

## Influence of Molecular Weight and Rheological Behavior on Electrospinning Cellulose Nanofibers from Ionic Liquids

Linda Härdelin,<sup>1,2,3</sup> Erik Perzon,<sup>1,3</sup> Bengt Hagström,<sup>1,3,4</sup> Pernilla Walkenström,<sup>1,3</sup> Paul Gatenholm<sup>2,3</sup>

<sup>1</sup>Swerea IVF, PO Box 104, Mölndal, SE-431 22, Sweden

<sup>2</sup>Department of Chemical and Biological Engineering, Chalmers University of Technology, Gothenburg, SE-412 96, Sweden

<sup>3</sup>Wallenberg Wood Science Center, Chalmers University of Technology, Gothenburg, SE-412 96, Sweden

<sup>4</sup>Department of Materials and Manufacturing Technology, Chalmers University of Technology, Gothenburg, SE-412 96, Sweden

Correspondence to: L. Härdelin (E-mail: linda.hardelin@swerea.se)

**ABSTRACT:** Dissolving pulp was depolymerized with 2.5M HCl into cellulose fractions with decreasing molecular weight relative to acid treatment time. The cellulose fractions were dissolved at various concentrations in the ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) with co-solvent DMSO at ratio 1 : 1 (w/w) and electrospun. Size exclusion chromatography was used to evaluate the molecular weight distributions and the rheological properties were characterized with a cone-and-plate rheometer. Scanning electron microscope was used to evaluate the fiber morphology, and thereby spinnability. Zero shear viscosity as a function of cellulose concentration show that all the solutions in this study are in the entangled semi-dilute regime; where the polymer concentration is large enough for significant overlap necessary for chain entanglement. However, within the intervals studied, neither cellulose concentration nor molecular weight seems to be decisive for if a solution can be electrospun into fibers or not. It is rather the viscosity of the solution that is decisive for electrospinnability, even though the solution is in the entangled semi-dilute regime. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2303–2310, 2013

**KEYWORDS:** electrospinning; cellulose; ionic liquids; viscosity; molecular weight

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### INTRODUCTION

Cellulose is a linear polysaccharide consisting of repeated D-glucose units and the world's most abundant biopolymer. It is renewable and an excellent source for producing new materials.<sup>1</sup> Since Swatloski et al.<sup>2</sup> dissolved cellulose in ionic liquids, the area has attracted a lot of interest among many researchers. The ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) is one of the ionic liquids best suited for cellulose dissolution.<sup>3,4</sup> Recently, ionic liquids have been used to dissolve cellulose for electrospinning nanofibers.<sup>5–10</sup>

In our previous study, we electrospun cellulose from the ionic liquid EmimAc with different co-solvents.<sup>7</sup> Dissolving pulp was used as cellulose source at one fixed concentration (2.5 wt %), which was dissolved in a solvent system consisting of EmimAc and a co-solvent at different ratios, to study the effect on electrospinnability. To continue that study we herein varied the concentration and molecular weight of the cellulose, in order to investigate the influence molecular weight and rheology has on electrospinning cellulose dissolved in ionic liquids. To the best of our knowledge this has not been done before.

The degree of polymerization (DP) of cellulose can be lowered with acid hydrolysis. The reaction is a three step process. The first step occurs on the glycosidic oxygen, which links two glucose units, where a proton from the acid interacts with the oxygen to form a conjugate acid. In the next step, the C–O bond is cleaved and the conjugate acid is broken down to an intermediate cyclic carbonium ion. Water is then rapidly added, and a proton and glucose are released.<sup>11</sup> When cellulose is hydrolyzed by acid a strong initial decrease in DP is observed, before it reaches a leveling-off degree of polymerization (LODP). Models of cellulose state that in the fibrils there are both crystalline regions and amorphous, less ordered regions.<sup>12</sup> The LODP values observed after acid hydrolysis are considered to correspond to the crystallite length in the cellulose chains.<sup>13</sup>

Solution viscosity 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.<sup>14</sup> 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.<sup>15,16</sup> An increase in molecular weight means that the average chain length per molecule increases, which gives more entanglements per volume.

The aim of this study was to investigate the relationship between cellulose molecular weight and fiber spinnability when electrospinning cellulose from ionic liquids.

## EXPERIMENTAL

### Materials

The cellulose source used in this study was a dissolving pulp from Domsjö Fabriker AB, Sweden. Viscosity of the dissolving pulp was in the range 500–900 mL/g, measured according to the standard SCAN-C15 : 88 and  $DP_v$  was between 620–1360 (according to the supplier).

Ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate (EmimAc) Lot# STBC3627V  $\geq 90\%$ , dimethyl sulfoxide (DMSO)  $\geq 99.5\%$ , and *N,N*-dimethylacetamide  $\geq 99.5\%$  were purchased from Sigma-Aldrich. Lithium chloride 99.5% was retrieved from KEBO-Lab AB, Sweden, and hydrochloric acid fuming 37% pro analysis from Merck. Methanol was of HPLC grade from Fisher Scientific. All chemicals were used without further purification.

### Methods

The pulp was disintegrated in a disintegrator according to the standard SCAN-C18 : 6 in order to achieve a more even distribution of the cellulose fibers. For each batch 30 g (dry weight) pulp was soaked in distilled water over night. The wet pulp was torn into small pieces, 2 L of distilled water was added and the disintegration started. The pulp slurry that was obtained had a cellulose concentration of 1.5 wt % after disintegration. 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 filtered and washed thoroughly with distilled water. The pulp was dried in an oven at 80°C for 12 h.

In accordance with our earlier study,<sup>7</sup> DMSO was chosen as co-solvent and used in ratio 1 : 1 (w/w) with the ionic liquid EmimAc for all solutions made in this study (see Table I for solution parameters). A co-solvent, here DMSO, is added to lower

**Table I.** Solution Parameters

Solution	Cellulose (wt %)	HCl 2.5M 70°C
5% 0 min	5	0 min
5% 5 min	5	5 min
5% 10 min	5	10 min
5% 15 min	5	15 min
5% 20 min	5	20 min
7.5% 5 min	7.5	5 min
7.5% 10 min	7.5	10 min
7.5% 15 min	7.5	15 min
7.5% 20 min	7.5	20 min
7.5% 30 min	7.5	30 min
7.5% 45 min	7.5	45 min
10% 5 min	10	5 min
10% 10 min	10	10 min
10% 15 min	10	15 min
10% 20 min	10	20 min
10% 30 min	10	30 min
10% 45 min	10	45 min
10% 75 min	10	75 min
12.5% 20 min	12.5	20 min
12.5% 30 min	12.5	30 min
12.5% 45 min	12.5	45 min
12.5% 75 min	12.5	75 min
15% 30 min	15	30 min
15% 45 min	15	45 min
15% 75 min	15	75 min

the viscosity without any cellulose precipitation. An appropriate amount of dry cellulose was weighed and placed in a small glass container. DMSO was added to the pulp and allowed to soak into the pulp over a period of time, roughly 1 min. EmimAc was then added to the mixture and the container was sealed. The sealed container was placed in an oil bath at 80°C for 24 h under stirring. The clear and homogenous solution was then subjected to electrospinning for 1 h.

The rheological properties of the solutions were characterized by means of a Bohlin Rheometer CS 30 (Malvern Instruments, 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. Stress sweep tests were performed on all solutions at a frequency of 1 Hz (6.28 rad s<sup>-1</sup>) to determine their linear viscoelastic region. 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 0.0628–125.6 rad s<sup>-1</sup>.

Molecular weight determination was performed using Size Exclusion Chromatography (SEC). 30 mg of each acid treated pulp fraction, as well as the untreated pulp, was activated in 30 mL deionized water for 3 h with magnetic stirrer. The water was removed with vacuum filtration and the pulp samples

subjected to solvent exchange with 30 mL methanol ( $3 \times 30$  min stirring) and then 30 mL DMAc ( $3 \times 30$  min stirring). A 3.8 mL of 8% LiCl/DMAc was added to each pulp sample and stirred at 4°C for 5 days. The solutions were diluted with 57 mL DMAc to a concentration of 0.5 wt % pulp. Before characterization the solutions were filtered through a 0.45  $\mu\text{m}$  polytetrafluorethylene (PTFE) syringe filter and stored in vials. The SEC system consisted of a DGU-20A<sub>3</sub> degasser (Shimadzu, Japan), a LC-20AD liquid chromatography (Shimadzu, Japan), a Rheodyne 7725i fixed loop (100  $\mu\text{L}$ ), and a RID-10A refractive index detector (Shimadzu, Japan). The separation system consisted of a mixed-A 20  $\mu\text{m}$  guard column ( $7.5 \times 50$  mm, Polymer Laboratories, UK) and three mixed-A 20  $\mu\text{m}$  columns ( $7.5 \times 300$  mm, Polymer Laboratories, UK) connected in series. The injection volume was 100  $\mu\text{L}$  and the flow rate was set at 0.5 mL/min. The columns were thermostated at 80°C and the mobile phase was 0.5% LiCl/DMAc. Each sample run lasted for 90 min. Pullulan standards with nominal masses of 800 kDa, 400 kDa, 200 kDa, 110 kDa, 50 kDa, 22 kDa, 12 kDa, 6 kDa, 1.3 kDa, and 320 Da (Fluka) were used for the calibration. The linear coefficient of determination ( $r^2$ ) was 0.996 for the curve of pullulan molecular weight versus the elution time. The system and data were controlled and evaluated with LC Solution software (Shimadzu, Japan).

Electrospinning was performed using a syringe capped with a blunt needle (0.6 mm i.d.) which was filled with cellulose solution. The solution was charged by applying a high voltage (10–50 kV) to the metallic needle. The distance between the tip of the needle and the collector was set to 10 cm. Solution flow rate was set at 0.5 mL/h and the grounded collector had a rotational speed of 25 rpm. The electrospinning setup was composed of a high voltage power supply (Gamma High Voltage Research, Ormond Beach, FL), a syringe pump (NE-1000 – New Era Pump Systems, Farmingdale, NY), and a rotating collector (diameter 10 cm) covered with an aluminum foil. The collector was partly submerged in a water bath in order to achieve precipitation of the cellulose solution into solid polymer fibers. To control surrounding atmosphere, the electrospinning equipment was set up in a room with constant relative humidity (RH 65%) and temperature (20°C).

A Scanning Electron Microscope (SEM; JSM-6610LV – JEOL) was used to investigate the fiber morphology and thereby evaluate the spinnability of the electrospun solutions. Fiber samples were cut out and mounted onto a holder, and the micrographs were taken at 500 $\times$  magnification in low vacuum.

## RESULTS AND DISCUSSION

### Molecular Weight Distributions

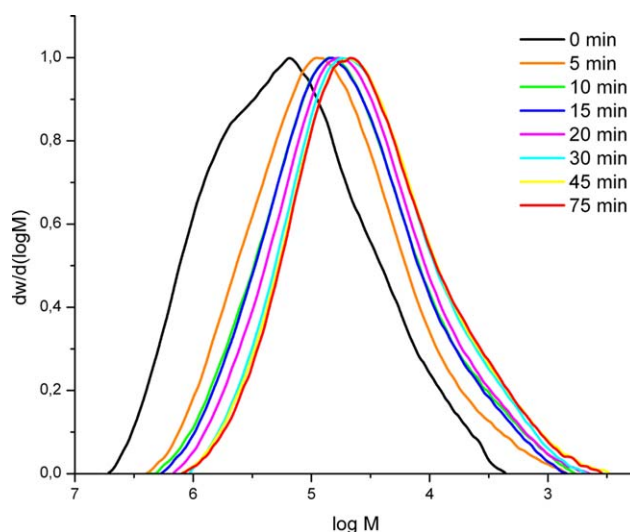
Table II shows the numerical evaluation of the molecular weight distribution of acid treated cellulose samples, where  $\bar{M}_w$  is the weight average molecular weight,  $\bar{M}_n$  is the number average molecular weight, and PDI is the polydispersity index ( $\bar{M}_w/\bar{M}_n$ ). The weight average molecular weight ( $\bar{M}_w$ ) for the untreated cellulose (0 min) is 385 kDa, which gives a DP of around 2380. The cellulose monomer ( $\text{C}_6\text{H}_{10}\text{O}_5$ ) has a molecular weight of 162 Da ( $385 \text{ kDa}/162 \text{ Da} = 2380$ ). The DP value given by the supplier ( $\text{DP}_v = 620\text{--}1360$ ) is based on the

**Table II.** Numerical Evaluation of Molecular Weight Distribution of Acid Treated Cellulose Samples

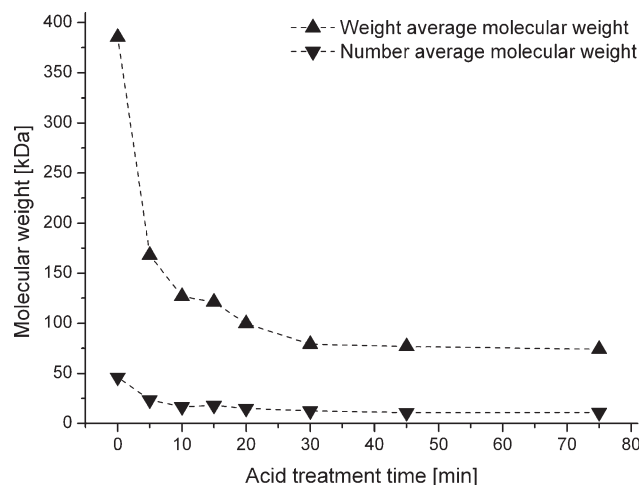
Acid treatment time	$\bar{M}_n$ (Da)	$\bar{M}_w$ (Da)	DP ( $\bar{M}_w/M$ )	PDI ( $\bar{M}_w/\bar{M}_n$ )
0 min	46,388	385,497	2380	8.31
5 min	23,417	168,210	1040	7.18
10 min	16,745	126,868	780	7.58
15 min	18,159	121,224	750	6.68
20 min	14,924	99,837	620	6.69
30 min	12,757	79,118	490	6.20
45 min	10,895	76,598	470	7.03
75 min	11,058	73,923	460	6.69

viscosity average molecular weight, and is thus lower than our measured DP value for the untreated cellulose based on  $\bar{M}_w$ . Which measurement technique used, is thus important to bear in mind when comparing different DP values.

In Figure 1 and Table II, the molecular weight distributions of the acid treated cellulose samples are all lower compared to the untreated sample (black line, 0 min in Figure 1). This confirms that the cellulose is hydrolyzed by the hydrochloric acid, and thereby depolymerized to various degrees depending on the time of acid treatment. Longer treatment time gives more chain scission. One point stands out, and that is the number average molecular weight after 75 min of acid treatment. It is slightly higher compared to after 45 min of acid treatment. However, both these points, and the one at 30 min, are all at the leveling-off degree of polymerization (Figure 2) and the small difference in  $\bar{M}_n$  ( $\sim 160$  Da) is therefore negligible. Noticeably, the polydispersity index (PDI) remains rather constant for all cellulose samples. This implies that the molecular weight distributions are all equally broad; they do not get narrower over time.



**Figure 1.** Molecular weight distributions of acid treated cellulose samples. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 2.** Molecular weight as a function of acid treatment time for cellulose samples.

However, it would be reasonable for the molecular weight distributions to get narrower over time, i.e., a decrease in PDI, which has previously been reported by others.<sup>17</sup> One could speculate that the reason why we do not see a decrease in PDI is that small water-soluble oligomers formed under the acid treatment are removed during the washing step, which follows the acid treatment, and that this loss of small water-soluble molecules could generate a PDI with constant value over acid treatment time.

In Figure 2, molecular weight, from Table II, is plotted against acid treatment time. The  $\bar{M}_w$  decreases rapidly from around 385 kDa, reaching a leveling-off degree of polymerization (LODP) value of less than 100 kDa. The LODP is reached after approximately 30 minutes, and after that the DP only decreases slightly. The compact cellulose crystallites are impermeable to water and acid catalysts, and only the amorphous regions are subjected to acid hydrolysis.<sup>18</sup> To reach a lower LODP-value for the cellulose used in this study, harsher acid conditions are needed (e.g., stronger acid or higher temperature). Microcrystalline cellulose (MCC) are usually produced by acid degradation of cellulose, mainly by hydrolysis with hydrochloric acid.<sup>19</sup>

### Structural Analysis

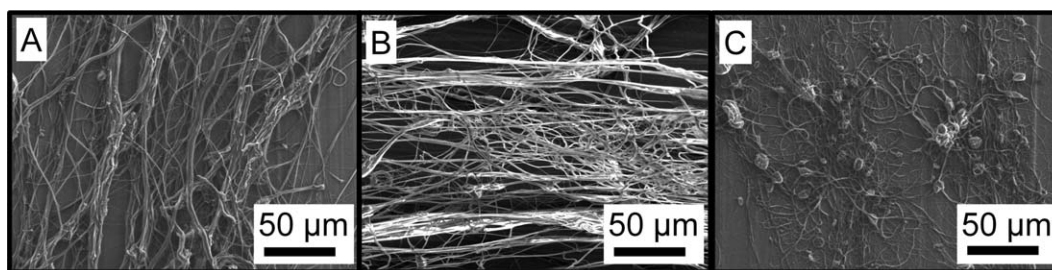
The fiber morphology was evaluated with SEM. Micrographs were taken of fibers from all spinnable solutions (spinnable solutions are denoted with triangular symbols in following

figures). The electrospinnable solutions could be divided into three sub-regions when relating fiber morphology to solution viscosity: a top region, a middle region, and a lower region. Figure 3(A) shows an example of how fibers can look when they are electrospun from the top region. There are thin fibers present in the micrograph, but many fibers are thick and seem to be made up of bundles of several individual fibers. In the middle region, the fibers may look as in Figure 3(B). In the lower region, but still high enough viscosity for fiber spinning, the electrospun fibers have more beads and drops as seen in Figure 3(C).

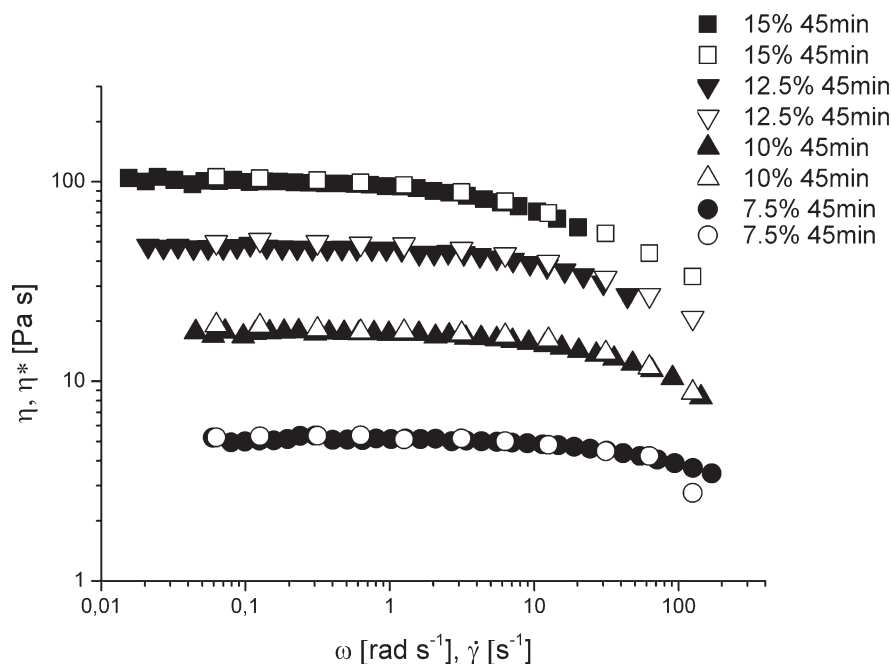
### Rheological Behavior

Figure 4 shows the steady-state shear viscosity as a function of shear rate and the magnitude of the complex viscosity as a function of angular frequency for 45 min of acid treated cellulose. Steady-state shear viscosity and complex viscosity was measured for all different acid treatment times. As the slopes all show the same tendencies and behavior when comparing the different acid treatment times, the 45 min of acid treatment time is used as an example of all their behavior. The viscosity increases as the cellulose concentration increases, which are to be expected for polymer solutions. All solutions show shear thinning behavior, i.e., the viscosity decreases as the shear rate increases. That is an indication of them all being non-Newtonian liquids. The shear thinning behavior also increases as the viscosity increases; solutions that have a high viscosity also have a higher degree of shear thinning. The empirical Cox–Merz rule<sup>20</sup> applies to our solutions as seen from the overlap of the complex viscosities (hollow symbols) and the shear viscosities (filled symbols). The Cox–Merz rule states that for linear viscoelastic liquids the magnitude of the complex viscosity  $\eta^*$  coincides with the steady state viscosity  $\eta$  when plotted versus angular frequency ( $\text{rad s}^{-1}$ ) and shear rate ( $\text{s}^{-1}$ ), respectively. Among researchers there is a disagreement whether or not the Cox–Merz rule can be applied to cellulose in ionic liquid-solutions. In previous studies it has been reported that the Cox–Merz rule does not apply for cellulose in ionic liquid-solutions,<sup>21,22</sup> but in our study as well as other studies it is shown that the rule does apply.<sup>23</sup> Worth mentioning are that these other systems, compared to ours, did not contain any co-solvents.

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 (shown below) indicate that the cellulose in our



**Figure 3.** (A–C) SEM micrographs of electrospun fibers. (A) Top region of the spinnable solutions, (B) middle region of the spinnable solutions, and (C) low region of the spinnable solutions. All micrographs are taken at 500× magnification.

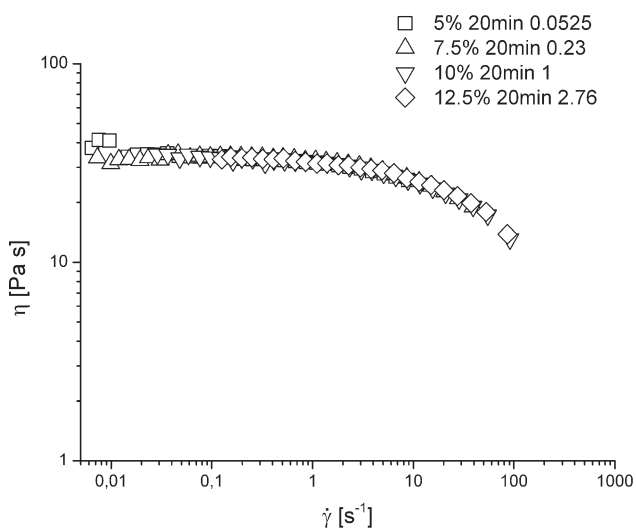


**Figure 4.** Viscosity as a function of shear rate (filled symbols) and complex viscosity as a function of angular frequency (hollow symbols) for acid treated (45 min) cellulose in DMSO : EmimAc 1 : 1 (w/w) at concentrations indicated. Round symbols exhibit too low viscosity for electrospinnability, triangular symbols can be electrospun, and square symbols are too viscous for good electrospinnability.

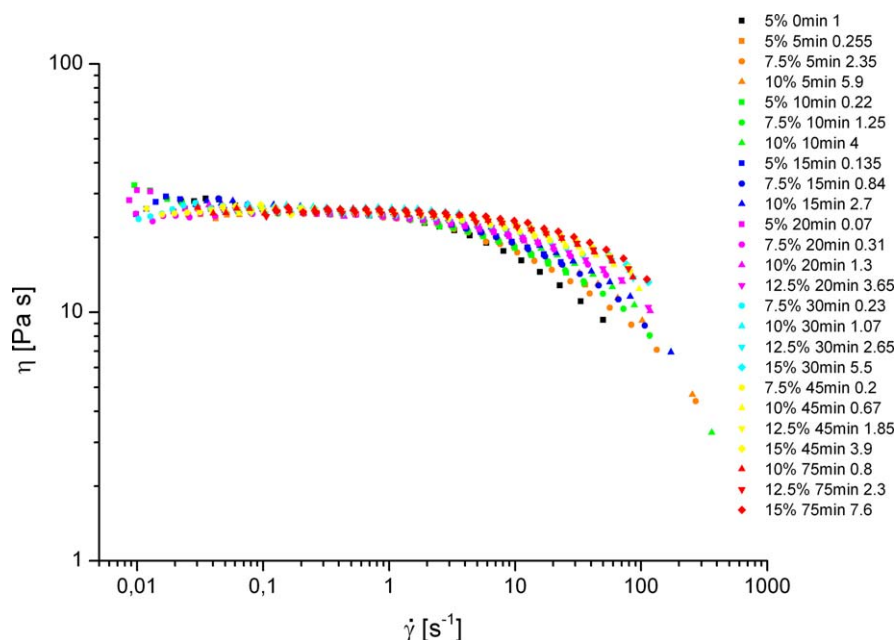
solutions is genuinely dissolved on the molecular level, forming flexible overlapping coils in the solvent, and that chain interactions are dominated by topological constraints (entanglements). For the acid treated cellulose samples, in the concentration range studied, the equation  $\eta_0 = Kc^\alpha M_w^\beta$ , described by Onogi et al.,<sup>24</sup> was found to produce a good correlation of zero shear viscosity to concentration ( $c$ ) and molecular weight ( $M_w$ ) with  $K = 1 \times 10^{-17}$ ,  $\alpha = 4.48$ ,  $\beta = 2.82$ , and with a linear coefficient of determination ( $r^2$ ) of 0.964. Onogi et al. found this type of power law correlation to be applicable to a number of concentrated polymer solutions involving flexible polymers (like polyvinyl acetate and polystyrene), the ratio  $\beta/\alpha$  being in the range 0.54–0.72 and tending to lower values for poor solvents.<sup>24</sup> The similar behavior of cellulose in EmimAc and DMSO ( $\beta/\alpha = 0.63$ ) seems to indicate that the cellulose molecules are quite flexible, forming random coils in the solvent system, and that the intramolecular hydrogen bonds in cellulose are largely broken by the interactions with the solvent.

We found that the shear viscosity curves for different cellulose concentrations, with a given acid treatment time, could be perfectly superimposed to form a single master curve by shifting along the “–1” slope in the  $\log(\eta)$  versus  $\log(\dot{\gamma})$  diagram. That is, multiplying shear rate and dividing shear viscosity with a concentration depending shift factor ( $f$ ). Figure 5 shows the celluloses with an acid treatment time of 20 min. We have chosen the 10% solution as the basis for the master curve ( $f = 1$  for this curve). All other curves are then shifted to get the best fit in the low shear rate region (same zero shear viscosity). However, superimposing curves representing cellulose solutions with different acid treatment times did not result in a unique single master curve. Figure 6 shows the shifted viscosity curves

for all solutions. The reference sample, i.e., 5% 0 min, is chosen as the basis for the master curve ( $f = 1$  for this curve). All other curves are shifted similar to previous figure. At high shear rates there is a divergence among the curves representing solutions of cellulose with different acid treatment time. The shear thinning starts at higher shear rates as the acid treatment time increases, hence as the molecular weight decreases. At very low shear rates there is also a deviation among the curves, this is attributed to the fact that the measurements were performed at lower shear rates than the instrument is capable of recording



**Figure 5.** Viscosity as a function of shear rate for 20 min acid treated cellulose solutions shifted along the “–1” slope. Solution properties and shift factors as denoted.

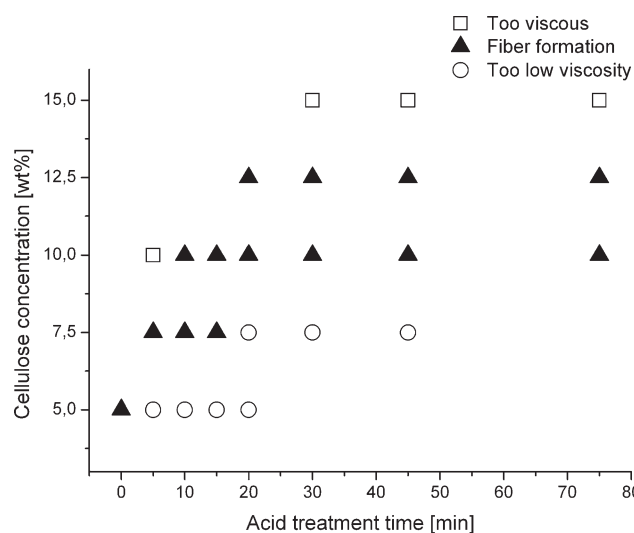


**Figure 6.** Viscosity as a function of shear rate for all solutions shifted along the “−1” slope. Solution properties and shift factors as denoted. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

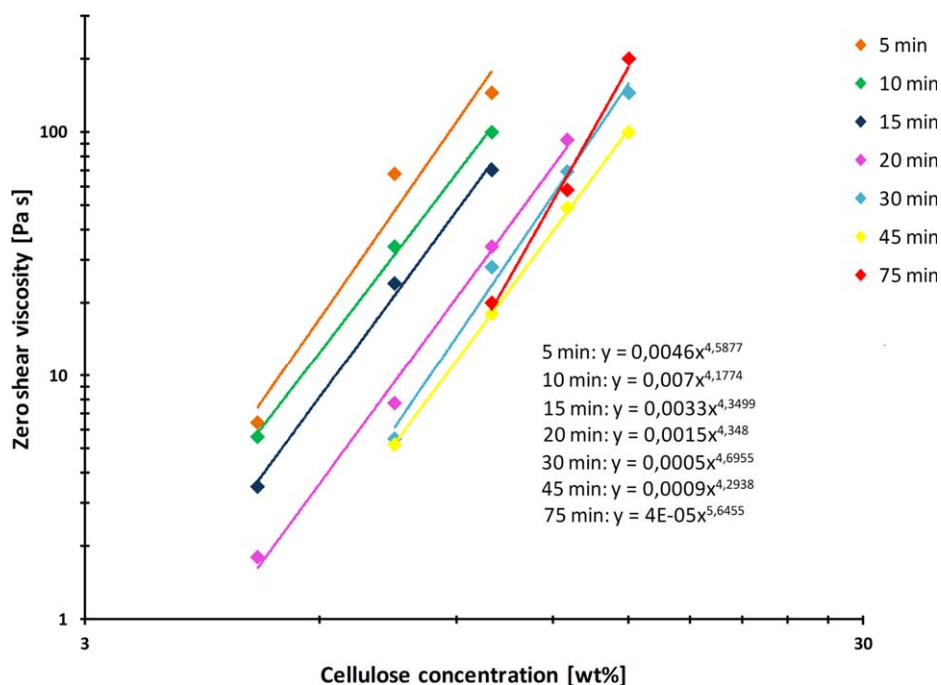
with reliability. Different acid treatment time is indicated in Figure 6 with different colors. This effect on shear thinning behavior that we see, i.e., the onset of shear thinning starts at lower shear rates as the molecular weight increases, is for a flexible polymer an indication that the molecular weight distributions have different polydispersity index (PDI). A polymer with a broad molecular weight distribution will start to shear thin at a lower shear rate than a polymer with a narrow molecular weight distribution, in our case, that the PDI decreases as the treatment time increases.<sup>25,26</sup> But from what can be seen from the size exclusion chromatography results in Table II and Figure 1, the PDI of the cellulose fractions remains rather constant with increased acid treatment time. This discrepancy in our data could be derived from slight differences in the high molecular weight tail of the molecular weight distribution. This high molecular weight tail consists of a few long chain molecules which, despite their very low number, have the capacity to affect the onset of shear thinning.<sup>27</sup> One possibility is that the contribution to the PDI (which is calculated from the  $\bar{M}_w$  and the  $\bar{M}_n$  obtained from SEC measurements) from these long chains is negligible considering their low number. Another possibility is the difficulty to detect the high molecular tail by SEC as stated by Wasserman and Graessley.<sup>27</sup>

Electrospinnability, defined as the ability of a solution to be electrospun into fibers, for the solutions studied, are shown in Figure 7 as filled triangular symbols. From the rheological measurements, exemplified by Figure 4, it can be deduced that the electrospinnable solutions show zero shear viscosities between 10 and 100 Pa s. Solutions that could not be electrospun are divided into two sub-groups: non-spinnable because of too high viscosity (denoted with hollow squares in Figure 7) and non-spinnable because of too low viscosity (denoted with hollow circles in Figure 7). From Figure 7, we see that, within the intervals studied and with the chosen parameters, neither cellulose concentration

nor acid treatment time, and thereby cellulose molecular weight, are solely decisive for whether or not a solution can be electrospun into fibers or not. It is rather the viscosity of the solution that is decisive for electrospinnability. The viscosity, in turn, is 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 electrospay instead of electrospin, hence no fibers are formed. Solutions with too high viscosity become difficult to handle and are thus non-spinnable. For instance, the solution transfer to



**Figure 7.** Electrospinnability for acid treated cellulose in DMSO : EmimAc 1 : 1 (w/w) at concentrations and acid treatment time indicated. Solutions indicated by round hollow symbols display too low viscosity, triangular filled symbols can be electrospun into fibers, and square hollow symbols are too viscous for good electrospinning.



**Figure 8.** Zero shear viscosity as a function of cellulose concentration. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

syringe is very difficult and there is a tendency for the needle to clog during electrospinning.

In Figure 8, the zero shear viscosity is plotted against cellulose concentration (wt %), and a power-law is fitted for each cellulose fraction. For all solutions there is a power-law dependence,  $\eta_0 \propto C^n$ . 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 et al.<sup>28</sup> reported scalings for cellulose in EmimAc solutions to be 4.4 at 0°C and Sescousse et al.<sup>29</sup> around 4 at low temperatures (0–40°C). Gericke et al.<sup>28</sup> also concluded that EmimAc is close to a theta solvent for cellulose. For neutral linear polymers in a theta solvent, the theoretical concentration scaling give slopes of 1, 2, and 14/3 in the dilute, semi-dilute unentangled, and semi-dilute entangled regimes, respectively.<sup>23</sup> These theoretical predictions indicate that all our cellulose fractions at the chosen concentrations are in the entangled semi-dilute regime, as seen in Figure 8. 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. Chain entanglement is important for stable fiber formation during electrospinning.<sup>30</sup> However, as seen from our results, some of the solutions show no electrospinnability (indicated with hollow circles and squares in Figure 7). 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.

## CONCLUSIONS

Depending on treatment conditions, acid depolymerization of cellulose reaches a leveling-off degree of polymerization

(LODP). Under our conditions, the LODP is reached after approximately 30 min of acid treatment. Results from size exclusion chromatography confirmed that the cellulose was depolymerized by the acid treatment into different molecular weight fractions. Longer acid treatment time yielded more chain scission, hence lower molecular weight.

From rheological measurements, we concluded that the empirical Cox–Merz rule can be applied to our solutions. The Cox–Merz rule states that the complex viscosity overlaps the steady-state shear viscosity at the same frequency and shear rate. From the rheological measurements and the evaluation of electrospinnability of our solutions, with the specific parameters used in this study, we can see that electrospinnable solutions exhibit zero shear viscosities between 10–100 Pa s.

The SEC data show no clear distinction among the polydispersity index values. But, from the rheology results, we see that the solutions exhibit a behavior that is an indication of a decrease in PDI values, i.e., the PDI values for the different celluloses decreases with acid treatment time, hence molecular weight. These different PDI values are clarified in Figure 6 as the onset of shear thinning starts at higher shear rate as the molecular weight decreases. This effect on the shear thinning behavior is most probable attributed to a few long polymer chains present. A high molecular weight tail can give little contribution to the PDI calculated from the SEC measurements but distinguishable when performing rheological measurements, which is why our results seem to differ.

In electrospinning cellulose fibers from ionic liquids, we have shown that the dominant property for fiber formation is solution viscosity. This is the case even though all our 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.

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