ASTM D-3985) as a function of a water vapour transmission rate (WVTR, modified ISO 2528:19958E) at 23°C and 50% RH.

Figure 3. Grease barriers of different coatings (the more orange, the poorer the barrier).

relatively low, although higher (weaker) than the reference. At higher humidity, the addition of nanoclay would have a more pronounced effect on the WVTR.

The bio-hybrid barrier dispersions showed excellent grease barrier properties (Figure 3; oil permeation = orange, modified Tappi T 507). Wood-derived xylan, agro-derived pectin and hydrophobic starch I coatings all fully restricted oil permeation. Oil permeated slightly through the hydrophobic starch II and the reference coating at an elevated temperature (60°C) during 24 hours. The base board did not resist the oil at all.

Boards coated with starch dispersions were heat sealable, most probably due to the more extensive modification of the polymers. A rough surface may worsen the printing and converting characteristics and result in uneven barrier properties. These issues could be overcome by, e.g., calendering. To summarize, we have demonstrated successful lab-scale and pilot-scale roll-to-roll coating of biohybrid materials with improved oxygen, water vapour and grease barrier properties. We have also further converted the coated board into packaging demonstrations. These materials can be regarded as environmentally sound alternatives for synthetic barrier materials in packaging applications.

Flexpakrenew: Nanoclay-reinforced xylan barriers

The aim of the Flexpakrenew project was to improve the barrier properties of xylan through bentonite reinforcement in aqueous medium. The bentonite particle dispersion in the coatings was investigated and water vapour and aroma barrier properties were analysed. In order to derive a high-value, pure xylan product, purification steps are needed to remove contaminants. Biorefinery processes need to be developed further in order to extract valuable components, like xylan, and derive more value from wood. Bleached pulp can be extracted by sodium hydroxide[3,6] and xylan precipitated by carbon dioxide followed by purification and ultrafiltration6.

Crack- and pinhole-free film formation is essential for barrier coatings. Xylan as such is not suitable for film formation due to its high internal cohesion, which results in fragile and fragmented films. Thus, xylan needs to be plasticized externally or internally. The barrier properties can be enhanced by dispersing bentonite (water-swellable nanoclay like smectites and montmorillonites) into a polymer. The individual plate-like particles of the bentonite function are impermeable additives that significantly increase the tortuosity of the path that diffusing molecules take through the coating. The slower diffusion of the permeating molecules results in enhanced protection against the inward movement of gases, water vapour and loss of aroma compounds. Intercalated or exfoliated structures may be obtained when swollen aqueous bentonite dispersion is mixed properly with hydrophilic polymer and subsequently dried. Intercalated structures are obtained when the polymer is located between the clay plates and the plates show regular ordering, whereas when the platy particles are completely dispersed within the polymer matrix, i.e. there is no alignment between individual clay plates, the structure formed is said to be exfoliated[7].

The xylans used in the study were, e.g., xylan extracted from ECF-bleached and com-

Table 1. The coat weight (g/m^2), contact angles of water and di-iodomethane (CH_2I_2) and dispersive (γ^d) and polar (γ^p) surface energy components of the various glycerol (G)-plasticized xylan (X and Xbkp) coatings reinforced with bentonite (A to D).

Coating	Coat weight	Contact angle (H_2O)	Contact angle (CH_2I_2)	γ^d	γ^p	γtotal
X	5	72.7±0.4	42.7±3.6	38.4	4.5	42.8
X.G	5	66.3±4.2	37.0±4.0	41.2	6.6	47.8
X.G.A	6	50.0±1.2	45.2±2.1	36.9	20.0	56.9
X.G.B	7	82.3±4.1	43.2±4.6	38.0	4.5	42.6
X.G.C	6	51.4±1.2	45.8±3.4	36.6	19.3	55.9
X.G.D	5	78.6±1.3	47.4±3.4	35.8	5.0	40.8

mercial birch kraft pulp using the VTT in-house method (Xbkp)[5]. One layer of xylan-bentonite composite was applied to a paper substrate (50 g/m^2) by an Erichsen film applicator using a wet thickness of 60 µm and a spreading speed of 24 mm/s. The temperature of the bentonite-reinforced coating solutions was kept at 60°C prior to coating. Excess water was evaporated in an oven at 105 °C for 1 min and completed at room temperature.

The so-called gallery spacing of the bentonite plates was determined by a wide-angle x-ray diffraction technique (XRD: Philips X'Pert, Cu tube at 40kV and 40 mA). The contact angles of the advancing water and di-iodomethane droplets (Table 1) were determined with a CAM 200 (KSV Instruments, Finland). Aroma permeability (d-limonene, cis-3-hexeol, isoamyl acetate and r-carvone) analyses were performed using equipment consisting of a test cell and gas chromatograph[8].

For the coating studies, an aqueous solution of 20% xylan was prepared. The viscosity of the solution has a significant role in the coating process[9]. The viscosities of the xylan solution with and without glycerol were similar. The bentonite dispersions were mixed with the plasticized xylan, resulting in homogeneous and viscous coating solutions. The viscosity of the bentonite-reinforced solutions increased depending on the bentonite used and its interactions with xylan. An increase in viscosity showed xylan interacting with bentonite plates. The water contact angles of xylan coating decreased (increased hydrophilicity) due to the addition of glycerol, which is required in order to obtain coherent coatings. The contact angle of water either decreased or increased depending on the nature and orientation of the bentonite added.

The xylan-bentonite coating XRD patterns (peaks 3.1-3.3° 2θ in Figure 4B) indicate that xylan has entered the gallery, an intercalated structure exists and the spacing has increased compared with dry bentonite powder (Figure 4A). The intensity of the peaks of, e.g., the coatings reinforced with clays indicates whether the platy particles are more aligned and ordered. Similar observations for bentonite-polymer composites have been reported in previous work[10].

As the glycerol was added, in an attempt to enhance xylan film formation, hydrophilicity increased and only a small decrease in water vapour barrier properties was observed (Figure 5A). The xylan coatings reinforced with bentonites A and C were the most hydrophilic, but interestingly they also exhibited the best water vapour barriers. It was anticipated that the birch xylan extracted from the bleached kraft pulp would have similar WVTR values to commercial xylan (X) if they were of equal

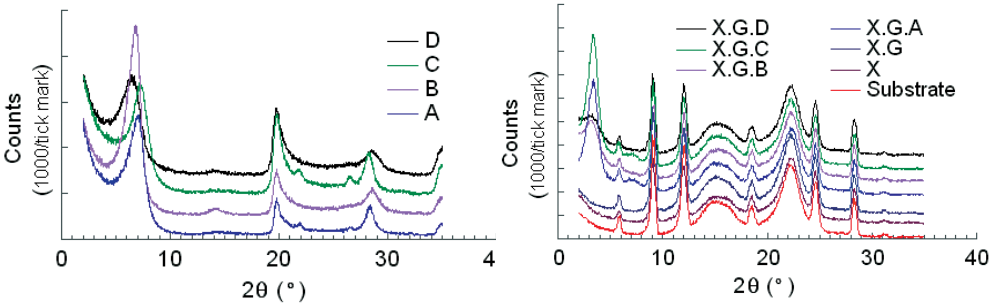

Figure 4. XRD diffraction patterns for A) the dry bentonite powders and B) the substrate and various xylan coatings. All the patterns are presented in corresponding order to the legends in which A to D, X and G represent the bentonites, xylan and glycerol respectively.

thickness. The best values obtained within this Flexpakrenew study are competitive with, e.g., PLA-coated board (20 g/m^2) with a WVTR of 68 gm^{-2}d^{-1}.[11]

Selected bentonites with birch xylan gave intact coatings and significantly enhanced water vapour barrier properties (WVTR). This indicates that the platy bentonite particles increased the tortuosity of the path of the diffusing molecules. This study clearly shows that when birch xylan, a natural polymer, is modified using bentonite it offers significant potential to form novel sustainable barrier coatings.

Results from the LigniVal project

Lignin is one of the most abundant natural polymers, together with cellulose and hemicellulose. The pulp and paper industry produces vast amounts of lignin each year, of which only 1–2% is used in specialty products. The rest of this material serves as fuel. Although the burning of lignin is a way to reduce the use of fossil fuels, lignin has significant potential as a raw material for the sustainable production of chemicals and materials. Furthermore, in the future, biorefineries processing lignocellulosic materials for the primary purpose of producing fermentable sugars from cellulose and hemicellulose will generate lignin in substantial quantities. Consequently, new avenues will open up for lignin use. One such use could, of course, be as a barrier material for fibre-based packaging materials. However, technical lignins as such have poor film-forming properties. Chemical functionalization is a potential route to introduce thermoplasticity and achieve films that can be used in barrier applications. Commercially available softwood and hardwood kraft lignins were esterified with palmitic acid and tested for application in coatings of fibre-based packaging material.

The aim was to improve the barrier properties against water vapour and oxygen of paperboard. The novel lignin derivatives were applied by a bar coater on the paperboard and formed a smooth surface on the board material. A significant decrease in WVTR was observed for all the lignin-coated board samples (Table 2). Furthermore, the contact angle of the modified lignin coatings was high and stable for the full measurement time of 120 seconds. For all the investigated lignin-coated board samples a significant decrease in the oxygen transmission rate (OTR) was observed (Table 2). According to the results, lignin palmitate can potentially be exploited as a sustainable alternative to petroleum-based barrier materials.

Polyesters based on hydroxy acids obtainable from black liquor

As an alternative to biopolymers extracted from biomass, materials can also be polym-

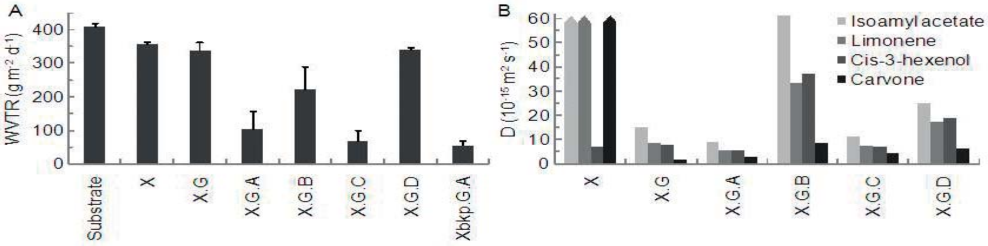

Figure 5. Permeability properties for the various xylan coatings with different nanoclay additives: A) water vapour transmission rates (WVTR) at 50% RH and 23°C and B) diffusion coefficient (10–15 m2/s) of the model aroma compounds at 23°C.

Table 2. Coat weight, WVTR and OTR for the paperboard and the coated paperboard samples. All the measurements were carried out at 23°C and 50% RH. L(SW)-PA – softwood kraft lignin palmitate, L(HW)-PA – hardwood kraft lignin palmitate and PA – palmitic acid.

Sample	Coat weight (g/m^2)	WVTR (g/m^{2}x24h) [a]	OTR (cm^3/m^{2}x24h)
Paperboard	-	740	>400 000
L(SW)-PA [b]	6.4 (±1.8)	190	37 800
L(SW)-PA [c]	12.0 (±2.7)	130	26 200
L(HW)-PA [b]	6.2 (±1.8)	190	2490
L(HW)-PA [c]	10.4 (±0.7)	40	1750
PA [b]	6.0 (±2.0)	410	2830

[a] Measured according to the wet cup method [b] single coat layer [c] double coat layer.

erized from biomonomers such as so-called hydroxy acids. These can be used to make, e.g., bioplastics (see Polyesters based on hydroxy acids obtainable from black liquor by Mehtiö et al.).

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Biaxially oriented PLA-montmorillonite-nanocomposite for barrier film applications

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Polymer-layered silicate nanocomposites are prepared by incorporating finely dispersed nanoclay in a polymer matrix. There is a need for sustainable solutions in the packaging industry for high-barrier food packages, which are used in massive volumes. Bio-based and bio-degradable polylactide (PLA) are therefore selected as matrix polymers in this study. Montmorillonite nanoclay has a high aspect ratio and unique intercalation/exfoliation potential and is selected as the nanofiller to improve the barrier properties of the film.

The dispersion of the plate-shaped nanoparticles in the polymer matrix is studied. The dispersion can be improved by adjusting the compounding process parameters. Some compatibilizers are also tested to generate optimal dispersion of the nanoclay. The PLA nanocomposite film is biaxially oriented to prepare a mechanically strong, thin film with the desired barrier properties. The best orientation parameters for the materials are searched for and tested. The transparency and oxygen permeability of the film are controlled by varying the weight fraction of the nanoclay and its dispersion in the polymer matrix.

Materials and methods

In this study, Ingeo Biopolymer 3051D and Ingeo Biopolymer 4032D, PLAs from NatureWorks LLC, were used as matrix polymers. The PLA packaging grades may be used as food packaging materials, U.S. FDA effective. The results of the compounds based on Ingeo 4032D are reported here.

In order to improve the barrier properties of biodegradable films, two surface-modified montmorillonite clays, Nanomer I.34TCN (surface-modified grade by Nanocor) and Cloisite 30B (ternary ammonium salt-modified grade by Southern Clay Products Inc.), were used as fillers. The results of using Nanomer I.34TCN as a filler are reported here.

Different compatibilizers were used and studied to improve the dispersion of the montmorillonite in the matrix polymer. These compatibilizers were based on polypropylene, polyethylene, styrene and styrene/ethylene/butylene triblock copolymer containing a reactive maleic anhydride (MAH) group. Epolene E-43 is a maleic anhydride-grafted polypropylene resin that has an acid number in the range 40.0-55.0 (mg-KOH). A laboratory-made maleic anhydride-grafted polylactide (PLA-g-MAH) was also used to improve compatibility and dispersion. Only the results of using Epolene E-43 as a compatibilizer are reported in this paper.

Processing

Nanocomposites based on montmorillonite and matrix polymers were compounded twice by the twin-screw extruder Berstorff ZE 25X48D at VTT. The reference sample BIPA 1 was compounded once using the same compounding parameters. Materials were dried according to the manufacturer's instructions prior to processing. Compounding was performed at temperatures of 190°C-200°C and the rotation speed of the screw was 250 rpm. Montmorillonite was gravimetrically dosed into the compounder's cylinder through the same filling opening as the polymer.

After compounding, the nanocomposites were dried and extruded with a Brabender Plasticorder single screw extruder (diameter 18 mm) using a flat die. The thickness of the cast film was 0.5-0.9 mm. Minimal flow orientation was induced during extrusion. The final film samples were prepared by biaxially orienting the cast film using a Brückner laboratory-scale stretch machine Karo IV.

Characterization

The Water vapour transmission rates of the films were determined gravimetrically using a modified ASTM E-96 procedure. Anhydrous calcium chloride was used as a desiccant and placed on the bottom of a circular aluminium dish. Paraffin wax was used to seal the samples tightly on the mouth area of the dishes. Samples were stored in test conditions of 38°C and 75% relative humidity and weighed periodically until a constant rate of weight addition was attained.

The Oxygen transmission measurements were performed with an Oxygen Permeation Analyser Model 8001 (Systech Instruments Ltd. UK). The tests were carried out at 23°C and 50% relative humidity.

The Light Absorbance of the oriented films was defined using an Ordior UV-Vis spectrophotometer (UV-2501PC). The wavelength used was 200–900 nm. The film thickness was measured and the absorbance value was converted to correspond to 100 µm film thickness.

Results and Discussion

Table 1 presents the compositions of the polymer nanocomposites and the numerical values for O_2 and moisture permeability.

Figure 1 shows a remarkable reduction in oxygen and moisture permeability in PLA when nanoclay is compounded into the polymer. Improved barrier properties are proof of exfoliation of the layered silicate platelets in the matrix. No big difference is seen between using and not using a compatibilizer. However, the orientation parameters were found to affect the permeability of the oriented film. The lowest permeability values were measured for PLA/montmorillonite-composite films without a compatibilizer.

Photographs of the prepared biaxially oriented films are presented in Figure 2. The high transparency of the PLA films is reached by 5 w% nanoclay loading in the compounds, the composite film without a compatibilizer being the brightest. The transparency of the film shows successful dispersion of nanoclay in the polymer matrix.

The light absorbance of the films is presented in Figure 3. The wavelength of the visible light is 380-750 nm. The smallest absorbance value is achieved with the reference film (BIPA 1), which is pure PLA. The highest absorbance value is achieved with the BIPA 27 film, which is slightly cloudy, though it has good transparency. The cut-off point for the different compounds is moved to higher wavelength values as a function of

Table 1. PLA-nanoclay composites, their composition and barrier properties.

Sample	Nanoclay w%	Compatibilizer w%	O_2 barrier cc*100µm/m²/day	H_2O barrier g*100µm/m²/day
BIPA1	0	0	273	40
BIPA18	5	0	118	20
BIPA19	5	1	145	22
BIPA27	5	5	149	21

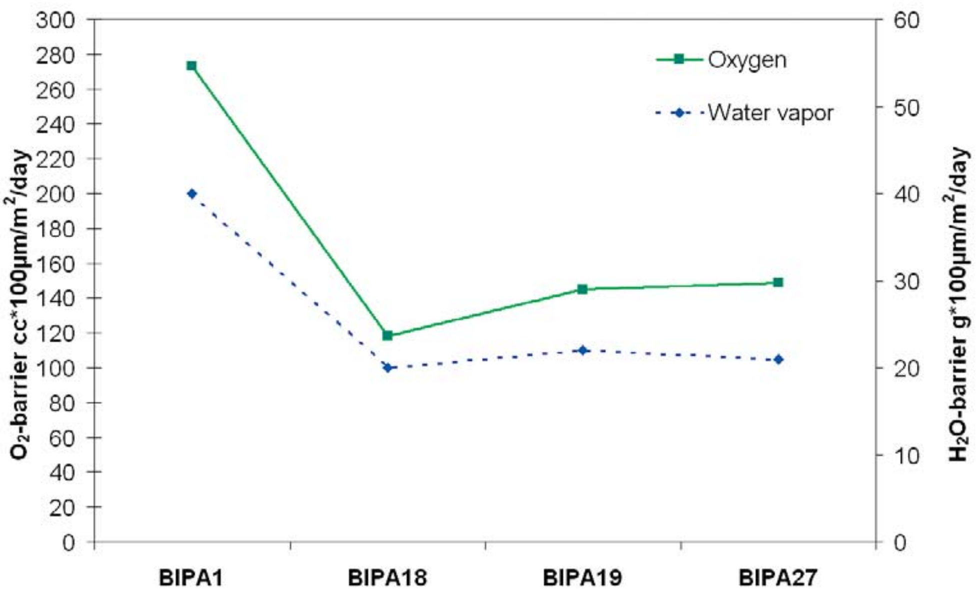

Figure 1. Oxygen and water vapour barrier values measured for reference PLA-film BIPA 1 and PLA/montmorillonite films BIPA 18, BIPA 19 and BIPA 27.

Figure 2. Biaxially oriented PLA-montmorillonite -nanocomposite films: BIPA18, BIPA19 and BIPA 27, from left to right.

the amount of the Epolene E-43. Due to the nanosize filler particles, higher light absorbance can be reached without any significant loss in the transparency of the film. This phenomenon is desirable, especially in the packing industry.

Conclusions

Biaxially oriented films made from PLA-Montmorillonite nanocomposites were prepared successfully. Compounding process parameters were found to have a crucial impact on nanoclay dispersion in a polymer matrix. Biaxial orientation parameters for the PLA nanocompound were searched and set to optimal values to produce films of uniform quality. The transparency of the oriented films is satisfactory for food and pharmaceutical packaging. The barrier properties of PLA were improved remarkably with a nanoclay loading of 5 w%, the oxygen permeability was reduced to less than half of the value of pure PLA and the moisture permeability was reduced to 50% of the numerical value for pure PLA.

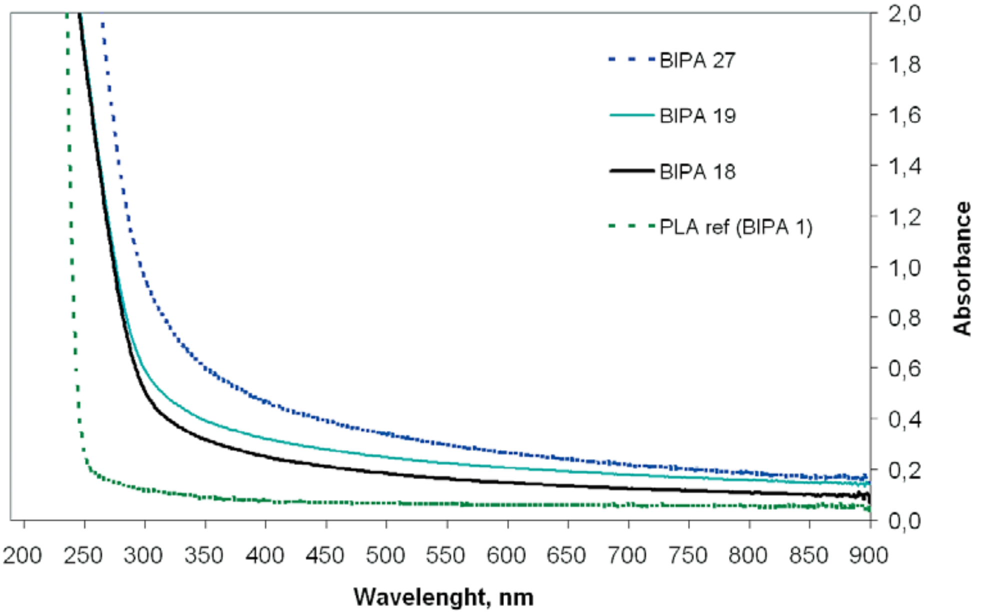

Figure 3. Light absorbance values as a function of the wavelength for PLA-montmorillonite – films BIPA 18, BIPA 19 and BIPA 27. The reference film is pure Ingeo 4032D PLA.

Different compatibilizers were tested to generate improved nanoparticle-matrix polymer interfacial interaction and fine dispersion or nanoparticles. However, the best barrier properties were achieved without an added compatibilizer in this study. Experimental work needs to be continued to understand the interfacial interaction at the nanoparticle level.

Publications

Härkki, O., Karttunen, M., Kortet, S., Koponen, M. and Harlin, A. 2011. Biaxially oriented PLA-montmorillonite-nanocomposite for barrier film applications. Poster presentation, Nanocomposites 2011, Paris-Est, Creteil University, 7–10 June 2011.

Atomic layer deposited thin-layers for upgrading bio-based materials

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Biopolymers can be upgraded with thin-film deposition techniques. Water vapour and oxygen barrier properties were both significantly improved with a 25-nm-thick layer of atomic layer deposited Al_2O_3. Pre-treating the substrate prior to the ALD and using ozone as a precursor instead of water further enhanced the barrier properties. Flexibility of inorganic layers can be improved by dividing the inorganic coating into thinner layers separated by hybrid layers prepared by atomic/molecular layer deposition techniques.

Renewable materials offer a means of mitigating the greenhouse effect[1]. However, the use of such materials is limited partly due to their inadequate barrier performance. Multilayer structures with metallic layers such as aluminium have typically been used to provide a barrier against gases, moisture and light[2,3]. For obvious environmental reasons, the replacement of aluminium has recently attracted considerable attention.

The atomic layer deposition (ALD) technique is a surface controlled layer-by-layer thin-film deposition process based on self-limiting gas-solid surface reactions. It is suitable for producing pinhole-free barrier coatings of uniform thickness. Nowadays, a wide range of ALD-grown materials and applications have been developed ranging from catalysts to electroluminescent displays to microelectronics and beyond[4]. In our previous work, thin inorganic coatings have been deposited by the ALD at a low temperature on various polymer-coated papers and boards, and polymer films[5-11]. Despite the promising results, an improvement in barrier performance is still needed to create coatings suitable for more demanding applications. One route is to pre-treat the substrate before the thin-layer deposition. The surface chemistry of the substrate may affect initial thin-film growth. Pre-treatment could enhance the uniformity of the thin layers and thus improve the barrier properties, especially those obtained with thin coatings.

Inorganic thin films often have poor mechanical properties, especially in the case of thick layers, which results in film cracking impairing the barrier properties[12-15]. An organic layer may act as a spacer between thin inorganic layers, thus improving the mechanical properties. Molecular layer deposition (MLD) is, in principle, similar to the ALD except for organic precursors. Interestingly, ALD and MLD can be combined to produce inorganic-organic thin hybrid films. These hybrid films have properties of both inorganic and organic components[4,16].

Materials and methods

Base substrates

A wide variety of polymer films and coated paperboards were tested, some of which are listed in Table 1. These samples included commercial samples and samples prepared on a pilot and laboratory scale. Pilot-coated boards were pretreated at the SUTCO coating line at VTT prior to the ALD.

Table 1. Examples of materials tested

Abbreviation	Material
BOPLA	Oriented polylactic acid film
Cellophane	Cellophane film
OPET	Oriented polyester film
PE coating	Low-density polyethylene coated paperboard
Pectin/nanoclay coating	Pectin/nanoclay coating on paperboard
PHB/HV	Oriented polyhydroxybutyrate-co-valerate film
PLA coating	Polylactic acid coated paperboard

Thin-film deposition

Films were deposited at VTT using Picosun SUNALE^{TM} R-series batch ALD reactor. The thin-layer depositions were carried out at 80 and 100ºC. The ALD precursors for the Al_2O_3 depositions were water, ozone and trimethylaluminum (TMA). The organic precursor for the hybrid layers was ethylene glycol (EG).

Thin-film characterization

The water vapour transmission rate (WVTR) was measured according to the modified gravimetric methods ISO 2528:1995 and SCAN P 22:68 and expressed as g/m^2/day. The test conditions were 23 °C and 50/75% relative humidity. The oxygen transmission rate (OTR) was determined at 23 °C and 50% relative humidity. OTR was expressed as cm3/m^2/d/105 Pa.

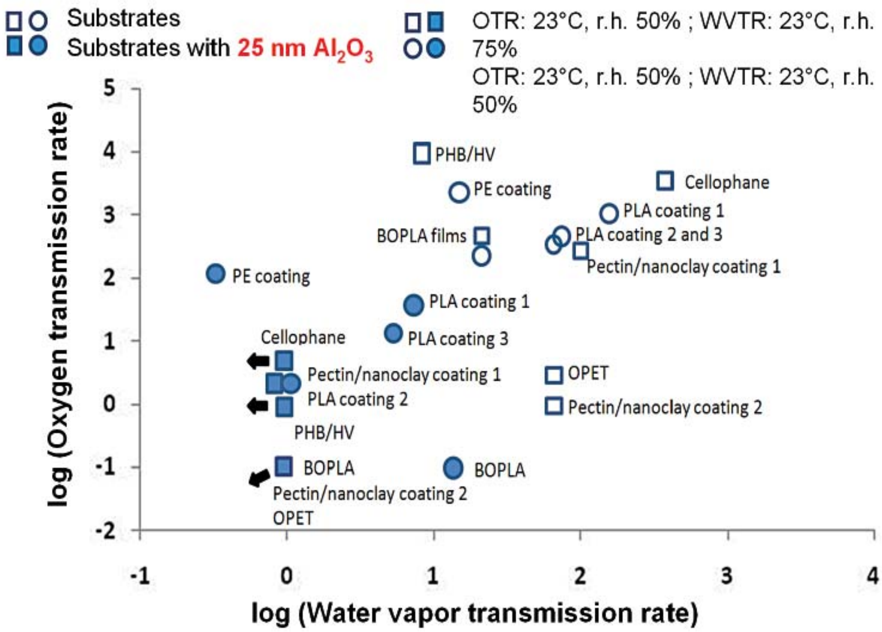

Figure 1. The effect of 25-nm-thick ALD-grown Al_2O_3 on oxygen and the water vapour barrier properties of various materials

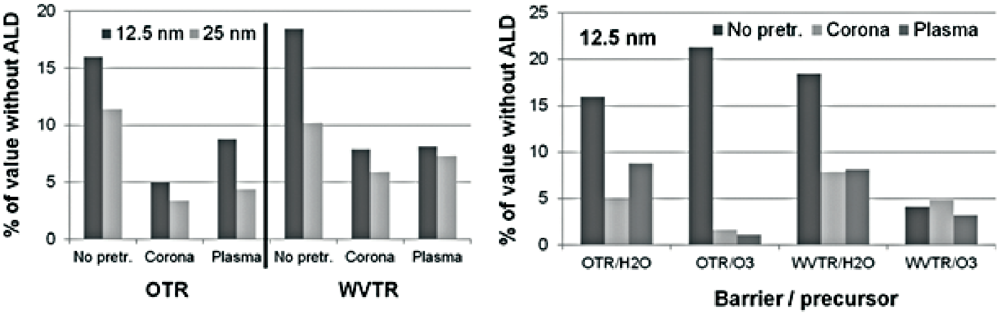

Figure 2. Relative effect of surface pretreatments (left) and oxidants (right) on the OTR and the WVTR of PLA coating

The actual coating thicknesses on the biopolymers could not be measured directly. Instead, the thicknesses were determined for coatings deposited with the same parameters on silicon wafers; the thickness determinations were carried out with ellipsometry (Sentech) and X-ray reflectivity (XRR).

Films were strained with a mechanical tensile tester (MTS) with a load cell of 200 N and test velocity of 12 mm/min. Samples were stretched below the maximum elongation at break. Scanning electron microscopy (SEM) was used to image the films.

Experimental part

Upgrading polymer films and coatings by ALD

Figure 1 demonstrates the effect of a 25 nm ALD-grown Al_2O_3 layer on a number of different packaging materials. The effect was profound, and the improvement obtained with the ALD thin-films was in many cases dramatic. Please note that the arrow refers to cases for which the exact barrier value was below our typical measurement range.

Corona and argon plasma pretreatments (50 Wmin/m^2) performed for PE and PLA coatings prior to the ALD improved the barrier somewhat, especially in the case of thin Al_2O_3 layers, as presented in Figure 2. Surface chemistry probably plays a role in the initial growth rate of Al_2O_3 thin-films. Likewise, the choice of oxidant affects the barrier properties achieved. Ozone as the precursor led to slightly better barrier properties than water.

Flexibility through nanolaminates

Flexibility is one of the key requirements of converting operations and many packaging applications. The objective was to study, experimentally, whether the flexibility of the ALD-grown Al_2O_3 film can be improved by adding hybrid material to the film with the ALD/MLD technique[17]. Inorganic Al_2O_3 and hybrid thin-films were deposited on the BOPLA and Cellophane. The barrier properties of Al_2O_3 thin-films, especially thick ones, were deteriorated by straining. Hybrid films were an even poorer barrier against oxygen and water vapour than Al_2O_3, probably due to the water sensitivity and porous structure of these films. The number of defects increased and the film density decreased with increasing hybrid film thickness. This is due to different growth mechanisms.

The ALD and the ALD/MLD techniques were both used to produce stable five-layer laminates (Table 2). The samples with the highest total thicknesses of Al_2O_3 provided the best barrier properties before straining. The OTR of the laminates increased less with straining than that of the plain Al_2O_3 (Figure 3). The flexibility of thin-films increased when the thickness of the individual Al2O3 layers decreased and/or a hybrid was used as a spacer between the Al_2O_3 layers. Likewise, the probability of defects extend-

Table 2. Structure of five-layer Al_2O_3/hybrid laminates on silicon wafers including the number of cycles, thickness and growth per cycle for single layers determined with X-ray reflectivity (XRR).

	1. Al_2O_3	2. Hybrid	3. Al_2O_3	4. Hybrid	5. Al_2O_3	Total
Laminate 1						
Cycles	150	50	150	50	150	
Thickness, nm	10.2 ± 0.4	9.27 ± 0.05	10.75 ± 0.04	9.12 ± 0.04	11.69 ± 0.04	51.1 ± 0.5
Growth per cycle, nm	0.068	0.185	0.072	0.182	0.078	
Laminate 2						
Cycles	50	100	50	100	50	
Thickness, nm	1.939	20.7 ± 0.15	1.73 ± 0.27	20.25 ± 0.1	2.58 ± 0.05	47.2 ± 0.6
Growth per cycle, nm	0.039	0.207	0.035	0.203	0.052	
Laminate 3						
Cycles	50	50	50	50	50	
Thickness, nm	4.31 ± 0.22	10.03 ± 0.03	2.49 ± 0.06	9.44 ± 0.02	2.66 ± 0.16	29.2 ± 0.4
Growth per cycle, nm	0.086	0.201	0.05	0.189	0.053	

ing through the whole multilayer structure is reduced. However, increasing the thickness of the hybrid layer decreases the growth rate and the stabilizing effect of the following Al_2O_3 layer.

Conclusions

Barrier properties of various bio-based materials can be improved significantly with inorganic Al_2O_3 thin-films applied by atomic layer deposition (ALD). The properties can be further improved by pretreating the substrate with corona and plasma prior to the ALD, and by optimizing the choice of the oxidant. This indicates that surface chemistry and interactions between the precursors and the base substrate are important for proper thin-film growth.

Thick inorganic coatings are brittle. Stable five-layer laminates of thin inorganic layers and hybrid spacer layers improved flexibility when compared with a single thick inorganic layer. In addition, the probability of defects extending through such a laminate is smaller. The properties of such laminates could be improved further by using ozone as a precursor instead of water. This way the detrimental interactions between water and the hybrid layer could be diminished. Likewise, testing alternative organic compounds in the hybrid layer could enable laminates with enhanced barrier performance against water vapour. In many practical applications, the thin-film could be laminated between two polymeric substrates. It would also be interesting to evaluate the performance of thin-films in such cases.

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Most of this study was performed as part of the RRALD (Roll-to-Roll ALD process devel-

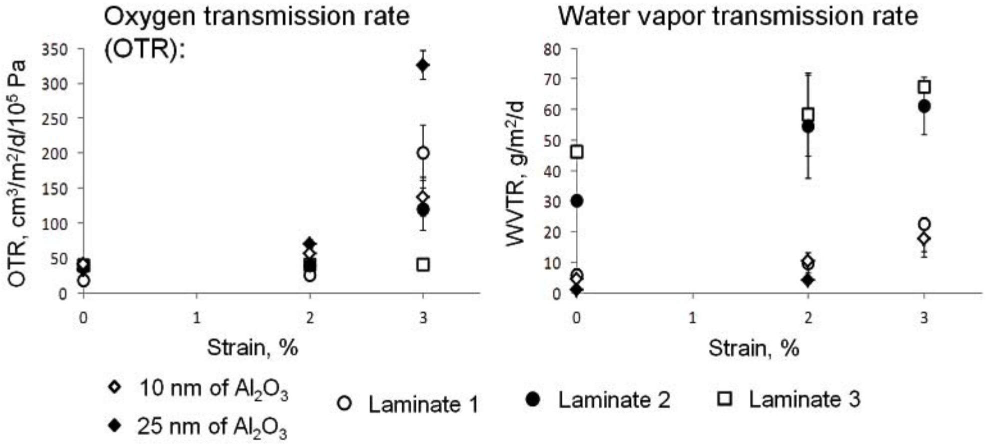

Figure 3. OTR (left) and WVTR (right) of Al_2O_3 and laminates of Al_2O_3 and hybrid on BOPLA as a function of strain.

opment) project. The authors would like to thank the Finnish Funding Agency for Technology and Innovation (TEKES) and the industrial partners for their funding and the material suppliers for providing them with the film samples. The authors would also like to thank Aalto University and Tampere University of Technology for their cooperation.

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Nanotubes and nano-coral by the fibre template method

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Tubes by fibre templates (TUFT) is a process that is used to fabricate tubular materials. The tube dimension depends on the template fibre size and coating thickness, while the tube regularity depends on the coating and template removal methods. We have studied the preparation of tubes using electrospun fibres of polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) and polyamide-66 (PA) as templates, atomic layer deposition (ALD) of Al_2O_3 as coating and dissolution as well as heat treatment in template removal. Smooth tubes were obtained in a dissolution of PVP and PA templates and when heat treatment was used as template removal. Dissolution of PVA, on the other hand, produced novel nanostructured and high surface area coral-like material. This material, which we have called 'nano-coral', has a relatively high surface area due to the interconnected cavities formed after the removal of the template. Nanotubular materials have potential in catalyst carriers, filtration and other application fields.

Tubes by fibre templates (TUFT) is a process that is used to fabricate tubular materials[1-5]. The process includes three steps: template preparation, coating and template removal. In the TUFT process, the tube dimensions depend on the template fibre size and coating thickness. The preparation of nanotubes requires the use of nano-sized templates and coating methods enabling nano-size coatings. Tube regularity, on the other hand, depends on the coating material and method as well as on the template removal method. Template removal methods include thermal decomposition, dissolution and biodegradation. Electrospinning and ALD are suitable for the preparation of nanotubes. While many nanomaterial manufacturing methods only produce a few grams or an even smaller amount of material, these manufacturing methods are suitable for large-scale production.

Electrospinning is a method that can be used to prepare polymeric or composite fibres with diameters typically in the sub-micron range[6-8]. In electrospinning, the polymer is dissolved in a suitable volatile solvent. The solution is fed into the electrostatic field, arranged between a nozzle and a collector, and the electrostatic field causes instabilities and stretches the polymer solution. The appearance of the deposition ranges from droplets to beaded fibres and finally smooth continuous fibres, depending on the solution properties, especially the viscoelasticity; process variables, particularly the strength of the electric field; the solution flow rate; and the ambient conditions. An optimally interconnected web composed of sub-micron or nanofibres is obtained. The principle of the process and appearance of the deposition are presented in Figure 1. Electrospun fibres can be prepared from a wide variety of polymers from natural to synthetic, and a wide variety of additives and fillers can also be used in order to modify the properties of the fibres. Metal containing nanofibres, for example, can be pyrolysed into ceramic nanofibres, and organic nanofibres

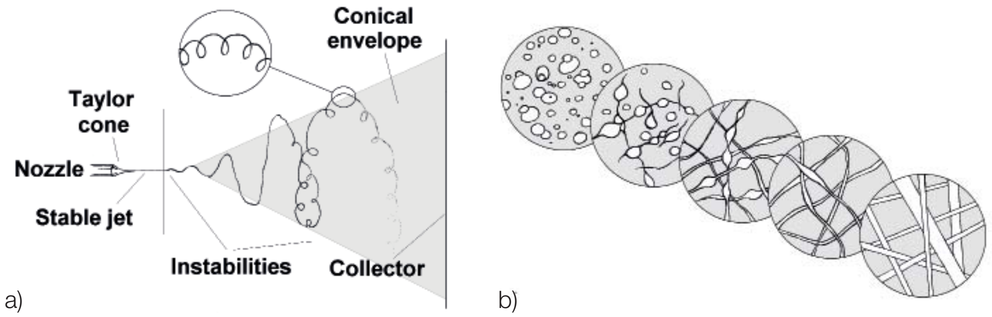


Figure 1 a) principle of electrospinning and b) appearance of deposition[8].

graphitized into carbon nanofibres. The small fibre diameter, small pore size and high surface area of the nanofibre web are properties that are advantageous for many applications. Application areas of electrospun fibres include filtration, reinforcement, tissue engineering, sensors, fuel cells and nanoelectronics. Electrospun fibres are typically smooth and form a randomly oriented fibre web with high porosity and an interconnected tube structure. High porosity is advantageous in a TUFT template material.

ALD enables preparation of coating layers in the nanometre range[9–12]. ALD is a surface-controlled layer-by-layer coating method. It is based on self-limiting gas-solid reactions leading to coatings with a low impurity content. Coatings are conformal, pinhole free and have a fixed thickness. In the ALD coating, the surface is exposed with the pulses of the reactants, which chemisorb onto the surface as a monolayer, one at a time. The excess of unreacted precursor and volatile reaction by-products is removed from the reaction chamber between reactant pulses. These cycles are repeated until the desired film thickness has been obtained. The coatings are typically ceramic (oxides, nitrides, sulphides, etc.) or metallic. There is a wide range of applications for ALD-grown materials, ranging from catalysts to electroluminescent displays in microelectronics and beyond to different kinds of protective and functional coatings. The use of ALD in the TUFT process has advantages over other coating methods, such as chemical vapour deposition (CVD), electroless deposition and in-situ polymerization. A challenge of many of the other processes is uneven coating of fibres in different parts of the web. However, ALD allows preparation of dense and pinhole-free inorganic films with a fixed thickness even inside deep pores and trenches of porous materials. This can be used in template processes.

A wide variety of materials can be used in tubes prepared by combining these two methods. The polymeric template is typically removed by calcination, leaving a smooth tube structure. Typical application areas are sensors and catalytic applications. Al2O3 nanotubes have been prepared[13-15]. Suitable materials include PVA template fibres and trimethyl aluminium (TMA) + H_2O as ALD reactants[13]. ZnO nanotubes have been prepared for gas sensing applications[16] using PVA as a template and diethylzinc + H_2O as ALD reactants. SnO_2 tubes have been prepared for gas sensors and lithium ion batteries[17] using polyacrylonitrile as a template and dibutyltin-diacetate and O_2 plasma as ALD reactants. Ir, IrO_2 and Pt tubes have been intended for catalyst applications[18]. Pure Ir was obtained in ALD using Iridium(III)acetylacetonate $Ir(acac)_3$ + O_2 or a three-step process $Ir(acac)_3$ + O_3 + H_2, IrO_2 using $Ir(acac)_3$ + O_3, and pure Pt using platinum(II)acetylacetonate + O_3. Photocatalytic TiO_2 nanotubes loaded with magnetic nanoparticles have also been prepared[19].

Table 1. Polymers used as a template

	Polyvinylalcohol	Polyamide-66	Polyvinylpyrrolidone
Properties	Mw = 72 000 g/mol, hydrolysation rate = 98%	Technical grade	Mw = 360 000 g/mol
Source	Merck	Fluka	Sigma-Aldrich
Solvent	Water	Formic acid	Ethanol

Functionalization was obtained by including metal-containing compounds (e.g. Ni, Co, Fe) in PVP solution, and the ALD reactants were $TiCl_4$ + H_2O. During the calcination, metal compounds turned into metallic nanoparticles located inside the tubes.

We have studied the preparation of Al_2O_3 nanotubes using three template polymers and different template removal methods. Work has been done in co-operation with Tampere University of Technology (TUT) and partly as the VTT-funded M.Sc. Thesis of Heidi Hildén.

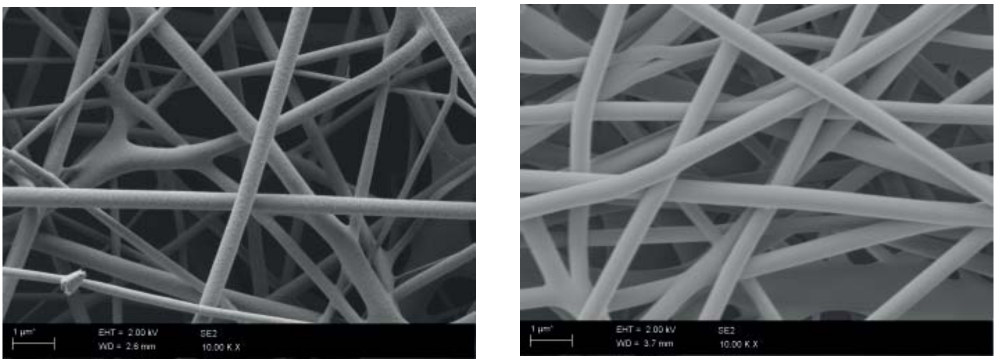
Experimental

Electrospinning was conducted using horizontal single- and multi-nozzle electrospinning set-ups (TUT). The ALD coating was prepared using the Picosun batch SUNALE^{TM} ALD reactor and trimethylaluminium (TMA) + H_2O as reactants (VTT). In a first study, we used PVA as a template and dissolution as the template removal method[3,4], and in the second study different polymers (PVA, polyamide-66 [PA] and polyvinyl pyrrolidone [PVP]; see Table 1) as templates, and removal was done by dissolving and by heating[4,5]. The formed Al2O3 nanotube structures were analysed with scanning electron microscopy (SEM). (For more details, see[3,4].)

Results and Discussion

Electrospinning of the PVA solution (10 wt%) produced a web composed of smooth, bead-free nanofibres that were ALD coated with Al2O3. The appearance of the coated fibres was similar to the template fibres, the only difference being the fibre diameter; see Figure 2. The surface of the ALD coating was smooth and conformal with the surface of the template fibres.

The dissolution process in heated water (2 h, 80°C) changed the structure of the tube walls and the smooth ALD coating was transformed into a highly complex, coral-like structure that consisted of continuous channels inside highly porous tubes (Figure 3).



a) b)

Figure 2 a). Template fibres and b) ALD-coated fibres (coating thickness 100 nm).

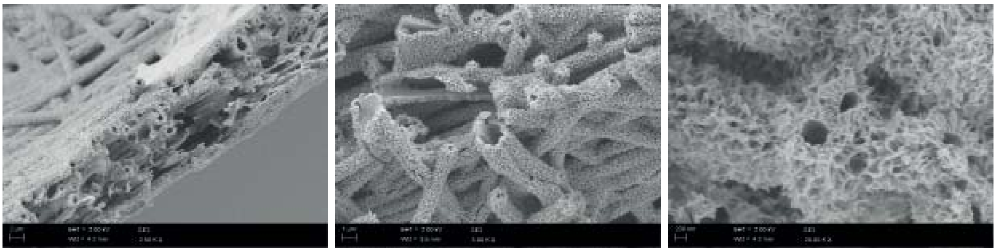
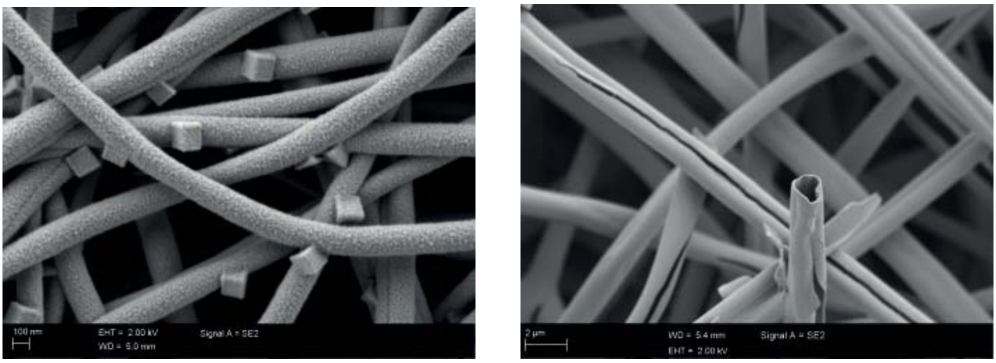

a) b) c)

Figure 3. Nano-coral obtained using dissolution in the removal of the PVA template.



a) b)

Figure 4. Nanotubes obtained by the dissolution of a) PA and b) PVP template fibres.


a) b) c)

Figure 5. Nanotubes obtained by thermal decomposition of a) PVA b) PA and c) PVP.

The probable cause of this change is polymer swelling and migration out of the structure. The formation of this structure depends on the dissolution temperature and time (see the results from[3,4]). This kind of material has potential applications, for example, in the fields of catalysts and filtration.

Further studies of nano-coral formation revealed that the polymer-dissolving method can produce at least three different kinds of nanotubes. In addition to porous nano-coral-structured nanotubes obtained with PVA fibres, smooth fibres were also observed. Cubic crystals appeared on the surface of the smooth tubes as a result of dissolving PA fibres, and the smooth tubes obtained by dissolving PVP fibres had cracked along the length of a tube (Figure 4). Smooth fibres were also obtained when template removal was conducted using heat treatment (Figure 5).

Conclusions

We have demonstrated the use of the TUFT method in the preparation of nanotubes of different structures by applying an ALD coating onto a porous electrospun template web. Typically, nanotube structures obtained in this way are smooth and resemble the coating. However, the unique nano-coral structure can be obtained using the dissolution technique for the removal of the fibrous template instead of the heat treatment. When PVA was used as a template, the resulting structure consists of a complex network of channel-like structures surrounding a highly porous tube. These channels enable permeability of gases or liquids through the structures. These novel nanotubular materials can be used for, for example, catalyst and filtration applications.

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Bio-based latexes and adhesives

Development of bio-based latexes for paper coating applications

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The purpose of this work is to demonstrate how α-methylstyrene can replace styrene in preparing styrene-butadiene-type latexes and compare the properties of the paper coating of the prepared α-methylstyrene-butadiene emulsion with the commercial styrene-butadiene latex reference sample. The measured paper properties for uncalandered and calandered coated samples proved α-methylstyrene to be adequate for replacing the oil-based styrene in commercial reference SB latexes. Even though, the emulsion polymerization for the α-methylstyrene butadiene latex was not optimized, almost all the tested properties were at least as good as in the commercial reference sample. α-methylstyrene-containing coating colours had slightly higher viscosity than the other coating colours. Coating colours containing α-methylstyrene seem to have an improved water retention compared with the reference styrene-butadiene latex-coating colour and the laboratory-prepared styrene-butadiene coating colour. The paper coated with the commercial reference latex-containing coating colour was less porous than the other coated papers. Despite that, the dry and wet surface strength were both at least as good as in the case of the commercial reference latex. The results are promising when considering the future development of the bio-based latexes.

Materials and Methods

Emulsion polymerization

Polymerization was carried out in the Mettler-Toledo RC1e reaction calorimetry (RC). The RC is a batch or semi-batchwise operated lab-scale reactor that is used to measure the thermochemical changes of endo- or exothermic reactions. Both isothermal and adiabatic running modes can be applied. It is equipped with sensitive thermostats, which are used to measure the inside temperature of the reactor and the temperature of the heat exchange medium circulated in the reactor jacket. The RC is mainly suited to the measurement of the heat of the reaction, the heat of mixing and the solution, providing temperature curves as a function of time and estimating the accumulated heat during the feed of the reactants. Emulsion polymerization is an exothermic reaction and RC allowed us to control the temperature profile accurately during the reaction time span and monitor the rate of the reaction by on-line heat release measurements. Three separated feed streams, i.e. monomer, initiator and butadiene streams, were operated during the run. It is extremely important to control accurately the mass flow rates of the relatively low rate of feed streams. The butadiene feed line was engineered based on an HPLC pump, and it was manually operated while the other two feed pumps were controlled by the computer. In addition to monomers, other chemicals are necessary, including emulsifiers, pH regulators and charge transfer agents, for the successful production of industrial latexes.

The characterization of the latex products included the dry content, glass transition temperature Tg, molecular mass determination and particle size distribution. Directly after polymerization, the dry content and glass transition temperature of all the latex products were determined. On the basis of these results, certain products were analysed in more detail, especially to obtain the molecular mass distribution and particle size distribution, which are important in various applications.

Coating colour and coated paper testing

The prepared latexes were used in a typical standard coating colour recipe and the coating colours were coated onto paper with a semi-pilot blade coater (Saukko, VTT) that also enables on-line measurement of the coating colour consolidation. All coated papers were calandered with a band calender. The coated paper quality was characterized by measuring paper properties and by laboratory printing tests.

The semi-pilot coater enables testing of interactions between the base paper and the coating colour, coating colour immobilization and consolidation in detail, and the related print quality at appropriate coater speeds (max. velocity 1200 m/min). The coating equipment is a jet applicator equipped with a blade-metering unit and two IR dryers (2x24 kW). The blade beam angle can be adjusted to a value between 15 and 60**°** and the dwell distance from the application to the blade can be varied between 235 and 730 mm. The coated width is 130 mm and the coated length approx. one metre. The device has an open structure so that measurement sensors can easily be placed along the web. A special feature is that the web can be accelerated to full speed as 1200 m/min in 0.1 second and decelerated to a complete stop in the same time period. The device can be used for the screening of coating colour formulations prior to a coating trial as it only uses small amounts of coating colour, making the screening easy and effective. Optical measurement sensors detect coating colour consolidation from several points on line or continuously from the stopped web. The consolidation process can be monitored from either a stopped or moving web using a high-speed video camera. More information related to coating testing is available[1].

Several coating colour properties were measured including temperature, pH and dry solids content. Viscosity was determined and measured at both small (0-3000 1/s) and high (typically $2x10^5$-$10^6$1/s) shear rates. The static water retention of the coating colours was determined with a gravimetric method. Standard coated paper properties were measured according to internal VTT instructions or to international standards (standards SFS-ISO 2470, SFS-EN ISO 8254-1, ISO 5636-5, ISO 9416 and ISO 8791-4:2007 were used). The picking resistance and delamination of the coated papers were evaluated with IGT AIC2-5 according to the SCAN-P 63:90 standard. The wet pick test was performed with a Prüfbau laboratory printer.

Results and discussion

Even though the emulsion polymerization for α-methylstyrene-butadiene latex was not optimized, almost all the properties were at least as good as in the commercial reference sample. The α-methylstyrene-containing coating colours had higher viscosity than the other coating colours. This was true for all shear rates. The dry and wet surface strengths were at least as good as in the case of the commercial reference latex. Coating colours containing α-methylstyrene seem to have improved water retention compared with the reference styrene-butadiene latex coating colour and the laboratory prepared styrene-butadiene coating colour. The α-methylstyrene-butadiene latex still contained a significant amount of monomers, and more work is needed to optimize the polymerization process.

The actual offset printing process also includes a fountain solution. The fountain

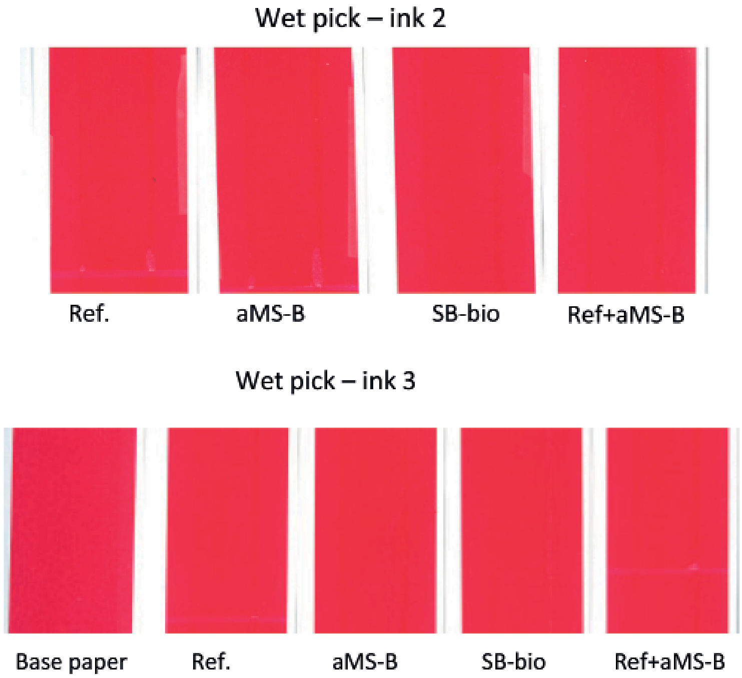

Figure 1. Wet pick test with Huber inks 2 and 3.

solution wets parts of the paper and has a tendency to loosen both the paper and coating layer structure. The so-called wet strength of the coated paper is therefore measured when evaluating new binders in coating colours. Figure 1 shows that no wet strength problems were observed for any of the tested latexes. The density (colour) of the strip is the same all over, which indicates that no wet pick is taking place. The test was performed with two different Huber test inks, no 2 and the more tacky ink no 3. This did not change the outcome of the measurement.

Conclusions

Based on the measured paper properties for uncalandered and calandered coated samples, α-methylstyrene seems to be adequate for replacing the oil-based styrene in commercial reference SB latexes. Terpenes, such as α-limonene and pinene, are a possible source of aromatics, and they can indeed be converted into p-cymene by catalytic dehydrogenation and aromatization. There are well known industrial hydrodealkylation and disproportionation processes developed by major petrochemical companies that can convert p-cymene further into BTX aromatics or simultaneously dehydrogenate the alkyl chain of p-cymene into styrenic monomers such as α-methylstyrene. In addition to potential biobased routes for α-methylstyrene production, oil-based α-methylstyrene is produced as a by-product in the cumene-based production of phenol. The results are promising when considering the future development of the biobased latexes.

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Bio-based adhesives

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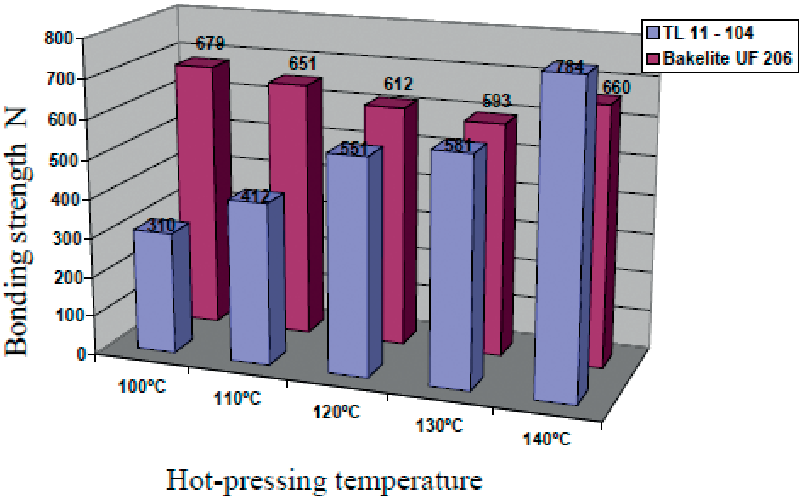
VTT has developed formulations and IP for price-competitive adhesives based on natural and renewable raw materials for environmentally friendly end products. The increase in the price of petroleum, along with the implementations of low-emission chemical regulations, is driving product and chemical manufacturers towards the use of bio-based adhesives. New challenges will also be faced when petroleum-based coatings are replaced with bio-based materials and the novel surfaces need to be glued. Fully bio-based packaging also requires the adhesive to be bio-based.

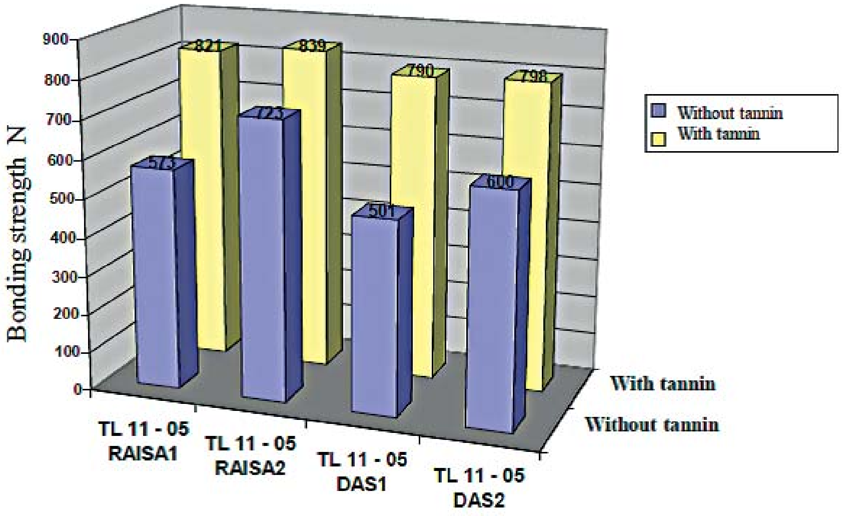
Thermoset resin for wood and rug gluing

VTT has developed formaldehyde-free starch-based adhesives for gluing fibre-based products. The adhesive formulation comprises transglycosylated starch and hydroxyl propylated starch, and the adhesive is hardened using a cross-linker. In Figure 1, the strength property as a function of compression temperature is shown for the starch-based adhesives and a commercially available urea formaldehyde resin. The formaldehyde-free adhesive formulation shows similar or better strength properties than the



TL 11 – 104 = starch based adhesive
(Tranglycosylated starch 90 %, hydroxypropylated starch 10 %)

Figure 1. Influence of compression temperature on bonding strength for starch-based adhesive and a commercial UF-resin.



RAISA = oxidized starch glue, DAS = dialdehyde starch
Glues contain 90 % transglycosylated starch and 10 % oxidized or dialdehyde starch

Figure 2. Bonding strength of wood veneers glued with a starch-based adhesive with and without the addition of tannin.

commercial resin, depending on the compression temperature.

Polyphenol adhesives are well known, and they have been used for gluing wood composites such as chipboard, plywood and fibreboard. The natural phenolic component can be lignin, resorcinol or tannin. In VTT's formulation, part of the tannin has been replaced by a combination of modified starches, i.e. transglycosylated starch and oxidized starch. The addition of different starches modificated with different molecular masses results in an adhesive formulation with a solid content of at least 40% and a low viscosity level. The novel adhesive compositions also have the benefit of moisture resistance as a result of the added modified starch products. Figure 2 shows the result of the strength properties of starch-based adhesive with and without the addition of tannin. The starch material tested is a mixture of transglycosylated starch and oxidized starch. The ultimate tensile load is clearly higher with the addition of tannin than the tannin-free starch-based adhesive.

It is also possible to combine the bio-based adhesive with a pre-treatment of the wood surface. The pre-treatment can either be chemical or enzymatic. The breaking load and the wood failure could also be increased with laccase treatment of the wood substrate as well as with succinate treatment and citrate treatment.

The starch-tannin-based glues also showed excellent performance as adhesive for rugs and carpets (Figure 3).

Hot melt adhesives based on starch

Starch ethers and esters (such as starch acetate) have been subjected to transglycosylation and used as a component in hot melts or as hydrophobic coating. The advantage of the translycosylated material is that lower melting products can be achieved and thereby be prepared by simple melting, i.e. no extrusion is required in contrast with normal starch-acetate-based hot melts. For the preparation of a typical hot melt adhesive, the transglycosylated starch acetate is mixed

Figure 3. Gluing carpet using a tannin-starch-based adhesive.

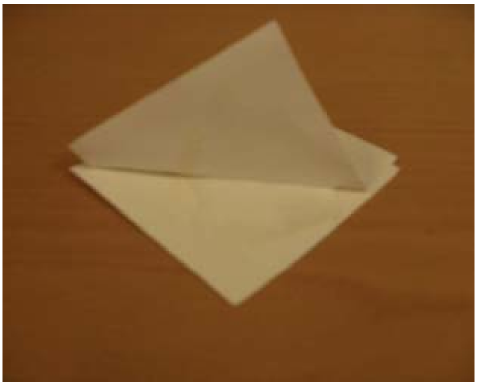


Figure 4. Gluing of paperboard using a starch-based hot melt.

with a plasticizer such as triethyl citrate. The adhesives are applied at temperatures of about 140°C. By varying the grade and proportion of the transglycosylated products and the plasticizer, it is possible to affect the melt viscosity and softness of the adhesive. Hot melt adhesives can also contain high molecular weight starch esters, as one component, especially when a non-contact application of a hot melt layer and high film strength is needed.

Paperboard was glued using a starch-based hot melt adhesive. As can be seen in Figure 4, the adhesive joint is stronger than the paperboard material. The hot melt adhesive is also well suited to gluing VTT's PLA/nanoclay composite films.

Figure 5. Gluing of cardboard using a water-based starch adhesive.

Water-based starch adhesives

Transglycosylated native starch has also been used in the preparation of aqueous adhesive formulations. VTT's starch-based aqueous adhesive formulation has the advantage of a high solids content, which results in less energy being needed for drying and, at the same time, it has low to moderate viscosity. The adhesive can be used in paper and board products and as a primer for other adhesives, as tested in cardboard gluing (Figure 5). The properties of this adhesive can be tailored for specific performance by varying the polymeric starch component, degree of modification, molecular weight and additives.

In the area of bio-based adhesives, VTT offers IP and development projects for both chemical manufacturers and end-users.

Demonstrators

Packaging demonstrators

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The aim of the packaging demonstrators during the Bipa project was to prepare sample demos containing translucent or transparent sections. The demos were manufactured to promote research sales by VTT Technical Research Centre of Finland and to present the patented 'translucent windows' technique to wide audience and target groups. One packaging demonstrator presented a completely transparent section made from hemicellulose-based film. The barrier layer in the demonstrator products, when applied, was bio-based dispersion (see Hartman et al. in this publication).

Translucent windows1 can be made with a new technology developed by VTT. The technology uses a novel bio-polymer-based formulation and a hot-press process.

The main benefits of the technique are

- Cost-efficiency due to an easy one-step method
- The possibility to integrate with existing production processes
- Provides translucency, increased strength and barrier properties with the minimum amount of material
- Bio-based and completely recyclable materials
- No need to assemble separate strip windows
- No weak spot in the package due to the window

The demos were related to food packaging and designed to be used as real commercial packages following examples found in grocery stores. Package designer Petri Huttunen designed the packages,

Figure 1. Bread package for daily use with a hemicellulose-based transparent window.

Figure 2. Airtight bread package with a translucent section on the lid (background) compared with a package with a completely transparent lid.

including the graphics, using personally taken photographs.

The base carton board material and thinner flexible packaging paper were chosen as base materials, and all the impregnation work required to produce translucent sections was carried out at the VTT Tampere unit by Samu Aalto.

Before impregnation and production of the translucent sections, the demo package billets were printed at the DMP printing house in Helsinki using digital printing methods to give the packages a colourful appearance to resemble real-life commercial packages.

After the translucent section impregnation and printing, the packages were cut using an Esko Graphics packaging table at VTT Espoo and assembled by hand.

The project was implemented during January-May in 2011. The VTT Tampere and Espoo units worked in close co-operation during the project. The targets set for the project were fulfilled with flying colours.

Three individual designs were chosen to be presented as demos.

Demonstrator 1: Bread package for daily use with a transparent circle made from hemicellulose-based film on the top part going over one bent edge.

This kind of package serves as support while the bread is being eaten. It also protects the product while it is in the sales counter. The package is of an open type so air and moisture have an effect on the product. This kind of package can be found in Finland at, for example, R-kioski.

Hemicelluloses such as xylans and glucomannans exist in high amounts in woods, and agricultural plants are potential raw materials for different kinds of novel materials and applications. The highly transparent and flexible films prepared from modified hemicelluloses, without any additives (softeners etc.), have had mechanical properties, for example, tensile strengths up to 44 MPa, elongation at break 5–22%, Young's modulus 500–1000 MPa, and reasonable barrier properties: water vapour permeability (5–10 g, mm/kPa, m^2, d) and oxygen permeability (12–30 cm^3, µm/kPa, m^2d). The properties are mainly dependent on modifications (type of substituent(s), degree of substitution etc.) but also on the amounts and type of additives used.

The inside of the package was coated using bio-based dispersion coating to prevent grease transfer from the bread and fillings.

Demonstrator 2: Air tight bread package aimed at longer use with a transparent lid

This kind on package serves as a container in, for example, vending machines for bread. The package can be made airtight so air and moisture do not affect the product. There are several bakeries that use this kind of package. Packages are most often made of plastic.

The package section on the lid was made using a transparent windows technique for flexible packaging paper.

Demonstrator 3: Candy bag with a translucent circle on the front

The plastic candy bags with a matte surface finish contain 'high value' candy and have appeared in stores in 2010. They contain a faint translucent area with an appearance just like that which can be attained using a translucent paper technique. The candy bag with a translucent circle impregnated using a translucent paper technique was intended as an alternative to these kinds of candy packages.

The assembly of the packages described above can be carried out using water-based starch dispersion glue or starch-based hot melt glue (see Bio-based Adhesives by Hult Mori et al. in this publication).

The packaging demonstrators above proved that making completely bio-based

Figure 3. Candy bag demos placed on counter.

and biodegradable packaging from renewable sources is possible. The challenge is to implement such products and their production technique on an industrial scale cost-effectively.

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VTT Research Highlights 2

Title	Research highlights in industrial biomaterials
Author(s)	Anghelescu-Hakala, A., Harlin, A., Hartman, J., Heikkilä, T., Hult Mori, E.-L., Härkki, O., Kunnari, V., Laine, C., Laitinen, A., Lattu, J., Mehtiö, T., Penttilä, M., Qvintus, P., Rämö, Setälä, H., Tammelin, T., Vähä-Nissi, M., V., Wiebe, M. and von Weymarn, N.
Abstract	Green VTT has commitment to develop technologies for the bio-economy to benefit society through prosperity through less environmental burden. Industrial biomaterials spearhead program is targeting new value added applications on non-food related biomass in the fields of marked industrial importance, such as packaging, composites and appliances. The development is based on long research activity in the fields of biomass fractionation and converting as well deep expertise on the material sciences, converting technologies and application. This Research Highlights focuses on novel biopolymers from forest industry side-streams that have been developed for bio-packing applications, like oxygen and grease barrier materials for fibre webs. Development of translucent and mouldable fibre based packaging and modification and regeneration of cellulose enabled new openings. The main achievement is, however, the nanocellulose development that has progressed to the international top level, enabling VTT partners to move to the industrial scale test runs and pilot decisions. Research and development in the area of industrial biomaterials has a positive impact on chemical, forest and packing industry.
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Nimeke	Research highlights in industrial biomaterials
Tekijä(t)	Anghelescu-Hakala, A., Harlin, A., Hartman, J., Heikkilä, T., Hult Mori, E.-L., Härkki, O., Kunnari, V., Laine, C., Laitinen, A., Lattu, J., Mehtiö, T., Penttilä, M., Qvintus, P., Rämö, Setälä, H., Tammelin, T., Vähä-Nissi, M., V., Wiebe, M. and von Weymarn, N.
Tiivistelmä	Vihreän VTT:n tavoitteena on toimia biotaloudessa ja kehittää teknologioita, joita hyödyttävät yhteiskuntaa ja edistävät taloutta, mutta kuormittavat vähemmän ympäristöä. Teolliset biomateriaalit – kärkiohjelma tähtää uusien biomassasta saatavien sovellusten kehittämiseen erityisesti pakkausten ja komposiittien alueella. Kehitystyö perustuu pitkäaikaiseen tutkimustoimintaan biomassan fraktioinnissa ja muokkauksessa sekä vahvaan materiaalitieteiden, jalostusteknologioiden ja sovellusten osaamiseen ja asiantuntemukseen. Research Highlights – julkaisussa tarkastellaan uusia metsäteollisuuden sivuvirroista saatuja ja muokattuja biopolymeerejä, joita on kehitetty biopakkaussovelluksiin, kuten kuitupohjaisten pakkausmateriaalien happi- ja rasvabarriereiksi. Läpikuultava ja muokattava kuitupohjainen pakkaus sekä selluloosan modifiointi ja regenerointi tuovat alalle uusia mahdollisuuksia. Vuoden 2011 pääsaavutus on kuitenkin nanoselluloosan kehitys kansainvälisesti katsottunakin huipputasolle, mikä on mahdollistanut VTT:n partnereiden etenemisen teollisen mittakaavan testeihin sekä pilot-mittakaavan tuotantoon. Tutkimus- ja kehitystoiminta teollisten biomateriaalien alueella edistää sekä tukee kemian-, metsä-, ja pakkausteollisuuden uudistumista.
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