

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

# Cellulose processing in ionic liquid based solvents

CARINA OLSSON

Department of Chemical and Biological Engineering  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2014

CELLULOSE PROCESSING IN IONIC LIQUID BASED SOLVENTS

Carina Olsson

ISBN 978-91-7385-999-8

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Doktorsavhandlingar vid Chalmers tekniska högskola

Ny serie nr: 3680

ISSN 0346-718X

Department of Chemical and Biological Engineering

Chalmers University of Technology

SE-412 96 Gothenburg

Sweden

Telephone + 46 (0)31-772 1000

Cover: Regenerated cellulose fibers and its raw material, wood.

Printed by Chalmers Reproservice

Gothenburg, Sweden 2014

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CARINA OLSSON

Department of Chemical and Biological Engineering  
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## ABSTRACT

As the most abundant polymer in nature, cellulose has an undisputed role among the raw materials to be used in a sustainable future. From its native form, in wood or straw, cellulose can be processed into products such as paper and board. Through dissolution and precipitation, the range of cellulose based products can be increased to include textile fibers, thin continuous films, foams and membranes. Since cellulose is insoluble in most conventional solvents, ongoing research worldwide aims to find new, efficient and environmentally friendly solvent systems for biomass in general, and for cellulose in particular.

In this thesis, the solvent of focus was 1-ethyl-3-methylimidazolium acetate, commonly abbreviated as EMIMAc. It is an ionic liquid, and belongs to a class of solvents which was basically unexploited by cellulose chemists until just over a decade ago.

Results show that cellulose that is dissolved in EMIMAc, with or without a cosolvent, can be spun into continuous textile fibers using airgap spinning or wet spinning, or be cast into films. The properties of the produced fiber vary depending on the solution, cellulose sources and spinning parameters, such as drawing. For example, the regeneration medium was found to be of great importance for the crystallinity of regenerated films. Properties of regenerated cellulose can be further altered by drying conditions. It was also shown that some residual coagulation medium (water), which is time-consuming to remove in a solvent recycling step, can be tolerated in the EMIMAc to some extent if cellulose concentration or degree of polymerization is low. Finally, esterification of cellulose in EMIMAc was found to be improved by using cosolvents to regulate unintended acetylation, which until now, has been the dominant result in such reactions.

Keywords: cellulose, ionic liquids, dissolution, rheology, solution spinning, cellulose derivatives, esterification, crystallinity, NMR spectroscopy



*Corpora non agunt nisi solute*



## List of publications

This thesis is based on the studies presented in the following papers, referred to in the text by their Roman numerals.

- I. Influence of water on swelling and dissolution of cellulose in 1-ethyl-3-methylimidazolium acetate**  
C. Olsson, A. Idström, L. Nordstierna and G. Westman  
Carbohydrate polymers 99:1 (2014) 438-446
- II. Effect of methylimidazole on cellulose/ionic liquid solutions and regenerated material therefrom**  
C. Olsson, A. Hedlund, A. Idström and G. Westman  
Journal of Materials Science, 49:9 (2014) 3423-3433
- III. Cosolvent facilitated in situ esterification of cellulose in 1-ethyl-3-methylimidazolium acetate**  
C. Olsson and G. Westman  
Manuscript
- IV. Wet spinning of cellulose from ionic liquid solutions - viscometry and mechanical performance**  
C. Olsson and G. Westman  
Journal of Applied Polymer Science, 127:6 (2013) 4542-4548
- V. Modification of crystallinity and pore size distribution in regenerated cellulose films**  
Å. Östlund, A. Idström, C. Olsson, P. T. Larsson and L. Nordstierna  
Cellulose, 20:4 (2013) 1657-1667
- VI. Direct Dissolution of Cellulose: Background, Means and Applications**  
C. Olsson, G. Westman  
Review book chapter published in Cellulose - Fundamental Aspects, 143-178. Intech, Rijeka, 2013

## Contribution report

The author's contribution to the papers presented in this thesis:

### **Paper I and Paper II:**

Main author. Responsible for experimental outline, experimental work, interpretation of results and manuscript preparation. Conducted all experimental work with the exception of solid state NMR spectroscopy, which was performed by Alexander Idström, and the fiber spinning (Paper II), which was performed together with Artur Hedlund.

### **Paper III and Paper IV:**

Main author. Responsible for experimental outline, experimental work, interpretation of results and manuscript preparation.

### **Paper V:**

Partly responsible for planning the experimental outline and minor contributor to the experimental work. Contributed to the interpretation and evaluation of results as well as preparing the manuscript.

### **Paper VI:**

Main author.

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## Conference presentations

The progress of the research presented in this thesis has also been presented at a number of seminars and conferences. Selected titles are listed below:

### **Dissolution and regeneration of wood saccharides in ionic liquids**

In 11<sup>th</sup> European Workshop on Lignocellulosics and Pulp, Proceedings. Hamburg, Germany, August 16-19, 2010, pp. 411-415 (poster)

### **Cellulose processing in ionic liquids using N-methylimidazole as cosolvent**

In Presentations and posters from the 2<sup>nd</sup> Avancell conference. Göteborg, Sweden, October 2-3, 2012, p. 3 (oral presentation)

### **Determination of cellulose II crystallinity index by solid state NMR**

In Presentations and posters from the 2<sup>nd</sup> Avancell conference. Göteborg, Sweden, October 2-3 2012, p. 9 (poster)

### **The role of 1-methylimidazole as a cosolvent for cellulose in imidazolium based IL solutions**

In 5<sup>th</sup> workshop on cellulose, regenerated cellulose and cellulose derivatives, Abstracts. Örnsköldsvik, Sweden, November 13-14 2012, pp. 8-12 (oral presentation)

### **Ionic liquids for cellulose processing - influence of water on swelling and dissolution of cellulose in EMIMAc**

In 3<sup>rd</sup> Avancell conference, Book of Abstracts. Göteborg, Sweden, October 8-9 2013, p. 63-64 (poster)

### **Influence of water on dissolution and swelling of cellulose in EMIMAc**

In Troëdsson seminar/COST ACTION FP1205 workshop on cellulose dissolution and regeneration, Abstracts. Göteborg, Sweden, December 3-4, 2013, p. 1 (oral presentation)

## Additional publications

Apart from the papers included in the thesis, the author has published the following closely related article.

**Solvation behavior of cellulose and xylan in the MIM/EMIMAc ionic liquid solvent system - parameters for small scale solvation**

S. Bylin, C. Olsson, G. Westman and H. Theliander

BioResources 9:1 (2014) 1038-1054

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# 1 Introduction

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We live in a finite world. If our natural resources are consumed faster than nature can regenerate them, they will eventually run out. Consequently, the interest in bio-based polymers as a platform for future processes and products is increasing due to the gradual depletion of petroleum reserves, as well as greater awareness of the need for carbon-neutral raw materials for energy and materials.

As the main structural component in plants, cellulose is, by far, the most abundant organic polymer in nature (Kamide 2005). In theory, cellulose is an inexhaustible resource that is produced in the range of  $1.5 \cdot 10^{12}$  tons of biomass every year (Klemm et al. 2005). Despite the fact that cellulose is available in all plants, the main part of the cellulose that is used today, for example in board, paper and textile, originates from wood pulp. Cotton is still the main source of cellulose for textile use, but the demand for wood based raw material is increasing in this field due to the environmental drawbacks of cotton cultivation and processing, such as the usage of water and pesticides.

Unlike many petroleum based polymers, cellulose cannot be melted and molded at elevated temperatures; it will catch fire and decompose. To be obtained in liquid form, cellulose must be dissolved or chemically modified into a thermoplastic that can be melted. Owing to its chemical composition, cellulose is insoluble, or only partly soluble, in most common solvents. Although quite a few alternatives have proven useful, the search for efficient and non-degrading solvents for cellulose is still ongoing, and in the light of current trends within sustainability and the exploration of alternatives for petroleum-based products, this search is now more important than ever.

## 1.1 Objective and outline of thesis

Assuming that cellulose is to be a key raw material in a new biobased economy, the aim of this research has been to evaluate the potential possibilities and challenges of using ionic liquid based solvents for cellulose. The focus was on 1-ethyl-3-methylimidazolium acetate, one of the most promising ionic liquids for cellulose processing so far. In this research, aspects of the entire process, from pulp to regenerated material, were investigated. This included studies of solution properties using different sources of cellulose, possibilities for processing cellulose in a binary solvent system including both an ionic liquid and an additional cosolvent, the need for separation in solvent recycling, and, finally, the mechanical properties of the regenerated materials. Additionally, it was also studied how these mechanical properties can be altered using different approaches both in the choice of solvents, raw material, coagulation media and post treatment. Appended to this thesis is also a review paper that deals with the direct dissolution of cellulose in a broader perspective.

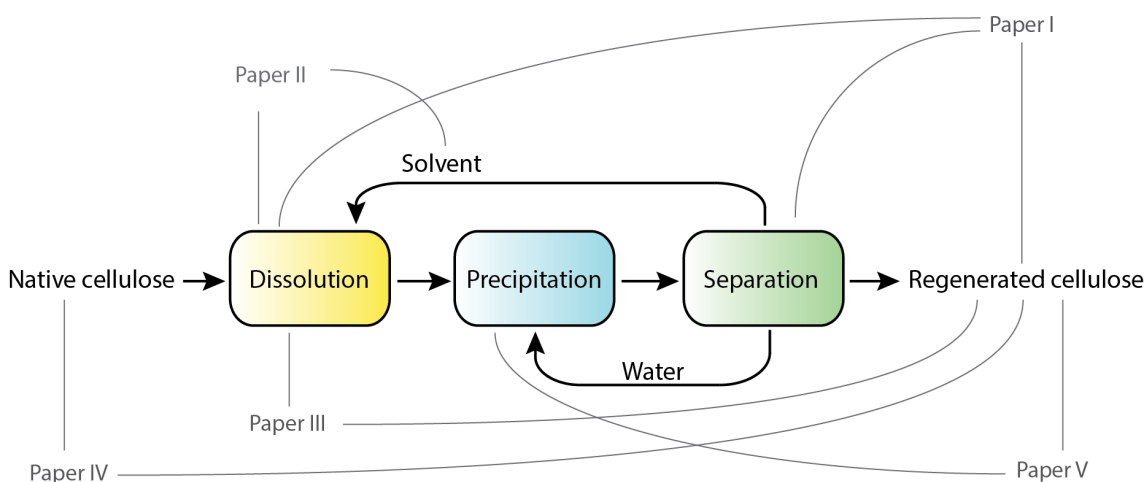


Figure 1. Overview of the papers, based on the experimental work, that are included in this thesis, and how their contents are related to the process cycle of a closed-loop process for producing regenerated cellulose in a direct (non-derivatizing) solvent system.

The outline of the present thesis can be summarized as follows: Chapter 2 provides an introduction to cellulose and cellulose dissolution, partly based on the appended review article Paper VI. Chapter 3 describes the experimental methods and materials used in the different projects. Chapters 4 through 6 summarize the results of Papers I through V. Finally, Chapter 7 and Chapter 8 provide the conclusions of the experimental part of the thesis along with reflections and suggestions for future work.

## 2 Cellulose

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The main amount of the cellulose used in industry is found in the secondary walls of higher plants, such as wood, where it is incorporated into a matrix of lignin and shorter heteropolysaccharides known as hemicelluloses and pectin.

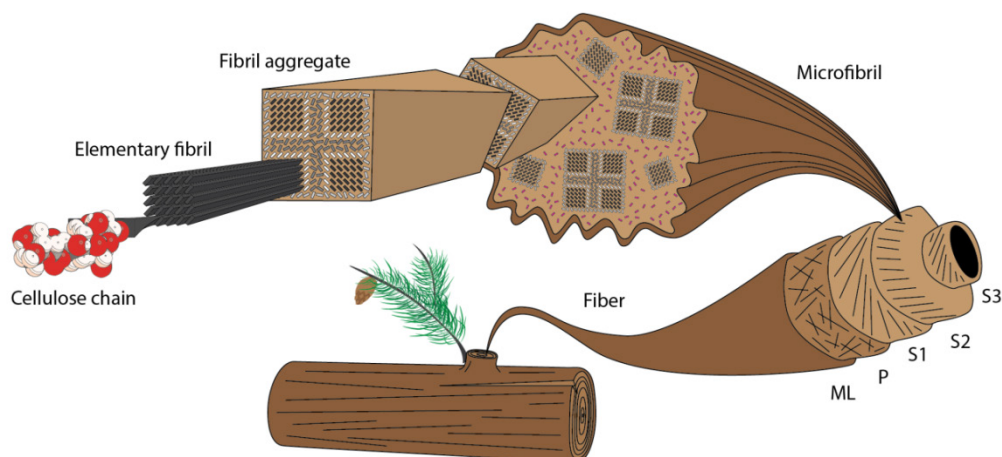


Figure 2. Structure of wood fiber. Lignin rich mid lamella (ML), primary layer (P), and secondary layers (S1, S2, S3) where most of the cellulose is found in fibril aggregates inside the microfibrils where it is surrounded by hemicelluloses. *Adapted from A. Idström, with permission.*

In a chemical process known as pulping, lignin is removed from wood and fibers are isolated in different purities as paper grade pulp for printing paper or as dissolving grade pulp for cellulose derivatives or regenerated cellulose. The two most common chemical pulping processes are the Kraft pulping process, also known as sulfate pulping, and the sulfite pulping process. There are also (thermo-)mechanical pulping and combined processes.

## 2.1 Cellulose structure and applications

Cellulose is a simple polymer, linear and with only one type of monomer, and nevertheless, it provides challenges at all levels of processing. Unlike some other biopolymers, such as proteins, cellulose in its native form is highly polydisperse. From monomer to bulk material, all levels present interesting features.

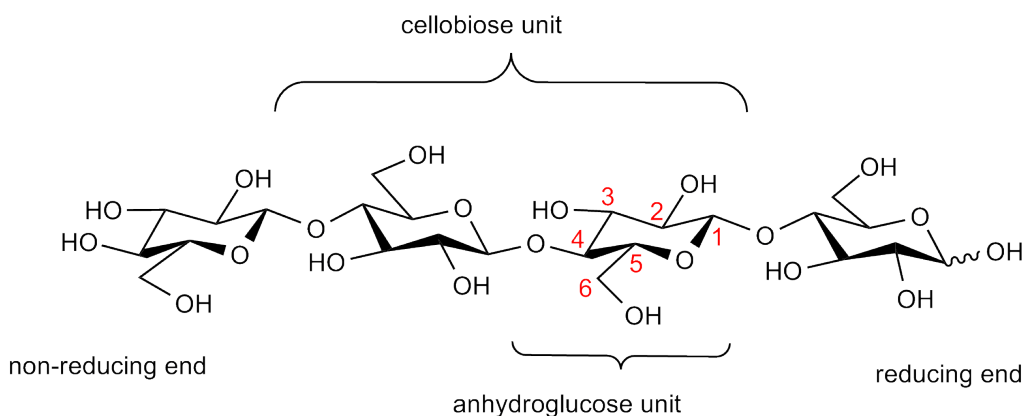


Figure 3. The molecular structure of cellulose, with anhydroglucose units (AGU) linked by  $(\beta)1 \rightarrow 4$  glucosidic bonds. Red numbers refer to carbon numbering in the AGU.

The molecular structure of cellulose is depicted in Figure 3. As can be seen, the glucose rings take on a chair formation (Ferrier 1963; Chu and Jeffrey 1968; Nehls et al. 1994). Three hydroxyl groups are present in the anhydroglucose unit; secondary on C2 and C3, and primary on C6. The rotational conformation of the primary alcohol on C6 can be altered, as shown in Figure 4, and this will have a profound impact on the hydrogen bonding pattern, and therefore the crystallinity, of the cellulose meta-structure (Nishiyama et al. 2002). The *tg* conformation is characteristic for the crystal structure of native cellulose, called cellulose I. *gt* is characteristic for regenerated or mercerized cellulose crystals, cellulose II (Langan et al. 2001). *gg* is found, together with *gt* and *tg*, in non-ordered regions.

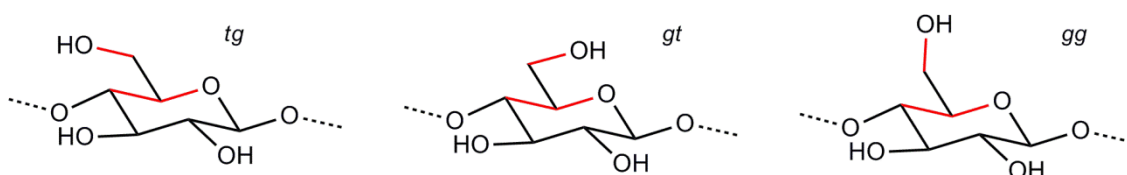


Figure 4. Possible rotational conformation of the cellulose hydroxymethyl group. *t* and *g* denote trans and gauche, meaning its dihedral angles of  $60^\circ$  and  $180^\circ$  relative to the ring oxygen and C4, marked by the red lines.



The reducing and non-reducing ends of cellulose, illustrated in Figure 3, show that the cellulose chain has an inherent directionality. At one end of the cellulose chain, the anomeric carbon, C1, is involved in a glycosidic bond. This is referred to as the non-reducing end. At the other end of the polymer, there is a free hydroxyl group at C1 and the structure is free to convert to its aldehyde form. This end is referred to as the reducing end. This chemical polarity of the cellulose chain is important when it comes to its different crystal structures. In native cellulose I crystals, all chains are parallel, while in cellulose II crystals they are anti-parallel (Kolpak and Blackwell 1978). It is still debated whether this anti-parallel ordering is due to chain-folding or to the interdiffusion of crystallites during dissolution. Cellulose I can be subdivided into cellulose I $\alpha$  and cellulose I $\beta$  (Atalla and VanderHart 1984; VanderHart and Atalla 1984), where the I $\alpha$  is dominant in bacteria and algae and I $\beta$  is dominating in higher plants. Recent work using X-ray and neutron diffraction suggests that cellulose I $\alpha$  is triclinic, while the I $\beta$  form is monoclinic (Finkenstadt and Millane 1998).

The number of AGU units in the cellulose chain defines its degree of polymerization (DP). The DP of several sources including native wood was first determined in 1962 (Goring and Timell 1962) to be between 9000 - 10000. Extraction methods and treatment of cellulose can degrade the polymers, and consequently, the DP of wood pulp can vary between 300-1700, whereas regenerated fibers from cellulose usually have a DP of around 250-500 (Klemm et al. 1998).

### **2.1.1 Nanocellulose**

Through chemical and/or mechanical treatment, the native cellulose fiber can be refined to nanocellulose in different forms, such as those illustrated in Figure 5. Nanofibrillated cellulose (NFC), or microfibrillated cellulose (MFC), is produced through mechanical treatment in devices such as high-pressure homogenizers. This treatment delaminates the cellulose fibers and liberates the microfibrils, which are around 20 nm in diameter. The process requires a high amount of energy, but can be facilitated by enzymatic or chemical treatment such as TEMPO oxidation (Saito et al. 2006; Henriksson et al. 2007).

Cellulose nanocrystals (CNCs), also known as nanocrystalline cellulose (NCC) or cellulose whiskers, consist of rod-like crystals, around 5–70 nm in diameter and between 100 nm and several micrometers long. They are produced through acid hydrolysis of amorphous sections of a lignin-free cellulose source such as pulp or cotton linters (Ranby 1951). After sulfuric acid

hydrolysis, these crystals form stable suspensions in water due to the incorporation of anionic sulfate ester groups on the surface (Hasani et al. 2008).

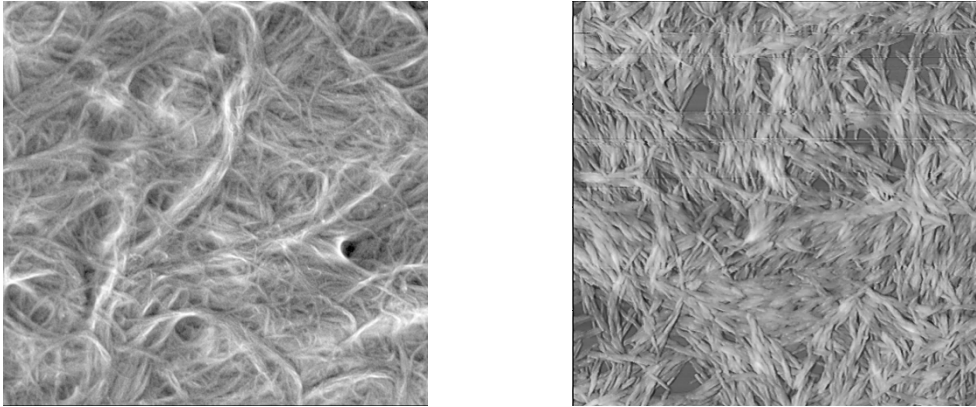


Figure 5. Microfibrillated cellulose (left) and cellulose nanocrystals (right). ©Merima Hasani, and Michael Obersriebnig, with permission.

Due to its extraordinary ability to hold water, as well as its mechanical properties, potential applications for MFC are seen in medical, pharmaceutical, cosmetic, and hygiene absorbent products as well as in textile, nanocomposites and paper and board reinforcements. The optical properties of CNC also make them suitable for security papers. With a strength eight times that of steel, combined with film-forming abilities, the crystals can also be used in high performance nanocomposites, paper, coatings, food packaging, and as gas barriers (Klemm et al. 2011).

### **2.1.2 Regenerated cellulose**

The most industrially important technique for dissolving and shaping cellulose is via the viscose process. This method is mainly used for textile production, and involves the conversion of cellulose to cellulose xanthate by means of a reaction in sodium hydroxide and carbon disulfide. This method was first described by Charles Frederick Cross, Edward John Bevan, and Clayton Beadle well over a hundred years ago (Cross et al. 1893). The resulting derivative, cellulose xanthate, is soluble in aqueous sodium hydroxide. The cellulose xanthate solution is subsequently in sulfuric acid, for simultaneous neutralization and regeneration of the pure cellulose in a wet spinning step. The viscose process yields high performance fibers, such as rayon, with excellent properties for various applications. However, it has some drawbacks. The sulfuric reagents, their byproducts and the heavy metals used in the regeneration baths are, despite a decrease in usage, still a problem from an

environmental point of view. Both air and water streams must be adequately purified to meet today's regulations. A recent competitor for making regenerated textile fiber on a commercial scale is the NMMO-system for the production of so called Lyocell fibers. So far, ionic liquids (ILs) for this purpose have not reached the commercial market although it is fully possible to produce all sorts of regenerated cellulose materials from IL/cellulose solutions, not only fibers but also aerogels and films (Kosan et al. 2008; Aaltonen and Jauhiainen 2009; Liu et al. 2011).

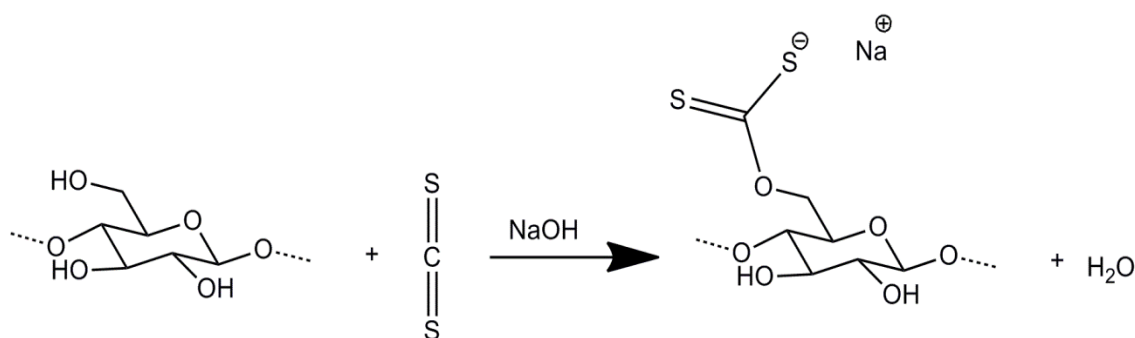


Figure 6. The reaction that forms cellulose xanthate, the starting material for making viscose. Cellulose reacts with carbon disulfide to form the cellulose derivative which is soluble in aqueous sodium hydroxide.

Recent applications for regenerated cellulose include non-woven filters made from nanofibers produced by electrospinning of cellulose from ionic liquid solutions, used for purification of water or air, (Xu et al. 2008; Härdelin et al. 2012).

### 2.1.3 Cellulose derivatives

Cellulose is a versatile polymer, with many areas of applications in itself, but through chemical modification it can become even more useful. For example, by acetylation of its OH groups, cellulose can be transformed into the easily dissolved and thermoplastic derivative cellulose acetate. This material can be used for many things, including filters tow for cigarettes, textile fibers and exclusive eyeglass frames.

Other cellulose esters can for example be used as compatibilizers in cellulose composites (Pasquini et al. 2007; Freire et al. 2008). Such cellulose esters include cellulose propionate, which has properties similar to cellulose acetate. Mixed esters are also common, e.g. cellulose acetate propionate and cellulose acetate

butyrate (Heinze and Liebert 2001). Cellulose esters are generally produced by reacting cellulose with the corresponding acid chloride or anhydride.

Cellulose ethers is another group of cellulose derivatives used in many every-day products, ranging from concrete to cosmetics, and even food additives such as emulsifiers (E461, E462, E463). Mixed ethers, e.g. hydroxypropylmethyl cellulose (HPMC), are especially common in tablet formulation.

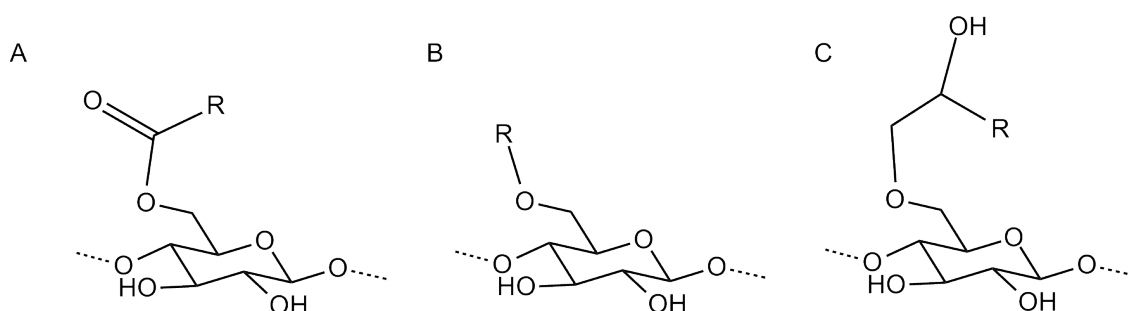


Figure 7. Example of a general cellulose ester (A), and general cellulose ethers; alkyl cellulose (B), and hydroxyalkyl cellulose (C). For esters and alkyl cellulose, R can be  $\text{CH}_3$  or a longer carbon chain, aliphatic or aromatic. For hydroxyalkyl cellulose, R can be a proton or a carbon chain. The substituents can also be found on C2 or C3.

Alkyl cellulose is generally produced via the Williamson ether synthesis route, where the corresponding alkyl chloride is used as the etherification agent in aqueous alkali. Hydroxyalkyl cellulose can be produced via an epoxide ring opening reaction in an inert solvent, such as isopropanol, with a catalytic amount of alkali.

Recent exploration of nanocellulose and its applications has resulted in surface-modified cellulose nanocrystals with properties that are significantly altered as compared to the original CNC particle. Such alteration increases the potential range of uses for cellulose-based products, both as stand-alone materials and as parts in composites.

Apart from paper, board, and tissue, there are indeed many products from cellulose that are used in everyday life today. With the extraordinary rate of research in the field at present, even more cellulose based products can be expected in the future.

## 2.2 Solubility of cellulose

At a first glance, cellulose looks very simple. Nevertheless, *dissolution* of cellulose is in fact quite complicated. Many factors contribute to make cellulose insoluble in most common solvents. Native cellulose has a high DP, which leads to a decrease in solubility due to a reduction in entropic gain in the dissolution process. Glucose, cellobiose, or any oligomer of cellulose structure up to a DP around ten are soluble in simple solvents, such as water. However, cellulose is not, so the length of the polymer is obviously a relevant factor (Liebert et al. 2008). An additional challenge is the interactions between the cellulose molecules. Three hydroxyl groups per AGU make complex patterns of hydrogen bonds possible. To break these bonds, solvents with a high capacity for hydrogen bonding are necessary.

Water alone cannot dissolve cellulose, yet both water - water, carbohydrate - water and carbohydrate - carbohydrate hydrogen bond strengths are around 5 kcal/mol (Lindman et al. 2010). Thus, hydrogen bonding is not the only relevant factor for a suitable solvent but other types of interaction must be taken into consideration. As shown in Figure 8, hydrogen bonds arrange cellulose chains in sheets, but stacking of these sheets into the three dimensional structure of the cellulose material involves hydrophobic interactions. In the last few years, some eye-opening papers have brought this matter up for discussion (Biermann et al. 2001; Bergenstr hle et al. 2008; Gross and Chu 2010; Lindman 2010; Lindman et al. 2010; Cho et al. 2011).

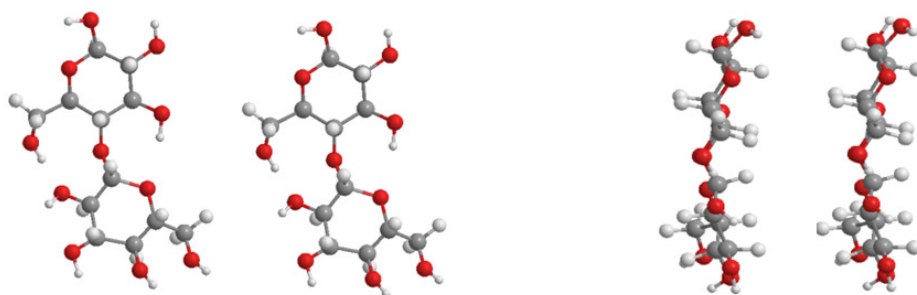


Figure 8. Cellulose simplified as a cellobiose. Equatorial hydrogen bonds arrange cellulose chains in sheets that are stacked onto each other in three-dimensional crystals by means of hydrophobic interactions.

Swelling of cellulose is a process in which a liquid molecule penetrates the fiber structure by interacting with the cellulose polymer to a certain extent, leaving the volume and physical properties of the cellulose significantly

changed, although the solid or semi-solid state remains. This occurs, for instance, in water and dilute lye. Dissolution, on the other hand, completely destroys the supramolecular structure (e.g. the fiber) due to a superior interaction between the solvent and the polymer, and results in a clear solution in which the polymers are molecularly dispersed.

Traditional solvents for cellulose include several types of derivatizing solvents, i.e. solvents that react with cellulose to form a more easily soluble cellulose derivative. One example of such a solvent system is CS<sub>2</sub> in NaOH used in the industrially important viscose process. Non-derivatizing solvents include for example N-methyl-morpholine-N-oxide (NMMO) and LiCl in dimethylsulfoxide (DMSO). In the last ten years, research on cellulose solubility has, to a large extent, been dominated by research on ionic liquids.

In a good solvent, dissolution is instantaneous and homogeneous – without any sign of heterogeneous fiber swelling. In hydrated samples, the dissolution is accompanied by a swelling process known as ballooning. The ballooning effect is known in less powerful solvents and has been studied in e.g. NaOH(aq), NMMO and some ionic liquids (Cuissinat and Navard 2006a, b). This effect is unique to fibrous materials. The same liquid may act as a solvent or merely a swelling agent, depending on the conditions used in the experiment. In some cases, temperature can be crucial. In general, five different modes of dissolution can describe fibrous cellulose swelling and dissolution in different solvents (Cuissinat and Navard 2006a):

- Mode 1: Fast dissolution through disintegration into rod-like fragments
- Mode 2: Swelling by ballooning, dissolution of the fiber
- Mode 3: Swelling by ballooning, followed by partial dissolution of the fiber
- Mode 4: Homogeneous swelling, but no dissolution of the fiber
- Mode 5: No swelling and no dissolution (in the case of a non-solvent)

As expected, a non-solvent (e.g. water) added to a solvent (e.g. NMMO), will shift the dissolution mode of cellulose from Mode 1 to Mode 2 and then at higher non-solvent concentrations to Mode 3. Finally, with sufficient amount of non-solvent added, the system will enter Mode 4 and will no longer be useful for homogeneous processing. On the other hand, by reversing the process, starting with Mode 4 and by removing the non-solvent from the system, significant advantages in mixing can be achieved. This technique can be used with success when dissolving cellulose in NMMO and in some ionic liquids.

## 2.3 Cellulose and ionic liquids

As early as in the 1930s, it was found that liquefied quaternary ammonium salts, alone or diluted in suitable solvents, can dissolve cellulose (Graenacher 1934). This was the first successful direct dissolution of cellulose in organic salt. However, at that time, these findings did not attract much attention. It took almost 70 years for this idea to blossom. In the early 2000s, it was found that neat 1-butyl-3-methylimidazolium chloride (BMIMCl) can dissolve cellulose quickly and without derivatization (Swatloski et al. 2002). This finding would set the spark to a formidable explosion in the so called *ionic liquid* research related to cellulose. Ionic liquids (ILs) represent chemicals simply defined as organic salts with a melting point below 100 °C. If an ionic liquid has a melting point below room temperature, it is often called *room temperature ionic liquid* (RTIL). The opportunity of pairing anions with cations yields an almost endless library of potential ionic liquids. The term *task specific ionic liquid* (TSIL) reveals the idea of this approach. ILs have industrial applications in as widespread areas as pharmaceuticals, analytical chemistry, extraction, materials science and as electrolytes in batteries. ILs have shown great versatility in the field of cellulose technology, including dissolution for regeneration purposes (Viswanathan et al. 2006; Kosan et al. 2008), homogeneous derivatization (Heinze et al. 2005; Gericke et al. 2011; Gericke et al. 2012), and biomass processing including wood component separation (Fort et al. 2007; Kilpeläinen et al. 2007; Sun et al. 2009; Froschauer et al. 2013). As shown in Figure 9, the number of publications in the field has, so far, increased year by year.

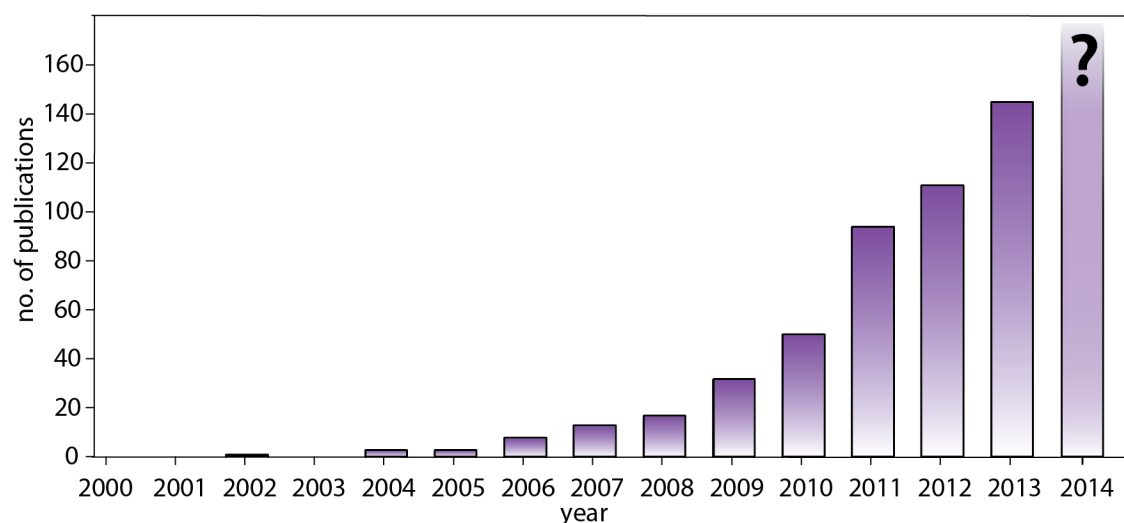


Figure 9. Number of publications found in PubMed using the search terms “ionic liquid/s” in combination with “cellulose” years 2000–2013.

The range of ionic liquids that are interesting from a cellulose processing point of view is broad. Some of the most common cations are imidazolium, pyridinium, ammonium and phosphonium derivatives, shown in Figure 10. Recently, tetramethylguanidinium based ILs have gained attention due to the possibility to recycle and purify them by distillation (King et al. 2011).

The most popular cation used today is the imidazolium cation with different alkyl substituents. Some of the imidazolium based ILs are very efficient as cellulose solvents but due to ecotoxicity and low biodegradability as well as high cost, an efficient method for recycling is needed (Romero et al. 2008). Life cycle assessment of an imidazolium ionic liquid for cellulose processing has shown that it is comparable to the commercial NMMO which is used in the Lyocell process. The main contribution to environmental impact is, in both cases, the synthesis of the solvents (Righi et al. 2011).

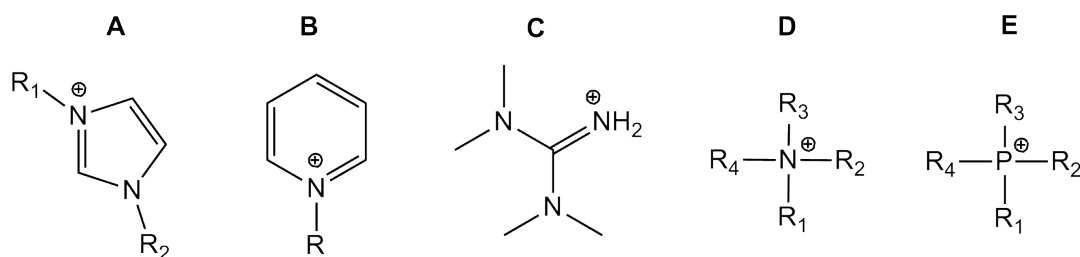


Figure 10. Technically relevant IL cations for cellulose processing: (A) imidazolium, (B) pyridinium, (C) tetramethylguanidinium, (D) ammonium, (E) phosphonium

The dissolution mechanism of cellulose in ionic liquids has long been argued to be all about hydrogen bond interactions. Several studies have confirmed that the anion of the ionic liquid penetrates the native cellulose structure and disassembles it by means of competitive hydrogen bonding (Zhang et al. 2005; Remsing et al. 2006; Zhang et al. 2010). The bonding patterns depend on which anion that is used. Some, like acetate, can bond not only to one but possibly to two sites along the cellulose chain (Rabideau et al. 2014). Others, like chloride, have instead been suggested to interfere with the cellulose disintegration mechanism and actually hinder further dissolution by bridging between two adjacent cellulose chains (Youngs et al. 2011).

The picture is not as clear for cations. Recent studies on the imidazolium cation have explained, in detail, the effect of cation asymmetry and show effects on glass temperature, viscosity and ion mobility (Zheng et al. 2011). Although the common view now is that it is the anion that is mainly responsible for the



dissolution of cellulose, the number of carbons in the alkyl chains of the imidazolium cations actually influences the dissolution ability of the corresponding ionic liquid. Longer alkyl chains in the cation leads to a decreased cellulose solubility (Swatloski et al. 2002; Vitz et al. 2009). The most peculiar influence is the odd-even effect of the cation alkyl chain length, in which odd numbers of carbons (3, 5) gives a less effective ionic liquid cellulose solvent than the corresponding cation with even numbers of carbons (2, 4 or 6), at least if chloride is used as the anion (Vitz et al. 2009). This odd-even effect can also be observed in other contexts, due to odd or even numbers of many different types of structural units such as CH<sub>2</sub> groups, metal atoms, or other more complicated units (Tao and Bernasek 2007). For example, solubility and molar Gibb's free energy of dicarboxylic acids in water have been shown to vary according to an odd-even pattern (Zhang et al. 2013). Another example is surfactants that have varying abilities to emulsify organic salts depending on odd or even numbers of carbons in their aliphatic chains (Varghese et al. 2013).

It has also been argued that since the anion acts as a hydrogen bond acceptor, the cation might act as a hydrogen bond donor, possibly at the most acidic proton at C2 (Lu et al. 2014). It has been revealed that if position C2 in the imidazolium ring is substituted with a methyl group, cellulose dissolution is less efficient and solution viscosity is higher (Kosan et al. 2008). Nevertheless, the precise role of the cation is still debated. Recent computer aided research based on molecular dynamic simulations shows, in detail, the contribution of both cation and anion in the interaction between cellulose and ionic liquid (Rabideau et al. 2014). However, such data must be confirmed experimentally in order to be properly understood and implemented.

Cellulose regeneration from non-derivatizing solvents, such as ionic liquids, cannot be described merely as a reversed dissolution process. The first, most obvious reason is that the regenerated cellulose does not recrystallize to its native allomorph (cellulose I). Instead, it forms either non-crystalline, amorphous cellulose, or the more thermodynamically stable allomorph of cellulose II. Furthermore, the amount of antisolvent, for example water, that is tolerated in a dissolution step and in a regeneration step in order for cellulose to be dissolved, or stay in solution, can vary dramatically, at least for some ionic liquids. Hauru et al. have studied the regeneration of cellulose from several different solvent systems and have shown that while the ionic liquid tetramethylguanidinium acetate can tolerate only 4 % water in the dissolution step, 24 % of water can be added to a cellulose solution of the same solvent before any sign of regeneration is noted. In this case, a more hydrophobic anti-

solvent was suggested in order to facilitate cellulose regeneration in this system, for example a water-alcohol mixture (Hauru et al. 2012). The different steps in the regeneration process were explained simply as gelation, particle formation, and a stepwise removal of IL and water from the cellulose particles. A more detailed view of the molecular interactions in the regeneration step has been provided from molecular dynamic studies of cellulose in 1-butyl-3-methylimidazolium acetate, where it has been suggested that water added as an anti-solvent will withdraw acetate anions from cellulose by competitive hydrogen bonding with the effect that the exposed cellulose chain will form hydrogen bonds with other cellulose chains, resulting in precipitation (Gupta et al. 2013). It should be noted that the experimental study performed by Hauru et al. was conducted with 1 wt% cellulose, while the computational modeling by Gupta et al. was performed on 11.4 wt% cellulose in solution.

In addition to solvents, secondary solvents, or so called cosolvents, can be useful in cellulose processing. Cosolvents are nonsolvents in the sense that they do not participate in the actual dissolution to a significant degree. However, they can be added to a cellulose solution in large amounts without causing immediate coagulation. In some cases, the amount of cosolvent added to the solution can far exceed the amount of actual solvent (Rinaldi 2011). In contrast, nonsolvents can also be antisolvents, which have more detrimental effects and are more likely to be used to facilitate the precipitation of the cellulose product. The boundary between these two are, however, vague and depends on each specific solvent/cellulose system and on the mutual interactions of all components (Huo et al. 2013).

## 3 Materials and methods

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Below is a summary of the materials and methods used in the experimental work behind this thesis. For details on how each technique was implemented in the different studies, please see further information in the appended papers.

### 3.1 Solvent systems

The focus of this work was on imidazolium based ionic liquids, especially 1-ethyl-3-methylimidazolium acetate (EMIMAc), which has the advantage over most other ILs of being liquid at room temperature. The closely related 1-butyl-3-methylimidazolium chloride (BMIMCl) was also used for some experiments. The cosolvents used were 1-methylimidazole (MIM), dimethylsulfoxid (DMSO) and N,N-dimethylacetamide (DMAc). These solvents are depicted in Figure 11. Suppliers and purity are provided in the individual papers.

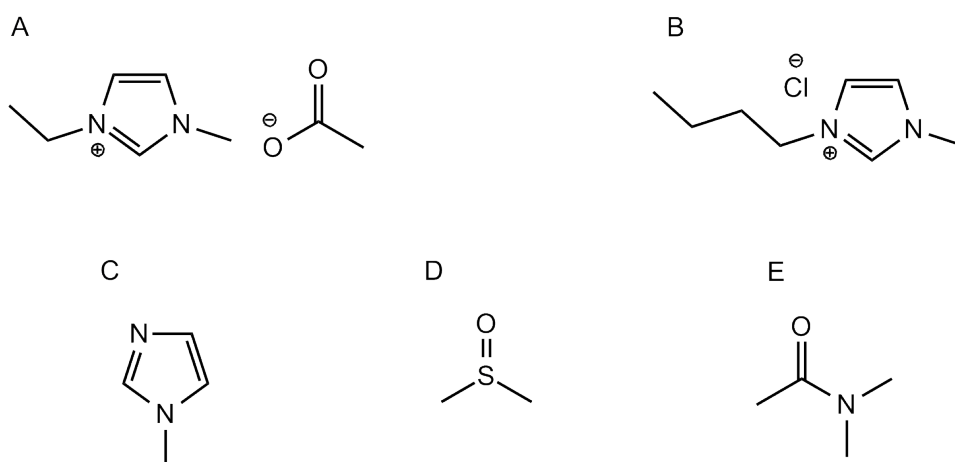


Figure 11. Solvents (A-B) and cosolvents (C-E) used in the included studies: (A) EMIMAc, (B) BMIMCl, (C) MIM, (D) DMSO, (E) DMAc.

## 3.2 Cellulose sources

Microcrystalline cellulose (MCC, Avicel PH-101) with high purity and low molecular weight was used in Papers I through IV. Two different dissolving grade pulps were used; pre-hydrolysis Kraft Eucalyptus pulp from the Bahia mill in Brazil (denoted hardwood pulp, HWP) was used in Papers I, II and IV, and sulfite Eucalyptus pulp from the Sappi Saiccor mill in South Africa was used in Paper V, as well as sulfite spruce pulp from the Borregaard mill in Norway (denoted softwood pulp, SWP) used in Paper I.

## 3.3 Dissolution of cellulose

The solubility of cellulose in different solvent systems was determined by using a number of techniques, including turbidity measurements, light microscopy and a Focused Beam Reflectance Measurement (FBRM) probe. All of these techniques measure particles on the micrometer scale, which means that only “macroscopic” dissolution can be determined. Dynamic and static light scattering experiments are necessary in order to determine if the polymers are actually molecularly dispersed in a solvent.

### 3.3.1 KF titration

Volumetric Karl Fischer (KF) titration (Metrohm Titrando 890) was performed in order to quantify the water content of the hygroscopic ionic liquids, with and without added water.

### 3.3.2 Turbidity - solubility

The turbidity of cellulose solutions was estimated using light absorbance measurements in a UV/vis spectrometer (Agilent 8453, G1103A), at three different wavelengths, 800, 825, and 849 nm. At these wavelengths, no actual molecular absorbance takes place. Consequently, it could be assumed that all apparent absorbance was actually light scattering from non-dissolved particles, and the turbidity could be calculated according to Equation 1.

$$\tau = Abs \cdot \frac{\ln 10}{L} \quad \text{Equation 1}$$

$\tau$  denotes turbidity,  $Abs$  denotes apparent absorbance and  $L$  denotes the length of the cuvette. By preparing a calibration curve for cellulose dispersed in each cosolvent that was going to be examined, it was possible to estimate the

solubility of the cellulose in each binary solvent system including each particular cosolvent. Calibration curves were prepared with microcrystalline cellulose particles, and cannot be translated to comprise the solubility of fibers, since the shape and light scattering ability of fibers and MCC is very different. The calibration curves for the cosolvents MIM, DMSO and DMAc are shown in Figure 12.

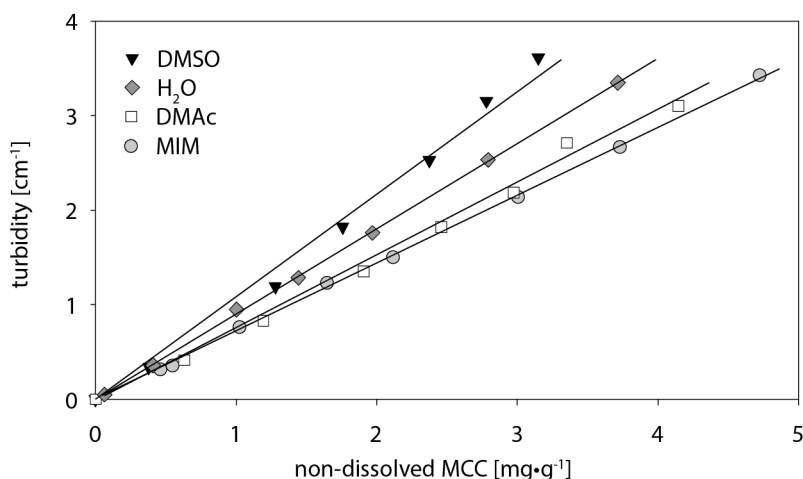


Figure 12. Calibration curves for MCC dispersed in cosolvents.

### 3.3.3 Light microscopy

Micrographs of selected solutions/ dispersions were captured with a Zeiss Discovery V12 microscope using a Canon Powershot G9 camera mounted on a Zeiss universal digital camera adapter d30 M37/52x0.75.

### 3.3.4 Rheology and viscometry

Oscillatory and rotational shear viscometry and/or capillary viscometry was used for further characterization of the solutions. Polymer solutions and gels are viscoelastic materials and do not behave as Newtonian fluids nor as Hookean solids under mechanical stress, but rather as a combination of the two. The two simplest models of this behavior are the Kelvin-Voigt and Maxwell spring and dashpot models depicted in Figure 13. In general, a dilute polymer solutions behaves more like a fluid, and a concentrated polymer solution, or a gel, behaves more like a solid.

One very important consequence of the viscoelasticity of polymer melts and solutions is their tendency to reduce their viscosity during shear, a behavior known as shear thinning. In a Newtonian fluid, viscosity is independent of shear rate, whereas in a polymer solution the molecules will align under shear

and the viscosity decreases. This is important in many process considerations, e.g. mixing and pumping. Viscoelastic data, if not stated otherwise, was collected with a Bohlin Instruments CS50 rheometer equipped with a 4°/4 mm cone and plate measuring system. The samples were analyzed in a closed container to avoid moisture uptake. Temperature has a major impact on viscosity, and therefore, was carefully selected for each sample series.

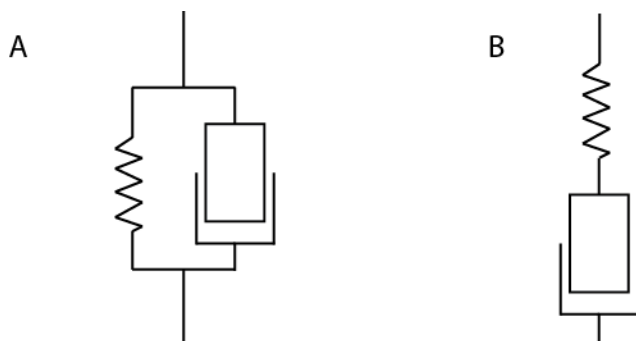


Figure 13. Spring and dashpot models of viscoelastic materials by Kelvin and Voigt (A) and Maxwell (B).

Capillary viscometry is always performed on very dilute solutions to avoid polymer entanglement. The purpose of this method is to determine the interaction between solvent and polymer by estimating the hydrodynamic radius of a single polymer molecule in solution. A good solvent will swell the polymer a lot, while a poor solvent will not. The time it takes for a polymer solution to flow in a capillary is recalculated to intrinsic viscosity by assuming  $t_s/t_0 = \eta_s/\eta_0$ , where  $t$  denotes efflux time and  $\eta$  denotes viscosity, and  $s$ -values represents the solution data, and zero-values represents the solvent data. The relative viscosity,  $\eta_{rel}$ , is equal to this ratio. The inherent viscosity,  $\eta_{inh}$ , is the relative viscosity divided by the polymer concentration. By plotting the inherent viscosity versus polymer concentration and extrapolating to zero, the intrinsic viscosity  $[\eta]$ , which corresponds to the hydrodynamic radius of the polymer divided by its molecular weight, can finally be calculated.

### 3.3.5 Focused Beam Reflectance Measurement

The dissolution rate was studied in situ in Paper II, using a Focused Beam Reflectance Measurement probe (FBRM G600, Mettler Toledo). It works by tracking the number of particles in a solution as a function of time, as illustrated in Figure 14. The probe collects data in a narrow volume immediately in front of its tip where the laser beam is in focus, in real time. An averaged particle size

distribution can be delivered at selected intervals. For fast processes like microcrystalline cellulose dissolution in EMIMAc/MIM, this is every 2 to 3 seconds. Since the FBRM probe measures chord length distribution, the actual meaning of the data can be complicated to interpret quantitatively in the case of needle-like particles like cellulose crystals, assuming some measurements will be along the particle and some will be across it. Identical data processing for all samples must be ensured, and the results cannot be quantitatively compared to spherical particles.

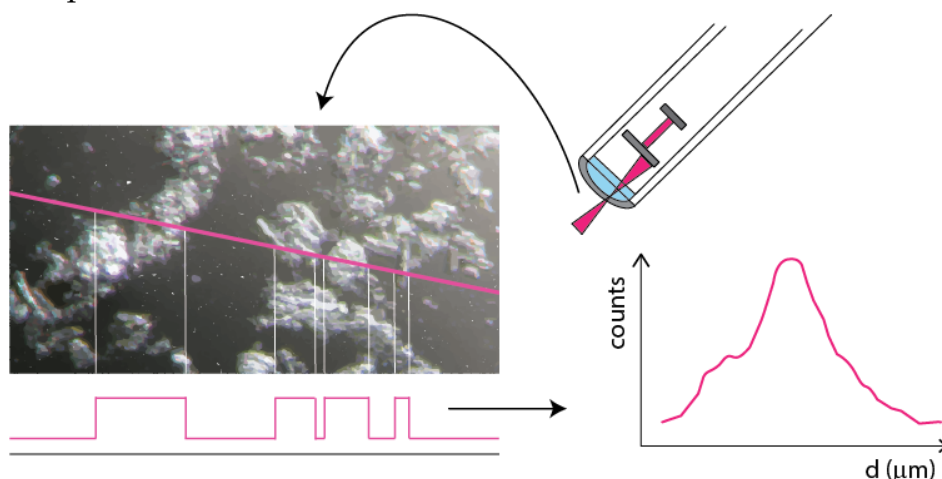


Figure 14. Simplified model of how the FBRM probe works: The rotating focused laser beam detects particle edges as chord lengths in the range of 1 – 1000  $\mu\text{m}$  by light reflectance. For a collection of particles, the chord length (particle size) distribution can be monitored in real time.

### 3.4 Cellulose derivatization

Homogeneous esterification of cellulose in ionic liquids has recently gained interest, and new synthetic routes have been explored. It has been proposed that, due to their good dissolution properties, the use of ionic liquids can aid in controlling the degree of substitution in for example acetylation and tosylation reactions, through the use of various ionic liquids, reaction conditions and reactants (Wu et al. 2004; Granström et al. 2008; Cao et al. 2009). Unlike in DMAc/LiCl solutions, no catalyst seems to be needed. By first dissolving the native cellulose in an ionic liquid and then adding the reagent, e.g. the acyl chloride or anhydride of the desired ester, the reaction becomes homogeneous rather than heterogeneous. So far, the most successful solvents for this purpose have been those ionic liquids with a chloride anion. Ionic liquids with an acetate anion as in EMIMAc are generally not preferred. This is because, in many cases, the acetate reacts with the cellulose as well, and interferes with the intended

esterification so that the reaction yields cellulose acetate, or at least a mixed result, no matter which ester that was intended (Köhler et al. 2007).

In the appended Paper III, esterification was performed in a binary solvent, using EMIMAc and two different cosolvents, in order to avoid, or at least control, undesired acetylation.  $^1\text{H}$  NMR spectra of two such esters, cellulose acetate and cellulose acetate propionate prepared in EMIMAc/MIM (1:1), are shown in Figure 15. Cellulose was first dissolved in the binary solvent, heated to the desired temperature and then mixed with anhydride. Time, temperature, the molar ratio of reagent and the relative amount of cosolvent were varied. After the reaction was completed, the resulting material was precipitated in methanol. All samples were washed and dialyzed in deionized water to remove any remaining solvent or reagent, and the final product was freeze dried before analysis.

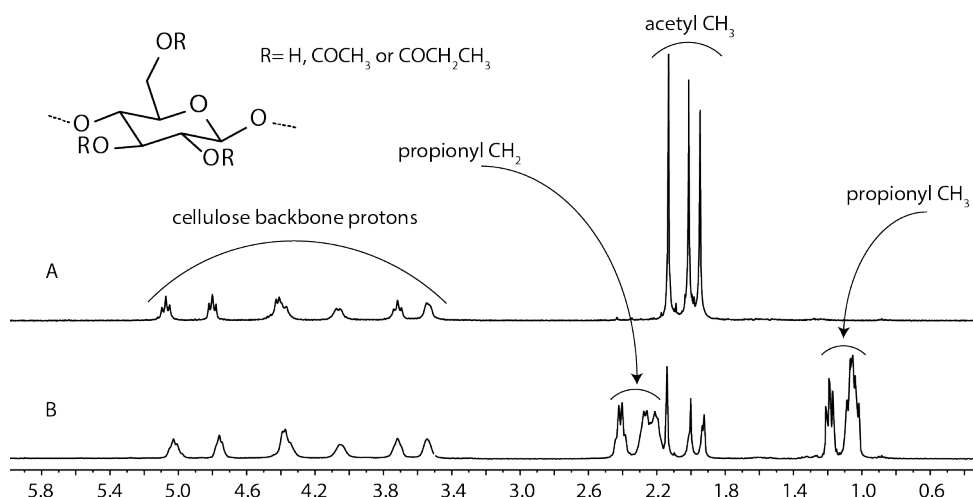


Figure 15. Cellulose acetate (A) and cellulose acetate propionate (B), the latter is a common result from trying to propionate cellulose in EMIMAc, in which the acetate ion from the solvent interferes with the desired reaction.

### 3.5 Experimental design

Design of experiments and interpretation of data for the cellulose derivatization were done using the software MODDE 9.1 (Umetrics). A reduced factorial design with four parameters (time, temperature, reagent/cellulose ratio and cosolvent/IL ratio) was set up using DMSO and MIM as cosolvents. The experiments were then conducted according to the MODDE design, and the impact of the different parameters was evaluated.



### **3.6 Regeneration of cellulose**

A cellulose solution can simply be poured into an anti-solvent such as water, and it will coagulate. The solvent will diffuse out of the material and end up in the surrounding liquid, and a regenerated cellulose material will have been produced. However, this method provides very little control over the regeneration process or the resulting material. The size, thickness and shape of the regenerated material is much more easily manipulated by using thin film preparation or fiber spinning.

Regenerated cellulose films were prepared in Papers I and V. In Paper I, the technique was very simple; cellulose solutions were poured onto a plastic surface and then covered with water until coagulation. In Paper V, a known amount of cellulose solution was pressed between glass plates to form a disc of controlled shape and weight before coagulation.

Regenerated cellulose textile-like fibers were produced in Paper II and IV. Two techniques were used; traditional wet spinning like in the Viscose process, and airgap spinning like in the Lyocell process. Both were done on a lab scale extruder modified to suit the selected technique. As the name implies, wet spinning means that the polymer solution is extruded directly into the coagulation bath which is filled with a liquid, usually water, that behaves as a solvent towards the polymer solvent and as an anti-solvent towards the polymer. In airgap spinning, which is a modified version of wet spinning, there is a small distance, called airgap, between the spinneret and the coagulation bath. Traditional wet spinning works best for spin dopes with lower viscosity while airgap spinning is used for high viscosity solutions. The spinning setups are described in detail in the appended papers. Part of the equipment, in the airgap spinning mode, is shown in Figure 16. As the spin dope, in the shape of the newly extruded fiber, comes in contact with the anti-solvent there is a two way mass transfer: the solvent which is contained in the spin dope diffuses towards the anti-solvent, and, at the same time, the anti-solvent diffuses towards the interior of the fiber. The formation of an outer, denser, gel surface (skin or shell) slows down the coagulation mechanism of the inner filament portion (core), due to the decrease in diffusion rate. This can create a more or less porous structure with randomly distributed voids as the fiber is formed (Andreoli and Freti 2004). By adjusting the speed of the take up rolls, different amounts of stretch can be applied to the newly formed fibers, causing their diameter and mechanical properties to change. This approach was used in Paper II with good results on stiffness, elongation and strength.

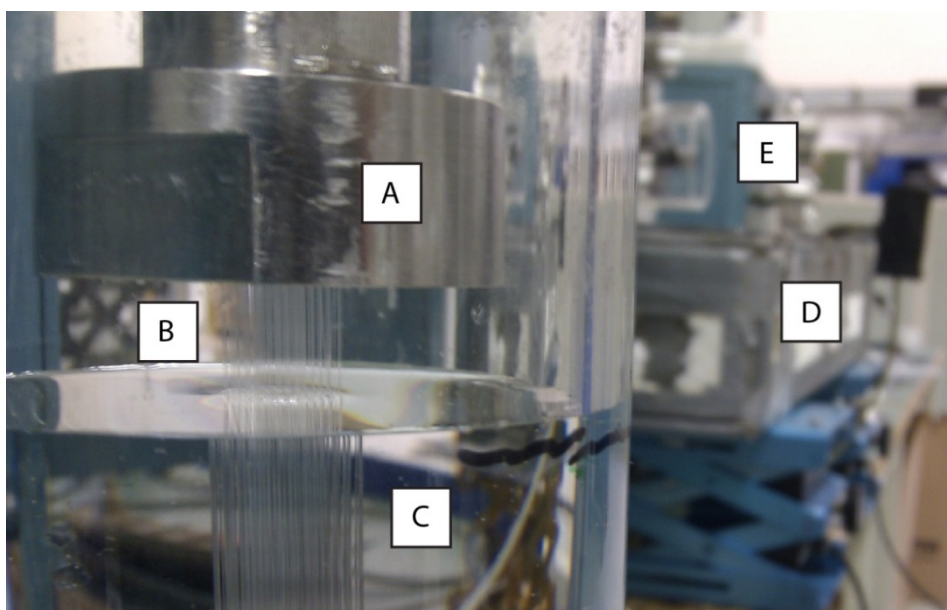


Figure 16. Detail of the spinning equipment used in Paper II, set to airgap spinning. The spinneret (A) and fibers in the airgap (B) and the coagulation liquid (C) are clearly visible in the foreground. In the background is the washing baths (D) and take-up roll (E).

### 3.7 Characterization of regenerated material

A number of different techniques were used in order to characterize the materials that were prepared in this thesis. Below is a short summary, and further information is provided in the appended papers.

#### 3.7.1 GPC

Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC), is used to determine the molecular weight distribution of a polymer such as cellulose. In this process, a dilute solution of the polymer is pushed through a column of porous material where large polymers exit first, while smaller polymers have a tendency to get trapped within pores and reach the detector later. Common detectors are based on refractive index (RI), viscometry and light scattering. Since no cellulose standards are available for calibration of the detectors, standard polymers of pullulan are common. However, since these standards have different molecular structures than cellulose, the quality of the quantitative MW data from such calibrations can be questioned. A combined detector system that includes multi-angle laser light scattering (MALLS) and RI is preferred to obtain the true molecular weight distribution without the use of a standard curve. The cellulose solvent and eluent was DMAc/LiCl in the GPC experiments, which were carried out using

a set of three columns, PLgel Mixed A (300x7.5mm) with a guard column (Polymer Laboratories Ltd.) and analyzed using a refractive index detector HP 1047 (Hewlett-Packard).

### 3.7.2 Fiber tensile testing

The mechanical performance of regenerated textile fibers was analyzed on bundles (Paper IV) or on single filaments (Paper II). By pulling the fiber(s) at a controlled rate, thereby applying a controlled *strain* and measuring the *stress*, a so called stress-strain curve, such as the one seen in Figure 17, can be constructed. Stiffness, strength, and elongation of the fiber can be derived from this curve. In order to calculate the tenacity, which is the standard measure of strength in a textile fiber, the linear density must also be determined. This is defined as mass per length, in grams per 10000 meters of fiber for the standard unit *tex*, and as grams per 9000 meters for the similar *denier* definition.

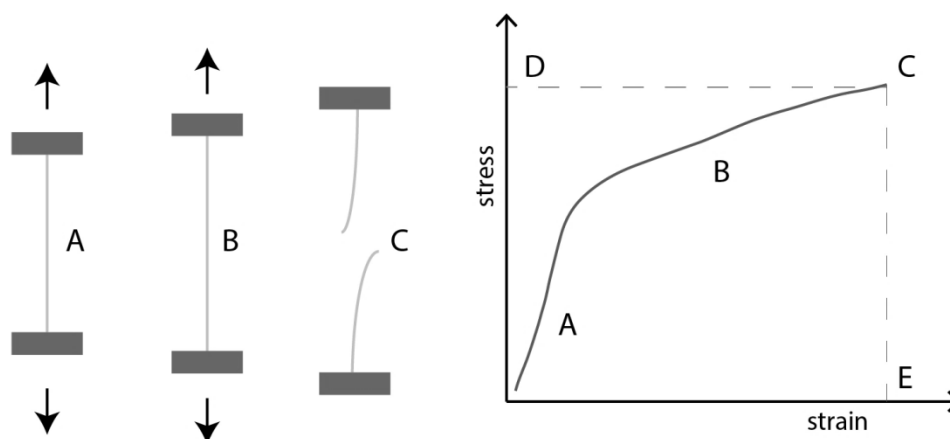


Figure 17. Tensile testing of fiber, clamped and pulled until the breaking point, and the resulting stress – strain curve. The initial part of the experiment (A) gives a slope of the curve that represents the stiffness of the fiber. Then the fiber is further pulled (B) until the breaking point (C), the values for tenacity (D) and elongation at break (E) are extracted.

The tensile testing of fibers (Paper II) was carried out on a Vibroskop/Vibrodyn instrument (Lenzing Technik GmbH & Co KG), and the tensile testing of fiber bundles (Paper IV) was carried out on a Zwick Roell 2.5Z tensile tester.

### 3.7.3 NMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy includes a range of powerful techniques to analyze the environment of an NMR active nucleus, such as a proton ( $^1\text{H}$ ) or a carbon ( $^{13}\text{C}$ ). The work included in this thesis relied on

standard  $^1\text{H}$  NMR spectroscopy for analyzing dissolved cellulose derivatives (Paper III), solid state CP/MAS  $^{13}\text{C}$  NMR spectroscopy for determining cellulose crystallinity (Papers I, II and V) and NMR cryoporometry for monitoring the pore size distribution of regenerated cellulose (Paper V). Experiments, instrumentation and setups are described in detail in the appended papers.

#### **3.7.4 SEM**

Scanning electron microscopy (SEM) was used in Paper IV to obtain a good visual representation of the surface and cross section of the wet spun regenerated fibers. By using this technique, the physical appearance of features down to the nanometer range could be monitored. All samples were sputtered with a thin layer of gold before analysis on the Leo Ultra 55 FEG Scanning Microscope.

#### **3.7.5 Ion chromatography**

For the cellulose derivatives in Paper III, the samples were hydrolyzed in 72 %  $\text{H}_2\text{SO}_4$  according to a standard procedure developed for carbohydrate component analysis (Theander and Westerlund 1986). The hydrolysates were analyzed for anions using ion chromatography (IC) in aqueous  $\text{Na}_2\text{CO}_3$  (3.6 mM) at 45 °C on a Metrohm 850 Professional IC Anion MCS equipped with a Metrosep A Supp 7 column, using the MagIC Net 3.0 software. The acetate- and propionate signals were quantified using acetate and propionate standards (Sigma Aldrich).

## 4 Cellulose in IL and water

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*This chapter is based on Paper I.*

When producing regenerated cellulose via the direct dissolution route, as is the case when using ionic liquids, the solvent is mixed with the coagulation medium (often water) in the precipitation step. The regenerated cellulose is collected in its desired shape and the water/solvent mixture is separated and recycled, see Figure 18. Some water can be removed from the ionic liquid by means of partial phase separation using  $K_3PO_4$  to bind the water before the enriched ionic liquid phase can be collected and further purified by evaporating the water (Gutowski et al. 2003). Due to the hygroscopic nature of ionic liquids and the relatively high boiling point of water, this step entails high energy costs in a large scale application. Understanding the effect of the water that remains in the ionic liquid is, therefore, fundamental.

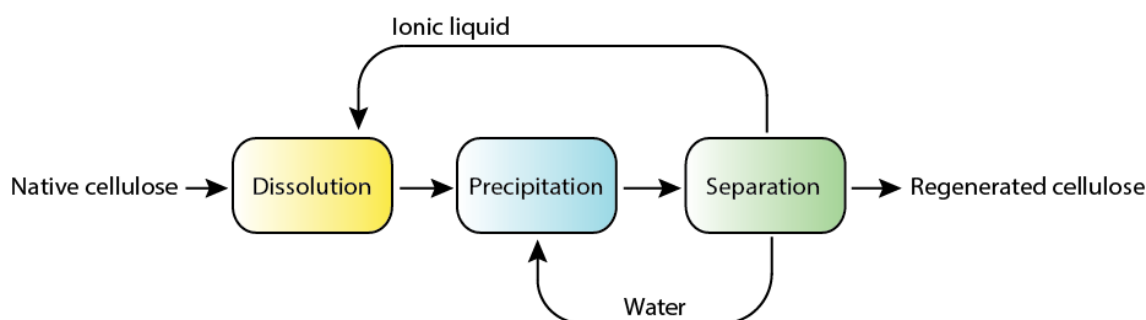


Figure 18. Simplified scheme of the direct dissolution and subsequent precipitation of cellulose in a closed-loop process. Note that both solvent (ionic liquid) and coagulation medium (water) are recycled and reused.

## 4.1 Influence of water on cellulose dissolution

The solubility of commercial microcrystalline cellulose and two different dissolving grade cellulose pulps in EMIMAc/water binary solvent mixtures was investigated using microscopy and turbidity.

The micrographs in Figure 19 show 2 wt% cellulose solutions/dispersions in a binary mixture of EMIMAc and water containing 10 wt% water. In this case, the pulp samples (both softwood pulp and hardwood pulp) show residual non-dissolved material in the form of swollen fibers while the microcrystalline cellulose has clearly been completely dissolved.

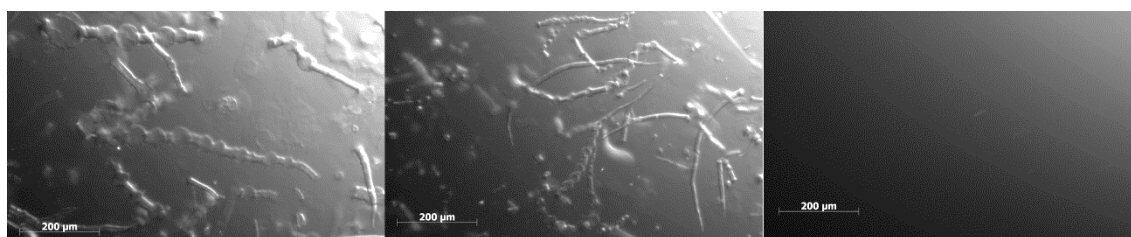


Figure 19. Micrographs showing 2 wt% soft wood pulp (left), hard wood pulp (center) and MCC (right) in EMIMAc containing 10 wt% water. A significant number of non-dissolved but ballooning fibers are found in the pulp samples, while the MCC has been completely dissolved.

The swelling in the two dissolving pulps can be seen to take place in the form of ballooning, which indicates that the solvent is not very efficient. In fact, according to the definition in Chapter 2.2, the dissolution was changed from Mode 1 dissolution to Mode 3 dissolution by the addition of water. In pure EMIMAc and other good cellulose solvents, this phenomenon is not noticed. Instead, dissolution takes place by immediate disintegration and the fibers never go through this state. No particles were visible in the MCC sample, and if they had been visible they would not have been seen in the shape of balloons, since ballooning is only seen in fibrous material (Cuissinat et al. 2008).

Additional micrographs can be found in the appended Paper I and in the electronic supplementary material that accompanies the article. There, it can be seen that MCC samples only show some residual solid material at 15 wt% water concentration in the solvent at 2 wt% cellulose content. For solutions with higher cellulose concentrations, the amount of water that can be tolerated declines for all different cellulose types.

Turbidity measurements show a similar result; microcrystalline cellulose forms turbid solutions only in EMIMAc with high water content, while the pulp samples are much more sensitive to water contamination. A summary of

turbidity measurements is shown in Figure 20 for MCC and HWP samples. The turbidity of SWP in water and EMIMAc was very similar to that of HWP.

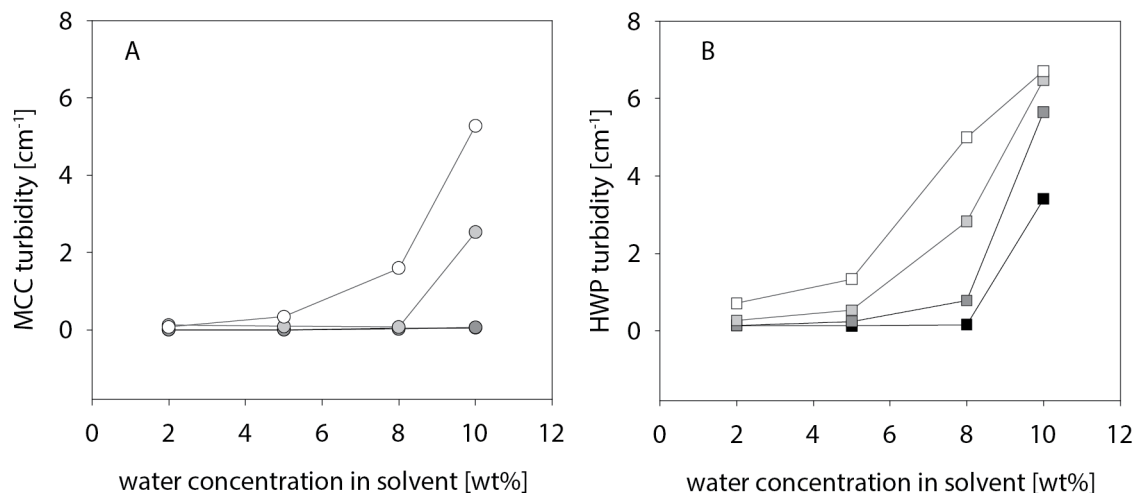


Figure 20. Turbidity of solutions as a function of water content in the EMIMAc/water binary solvent; A is MCC and B is HWP. Symbol color denotes cellulose concentrations according to: black = 2 wt%, dark grey = 5 wt%, light grey = 8 wt%, white = 10 wt%.

Light microscopy and turbidity measurements are only valid for solubility estimations on the macroscopic scale. These techniques, alone, are not sufficient for investigating if, and how, polymers aggregate on the molecular level. In order to determine if and how polymers aggregate on the molecular level, static and/or dynamic light scattering and intrinsic viscosity measurements are preferred, and have, to some extent, been used in previous research (Kuzina et al. 2010; Le et al. 2012). However, these techniques usually demand dilute solutions, and, consequently, the effect of cellulose concentration is difficult to investigate. In this work, rotational and oscillatory rheology was used instead. Figure 21 shows the results from some of these studies on MCC. In Figure 21A, it can be noted that the viscosity of relatively concentrated cellulose solutions (10 wt%) decreased if a moderate amount of water (5 wt%) was added to the EMIMAc solvent. For the sample with 10 wt% water in the solvent, the sample no longer displays a Newtonian plateau at low shear rates. Instead, a shear thinning behavior throughout the measurement, much like in a suspension, was observed. A decrease in solvent preference for the polymer in the presence of water should be reflected in a more contracted polymer conformation, or even aggregation between polymer chains, leading to an increased amount of free solvent and a lower viscosity. The same type of result is shown in Figure 21B for  $\tan(\delta)$  values derived from the elastic and viscous moduli ( $G'$  and  $G''$ )

obtained from oscillatory measurements of the same samples. In that figure, the viscous contribution to the material properties is the largest in the sample with 5 wt% water in the solvent, whereas the sample with 10 wt% water in the solvent behaves like a gel with a typical plateau at lower frequencies.

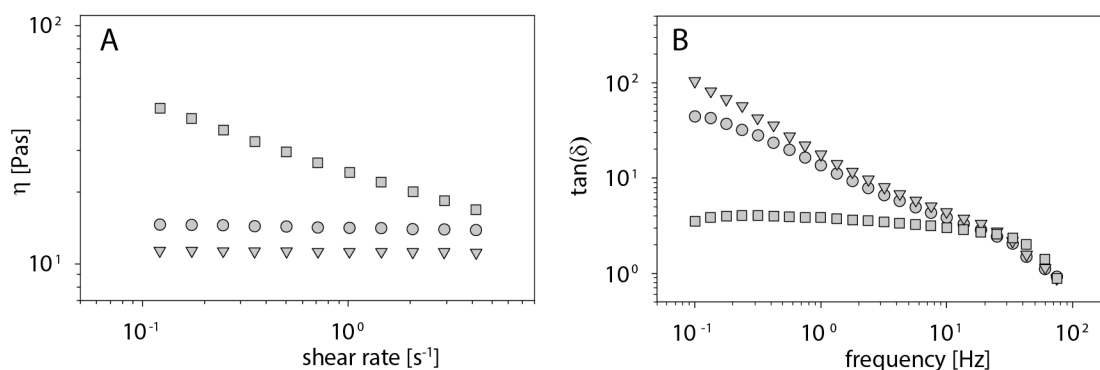


Figure 21. Flow curves at low shear rates (A) and  $\tan(\delta)$  as a function of frequency (B), for 10 wt% MCC solutions in different amounts of water in the EMIMAc/water binary solvent: circles 0 wt%, triangles 5 wt% and squares 10 wt%.

A similar tendency can be noticed in the HWP solutions in Figure 22, although not as clear as in the case of MCC. The viscous contribution to the flow characteristics clearly dominates in the 2 wt% and 5 wt% HWP samples, regardless of water content (0 or 10 wt%), while a gel-like behavior is observed in the 8 wt% HWP samples in the presence of 10 wt% of water.

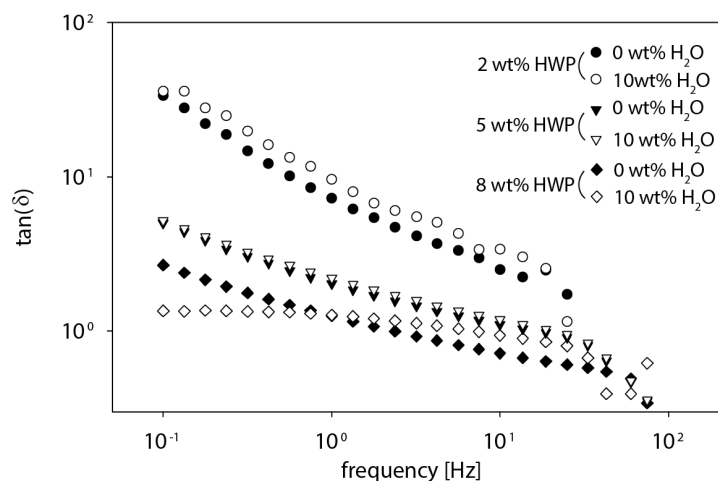


Figure 22.  $\tan(\delta)$  as a function of frequency, cellulose concentration and water concentration in EMIMAc for HWP samples measured at 50 °C.



As indicated by the micrographs and the turbidity data in Figure 19 and Figure 20, HWP shows incomplete dissolution in EMIMAc that contains 10 wt% water, even for the samples with only 2 wt% pulp. Several different effects are introduced as the water content increases. For example, more water will lead to a decrease in overall solvent viscosity and possibly an increase in the mobility of dissolved cellulose below the overlap concentration of the polymer. More water will also lead to a decrease in the number of accessible ILs, leading to a decrease in the solubility of the cellulose. A result of this is that some of the cellulose will not be perfectly dissolved, and, consequently, fewer polymers will be involved in entanglements. This will lead to a decrease in the viscosity of the system. At the same time, non-dissolved particles can act as fillers which, instead, increase the viscosity of the system, at least at higher cellulose concentrations. Furthermore, if some dynamic effects are assumed, like rearrangements of IL-cellulose-water interactions over time, it can be expected that dissolved cellulose may re-aggregate chain-to-chain at higher water contents, i.e. without a surplus of IL. This may lead to a sort of physically cross-linked gel like structure and again an increase in viscosity.



## 5 Cellulose in IL and organic cosolvents

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*This chapter is based on Paper II and Paper III.*

Mixed solvent systems provide further possibilities for cellulose processing. The addition of a cosolvent might lower the viscosity of a solution and thereby facilitate a fast dissolution rate and overall ease of handling. Mixtures of ionic liquids and organic solvents include BMIMCl in 1,3-dimethyl-2-imidazolidinone (DMI) which, owing to its low viscosity, allows for efficient mixing and without agglomeration. This system is claimed to dissolve 10 % cellulose (Avicel) within a few minutes at 100 °C (Rinaldi 2011). This behavior is explained by the fact that only a fraction of IL in a proper molecular solvent can shift the solvatochromic Kamlet Taft parameters  $\alpha$ ,  $\beta$  and  $\pi^*$  to the point at which the cellulose is dissolved. Remsing and co-workers have studied the molecular interactions of BMIMCl in water and DMSO, respectively, and have found that while water completely solvates the ions already at low concentrations, high density clusters of ionic liquid were found even at concentrations as low as 10 %. The poor interaction between ions and DMSO thereby showed suggests that DMSO can be used as a rather inert cosolvent, leaving the ionic liquid intact to act as a solvent (Remsing et al. 2008).

Homogeneous reactions as a route to adding functionality to the reactive cellulose hydroxyl groups provides better control of the total degree of substitution and substitution pattern since each part of the cellulose is, at least in theory, exposed to reagents and solvent. Some unexpected results in ionic liquids have been observed, for example spontaneous acetylation of cellulose when using EMIMAc as a solvent (Köhler et al. 2007). This was first discovered as a surprising side reaction in the ionic liquid EMIMAc when, in fact, the goal

was to react cellulose with acid chlorides, trityl chlorides and tosyl chlorides. The resulting polymer was acetylated, meaning that parts of the solvent, the acetate anions of the IL, were consumed. In large scale applications this might turn out to be a serious problem, since recycling of the solvent requires that it does not degrade or react during the process. Not only will the recycling become more complicated due to side products, it will also be incomplete. In large scale applications, recycling of the solvent is necessary for both economic and environmental reasons (Ebner et al. 2008).

### 5.1 Dissolution of cellulose in EMIMAc and cosolvents

The four different molecular solvents in Figure 23 were evaluated as cosolvents: 1-methylimidazole (MIM), dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc) and water (H<sub>2</sub>O). Of these, only the first three can be regarded as non-solvents, and were evaluated in Paper II. The fourth can be regarded as an antisolvent, see Chapter 2.3.

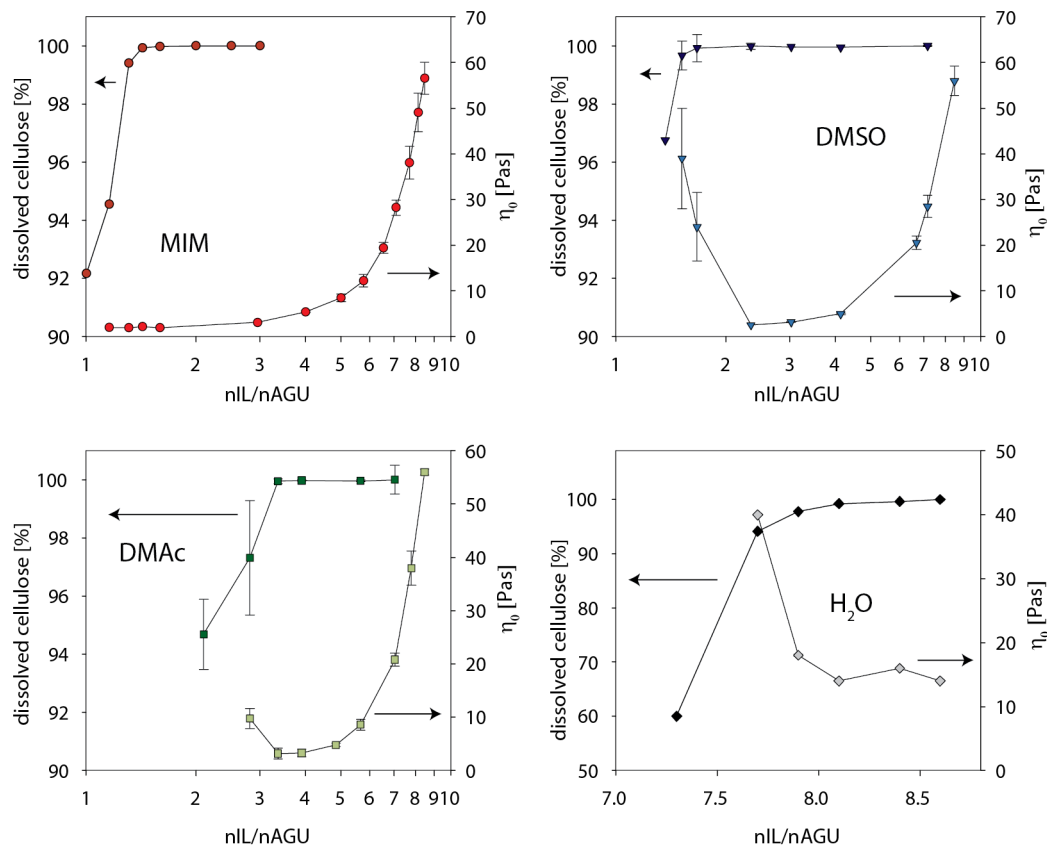


Figure 23. Effect of different cosolvents on the solubility and zero shear viscosity of 10 wt% cellulose (MCC) solutions. Viscosity was measured at 30 °C for all solutions except the one with water, which was measured at 50 °C. Note that the H<sub>2</sub>O plot has a different scale on the x-axis.

MIM was found to be a good cosolvent candidate in combination with EMIMAc, based on the viscometry and solubility data confirmed using light microscopy (Figure 24). Additional experiments were conducted using this cosolvent. For MCC in EMIMAc and MIM, only as little as 9 mol% EMIMAc in the binary solvent mixture ( $x_{IL} = 0.09$ ), corresponding to a molar ratio  $n_{IL}/n_{AGU}$  of 1.43, was needed to dissolve 10 wt% cellulose. Interestingly, when using MIM together with BMIMCl as the active solvent component, MCC was not soluble in BMIMCl/MIM until the molar fraction of ionic liquid in the solvent reached 50 % ( $x_{IL} = 0.5$ ), corresponding to a molar ratio  $n_{IL}/n_{AGU}$  of 5.7 for the 10 wt% cellulose samples. This result was valid regardless of temperature, in the range from 50 °C to 110 °C. For this reason, BMIMCl was discarded from further study.

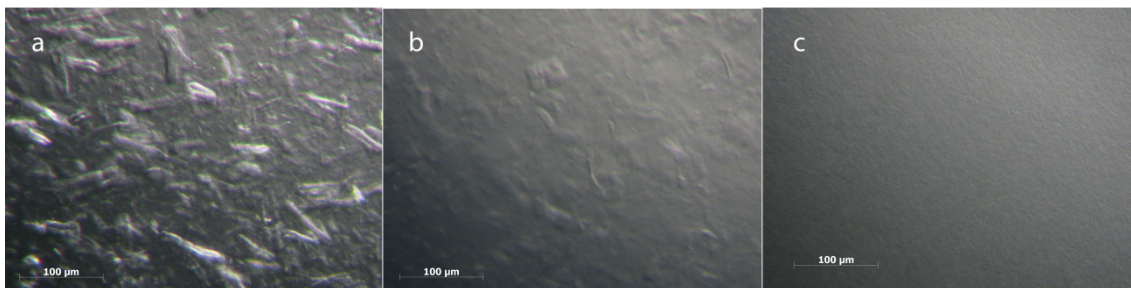


Figure 24. Micrographs showing the transition from the non-dissolved to the dissolved state of 10 % MCC with an increase in the IL ratio from a)  $n_{IL}/n_{AGU} = 1.16$ ;  $x_{IL} = 0.07$  to b)  $n_{IL}/n_{AGU} = 1.31$ ;  $x_{IL} = 0.08$  and c)  $n_{IL}/n_{AGU} = 1.43$ ;  $x_{IL} = 0.09$ .

Intrinsic viscosity describes the volume of the polymer chain in the solvent and is inversely proportional to the overlap concentration. This was used to follow the polymer conformation in the binary solvent EMIMAc/MIM. Cellulose concentrations around 1 % are stated to be well below the overlap concentration and, therefore, were used in order to avoid polymer - polymer interactions that could influence the result. Owing to instrument limitations only solvent mixtures with EMIMAc contents of up to 60 % in the solvent could be used. All binary solvent mixtures with more EMIMAc had a viscosity that was too high to be measured in the equipment. The intrinsic viscosity of dissolved MCC increased with an increased amount of EMIMAc in the binary solvent mixture over the entire range of solvent compositions ( $x_{IL} = 0.1 - 0.6$ ). This was interpreted as an increase in polymer - solvent interaction. This means that even if dissolution occurs at an EMIMAc/AGU ratio of 1.4 for the 10 wt% solutions in Figure 23, there is still some difference in polymer conformation on the molecular level if the relative amount of IL increases beyond this point.

Dissolution of pulp is different from dissolution of MCC, which was also seen in the binary solvent system EMIMAc/H<sub>2</sub>O described in Chapter 4.1. In order to completely dissolve pulp, both hardwood (HWP) and softwood (SWP) dissolving grade pulp, a higher relative amount of EMIMAc is needed in the binary solvent mixture. For HWP, the limiting ratio was found to be around 2.4 mol EMIMAc per mol AGU while for SWP it was found to be at least above 3 mol EMIMAc per mol AGU (Bylin et al. 2013). This limiting amount of EMIMAc was not dependent on the cellulose concentration in the pulp samples, whereas it was in the MCC samples.

The impact of MIM on the dissolution rate was investigated using the FBRM probe which counts particles in situ during the dissolution process. The results are presented in Figure 25, both as raw data and as the calculated initial dissolution rate in three different solutions.

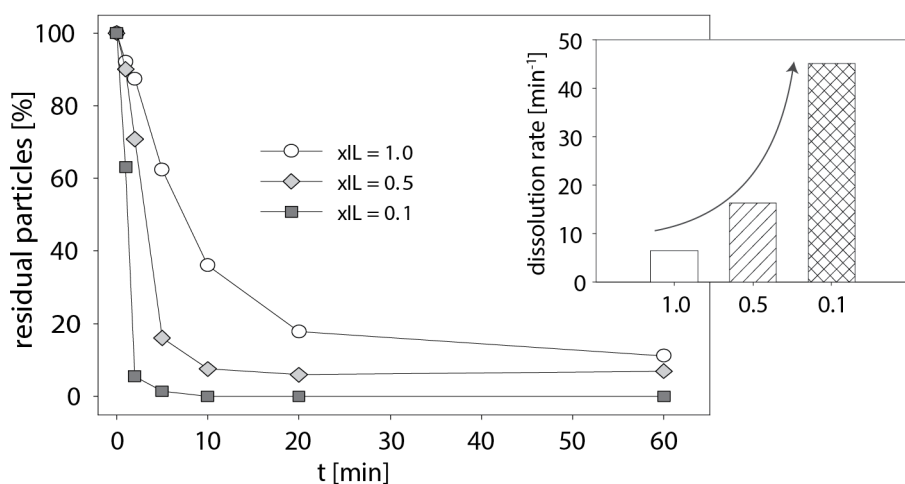


Figure 25. Dissolution rate of MCC in binary mixtures of EMIMAc/MIM at molar ratios  $x_{IL} = 1.0, 0.5$  and  $0.1$ , at  $30\text{ }^{\circ}\text{C}$ . The main plot shows FBRM data as particle counts over time while the inset depicts the initial slope of the three FBRM data curves.

The data is based on FBRM readings at  $30\text{ }\mu\text{m}$ , as this turned out to be the average particle size in the initial MCC particle size distribution in pure MIM. As shown in Figure 25, the dissolution rate could clearly be substantially increased using MIM as a cosolvent.

A small study on cellulose degradation in the EMIMAc/MIM solvent system was performed, and it was concluded that very little degradation, three percent or less, took place at mild temperature conditions.

## 5.2 Cosolvent facilitated in situ derivatization

The homogeneous reaction of cellulose with propionic anhydride in EMIMAc with and without a cosolvent was studied in Paper III. The experimental design included time, temperature, amount of reagent, and solvent composition. The relative degree of propionate over acetate substitution was calculated after ion chromatography of hydrolyzed products. The impact of the different parameters in the experimental design was calculated with the software MODDE 9.1. It was found that only two of the parameters that were varied in the experiments were significant, see Figure 26.

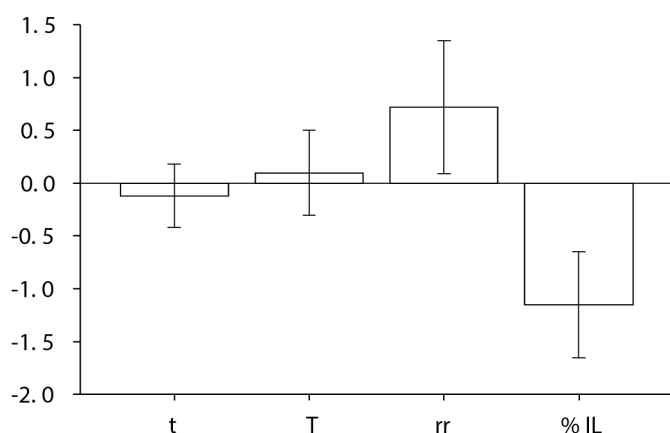


Figure 26. Impact on propionate degree of substitution for experiment parameters time (t), temperature (T), amount of reagent (rr) and solvent composition (% IL) according to MODDE. Only rr and % IL were significant, with rr positive and % IL negative.

The amount of reagent showed a positive correlation, and the solvent composition  $x_{IL}$  showed a negative correlation. This means that by increasing the amount of propionic anhydride reagent and decreasing the ratio of EMIMAc in the solvent mixture, the resulting product will have a higher propionate degree of substitution (DS).

The DS of propionate relative to the DS of acetate in the hydrolyzed products for both the sample series with DMSO and MIM as cosolvent are shown in Figure 27. It can be seen that all samples without a cosolvent ( $x_{IL} = 1$ ) had low propionate contents. For the samples prepared in 50 % EMIMAc and 50 % cosolvent ( $x_{IL} = 0.5$ ), the results were somewhat more varied, but nevertheless very low in propionate content. For samples prepared in 10 % EMIMAc and 90 % cosolvent ( $x_{IL} = 0.1$ ), the propionate content was much higher, and the propionate/acetate ratio was also clearly related to the amount of reagent that was added to the reaction mixture.

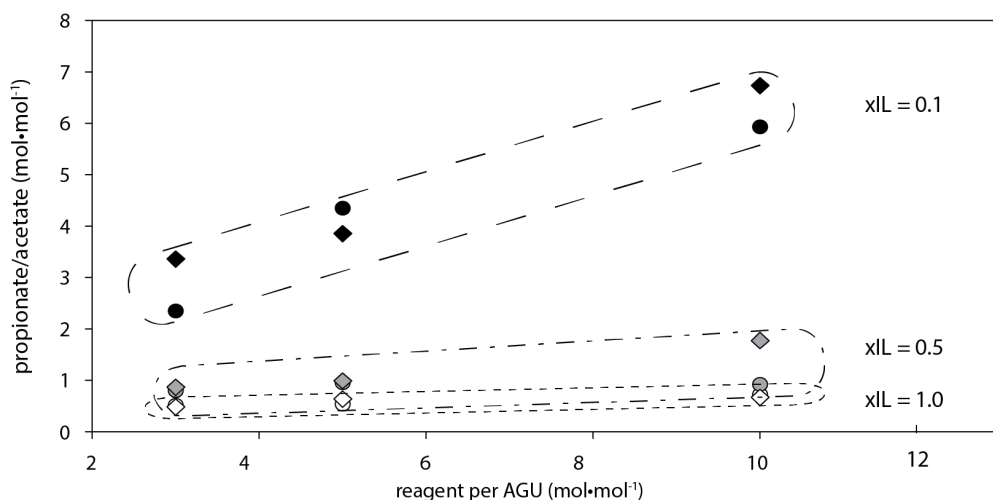


Figure 27. Amount of propionate, relative to acetate, in cellulose derivatives produced in EMIMAc/cosolvent. The xIL in the solvent is 0.1 (black), 0.5 (grey) and 1.0 (white) as a function of the molar ratio of propionic anhydride reagent per AGU. Dots represent samples with DMSO as cosolvent, diamonds represent samples with MIM as cosolvent.

The ion chromatography results were validated with <sup>1</sup>H and <sup>13</sup>C NMR spectrometry of unhydrolyzed samples. It was further found that both propionate and acetate appeared as three distinct peaks, showing the substituents covalently bound and evenly distributed at three different sites (C2, C3 and C6).

MIM is known to catalyze some reactions. For example, it has been found that MIM has an impact on the degree of substitution in the final product for trimethylsilylation of cellulose in imidazolium based ionic liquids (Köhler et al. 2008). Furthermore, in DMAc/LiCl, esterification of cellulose by carboxylic acid anhydrides is efficiently catalyzed by the analogous molecule imidazole (Nawaz et al. 2013). In Figure 27, there seems to be no major difference between using DMSO or MIM as the cosolvent in this case, which to some degree seems surprising. However, it must be emphasized that a crude quality of EMIMAc, which is known to contain some MIM, was used in these experiments. Thus, the potential catalytic effect of MIM would, in this case, be noticed even in the case when no extra MIM has been added.

Traces of acetate were found, in different amounts, in all samples, regardless of characterization method. This suggests that the acetate anion is indeed very reactive under certain conditions. While this method might be a facile route to mixed esters at different ratios, the main disadvantage is, of course, that the solvent is consumed to some extent. Consequently, recycling is not an option in this case, at least not without extensive purification and material loss.



## 6 Regenerated cellulose properties

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*This chapter is based on Papers I-II and Papers IV-V.*

Solvent composition, choice of coagulant and polymer concentration are some of the parameters that are likely to affect regeneration and the properties of a regenerated cellulosic material (Fink et al. 2001). Regenerated fibers and films were characterized to determine e.g. strength, elongation, crystallinity and porosity. This provides information about the structure of the material that can be important for its mechanical performance and reactivity.

### 6.1 Mechanical properties

The mechanical properties of any material are, of course, utterly important. For textile like fibers, which were investigated in this case, two very important properties are strength, or tenacity, and elongation. The method for testing these properties is briefly discussed in Chapter 3.7.2.

#### 6.1.1 The effect of cellulose DP distribution

In Paper IV, spin dopes were prepared and regenerated textile-like fibers were produced by wet spinning in water from cellulose mixes consisting of MCC and pulp. Mechanical properties of the resulting fibers are shown in Figure 28. It can be seen that tenacity in the dry state depends the average DP of cellulose, while in the wet state the trend is much weaker. For elongation, the difference between wet and dry samples, as well as between samples with different DP, is surprisingly small.

The mechanical properties of the fibers presented in Figure 28 are further described in the appended full paper. In this case, the measurements were done

on fiber bundles and the results had to be recalculated to single filaments, assuming that all fiber bundles were perfect. This method was, of course, not optimal and some error was most probably introduced into the data.

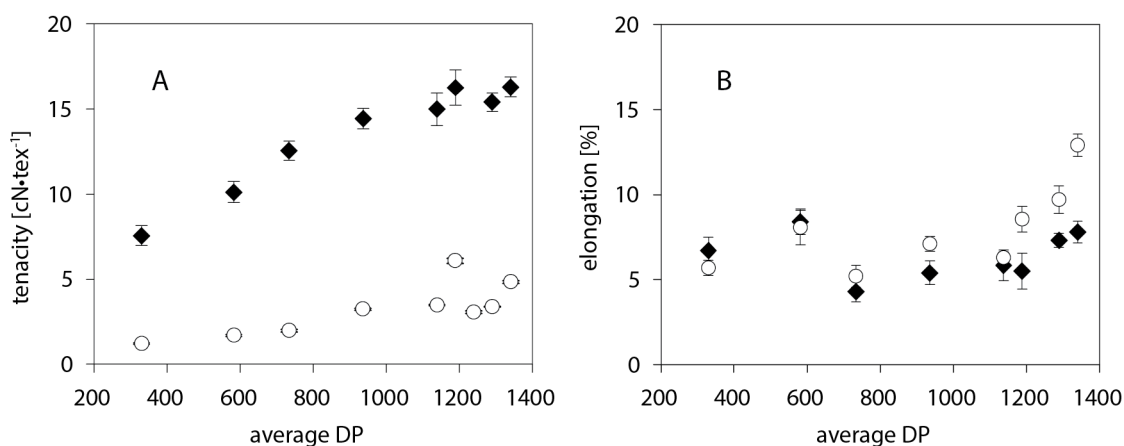


Figure 28. Tenacity (A) and elongation (B) as a function of average DP of mixed cellulose spin dopes, measured in dry (black diamonds) and wet (white dots) states for fiber bundles.

### 6.1.2 The effect of cosolvent addition

In Paper II, the impact of the addition of a cosolvent on fiber properties was studied using equipment that was optimized for single filament analysis. The data from this study is presented in Table 1. In this study, fibers were produced both via wet spinning and airgap spinning. Fibers spun via airgap spinning are, overall, stronger than fibers spun via wet spinning due to the orientation of polymers that takes place in the airgap before the fiber is solidified in the coagulation bath.

The strongest fibers in this study had a tenacity of around 35 cN/tex, which is in the range of, but not quite as strong as, previously reported results for EMIMAc and similar solvent systems. However, in that previous study, a much larger airgap was applied and even though no draft ratio was described, the fineness of the filaments was reported to be very low, between 1 and 2 dtex and it can be speculated that some drawing might have been applied, which would additionally explain the high tenacities (Kosan et al. 2008).

For the samples with MIM as a cosolvent, it appears that the amount of stretching necessary to reach high tenacities is greater for solutions with more cosolvent. This can be explained by the fact that these solutions have a lower viscosity and will relax more quickly in the airgap, and the macromolecular structuring and the stresses caused by elongational deformation cannot be preserved until the point of coagulation. This can, in fact, be seen in the case of

xIL = 0.5, listed in Table 1. This means that a very strong fiber cannot be achieved when using high amounts of cosolvent for the cellulose concentrations studied. However, it appears that intermediate amounts of cosolvent can be used, as the drawability of the xIL = 0.7 was reasonable and gave decent strengths over a wide range of stretch.

Although it generally gives weaker fibers than air-gap spinning, traditional wet spinning of EMIMAc-MIM-cellulose solutions was very stable and allowed for a surprisingly large stretch, both between spinneret and the first roll and between the first roll and the take-up roll in the stretch bath. This is an important difference to ordinary solutions of IL and cellulose, which will die-swell several times upon extrusion.

Table 1. Summary of data from fibers of EMIMAc/MIM dissolved cellulose, with standard deviation within parentheses.

xIL	pulp conc.(%)	draft ratio	titer (dtex)	tenacity (cN/tex)	elongation (%)	Young modulus (cN/tex)
0.5	15	1	8.48 (1.19)	22.5 (2.4)	15.6 (2.3)	783 (73)
0.5	15	1	10.62 (1.3)	20.9 (1.0)	24 (3.9)	676 (31)
0.5	15	1.3	7.18 (0.63)	24.7 (1.6)	13.4 (2.5)	878 (55)
0.5	15	2	5.42 (0.46)	26.1 (2.1)	13.3 (1.8)	914 (77)
0.7	15	1	10.08 (0.76)	26.0 (2.2)	15.5 (2.7)	860 (34)
0.7	15	1.5	10.18 (0.74)	25.5 (2.2)	18.1 (1.9)	724 (83)
0.7	15	2	5.12 (0.28)	32.3 (1.7)	9.7 (1.6)	1124 (81)
0.7	15	3	3.42 (0.35)	35.1 (2.0)	9 (1.7)	1177 (96)
0.7	15	3	3.27 (0.37)	35.0 (2.2)	9.3 (1.2)	1190 (65)
1	15	1	23.84 (2.3)	31.3 (3.1)	10 (1.4)	1045 (99)
1	15	2	15.3 (2.15)	30.8 (2.1)	8.8 (1.5)	1078 (56)
1	15	3	11.14 (2.22)	34.9 (2.7)	8.8 (0.8)	1203 (82)
0.5	8*	2	2.84 (0.18)	11.2 (0.5)	11.5 (1.5)	492 (27)
0.5	8*	3	5.61 (0.66)	12.6 (1.0)	12.4 (2.3)	532 (36)
0.5	8*	4	2.21 (0.04)	13.0 (0.8)	7.3 (0.7)	580 (29)
0.9	8*	2	4.01 (0.47)	13.7 (0.8)	13.7 (2.4)	497 (59)
0.9	8*	3	2.32 (0.07)	15.9 (0.64)	7.3 (0.8)	691 (38)
0.9	8*	1.1	5.36 (0.84)	15.5 (0.6)	6.1 (0.8)	718 (49)
0.9	8	1	5.1 (1.06)	21.8 (3.8)	13.2 (3.7)	751 (101)
0.9	8	2	3.15 (0.43)	27.0 (1.0)	14.1 (1.4)	744 (90)
0.9	8	3.5	1.68 (0.34)	31.2 (2.4)	10.1 (1.3)	951 (56)

\* = wet spinning

## 6.2 Crystallinity and pore size distribution

Crystallinity is claimed to be an important factor for fiber properties such as strength (Röder et al. 2013). Consequently, this was one of the parameters that were investigated for regenerated cellulose samples in Paper I, Paper II and Paper V. Pore size distribution was investigated as a part of the regenerated cellulose hornification study in Paper V.

### 6.2.1 The effect of cosolvent addition

Selected samples from fibers spun from dopes of cellulose in binary solvents of EMIMAc/MIM in Paper II were analyzed using solid-state NMR. A complete transformation from the crystal structure of native cellulose could be noticed, indicating complete dissolution in all samples. As seen in Figure 29, the peak at around 66 ppm which is typical for the cellulose I crystal structure is entirely absent from all fiber samples. The crystallinity of the regenerated fibers can be calculated from the peak height at around 108 ppm. The measured crystallinity was high for the reference fiber (from a pure EMIMAc solution) and increased as a result of increased amount of cosolvent. There is a clear difference between the EMIMAc sample and the first EMIMAc/MIM sample, but there is almost no difference between the sample with 30% cosolvent (Figure 29C) and the one with 50% cosolvent (Figure 29D).

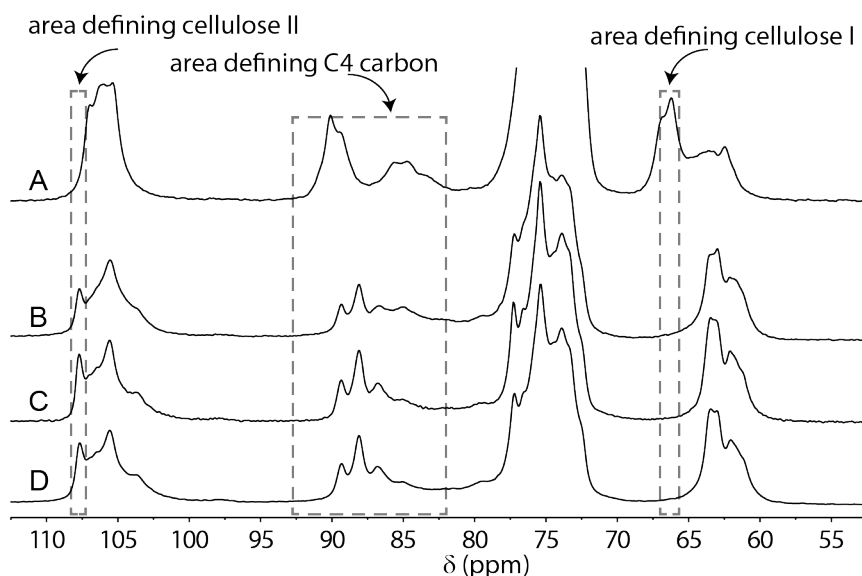


Figure 29. Solid-state NMR spectra of native dissolving pulp (a) and regenerated cellulose fibers from 15 wt% pulp spin dopes with 100 mol% EMIMAc (b), 70 mol% EMIMAc (c) and 50 mol% EMIMAc (d) in the binary solvent system EMIMAc/MIM. Signals from crystalline parts are shown for cellulose I (65.6 ppm) and cellulose II (107.6 ppm). The fingerprint of the C4 carbon is also highlighted.

In order to find other morphological differences between these two fibers, a simple technique for revealing anisotropy was used. The fibers were mounted between two polarized glass plates at 90 ° rotation relative to each other to obtain a visual representation of the birefringence of each fiber. As can be seen in Figure 30, there is a difference in color between the two fibers spun from binary EMIMAc/MIM solvents, which means that they are indeed not identical in terms of overall anisotropy. As a reference, the fiber spun from only EMIMAc is also shown.

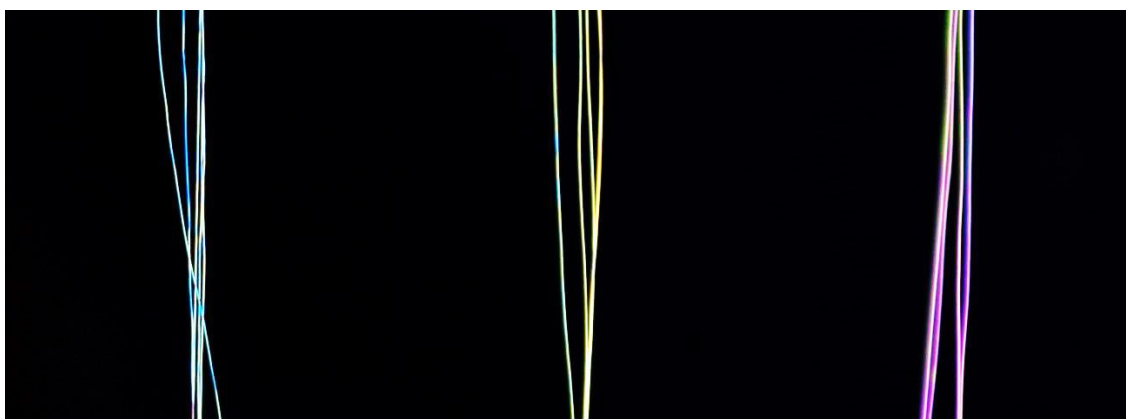


Figure 30. Birefringence, seen as colors between polarized glass plates, in regenerated cellulose fibers as a consequence of polymer orientation. Fibers were spun from 15 wt% pulp with different ratios EMIMAc/MIM. From left to right: 50 % EMIMAc (blue), 70 % EMIMAc (yellow) and 100 % EMIMAc (pink).

The coagulation mechanism for cellulose dissolved in non-derivatizing solvents can be described as a two-way diffusion controlled process, in which diffusion coefficients change during the gelation of the sample (Biganska and Navard 2005). The coagulant and the solvent do not necessarily have the same diffusion rate. This suggests a two-step regeneration in which the coagulant first dilutes the solvent, and then removes the rest of the solvent bound to the cellulose. This process has been suggested for several solvents including EMIMAc (Sescousse et al. 2011). If the ionic liquid is diluted with a highly water-soluble small molecular solvent, in this case MIM, the crystallinity of the regenerated material increases if all other factors remain unchanged. This can be interpreted as an effect of the change in the diffusion of bulk solvent (the cosolvent fraction) from the cellulose dope into the coagulation bath and of the coagulation medium into the cellulose dope.

### 6.2.2 The effect of water impurities in the solvent

Cellulose was regenerated in the form of films from binary solvents of different EMIMAc/H<sub>2</sub>O mixtures in Paper I. The water concentration in the solvents, as well as the cellulose concentration in the solution, was varied.

The crystallinity of the films was estimated with solid-state NMR, and the results are shown in Table 2. The highest conversion from cellulose I to cellulose II was found when there was a low water concentration in the solvent and at low cellulose concentrations. A significant amount of amorphous material was found in the product if the initial solution contained 8 wt% of cellulose, or more. This can be explained by the high degree of entanglement, partly “locked” by parts of cellulose deprived of solvent ions and, consequently, prone to random aggregation.

Furthermore, computer models of cellulose in water have suggested that the C6 hydroxymethyl group will be found in the gg position, which might inhibit the formation of cellulose II and promote the formation of an amorphous structure (Liu et al. 2012). At high water content and high cellulose content, residues of remaining cellulose I were detected in the product. No conversion whatsoever from cellulose I to cellulose II was observed in samples with more than 10 wt% water in the initial solution.

It should, however, be noted that there was still some conversion from cellulose I to amorphous material, since the crystallinity index of the native pulp exceeded that of all samples treated with EMIMAc/water. This means that the ionic liquid was able to, at least partly, dissolve/swell crystalline cellulose I, even in the presence of high water content. This is in line with the swelling type of Mode 4 in the model of dissolution described above in Chapter 2.2.

Table 2. Results for crystallinity index measurements from solid-state <sup>13</sup>C NMR of regenerated cellulose, as a function of water and HWP concentration in the cellulose solution. Increasing crystallinity is highlighted by the increase in color intensity; green for cellulose II (A) and red for cellulose I (B). Crystallinity index for native HWP was 0.65.

H <sub>2</sub> O content (wt%)	<b>A</b> HWP concentration (wt%)				<b>B</b> HWP concentration (wt%)			
	2	5	8	10	2	5	8	10
0	0.70	0.47	0.25	0.29	0.00	0.00	0.03	0.02
2	0.70	0.57	0.30	0.25	0.01	0.01	0.01	0.03
5	0.68	0.56	0.31	0.23	0.00	0.04	0.01	0.03
8	0.63	0.34	0.18	0.13	-0.03	0.01	0.02	0.07
10	0.40	0.33	0.17	0.09	0.04	0.07	0.14	0.15
15	0.02	0.00	0.00	0.00	0.46	0.53	0.55	0.58

A closer look at Table 2 reveals that there is an apparent maximum conversion to cellulose II for samples with water contents at around 2-5 wt% in the ionic liquid. This suggests, surprisingly enough, that the addition of a small amount of water might aid dissolution on the molecular level since the cellulose must be arranged linearly, polymer by polymer, in order to form crystals. In a cellulose solution in which most polymers form small, poorly dissolved aggregates, this would not be likely since a transition from cellulose I to cellulose II forces the polymers to go from a parallel orientation with respect to their closest neighbors, to an antiparallel orientation.

Since the hydrogen bonds between cellulose and IL are stated to be stronger than the bonds between water and IL (Liu et al. 2010; Hauru et al. 2012), the cellulose-IL interaction should still be preferred even in the presence of a small amount of water, which would explain these results. The strength of the cellulose-IL hydrogen bonds would also explain the reduction in viscosity at low water contents as the “free bulk solvent”, not engaged in polymer solvation, would have a lower viscosity due to the dilution by water.

### **6.2.3 The effect of the coagulation medium**

Coagulation of a cellulose solution to a solid material is a complex process involving diffusion of both solvent and coagulation medium in an increasingly stiffer material that undergoes gelation as well as polymer orientation and crystallization. Consequently, there are many factors that can and will affect the properties of the regenerated material. In Paper V, the effect of different coagulation media on crystallinity was investigated.

Thin regenerated cellulose films were prepared in different coagulation media. Water, which has a high polarity, was compared with two less polar coagulation media: ethanol and propanol. A coagulation medium with even lower polarity, such as acetone, would reduce its mutual solubility in the ionic liquid solvent, and thus inhibit cellulose precipitation.

By using solid-state NMR spectrometry it was found that water as the coagulation medium gives a material with a significantly higher amount of cellulose II crystals than ethanol and propanol does. This is shown in the NMR spectra in Figure 31. No difference was noted between the two samples coagulated in alcohols. The difference between samples coagulated in water or alcohol can be explained by the altered preference of EMIMAc to diffuse out of the cellulose matrix and into the coagulation media. Water, which is highly miscible with EMIMAc, induces a higher rate of exchange of the ionic liquid and the coagulation media within the cellulose gel matrix.

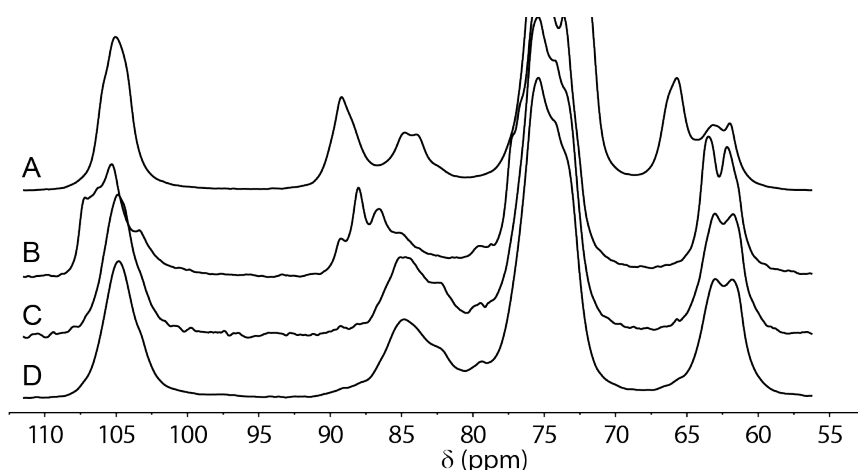


Figure 31.  $^{13}\text{C}$  solid state NMR spectra of cellulose. Reference material dissolving pulp (A) and cellulose regenerated in water (B), ethanol (C) or propanol (D).

According to molecular modeling of cellulose in EMIMAc (Liu et al. 2012), the hydroxymethyl group at C6 has a preference for the *gt* conformation. The same conformation is found in cellulose II. During a rapid coagulation of cellulose, as is the case when using water as the coagulation medium, this conformation seems to be preserved. It can be speculated that a slower solvent exchange, as when alcohols are used as the coagulation media, would allow slower solidification and more time for conformational rearrangement.

It was also noted that the pore size distribution, measured with NMR cryoporometry, was broader for films coagulated in alcohol than for films coagulated in water. This is in accordance with previous research, in which films coagulated in water were found to have lower water permeability and presumably a denser structure than films coagulated in ethanol (Liu and Budtova 2012).

#### 6.2.4 The effect of drying conditions

Cellulose films, coagulated in water, were subjected to different drying treatments in Paper V. A never dried film was compared to films dried in relative humidities of 75 % and 11 %, respectively, an oven-dried film and a film that was oven-dried, rewetted and oven-dried again for five cycles. All samples were submerged in water and centrifuged at 3000 g for 15 minutes prior to NMR measurements.

The effect of different drying treatments in regenerated cellulose is shown in Figure 32. It was found that the cellulose II content of regenerated cellulose could be increased by drying, a form of hornification, which has previously mostly been observed in cellulose I. It can be noted that the peaks that originate



from cellulose II crystal interior C4 carbons increased when harsher drying conditions were applied, whereas signals that originate from C4s at surfaces decreased. This can be interpreted as co-crystallization, previously detected for cellulose I using the same corresponding technique (Idström et al. 2013). Figure 32 also shows the pore size distribution, measured with NMR cryoporometry, for all of the samples. A clear bimodal distribution (3 and ~5 nm) of the pores in all of the materials except the one that had the harshest drying treatment (only 3 nm) was observed, in accordance to previous research (Isobe et al. 2011). Consequently, a pore collapse occurred at the most intense drying treatment. This can be interpreted as another sign of a form of cellulose II type hornification.

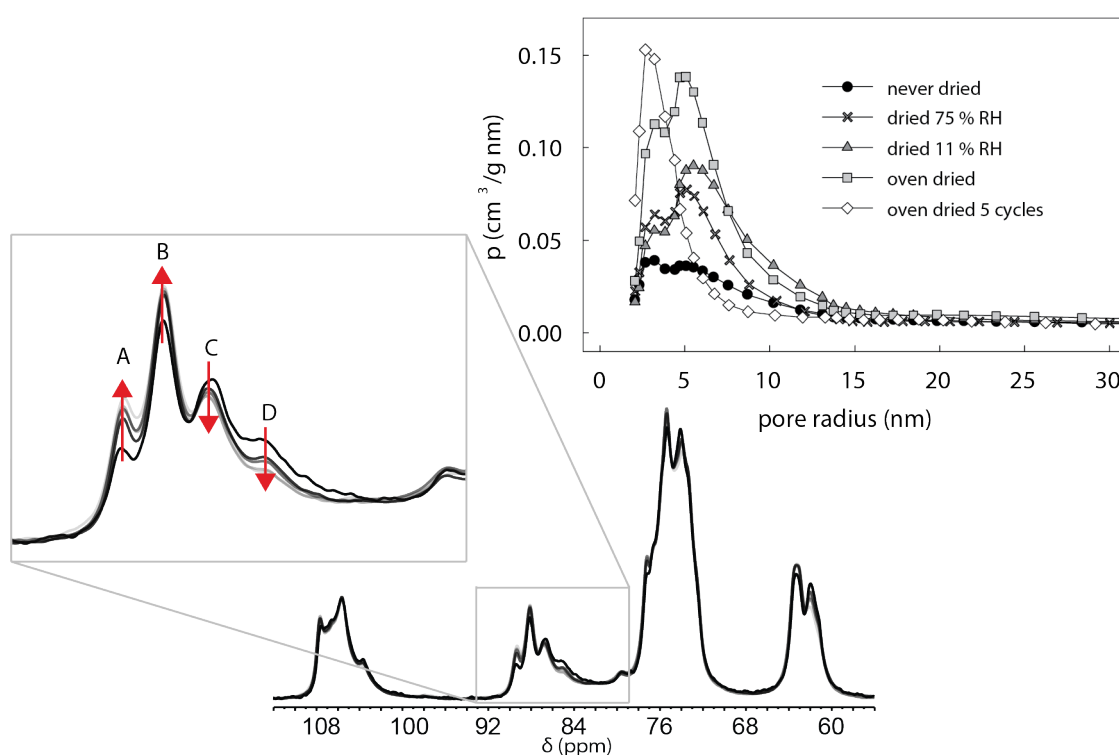


Figure 32.  $^{13}\text{C}$  solid-state NMR spectra and pore size distributions, measured by NMR cryoporometry, of regenerated cellulose; never-dried (black), dried in 75 % RH (dark grey), dried in 11 % RH (grey), oven dried (light grey), oven dried 5 cycles (very light grey). Peaks A and B originate from crystal interior, peaks C and D originate from surfaces.



## 7 Summary of papers and conclusions

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*In this thesis, different aspects of cellulose processing in ionic liquid based solvents have been investigated. The main results from the experimental work are summarized below.*

In **Paper I**, the influence of water on dissolution of cellulose in EMIMAc was investigated. It was found that a certain amount of water in the solvent can be accepted, but that the impact of water differs very much depending on the cellulose type. For instance, MCC is not as sensitive as pulp. However, the difference between hardwood pulp and softwood pulp was surprisingly small even though the degree of polymerization of the softwood pulp was around twice that of hardwood pulp. Microscopy showed that pulp swelled by ballooning in EMIMAc with water contents between 5 and 15 wt%. Some solutions reached an apparent critical gel-point at a molar ratio EMIMAc/water of 1:1 (10 wt% water). However, undissolved material acting as filler can cause a similar effect. Increasing the water content over 10 wt% inhibited dissolution severely, and light microscopy measurements revealed plenty of non-dissolved material at a water content of 15 wt%, at all concentrations and for all DPs of cellulose. A low amount of cellulose and low amounts of water in the solution generally resulted in a regenerated cellulose material of high crystallinity. The same samples were found to be well dissolved. This means that complete dissolution facilitates not only the destruction of the native cellulose I structure, but also the re-crystallization to cellulose II. At the same time, an apparent maximum in conversion to cellulose II was noted at 2-5 wt% water in the solvent, which correlates to viscosity measurements that show a minimum at the same water content.

In **Paper II**, molecular organic solvents, especially N-methylimidazole (MIM) which is a precursor to imidazolium based ionic liquids, were evaluated as cosolvents for cellulose solutions in ionic liquids, EMIMAc and BMIMCl. After initial viscosity and solubility experiments, MIM and EMIMAc were selected for further study. Solutions of pulp, EMIMAc and cosolvent were regenerated by wet spinning and airgap spinning. It was found that air-gap spinning can give good textile quality fibers if intermediate amounts of cosolvent are used. Wet-spinning gives weaker regenerated fibers, but some process issues, such as die-swell and low drawability, were significantly improved using the binary solvent mixture instead of pure EMIMAc. Even though the tenacity did not increase for fibers spun from binary solvents, these fibers showed significantly higher crystallinity than fibers from pure ionic liquid solutions.

In **Paper III**, the cosolvents DMSO and MIM were used to adjust the amount of solvent induced acetylation while producing cellulose propionate in the ionic liquid EMIMAc. Ion chromatography of hydrolyzed product was used to quantify the amount of propionate and acetate, respectively, in the product. The amount of cosolvent and the amount of reagent turned out to be significant parameters for diminishing the unwanted acetylation, while time and temperature of the reaction were not. <sup>1</sup>H NMR spectrometry of dissolved polymeric material confirmed ester formation at C2, C3 and C6, as well as the trend already established by IC. In no case was acetylation fully avoided.

In **Paper IV**, a series of cellulose solutions in EMIMAc were prepared from microcrystalline cellulose and/or pulp. The average degree of polymerization (DP) of the cellulose in the solutions ranged from 330 to 1340. The viscosity of the solutions increased with DP, and the crossover of elastic and viscous modulus were found to vary linearly in two different regimes at different DP intervals. Wet spinning of the cellulose in hot water without drawing generated fibers of varying mechanical properties. These properties did not always vary linearly with respect to average DP. Elongation did not seem to be affected to the same extent as tenacity and stiffness, both of which increased steeply with an increase in the DP of the polymers in the tested fibers.

In **Paper V**, the effect of different coagulation media and different drying conditions on crystallinity and pore sizes in cellulose that is regenerated from EMIMAc solutions was studied. It was concluded that both the coagulation route and the method of post-treatment influence the regenerated cellulose films. A complete conversion from cellulose I was seen for all different coagulation media (water and two alcohols), ranging from mainly crystalline cellulose II after coagulation in water, to a mainly non-crystalline structure after

coagulation in an alcohol. After drying of the regenerated cellulose films coagulated in water, clear signs of hornification were seen in the form of an increase in NMR signals originating from crystalline interiors and a decrease in signals from cellulose crystal surfaces. A bimodal pore size pattern with pore sizes of 3 and 5 nm was found in the samples exposed to all but the harshest drying treatment, in which instead a monomodal pore size pattern mainly consisting of 3 nm pores was seen. Porosity and crystallinity were found to be more tunable for a cellulose hydrogel coagulated in water than for corresponding gels coagulated in alcohols.

From the above summaries, it appears that dissolved cellulose has a tendency to recrystallize into cellulose II if:

- 1) it is fully dissolved
- 2) it is either in low concentration or aligned
- 3) regeneration is fast

The first statement was demonstrated in Paper I. in which it was found that crystallinity trends coincides with solubility trends seen in turbidity measurements and by the visual inspection using a microscope. In the solutions where particles are visible, the regenerated material has lower crystallinity.

The second statement has to do with the fact that high crystallinity was found in samples in which the cellulose concentration in the solutions was low, such as in some samples in Paper I and all of the samples in Paper V. In Paper I, solutions with high cellulose concentrations gives regenerated materials of low crystallinity. However, in Paper II, there are samples with exceptionally high crystallinity, and those are produced from 15 wt% cellulose solutions. In that study, however, the cellulose molecules had been aligned in the spinning equipment before precipitation.

The last statement has to do with findings in Paper II and Paper V. In Paper II, the solutions with higher amounts of cosolvent in the binary solvent mixture resulted in regenerated materials with higher crystallinity. It can be hypothesized that the smaller, water-soluble, cosolvent molecules can diffuse fast, and leave the polymer solution and enter the water phase faster than the bulky ions, which make up the other part of the solvent, can. In Paper V it was noticed that coagulation in water gives a regenerated cellulose material with higher crystallinity than coagulation in propanol and ethanol. This is due to the limited solubility of EMIMAc in the alcohols, which means that coagulation of cellulose will be slower.



## 8 Future work and outlook

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*Suggestions for further work in this field are listed below. They are based on the results reported in this thesis and on related issues that arose, but were not explored, during the course of this research.*

- The molecular interactions between cellulose and many solvents are still hypothetical. Such solvents include ionic liquids such as the imidazolium type ILs, where researchers are still arguing about the role of the cation. A deeper understanding of the mechanisms that govern cellulose solubility is required to optimize solvent systems for different applications. Molecular modeling should be a powerful tool in this pursuit.
- Once the nature of these interactions are established, research should focus on the influence of different cosolvents, and the mechanisms involved in matching a solvent with a suitable cosolvent in order to obtain preferred solution properties.
- The influence of cosolvents should also be further investigated with regard to the coagulation step and the properties of the final regenerated material. The same attention should be given to the study of contaminants, such as water and degradation products.
- Fundamental rheological studies of spinning solutions, both shear and elongational, are necessary in order to determine the required properties of the solution in order to attain stable spinning conditions and an end product with desired properties.
- More research on the structure formation and the phenomenon of coagulation is needed in order to understand how different properties in

the regenerated material can be optimized. To meet this purpose, solutions, air-gap and coagulation baths must be studied, as well as the drying process.

- In order to achieve economically feasible, and ecologically acceptable, processes, the recycling procedure of solvent and cosolvent, if present in a process, must be further improved. It must be ensured that the least amount of energy possible is used, and that the quality of the solvents is maintained over a large number of cycles.
- Future work should also include integrated methods for polymer derivatization, such as cross-linking in fibers with the purpose of further improving for example stiffness and strength. Other strategies for specialty fiber optimization include the addition of a secondary polymer in the spin dope. The use of additives and/or hydrophobic modification of cellulose might be necessary to achieve this.

Finally, there is a need for future development of wood based textiles that can, to a large extent, replace petroleum based textiles and cotton, and fill the growing gap between supply and demand on the textile market. However, this requires that individual researchers, research institutes, academia and industry make joint efforts to combine their individual strengths. A lot of cellulose processing today is based on know-how, but many now strongly believe that proper understanding of the molecular interactions is necessary to take the research to the next level. This thesis is a small step forward in this direction, a tiny piece in the great jigsaw puzzle that is research.



# Acknowledgements

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This thesis and the work behind it were financed by the research foundation *Södra Skogsägarnas stiftelse för forskning, utveckling och utbildning* via the research network *Avancell - Centre for Fibre Engineering*, a collaboration between Södra Innovation and Chalmers University of Technology. The practical work behind this thesis was carried out at Chalmers University of Technology, Södra Innovation, Swerea IVF, Swedish NMR Centre and Artimplant AB, by me or by my co-authors.

Obviously, this thesis would not have been possible without the inspiration and support of a number of people:

- Gunnar Westman, my advisor, for a never ending stream of ideas and a fearless approach to science.
- Everyone involved in Avancell, for including me in this inspiring and growing network. I wish the next Avancell cycle good luck and hope to see great results in the future.
- My co-authors and everyone who helped out in the various labs, for contributing to the papers in this thesis with their expertise, effort and enthusiasm. I really appreciated your input. Let's do it again sometime!
- All my colleagues, especially former and present members of Group GW and the rest of Floor 9, for making these years what they were.
- ♥ My friends and family, especially Alex, for support and encouragement. Life is so much easier with you by my side.



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