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Shapeable cellulosic materials

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ABSTRACT

A palette of materials has been developed by the oil and gas sector. The expected depletion of fossil resources and the stress on the climate from burning them has, however, turned the world's attention to renewable resources. To develop competitive high quality products from renewable resources, is indeed a challenge for the research community.

Cellulose is a renewable material with a variety of properties depending on source, processing and other modifications. In liquid food packaging the cellulose-based carton is combined with plastics to make the package impermeable to water. The production of carton packages with a shapeable cellulosic material would be an interesting way to enhance its function, reduce the amount of fossil-based material in it and to make it more competitive towards plastic bottles.

In this work, cellulose was made shapeable through blending with moldable polyethene. Esterified cellulose was used in order to increase the interfacial adhesion and the dispersion of cellulose in composites. Esters with various hydrophobicities, carbonyl hydrogen-bonding and degree of substitution were prepared. It was concluded that the fiber dispersion in the composites could be both improved and impaired by the esterification. Moreover, the eventual benefits of esterification on the interfacial adhesion, was counteracted by weakening and fragmentation of the fibers because of the chemical treatment and the mechanical processing.

Cellulose was also made shapeable through coagulation of the cellulose-ionic liquid solutions with a coagulation agent (e.g. water), to obtain shapeable three-component gels. The strength, the stiffness and the thermal degradation, were found to depend on the types and amounts of the gel constituents. By regeneration of cellulose, from the gels, stiff regenerated cellulose was obtained.

Keywords: cellulose, ionic liquid, coagulation, gel, cellulose ester, polyethylene, composite, interactions, material properties

List of publications

1 PAPER I

PREPARATION AND CHARACTERIZATION OF CELLULOSE ESTERS AND THEIR POLYETHYLENE COMPOSITES
Malin Brodin, Gisela Richardson and Gunnar Westman
Submitted manuscript

2 PAPER II

THERMAL AND VISCOELASTIC PROPERTIES OF CELLULOSIC GELS WITH DIFFERENT IONIC LIQUIDS AND COAGULATION AGENTS
Ruth Ariño, Malin Brodin, Antal Boldizar and Gunnar Westman
Submitted manuscript

Work related to the thesis has been presented at the following conferences:

The 4th workshop on cellulose, regenerated cellulose and cellulose derivatives
Karlstad 2009 (oral presentation)

Polysaccharides as a source of advanced materials, European polysaccharide network of excellence
Turku 2009 (poster presentation)

Ekmandagarna
Stockholm 2010 (oral presentation)

2nd Avancell conference
Göteborg 2012 (poster presentation)

Content

1 Introduction

Resources have to be used in a responsible way to ensure the world's future need for materials. The use of renewable resources is one path towards a more sustainable future. In line with this, it would be interesting to develop shapeable materials from wood-based cellulose. In this work, gels with cellulose, ionic liquids and coagulation agents are studied, as well as, composites with cellulose esters and a thermoplastics.

1.1 BACKGROUND

The expected depletion of fossil resources and the stress on global climate from burning them is turning the world's attention to renewable resources. With rising oil and gas prices, the production of plastic commodity products will eventually become expensive. The development of materials from more sustainable resources has, besides recycling and re-using plastic, become an increasingly more important route to ensure future's need for materials.

An amazing palette of materials has been developed from fossil feedstocks, which are suitable for applications ranging from fuels through disposables to computer components. In addition, the oil and gas industry is well developed when it comes to equipment, implementation, plants, transportation and logistics. It is indeed a challenge for the research community to develop high-quality products from renewable resources that are competitive with these materials and their industry. An advantage would be if the production of new materials could be incorporated into the systems of the oil and gas industry. It is also desirable that the production of materials is performed in a sustainable way and that it does not compete with food production in developing areas. One responsible way to utilizing our resources would be to develop good recycling chains. For example, an alternative to using excellent wood as bio-fuel would be to first build a wooden house and, when the house is worn-out, make a chair, followed by making paper pulp of the chair and, later, textile fibers of the recycled paper. Burning the worn-out textile for energy would be the final step. It is not probable that any single resource will replace all applications where fossil-based products have dominated. More likely, an increase in the use of several resources will be seen. Furthermore, research on alternative feedstocks is likely to bring about products with properties and applications that are completely new to us. There are several examples of products from renewable resources. 'Bio-ethanol' can be made from Sugarcane bagasse (Uma, Muthulakshmi *et al.* 2010) and used in 'Green polyethene' production. Lactic acid obtained from e.g. wastepaper (Schmidt and Padukone 1997) or wheat straw (Saito, Hasa *et al.* 2012), can be used for the production of polylactic acid (PLA). Rayon is made using the viscose process from the cellulosic feed-stock (Hermanutz, Gähr *et al.* 2008) and 'Bio-oil' can been made through the pyrolysis of e.g. wood (Mohan, Pittman *et al.* 2006) and swine manure (Fini, Kalberer *et al.* 2011).

Cellulose is a widely abundant renewable material. The biopolymer is produced by green plants, algae, some bacteria and a few animals. Bulk quantities can be isolated from forest trees and cotton. Cellulosic materials have a large number of different properties, depending on the resource, processing and other modifications. The many possibilities for tailoring cellulosic materials for different applications will become increasingly important in meeting future material needs. Cellulose-rich paper pulp is used in carton packages to provide strength. In liquid food packaging, the carton is combined with plastic films which makes the package impermeable to water. An interesting way to enhance the function of a carton package is to make it with a shapeable cellulosic material to reduce the amount of fossil-based material in it and to make it more competitive towards plastic bottles. Shapeable cellulose could be used in such packages e.g. by replacing some of the plastic films with cellulosic film or by replacing the plastic caps with a composite containing a fraction of cellulose.

There are different possible approaches to making shapeable cellulosic materials. One is to dissolve cellulose, shape it, and then regenerate it by adding an anti-solvent. Cellulose has been regenerated e.g. as films, beads and fibers with this method (Turner, Spear *et al.* 2005; Viswanathan, Murugesan *et al.* 2006). Another approach is to blend a thermoplastic with cellulose, and thus decrease the amount of plastic needed. In the obtained composite, the thermoplastic provides shapeability to the cellulose-containing material by becoming soft and shapeable at elevated temperatures. Another advantage of these materials is that they will presumably possess other properties than comparable fossil-based materials.

For these types of shapeable materials the influences of physical and chemical interactions and structure on the material behavior, are far from being fully understood. For instance the interactions and the chemical structure of cellulose, cellulose derivatives, reagents and solvents as well as the interactions between all the components of cellulosic solutions, and also the effect of chemical treatments on the involved materials. Obviously, optimization of isolated parameters would not add much to the general understanding of the materials. On the other hand it is also futile to study all parameters at the same time since the massive amount of data obtained would be unmanageable. To understand these complex material mixtures studies extending from a molecular level, through processing methods, to material properties are needed.

1.2 OBJECTIVES

The objective of this thesis is to make shapeable cellulosic materials, to study their structure and behavior, and to address the importance of their molecular interactions. The thesis concerns two types of materials.

Composites of cellulose esters and polyethene (PE) were studied. From this approach the strong and stiff cellulose was made shapeable by combining it with a thermoplastic matrix. Cellulose esters were prepared and used to increase surface adhesion and to decrease agglomeration in PE-composites, and consequently improving the suitability of the cellulosic material for the composite application. Special attention was given to connecting the cellulose ester characteristics to composite properties, and to interactions in cellulose esters and their composites.

Three-component gels made of cellulose, ionic liquid and a coagulation agent (e.g. water) were prepared and studied. Using this approach cellulose could be made shapeable by disrupting the interactions that make cellulose strong and stiff, i.e. by dissolution. The processing behavior of the gels was studied, and the amounts and types of components in the gels were varied in order to understand their influence on the gels characteristics.

2 Theory

Cellulose is a material built up by nature in a most extraordinary way. There are large diversities in the structure of the material at different magnifications, in different species and in different parts of the same species. If such a complex material is blended with plastics or solvents, the mixtures are even more intricate. Care has to be taken that no important factors are overlooked.

2.1 CELLULOSE

With trees being high, comparably thin and still standing strong, it is obvious that wood is a remarkable material. It is also obvious that one tree can be very different from another, both by appearance but also by the way they burn in a campfire or by the utility of their wood in the hull of a wooden yacht (Figure 1). Such differences between wood-types depend on variations in types and amounts of their constituents. Wood is made up by wood-cells, with thick and strong cell-walls, referred to as wood fibers. The wood fibers are made up by cellulose, hemicellulose, lignin and extractives. When a cell dies, the wood fiber remains in the wood, and continues to support the tree with strength, stiffness and flexibility. Wood fibers are different in different tree-types and also in different parts of the same tree, which explains why no two trees are the same (Rowell 2005) (Figure 1). Softwood (e.g. pine and spruce) has one main type of fibers (tracheids) that are long, have large lumen and are used by the tree, both for mechanical strength and liquid transportation. Hardwood (e.g. birch and maple) however has thin and short fibers (libriform cells/fiber tracheids) for mechanical strength, and short fibers with large lumen (vessels) for liquid transportation. There are also other specialized fibers in a tree. A typical cellulose content of wood is 40-50 % (Lennholm, Blomqvist *et al.* 2004).

Figure 1 Photographs of different tree species (left) and a wood log (middle), beside a drawing of different softwood and hardwood fibers (right).

Large bulk quantities of cellulose pulp, from both softwood and hardwood, are used for paper making and cardboard production (Figure 2). Wood is processed into cellulose-rich pulp by hydrolyzing and dissolving hemicellulose, lignin and extractives. In the kraft pulping process the wood is impregnated and heated in a water solution with hydroxide and hydrosulphide ions as the active ingredients. The pulping is often combined with bleaching either to further reduce the amount of lignin and hemicellulose or to reduce their color by modifying them. After pulping and bleaching the cellulose is exposed, resembles the shape of the cell-wall, and is referred to as fibers or pulp fibers. This pulp will still contain residues of hemicellulose and lignin, but will have different properties depending on the wood source and the type of chemical process.

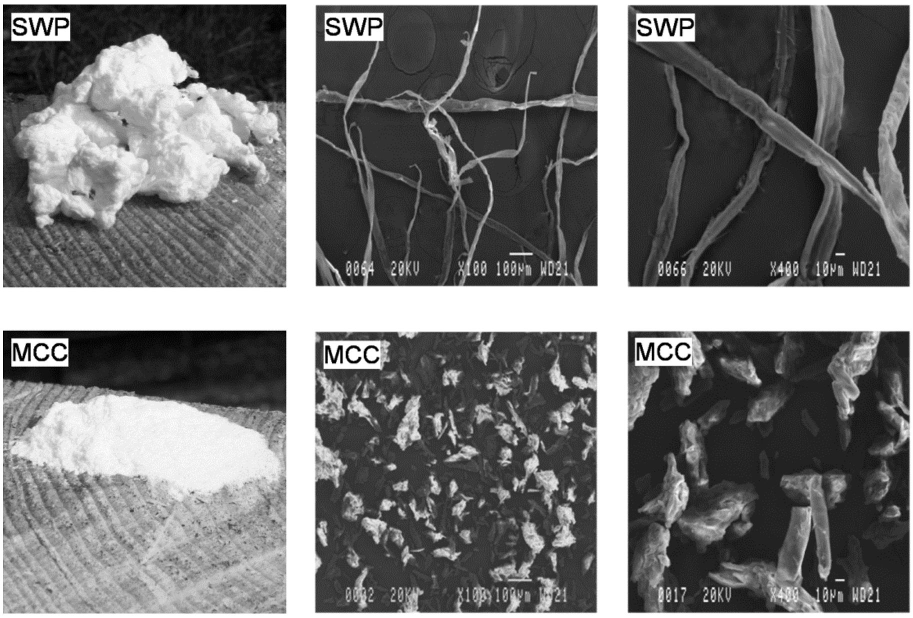


Figure 2 Ordinary photographs and SEM micrographs of softwood kraft pulp (SWP) and microcrystalline cellulose (MCC).

A pulp with higher cellulose content, called dissolving pulp, is obtained either through an acid sulfite process or through a pre-hydrolysis step added to the kraft pulping process, followed by alkali extraction (Biermann 1996). If pulp is subjected to acid hydrolysis after pulping the result is microcrystalline cellulose (MCC) (Battista 1950; Virtanen, Svedstrom *et al.* 2012). During that treatment more of the hemicellulose and the lignin is hydrolyzed and dissolved, but so is some of the amorphous cellulose. This results in smaller microcrystalline fragments of fiber (Figure 2). Severe acid hydrolysis treatment is used to obtain nanocrystalline cellulose (NCC), which is of even smaller and rather uniform crystalline fragments.

Cellulose is produced in nature also by other species than wood (e.g. cotton, tunicate and some bacteria). Common for all species is that cellulose is useful because it provides strength and stiffness. In the cellulose biosynthesis of wood, groups of cell-wall proteins (so-called rosettes), synthesize one cellulose molecule per protein. Simultaneously, the cellulose strands agglomerate and form crystalline segments of several cellulose polymers, which are mixed with other cell-wall components in a refined way to form the advanced cell-wall structure of wood (Figure 3). Amorphous cellulose is produced as well, thus wood cellulose is semi-crystalline (Lennholm, Blomqvist *et al.* 2004). The degree of polymerization (DP) of cellulose in wood is about 30000, but after pulping the DP is reduced to about 10000 (Godavarti 2005).

Cellulose is a polymer built of anhydroglucose units (AGUs) linked to each other with glucosidic bonds between carbon 1 of the first AGU, and carbon 4 of the next (Figure 3). The configuration at carbon 1 is β, which results in each AGU being rotated by 180° relative to its neighbors. Thus the actual repeating unit of cellulose is cellobiose. This rotation is further stabilized by hydrogen bonds between the AGUs. This configuration results in the cellulose molecule being both planar and linear, with hydrophilic hydroxyl groups – capable of interacting with other hydrophilic groups – in the plane, and comparably hydrophobic regions – capable of interacting with other hydrophobic regions – above and below the plane. In this way the polymer organizes itself as a strong three-dimensional, sheet-like structure. The AGUs at the two ends of the polymer are not similar due to the carbon 1 to carbon 4 arrangement in the glucosidic bond, and are referred to as the reducing end (with the hemiacetal) and the non-reducing end (with the hydroxyl) of the molecule (Lennholm, Blomqvist *et al.* 2004). The hydrophilic regions (hydrogen bonds) and hydrophobic regions (hydrophobic interactions and van der Waals forces) in cellulose, are important when cellulose molecules are organized into microfibrils, fibrils and fibers (Lennholm, Blomqvist *et al.* 2004) (Figure 3).

Although each single interaction is weak, the large amount of interacting points make cellulose, strong, stiff and difficult to access. If the configuration at carbon 1 had been α instead of β, hydrogen bonds between neighboring AGUs would not exist, and the polymer would not organize itself in such an ordered way. This is exactly the case with starch which has very different properties compared to cellulose. Starch is a flexible and rather amorphous polymer, found in nature as water-soluble energy storage.

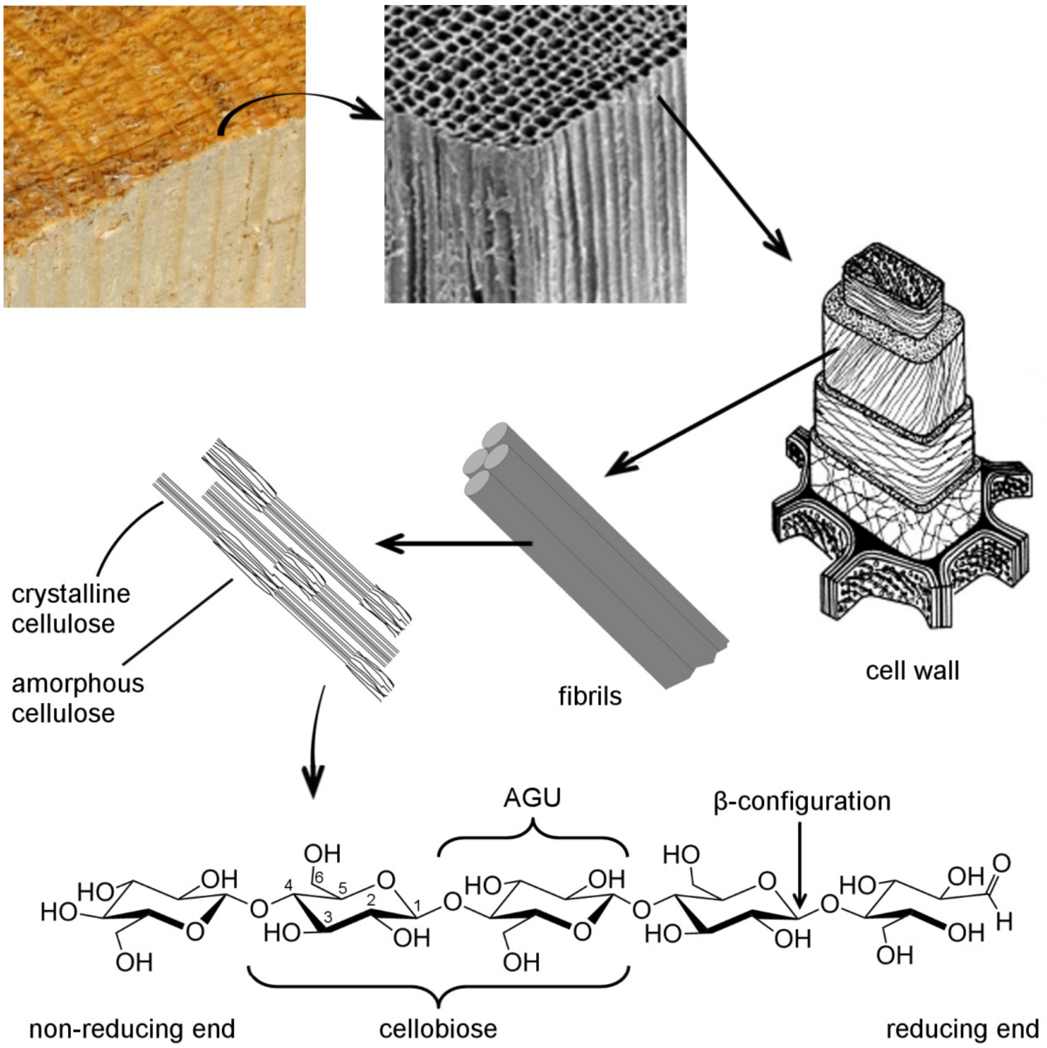
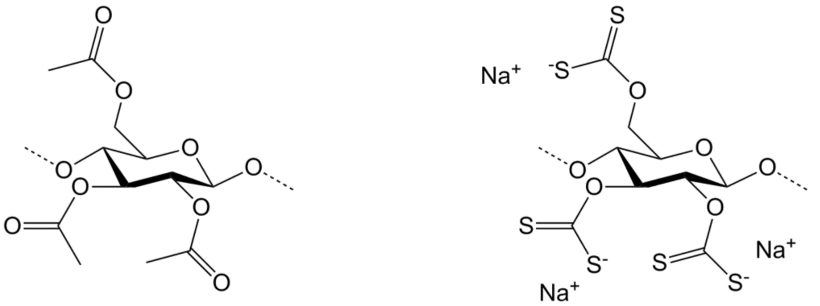


Figure 3 A schematic figure of the wood structure and the chemical structure of cellulose.

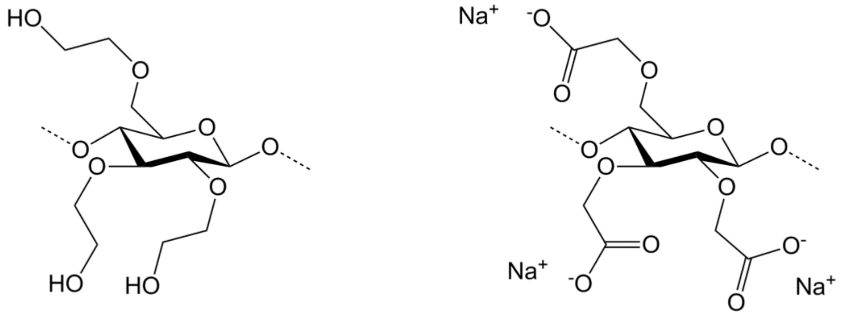
2.2 CELLULOSE DERIVATIZATION

Chemical modification increases the diversity of areas where cellulosic materials may be used, and cellulose derivatives are found in various advanced applications (Figure 4). Some of these are the optical films of cellulose triacetate which are used in liquid crystal displays (LCD) (Edgar, Buchanan *et al.* 2001), cellulose xanthate which is wet-spun to form textile fibers in the viscose process (Wilkes 2001), cellulose ethers (i.e. hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose) which are used as excipients for controlled drug release in pharmaceutical formulations (Baumgartner, Kristl *et al.* 2002) and sodium carboxymethyl cellulose/MCC mixtures which are used to suspend insoluble components in beverages (Tuason, Krawczyk *et al.* 2010).



Cellulose triacetate

Sodium cellulose xanthate



Hydroxyethyl cellulose

Sodium carboxymethyl cellulose

Figure 4 Chemical structures of substituted AGUs of four cellulose derivatives.

Cellulosic materials with different properties can be obtained by chemical modification. Different cellulose derivatives can be obtained through nucleophilic substitution reactions, of cellulose hydroxyl or hydroxylate groups e.g. with carboxylic acid derivatives (Uschanov, Johansson *et al.* 2011), epoxides (Hasani, Cranston *et al.* 2008), silanes (Schuyten, Weaver *et al.* 1948), and alkyl halides (Koschella, Heinze *et al.* 2001). Hydroxyl groups can also be modified through oxidation to form aldehyde or carboxylic moieties.

The many hydroxyl groups of cellulose can be reacted to different extent. The degree of substitution (DS) is defined as the average number of reacted hydroxyl groups per AGU. Since each AGU has three hydroxyl groups, the DS of cellulose derivatives ranges from 1 to 3. Under heterogeneous reaction conditions cellulose is not dissolved in the reaction medium. Thus, some AGUs in the fiber are not available to the reagents. AGUs in pores and on the surface of a fiber are more available to the reaction medium, than AGUs inside the fiber-wall. Some AGUs may not be available at all. Thus, the DS obtained from heterogeneous reactions cannot be as high as 3, and the distribution of substituents is not even, on and between fibers. With some reagents (e.g. acetic anhydride), the substituted product is dissolved in the reaction medium during the reaction. Then the fully substituted product becomes acquirable since the hydroxyl groups hidden in the fiber-wall become exposed to the reaction medium during the reaction. Cellulose derivatization can also be conducted under homogeneous reaction conditions. Then cellulose is dissolved in the reaction medium prior to derivatization. It should be stressed however that once cellulose has been dissolved, the same strong and stiff structure that is obtained during biosynthesis cannot be regained.

Strong and stiff fibers are desired in composites, consequently, heterogeneous reaction conditions are the most interesting when modifying cellulose for such applications. Furthermore, heterogeneous reaction conditions are usually considered less energy demanding. Nucleophilic substitution reactions, where the reagent is reacted with hydroxyl groups of cellulose, are commonly used to modify cellulose for composites.

2.3 THERMOPLASTICS AND COMPOSITES

Thermoplastics is a term that commonly refers to linear or branched synthetic polymers, that possess melting temperatures lower than their decomposition temperatures (Gnanou and Fontanille 2008; Pritchard 1999). When a thermoplastic is heated many interactions in the polymer are broken, and above a certain temperature the thermoplastic flows. Above its melting temperature the thermoplastic polymer can be shaped and processed after which it can be cooled to become solid. This is a very convenient property that opens up alternatives for processing and material recycling. Polyethene (PE) is one of the most common synthetic polymers (Figure 5). It is a thermoplastic produced from ethene through catalyzed or free radical polymerization. Ethene is mainly obtained from the thermal cracking of gas and therefore most PE produced is dependent on the fossil feedstock (Gnanou and Fontanille 2008). The polymerization of ethene made from sugarcane ethanol results in a plastic called ‘Green polyethene’. Ethanol can also be produced on a pilot-scale from lignocellulosic materials (Arshadi and Grundberg 2011). By varying the polymerization method or the reaction conditions PE can be produced with e.g. different molecular weights, densities, degrees of crystallinity, polydispersity, degrees of branching and glass transition temperatures. PE is used in different applications depending on its service and processing characteristics. Fossil-based thermoplastics are used plentifully in modern society such as in as textile fibers, in automotive applications, in synthetic ropes, in tires, tubing and pipes, as insulation foams, as plastic bottles and in adhesives (Gnanou and Fontanille 2008). In dairy carton packages PE is used to hot-seal the packages, as a water resistant laminate and in plastic screw-cap seals.

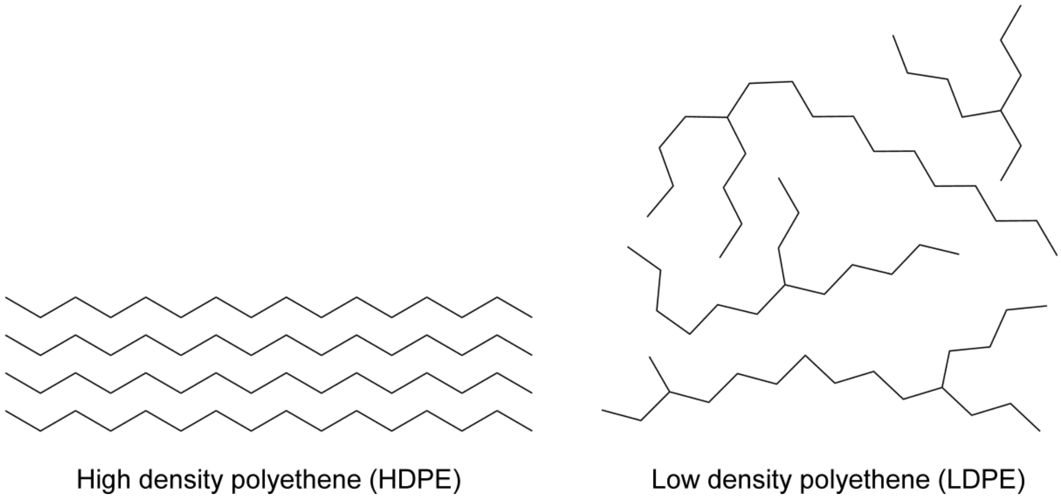


Figure 5 Schematically drawn structures of linear and more crystalline PE, and branched and less crystalline PE.

Composites can be obtained by mixing a thermoplastic with a strong and stiff reinforcing material (e.g. carbon fiber, glass fiber or cellulose fiber). Such reinforced thermoplastics possess properties found neither in the thermoplastic nor in the reinforcement. They are often stiffer and stronger than the thermoplastic, but yet shapeable if the thermoplastic matrix is heated above its melting temperature.

Cellulose as a reinforcement in hydrophobic, commodity thermoplastics compares well with glass fibers in terms of mechanical properties (Zugenmaier 2006). Cellulose nanocrystals possess tensile strength and stiffness high enough to compete with glass and steel (Eichhorn, Dufresne *et al.* 2010). For the composite to obtain the desired material and rheological properties, however, some obstacles need to be overcome.

The complicated structure of cellulose, with hydrophilic and hydrophobic regions and high surface energy is important for its strength, but also causes difficulties in composite preparations. PE is a hydrophobic polymer with a low surface energy. This difference in surface energy between cellulose and polyethene results in limited interfacial adhesion between them. Due to the poor interfacial adhesion, the stress transfer between the matrix and the reinforcement is poor, resulting in a weak composite. Furthermore, the cellulose molecules interact well with other cellulose molecules which leads to agglomeration of cellulose aggregates in the matrix. More aggregation results in less surface available for interaction with the matrix and thus an additional reduction in stress transfer. This insufficient compatibility between cellulose and hydrophobic thermoplastics may, however, be counteracted by improving the interfacial adhesion between cellulose and PE, which may also result in a reduction in the agglomeration of cellulose (Herrera Franco and Valadez-González 2005).

Different ways of addressing these issues include modifying the composite preparation method, the addition of surface active agents, modifying of the matrix, and modifying the reinforcement. The agglomeration in the composite can be reduced during composite preparation by specific mechanical processing methods (Ariño and Boldizar 2012). Short matrix polymers can be modified chemically e.g. maleic anhydride to increase the adhesion between cellulose and matrix (Barkoula and Peijs 2011). Examples of physico-chemical methods to treat cellulose surfaces are corona treatment (Uehara 1990) and plasma treatment (Wang, Kaliacuine *et al.* 1993).

There are several chemical cellulose surface treatment methods (Belgacem and Gandini 2005; Cetin and Hill 1999; Joly, Kofman *et al.* 1996). Grafting is a method where cellulose is reacted with a reagent that possesses two different reactive functionalities (Figure 6). The obtained derivative is then reacted with a monomer of a type similar to the thermoplastic matrix to receive the grafted cellulose which is expected to interact and become entangled with the matrix. Through compatibilization cellulose is reacted with a reagent which in itself is expected to induce better interaction with the matrix (Figure 7). Examples of compatibilization reagents are carboxylic acids and their derivatives. Cellulose esters are obtained after their reaction with cellulose hydroxyl groups.

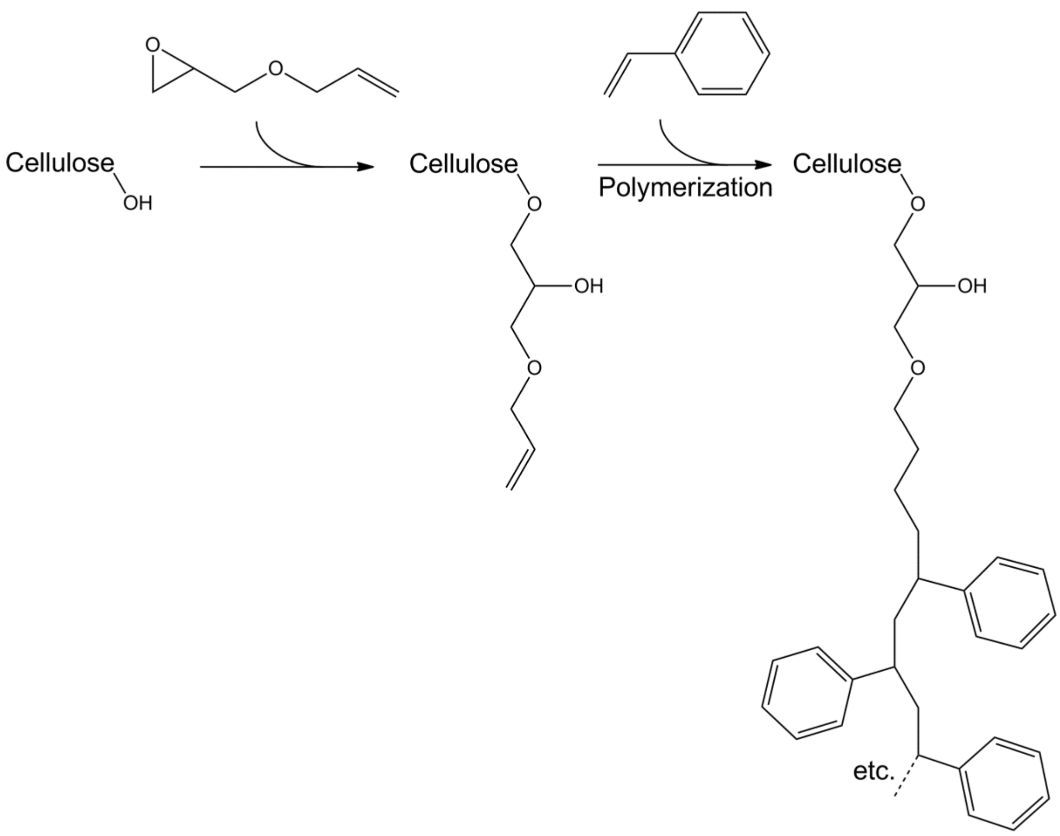


Figure 6 Schematic figure of the reaction of cellulose with allyl glycidyl ether, followed by grafting of styrene.

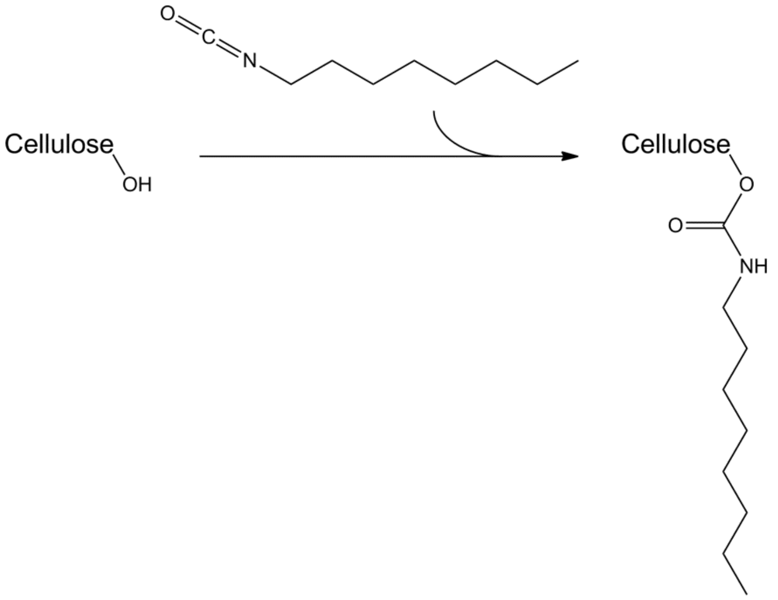


Figure 7 Schematic figure of the compatibilization of cellulose with octyl isocyanate.

2.4 DISSOLUTION AND REGENERATION OF CELLULOSE

The large amount of hydrophilic and hydrophobic interactions is the key to cellulose's rigidity and strength. One way to alter cellulose properties is to alter these interactions through dissolution and regeneration processes. Water and common organic solvents fail to dissolve cellulose, but solvents for cellulose have been found (Figure 8). These include N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) (Edgar, Arnold *et al.* 1995), dimethylsulfoxide/tetrabutylammonium fluoride (DMSO/TBAF) (Heinze, Dicke *et al.* 2000), sodium hydroxide/urea/water (Cai, Zhang *et al.* 2007), N-methylmorpholine-N-oxide monohydrate (NMMO*H_2O) (Rosenau, Potthast *et al.* 2001), and molten salt hydrates (e.g. lithium perchlorate trihydrate) (Fischer, Leipner *et al.* 2003). A group of solvents, first published by Graenacher *et al.* in 1934 (Graenacher 1934), that has been rigorously examined lately, are the ionic liquids.

Imidazolium-based salts are a group of ionic liquids, some of which dissolve cellulose (Figure 8). They are liquid at lower temperature than many other salts (e.g. the melting temperature of 1-butyl-3-methylimidazolium chloride (BMIMCl) is 70 °C and the melting temperature of 1-ethyl-3-methylimidazolium acetate (EMIMAc) is -20 °C), and are constituted of an organic, asymmetric and amphiphilic imidazolium cation and an organic or inorganic anion. By altering the anion or the alkyl chains on the imidazolium moiety, different dissolution properties can be obtained. Solutions with cellulose contents as high as 25 % in BMIMCl have been reported (Swatloski, Spear *et al.* 2002). Ionic liquids as cellulose solvents are commercially interesting as an alternative to the Lyocell process. In the Lyocell process cellulose is dissolved in NMMO*H_2O and regenerated as man-made fibers. This process suffers, however, from thermal degradation and other side-reactions (Rosenau, Potthast *et al.* 2001). Properties such as thermal and chemical stability as well as low vapor pressure, have been reported for various imidazolium-based ionic liquids. Thus it is expected that their exposure to workers and environment can be controlled and minimized. For the same reasons, these solvents can be candidates for replacing volatile organic solvents (VOCs) in industrial chemistry (Meindersma, Maase *et al.* 2007). Some important draw-backs of many ionic liquids are, their high viscosity and difficulties in recycling the solvent on an industrial scale. It has also been reported, that some imidazolium-based ionic solvents hydrolyzes cellulose and reacts with its reducing end-groups (Ebner, Schiehser *et al.* 2008), making it obvious that many issues need more study and that generalizations may be misleading.

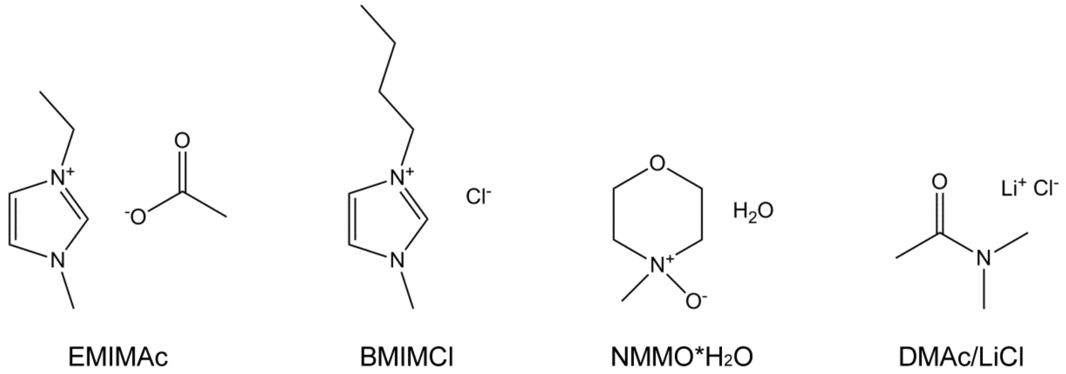


Figure 8 Structures of some cellulose solvents; i.e. the imidazolium-based ionic liquids EMIMAc and BMIMCl, beside NMMOH_2O and DMAc/LiCl.*

Common for several cellulose solvent systems is that they are ionic, that their anions are good hydrogen bond acceptor and that their cations are amphiphilic and asymmetric. The three-dimensional sheet-like structure of cellulose is strong because of hydrogen bonding as well as hydrophobic interactions. To dissolve cellulose, these interactions need to be disrupted. The actual mechanism of cellulose dissolution, however, is debated (Glasser, Atalla *et al.* 2012; Medronho, Romano *et al.* 2012). A probable dissolution mechanism is that the anion of the solvent forms hydrogen bonds to cellulose hydroxyl groups and thus competes with cellulose-cellulose and solvent-solvent hydrogen bonds. In addition to that, the hydrophobic part of the amphiphilic solvent cation, is likely to interact with hydrophobic parts of cellulose and thus enters between the sheets of the cellulose structure. It is most probably that both mechanisms operate simultaneously.

There are several studies on solutions of cellulose (or a model substance) in ionic liquids. It has been reported that more cellulose could be dissolved in imidazolium-based ionic liquids if the anion was a strong hydrogen bond acceptor (i.e. the anion is a strong hydrogen bond base) (chloride) (Fukaya, Hayashi *et al.* 2008; Swatloski, Spear *et al.* 2002). ^{13}C NMR, $^{35/37}$C NMR and diffusion NMR studies of D-cellobiose in imidazolium-based ionic liquids have shown that the anions interact with cellulose hydroxyl groups (Remsing, Hernandez *et al.* 2008). It has also been found that the zero shear viscosity of cellulose ionic liquid solutions, decreased when the anion was changed from chloride to acetate (Kosan, Michels *et al.* 2008).

From ^{13}C NMR and $^{35/37}$Cl NMR relaxation studies of glucose, cellobiose and glucose pentaacetate dissolved in BMIMCl, it has been reported that there are no direct interactions between solute hydroxyl groups and cations of ionic liquids (Remsing, Swatloski *et al.* 2006). Studies show, however, that the solution properties are also dependent on the cation. Rheological measurements of cellulose-ionic liquid solutions have shown that the zero shear viscosity decreases when the cation of the ionic liquid is changed, from BMIM to the smaller EMIM (Kosan, Michels *et al.* 2008). Moreover, COSMO-RS modeling studies of cellulose-ionic liquid solutions, have shown that for some anions, the choice of cation affects the solubility of cellulose (Kahlen, Masuch *et al.* 2010). If hydrophobic interactions are important in the dissolution of cellulose, it is reasonable that the amphiphilic cation affects the solubility. One plausible model for the cellulose-ionic liquid solution is that anions cover the surface of cellulose by forming hydrogen bonds to its hydroxyl groups and that cations form a layer outside the anions. If that is the case, it would not be surprising if the cations affect the solution behaviors (e.g. the zero shear viscosity mentioned).

Initiatives to decrease the viscosity of cellulose-ionic liquid solutions, have led to the conclusions that, cellulose could be dissolved in smaller amounts of imidazolium-based ionic liquid, if a co-solvent (e.g. pyridine, DMSO, N-methylpyrrolidinone) was used (Evlampieva, Vitz *et al.* 2009; Rinaldi 2011). This indicates that the ionic liquid in cellulose-ionic liquid solutions, have both a direct function of dissolving cellulose and an indirect function in which it can be replaced by a co-solvent.

Whereas cellulose-ionic liquid solutions have been studied using NMR, rheology and solubility methods, the regeneration of cellulose from a solution has been less examined. One theory is that when cellulose is regenerated from a solution by the addition of an anti-solvent (e.g. water or alcohol), the anti-solvent interacts with the solvent anions. Consequently, inter and intramolecular cellulose hydrogen bonds can be formed again. Regenerated cellulose is obtained after removal of the solvent and the anti-solvent. Although the regenerated material consists of only cellulose, the structure is not the same as the complex structure of native cellulose. Cellulose can be regenerated from ionic liquids in several shapes depending on the choice of regeneration process. Zhang *et al.* have regenerated carbon nanotube/cellulose composites from solutions of pulp in AMIMCl (Zhang, Wang *et al.* 2007). Cellulose-polyamine materials for biocatalyst immobilization have been prepared by regenerating films and beads from MCC-BMIMCl solutions (Turner, Spear *et al.* 2005). Cellulose has also been regenerated as foam (Deng, Zhou *et al.* 2009) and electrospun as man-made fiber (Viswanathan, Murugesan *et al.* 2006). There are no full-scale facilities that spin fibers from cellulose ionic liquid solutions yet, but there is lab scale devices (Kosan, Michels *et al.* 2008; Viswanathan, Murugesan *et al.* 2006). In some cases, the regeneration process may go through a gel stage.

2.5 CELLULOSE-BASED GELS

Gels are defined as soft, solid or solid-like materials made from two or more components, one of which is liquid and present in a considerable amount (Almdal, Dyre *et al.* 1993). The solid behavior of gels is an effect of a cross-linking in the material which may arise from covalent bonds, crystallites or some other junction (Ferry 1980). When a gel is formed from a solution, the solute forms cross-links, which are thus not necessarily of covalent nature. Examples of solutes are polymeric chains that crystallize locally during gel formation, and monomers in a solution that polymerize so that a cross-linked polymer is eventually formed. When the amount of cross-links is such that the material starts to behave as a viscoelastic material rather than as a liquid, the gel point has been reached and the material is considered a gel (Pierre 1998). These polymeric gels should not be confused with the classical gels described by the sol-gel theory, which are colloidal gels with a solid network of colloidal particles and a liquid solvent (Pierre 1998).

If the liquid/solvent in the gel is water or an alcohol the gel is a hydrogel or an alcogel, respectively (Pierre 1998). Cellulosic hydrogels have been prepared by the addition of water to solutions of cellulose. That way the solvent is washed out of the cellulosic material by the water resulting in a gel consisting of cellulose and water. Hydrogels have been made from cellulose dissolved in e.g. NaOH/water (Gavillon and Budtova 2007), N-methylmorpholine-N-oxide(NMMO)/water (Gavillon and Budtova 2007), 1-allyl-3-methylimidazolium chloride (AMIMCl) (Li, Lin *et al.* 2009), NaOH/urea/water (Yang, Fukuzumi *et al.* 2011), and DMAc/LiCl (De Oliveira and Glasser 1996). If the hydrogel or alcogel is dried through evaporation, the gel shrinks and forms a dry xerogel (Pierre 1998). If the hydrogel or alcogel is instead dried under supercritical conditions, the porous dry gel received is an aerogel (Pierre 1998). Besides processing techniques, the properties of gels depend on factors such as concentration, components and the time of gel formation. Kadokawa *et al.* have prepared three-component gels consisting of MCC, BMIMCl and water by the slow addition of water to the MCC-BMIMCl solution (Kadokawa, Murakami *et al.* 2008). They obtained a flexible gel that could be shaped and re-shaped by heating. The addition of water to the MCC-BMIMCl solution induced the formation of non-crystalline but ordered aggregates in the gel.

3 Materials and Characterization

Complex materials need to be studied at several levels in order to get a reliable result. The cellulosic materials are studied on a molecular level as well as on a microscopic level. Material properties of composites and gels are also studied. Still the observer needs to keep a critical attitude towards the results.

3.1 MATERIALS

Bleached softwood kraft pulp (SWP) were generously provided by Södra. Prior to usage the wet pulp was washed with distilled water and acetone, and then bench-dried for several days. Avicel PH-101 (MCC) was purchased from Sigma-Aldrich and oven-dried (~105 °C) over night prior to usage. Treated ref-SWP and Treated ref-MCC for Paper I were prepared the same way as the esters, except that no acid chloride or 2,2,6-Trimethyl-4*H*-1,3-dioxin-4-one was added. Reference-SWP refers to SWP pretreated as above, whereas Reference-MCC refers to ethanol-washed and bench-dried MCC. Low-density polyethene (density: 920 kg/m^3, T_m: 100-140 ºC, melt flow rate: 7.5 g/10 min) was obtained from Borealis. All other laboratory chemicals were purchased from Sigma-Aldrich. Pyridine, triethylamine and N,N-dimethylformamide (DMF) were pre-dried over molecular sieves (pore size 4 Å) over night. Acid chlorides (butanoyl chloride, hexanoyl chloride, dodecanoyl chloride, 2-ethylhexanoyl chloride) and 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one were used as obtained. 1-Butyl-3-methylimidazolium chloride (BMIMCl) and 1-ethyl-3-methylimidazolium acetate (EMIMAc) were dried at 55 ºC, under reduced pressure for 3 h before usage.

PREPARATION OF ALKYL ACID CELLULOSE ESTERS

A typical preparation of alkyl acid cellulose esters has been reported before (Freire, Silvestre *et al.* 2006), and was applied as follows: Acid chloride (butanoyl chloride, hexanoyl chloride, dodecanoyl chloride or 2-ethylhexanoyl chloride, 1 or 3 eq/AGU), base (pyridine or triethylamine, 1 or 3 eq/AGU) and dimethylformamide (30 or 50 mL/g cellulose) were mixed in a flask. Cellulose (MCC or SWP, ~4 g) was added, and the heterogeneous reaction mixture was heated to 115 °C, for 6 h. After cooling, the reaction mixture was filtered and the solid was washed with DMF, acetone, ethanol, water and again with ethanol. The obtained cellulose ester was bench-dried for several days.

PREPARATION OF β–KETOBUTANOIC ACID CELLULOSE ESTERS

β-Ketobutanoic acid cellulose ester (β-ketoBACE) was prepared in a manner similar to that of the alkyl adic cellulose esters, with some modifications. 2,2,6-Trimethyl-4H-1,3-dioxin-4-one (1 or 3 eq/AGU) and dimethylformamide were mixed in a flask. Cellulose (MCC or SWP, ~4 g) was added and the heterogeneous reaction mixture was heated to 80 °C for 6 h. After cooling, the reaction mixture was filtered and the solid was washed with DMF, acetone, ethanol, water and again with ethanol. The obtained cellulose ester was bench-dried for several days.

PREPARATION OF COMPOSITES

Cellulosic samples (~0.32 g) were mixed with PE (2.88 g) and compounded in a Haake MiniLab twin-screw compounder, at 60 rpm and 150 °C, for 10 min. ~2 g of each composite was obtained. Fibrous samples were milled before compounding, since the compounder otherwise became clogged.

PREPARATION OF GELS

To obtain solutions with cellulose-ionic liquid ratios of 1:20 and 1:10, cellulose (MCC or DACE, 0.5 g) was dissolved in ionic liquid (BMIMCl of EMIMAc, 5 or 10 g) in a closed flask at 70 °C overnight. The solution was poured into petri dishes (diameter 50 mm, 4 g in each dish) and put in an oven (~105 °C, 10 min) to minimize heterogeneity in the solution and to remove residual bubbles. To obtain a slow absorption of the coagulation agent to the solution, the petri dishes with solution and petri dishes with coagulation agent (water or ethanol) were put under an overturned glass bowl (Figure 9). The glass bowl was kept in the dark in order to avoid any side-effects from light exposure. The solutions were coagulated for 4 days. Excess ionic liquid was rinsed off with a coagulation agent and the gels were bench-dried for 2 days.

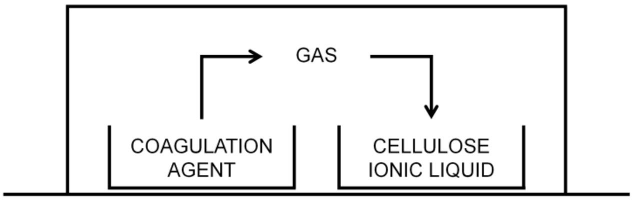


Figure 9 Illustration of the gel preparation.

PREPARATION OF REGENERATED CELLULOSE

The gel was put in a large excess of coagulation agent for 3 days and then bench-dried for 3 days.

3.2 CHARACTERIZATION

FOURIER TRANSFER INFRARED SPECTROSCOPY (FTIR)

In an infrared spectrometer radiation is emitted and split into two beams. One beam is passed through the sample, by which some of the radiation may be absorbed. The intensity of the sample beam and the reference beam, are compared. Absorption (or transmittance) is plotted against frequency (or wavenumber), and the frequencies of the absorption bands are used to determine the functional groups that are present in a sample. A molecule can vibrate if it is a dipole, and the radiation energy equal to such a vibration, is absorbed. Different modes of vibration are stretching (symmetric and asymmetric) and bending (rocking, scissoring, wagging and twisting). Differences in the surroundings of the dipole changes the frequency of its vibration and consequently the frequency absorbed in FTIR spectroscopy. For example, carbonyl (C=O) stretching of saturated esters, absorbs energy at about 1750-1735 cm^{-1}, whereas carbonyl stretching of saturated carboxylic acids, absorbs energy at about 1725-1700 cm^{-1}.

FTIR was performed on potassium bromide tablets using a Perkin Elmer Spectrum One instrument.

WATER RETENTION VALUE (WRV)

Water retention value (WRV) is a readily used technique for studying the ability of a pulp to hold water. The standards for the measurement are given in Tappi 2011 (Tappi 2011). It is defined as the mass of the water the pulp sample can hold, under centrifugation, divided by the mass of the dry pulp sample (Equation 1).

$$WRV = \frac{m_{water}}{m_{dry\ sample}} = \frac{m_{wet\ sample} - m_{dry\ sample}}{m_{dry\ sample}} \qquad \text{Equation 1}$$

Cellulose (SWP, MCC or derivative, ~0.4 g) was soaked in distilled water, centrifuged in Vivaspin tubes (4000 rpm, 10 min) and oven-dried (~100 °C). A Thermo Scientific Heraeus Megafuge 40 centrifuge was used. The samples were weighed before ($m_{wet\ sample}$) and after ($m_{dry\ sample}$) drying. The WRV were calculated using Equation 1.

ELEMENTAL ANALYSIS

The degree of substitution (DS) of cellulose esters can be accessed from elemental analysis by using a method previously reported (Vaca-Garcia, Borredon *et al.* 2001). The ratio of carbon to oxygen and hydrogen in the sample is measured in the elemental analysis. By adding a substituent with a different ratio of carbon than cellulose has, the values changes. For some substituents in this study, however, this ratio did not differ much from that of cellulose, and the difference measured was minor. Therefore, focus should be on trends, and not on the exact numbers of the DS. For this reason no DS values for β-ketoBACE are reported here.

Elemental analyses for determining DS were performed by Mikroanalytisches Laboratorium Kolbe (Germany), and the DS values were calculated according to the description by Vaca-Garcia *et al.* (Vaca-Garcia, Borredon *et al.* 2001).

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

In a differential scanning calorimeter (DSC) the difference in heat flow between a sample and a reference sample upon heating or cooling is studied. The difference in power (heat energy per time unit) needed to maintain the sample and the reference at the same temperature is measured. By plotting heat flow to temperature, the glass transition temperature (Tg), crystallization (Tc), melting (Tm) and other thermal transitions can be seen.

DSC measurements of gels were performed in an inert atmosphere, with a Perkin Elmer DSC7 equipped with an intracooler. The heating rate was 10 °C/min from 10 to 300 °C.

THERMOGRAVIMETRIC ANALYSIS (TGA)

A thermogravimetric analyzer (TGA) records the mass of a sample while it is heated in a controlled atmosphere. Plotting weight to temperature gives information about decompositions, oxidations (if oxygen is present), vaporizations, sublimations and desorptions. The content of different components of multicomponent samples can be obtained if they e.g. vaporize at different temperatures.

For the TGA measurements a Perkin Elmer TGA 7 instrument was used. The heating rate for gels was 5 ºC/min from 20 to 150 ºC followed by 10 ºC/min from 150 ºC to 400 ºC and the heating rate for composites it was 5 ºC/min from 25 to 550 ºC.

DYNAMIC MECHANICAL AND RHEOLOGICAL MEASUREMENTS

Using dynamic and rheological methods a sample is exposed to an oscillating (sinusoidal) stress, and its response is measured. In dynamic mechanical analyses (DMA) of composites, a rectangular bar of sample is clamped at the short ends. One clamp is fixed, whereas the other stretches the composite. In the rheological measurements of gels, a parallel plate geometry is used, in which the gel is placed between two horizontal plates. The lower one is fixed, whereas the upper one is rotated. In DMA measurements, a tensile stress is applied, and the tensile storage and loss moduli (which are the elastic and viscous components of the complex modulus) obtained, are abbreviated as E' and E''. In parallel plate rheometry, a shear stress is applied, and the shear storage and loss moduli obtained, are abbreviated as G' and G''. Moreover, the phase angle between the sinusoidal stress and strain (tan δ), which depends on the storage and loss moduli of the material, can be quantified. Different experiments can be designed by varying e.g. the frequency of the oscillation, the temperature or the applied stress.

DMA measurements of composites were performed using a Q800 DMA (TA Instruments), in tension film mode. Samples with gauge dimensions of about 15x6x0.6 mm were cut, and incubated at 23 °C, 50% RH (relative humidity) at least 24 h. Three replicates of each sample were tested. Experiments were performed with a 0.5 °C/min ramp, from 23 to 85 °C (50% RH, 0.05 % strain), at 1 Hz.

Rheological measurements on gels were performed using a stress-controlled Rheometrics SR200 rheometer, with parallel-plate geometry. The gel samples were disks with a diameter of 25 mm diameter and a thickness of ~2 mm. Isothermal stress sweeps at 25 and 70 ºC, were performed between 0.4 and 1500 Pa and at a circular frequency of 1 Hz. A temperature sweep was performed between 25 and 180 ºC with a heating rate of 5 ºC/min, a stress of 50 Pa and a circular frequency of 1 Hz. A frequency sweep was performed between 0.01 and 10 Hz, at 25 ºC and a stress of 50 Pa.

TENSILE TEST

In a tensile test a sample shaped like a dog-bone is clamped at the ends of the sample. One clamp is fixed, whereas the other stretches the sample in a linear mode. Strain controlled equipment measures the stress needed to obtain a defined strain, at a certain speed. Parameters such as tensile modulus (Young's modulus), strain at break and ultimate tensile strength (defined here as the first stress maximum in a test) of a sample, can be obtained.

Tensile tests of composites were performed with an Instron 5565A. Samples were hot pressed, cut into dog-bone shaped samples with gauged dimensions of about 22x6x0.6 mm, and incubated at 23 °C and 50% RH for at least 24 h before testing. Three replicates of each composite were tested and the applied strain rate was about $2 \cdot 10^{-3}$ s^{-1}.

SCANNING ELECTRON MICROSCOPY (SEM)

In a scanning electron microscope (SEM) an electron beam is swept over the sample in a raster pattern. This results in many signals from the sample, but the ones detected in the SEM are secondary electrons and a surface map of the sample is obtained in this manner. It is easier to study conductive samples since these are well grounded. The build-up of charge in un-conductive samples generates instrumental artifacts, as well as the risk of burning the sample. To avoid these disadvantages, un-conductive samples are often coated with a metallic film (e.g. by sputtering). SEM results are obtained as a magnified visual map (not an actual image) of a sample, that reveals things hidden from the naked eye. This method is commonly used in the cellulosic field to visualize fibers or fiber surfaces. Composite fracture surfaces can also be studied with SEM. The resolution is, however, not high enough to study single polymer chains of cellulose.

SEM was performed on gold sputtered samples of cellulose and of cellulose-PE composites using a JEOL JSM-829 microscope at 20 kV. To obtain the fracture surfaces of composite samples, they were frozen with liquid nitrogen prior to breakage.

CONFOCAL LASER SCANNING MICROSCOPY (CLSM)

With a confocal laser scanning microscope (CLSM) a laser beam is focused at a spot just below the surface of a sample. Electrons in that spot are excited and their relaxation is detected. A larger area can be scanned this way giving an image of the interior of a sample. Some samples need to be stained for the relaxation to be detectable. Cellulose, however, has some autofluorescence, and can sometimes be studied without staining. The cellulose inside a composite can thus be studied with this method, without destroying or affecting the sample.

CLSM of composite samples was performed with a Leica SP2 confocal laser scanning microscope. Samples were hot pressed before examination and, when necessary, samples were stained with acridine orange. The objectives used were, 10 × (N.A. 0.30) and 50 × (N.A. 0.55) air objectives. The excitation wavelength from the Ar/Kr laser was 488 nm, and emission wavelengths above 500 nm were detected. Images were obtained from about 15-50 μm below the surface.

4 Cellulose esters and composites – Paper I

5 Cellulose-based gels – Paper II

6 Concluding remarks

Two types of shapeable cellulosic materials have been prepared and studied.

The study of chemically modified cellulose and its composite applications acknowledges the complexity of such materials. The large amount of processing steps (e.g. pretreatment, chemical modification, rinsing, milling, compounding, hot pressing and sample preparation for characterization), makes it difficult to assign results to only a few parameters. In many of these steps the cellulosic material, the plastic, or interactions within or between them are affected in more than one way, and have major effects on the performance of the composite. To obtain good thermoplastic composites with cellulose esters, and to better study the influence of different side chains and substitution patterns, the chemical treatments would need to be less harsh in order reduce the effect on fiber morphology. It would also have been interesting to prepare SWP esters with an un-swelling reaction medium (substitution limited to the fiber surface), to see if higher storage moduli could be obtained for the fiber-PE composites.

The study of shapeable cellulose-based gels has increased knowledge about such gels by examining the effect on gel properties by using different amounts and types of constituents, and thus affecting the strength of interactions in gels. To be able to better predict and design regenerated cellulosic materials it would be interesting to correlate the structure and properties of these types of gels with structure and properties of corresponding regenerated cellulose.

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