



Developments in advanced biocomposites

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Ali Harlin & Minna Vikman (eds.)



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Abstract

VTT has long experience in developing biocomposites for several application areas. Biocomposites are materials consisting of bioplastics, natural fibres and/or fillers and additives, which are also preferred to be biomass-based. The utilisation of non-food resources will be one of the main issues and drivers in material development. The variety of biomaterials, the number of material combinations, processing technologies and potential applications offer extensive opportunities but there are many challenges that must be overcome during the development of biocomposites and bioplastics. The next generation of biomaterials are being developed through advanced processing and nanotechnology. This publication gives overview of the research activities and main achievements at VTT in this area.

Preface

A good starting point for this publication was Biocomposite-workshop which was held in Tampere 25th of March, 2010. The workshop was organized as a part of Industrial Biomaterial spearhead programme and it's aim was to review the research activities and main achievements at VTT in the field of the biocomposites. This publication was prepared on the basis of the presentations held in the workshop, but in addition some other relevant research topics in this field are included.

I want to thank all the writers of this publication for their valuable contribution.

Ali Harlin

Professor, Programme Manager

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Biogenic and nano components are renewing composites

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A biogenic substance is a substance produced by life processes, which may be either constituents or secretions of plants or animals. There are three strategies for converting biogenic substances to precursor and further into value added chemicals, namely, gasification to synthesis gas, thermal conversions to simple precursors, and utilization of highly selective catalysis (Gallezot, 2007). However biomaterials like agrofibre and wood are bio-based composites as such. A combination of proven composite technologies and novel biogenic and nano components will lead us to the next generation of bio-based materials.

Biogenic raw materials

Attention has been drawn to the use of biomass as a source of energy and, more specifically to their use in transportation fuels. (Huber et al., 2005; Huber et al., 2006; Petrus & Noordemeer, 2006; Ragauskas et al., 2006) In order to implement the Rio declaration (Report, 2007), the US chemical industry prepared a Vision 2020 program (Technology Vision, 2007), one recommendation of which was to use renewable feed stocks – especially cellulose sources – for valuable chemicals. Goals for the chemical industry to achieve sustainable development were defined in the workshop report in July 2001 (Workshop report, 2001). In particular, it was stated that the use of renewable raw materials should be increased by 13% until 2020. Furthermore, the EU has established a platform for

sustainable chemistry demanding that 30% of chemicals should be prepared from renewable resources by 2025 (CEFIC, 2007).

In direct analogy to a petroleum refinery, an economically attractive bio-refinery should produce multiple products, including fuel, power, and bulk or fine chemicals, from biomass (Zhang, 2008). In addition, the valorisation of all components of biomass is essential for a viable bio-refinery (Bozell et al., 2007). In the review of Gum et al. (1992), a value added class of compounds called reaction polymers are discussed in more detail. The compounds include polyurethanes, epoxies, unsaturated polyesters, and phenolics. Biomass carbohydrates are the most abundant renewable resources available, beyond even lignin, and they are currently viewed as a feedstock for the Green Chemistry of the future (Lichtenthaler, 1998, 2002 and 2004).

Wood composites

The development of traditional wood composites has declined since particle board and plywood volumes have reduced in construction applications even if their position in the furniture industry is still marked. Renewed interest can be expected in bio-based adhesives, glues, preservatives and coatings. New products could also be expected if treated wood will be converted further into assembly series or ready products.

It seems that suitable waste streams for wood polymer composites (WPC) are difficult to predict. Saw mills side streams find use in energy production and as raw material in pulp mills. Heat treated wood can be used in energy production as well. Pressure preserved wood is most suitable for material recycling, but at the same time value chains and consumption habits have favoured preserved and heat treated wood instead of wood plastic products, which have grown markedly in other markets.

Wood fibre composites

Typically wood fibre composites are used in packaging materials like fibre mouldings and strengthening elements, where recycled and second hand fibre sources and low technology are used.

Wood fibre as such has not been seen as a very efficient composite material due to its limited aspect ratio and high water uptake.

However, it has been possible to chemically modify the fibre to be compatible with most of the plastics and simultaneously markedly hydrophobic. It has also

been observed that mechanical properties can be improved through the use of fibre webs like recycled paper and especially packaging waste. Clearly with enhanced high consistency sieving, mixing and extruding technologies, the product qualities and production efficiency could be improved and WFPC could find added value in use elsewhere.

Natural fibre composites

Natural fibre is markedly more expensive, but due to its high aspect ratio may provide higher performance as well. For the natural fibre composites NFPC improved compatibility is required, which has been possible to develop through different kinds of chemical and chemo enzymatic methods. In bulk products this route has been seen as overkill mean while the actual engineering applications seem to be technically too far.

Several interesting experiments have been conducted to apply natural components, like straws, rumen, feathers and peat. Both particle board technology and thermoplastic compounding has been applied, when new biopolymers are also necessary elements of the novel materials. Applications finding increasing market potential are found especially in appliances and furniture. Here consumer preferences for more sustainable solutions combined with design, unique tactile and visual properties play a vital role.

New materials

The performance of the composite especially in the engineering application is valorised as a ratio between mechanical performance term and density. What is targeted is high performance with minimum weight. Vehicles are a typical example, where light weight materials improve both fuel economy and transportation efficiency. The benefits are also typical for packaging.

Nano fibril cellulose (NFC) is an emerging bio-material carrying many promises of high mechanical strength. NFC has expected strengths similar to aromatic polyesters like Kevlar while it is available practically everywhere in growing plants. Like other nanomaterials, NFC has compatibility issues related to a very high surface area in the material. NFC is hydroscopic due to free hydroxyls, which on the other hand may help bonding. Also other nanomaterials like nano clays may open a new avenue for development.

Foams are generic platforms enabling the reduction of weight. Rigid foams can be placed in the composite structure in less load bearing areas like the middle. Foams also enable the control of composite structure.

Technical solutions

There is an obvious need for processing technologies capable of gently but efficiently handling high viscosity pulps and mixtures with high consistency. Simultaneously required is very efficient mixing, control of orientation and breakage avoidance in composite fibre. Certain answers may be found in the rubber, paint and food processing industries.

Surface treatments of biopolymers not only enable tailoring for scratch resistance and stain repellence but also for tactile and visual properties. There are several advanced modifications of basic coating and surface treatments. Beyond methods like the sol-gel coatings are coming thin layer methods like thermal spray, plasma deposition and atomic layer deposition are being developed.

Combining new biogenic polymers with nanotechnology can be expected to produce technical breakthroughs. Further, more emphasis has to be put on material physics and modelling than on converting. Material structure and behaviour has to be better understood.

On the other hand, high volume waste management issues may introduce new raw materials for construction applications. In this sector technical performance is important but also easy-handling and ease-of-maintenance are marked issues. Depending on legislation and the development of raw materials prices, especially oil, the existing balance of contemporary material usage may rapidly change.

Conclusions

VTT has long experience in developing biogenic composites. In construction materials an actual breakthrough has not yet happened. Simultaneously, more focus is put on packaging and its sustainability. The next generation of biomaterials are being developed through advanced processing and nanotechnology. The development of new technologies for biogenic composites will enable the commercialisation of the WFPC technologies when the time is appropriate.

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Trends in bioplastics and biocomposites

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Abstract

Natural fibres have found their way onto the composite market as reinforcements or fillers, mainly in polyolefin-based WPC products. Currently, bio-based materials are widely researched with the aim of replacing polyolefins and other oil-based plastics. The current 'bulk' bio-plastic polylactic acid (PLA) is being accompanied by other commercial bio-polymers such as starch-based polymers, PHB and biopolymer blends. There are also many expectations towards new polyester-, polyamide- and protein-based biopolymers, which are globally under development.

All the components in biocomposites – polymers, fibres, fillers, compatibilisers and additives – are preferred to be bio-based. While aiming towards competitive, high-performance and sustainable biocomposites by mixing these novel biobased components, the material formula and the processing techniques need to be thoroughly studied, developed and optimised to be able to meet the requirements of different applications, industries and markets.

The variety of biomaterials, the number of material combinations, processing technologies and potential applications offer tremendous opportunities; however, there are many challenges that must be overcome during the development of bioplastics and biocomposites for different industrial sectors such as transportation, packaging, furniture, agriculture, construction and consumer products.

Drivers

Legislation, changes in raw material resources and prices, consumer demand, land filling, innovations, global warming and the 'green image' are all driving the market of biomass-based products, namely bioplastics and biocomposites.

The oil/petroleum-derived plastics industry is faced with important issues such as the increase in oil prices and the continuous fluctuations in petroleum prices, which have resulted in price volatility. Further, the sources for synthetic plastics – fossil fuel reserves – are diminishing and the demand for renewable materials is increasing. However, the raw materials used for bioplastics are agricultural resources that are renewable and present in abundance, thereby establishing bioplastics as a sustainable industry.

The synthetic plastics industry is also burdened with environmental issues. When fossil fuels are utilised, it leads to more CO₂ release than CO₂ utilisation, thereby leading to an increase in global warming. Thus, concerns are rising about the sustainability of the synthetic plastics industry. Global climatic changes (greenhouse effect) and waste disposal issues are some weaknesses of the synthetic plastics industry. Biopolymers can play an important role in the CO₂ cycle as with greater agricultural production, more CO₂ (which has resulted from biopolymer degradation) is absorbed and, hence, CO₂ released to the atmosphere is reduced, thereby leading to reduction in global warming. Environmental awareness movements are very strong, especially in the European Union (EU), Japan, and the United States, and bioplastics can meet the increasing demands for biodegradable products. The compostability of the materials is certified by the European Standard EN 13432 and third parties. The biodegradability of bioplastics is covered under the European Packaging Directive 94/62/EC, which has been amended by a new Packaging Directive 2004/12/EC; this includes both the aerobic (composting) and anaerobic treatment of biodegradable packaging as organic recycling. This means that biodegradable plastics are considered beneficial as recycled plastics as they reduce the waste that goes to the landfill. This creates an advantage for biodegradable plastics over conventional ones (Frost & Sullivan, 2007).

Improved properties, the increase in the number of producers, the growing variety of different types of bioplastics, the depreciating prices of bioplastics and availability are all factors that will increase the usage of bioplastics and open up new possibilities and application areas for bioplastics, and further for biofoams and biocomposites.

Bioplastics

The definition of bioplastics is expanding from biodegradable plastics to bio-mass-based/ bio-sourced/ renewable sources plastics. The standardisation work of bioplastics was initiated in Europe and the USA; to date, however, there is no universal, established practice on the definitions for bioplastics. Furthermore, there is no legislation regulating the amount of renewable sourced material that needs to be present in a plastic, for it to be called ‘bioplastic’ nor for the measurement and reporting of renewable content of a bioplastic. It is therefore open to individual players in the market to assess this particular issue. The ultimate goal, beyond the mere reporting of renewable content, is likely to be a framework for providing a fuller assessment of each material's life-cycle and carbon footprint (Frost & Sullivan, 2007).

Definition of bioplastics

Renewable resources	3 Biobased: PE, PA11 etc.	1 Starch PLA PHA
Petro resources	4 PE, PP, PET, PC, PVC, PUR, PA, ABS, etc.	2 PVA PCL PBS
	Non Biodegradable	Biodegradable

According to the latest definitions, biopolymers and bioplastics can refer to:

- 1) bio-based and biodegradable plastics like PLA, PHA and starch acetate (SA);
- 2) bio-based, non biodegradable plastics like polyamides and bio-based PE;
- 3) synthetic biodegradable polymers, e.g. PCL, PBS and PVA;
- 4) conventional plastics; and
- 5) combinations of the above

Figure 1. Division of bioplastics.

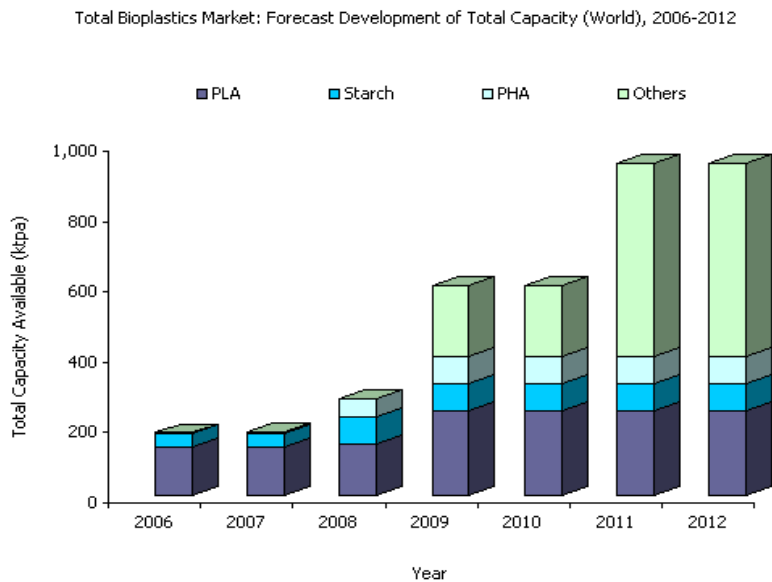
The fastest growing and most interesting group of the above (Figure 1) is the bio-based/ renewable resourced plastics, which are introducing to the market a number of bio-based plastics with the same properties as conventional plastics.

At present, the most commonly used commercial bioplastics are PLA and starch-based plastics. PHAs, biopolymer blends and some bio-sourced thermoset materials, such as furan resin, also exist. (Frost & Sullivan, 2007).

Production and markets

The worldwide production of bioplastics is growing and the usage of bioplastics is expanding into several industrial sectors. The bioplastics market is growing more than 8% to 10% per year. Bioplastics cover approximately 10% to 15 % of the total plastics market and is estimated to increase its market share to 25% to 30 % by 2020. The market itself is huge and is expected to increase from over USD 1 billion in 2007 to more than USD 10 billion by 2020 (Shen et al., 2009).

According to Frost & Sullivan's report (European Markets for Bioplastics', December 2007), the production of bioplastics is estimated to grow from 200,000 tons in 2006 to one million tons in 2011. As shown in Figure 2, the growth is forecast to occur in the sector 'other bioplastics' rather than in PLA, PHA or starch-based plastics, which are at present mainly used for packaging applications. The 'other' segment includes bioplastics such polyamide, cellulose-based biopolymers, blends, lignin and biomass-based polyethylene (PE). (Frost & Sullivan, 2007).



Note: Others include bio-sourced polyethylene

Figure 2. World's bioplastic production capacity in tons in 2006–2012.

The production capacity of bioplastics will grow as there are more and more companies entering and investing in the market. Currently, some 20 companies hold 90% of the market share; however, by 2015 it is estimated that there will be over 250 and by 2020 over 2,000 companies in the market. Asian has the highest growth rates and investments to 2020 (Shen et al., 2009).

Table 1 gives the key industrial producers of bioplastics in the world in 2007, 2009, 2013 and 2020 (Shen et al., 2009; European plastic news, 2010).

Table 1. Worldwide producers of bioplastics and forecast of production capacity (Shen et al., 2009).

Producer		Polymer type	Trade name	World Capacity (kton/a)			
				2007	2009	2013	2020
NatureWorks	US	PLA	Ingeo	140	140	300	450
PURAC	TH	L-lactide, D-lactide	PURAC	75	75	150	300
Teijin/ Musashino	JP	Heat resist. PLA	BIOFRONT	0,2	1,2	10	10
Pyramid	DE	PLA	Pyramid PLA				60
Novamont	IT	Starch blends	Mater-Bi	40	60	100	200
Rodenburg	NL	Part. ferm. starch	Solanyl	40	40	40	40
BIOP	DE/NL	Starch blends, SA	Biopar & Bioparen	5	5	80	150
LIVAN	CN/HU	Starch blends	Livan	10	60	60	110
Cereplast	US	Starch blends	Cereplast Compost.				
Tianan	CN	PHB-V	Enmat	2	10	50	50
Telles	US	Metabolix PHA	Mirel	0,25	50	50	50
PHB Industrial	BR	Biocycle	PHB-V	0,05	10	10	10
Tianjin /DSM	CN	P(3HB-co-4HB)	Green Bio		10	10	10
Innovia	UK	Reg. cellulose film	NatureFlex	5	5	20	20
BASF	DE	PBAT	EcoFlex	14	14	60	60
Mitsubishi Chemicals	JP	PBSL	GSPla	3	3	10	10
Arkema	FR, US,CN	PA11	Rilsan 11	5	5	5	5
Braskem		for PE		5	200	200	200
Dow-Crystalsev		for PE				350	350
Solvay		Ethylene for PVC				60	60

The variety of bioplastics will offer tremendous opportunities for the development of distinct biocomposites for different applications.

Biocomposites

Biocomposites are composites consisting of bioplastics, natural fibres and/or fillers and additives, which are also preferred to be biomass-based. It is common knowledge that the interaction between the fibres and matrix determine the properties of a composite. Many research and development activities have been and are being carried out with the aim of improving the performances of natural fibre composites (NFC), wood plastic composites (WPC) and biocomposites.

These activities include improvements of the properties of natural fibres: optimal fibre length and aspect ratio, and distinct fibre treatments. In addition, new biomass-based additives, such as impact modifiers, fire retardants and biocides, are globally under development. Nevertheless, the development of new bioplastics is crucial for the properties and future of biocomposites.

Markets

Biocomposites are one of the newest classes of composites; in most cases they are included in wood plastic composites or natural fibre composites. The production of Wood Plastic Composites (WPCs) has increased substantially over the last ten years. The production capacity grew 40% in the USA, 100% in Europe, and 13% in Japan from 2000 to 2005 (Figure 3). Although production of WPCs began in the USA – the production and market leader – the fastest growing market is in Europe. (Asta Eder, 2007)

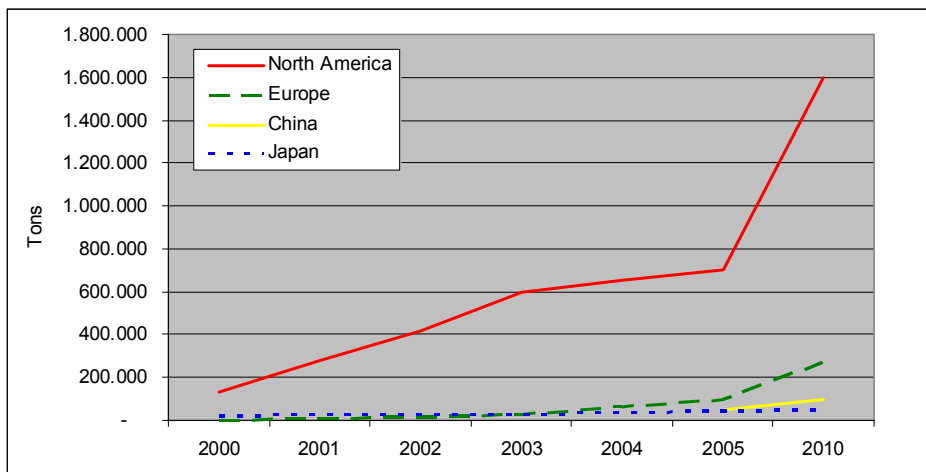


Figure 3. WPC Production growth rates (Asta Eder, 2007).

The market forecasts shown in Figure 4 for naturally reinforced Plastic Composites (NRPC) and for natural fibre composites (NFC) are promising, as is the market growth of biocomposites due to the variety in terminology and the fact that the greener it gets the better. The annual growth rate predicted for European biocomposites is 21%. The volume of biocomposites is predicted to increase from 129,000 tons in 2008 to 427,000 tons in 2014. Furthermore, natural fibres and fillers are the fastest growing plastics ‘additives’. Injection moulding mate-

rials are at an early stage and significant growth can be expected in the medium term.

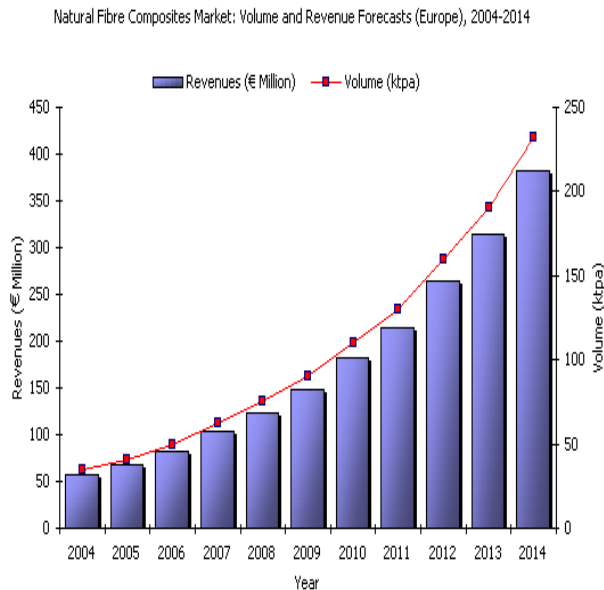
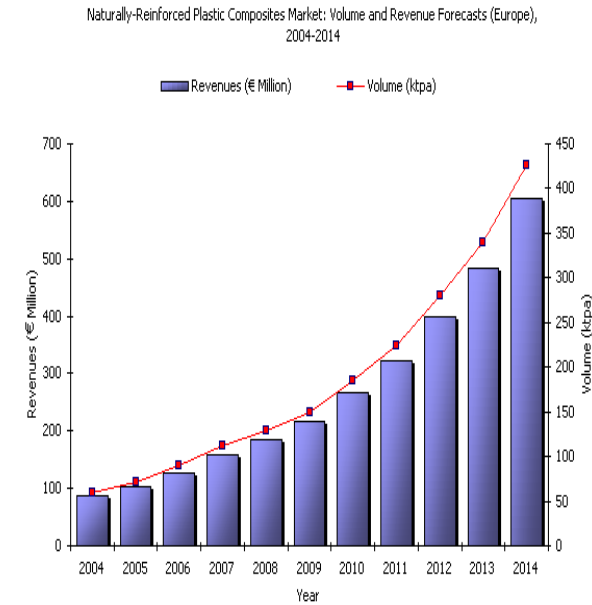


Figure 4. Forecast of NRPC and NFC Composites in Europe, 2004–2014 (Frost & Sullivan, 2008b).

Applications

Some 65% of bioplastics were used in packaging and food related applications in 2007 and in 2025, the share is estimated to be 40%. Automotive and electronics are forecasted to reach over 25% of the market share by 2025 with a higher profit potential compared to the packaging and food industry. (Frost & Sullivan, 2008a).

The most commonly used polymers for biodegradable packaging are starch-based polymers. Starch accounted for 50% of the share of biodegradable packaging globally in 2007. Starch-based polymers are commonly used polymers in biodegradable packaging in applications such as compostable bags, consumer goods packaging and fresh food packaging for fruits, vegetables and bakery products. They are also used in food service packaging such as disposable packaging. Starch is followed by PLA which accounted for 40% of the share by volume (Frost & Sullivan, 2008a).

PLA dominates the fresh food packaging sector. The rapid capacity expansion of this polymer is set to boost the growth of biodegradable packaging applications of PLA. The other polymers, such as PHA, and polyesters accounted for the remaining 10% of the share.

Figure 5 shows the volume share by polymer type in the global biodegradable packaging market in 2007 (Frost & Sullivan, 2008a).

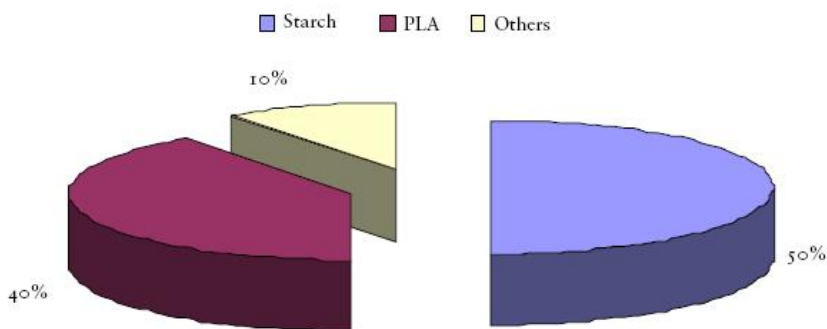


Figure 5. Biodegradable Packaging Market: Volume Share by Polymer Type (World), 2007. (Frost & Sullivan, 2008a).

Two of the key issues in transportation, packaging, construction, electronics and consumer goods are light weights and the reduction of raw material consumption. New bio-sourced biopolymers are developed to meet the requirements of

novel applications. Common requirements for distinct materials in mass production are low-price, processability, appropriate performance and light weight. The weight reduction in products can be achieved by design, material choices and eventually by foaming. The variety of biomaterials, number of material combinations, processing technologies and applications offer tremendous opportunities; however, there are many challenges that must be met during the development of bioplastics and biocomposites in order to meet the demands of different industrial sectors.

Conclusions

The drivers represented in this paper will lead to an increase in the number and volume of bioplastics and biocomposites. The competitiveness of bioplastics compared to plastics will be improved thanks to higher production volumes and the increase in oil and plastic prices. Improved and tailored properties as well as enhanced processing technologies will offer tremendous opportunities for the utilisation of bioplastics and biocomposites in a large number of commercial applications in the future. The utilisation of non-food resources will be one of the main issues and drivers in material development.

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Peat fibre composites

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Abstract

In this study, we compared properties of peat fibre containing composites with other cellulose containing composites such as reed canary grass, sawdust and cellulose. Peat fibre containing composite material has been studied at the VTT in several projects including TULI-POC project, a market study and a production study together with the Aalto University Design Factory. A patent application concerning biodegradable peat fibre containing materials was submitted in 2007.

Peat fibre and reed canary grass are potential filler/reinforcement fibres in WPC and bio-based composites in addition to commonly used sawdust and cellulose fibres. Here, some results of PP and PLA composites with fibre contents of 20% and 40% are presented. If the performance of these different fibres is compared, cellulose can be said to have potential in high tensile strength bio-composites. The strength of sawdust lies in being a cheap side-stream material with adequate properties. The performance of reed canary grass composites, the strengths of which are a 'natural' visual appearance and easy availability, is similar to that of sawdust composites. Peat fibres showed surprisingly low water absorption, good impact strength properties and better fire retarding properties than other fibres. Biodegradable products can be tailored from all of the presented fibre materials using biodegradable polymers in a matrix. Potential products for peat fibre containing composite materials could be different injection- or extrusion-moulded items.

Introduction

The increasing concern for our environment and interest in materials with a low CO₂-footprint together with a lower price than fossil-based materials have increased research activity into bio-based materials all over the world. The research activity brings new bio-based polymers to the market with properties similar to those of engineering polymers. Adding natural fibres to polymers in addition to form composite materials reduces the price of the materials, gives a 'natural' look and feel to composite materials and, in the best cases, also property enhancement. New environmental laws and regulations are, in their way, pushing industry to adapt new materials. The interest by the industry can also be seen in the way new recycling and post-treatment possibilities have been created.

The production and customer demand for natural fibre-reinforced composites is also increasing in Europe. In North America, the productisation is much bigger, including, for example, decking, window frames, siding, terrace parts and car parts. The naturally reinforced plastic composite market is estimated to double in the next four years to 380 ktpa (Source: Frost & Sullivan).

The research into wood polymer composites (WPC) and bio-based composites concentrates mainly on natural fibres such as flax, hemp, bast fibre, wood, bamboo, cork and sawdust, and it is compounded with polymers such as polypropylene (PP), polyethylene (PE), polylactide acid (PLA) and thermoset matrices (e.g., polyesters).

Cellulose containing peat fibres could be one good domestic choice as a filler or reinforcement material in composites. Finland is the sixth highest peat-containing land in terms of land area, with 31% of Finland covered with peat (Minkinen & Laine, 2001). Less than 2% of this area is used, and then mainly for energy production, for which contradictory discussions are ongoing. Peat fibre composites could be one way to improve the image of peat heaving due to the relatively low amounts needed compared with energy production, positive utilisation of domestic natural resources and the good properties of peat composites. Peat composites could be one positive way to add value to peat as a raw material.

This study compared the properties of peat fibre containing composites with other cellulose containing composites such as reed canary grass, sawdust and cellulose.

Materials and methods

The fibre materials used in this research were milled peat, reed canary grass, sawdust and cellulose. **Peat fibre** was used in milled form straight from heaving and drying. It consists of cellulose, hemicellulose, lignin, different natural acids and resins and has a wide particle size distribution that also includes nanoparticles.

Reed canary grass, which is also cultivated in peat areas after heaving peat for energy use, is ended. It works as a green house gas absorbing vegetation. Its main use is also for energy purposes. It resembles straw and provides a good reference for straw containing materials in composites. Reed canary grass contains cellulose, hemicellulose, lignin, different extract and inorganic particles such as silicates, Fe, Mn, K, Cu and Ca. The reed canary grass used was chopped into 8 mm pieces.

Sawdust or wood flour is a widely used raw material in WPCs and can be obtained from side chains of the wood industry. It is cheap filler, which can compensate for the high cost of polymers, and it contains all wood ingredients, cellulose, hemicellulose, lignin and extracts.

Cellulose offers a wide variation of possibilities as raw material in composites. The properties of composites are affected by the origin of the cellulose (fibre size, shape and fibrillation) and the production type (hemicellulose and lignin content). It can be modified physically, chemically and enzymatically, aimed at compatibility improvement through covalent and electrostatic interactions between the fibre and matrix polymers and thereby high performance. In this study, we used bleached birch pulp cellulose.

The polymer matrix materials used here were polylactide (PLA) from Hycail and polypropylene (PP BH345) from Borealis.

The materials were compounded to fibre contents of 20% and 40% using the Berstorff ZE 25 x 33 twin-screw extruder followed by injection moulding with the Engel 200/50 HL to dog-bone-shaped test bars or extrusion with a Dolci extruder to 3-cm round extrusion profiles. The processing was performed at temperatures below 200°C for all the material combinations.

Tensile strength tests were conducted according to standard SFS-EN ISO 3167:2003 using Instron 4505 and Charpy impact strength (unnotched) according to standard ISO179. The water absorption measurement was made according to the ISO 62 standard and biological degradation according to ASTM D6400.

The fire resistance test used a standard EN ISO 11925-2:2002, in which the sample is placed in an upright position and lighted from the top with a torch.

Results

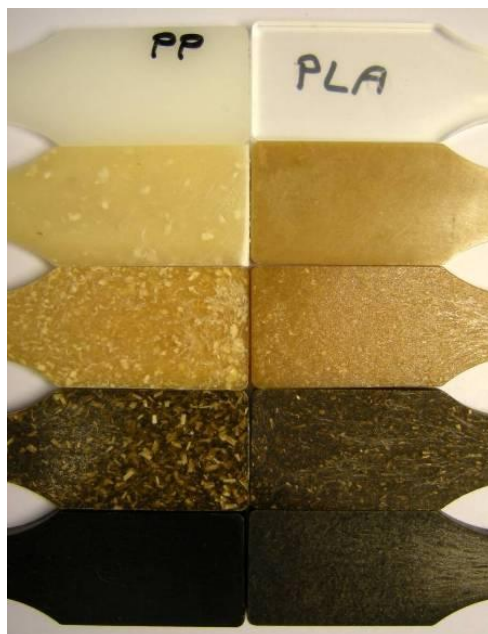


Figure 1. PP and PLA composites with cellulose, saw dust, reed canary grass and peat fibres in fibre content 40%.

Peat fibre composites are dark brown or almost black in PP but have some silvery shades in PLA composites. To disperse pure cellulose effectively into hydrophobic matrices (PP), some dispersion agents or hydrophobisation of fibre seem to be needed. The incompatibility of cellulose and sawdust with PP could be seen as small gaps between the fibre and matrix in the SEM pictures. Peat fibre had the most homogeneous and even material distribution in the PP, which indicates good compatibility, possibly due to hydrophobic resinous ingredients of the peat. In the PLA composites, the cellulose dispersed quite evenly to the matrix and reed canary grass and the sawdust had nice dispersion with big particles. The PLA peat fibres also had the most even distribution as well as some 1- μm size pores in the matrix. These may have been due to the resinous and acidic

ingredient causing changes during the crystallisation of the PLA or gasification of those compounds.

The tensile strengths of different fibre-filled PP composites all performed at the same level of around 20 MPa. The only exception was the maleic anhydride (MAH) cross-linked peat fibre (40% fibre) with 14% higher tensile strength compared with composites with other fibres. In the PLA composites, the birch pulp performed best, having a tensile strength of over 70 MPa, which is even higher than for PLA without fibre (64 MPa). The poorest performance was by PLA with 40% peat fibre with a tensile strength of 31 MPa. This may have been due to the porous structure.

The impact strength (Figure 2) in PP composites with 20% peat fibre was 33% higher than with the second best reed canary grass (42 kJ/m² vs. 28 kJ/m²). In the 40% fibre content, no difference could be seen in the results between the different fibres, and all the results were at the 16 kJ/m² level. PLA composites with 20% peat fibre had 25% higher impact strength than the second best with cellulose fibres (19 kJ/m² vs. 15 kJ/m²). The peat fibres also had a small positive effect on the 40% fibre content with 18% higher results compared with next best cellulose fibre composites (11 kJ/m² vs. 9.6 kJ/m²). Therefore, it seems that micropores in peat fibre composites do not have an effect on impact strength.

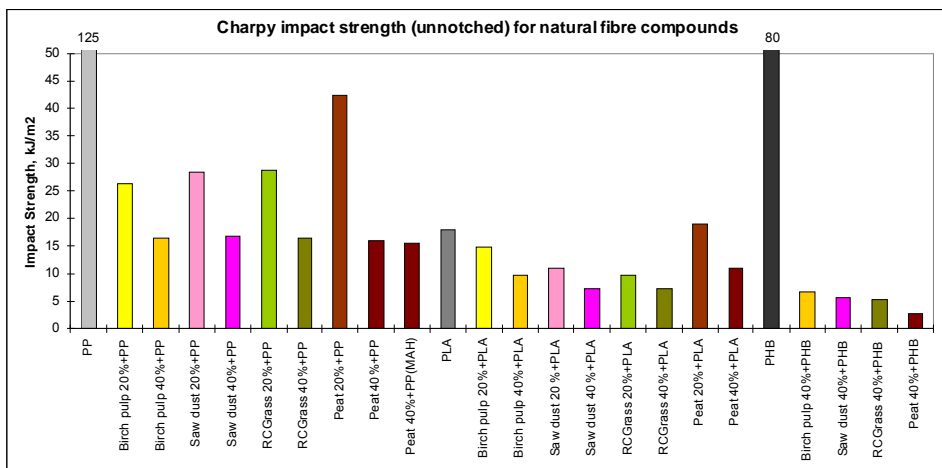


Figure 2. Charpy impact strength for natural fibre compounds with PP, PLA and PHB matrices.

The water absorption (Figure 3) in injection-moulded PP samples with 40% peat fibre was > 80% lower than with other fibres, being < 1 w-% with peat fibres and > 5 w-% with other fibres after one week tests. Peat fibre containing PLA composites had > 20% lower water absorption than with other fibres, being 1.6 w-% with peat fibres, 2 w-% with cellulose fibres and about 2.5 w-% with saw-dust and reed canary grass after a 96-hour test.

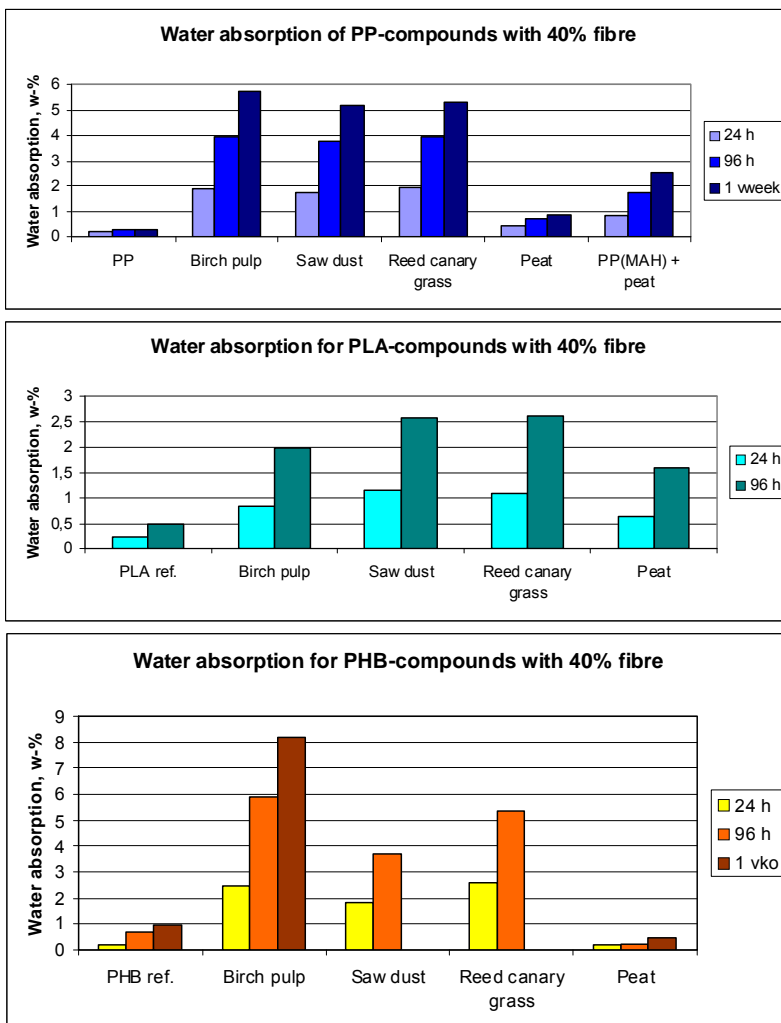


Figure 3. Water absorption for natural fibre compounds with 40% fibre content and PP, PLA and PHB matrices.

The fire properties were tested with composites containing 40% fibre. Compared with the actual burning of PLA composites, the burning proceeded with a clear flame in cellulose, sawdust and reed canary grass composites, being fastest in reed canary grass containing material. With peat fibres, the fire progress was more like smouldering and it even stopped in some samples. The speed of the fire progress with peat fibres was about 25% slower than with cellulose and sawdust containing fibres those performed similarly. Peat fibres containing PP composites were compared with pure PP and it was found that in peat fibre containing composite material the fire speed was about 40% slower than with pure PP. This indicates that peat fibre containing composites could be used in fire retarding composite materials.

Biodegradation of the PLA composites containing 40% fibre was analysed in standard composting conditions during a 12 week period (84 days). After the test, all the samples became very brittle and lost their elasticity. The weight lost in the cellulose fibre samples was 32.8%, the sawdust samples 32.2%, the reed canary grass samples 32.5% and the peat fibre samples 31.0%. This indicates that all the tested composite materials are biodegradable according to standard requirements, which means 60% degradation during a 180-day period (6 months).

Conclusions

Peat fibre and reed canary grass are potential filler/reinforcement fibres in WPC and bio-based composites in addition to commonly used sawdust and cellulose fibres. If the performance of these different fibres is compared, it can be said that cellulose has potential in high tensile strength biocomposites. The strength of sawdust lies in being a cheap side-stream material with adequate properties. The performance of reed canary grass composites, the strengths of which are a 'natural' visual appearance and easy availability, is similar to that of sawdust composites. Peat fibres showed surprisingly low water absorption, good impact strength properties and better fire retarding properties than other fibres. Biodegradable products can be tailored from all of the presented fibre materials using biodegradable polymers in a matrix.

From the research point of view, the focus of cellulose, sawdust and reed canary grass containing composites should be put on fibre matrix adhesion and hydrophobisation. The main focus of peat fibre composites should be the selection of fibre type and matrix crystallisation behaviour. Potential products for

peat fibre containing composite materials could be different injection- or extrusion-moulded items such as biodegradable planting pots, growing pots for herbs, plant shelters to be left in nature, geotextiles, burial items (flower holders, coffins, urns, candle holders, etc.), sport items (golf tees, shooting discs, etc.), shelters and injection-moulded items to be used as garden decorations, ploughing signs, door and window garnish mouldings, shelter pieces in packaging, etc. This is only part of the potential product portfolio for which peat fibres could be used.

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BioComp: processing and properties of starch acetate – bast fibre composites

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Abstract

Composite compounds based on hemp and flax fibres in triethyl-citrate-plasticised starch acetate were prepared by melt processing. Composite samples were prepared with fibre contents up to 50w%. A stiffness of 8.3 GPa and stress at a maximum load of 51 MPa were obtained with 40w% flax fibre in plasticised starch acetate with 20w% triethyl citrate. A nearly linear relation between fibre content and tensile properties was found. The impact strength of the composites was increased with the plasticiser content. The porosity content was low even at high fibre content.

Introduction

Unlike most fossil-based fibre-reinforced polymers (such as glass fibre/polyester composites), bio-based composites can be disposed of or recycled by composting. If incinerated, they typically have much lower ash production than fossil-based composites (Wollerdorfer & Bader, 1998).

The acetylation of starch makes the material less brittle by decreasing the modulus and by increasing the elongation at break and the impact strength. To improve further the processability of starch acetates (SAs), they are typically plasticised to bring down the glass transition temperature (T_g). Plasticising can be done by internal or external plasticising agents. In internal plasticising, the

hydroxymethyl groups of native starch are substituted with longer alky chains such as hydroxypropyl or the like, reducing the crystallinity and lowering the T_g . External plasticising is based on a similar mechanism, but there is no covalent bond between the plasticiser and the starch polymer chains. Triacetine (TriAc) and triethyl citrate (TEC) can be used for this purpose (Happonen et al., 1997). The plasticising effect of water is based on its hydrogen bonding capability with the native starch. When using TEC, with weaker intermolecular interactions to the SA, however, a gradual change in mechanical properties is observed along the increased plasticiser content. The stiffness of cellulosic fibres (eg, flax and hemp) is in the range of 30–70 GPa, and this is comparable with the stiffness of glass fibres (GF) of about 70 GPa (Lilholt & Lawther, 2000). In terms of stress at maximum load, GF perform better: the strength of cellulosic fibres is in the range 300–1500 MPa, whereas for GF (E-glass) it is about 2000 MPa (Kimura, 2001). Cellulosic fibres are about 40% lighter than GF (fibre densities of about 1.5 and 2.6 g/cm³, respectively), however, giving them potentially higher specific properties.

To be able to exploit fully the good tensile properties of cellulosic fibres, good fibre-matrix adhesion needs to be accomplished. It has been reported that incompatibility of cellulosic fibres and the SA matrix results in a weak interface between the two composite constituents (Matuana et al., 1997), leading to inadequate mechanical performance. Even with an SA with DS equal to 2.5, and subsequently good melt processability, every sixth hydroxyl functionality of the native starch starting material is still available for hydrogen bonding with the fibres however. Thus, in composites with an SA matrix with this DS, the interactions between the fibres and the matrix will be relatively abundant. In order to produce a starch-acetate-based matrix compatible with cellulosic fibres in composites, a series of plasticised starch acetates (PSAs) was prepared with variable plasticiser content from 20 to 35 w-%. Two kinds of cellulosic bast fibres, hemp and flax, were used at fibre contents ranging from 10 to 50 w-% in the composite to compare the performance of the fibres and the reinforcement effect. The stiffness, stress at maximum load, and impact strength were determined for the neat PSAs and the composites. SEM analysis of fracture surfaces was performed to evaluate the compatibility between the PSA matrix and the cellulosic fibres, and the dispersion of the fibres in the matrix. Finally, the processability and suitability for sample production of the PSA/cellulosic fibre composite compounds was evaluated by producing a number of demonstrator objects. (Nättinen et al., 2010).

Experimental

Materials

Matrix and fibres

Amylose-rich corn starch was supplied by Gargill, USA (Cerestar Amylogel 03003: 65w% amylose, 35w% amylopectin). The acetylation of starch was performed according to the method described by Lammers & Tiitola. (1998). Hemp and flax fibres with lengths of 10–20 and 4 mm, respectively, were used in the composites. The fibres were supplied by Ekotex, Poland.

Processing

The plasticiser was added to the SA using a liquid pump and mixed with a twin-screw extruder (ZE25x48D, Berstorff GmbH, Hannover, Germany) with modified co-rotating mixing screws. The granulates obtained by compounding were injection moulded with the Engel injection moulder (ES 200/50 HL, Engel Austria GmbH, Schwertberg, Austria) into an ISO 3167 tensile test specimen. The details of the processing are presented in a paper by Nättinen *et al.* (2010).

Characterisation

Impact strengths, tensile properties, density, volume fractions and other properties of the neat PSAs and the composites were determined. The details of the characterisations are presented in a paper by Nättinen *et al.* (2010).

Tensile tests

The tensile properties of the neat PSAs and the composites were measured according to the ISO 527 standard on an Instron 4505 Universal Tensile Tester with a 10 kN load cell and 5 mm/min cross-head speed. The strain was measured by an Instron 2665 Series High Resolution Digital Automatic Extensometer. The testing was performed in controlled ambient conditions: 23°C and relative humidity of 50%.

Results and discussion

Materials development

Plasticiser

In Figure 1 the specific volume (*ie*, reciprocal of the density) of the PSAs is plotted as a function of the weight fraction of the plasticiser. The relationship is well predicted by a linear relationship.

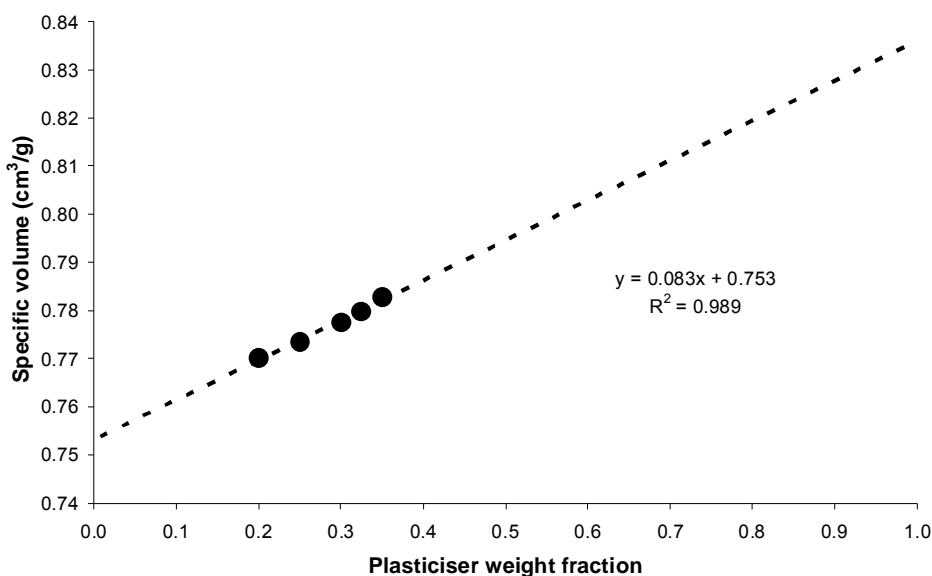


Figure 1. The specific volume (*ie*, the reciprocal of the density) as a function of the plasticiser weight fraction of SA compounds. The dotted line is a linear regression line. (Nättinen et al., 2010).

Figure 2 shows stiffness and stress at maximum load as a function of the plasticiser volume fraction. The results indicate that the relationship between the tensile properties and the plasticiser content is linear. According to these linear relationships, the tensile properties (both stiffness and stress at maximum load) approach zero when the plasticiser volume fraction approaches 0.40, which points to this being the equilibrium content of the plasticiser in the SA. For neat SA (at a plasticiser content of zero), the linear regression lines predict a stiffness of 3.6 GPa and stress at a maximum load of 50 MPa. These tensile property val-

ues, typical of a thermosetting polymer such as unsaturated polyester, are a result of a highly ordered structure with frequent hydrogen bonds between the carbonyl oxygen acceptors and the hydroxyl as well as the methyl and methylene donors. The introduction of plasticiser increases the degree of freedom for the movement of the polymer chains and renders the material more ductile and less brittle (Marcilla & Beltrán 2004). Even if the linear regression lines in Figure 2 do not reflect real material model predictions, they provide good empirical guidelines for the tensile performance of neat PSA compounds; *ie*, for a compound with a given plasticiser content, the tensile properties can be calculated from the equations of the linear regression lines.

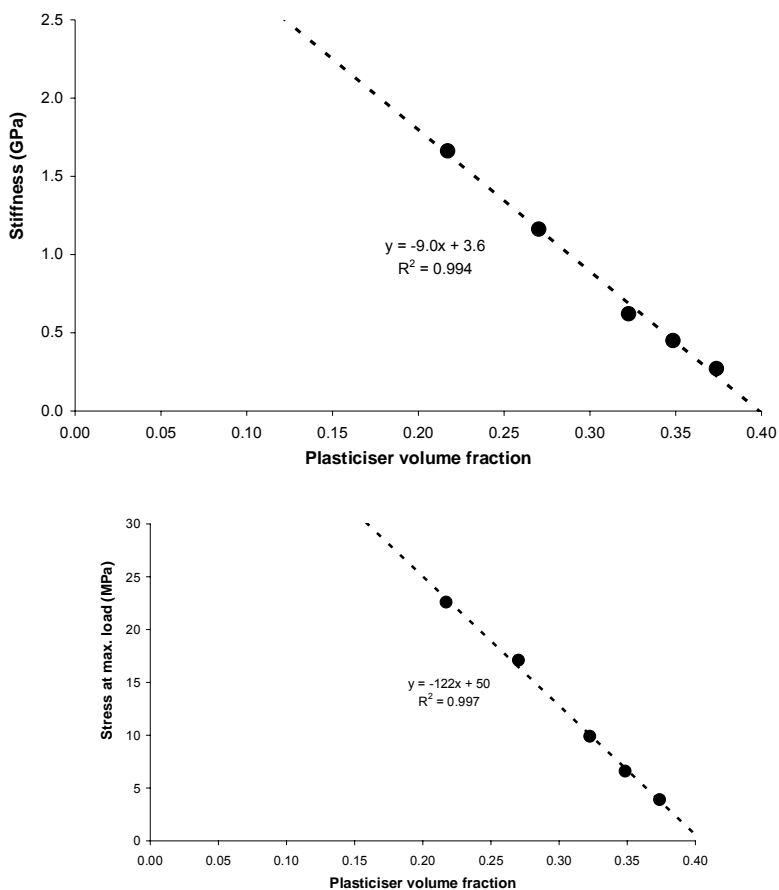


Figure 2. Stiffness (top) and stress at maximum load (bottom) as a function of the plasticiser volume fraction of neat PSA compounds. The dotted lines are linear regression lines. (Nättinen et al., 2010).

Figure 3 shows the effect of the plasticiser content on the mechanical properties of PSA/cellulosic fibre composites. As expected from the results of the neat PSAs, the stiffness and stress at maximum load of the composites are consistently reduced when the plasticiser content is increased. In contrast, the impact strength of the composites increases with the plasticiser content, and this can be explained by the greater toughness (or ductility) of the composites due to the larger plasticiser content.

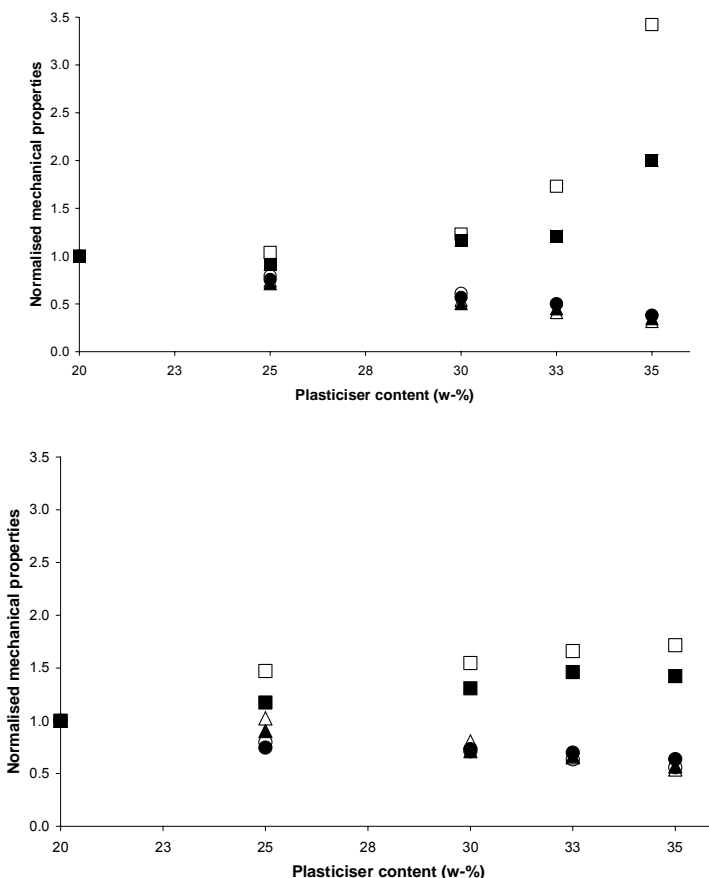


Figure 3. Stiffness (spheres), stress at maximum load (triangles) and impact strength (squares) of 10 (top) and 40w% (bottom) hemp (open symbols) and flax (closed symbols) fibre composites as a function of plasticiser content normalised with respect to the 20w% plasticiser content values. (Nättinen et al., 2010).

Fibre type and content

Figure 4 shows the normalised mechanical properties of PSA1.1 matrix composites with 10, 20, 40 and 50 w-% flax and hemp fibres. Stiffness and stress at maximum load are increased consistently and almost linearly as a function of the fibre content. In contrast, impact strength is affected less consistently by the fibre content: first it is increased when the fibre content is increased from 10 to 20 w-%, and then it is gradually decreased when the fibre content is increased to 50 w-%. For these composites, the highest stiffness of 3.6 GPa and stress at a maximum load of 21.2 MPa are obtained with the maximum content of 50w% hemp fibres. The highest impact strength of 23 kJ/m² was obtained with 20 w-% flax fibres.

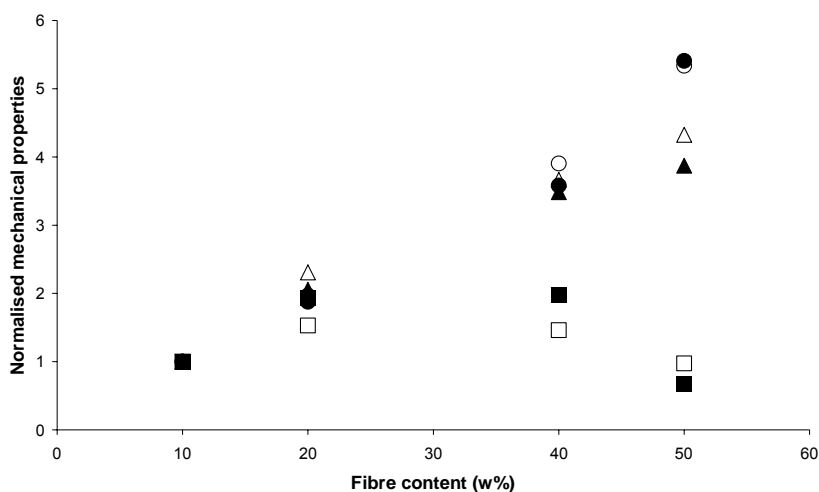


Figure 4. The stiffness (spheres), stress at maximum load (triangles) and impact strength (squares) of PSA1.1 matrix composites with hemp (open symbols) and flax fibres (closed symbols) as a function of fibre content. The data are normalised with respect to composites with 10 w-% fibres. (Nättinen et al., 2010).

The best tensile performance was observed for composites with a PSA2.2 matrix and 40 w-% flax fibres with a stiffness of 8.3 GPa and stress at the maximum load of 51 MPa. These properties are directly comparable to (and even larger than) typical values reported for short fibre composites with a thermoplastic matrix (Rana et al., 1998).

Material applications

Boxes with walls of 1 mm thickness and respirator casings with a grid of similar limiting dimensions were injection moulded to test the processability of the PSA-based composite material in applications requiring good processability and melt flow. A sample specimen of good quality could be produced from these materials. In addition and contrary to the fibre content limit of 50 w-% detected in the injection moulding and compounding processes, rectangular beams were produced by profile extrusion of PSA composite compounds with a hemp fibre content of 60w%. The boxes and respirator casings were moulded at Haidlmair GmbH (Austria) and Medop (Spain), respectively. The rectangular profile beams were produced at Maillefer (Finland) with a Conenor Conex Wood Extruder CWE-380-1. The manufacturing chain and the objects prepared in the project are shown in Figure 5.

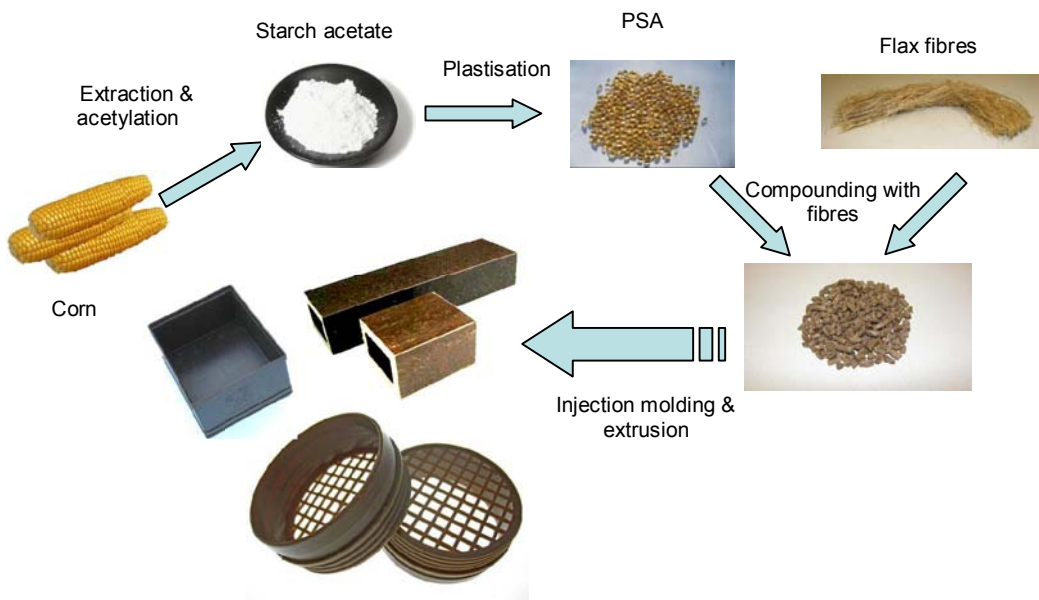


Figure 5. The manufacturing chain for natural fibre composites and sample objects prepared by injection moulding (thin walled boxes and respirator casings) and extrusion (rectangular profile). The outer dimensions of the boxes and the casings are (mm): 65 x 100 x 120 and 25 x 63 (Ø), respectively.

Conclusions

Cellulosic fibre composite compounds based on hemp and flax fibres in TEC plasticised SAs were prepared by melt processing. A stiffness of 8.3 GPa and stress at a maximum load of 51 MPa were obtained with 40% flax fibre in a PSA matrix with 20% TEC. At low plasticiser content and high fibre content, materials with good tensile properties were obtained. The higher the plasticiser content, the higher the impact strength. The increase in the fibre content first improved the impact strength, but higher fibre contents resulted in reduced impact strength. An almost linear correlation between the fibre weight fraction and the mechanical properties was demonstrated. Generally, it was shown that materials with good mechanical properties and good processability could be prepared from PSA/cellulosic fibre composites by melt processing up to a fibre content of at least 40 w-%.

Acknowledgements

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WOODY – Innovative advanced WOODbased composite

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Abstract

Currently, the world of polymeric composite materials is almost exclusively based on fossil-derived components. The non-renewable global oil resources are being increasingly exploited each year as a consequence of the growing demand for plastics engineering materials. As a solution to the increasing volumes of building and construction materials processed and transformed by industries in almost all sectors, renewable resources need to be exploited in order to reduce the depletion of oil reservoirs. The WOODY project (THEME NMP 2007 - 4.0-1 Advanced wood-based composites and their production Grant Agreement for: Collaborative Project) aims to develop new composite structures from renewable materials – namely wood-derived cellulose fibres and resins obtained from natural raw materials. The related manufacturing processes for advanced composite components, such as nanomaterials, will also be explored both as reinforcing fibres and as additives to bring new functionalities to structural composites.

Introduction

The WOODY project is aimed at introducing a fully innovative paradigm in the composite industry – thanks to the development of materials derived from natural resources – enabling it to cover the whole necessities of the components: fibre, matrix and core. The goal of the project is to develop new composite panels and laminates from wood-derived renewable materials, which deliver performances competitive to those of traditional composites.

The breakthrough innovation in materials is backed by an innovative approach in design of composite products – or ‘Composite Thinking’ – starting from the phase of conception to the production and installation, enabling a rethink of the products and fully exploiting the potentialities of composites. Figure 1 shows the approach and processes of the project.

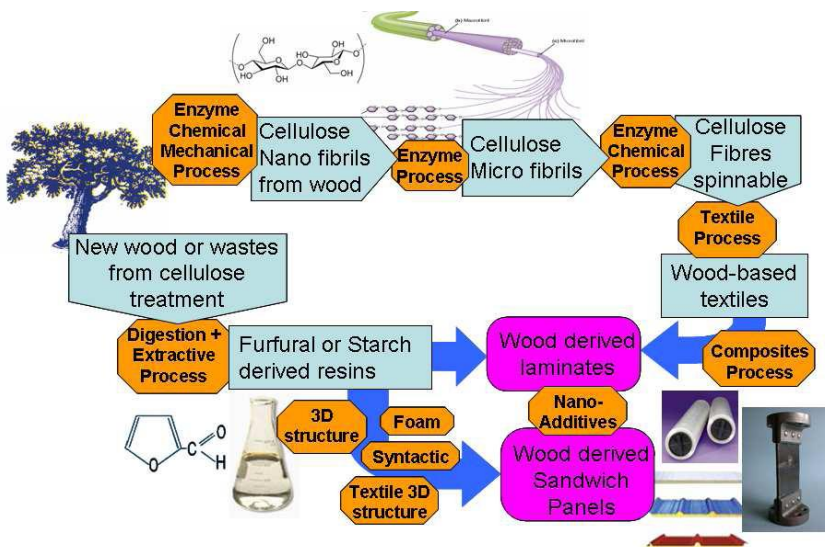


Figure 1. Schematization of WOODY Processes and the approach from raw material to finished products.

The quality of the approach is based on multidisciplinary research and on the target oriented to the redefinition of the whole processing value-chain for wood-derived cellulose, nano-fibrils and resins derived from natural raw materials, as well as on the related manufacturing process for advanced composite components. The project aimed to set the basis for the development of a new class of products, optimising the use of the natural resources.

Main innovations

This innovative project involving wood-derived is oriented towards a Composite Thinking approach: the radical renewing of the basic elements of construction (plates, pillars and beams) introduced at the design stage; and the concept of shells developed on the basis of the specific applications. Such requisites, devel-

oped in close cooperation with the innovative materials, are to be complemented by their mechanical and physical properties, enabling the maximum exploitation of the performances. The Scientific / Technological Objectives are listed below:

- Raw Materials:
 - Cellulose fibrils extracted from wood.
 - New processes for the high yield production of furfural from biomass.
 - The selection and development of nano-based natural components for functionalising the wood based materials.
- Treatments:
 - Light chemical treatment of cellulose to remove lignin and other materials before the fibrillation step with a super mass colloidiser and high shear mixing processes to reduce energy consumption.
 - Chemical treatment.
 - Enzymatic recombined CBD-based pretreatments for nanofibril production with a combined functionalising process and a protein-mineral fibril combination.
 - Treatments for nanofibril and whiskers separation, relying on chemo-mechanical and thermal treatments with high throughput.
 - Recombinant enzymatic treatment to increase the quality of the fibrils-to-fibre build-up, leading to a fibrous material suitable for the textile reinforcements of the composite laminates.
 - Treatments to strongly limit the moisture sensitivity of the composites, fully compliant with the base constituents and with the functionalising additives.
 - Modified textile processing to cost-effectively transform the fibres into yarns, webs, woven or knitted textiles, thus producing the reinforcing elements of the laminates.
- Composite Materials:
 - Laminate panels: reinforcement fabric, matrix material and additives based on wood-based cellulose, wood treatment and other eco sustainable materials.
 - Sandwich panels: foam core, skin layer and adhesion promotion agents.

The main target for VTT in WOODY is to develop novel bio-based and/or biodegradable thermoplastic foamed structures to be used as core layers in sand-

wich or laminate composite structures. The properties required from the bio-based and/or biodegradable thermoplastic core layers are: light weight, high modulus, high bending and compression strength, low density, closed cell structure, good processability and thermal stability.

Materials and methods

The results of the development of the biobased foamed core structure during the first year of WOODY are presented here. The bio-based polymers, chosen as matrix materials in the development of foamed core structure in the beginning of the WOODY project were starch derivatives and PLA. Other bioplastics are evaluated during the project according to their availability, applicability, processability, properties and price.

Thermoplastic matrix materials are foamed with different foaming technologies, such as soluble foaming with the physical blowing agent (PBA) CO₂ and/or chemical blowing agents (CBA) in the extrusion or injection moulding process, and also with batch foaming technology with PBA. The knowledge and results achieved in the core material and process development are exploited for modelling and further exploitation of developed materials, processes and structures in the design and manufacture of components and composites on an industrial scale.

Results

Foaming experiments with plasticised starch

The first foaming experiments in the WOODY project were accomplished with starch. Due to a number of inventions, patents and extensive knowledge attained during the last twenty years at VTT of starch, its processing, properties and applications, native starch was chosen to be used as a matrix polymer in the first foaming experiments. In these preliminary foaming trials, native starch and glycerol as a plasticiser were compounded in a Berstorff twin screw extruder with two different blowing agents – sodium bicarbonate and water. Sodium bicarbonate was compounded at a temperature of approximately 100°C to compose a material combination consisting 69% potato starch, 29% glycerol and 2% NaHCO₃. This compound was further expanded for two hours at 150°C in an oven immediately after compounding to form the cellular structure. Figure 2 shows the samples of the expanded starch core structures. Unfortunately, the extruded

starch compound was perceived to be unstable and not expandable after a couple of weeks of storage. Additionally, the expanded starch samples mainly had an open cell structure, which is not desirable for core layers.



Figure 2. Starch compound (i) after extrusion, (ii) expansion in an oven, and (iii) expanded starch.

In addition to sodium bicarbonate, water was used as a blowing agent for the potato starch in the extrusion foaming process. The extrusion foaming trials, run with a Berstorff twin screw extruder with water as a blowing agent, were carried out with two different recipes:

- 50% starch + 5.6 % glycerol + 44.4% water
- 60% starch + 15% glycerol + 25% water.

In the extrusion foaming process, starch and glycerol, as a plasticiser, were first melted and mixed with water (the blowing agent); the molten mass was then forced through a die to cause foam expansion. During the extrusion foaming, it was discovered that the screw geometry, pressure, cooling ability, moisture content, temperature distribution and temperature control have a huge influence on controlling the foam density and properties. The challenge is to increase the percentage of closed cells and to eliminate corrugation. The appearance of the extrusion foamed starch with water as a blowing agent is shown in [Figure 3](#). These foams are brittle, corrugated, tough and hydrophilic with a large cell size.



Figure 3. Plasticised starch foamed with water in an extruder.

Starch foams are in commercial use mainly in some packaging applications and can be used as a reference matrix material for the comparison of mechanical, thermal and water absorbent properties with other bio-based plastics. Due to the poor processing stability and properties such as hydrophilicity, poor mechanical properties and low thermal stability, the foaming of starch is mainly continued with micro- and/or nanocellulose reinforcements.

Foaming of PLA with a chemical blowing agent

Extrusion foaming trials were performed with NatureWorks PLA 2002D and the chemical blowing agent (CBA) Hydrocerol CT 3108 with 1% to 4% content. Hydrocerol is commercially available and, due to its totally biodegradable nature, it is also an ecological choice for use as a blowing agent for PLA. Extrusion trials were run at VTT with a Dolci cast extrusion line.

By using a Dolci extrusion line and sheet extrusion die, foamed PLA sheets of 300 mm width and 1 mm thickness with 2%, 3% and 4% of Hydrocerol content were successfully processed. The process parameters were optimised and Talc (Finntalc M15) was used as a nucleating agent. The best results were obtained with 4% Hydrocerol content and 1% talc as the nucleating agent. The density of the foams were analysed by gravimetric methods and the lowest density achieved was as low as 560 kg/m³, which is considered to be a good result with chemical blowing agents. The Dolci sheet extrusion line and extrusion foamed sheet is shown in Figure 4.

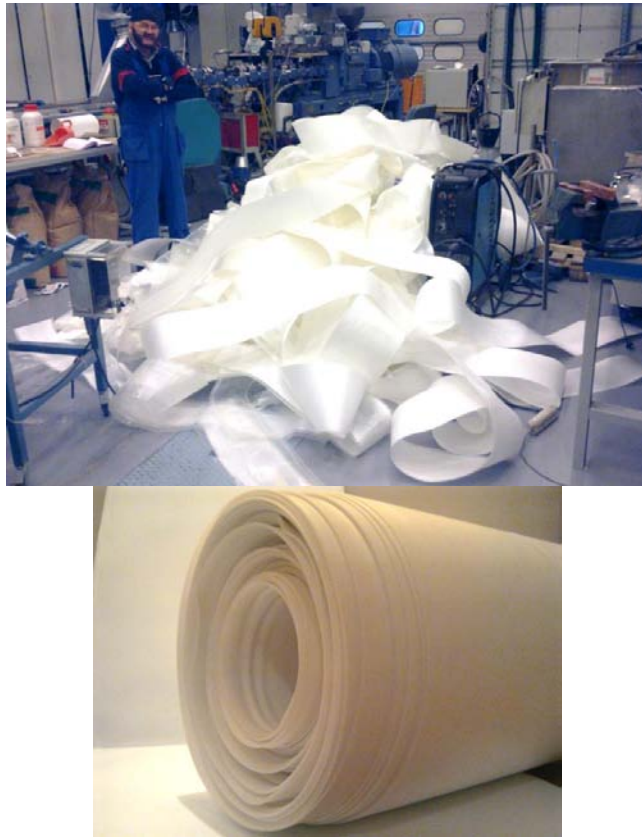


Figure 4. Foamed PLA sheet extrusion trials and foamed PLA sheet.

The SEM picture of the extrusion foamed sheet in [Figure 5](#) reveals both closed and open cells; it has a quite even cellular structure with some variation in cell size.

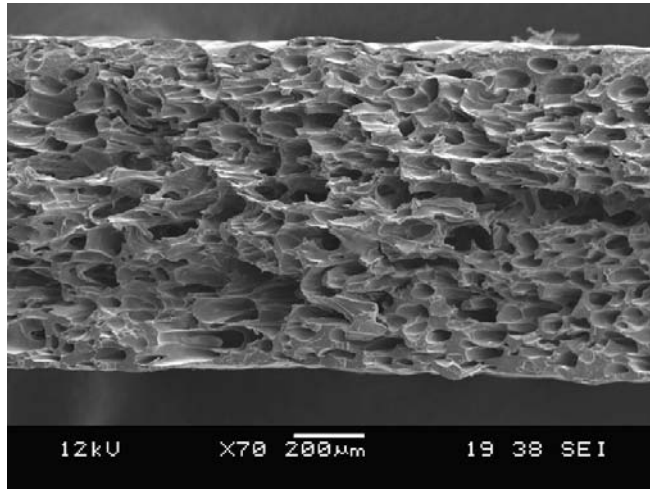


Figure 5. SEM picture of an extrusion foamed PLA sheet.

Conclusions

WOODY (01.01.2009–31.12.2012) is an innovative and ambitious EU project aiming to develop new composite structures from renewable materials – namely wood derived cellulose fibres and resins obtained from natural raw materials (Figure 6). The related manufacturing processes for advanced composite components are also being explored. The targeted applications of the proposed renewable structural composites are in the transportation and construction fields. This represents a significant step forward with respect to the current state-of-the-art wood composites processing, where wood panels are obtained by directly cutting wood pieces, or by pressing in polymeric matrix short wood fibres or wood powder as fillers in extrusion-like processes.



Figure 6. Project value chain and steps of innovation.

Consortium of the project

The WOODY consortium comprises 19 partners: ten small and medium enterprises; two large enterprises; one European Industrial association, and six research entities representing the excellence of the European area's fundamental and applied research. The partners are from seven EU countries plus Israel.

The coordinator of the project is CETMA from Italy and the consortium consists of the industrial partners: APC Composite, AP&M LDA, D'Appolonia S.p.A, Extreme Materials, Fapes, Gianazza Angelo SpA, Lindbäcksbygg, KAPENA SA, Marbo, Sicomp, Transfuran Chemicals, Volvo, and European Composites Industry Association EuCIA. The research partners are: Centexbel, the Hebrew University of Jerusalem, Luleå Tekniska Universitet, the Technical University of Denmark and VTT.

Each partner is strongly committed towards the final purpose of maximising the quality of the work to be performed, i.e. introducing an innovative class of composites starting from wood materials. The WOODY Project Consortium

shows complementarity of the multidisciplinary skills of the partners involved in the different fields of research, thanks to which, the achievement of Scientific and Technological objectives are achieved.

Acknowledgements

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Additional information of the project can be found on WOODY's internet pages:
www.woodyproject.eu

Lignin-compatible biocomposites

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Abstract

In the project, lignin was used as a bio-based compatibiliser in natural fibre-reinforced biocomposites. Birch pulp and flax fibres were treated with pine kraft lignin and/or lignosulphonate solutions. The treated fibres were compounded with polylactic acid (PLA) by melt processing to a fibre content of 30 w-%. The compounded materials were then injection moulded and the mechanical properties of the composite samples were determined. As a result, lignins showed great potential as biocomposite compatibilisers.

Introduction

Although the use of natural fibres to reinforce plastics has many advantages, such as low weight and price, renewability and easy availability, the composite properties do not always meet the material requirements of the desired applications. One reason for this is the weak adhesion between the hydrophilic fibres and hydrophobic matrix material. One of the most common solutions to the problem is the use of maleic anhydride (MAH) as a compatibiliser. When grafted onto the surface of the polymer, MAH acts as a coupling agent between the polymer and the fibres. MAH is widely used in polypropylene-based composites, and improved mechanical properties have been reported (Stark & Rowlands, 2003). In the Tekes-funded project 'Biocomposites as constructive materials – BIKO' (Tekes Technology Programme Report, 1/2004), MAH was

grafted onto polylactic acid (PLA) with peroxide and PLA. Flax fibre composites with improved mechanical properties were reported.

The use of lignin as a coupling agent in natural fibre composites has also been studied. Attached to the fibre surface by its inherent bonding capability with cellulosic fibres, hydrophobic lignin acts as a compatibiliser between the hydrophilic fibres and hydrophobic matrix polymer, thus strengthening the fibre-matrix interface. Lignin treatments of hemp fibres (Thielemans & Wool, 2005) and flax fibres (Thielemans et al., 2002) have been shown to improve compatibility between fibres and the thermoset matrix, thus also improving the mechanical properties of the composites. Graupner (2008) reported increased tensile properties of compression-moulded PLA-cotton composites when the fibres were treated with lignin. The results of lignin-treated fibres in thermoplastic, injection-moulded biocomposites have not been yet published however.

In addition to better material properties, the use of lignins as compatibilisers also preserves the potentially required bio-based nature of the biocomposites, embracing biodegradability as well as renewable characteristics. The aim of the research was to produce biocomposites that 1) are 100% bio-based; 2) use industry side streams; 3) have improved mechanical properties compared with existing biocomposites; 4) meet the properties of conventional, not bio-based materials. Agro and pulp fibres were treated with kraft lignin and lignosulphonates and compounded with polylactic acid to produce biocomposites with improved properties.

Materials and methods

Lignin treatments

Lignin-free, chemically bleached birch pulp (Stora Enso Oyj, Finland) and flax fibres (Ekotex, Poland) were selected as fibres. Pine kraft lignin was obtained from MeadWestVaco Corp., USA, and lignosulphonates from the Borregaard Group, Norway.

For the kraft lignin treatments, 1% and 3% pine kraft lignin water solutions were prepared. NaOH was added to the water-lignin solution to reach a pH >11: this was needed to dissolve the water-insoluble kraft lignin. The fibres were immersed in the solutions for 10 minutes and the excess water was then extracted by spin-drying, and finally the fibres were dried in a hot-air drier.

For the lignosulphonate treatments, two 1% lignosulphonate-water solutions (Na- and Ca-lignosulphonates) were prepared by mixing. Lignosulphonates are water soluble in nature, so no NaOH was needed. Fibre treatments were performed as described above.

Biocomposite processing

For the composite production, polylactic acid- (PLA) grade PLA 3001D (NatureWorks, USA) was used as a matrix polymer. Composites containing 30 w-% fibres were produced using a co-rotating twin-screw extruder (Berstorff ZE 25x33D). The compounds were then injection moulded with an injection-moulding machine (Engel ES 200/50 HL) into tensile test specimens, followed by normal mechanical testing of the specimens (ISO-527, ISO-179).

Results

PLA – flax fibre composites

NaOH treatment of flax fibres improved the impact strength of the PLA composites (Table 1), probably due to the roughening of the surface of the fibres. The addition of small amounts of kraft lignin (1% solution) maintained the impact strength values and clearly improved the tensile strength and strain at break of the composites, thus compatibilising the material. When more kraft lignin was added, a decrease in mechanical properties was seen, so the optimum lignin content in the solution seems to be less than 3%.

Table 1. The effect of lignin treatments on PLA – flax composite properties.

Treatment	Tensile strength	Impact strength	Elastic modulus	Strain at break
None	0 %	0 %	0 %	0 %
NaOH treated	-0.3 %	65.5 %	1.6 %	-17.3 %
NaOH + kraft-lignin treated (1%)	13.5 %	61.8 %	4.2 %	27.7 %
NaOH + kraft-lignin treated (3%)	9.4 %	60.2 %	4.3 %	-1.7 %

PLA – birch pulp composites

NaOH treatment of birch pulp fibres also improved the impact strength of the PLA composites, but other properties were reduced or remained at the same level as the composite containing untreated fibres (Table 2). The addition of 1% kraft lignin solution increased the elongation and tensile strength slightly.

Table 2. The effect of lignin treatments on PLA – birch pulp composite properties.

Treatment	Tensile strength	Impact strength	Elastic modulus	Strain at break
None	0 %	0 %	0 %	0 %
NaOH treated	-7.9 %	56.2 %	2.3 %	-17.6 %
NaOH + kraft-lignin treated (1% sol.)	-1.3 %	49.3 %	-2.4 %	2.0 %
NaOH + kraft-lignin treated (3% sol.)	-28.3 %	16.5 %	-9.2 %	-33.1 %
Na-lignosulphonate (1% solution)	6.6 %	59.0 %	-4.5 %	52.0 %
Ca-lignosulphonate (1% solution)	-4.5 %	2.7 %	-6.4 %	-1.4 %

Na-lignosulphonate treatment of birch pulp fibres had a significant effect on the mechanical properties of PLA composites (Table 2). The impact strength increased by 59%, elongation by 52% and tensile strength by 6.6%. The elastic modulus decreased slightly. Ca-lignosulphonate treatment, however, had no notable influence on the composite properties.

Conclusions

Lignin showed great potential as a compatibiliser of PLA – natural fibre composites. By treating fibres with NaOH + kraft lignin or Na-lignosulphonate solutions, biocomposites with improved mechanical properties were obtained. Compared with the commercially available and widely used compatibiliser MAH, the use of lignin offers even better mechanical properties at the same time as it provides a completely bio-based product. The influence of various coupling agents on the mechanical properties of composites has been collected in Table 3.

Table 3. The influence of various coupling agents on the mechanical properties of materials.

Reference	Matrix + fibre	Processing	Coupling agent	Tensile strength	Elastic modulus	Strain at break	Impact strength
<i>Graupner, 2008</i>	PLA + 40 w-% cotton	Compr. moulding	Kraft lignin (euca)	9 %	19 %	-20 %	-17 %
<i>Thielemans et al. 2001</i>	VE + 20 w-% hemp	RTM	Kraft lignin (pine) 1%	-16 %	10 %		
<i>Stark & Rowlands, 2003</i>	PP + 40 w-% wood flour	Injection moulding	3% MAPP (MAH+PP)	27 %	6 %	0 %	7 %
<i>BIKO (Tekes), 2003</i>	PLA + 30 w-% flax	Injection moulding	0.25% MAH, 0.25% peroxide	23 %	4 %	65 %	28 %
'Lignin compatibilised biocomposites'	PLA + 30 w-% flax	Injection moulding	Kraft lignin (pine) 1%	14 %	4 %	28 %	62 %
'Lignin compatibilised biocomposites'	PLA + 30 w-% birch pulp	Injection moulding	Na-lignosulphonate, 1%	7 %	-5 %	52 %	59 %

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ECOplast – Research into new biomass-based composites from renewable resources with improved properties for vehicle parts moulding

Introduction to starting a European research project

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Abstract

Lightweight materials with advanced mechanical properties are regularly used, for example, in the construction of vehicles, to improve performance and to reduce fuel consumption. The reduction in vehicle weight is increasingly important due to the added weight of safety equipment and further power-train inventions like hybrid drive systems.

The heterogeneous composition of composite materials is based predominantly on inorganic reinforcement and is in the micrometre to millimetre range. It has recently become clear that reducing the size of the reinforcement units to the same organic building block level results in emerging possibilities for further fine-tuning of material properties on a molecular and nanoscale level.

Novel hybrid materials can be applied to many branches of materials chemistry because they are simple to process and amenable to design on a molecular scale. There are currently four main topics in the synthesis of inorganic-organic materials: (a) their molecular engineering, (b) their nanometre- and micrometre-sized organization, (c) the transition from functional to multifunctional hybrids, and (d) their combination with bioactive components.

The novel materials not only enable characteristics between the two original phases but may also reach new levels of properties. Furthermore, the traditional composite materials are considered a significant problem in the recycling of combined materials. Possibilities of particular interest open up when combining nano-materials into biocomposites.

Impacts of project

With the oil supply diminishing every day, the pressure to become more independent of oil derivatives is a major subject of concern. A paradigm shift has been witnessed – a move from an all-petroleum-based industrial economy to one that encompasses a broader base of materials, including plant-derived products and fermentation by-products. In addition, the recent themes of discussion regarding the preservation of sustainable resources and recycling have led to renewed interest in biopolymers, with special focus on renewable raw materials. The advances in natural fibre development, genetic engineering and composite science have provided significant opportunities for improved materials from renewable resources with enhanced support for global sustainability. Due to growing environmental awareness and the demands of legislative authorities, the use and removal of traditional composite structures are considered critical.

The potential market for the biocomposites developed in ECOplast can be determined taking into account three fundamental factors: the potential of substitution acquired by novel biocomposites, automobile OEM demands and the production capacity of the base biopolymers.

Before analysing the potential market of novel biocomposites, the decisive factor of the impact on the European automobile sector, especially SMEs, is the economic feasibility of the developed materials to guarantee benefit margins and profitability. In fact, the polymer matrices used at ECOplast have been selected for their similarity in performance to conventional plastics used in vehicles to favour their substitution.

Challenges of the project

When aiming for a reduction in the dependence on fossil resources through the development of novel biocomposites with a biomass content of more than 90%, based on PLA and PHB biopolymers enhanced with natural fibres, nanofillers and mineral fillers from organic residual resources, there are several challenges.

There is limited validation even for the suitability of novel thermoplastic and commercially viable, biomass-based composites to meet the automobile requirements for integration into vehicles and tailoring of their properties.

Another important goal of this project is the adaptation of conventional processing techniques (polymer compounding, injection moulding and thermoforming) widely used in the automotive industry and the design of new ones tailored to these biocomposites. Here, the challenge will be to overcome the problem of degradation due to extreme thermal conditions and moisture absorbency.

This is not only to establish and evaluate biomaterial concepts but also to ensure maximum industrial relevance and economic impact of ECOplast results covering the two most widely used plastic processes, injection moulding and thermoforming, in the automobile industry. This is especially important for SMEs that are plastic processors in the automobile industry, as this sector is composed of a high number of industrial SMEs.

Scientific and technical objectives

The main objective of the project is the development of novel biocomposites based on new biopolymers as base matrices reinforced with natural fibres, nanofillers, mineral fillers and additives, adapting the conventional processing techniques used most in the automobile industry and other innovative processing technologies to tailor their properties for validation for their introduction into vehicles. The principal research line will focus on the adaptation of available biopolymers (PLA, PHB) and the creation of a new protein-based biopolymer (SELP) for use as the base matrix to meet the automotive standard requirements. To achieve this advance, it is essential to improve the thermal characteristics of these polymers as well as their hydrolysis resistance, dimensional stability and volatile emission.

Project ECOplast will develop several new reinforcements and novel additives such as nanofillers, mineral fillers and treated natural fibres, including nanocellulose, to be compounded with these base polymers in order to create new biocomposites with enhanced performance levels:

- Nanofillers to increase thermal resistance
- Natural fibres and nanocellulose to enhance dimensional stability and mechanical resistance
- Mineral fillers to reduce moisture absorbency.

The main challenges are the maturity of the new material concepts, their ability to improve the properties of biopolymers and enable adaptation of conventional plastic processing techniques as well as the exploration of novel processing technologies.

Research in detail

Material development

Suitable biopolymers will be developed through new synthesis or modulation of their structures to provide the necessary functionalities and properties for use as the base of novel bio-composites. This will be done by developing a PLA stereocomplex via the combination of PDLA as a nucleating agent, the development of a PLA copolymer via transesterification of PLA and by developing a new protein-based copolymer using silk-like crystalline and elastine-like flexible blocks.

Novel reinforcements and nanofillers will be tailored to enhance the biopolymer formulation achieved in the previous WP: a selection of the necessary natural fibre additives and their modification to guarantee optimal composite properties and processing, and a selection of the necessary mineral fillers and additives to guarantee their optimum properties and processing. This is done by developing new fibrillar natural nanofillers, developing wood base reinforcements, including cellulose and nanocellulose, and by developing natural fibres and selecting the adequate mineral fillers and additives to enhance the formulation.

Technology adaptation

Conventional mixing techniques will be adapted to the new biocomposites that will be developed, tailoring the processing parameters, machine configuration and structure. The exploration of innovative processing techniques is designed to overcome the excess of volatile emissions in some of the mixtures defined in the first WP. This will be done by compounding PLA-based biocomposites, cast-sheet extrusion of PHB-based biocomposites, applying a sheet containing long fibres and compounding biocomposites based on the new protein-based copolymer.

Conventional processing techniques will be applied to the new biocomposites that will be developed, tailoring the processing parameters, machine configuration and structure. The exploration of innovative processing techniques is designed to overcome the problems presented by these kinds of sensitive materials

regarding thermo-mechanical loads and residence times. This will be done by applying injection moulding to test samples, thermoforming test samples and integrated compounding-injection moulding.

The re-engineering, cyclic system will be programmed to adjust suitable bio-composite formulations, and it will be composed of three purging cycles. It will use the statistical method for experiment design called Multi-Level Factorial to determine the most effective combinations in the material matrices, taking into account interactions among the different added materials and achieving the most accurate information possible with the minimum tests required.

Biocomposite valorization

Evaluation of biocomposite behaviour in a pilot plant with conditions similar to real industrial facilities, determining processability and economic feasibility in order to enhance the expected economic impact and transference of knowledge to facilitate possible future industrialization, especially in European SMEs belonging to the automobile and plastic processing sectors. This will also include the scale-up studies for all processing.

Recyclability and biodegradability analyses of new developed composites and the environmental suitability of the new product by a Life Cycle Assessment (LCA). Eco-toxicity test of materials to reduce the risks to plants and animals. Assessment of the economic and legal viability of the material.

Research coalition of the project

Development of new biomass-based composites validated for the automotive industry by means of the adaptation of base biopolymers and the generation of new ones using innovative treatments for fibre reinforcements and the addition of the base polymer with novel fillers and nanofillers. For this purpose, the established research coalition of the project consist of the Spanish CTAG and AIMPLAST, the Portuguese PIEP and the University of MINHO, the German Fraunhofer UMSICHT and the Finnish VTT. The industrial partners are the German FKUR Kunststoff, BIOMER and PALLMANN, the Spanish Nanobiomaterials R&D, GRUPO ANTOLIN and MEGATECH and the Dutch PURAC. The coordinator is CTAG.

ECOplast – Research into new biomass-based composites from renewable resources with improved properties for vehicle parts moulding

References

The ECOplast project (Collaborative project for FP7-NMP-2009-SME-3) is coordinated by CTAG, which is a Spanish technological SME.

For more information about the ECOplast project, see its website: www.ctag.com.

Preparation of cellulose-starch and cellulose-lignin films

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Abstract

Composite cellulose films provide a platform for emerging film and membrane applications. This work provides some simple demonstrations of cellulose, starch and lignin composite film preparation in water-based solutions.

Background

Different approaches to prepare cellulose, starch and lignin composites have been studied. They dissolved all the polymers in ionic liquid (AmimCl) and coagulated films from the blend solution (Wu et al., 2009). The preparation of cellulose films has been known about for over a hundred years, and commercial cellulose fibres are currently produced by the viscose and Lyocell (NMMO) methods. The enzyme-assisted process to produce cellulose is an alternative way to make cellulose films. In the process, enzymes are used to modify the cellulose in alkaline-soluble form without the need for any chemical treatments. (Vehviläinen et al., 2008; Vehviläinen et al., 2009).

Structural considerations

As one of the most important and abundant polysaccharides in nature, starch has been the subject of much research. It is used widely in industry to provide functional properties such as gelling, thickening, bonding and adhesion (Soares et al., 2005). Starch is a high Mw polymer of hydro-glucose units linked by α -D-glycoside bonds. Starch molecules usually contain linear amylose and branched amylopectin (Maurer, 2001). Amylose is responsible for the film-forming capacity however (Romero-bastida et al., 2005). Pure native starch films are brittle compared with synthetic polymers such as polyethylene and usually need to be plasticized. The addition of plasticizers such as polyols can prevent cracking of the film during handling and storage (Arvanitoyannis & Biliaderis, 1998)

Structural arguments have been expressed for associative interactions between polysaccharides and lignin precursors (Terashima et al., 1995; Terashima et al., 1996). It has been suggested that dominant, organizing influence on the lignin ultrastructure is provided by strong associative interaction between the lignin precursors and the polysaccharide matrix. (Atalla, 1998). Strong associative interactions should lead to rapid adsorption of the lignols from an aqueous medium onto cellulose (Houtman & Atalla, 1995). A large number of adsorption sites should result from the stacking interactions between lignin aromatic rings and C-H groups of cellulose, which should enable cellulose-lignin film formation. (Besombes & Mazeau, 2005)

Application of polysaccharide films

Starch is considered a promising candidate for biodegradable and edible films. (Araujo-Ferro et al., 2010; Hernandez et al., 2008; Jansson & Thuvander, 2004; Talja et al., 2008). One way to improve the poor mechanical properties and water sensitivity of starch films is to add cellulose into the structure. Cellulose-starch composite films are usually prepared by casting films from gelatinized starch with added insoluble cellulose microfibrils, nanocrystals or nanoparticles. (Cao et al., 2008; Chang et al., 2010; Dufresne et al., 2000).

Membranes for chiral separation systems were developed by covalently binding functional substances onto the surface of commercial cellulose membranes. (Xiao & Chung, 2007) Active substances such as acetylated β -cyclodextrin are immobilized on a cellulose dialysis membrane. (Xiao et al., 2007) As an example, membranes were improved against blood coagulation by appropriate drug

treatments such as an antithrombogenic compound bonding chemically (German Pat. No. 27 05 735) or heparin salt bonding (German Off. No. 17 20 087), phospholipid surfactant coordination or even further graft polymerization (Nakabayashi, 2004) of the cellulose membranes.

Experimental results

Cellulose solution

The cellulose material was a commercial, dissolving-grade softwood TCF sulphite pulp. The pulp was first shredded mechanically and thereafter treated with a commercial endoglucanase-rich enzyme preparation. The enzyme treatment released about 3% of the pulp as soluble sugars, measured using the DNS method (Bernfeld, 1955), and decreased the viscosity from 405 ml/g to 270 ml/g (SCAN-CM 15:88).

The mechanically and enzymatically treated pulp was dissolved in aqueous sodium zincate according to the EP application 08397510.2. Cellulose xanthate solution prepared from softwood-based dissolving pulp was used as a reference. The cellulose content of the solution was 9 wt-%.

Starch films

Film experiments were achieved using two separate 12wt% starch solutions consisting of sodium hydroxide as well both sodium hydroxide and potassium hydroxide to explore the effects of an alkali used in starch solutions on the coagulation rate, resistance during the water washing and the properties of the final film. It was observed that about 1.5–2 hours is required before solutions level out and reach sufficient rheology for film formation. The starch used was commercial, unmodified native potato starch. Native potato starch is composed of granules, which must first be dissolved in polymer form using an alkali. The sodium hydroxide (NaOH) and potassium hydroxide (KOH) concentrations for dissolving starch granules were determined using the method described in the patent US 4,144,079.

The acid coagulants illustrated that not all of these acids, irrespective of acid concentration, were capable of precipitating starch solutions. In contrast, the ammonium ion (NH_4^+) containing ammonium sulphate close to the saturation concentration is capable of coagulating starch films. Different ammonium compounds were tested. The highest ammonium ion concentration can be attained

using $(\text{NH}_4)_2\text{SO}_4$. A short study of the ammonium ion release of the common and harmless ammonium compounds illustrated that a 43% $(\text{NH}_4)_2\text{SO}_4$ solution is needed for starch coagulation. An additional benefit of ammonium coagulation is that the used coagulation solution had pH 7.82, while typical acid solutions are below pH 2, causing a side reaction for the starch.

Films were formed using a 43% $(\text{NH}_4)_2\text{SO}_4$ solution at room temperature. The first signs of precipitation were observed approximately 8–10 seconds after the introduction of the starch solution into the coagulant solution. As the precipitation proceeded, a whitish opaque film was observed, irrespective of the alkali composition used in the starch solution. The NaOH containing starch solution, however, seems to require a longer coagulation time for the same film thickness compared with both the alkali containing starch solution. Further NaOH containing solutions were weaker and the films seemed to have more problems keeping their integrity, opacity and thickness during the water washing. In the case of the higher concentration and temperature, the coagulation rate was increased and similar differences between the used coagulants were achieved, although films prepared from this solution were slightly weaker and vulnerable.



Figure 1. Film precipitated from 6 g of starch solution containing 4:1 of KOH and NaOH.

Cellulose-starch films

While the starch films were mechanically weak after drying, they could be plasticized either externally with substances like polyols or internally by means of grafting. This study was aimed at pure natural polymer films, however, and the

experiments were therefore performed using two cellulose-starch solutions in which the cellulose-starch dry content ratios were 3:1 and 1:1. The solution was prepared mixing 5.5wt% cellulose enzyme-assisted zincate solution with 11wt% starch solution to achieve the desired mixing ratio.

Until now, the best available coagulant solution for starch solution that had been detected was 43% $(\text{NH}_4)_2\text{SO}_4$ solution, but it was not known how cellulose behaves with this coagulant. Cellulose solutions were typically precipitated with 10% sulphuric acid (H_2SO_4) or combinations of H_2SO_4 and sodium sulphate (Na_2SO_4). For this reason, a new type of coagulant based on ammonium sulphate, sodium sulphate and sulphuric acid, enabling sufficient SO_4^{2+} ions in the ammonium solution.

In the developed coagulant solutions, coagulation happened fast, and even one-minute precipitation generated clear, transparent cellulose films that were equal in their thickness, transparency and water resistance. When more than 30% of the starch was lost at a temperature of 60°C , only 7% of the 1:1 cellulose-starch films were lost.



Figure 2. Cellulose films precipitated with a combination coagulant contained some 1:1 of $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 in dilute H_2SO_4 .

Cellulose-lignophenol solutions

The purified softwood lignophenol sample was prepared by Mitsuru Aoyagi and kindly provided to the TUT by Professor Masamitsu Funaoka from Mie University, Japan (Funaoka, 1989). It was isolated by hydrolyzing the extractive-free wood flour (ethanol-benzene, 80 mesh pass) with concentrated sulphuric acid after solvation with cresol (a two-step process with a cresol/acetone solution). The lignophenol powder was dissolved in 5.5 wt-% NaOH to form a solution containing 13 wt-% lignophenol at $M_w = 11700$ g/mol.

The lignophenol/NaOH solution was added to cellulose or cellulose xanthate solution and mixed at 150 rpm for 5 minutes using a laboratory stirrer. The obtained mixture solutions contained approximately 5 wt-% lignophenol and 95 wt-% cellulose.

Cellulose-lignophenol films

The films were prepared from pure cellulose and cellulose xanthate solutions and from the same solutions mixed with lignophenol. The solution was spread evenly using a spatula inside a metal frame that was placed on top of the glass plate to adjust the thickness of the solution layer. After application, the frame was removed and the plate immersed in 10% sulphuric acid to coagulate the solution. The obtained film was transferred from the coagulation bath into distilled water and washed until it was free from salts, as measured with a conductivity meter. The purified films were dried under tension at 20–22°C in order to obtain even films for characterization.

The crystallinity and morphology of the cellulose/lignophenol films were measured by SAXS. The reference samples give typical X-ray diffraction patterns of cellulose II. According to the measurement, the lignophenol addition leads to more amorphous films. The FTIR analysis of the cellulose/lignophenol films indicated no clear difference compared with the pure cellulose reference. SEM images of the cellulose/lignophenol films indicated a homogeneous surface structure. A few more sieves of fibrils could be observed in the lignophenol-containing films, but the differences from the reference are only indicative in nature.

The cellulose and lignophenol have close interaction, and lignophenol is able to soften the cellulose to a certain extent. The interaction has not been shown to be caused by bonding between the phases, though dissolving polymeric lignophenol evidently enables softening of cellulose II films. The films may enable further development of cellulose membranes and modification thereof.

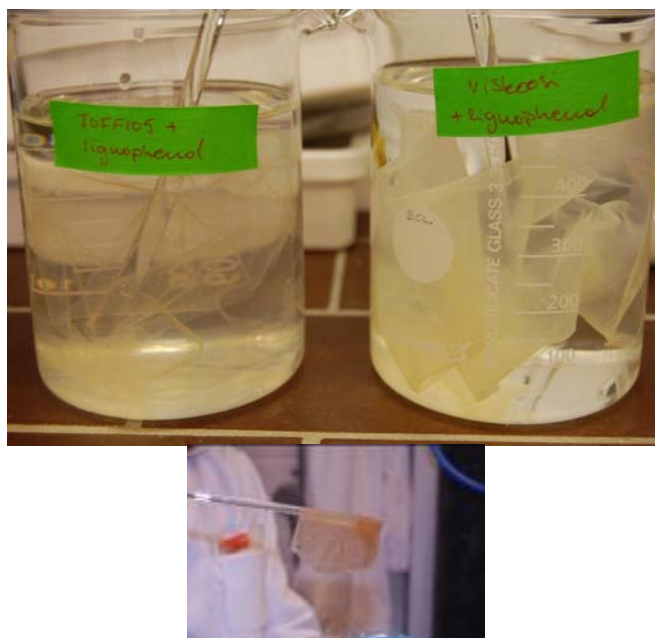


Figure 3. Cellulose-lignophenol films from cellulose-lignophenol solution (left) and from cellulose xanthate-lignophenol solution (right). Additionally, a picture of the film in the air.

Conclusions

Regenerated cellulose can be converted into a thin, transparent film with low permeability to air, oils, greases and bacteria, making the material useful in food packaging. In this work, we have simply demonstrated the possibility of forming cellulose-starch and cellulose-lignin films from water solutions. The cellulose films may find several industrial applications, such as a base for tapes, a semi-permeable membrane for batteries, a stationary phase for thin layer chromatography and dialysis media. In current research, dissolved cellulose was intimately combined with starch to provide ductile cellulose films and lignophenolate-enabling development of new functionalized membranes.

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Preparation of cellulose-starch and cellulose-lignin films

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From nanocellulose science towards applications

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Abstract

Scientific nanocellulose research has focused mainly on the study of structure-properties relationships of nanocellulosic fibres and materials made from these. Wide property ranges have been described, depending on the raw material sources, production methods, pre-treatments and functionalization. These results offer the bases for identifying the specific advantages and possibilities of this new class of nanomaterials. Comparing these with other applied materials and alternative technologies enables the identification of technically and economically feasible applications of nanocellulose-based technologies.

Introduction

Nanofibrillated celluloses (NFC) have been objects of scientific investigations for more than three decades. Like other areas of nanomaterial research, the first studies were motivated by novel physical and analytical methods of nanomaterial characterization and production. Since the first discovery in the late 1970s, nanocellulose research activities have intensified and attracted increasing interest, especially since the early 2000s. Though nanocelluloses resemble a class of quite different materials, the scientific interest is based mainly on a few outstanding, basic properties that these materials have in common, *i.e.*, large-scale availability as a renewable material, extraordinary mechanical strength, high

specific surface areas and aspect ratios, barrier properties, dimensional stability, biodegradability and biocompatibility (Eichhorn et al., 2010).

Based on recent and ongoing research achievements related to nanocellulose production, characterization and the production of nanocellulose-based materials, intense efforts in product development for nanocellulose applications are currently ongoing. This paper summarizes some of the most promising developments and future perspectives to give an overview of this fascinating, very versatile and promising area of applied materials science.

Nanocelluloses – A new class of nanomaterials

The term nanocellulose is widely used to describe a wide range of different cellulose-based nanomaterials. The differences are due to not only a wide variety of available raw material sources (Abe & Yano, 2009) *e.g.*, wood, straw, crop residues and bacteria, but also to different top-down and bottom-up production methods, including physical and chemical modification. For instance, the term nanocellulosic materials covers the whole range from ground cellulose fibres, such as microfibrillated cellulose (MFC) and oxidized nanocelluloses (*e.g.*, by TEMPO oxidation), to hydrolyzed, crystalline nanocelluloses (NCC, or cellulose nanowhiskers). The characteristic diameters and lengths of these materials typically vary between 5 and 500nm, *i.e.*, 10s of nanometre and 100s of microns respectively. The specific surface areas may be in the range of 10s to 100s of square metres, and the crystallinity and surface properties (*e.g.*, surface charges, functional groups) may also vary greatly.

Structure-properties relationships and potential applications

The different types of nanocelluloses, with their different morphologies, size dimensions, aspect ratios and functionalities, can be compared with other applied materials, such as microfibers, nanoparticles and polyelectrolytes (Figure 1). As for any other technical development, it is important to consider both perspectives: ‘market pull’ and ‘technology push’, to identify the most promising overlap.

Owing to the differences in specific structure-properties relationships, the specific application potential of different nanocelluloses can be derived. Some of these are outlined in the following (Figure 2).

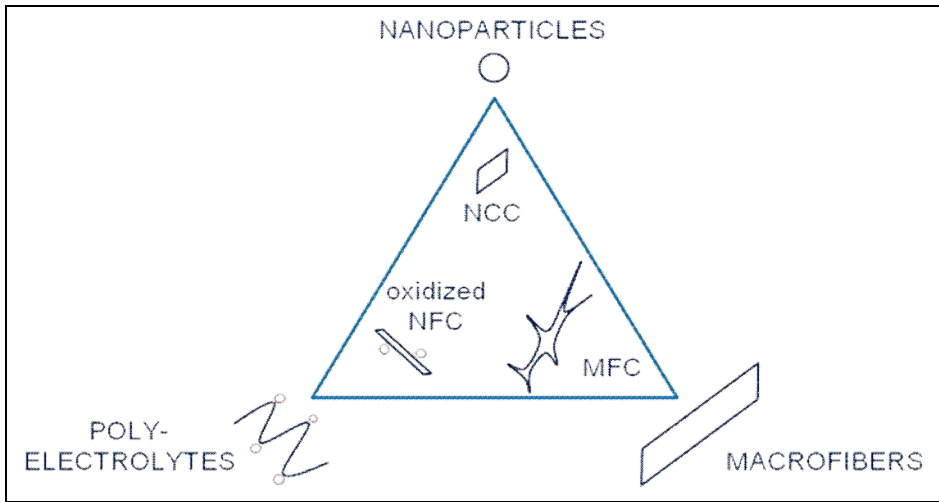


Figure 1. Nanocelluloses – A new class of nanomaterials: Scheme of different nanocellulosic materials and their comparison with other materials, *i.e.* polyelectrolytes, nanoparticles, and macrofibers.

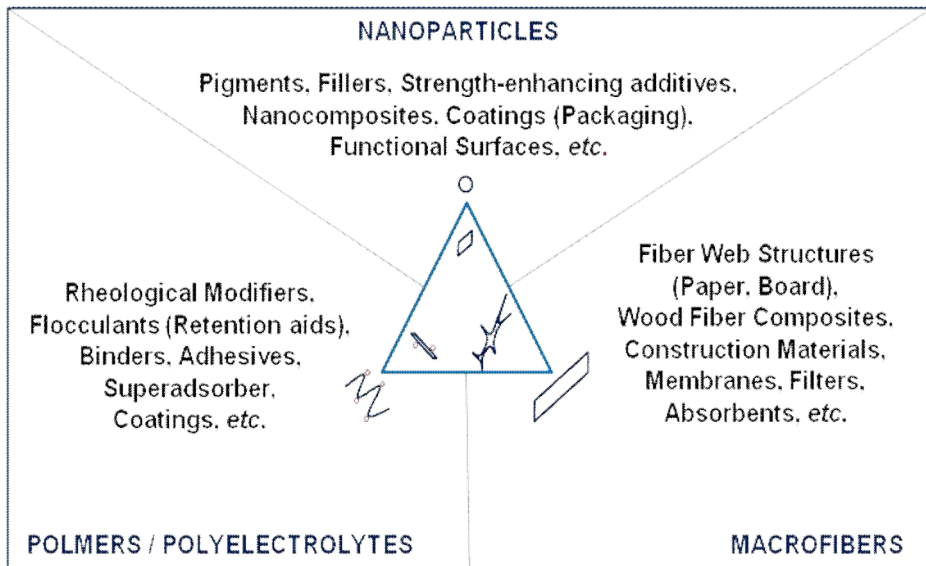


Figure 2. Potential application areas of different types of nanocelluloses based on their specific structure-properties relationships.

Composites and Construction Materials – The main application of nanocelluloses as strength-enhancing additives is in composite materials, especially poly-

mer composites (Okubo et al., 2005; Juntaro et al., 2008; Zoppe et al., 2009), but also, for example, in concrete (Nanocrete, In polymer composite applications, nanocelluloses are typically used as ‘hard segments’ for improved strength and toughness, *e.g.*, for large, flexible and transparent displays (Nakagaito et al., 2010; Okahisa et al., 2009). They can also induce additional properties such as improved sound propagation for loudspeaker membranes. In addition, nanocelluloses can show high dimensional stability and transparency, which is of special importance for, for example, their use as additives in flexible displays. For strength enhancement, high aspect ratio nanocelluloses are typically preferred. Additional surface modification can improve the compatibility and binding to the matrix material.

Porous Materials and Fibre Web Structures – Owing to their high aspect ratios, nanocelluloses also exhibit excellent properties for the formation or strengthening of porous materials, such as paper (increase in fibre-fibre interactions) (Gardner et al., 2008; Eriksen et al., 2008) aerogels (Svagan et al., 2008; Hentze & Sievänen, 2009) insulation materials, membranes and filters. For these applications, the surface properties of nanocelluloses also play an important role in the structure formation, additional functionalities and material performances. Due to their biocompatibility and purity, bacterial nanocelluloses, in particular, attract strong interest for biomedical applications, *e.g.*, as wound dressings or scaffold materials for tissue engineering and implants (Bodin et al., 2007).

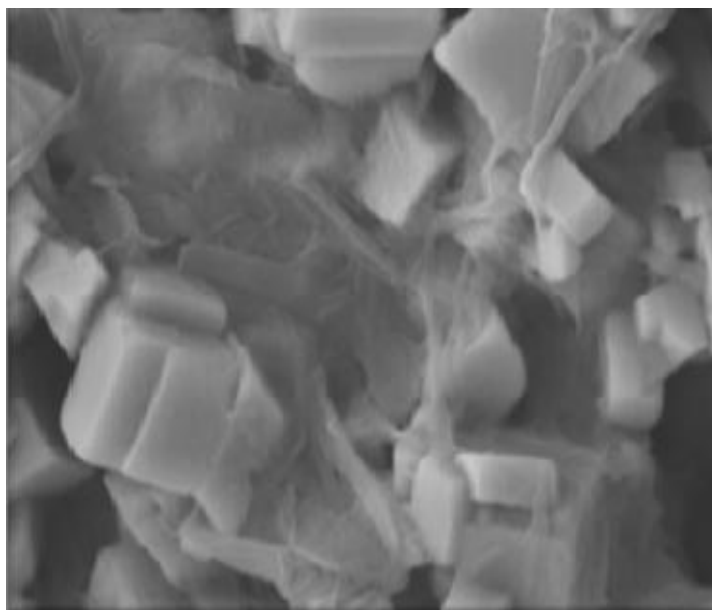


Figure 3. Calcium carbonate filler particles embedded in a nanocellulose matrix.

Coatings and Functional Surfaces – Based on their film formation capability and barrier properties, especially as oxygen barriers, nanocelluloses are studied intensively in coating formulations, *e.g.*, for food packaging (Hult et al., 2010). In addition, modified NFCs enable additional surface functionalities, such as specific binding sites for antimicrobial coatings, sensors, diagnostics and bioactive papers.

Functional Additives – One of the earliest applications of nanocelluloses was food additives. Nanocelluloses with very high aspect ratios, in particular, can be used as thixotropic rheological modifiers in different kinds of formulations. Due to their dimensional stability, *e.g.*, against high temperatures and salt concentrations, they exhibit specific advantages compared with commonly used, macromolecular polyelectrolytes. Specific application potential therefore exists for, for example, enhanced oil recovery, superabsorbents, paints and generally as a thickener in formulations with high salt contents. Another advantage compared with polyelectrolytes is high collision efficiency with particles of a similar size in flocculation applications, *e.g.*, as retention aids in papermaking or water treatment. Other applications as functional additives in papermaking include wet- and dry-strength additives. Like certain cellulose derivatives, nanocellulose

particles with amphiphilic surface properties can also be used as stabilizers for dispersions.

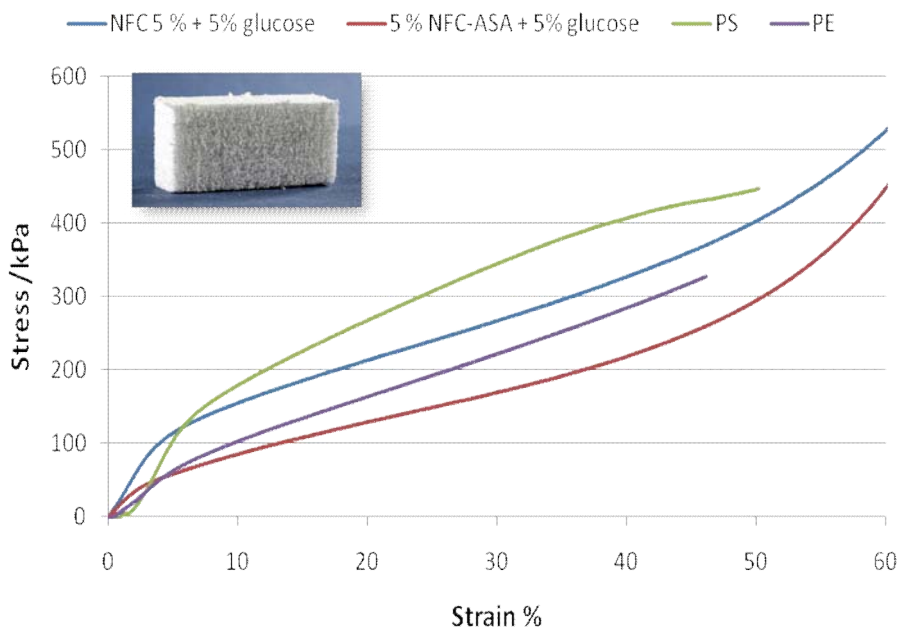


Figure 4. Stress-strain curves of nanocellulose aerogels (inset) compared to polyethylene (PE) and polystyrene (PS) foams.

Other Applications – In addition to the listed applications with most potential, further opportunities will arise as a synergistic effect of parallel developments in other areas of nanotechnologies and biomaterials. Some of these cover, for example, electronic applications, biomimetic materials (Walther et al., 2010; Capadona et al., 2008), and optical and energy devices (Nyström et al., 2009) such as battery separators.

For all of the outlined applications, there are important additional aspects related to NFC characterization, safe handling of nanomaterials, life cycle analysis, and theoretical modelling to enable optimized product performances.

Conclusions and outlook

Nanocelluloses are a new class of nanomaterials that can be produced and modified in manifold ways. They therefore resemble cellulose-based, nanostructured building blocks with a wide variety of properties and functionalities for a huge

range of material applications. Some of the most relevant potential application areas are composites and construction materials, porous materials, paper and board, coatings, functional surfaces and functional additives.

For paper and board applications, barrier coatings and strength enhancement are two major topics. In addition, nanocelluloses offer potential for future technologies, such as wood-free or water-free papermaking.

Beside the development of new materials and processes based on nanocelluloses, the involved study of material interactions on the nanometer scale will also enable a better understanding and improvement of technologies and materials we already use today (Ozin & Cademartiri, 2009).

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Graftplast – Grafted PLA, modified cellulose and starch

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Abstract

The project focus is on research into in-line grafting and modification of cellulose towards continuous processing methods using reactive extrusion in cellulose-based composite manufacturing. Products of the project are for deep-drawn plastic products, films and foams. Three different cellulosic material modification approaches were used to find ways towards these products. The cellulosic fibre length varies greatly depending on the origin and growing season of the wood, so four different cellulosic fibres were chosen as the fibre base for PLA biocomposites. They were eucalyptus pulp, and earlywood and latewood from stump-based pine and spruce fibre. The second modification approach was to polymerise lactic acid into polylactid acid on a cellulose surface using in-line reactive extrusion, which was assumed to improve the compatibility of cellulose with the PLA matrix and that way improve the mechanical properties of biocomposite material. The third approach was to analyse the suitability of reactive extrusion as continuous in-line manufacturing of cellulose acetate, which in theory is the most rational way to produce thermoplastic cellulose material.

Introduction, targets

The general objective of the project is to improve compatibility between cellulosic fibres and the PLA matrix and thus improve mechanical and other properties of such fully biobased composite structures. The project consists of three separate sub-tasks. The integrating issue for all the tasks is the use of compounding equipment that is typical of plastic reactive processing. In our case, the key equipment is the double screw compounder W&P D40 mm L/D 60. This device opens new possibilities for processing biobased fibres and plastics.

The plastic processing techniques of interest are injection moulding, extrusion and rotational moulding. More specifically, materials will be tested for deep drawing and foaming applications. The compounding technique will provide granulated materials for these applications.

Two different approaches are:

- Cellulosic fibres are fractionated by a novel technique according the cultivation season, and the fibres' origin from stumps is also of interest. The study is carried out for eucalyptus cellulose – as a reference fibre – and for pine stumps and latewood and earlywood fibre.
- PLA grafting onto a cellulose molecular backbone is applied by a few catalytic agents, first in a small lab scale compounder and then by an industrial scale W&P compounder.

Materials and methods

Fractioned cellulose fibre

Eucalyptus pulp from Metsa-Botnia and three different pulps prepared at the VTT Jyväskylä were compared in composite filler material. The prepared pulps were earlywood and latewood fractions from pine and pulp from spruce stumps. Pin chips from pine were fractionated according to density into earlywood and latewood fractions. The density of the earlywood fraction was 339 kg/m³ and of the latewood 487 kg/m³. After fractionation, the earlywood and latewood fractions were refined using the VTT experimental refiner. Spruce stumps were first chipped and then refined into pulp. All the pulp fractions were refined to the same freeness (CSF) level of about 80 ml.

The PLA for biocomposite preparation was PLA 3001D from Natureworks. The compounding to fibre contents of 20% and 40% was done using the Ber-

storrff ZE 25x33 twin-screw extruder followed by injection moulding with the Engel 200/50 HL into dog-bone shaped test bars.

Poly lactid acid grafting on cellulose

The idea of the cellulose grafting was to polymerise lactic acid into polylactid acid on a cellulose surface using in-line reactive extrusion, which was assumed to improve the compatibility of cellulose with the PLA matrix and that way improve the mechanical properties of biocomposite material. The materials used in the polymerisation were technical grade lactic acid (80% in water, Purac), birch pulp cellulose, dissolving pulp (Borregaard LV-U) and milled cellulose BE 600/10 TC (Rettenmaier & Söhne). The ring polymerisation route was also tested starting with the L-Lactide (99.5% from Altasorp). The polymerisation catalysts tested were potassium acetate, dibutyl tin octoate and p-toluenesulphonic acid. The mixtures at the first stage were made by Brabender and injection moulding using the Thermo Haake MiniJet equipment. For the larger-scale processing, the Werner Pfleiderer ZSK40 F 32.5 E (40 x 58 D) twin-screw extruder with gravimetric feeders, liquid feeding and vacuum was used.

Results and conclusions

The material properties of the fractioned fibres are presented in Table 1 and the results of the mechanical tests are shown below in Figures 1–3:

Table 1. Properties of fibres.

Property	Eucalyptus	Pine early-wood	Pine late-wood	Spruce stump
Fibre length before processing, μm		1070	1160	1030
Fibre width before processing, μm		36.4	36.8	36.7
Fibre length after processing, μm	156	172	192	154
Fibre width after processing, μm	18.9	26	26.7	24.1
Density as paper sheet, kg/m^3		320	280	240
Tensile index in sheet, Nm/g		27	26	21

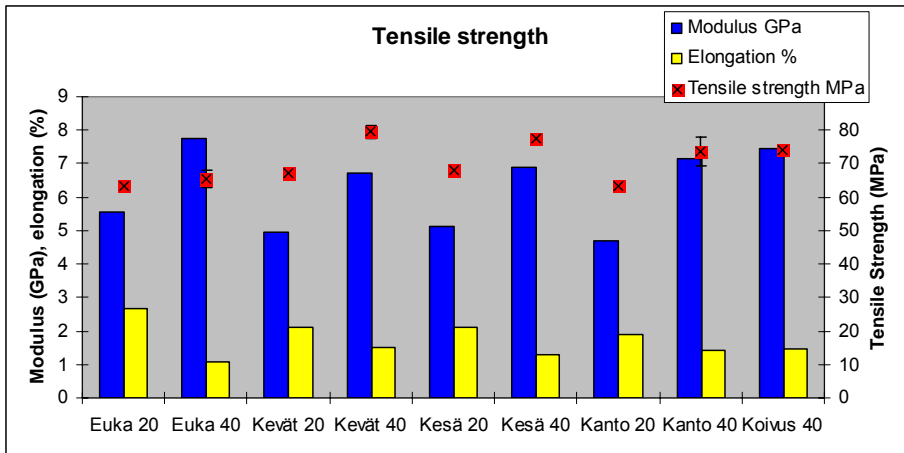


Figure 1. Comparison of results for mechanical testing. The label 'Kevät' refers to fibres cultivated in spring and 'Kesä' in summer. The label 'Kanto' refers to fibres from stumps and 'Koivu' is a reference to birch fibre. The number in the label refers to the amount of fibre in the PLA.

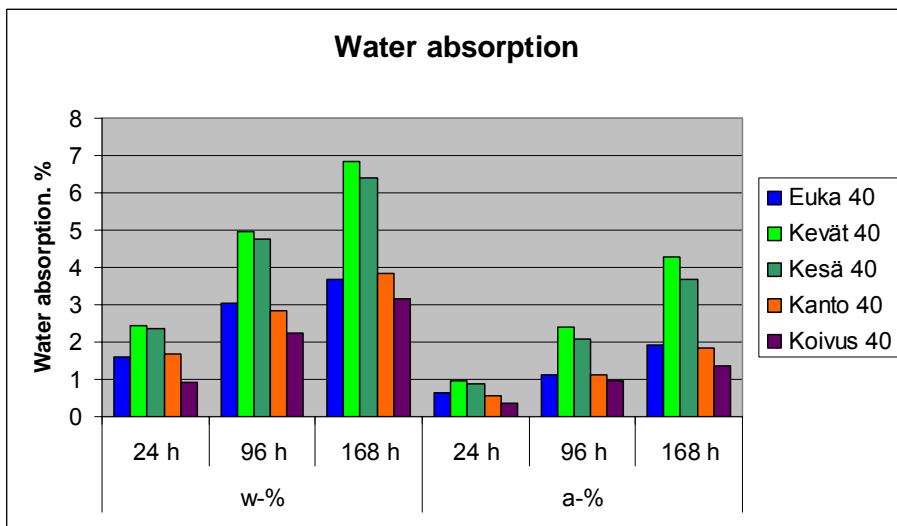


Figure 2. Comparison of results for the water absorption test. Labels as in Fig 1.

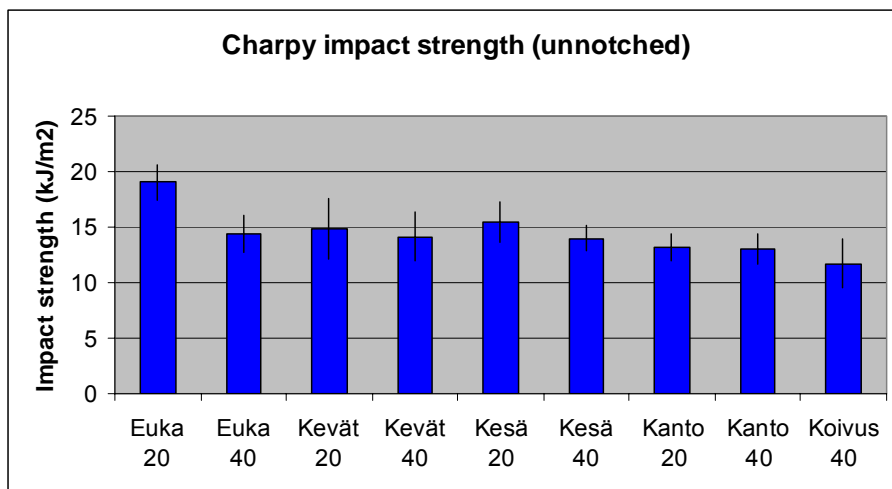


Figure 3. Comparison of results for mechanical impact test. Labels as in Fig 1.

According to the tensile strength results, there was no significant difference between the earlywood and latewood pine fractions in the injection-moulded composite materials that contained 40% fibre in the PLA. Both performed well giving a tensile strength > 77 MPa and a modulus > 6.7 GPa. In this series, the spruce stumps and reference birch pulp performed similarly with a tensile strength of 74 MPa and a modulus > 7.1 GPa. Eucalyptus gave about 15% lower tensile strength results compared with the others, but the elongation in the 20% eucalyptus-containing fibres was quite high at 2.7% compared with the others with $< 2\%$ elongation.

The impact strength value of 20% eucalyptus-containing PLA composite was significant at about 25%, higher than for the other fibres. In terms of impact strength, the pine earlywood and latewood also performed identically with impact strength of 14 kJ/m² for 40% fibre content, while spruce stumps gave a value of 13 kJ/m².

One of the main challenges of biocomposites is the control of moisture behaviour. Here, the water absorption results showed clear differences between the fibres. The reference, 40% birch fibre in PLA, gave the lowest water absorption value of 3.2 w-% after a one-week test. The second best was 40% eucalyptus in PLA with a 3.7% w-% absorption value and the spruce stump with 3.8 w-%. Here, pine earlywood and latewood also performed similarly with more than 6 w-% water absorption.

Process for cellulose modification and reactive compounding with PLA was performed according to Figure 4. The Figure 5 represents how the oligometric PLA is embracing cellulose fibres and makes them compatible with surrounding PLA matrix. As a reference a Figure 6 represents injection moulded sample of PLA with 40% cellulose fibre without modification or added compiling agents. Figure 7 is showing a DSC chromatograph of lactide grafted cellulose, where oligometric lactic acid is clearly present.

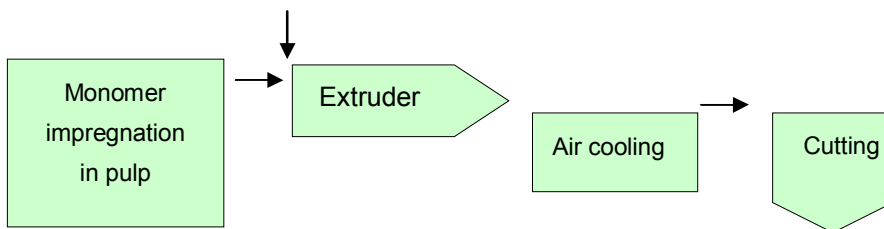


Figure 4. Processing layout for PLA grafting.

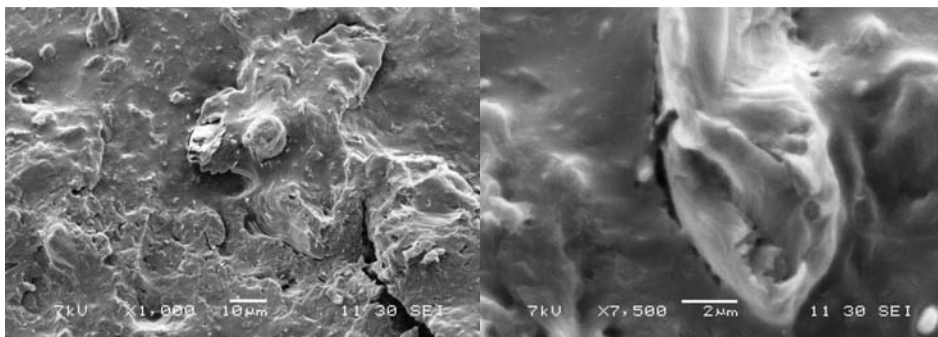


Figure 5. SEM pictures of oligomeric PLA embracing cellulose fibre.

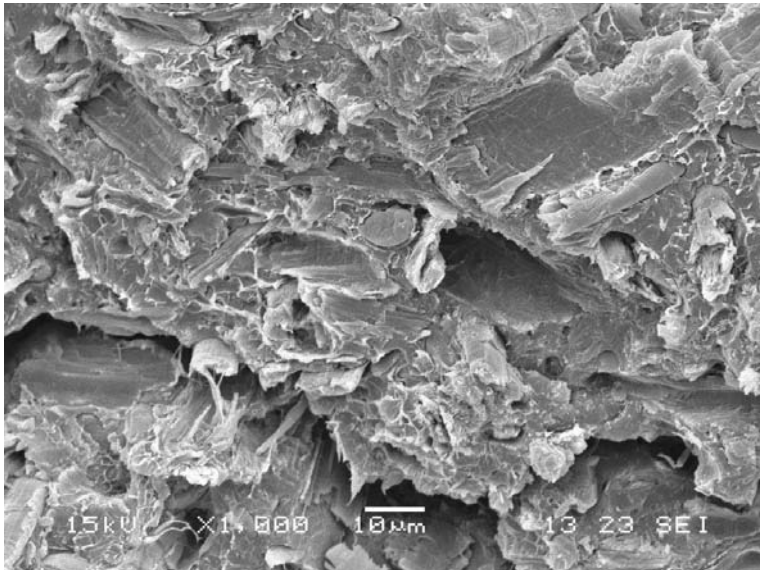


Figure 6. SEM picture of injection moulded sample PLA with 40% cellulose fibre without modification.

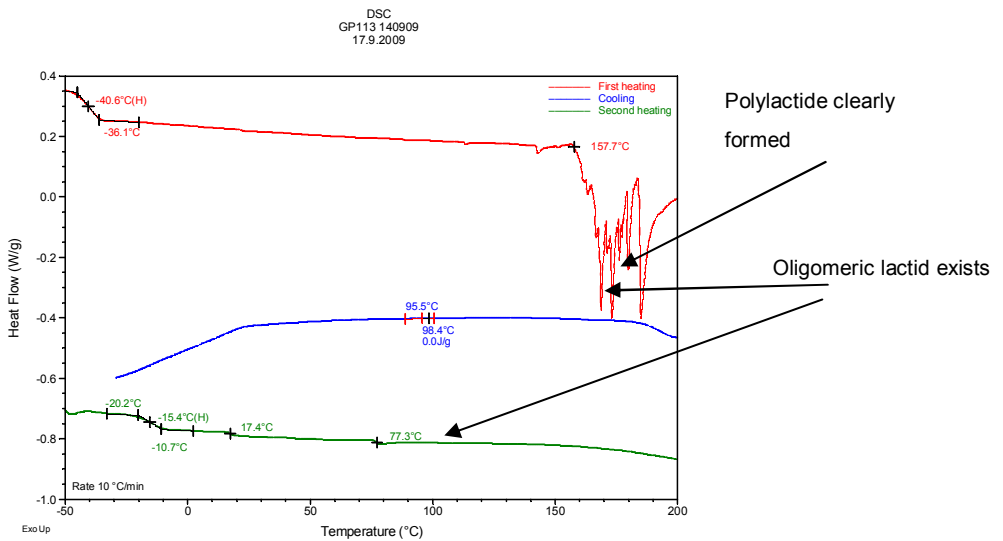


Figure 7. DSC of lactide-grafted cellulose. Notation 'Polylactide clearly formed' = there is a clear build-up of polylactide; 'Oligomeric lactid exists' = part of the lactide is still in the form of oligomers.

Conclusions

Based on the experiments, there is no significant reason to base wood fractionation on the season. At the same time, it was observed that birch and euca are similar: birch has slightly higher strength while euca has better impact and lower water absorption. Neither of the pine stumps offer any benefits. Eucalyptus fibre provided good elongation compared with the others however.

For the lactic acid grafting on the cellulose, we succeeded in attaching oligomeric polylactide groups to the cellulose surface, allowing better distribution and attachment of fibres to the PLA matrix. The maximum cellulose content applied to pilot-scale reactive extrusion was 70%. Potassium acetate was a suitable polymerisation catalyst. Drawbacks of these polymerisations were partial degradation of the cellulose fibre and oligomeric lactic acid function mainly as a plasticizing agent without strengthening the material. An interesting phenomenon was that several of the produced materials showed elastic properties that could be utilised to some extent.

Litterature

Immonen, K., Malm, T. & Valta, K. Polyaktidi-selluloosakuitukompaundi ja m enetelmä sen valmistamiseksi reaktiivisella ekstruusiolla (polylactide and cellulose fibre compound and method of making such). Invention filed 3.4.2009, taken over by the VTT. (In Finnish)

The durability and decay resistance of coated plywood, Thermowood® and wood plastic composites (WPC)

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Introduction

A building is subjected to different water sources, ageing processes and damage during its lifetime. For wood material, microbes often play a key role in its durability, especially in high humidity conditions. Moisture stress and biological factors, such as mould and decay fungi, are often critical, especially in cladding and decking structures in exterior use conditions. To evaluate durability, different test systems can be used. This paper briefly presents the use conditions and accelerated testing of different wood products.

The use conditions of wood and wood-based products

According to standard EN 335-1, the use conditions of wood and wood products are classified based on the eventual activity of different biological agents on the wooden structure. While the classification is very general, in reality many details are often important for the durability and service life of the whole structure or building. Under dry conditions, the risk of bio-deterioration is always accidental for wood used in inside construction or Use Class 1 (UC 1). When wood is under cover and not exposed to the weather (UC 2), condensation of water on the surface of the wood products may occur (risk of mould growth). In UC 3, the wood is above the ground and exposed to the weather; in UC 3.1 it is under wet conditions for limited periods; and in UC 3.2, the wetness can be prolonged but

The durability and decay resistance of coated plywood, Thermowood® and wood plastic composites (WPC)

not continuous. In UC 4 situations, however, the wood is in direct contact with ground and/or fresh water and thus the risk of bio-deterioration is high.

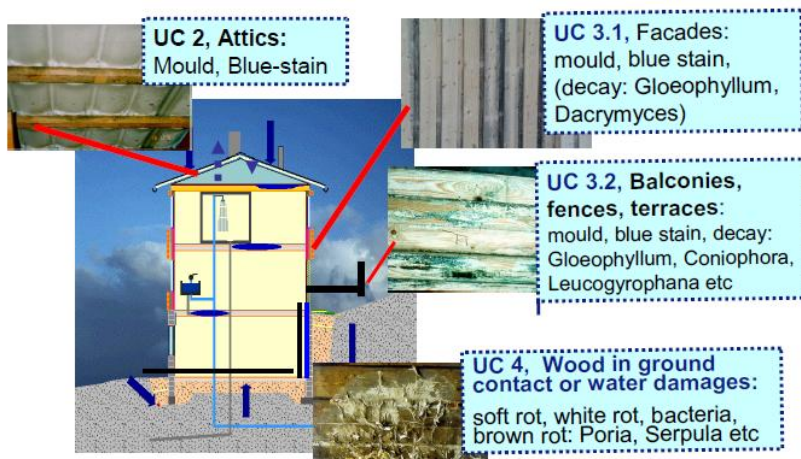


Figure 1. Example of the fungi causing damage in different parts of buildings and different use classes (UC 2 – UC 4). The damages are caused by moisture that has exceeded the tolerances of the materials and structure, e.g. by water leakage and faults in the structure, especially critical details.

For damage to develop, several different organisms can be involved (Figure 1). The accelerated laboratory tests are normally very hazardous for the materials – usually simulating the worst case scenario – compared to their intended use conditions above ground. The intended use conditions should carefully considered in order to evaluate the required durability of wood products, especially in UC 2 and 3.1 (claddings) situations.

The damage cases in cladding are mainly caused by excess water due to the malfunction of the structure. High exposure conditions, however, exist for wood in decking, docks or wood in ground contact; for this reason, more aggressive test conditions are needed. The most critical parts of the cladding and decking are the details where water can accumulate and thus initiate the decay process. The risk is lower in the Nordic Countries than in the Atlantic Climate area where unprotected and uncovered decking is more exposed to the weather and thus more prone to decay (Viitanen et al., 2010). In these use conditions, more durable materials and products are needed. The classification of the natural durability of heartwood of different wood species is presented in standard EN 350-2.

As exposure to the weather is important when evaluating the durability of wood-based products such as fences and cladding, it should be part of the test procedure. In the next sections, the testing of different wood-based materials is presented.

The durability and decay resistance of coated plywood

The first steps taken in evaluating the durability of the products are the accelerated screening tests carried out in the laboratory. They include different test methods for bacteria, discolouring fungi (mould and blue-stain) and decay fungi or algae. Mould and blue-stain fungi are often the first colonisers and can cause damage to the surface of materials and coatings. Discoloration is a common term for the problem, especially on paint films. Mould fungi will grow on outer surface of materials; blue-stain fungi will also penetrate into the material and cause damage in coatings and paint films.

The task of the EU project ‘Plybiotest’ was to determine the critical factors that affect the durability of coated plywood products. In addition, it aimed to find the adequate interactions of outdoor weathering (Figure 2) and laboratory test methodology in order to identify the critical parameters and cut-off values for the durability, performance and service life of coated plywood.



Figure 2. Outdoor test systems for coated plywood products at VTT Otaniemi.

The water permeability of a wood product is a very important part of its durability. In Figure 3, the water absorption / water permeability of different plywood

The durability and decay resistance of coated plywood, Thermowood® and wood plastic composites (WPC)

products is shown. The water permeability of plywood with a thin phenol film was accelerated during the test period faster than that of the melamine film, the paint base film, and the coated and painted birch plywood. The water permeability of uncoated plywood was high and mould growth and blue-stain development was significant after the first summer exposure period.

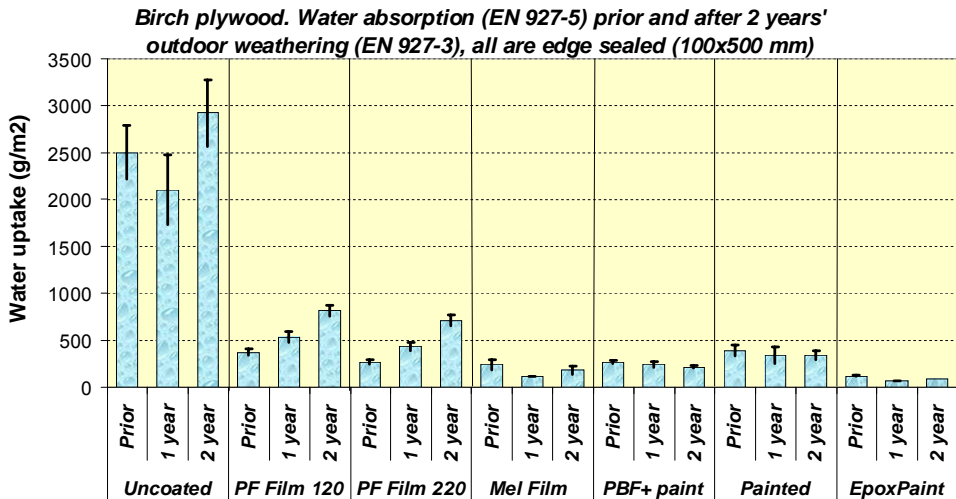


Figure 3. Water permeability / water absorption of different plywood products prior to, and after one year and two years' outdoor exposure (Viitanen et al., 2008).

The decay test after weathering was designed to be very aggressive in order to evaluate the effect of the coatings on the decay resistance on the plywood material (Figure 4). The decay test, performed after one year of weathering, found a slight effect of weathering on the decay resistance. The edge sealing of the coated plywood protected the birch plywood well against brown rot fungus; however, the effect was lower for spruce plywood. Similarly, the edge sealing also added to the resistance of uncoated plywood (Figure 5).

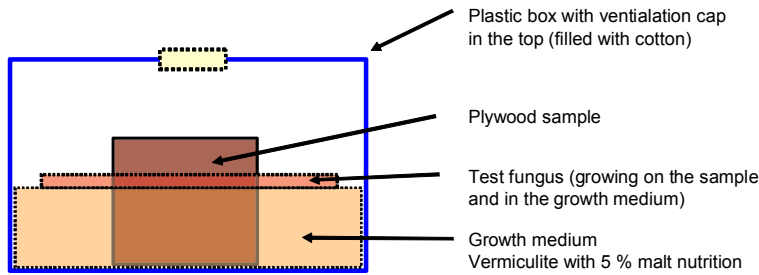


Figure 4. Decay test of plywood samples in a chamber with wet vermiculite and brown rot fungi *Coniophora puteana*. Small samples of 50 x 50 mm were used for the decay tests (embedded in to the vermiculite in a vertical position 2 / 3 of their width). After incubation, the mass loss and moisture content of the samples were analysed. The incubation time of boxes was 16 weeks at RH 70% and 22°C.

The uncoated birch and spruce plywood showed low decay resistance in high exposure conditions. The coated and edge sealed plywood performed well in the tests. The mould resistance of plywood products was also evaluated; the resistance was based on the performance of the coatings as well as on the surface quality of wood. It was found that the durability of coated plywood is less dependent on the natural durability of wood species; further, the input of coating system in several cases is higher.

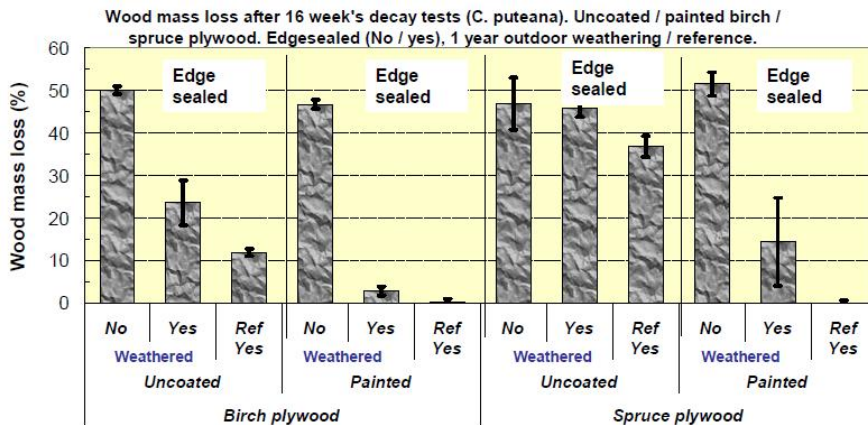


Figure 5. Mass loss of birch and spruce plywood after 16 weeks' decay test in vermiculite, the test fungus was *Coniophora puteana*. Uncoated and painted, edge sealed (yes) and not edge sealed (no) samples (50 x 50 mm) were used. The material was weathered one year prior the decay test. Un-weathered material was used as a reference.

Thermowood® and wood plastic composites

Thermal modification has been developed for an industrial method to increase the biological durability and dimensional stability of wood. Thermowood class D and the wood plastic composites are intended to be used as a decking material, which is exposed to high weathering and water exposure conditions. In this paper, the effects of the thermal modification on the resistance against the soft rotting fungi of sapwood and the heartwood of Scots pine and Norway spruce by using laboratory test methods are presented. The resistance to soft-rot fungi was measured using mass loss and the change of modulus of elasticity (MOE). The decay resistance of the wood plastic composite using the same test procedure is also presented.

Thermal modification was performed at four different temperatures (170°C, 190°C, 210°C, and 230°C) for three hours in the sapwood and heartwood of Scots pine and Norway spruce. The natural durability against the soft-rot micro-fungi was determined according to CEN/TS 15083-2 by measuring the mass loss and modulus of elasticity (MOE) loss after an incubation period of 32 weeks (Metsä-Kortelainen and Viitanen 2009).

The wood plastic composites are products with low wood content. The decay in this material will mainly develop in the cellulose material when the mass loss is directly correlated with the mass of the total amount of organic material. In this case, the main change will be notified as the changes of modulus of elasticity (MOE) and modulus of rupture (MOR). In Table 1, the results of the test series on two different WPC products are given.

In general, the thermal modification increased the decay resistance of the wood material. The mass loss and MOE loss differences between the sapwood and the heartwood were more evident with pine than with spruce. The difference between the sapwood and heartwood of spruce is not significant; this indicates that the heartwood of spruce is not durable against decay. It appears that a sufficiently high thermal modification temperature of 210–230°C reduces the differences between different wood materials and clearly gives better decay resistance.

Table 1. Density and moisture content before and after the decay test, the average MOE and mass loss of the soft-rot samples (Metsä-Kortelainen and Viitanen, 2009), and the test performed on WoodPlasticComposites (WPC) at VTT.

	Heat Treatment (°C)	Density kg/m ³	Moisture content (%)	Moisture content (%)	MOE loss (%)	Mass loss (%)	Decay rate (0–4)
			RH65%	After the test			
Spruce, sapwood	untreated	446	12	274	74	21	4
	170°C	430	10	266	73	18	4
	190°C	423	9	248	60	14	3
	210°C	413	7	231	37	8	2
	230°C	384	6	222	8	4	1
Spruce, heartwood	untreated	434	12	276	71	19	4
	170°C	449	9	241	65	15	4
	190°C	429	9	235	54	12	3
	210°C	414	7	225	35	7	2
	230°C	381	6	221	6	3	1
Pine, sapwood	untreated	501	11	247	71	21	4
	170°C	490	10	239	70	18	4
	190°C	478	9	229	67	16	4
	210°C	488	7	192	40	8	2
	230°C	476	6	182	19	5	1
Pine, heartwood	untreated	554	11	192	55	15	4
	170°C	551	8	184	54	13	4
	190°C	524	8	182	45	9	2
	210°C	520	7	167	25	6	2
	230°C	467	6	175	8	3	1
WPC	1	-	-	13	23	4	2
WPC	2	-	-	11	16	2	1
Pine sapwood	Untreated			111	81	38	4

For the untreated pine sapwood (reference samples), the MOE loss was significant after 16 weeks' exposure. The decay rate was high and the average mass loss of untreated pine sapwood varied between 21% to 38% and the MOE loss 71% to 81%. The wood moisture content was high during the test, but clearly lower in WPC products, where the loss of MOE and the mass loss were low. The decay resistance of WPC material was significantly higher than that of untreated pine sapwood. No weathering prior to the test was used, which may have had an effect on the results. Further, a performance test in exterior conditions is needed to evaluate the durability and service life of WPC products.

The correlation between the loss of mass and MOE is very high (Figure 6). This confirms the view that it is possible to measure the MOE loss many times during the incubation of the soft-rot test in order to measure the durability and the resistance of the test samples.

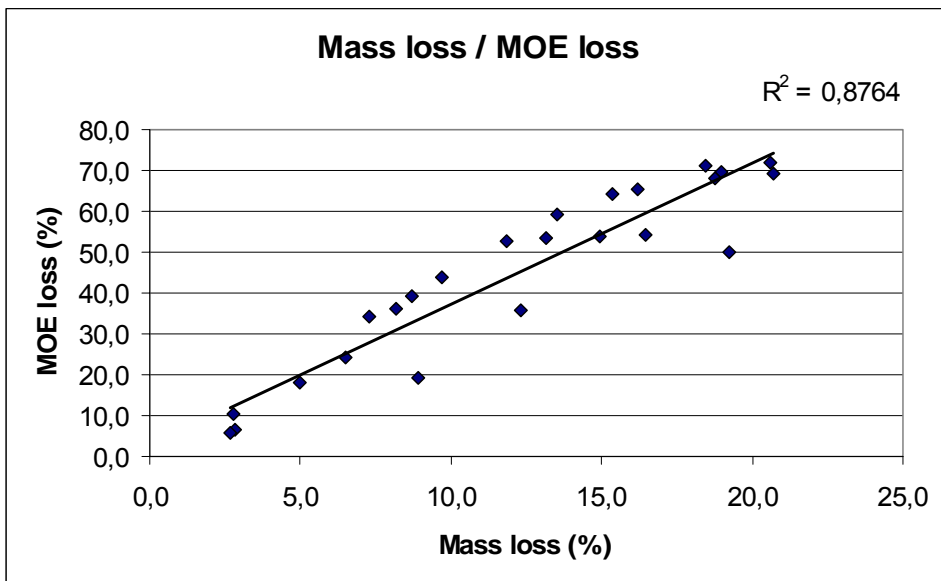


Figure 6. Correlation between the mass loss and MOE loss, soft-rot test (Metsä-Kortelainen and Viitanen 2009).

Competence of VTT on the durability and service life of wooden products and composites (e.g. wood plastic composites)

- Develop methods to evaluate the performance, durability and service life of wood-based products and composites.
- The producers and manufactures of new materials and products want to know the performance and durability / resistance of their products, especially if the products will be used under use conditions according to EN 335-1 UC 3-2 (terrace, fence, decking) or UC 4 (product in ground contact).
- VTT has extensive experience in factors affecting the durability, resistance and service life of wood products as well as the concepts of different test procedures. Several different test systems exist (laboratory–field).
- The resistance of wood products will be analyzed according normal process using standardized methods:
 - combinations of different types of exposure conditions -->
 - outdoor weathering / QUV weathering in a laboratory
 - accelerated laboratory tests: mould / blue-stain / decay fungi.
- For new products where wood is only a minor part of the overall materials (like plastics, WPC), other methods (like MOE changes) are employed.
- The producers and manufactures of new materials and products want to know the performance and durability/resistance of their products, especially if the products are to be used under use conditions according to EN 335-1 UC 3-2 (terrace, fence, decking) or UC 4 (products in contact with the ground).
- Tests in high exposure conditions yield faster results.
- Evaluation of the resistance of the product against:
 - mould growth, discoloration (blue-stain) and decay (in decay tests, the modulus of elasticity ‘MOE’ will be analyzed when needed)

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VTT Research Notes 2558
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Author(s) Ali Harlin & Minna Vikman (eds.)		
Title Developments in advanced biocomposites		
Abstract <p>VTT has long experience in developing biocomposites for several application areas. Biocomposites are materials consisting of bioplastics, natural fibres and/or fillers and additives, which are also preferred to be biomass-based. The utilisation of non-food resources will be one of the main issues and drivers in material development. The variety of biomaterials, the number of material combinations, processing technologies and potential applications offer extensive opportunities but there are many challenges that must be overcome during the development of biocomposites and bioplastics. The next generation of biomaterials are being developed through advanced processing and nanotechnology. This publication gives overview of the research activities and main achievements at VTT in this area.</p>		
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