

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

# Electrospinning Nanofibres from Cellulose Dissolved in Ionic Liquid

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CHALMERS UNIVERSITY OF TECHNOLOGY

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Cover: SEM micrograph of electrospun cellulose fibres

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## ABSTRACT

This thesis investigates the electrospinning of cellulose nanofibres from ionic liquids. Cellulose nanofibres produced by an environmentally friendly process have the potential to replace synthetic nanofibres produced with volatile and harmful solvents.

The influence of a co-solvent was studied by investigating how three well-known co-solvents (DMSO, DMAc and DMF) affect spinnability. The solution parameters viscosity, surface tension and conductivity were investigated in detail and related to spinnability and fibre formation. To form fibres, regardless of co-solvent used, a certain degree of viscosity and surface tension was needed. The system with DMSO as co-solvent was found to give the best fibre formation, be spinnable at a lower EmimAc content, and show more pronounced shear thinning. Compared to DMSO, both DMAc and DMF have a molecular structure which can present a resonance form and consequently stronger interaction between ionic liquid and co-solvent.

The effect of the molecular weight of the cellulose and cellulose concentration on fibre spinnability has also been investigated. Cellulose was depolymerised with hydrochloric acid to yield fractions of cellulose with different molecular weight distributions. Size Exclusion Chromatography confirmed that the cellulose was degraded into different molecular weight fractions, where longer acid treatment time yielded more chain scission, hence a lower molecular weight. The dominant property for electrospun cellulose fibres from ionic liquids to be formed is solution viscosity, a property controlled by, e.g., polymer concentration or molecular weight.

Keywords: Electrospinning, cellulose, nanofibres, ionic liquids, dissolution, rheology, molecular weight distribution



## List of Publications

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

### Paper I

#### **Electrospinning of Cellulose Nanofibers from Ionic Liquids: The Effect of Different Cosolvents**

**Linda Härdelin**, Johannes Thunberg, Erik Perzon, Gunnar Westman, Pernilla Walkenström and Paul Gatenholm

Published, *Journal of Applied Polymer Science*, (2012), 125(3), pp. 1901-1909

### Paper II

#### **Influence of Rheology and Molecular Weight on Electrospinning Cellulose from Ionic Liquid**

**Linda Härdelin**, Erik Perzon, Bengt Hagström, Pernilla Walkenström and Paul Gatenholm

*Submitted to Journal of Applied Polymer Science 2012-11-19*



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# 1. Introduction

Cellulose as a raw material has been used by man for many centuries in building material (wood) and textile fibres (cotton or flax), to name a few examples. In the past years the cellulose research field has grown immensely in response to the growing global awareness of renewable resources and environmentally friendly materials [1].

Nanofibres are fibres with a diameter less than 100 nanometres. When the fibre diameter is decreased from micrometres to nanometres, the surface-to-volume ratio is greatly enhanced. A multitude of applications for nanofibres has been proposed. Examples are filters [2, 3], drug delivery and tissue engineering [4], biosensors [5], energy and environmental applications [6, 7], reinforcement material [8] and protective clothing [9]. Electrospinning is a versatile and low cost manufacturing process for producing nanofibres [10]. Cellulose nanofibres produced by an environmentally friendly process has the potential to replace synthetic nanofibres produced with volatile and harmful solvents but has not yet been fully investigated.

## 1.1 Aim of thesis

The overall objective of this work has been to develop and study the electrospinning process for producing cellulose nanofibres from ionic liquid solutions.

In **paper I**, the aim was to investigate the role of co-solvents when electrospinning cellulose dissolved in ionic liquids into fibres. The relations of spinnability and fibre formation to rheological properties, surface tension and conductivity of the solutions were studied. Cellulose from one source and at one concentration was used in this study.

**Paper II** focused on the impact that the cellulose molecular weight has on electrospinning. The cellulose was therefore acid treated to achieve cellulose fractions of different molecular weight distributions, which were then electrospun at different cellulose concentrations.

## 1.2 Cellulose

Cellulose was first described by the French chemist Anselme Payen in 1838 as a fibrous material that remained after acid treatment of wood. It is a biopolymer and is found in the cell wall of all green plants, where it functions as a skeletal component giving the plant its structural integrity. Cellulose is the most abundant biopolymer in the world, and can be considered an almost inexhaustible source of raw material since it is regularly regenerated on earth. The molecular formula of the cellulose monomer is  $C_6H_{10}O_5$  and its molecular weight 162 Da. The cellulose molecule (shown in Figure 1) is a linear polysaccharide consisting of D-glucopyranose units (also known as anhydroglucose units (AGU)) linked by  $\beta$ -1,4-glycosidic bonds formed between carbon atom  $C_1$  and  $C_4$  of an adjacent unit. The hydroxyl groups are positioned in the equatorial plane at the  $C_2$ ,  $C_3$  and  $C_6$  atoms and the hydrogen atoms positioned in the axial plane. In the cellulose chain, every second AGU unit is rotated  $180^\circ$  in order to accommodate the bond angles of the  $\beta$ -1,4-glycosidic bonds [11, 12].

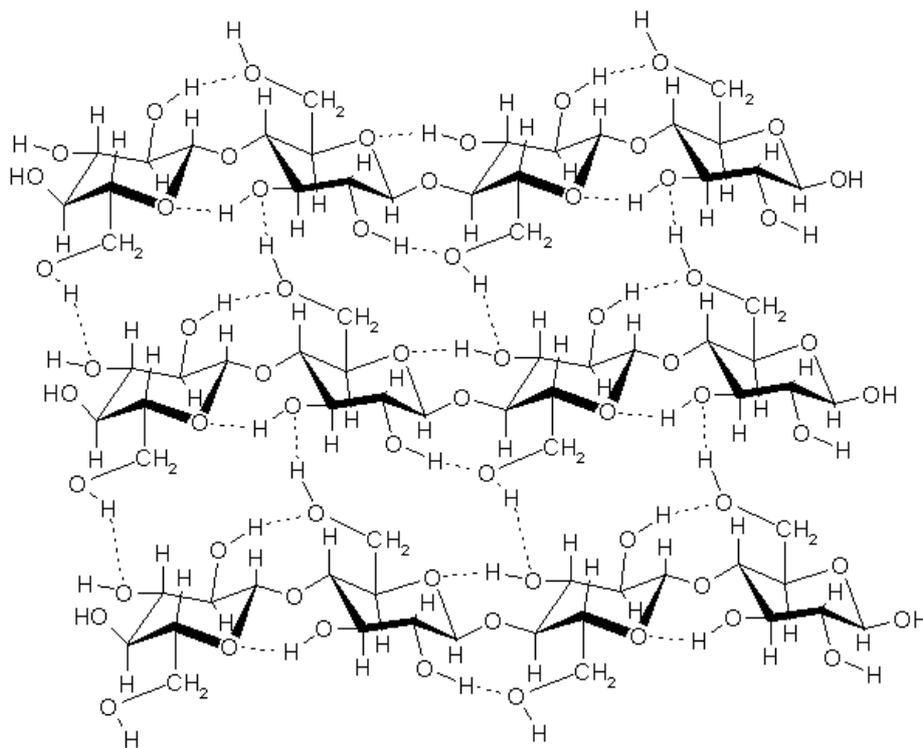
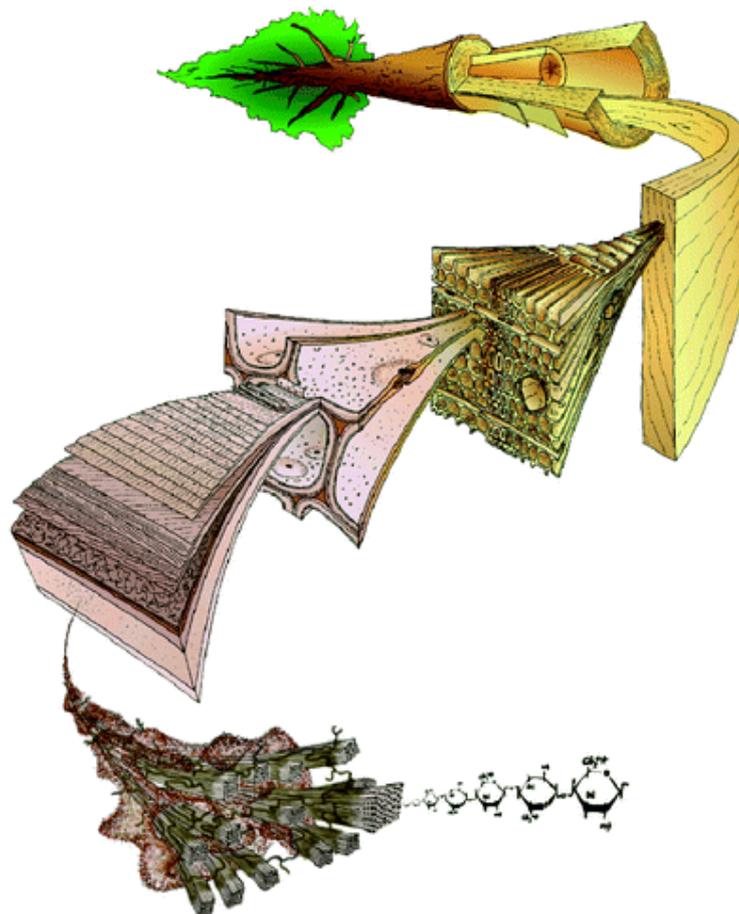


Figure 1. Structure of cellulose [13]. © 2004-2012 University of Cambridge.

Intramolecular (i.e., within a molecule) hydrogen bonds are formed between the hydroxyl group on C<sub>3</sub> to O<sub>5</sub>, and between the hydroxyl groups on C<sub>2</sub> and C<sub>6</sub>, along both sides of the cellulose chain [14]. These intramolecular hydrogen bonds make the cellulose chain stiff and rigid. Native cellulose can also form intermolecular (i.e., between molecules) hydrogen bonds between the hydroxyl group on C<sub>6</sub> of one chain and C<sub>3</sub> of the neighbouring chain. Both types of hydrogen bonds are shown in Figure 1. The hydrogen bonding network, van der Waals forces, and hydrophobic interactions arrange the cellulose chains into microfibrils, which aggregate into macrofibrils. The role played by the hydrogen bonding network and hydrophobic interactions in the dissolution of cellulose, has recently been debated [15, 16]. In the microfibrils the cellulose can be arranged in a highly ordered manner, termed crystalline cellulose, and in a less ordered manner, called amorphous cellulose or para-crystalline cellulose [12]. The cell wall in wood has these cellulose macrofibrils as the main component and their organization make up the hierarchical structure of wood as illustrated in Figure 2.



*Figure 2. Hierarchical structure of wood [17]. © University of Canterbury, 1996. Artwork by Mark Harrington.*

## 1.3 Dissolution of cellulose

Cellulose does not melt; instead it decomposes at high temperatures and must therefore be dissolved before it can be processed, e.g. into fibres. On account of the supramolecular structure of cellulose, it is insoluble in most common solvents. Heinze and Koschella classified cellulose solvents into two categories: derivatizing solvents and non-derivatizing solvents, where the latter is divided into the two sub-categories; aqueous media and non-aqueous media [18]. Derivatizing solvents dissolve cellulose by reacting with hydroxyl group/s of the cellulose molecule, thus making it soluble in a wide variety of common organic solvents. The dissolved cellulose derivative may then be converted back to cellulose in, e.g. a coagulation bath yielding a cellulose fibre. The most industrially important method for dissolving cellulose is the viscose process. In the viscose process, cellulose is first swollen in sodium hydroxide solution and then allowed to react with carbon disulphide forming cellulose xanthate, which is dissolved in dilute sodium hydroxide and converted back to cellulose via sulphuric acid [19]. Non-derivatizing solvents dissolve the cellulose directly by intermolecular interactions, i.e. without any chemical modification. The two most commonly used aqueous non-derivatizing solvents today are cuprammonium hydroxide (Cuam) and cupriethylenediamine hydroxide (Cuen). Examples of non-aqueous non-derivatizing solvents are lithium chloride/dimethylacetamide (LiCl/DMAc), *N*-methyl morpholine-*N*-oxide (NMMO), tetrabutylammonium fluoride and dimethyl sulfoxide (TBAF/DMSO), and ionic liquids [18]. The field of dissolution of cellulose in ionic liquids has grown significantly during the past ten years [20].

### 1.3.1 Dissolution of cellulose in ionic liquids

In a patent in 1934, Graenacher showed that molten salts could dissolve cellulose [21]. But it was not until Swatloski and co-workers in 2002 examined the solubility in several ionic liquids that the research area experienced substantial growth [22]. Ionic liquids are organic salts consisting of anions and cations, with relatively low melting points. Thus they form stable liquids at temperatures below 100 °C. Some of their outstanding properties are that they are chemically and thermally stable, non-flammable, and exhibit low vapour pressure. Due to their much desired properties, they are sometimes referred to as “green” solvents [23].

Ionic liquids, and other non-derivatizing solvents, are thought to dissolve cellulose by disrupting the hydrogen bonding network [24]. To separate the polymer chains from each other, the solvents should be able to compete for the existing intermolecular hydrogen bond interactions and thereby dissolve the cellulose. The dissolution mechanism has been investigated by NMR spectroscopy [25, 26] as well as molecular dynamics (MD) simulations [27, 28]. These studies conclude that dissolution of cellulose involves formation of hydrogen bonds between anion and hydroxyl groups of the cellulose. The cation has been shown to have a secondary role in the dissolution mechanism, but should not be neglected [29].

Some of the most frequently used ionic liquids for dissolution of cellulose are the imidazolium based ionic liquids. The structures of imidazolium cations are shown in Figure 3. However, not all ionic liquids have the ability to dissolve cellulose and, of the ones that do, there is a difference in dissolution efficiency. Factors that affect dissolution efficiency are, e.g. viscosity and water content in the ionic liquid. If the viscosity increases, and thereby decreases ion mobility, the dissolution efficiency decreases as well. Water, which is used for regeneration of cellulose, decreases the dissolution efficiency. It may also be so that the best cellulose dissolving ionic liquid has yet to be developed [20, 30].

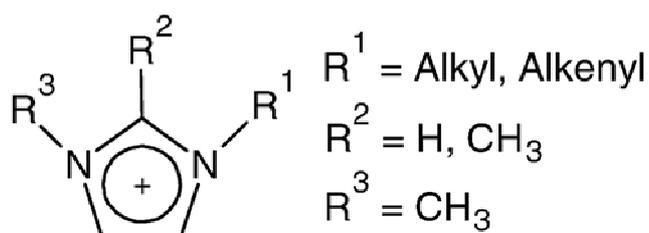


Figure 3. Structures of imidazolium cations. Adapted with permission from El Seoud et al. [31]. © (2007) American Chemical Society.

Pinkert and co-workers identified structural similarities between cellulose solvents and concluded that all non-derivatizing cellulose solvents could form hypothetical cyclic arrangements with themselves. They concluded that the solvents could break the intermolecular hydrogen bonds between cellulose chains and form new hydrogen bonds between the solvents and the cellulose chains, because the newly formed hydrogen bonds were more stable than the initial intermolecular hydrogen bonds

## Introduction

between cellulose chains. This might be because the ionic liquids that could dissolve cellulose were able to arrange their dipoles in such a way that an energetically favoured cyclic arrangement with cellulose could be formed [30].

One of the greatest advantages of the ionic liquids is the ability to tailor the chemical and physical properties by the anions and cations that are chosen [32]. For an ionic liquid to be used in an industrial process, it should meet certain requirements, e.g. low melting point and high decomposition point, no decomposition of cellulose, non-toxic, low viscosity and easy to use in an industrial process. Taking these requirements into consideration, the ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) is one of the ionic liquids best suited for cellulose dissolution and fibre spinning [33, 34]. The many desired properties of ionic liquids, and particularly those of EmimAc, are the reasons why EmimAc is chosen as the cellulose solvent throughout this work.

## 1.4 Polymer solutions

The viscosity of a solution depends on both polymer concentration and molecular weight (and other factors such as temperature and pressure); thus the viscosity increases as the size of the molecules and number of molecules increases [35]. Polymer solutions can be classified into four concentration dependent areas: the dilute regime, the unentangled semi-dilute regime, the entangled semi-dilute regime and the concentrated regime. In the dilute regime, where  $c < c^*$  ( $c^*$  is the critical chain overlap concentration), the polymer chains are individual, well separated, chains. When the concentration is increased, the chains start to overlap at the critical chain overlap concentration ( $c^*$ ). Above this concentration is the semi-dilute regime ( $c > c^*$ ), which is divided into unentangled and entangled semi-dilute regimes. The boundary between the unentangled semi-dilute regime and the entangled semi-dilute regime is the critical entanglement concentration,  $c_e$ , and is the concentration where polymer chain entanglement starts to occur. The reason why chain entanglement does not occur until  $c_e$  is reached compared to  $c^*$  is that a significant amount of overlap is necessary for polymer chains to entangle. The unentangled semi-dilute regime is defined as  $c^* < c < c_e$ , and here the polymer chains partly overlap but not enough for entanglement. The entangled semi-dilute regime is defined as  $c > c_e$ , and here the polymer chains entangle

[36, 37]. The dilute regime, the unentangled semi-dilute regime and the entangled semi-dilute regime are illustrated in Figure 4.

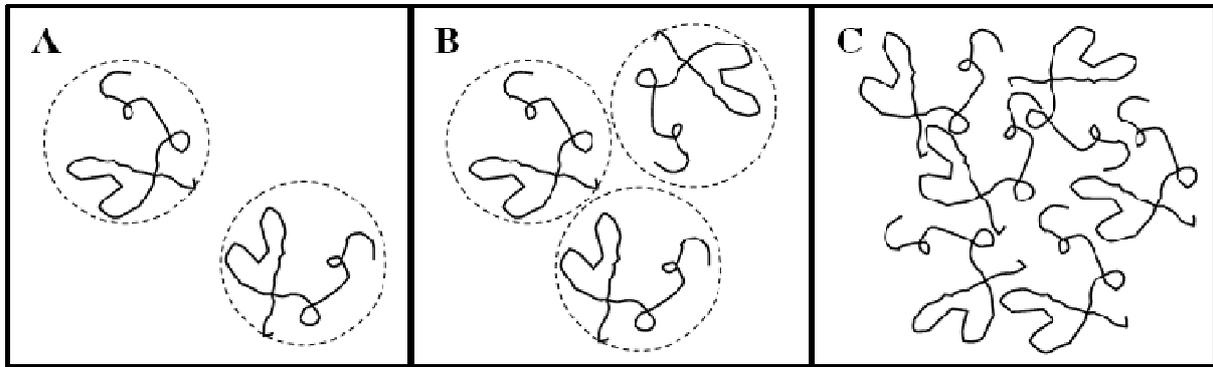


Figure 4. Illustrations showing concentrations of polymers in: A) dilute regime, B) unentangled semi-dilute regime and C) entangled semi-dilute regime.

### 1.4.1 Solution rheology

The viscosity of a solution is of great significance for processing the solution into, e.g., a fibre. Addition of a polymer, such as cellulose, to a solution will increase the viscosity of the solution in direct proportion with the polymer concentration, in the dilute regime. Here, where the polymer concentration is low, there is no strong interaction between the polymer molecules. At a given concentration ( $c_e$ ), the polymer concentration is high enough for interactions to occur between polymer chains, and the viscosity of the solution will then increase with a power-law dependence. This change in concentration dependence is attributed to the formation of polymer entanglements in the solution. The polymer chain length is the main contributing factor to the viscosity. A longer chain will occupy a larger volume in the solution, thus rendering a higher viscosity compared to a polymer chain of shorter length [38].

## 1.5 Fibre spinning

There are several ways of producing man-made fibres. Three of the most common spinning techniques are melt spinning, solution or wet spinning, and electrospinning. Among these, melt spinning is the most common way of producing synthetic fibres. In melt spinning, a polymer melt is pumped through a spinneret with small holes; the number of holes can range from one to a thousand. The fibre produced is stretched,

## Introduction

cooled, solidified and then wound up. Since cellulose does not melt, it is not possible to melt spin cellulose.

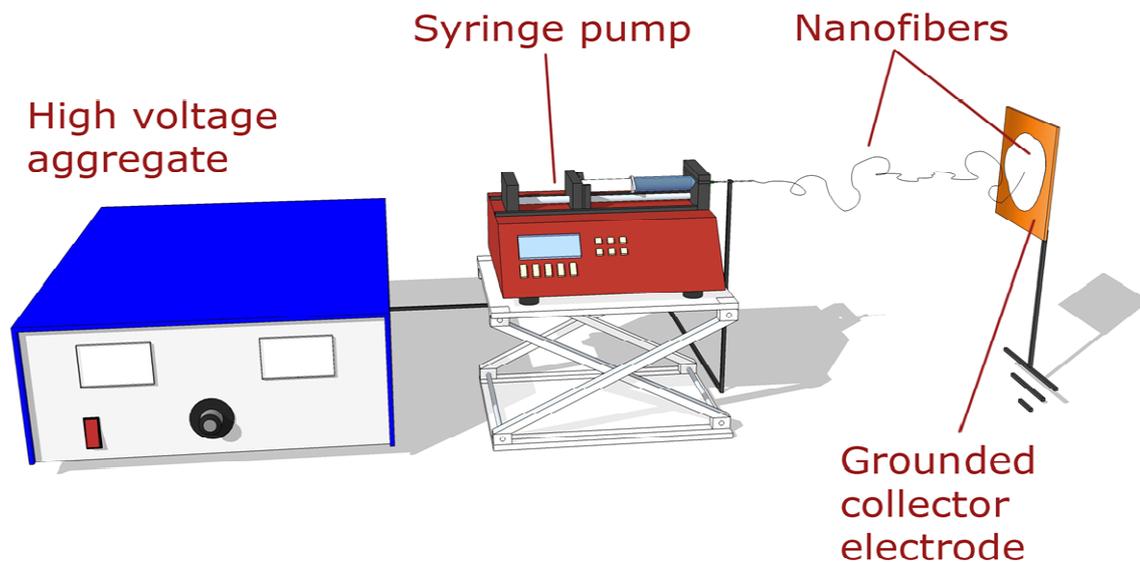
Instead, wet spinning can be used to produce cellulose fibres, where the viscose (or rayon) process has been the dominating process over the past 100 years, with an annual world production of two million tons by the year 2000. It was first patented in 1893 by Cross and Bevan and, even though the process has been refined over the years, the basic chemistry is still the same. The chemistry of the viscose process is described briefly in section 1.3 Dissolution of cellulose. The fibre filaments are formed by extrusion through a spinneret into a spin bath. In the spin bath, containing sulphuric acid, the cellulose xanthate coagulates into cellulose fibres, which are stretched and washed and then wound up [19]. However, the viscose process possesses some serious drawbacks, such as the requirement for high quality dissolving pulp as cellulose source, the use of carbon disulphide that causes high environmental loads, the use of heavy metals in the precipitation process and the production of by-products [11]. In the beginning of the 1980s, production began of the Lyocell fibre in a search for a more environmentally friendly production process and fibres with higher wet strength. The wood pulp is dissolved directly in hot *N*-methyl morpholine-*N*-oxide (NMMO) and spun into fibres, using the dry jet wet spinning process. Over 99% of the solvent is recovered and it is non-toxic in itself. However, the Lyocell process also has some significant disadvantages, such as thermal instability of the solvent, side reactions, high energy consumption and fibrillation of the fibres [19].

Ionic liquids as direct solvent of cellulose have the potential to become the future choice in the processing and manufacturing of cellulose fibres.

### **1.5.1 Electrospinning of cellulose**

The formation of filaments from polymer solutions by electrospinning was first described by Formhals in a patent in 1934 [39]. There had only been a few publications on the subject up to the 1990s, but the area was revived during that decade and grew substantially. Since then the annual number of publications on the subject of electrospinning has increased exponentially. During 2011, 1,490 articles were published according to the Scopus search engine (keyword: electrospinning).

Compared to conventional spinning techniques, electrospinning can produce fibres with thinner diameters from solutions and melts. In electrospinning, electrostatic forces are used to produce fibres with diameters down to the nanometre scale. However, they can be meters long. The basic set-up consists of a syringe filled with polymer solution, a metallic needle connected to a high voltage aggregate, a syringe pump and a grounded collector (see Figure 5).

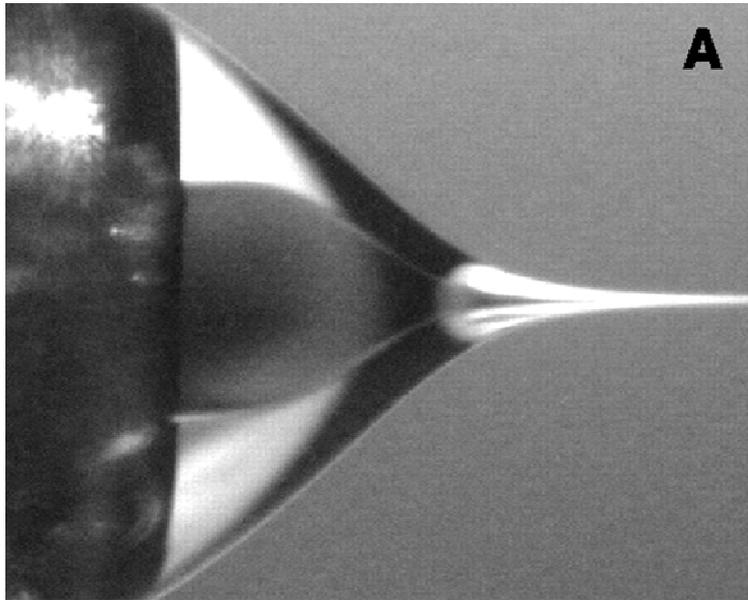


*Figure 5. Electrospinning set-up.*

The set-up can either be arranged vertically or horizontally. The horizontal arrangement is often preferred to avoid possible drops on the collector. The polymer solution in the syringe is fed by the pump through the needle, forming a droplet at the tip of needle. When a high voltage is applied to the polymer solution, an electric charge is induced in the liquid and the droplet takes on a conical shape. Studies of the jet forming process were conducted in the 1960s by Taylor. He examined the disintegration of water drops in an electric field and concluded that the shape of the droplet at the tip of the needle must have an angle of  $49.3^\circ$  to balance the surface tension with the electrostatic force [40]. This conical jet shape is referred to as the Taylor cone (see Figure 6). The liquid is held together by its surface tension and, when the repulsive electrical forces overcome the surface tension, a jet is ejected from the Taylor cone towards the grounded collector. The jet is very unstable due to the repulsion of charges and undergoes a whipping motion caused by a bending instability in the jet, which stretches and elongates the fibres prior to deposition on the collector.

## Introduction

The bending instability and fibre elongation process has been the subject of many investigations and modelled by, e.g., Reneker and co-workers [41, 42].



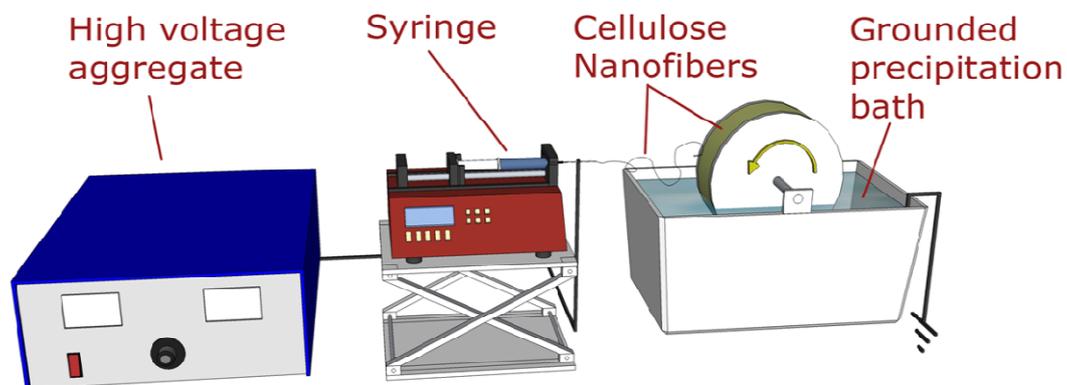
*Figure 6. Taylor cone. From [43]. Reprinted with permission from AAAS.*

There are three main groups of electrospinning parameters that affect fibre formation. These groups are: process parameters (e.g., applied voltage, solution flow rate and spinning distance), solution parameters (e.g., concentration, viscosity, polymer molecular weight, surface tension and conductivity) and ambient conditions (e.g., temperature and humidity) [44-47].

### **1.6 Regeneration of cellulose**

Although the powerful dissolving properties of ionic liquids are certainly attractive for enabling the preparation of cellulose nanofibers by electrospinning, a drawback of these solvents is their lack of vapour pressure. This means that the solvents will not evaporate during electrospinning, which is the normal behaviour in any electrospinning procedure. Instead, the elongated jets of polymer solution that are formed in the process have to be collected into a coagulation bath so that the polymer will precipitate and form a fibre. However, it is not sufficient to perform the electrospinning onto the static surface of a coagulant since precipitated fibres and extracted ionic liquid from these fibres will assemble there. Thus, after a short period of electrospinning, the precipitation will not be very effective. To circumvent this, a new type of collector was

designed and constructed where a rotating collector wheel was submerged into the grounded precipitation bath, shown in Figure 7. The rotation of the wheel allowed any residual ionic liquid to be continuously removed from the precipitated fibres.



*Figure 7. Electrospinning set-up with coagulation bath. (paper I)*

## **2. Experimental**

The experimental methods involved in this work are summarized below. For further details the reader is referred to the appended papers.

### **2.1 Conductivity (paper I)**

Conductivity was measured with a CON 5/TDS 5 Conductivity meter (Eutech Instruments Pte Ltd, Singapore/ Oakton Instruments, Vernon Hills, IL, USA). The conductivity meter was calibrated before use with conductivity standards of 12880  $\mu\text{S}/\text{cm}$  and 1413  $\mu\text{S}/\text{cm}$  from Hanna Instruments, USA.

### **2.2 Surface tension (paper I)**

Surface tension was measured using the pendant drop technique. The instrument used was a VCA Video Contact Angle System 2500 (AST Inc., Billerica, MA, USA). The needle size used was 25 gauge (0.2540 mm i.d.) and the focus of the camera was calibrated with methanol. The VCAOptimaXC software was used to capture the image of the pendant drop and to fit the curvature of the drop to the Young-Laplace equation, which gave a value of the surface tension.

### **2.3 Cellulose dissolution (papers I and II)**

The pulp (dissolving pulp, Domsjö AB, Sweden) was dried in an oven at 80 °C for 12 hrs before use. An appropriate amount of pulp was weighed and placed in a small glass container and the chosen co-solvent (dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc) or dimethyl formamide (DMF)) was added to the pulp. The pulp absorbed the co-solvent, over a period of roughly one minute, and the ionic liquid EmimAc was then added to the mixture and the container was sealed. The sealed container containing a mixture of pulp, co-solvent, and EmimAc was then stirred in an oil bath at 80 °C for 12 hours, which generated a clear and homogenous solution. The reason for first adding co-solvent to the pulp followed by ionic liquid was to enhance the ionic liquid diffusion rate into the pulp. It was found that, the dissolution process was simplified and less time consuming by using this method.

## 2.4 Rheology (papers I and II)

The rheological properties of the solutions were characterized with a Bohlin Rheometer CS 30 (Malvern Instruments Ltd, UK). The measurements were conducted using a cone-and-plate geometry with a diameter of 25 mm and a cone angle of 5.4° at room temperature, approximately 25 °C. Steady state shear viscosity was measured at shear stresses in the range 0.24 – 1500 Pa, as set by the viscosity of the solutions. Complex viscosity was measured by performing dynamic oscillatory shear tests from the angular frequency 0.0628 rad/s to 125.6 rad/s.

## 2.5 Structural analysis (papers I and II)

Scanning Electron Microscope (SEM) was used to evaluate the fibre morphology. A JEOL JSM-5300 (JEOL, Tokyo, Japan) was used in paper I, and there the fibre samples were first subjected to gold sputtering to avoid electrostatic charging of the samples. In paper II, a low vacuum SEM (JSM-6610LV – JEOL, USA) was used.

## 2.6 Molecular weight (paper II)

The molecular weight of the untreated pulp and acid treated pulp was determined using Size Exclusion Chromatography (SEC). 30 mg of each pulp sample was dissolved in 8% LiCl/DMAc and diluted to a pulp concentration of 0.5 wt% prior to characterization. Pullulan standards were used for calibration, and the linear coefficient of determination ( $r^2$ ) was 0.996 for the curve of pullulan molecular weight versus elution time.

## 2.7 Acid treatment (paper II)

The pulp was disintegrated according to the standard SCAN-C18:65 to achieve a more even distribution of the pulp fibres. An appropriate amount of disintegrated pulp slurry (5 g dry weight pulp) was placed in an Erlenmeyer flask and stirred with a magnetic stirrer, in a water bath at 70 °C. Hydrochloric acid was added and stirred for set times. The dispersion was then filtrated and washed thoroughly with distilled water. The pulp was dried in an oven at 80 °C for 12 hours.

### 3. Results and discussion

#### 3.1 Electrospinning cellulose from ionic liquids with different co-solvents (paper I)

Polymer solutions with a very high viscosity are not suitable for electrospinning. To circumvent this issue, a co-solvent can be added to the solution to lower the viscosity, but without any precipitation of the cellulose. The co-solvent affects the ionic liquids' interaction with cellulose and thus the solubility of cellulose [48]. The aim of this study was to investigate in detail how three well-known co-solvents affect spinnability when added in varying amounts.

Three different co-solvents (DMSO, DMAc and DMF) were used to study solution parameters (viscosity, surface tension and conductivity) and relate them to spinnability and fibre formation. The molecular structures of the co-solvents are shown in Figure 8. The spinning solutions had a fixed cellulose concentration of 2.5 wt%, and the solvent systems consisted of the ionic liquid EmimAc and co-solvent (DMF, DMAc, or DMSO) at various ratios ranging from 10 wt% to 90 wt%, respectively (see Table 1). When dissolving cellulose in EmimAc, the viscosity of the solution increases substantially with only a few wt% of cellulose.

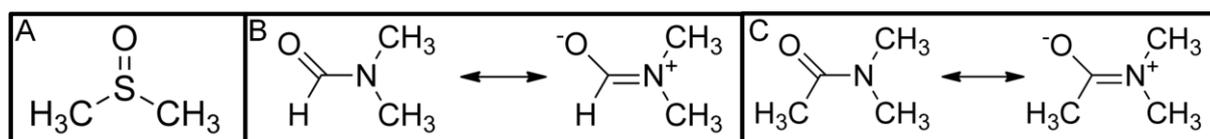


Figure 8. Molecular structure of A) DMSO, resonance forms of B) DMF and C) DMAc. (paper I)

Studies of the interaction between ionic liquids and co-solvents have shown that there is a stronger interaction between ionic liquid and DMF than between ionic liquid and DMSO [32, 49]. The authors state that, since DMF and DMAc have a molecular structure that allows for a resonance form with a negative pole on the oxygen atom, it can act as a hydrogen bond acceptor. DMSO lacks this property, see Figure 8. This structural difference between the co-solvents can explain why a wider solubility range

is seen when DMSO is used as co-solvent compared to DMF and DMAc, which is seen in Table 1 where solutions 1A and 1B could not form solutions as a result of too high co-solvent content.

### 3.1.1 Rheological behaviour

Steady state shear viscosity of the solutions increases with EmimAc content, as seen in Figure 9.

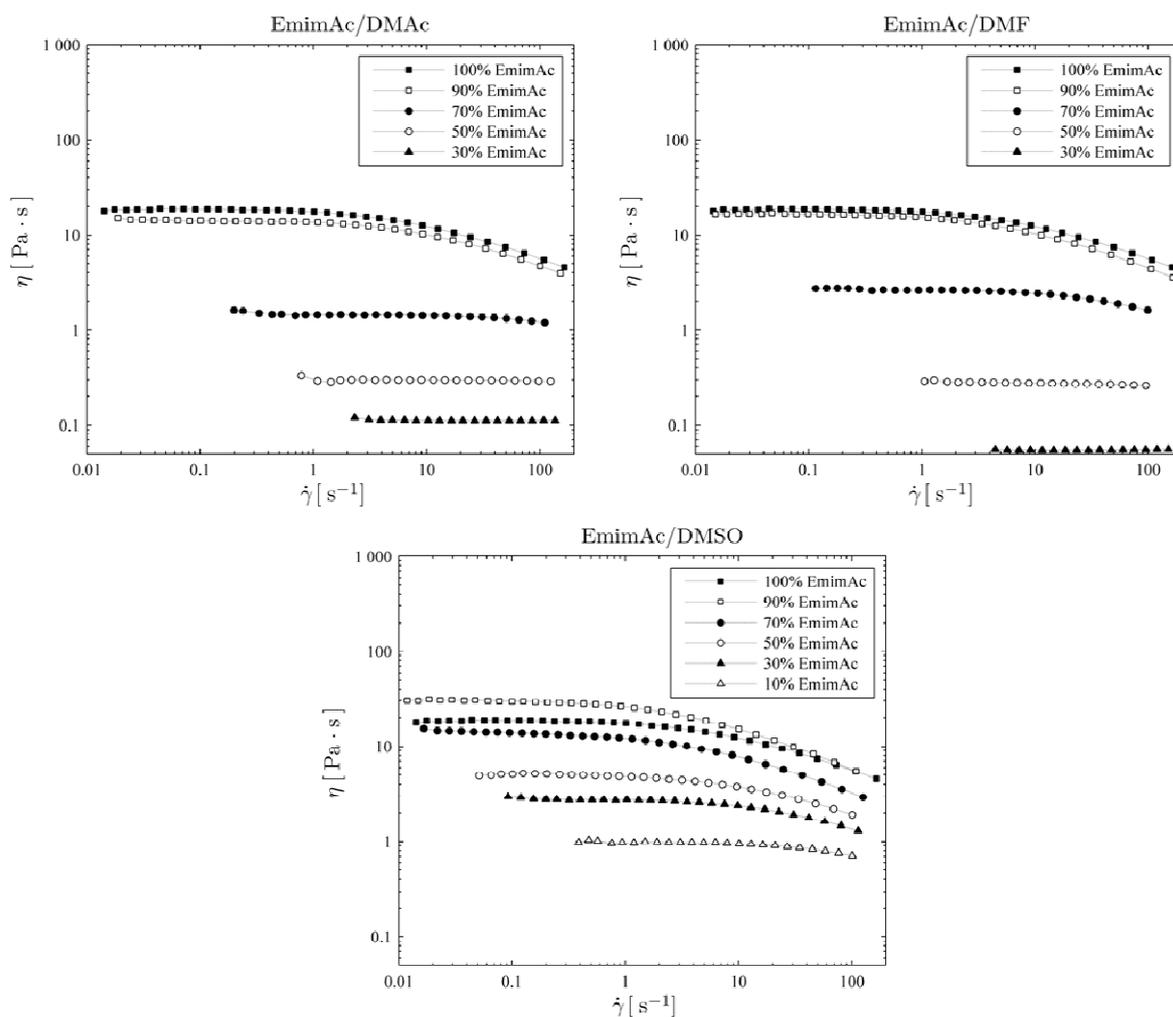


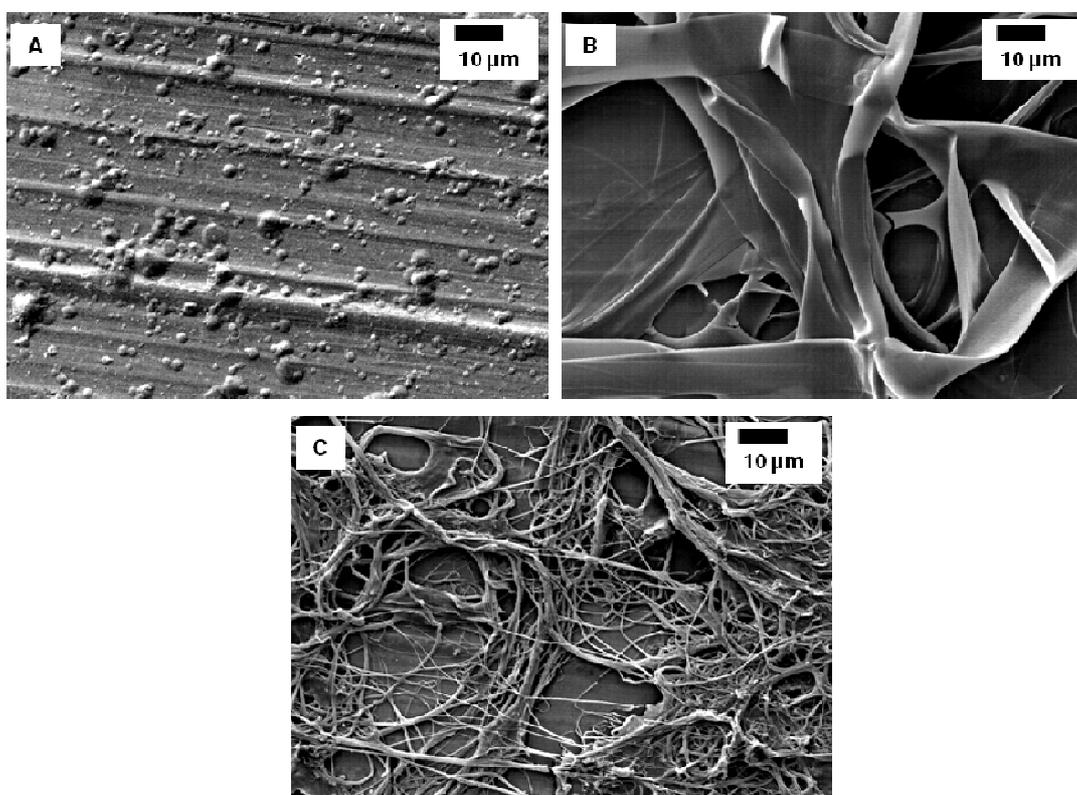
Figure 9. Viscosity as a function of shear rate on cellulose dissolved in EmimAc with different co-solvents. Solvent ratios as denoted. (paper I)

At high ratios of EmimAc, the dissolved cellulose molecules will adapt a random coil conformation with a relatively large radius of gyration, giving a high viscosity. Analogously, with an increased fraction of co-solvent, the reduced solubility will force the cellulose molecules to adapt a conformation with a lower gyration radius.

## Results and discussion

Consequently, the viscosity of the system is reduced. Shear thinning behaviour is exhibited by the solutions, especially at high fractions of EmimAc. As shear thinning is an indication of shear induced change in polymer conformation and/or reduced entanglement density, it is understandable that the solutions with the best cellulose solubility and thereby largest gyration radii and random coil flexibility show the greatest shear thinning tendency. Shear thinning can be interpreted as a result of a decreasing entanglement density as a consequence of shear.

When comparing the three systems, higher viscosity and more pronounced shear thinning behaviour are noted for the DMSO-based system. This is explained by the weaker interaction between the DMSO and the ionic liquid compared to the DMF/DMAc-based systems, rendering differences in polymer coil radius and flexibility which are manifested through the differences in rheological behaviour. SEM pictures were taken of all samples (see Table 1) and classified according to fibres formed. Fibre formation was ranked from +: no fibres formed to +++: fibre formation. Examples of the different classes are shown in Figure 10.



*Figure 10. SEM micrographs of electrospun cellulose fibres; A) example of classification +: no fibre formation (see Table 1); B) example of classification ++: tendencies to form fibres; C) example of classification +++: fibre formation. (paper I)*

*Table 1. Solution parameters and classification of fibre formation of cellulose dissolved in EmimAc. (paper I)*

Sample	Cellulose (wt%)	Co-solvent (wt%)	Fibre formation test 1	Fibre formation test 2	Fibre formation test 3
1A	2.5 wt%	90 wt% DMF	-	-	-
2A	2.5 wt%	70 wt% DMF	+	+	+
3A	2.5 wt%	50 wt% DMF	+	+	+
4A	2.5 wt%	30 wt% DMF	+	++	+++
5A	2.5 wt%	10 wt% DMF	+++	+++	+++
1B	2.5 wt%	90 wt% DMAc	-	-	-
2B	2.5 wt%	70 wt% DMAc	+	+	+
3B	2.5 wt%	50 wt% DMAc	+	+	+
4B	2.5 wt%	30 wt% DMAc	+	+	+
5B	2.5 wt%	10 wt% DMAc	++	++	+++
1C	2.5 wt%	90 wt% DMSO	+	+	+++
2C	2.5 wt%	70 wt% DMSO	+++	+	+++
3C	2.5 wt%	50 wt% DMSO	+++	+++	+++
4C	2.5 wt%	30 wt% DMSO	+++	+++	+++
5C	2.5 wt%	10 wt% DMSO	+++	++	+++
ABC0	2.5 wt%	0 wt%	+++	++	++

-            *could not be electrospun*  
 +            *no fibre formation*  
 ++          *fibre formation tendencies*  
 +++        *fibre formation*

Results off the electrospinning trials are shown in Table 1, and there it is clear that the EmimAc/DMSO-based system is the best fibre forming system. This is related to the different dissolution power of the EmimAc/DMSO system as opposed to the other two, as discussed above. In this system, the dissolved cellulose will probably adapt a

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conformation, entanglements and/or radius of gyration more suitable for fibre formation. All systems show that a rather high content of EmimAc is required to form fibres, although not too high, considering that pure EmimAc (sample ABC0) did not give the best fibre formation.

We see in Figure 9 and Table 1 that a certain level of viscosity is needed in order to achieve good fibre formation. It is difficult to say whether the shear thinning behaviour is beneficial in itself for fibre formation. By plotting the degree of shear thinning (reduction in viscosity over the measured stress interval divided by zero shear viscosity) versus zero shear viscosity (Figure 11), the region with the most pronounced shear thinning proves to be where the best fibre formation occurs. Unfortunately, the dependence of shear thinning behaviour cannot be completely decoupled from initial viscosity as the best fibre forming samples, i.e., those with the most pronounced shear thinning behaviour are also those with the highest zero shear viscosities.

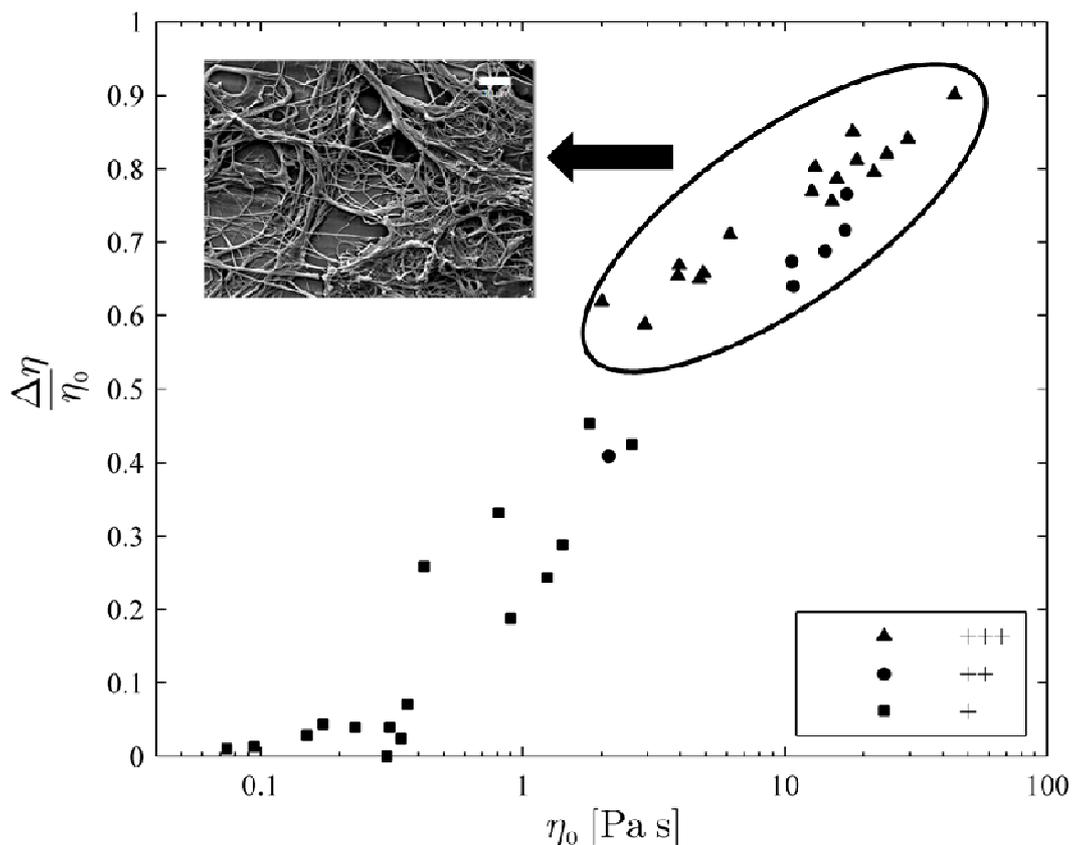


Figure 11. Shear thinning and fibre forming ability. (paper I)

### 3.1.2 Surface tension

Surface tension was measured for all three solvent systems and the surface tension decreases with decreased molar fraction EmimAc, as seen in Figure 12.

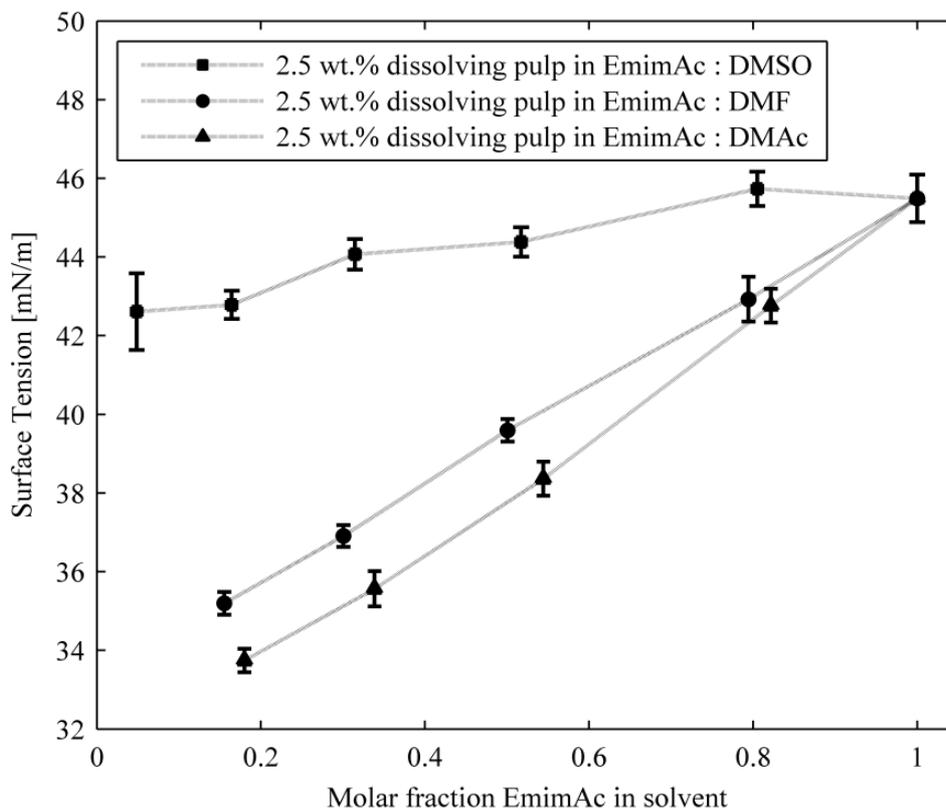


Figure 12. Surface tension as a function of molar fraction EmimAc in solvent. (paper I)

Using DMF or DMAc as co-solvent, the surface tension of the spinning dope decreases to a larger extent than by using DMSO as co-solvent. The DMSO-based system had the highest surface tension regardless of molar fraction EmimAc. The differences in surface tension reduction between the different co-solvents are simply related to the different surface tensions of the pure co-solvents.

Fibres could be electrospun from solutions with a surface tension greater than 42 mN/m, regardless of molar fraction EmimAc and co-solvent. This indicates that a certain degree of surface tension is beneficial for fibre formation. As for shear thinning, the dependence of surface tension cannot be fully decoupled from viscosity; most of the fibre forming samples with the highest surface tensions had relatively high zero shear viscosities.

### 3.1.3 Conductivity

The results off the conductivity measurements are shown in Figure 13, and no clear connections between spinnability and conductivity could be drawn from them. The only conclusion that could be made is that all three solvent systems exhibit similar values of conductivity and that they all show a conductivity maximum in the lower region of the EmimAc fraction. Solutions with conductivity values between 3 and 11  $\text{mS cm}^{-1}$  (i.e., the range investigated) could electrospin fibres. However, the conductivity range is not very large, and it is likely that a conductivity dependence on fibre formation would have been seen if a wider range of conductivities had been studied.

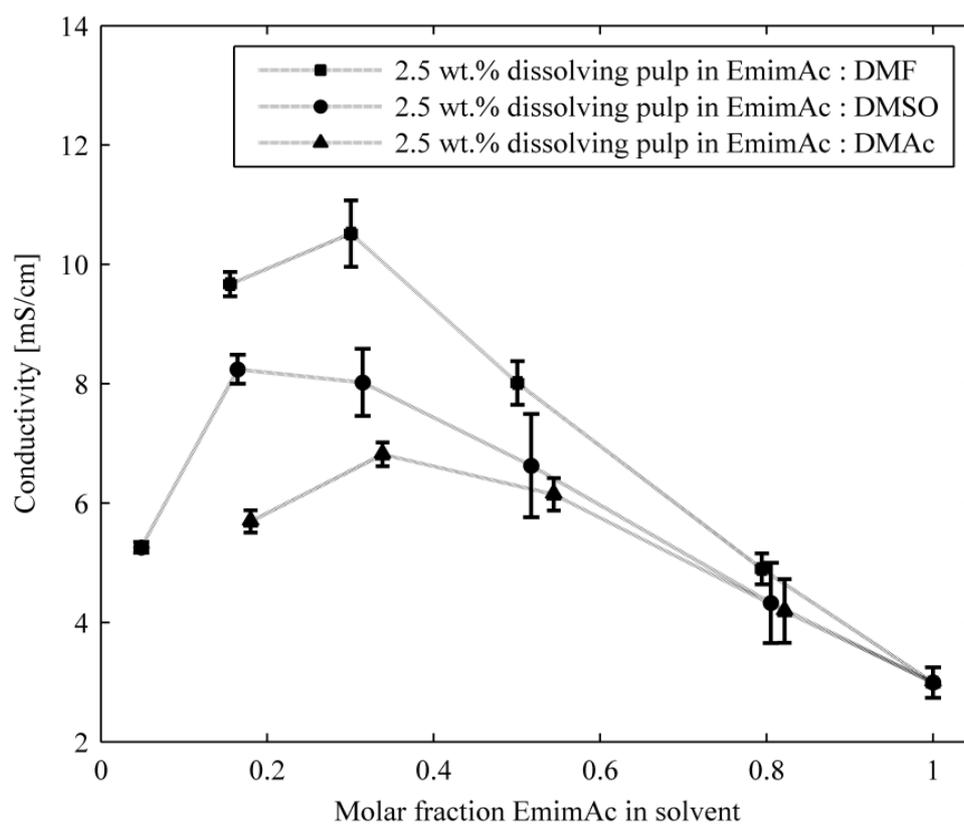


Figure 13. Conductivity as a function of molar fraction EmimAc in solvent. (paper I)

### 3.2 Electrospinning cellulose from ionic liquids with different molecular weight and concentration (paper II)

To continue the first study, where the cellulose concentration and molecular weight was unchanged, we investigated the influence that molecular weight and rheology have on electrospinning cellulose dissolved in ionic liquids, by varying the concentration and molecular weight of the cellulose. Based on the results off the first study, DMSO was chosen as co-solvent and used in a ratio of 1:1 (w/w) with the ionic liquid EmimAc. Cellulose was depolymerised with hydrochloric acid to yield fractions of cellulose with gradient of molecular weight distributions. Results off Size Exclusion Chromatography (see Figure 14) confirmed that the cellulose was depolymerised by the acid treatment into different molecular weight fractions. A longer acid treatment time yielded more chain scission, hence a lower molecular weight.

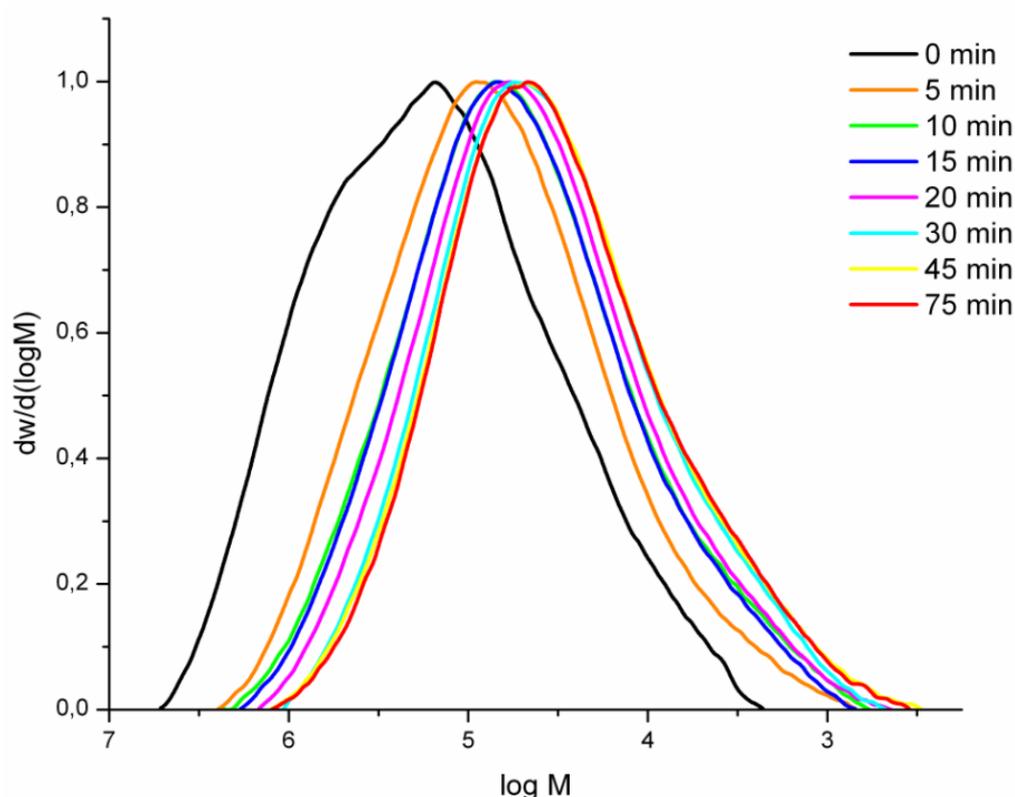


Figure 14. Molecular weight distributions of acid treated cellulose samples. (paper II)

Acid depolymerisation of cellulose reaches a levelling-off degree of polymerisation (LODP) that depends on treatment conditions [50]. In Figure 15, molecular weight is

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plotted against acid treatment time. Under the conditions used, the LODP were reached after approximately 30 minutes of acid treatment. For the cellulose used in this study, harsher acid conditions are needed (e.g., stronger acid or higher temperature) to reach a lower LODP value.

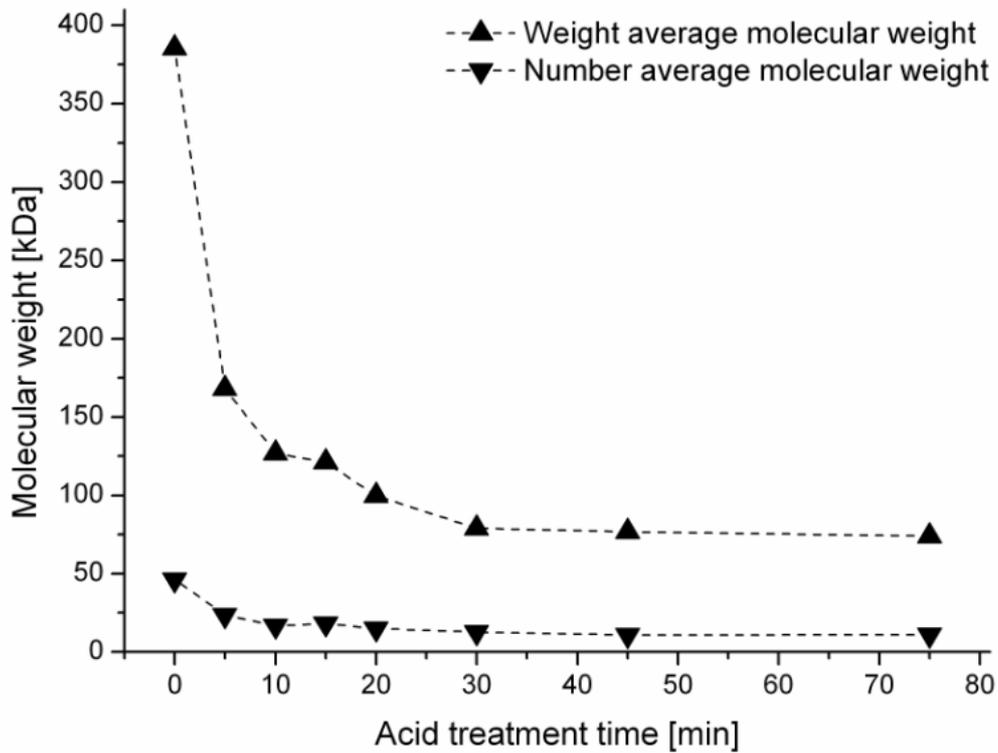


Figure 15. Molecular weight as a function of acid treatment time for cellulose samples. (paper II)

The fibre morphology of the electrospun fibres was evaluated with SEM. The electrospinnable solutions could be divided into three sub-regions when relating fibre morphology to solution viscosity: a top region, a middle region and a lower region. In the top region, many fibres are thick and seem to be made up of bundles of several individual fibres, as seen in Figure 16A. Figure 16B shows an example of how fibres can look when they are electrospun from the middle region. In the lower region, but still high enough viscosity for fibre spinning, the electrospun fibres have more beads and drops, as seen in Figure 16C.

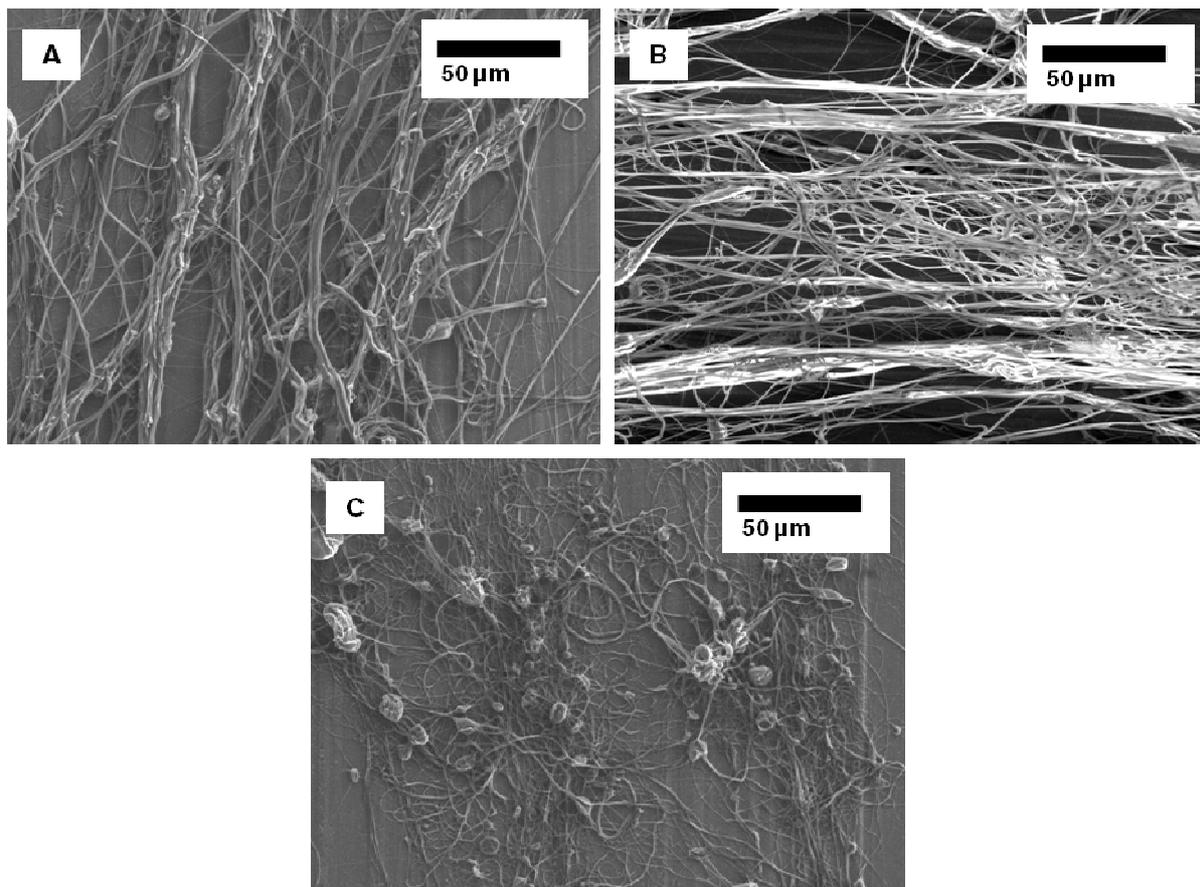


Figure 16. SEM micrographs of electrospun fibres. A) top region of the spinnable solutions, B) middle region of the spinnable solutions and C) low region of the spinnable solutions. (paper II)

The rheological properties of all solutions were characterized and, as expected for polymer solutions, the viscosity increased as the cellulose concentration increased. All solutions showed shear thinning behaviour, i.e., the viscosity decreased as the shear rate increased. Shear thinning behaviour is an indication of them all being non-Newtonian liquids. The shear thinning behaviour also increased as the viscosity increased; solutions that had a high viscosity also had a higher degree of shear thinning. The empirical Cox-Merz rule states that, for linear viscoelastic liquids, the magnitude of the complex viscosity coincides with the steady state viscosity when plotted versus angular frequency (rad/s) and shear rate (1/s), respectively [51]. The rheological measurements concluded that the Cox-Merz rule can be applied to our solutions.

Electrospinnability can be defined as the ability of a solution to be electrospun into fibres. Figure 17 shows the electrospinnability for the solutions studied here. Solutions that could be electrospun are denoted with green triangles in Figure 17. The solutions

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that could not form fibres, i.e., non-spinnable solutions, are divided into two sub-groups: non-spinnable because of too high viscosity (denoted with red squares in Figure 17) and non-spinnable because of too low viscosity (denoted with red circles in Figure 17). From Figure 17 we see that, within the intervals studied, neither cellulose concentration nor acid treatment time, and thereby cellulose molecular weight, seems to be decisive for whether or not a solution can be electrospun into fibres. It is rather the viscosity of the solution that is decisive for electrospinnability. The viscosity is, in turn, determined by the internal forces in the liquid, and similar viscosities can be achieved by, e.g., polymer concentration or molecular weight. Solutions exhibiting too low viscosity, either caused by low cellulose concentration or long acid treatment time, appear to electrospray instead of electrospin, hence not forming fibres. Solutions with too high viscosity become difficult to handle and are thus non-spinnable. For instance, the solution transfer to syringe is very difficult and there is a tendency for the needle to clog during electrospinning.

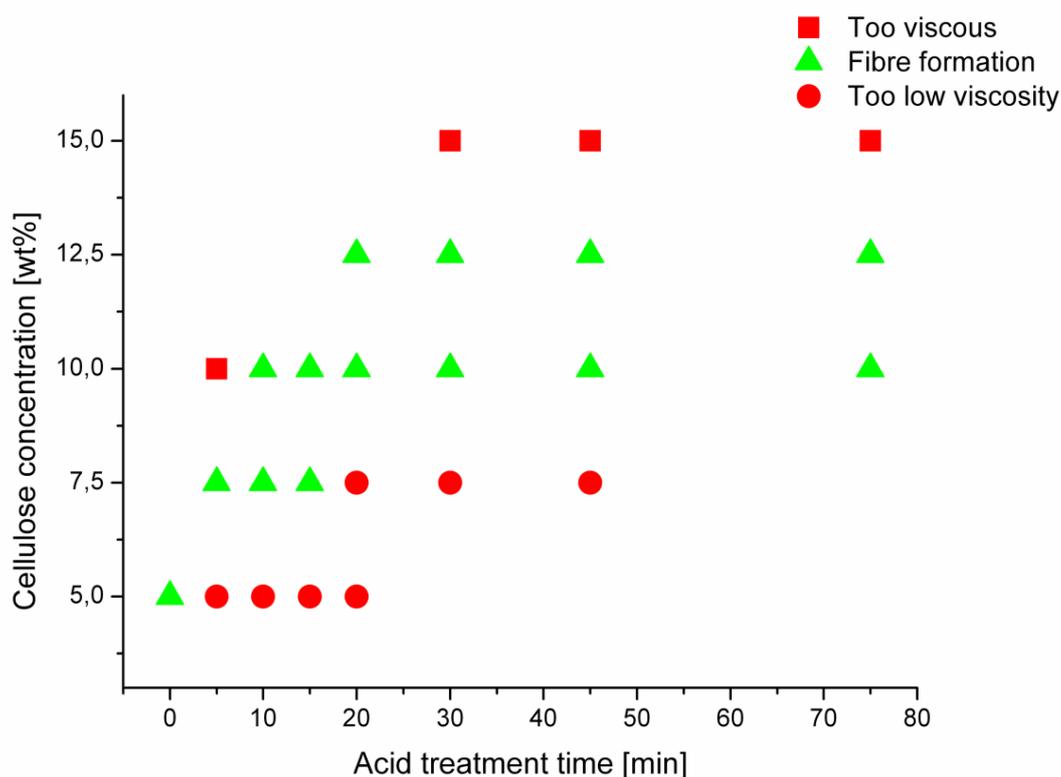


Figure 17. Electrospinnability for acid treated cellulose in EmimAc:DMSO 1:1 (w/w) at concentration and acid treatment time indicated. Solutions indicated by round red symbols display too low viscosity, triangular green symbols can be electrospun into fibres and square red symbols are too viscous for good electrospinning. (paper II)

A related important factor for successful electrospinning is polymer concentration. By plotting the zero shear viscosity of the solutions as a function of cellulose concentration (wt%), seen in Figure 18, a power-law dependence can be seen,  $\eta_0 \propto C^n$ , for each cellulose fraction. The power-law scaling of  $\eta_0$  for our solutions has exponents ranging from 4.1 to 5.6, with a mean value of 4.6. In relation to other scaling reported for cellulose dissolved in EmimAc our values are comparable (Gericke and co-workers reported scalings for cellulose in EmimAc solutions to be 4.4 at 0 °C [52] and Sescousse and co-workers around 4 at low temperatures (0-40 °C) [53]). Gericke and co-workers also concluded that EmimAc is close to a theta solvent for cellulose [52]. In a theta solvent, the polymer will remain in its unperturbed state as compared to in a poor solvent, where the polymer coil will contract, or in a good solvent, where the polymer coil will expand. The theoretical concentration scaling for neutral linear polymers in a theta solvent gives slopes of 1, 2 and 14/3 in the dilute, semi-dilute unentangled and semi-dilute entangled regimes, respectively [54]. These theoretical predictions indicate that all our cellulose fractions at the chosen concentrations are in the entangled semi-dilute regime, as seen in Figure 18. In the entangled semi-dilute regime, defined as  $c > c_e$ , the polymer concentration is large enough for the significant overlap necessary for chain entanglement. The importance of chain entanglement for stable electrospinning has been established by Shenoy and co-workers [55]. However, as seen from our results, some of the solutions show no electrospinnability (indicated with red circles and squares in Figure 17). Our conclusion is that, for electrospinning to occur, even though being in the entangled semi-dilute regime, the solution viscosity, either controlled by polymer concentration or molecular weight, also needs to be within a certain interval.

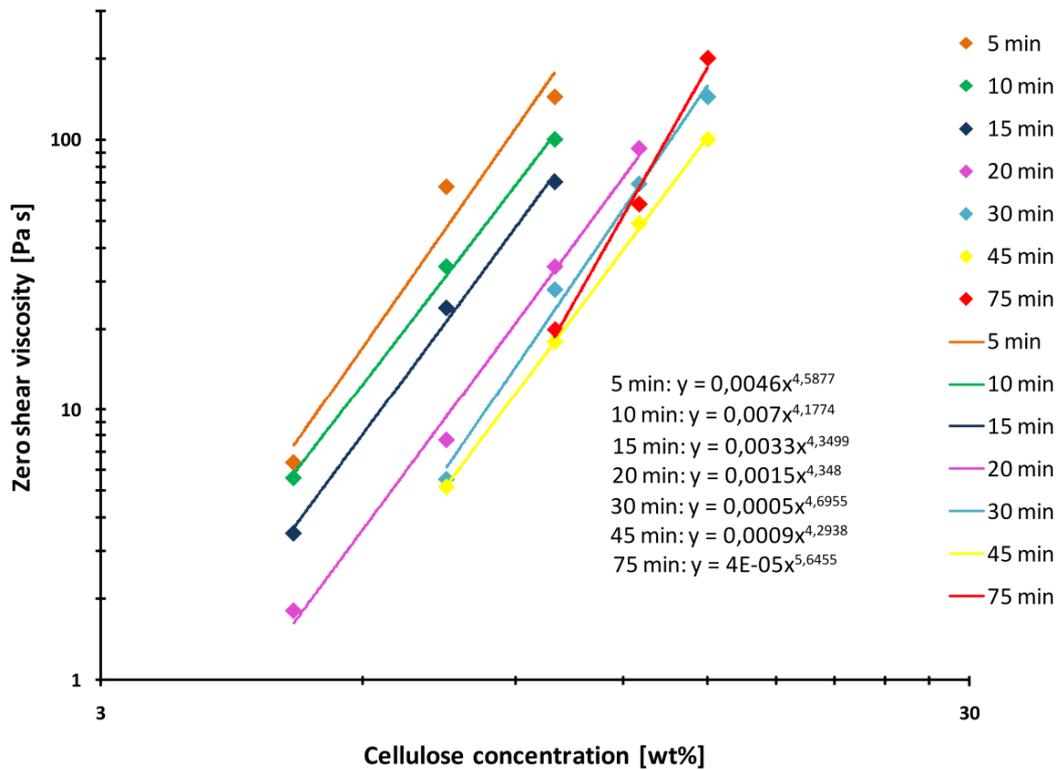


Figure 18. Zero shear viscosity as a function of cellulose concentration. (paper II)

The existence of a well defined zero shear viscosity and the facts that the Cox-Merz rule applies and that the viscosity scale has a concentration according to the theory for entangled semi-dilute polymers indicate that the cellulose in the EmimAc:DMSO 1:1 (w/w) solutions is genuinely dissolved on the molecular level, forming flexible overlapping coils in the solvent, and that chain interactions are dominated by topological constraints (entanglements).

## 4. Concluding remarks

Cellulose dissolved in the ionic liquid EmimAc has been successfully electrospun. Three different co-solvents (DMF, DMAc and DMSO) were used to study solution parameters (viscosity, surface tension and conductivity) and relate them to spinnability and fibre formation. To form fibres, regardless of which co-solvent is used, a certain degree of viscosity and surface tension is needed. The DMSO-based system is spinnable at a lower content of EmimAc than the DMAc-based and DMF-based systems, due to the higher viscosity values that were exhibited. The surface tension of the solvent mixtures is less affected when DMSO is used as co-solvent in comparison to the other two co-solvents. No clear connections could be drawn between conductivity and spinnability. The system with DMSO as co-solvent was found to give the best fibre formation, which is linked to the solubility of cellulose in ionic liquids with different co-solvents. In contrast to DMSO, both DMAc and DMF have a molecular structure that can present a resonance form and consequently a stronger interaction between the ionic liquid and co-solvent (DMAc or DMF) compared to the interaction between ionic liquid and DMSO. Interestingly, the solutions with the most pronounced shear thinning behaviour, i.e., the DMSO-based system, are also the best fibre forming solutions.

The effect of the molecular weight of the cellulose and cellulose concentration on fibre spinnability was also investigated. Cellulose was depolymerised with hydrochloric acid to yield fractions with different molecular weight distributions. Depending on the acid treatment conditions, acid depolymerisation of cellulose reaches a levelling-off degree of polymerisation (LODP); here it is reached after approximately 30 minutes. Size Exclusion Chromatography confirmed that the cellulose was degraded into different molecular weight fractions, where longer acid treatment time yielded more chain scission, hence a lower molecular weight. The dominant property for electrospun cellulose fibres from ionic liquids to be formed is solution viscosity. This is the case even though all EmimAc:DMSO 1:1 (w/w) solutions, with various concentrations and/or molecular weights, were in the entangled semi-dilute regime. The solution viscosity can be controlled with, e.g., polymer concentration or molecular weight.

## 5. Future work

To continue the work done in this thesis, it would be of great interest to combine the many advantages of dissolution of cellulose in ionic liquids with the larger production rate of the solution spinning method.

The solvents and coagulation bath used in this present study has proven to be suitable for electrospinning. A first task would be to apply this system, consisting of the ionic liquid EmimAc as solvent and water as coagulant, to the solution spinning process. To investigate suitable process conditions, e.g. co-solvent, speed and draw ratio, for successful solution spinning of cellulose dissolved in ionic liquids, and to characterize the properties of the formed fibres.

Another aspect would be to investigate the possibility of functionalize solution spun cellulose fibres by adding other substances to the spin dope. These substances could be dissolved on the molecular level or added as nanoparticles or being dispersed as droplets in the spin dope. Examples could be carbonaceous nanoparticles like carbon black, carbon nanotubes and graphite nanoplatelets, producing conductive cellulose based fibres. Another option is incorporation of compounds for controlled release of drug molecules. Such fibres could find applications in wound care for example. The possibility to spin fibres at low temperatures is here of particular relevance to protect degradation of additives.

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