

Wet Spinning of Cellulose from Ionic Liquid Solutions—Viscometry and Mechanical Performance

Carina Olsson, Gunnar Westman

Department of Chemical and Biological Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden

Correspondence to: C. Olsson (E-mail: carina.olsson@chalmers.se)

ABSTRACT: A series of regenerated cellulose fibers was produced from dopes prepared by mixing and dissolving cellulose of two different degrees of polymerization in different ratios in the ionic liquid 1-ethyl-3-methyl-imidazolium acetate. Viscoelastic properties of the spin dopes were characterized by controlled stress rheometry. The cellulose solutions were solidified in pure water by the traditional wet spinning technique. The resulting fibers were characterized by means of wet and dry tensile testing and scanning electron microscopy. The characterization revealed a compact and homogeneous fiber. A nonlinear relationship between degree of polymerization and fiber properties was observed with a moderate difference in mechanical properties in a broad interval of fibers while fibers composed of polymers with the highest degree of polymerization stood out as stronger and stiffer. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: ionic liquids; wet spinning; fibers; regenerated cellulose; rheology

Received 14 March 2012; accepted 14 May 2012; published online

DOI: 10.1002/app.38064

INTRODUCTION

New materials from sustainable resources have gained attention both in academia and industry over the past years. Plant biopolymers are considered a good alternative to fossil based polymers as they are vastly abundant, biodegradable, and renewable on a reasonable time scale. Cellulose, used today in a wide range of products, is the most abundant of these polymers and has gained significant attention in the development of new “green” materials where not only the raw material but also the chemistry to get the product is considered sustainable and eco friendly. As cellulose will decompose before melting, shaping the polymer into new materials requires dissolution. Due to the intricate hydrogen bonding network and dense packing of polymer sheets by hydrophobic interaction, a low solubility of cellulose in most common solvents is observed. Nonetheless, a multitude of both derivatizing and nonderivatizing solvents for cellulose are being applied for this purpose.¹

Fiber for textile applications is one of the most important uses of cellulose, and it is a fast growing sector. Cotton is still today the most common raw material for textile, but an increase in the use of regenerated fibers is urgent due to the large amount of valuable water and toxic pesticides that is wasted on this crop, not to mention the unwise use of agricultural land that could be used for growing edible plants. Regenerated cellulose fibers, on the other hand, can be produced from wood pulp.

Still today the dominating route to regenerated cellulose fibers is the viscose process, invented in the 19th century.² This process works well enough but includes several process steps due to a derivatization step in the order to dissolve the cellulose but also gives rise to hazardous gaseous and aqueous sulphuric byproducts.³ New methods using the same idea but different cellulose derivatives are being developed, especially in Finland, where large scale implementation of the so called carbamate process is planned.⁴ To decrease the number of process steps, a solvent system for direct dissolution may be used, such as amine oxides,⁵ concentrated acids,⁶ aqueous NaOH with^{7,8} or without additives⁹ and some specific transition metal complexes.¹⁰ The most successful of these solvents so far is the N-methylmorpholine N-oxide (NMMO) which today represents a significant and growing industry for producing textile fibers under the generic name Lyocell. To get an efficient and sustainable process, a great deal of process optimizing has been required to minimize byproduct formation and to properly recover the solvent.^{11–14}

New solvents for cellulose are constantly being developed. One relatively new and growing class of solvents is the multipurpose family of ionic liquids, salts with a melting point below 100°C composed of a bulky organic cation paired with an inorganic or organic anion. In 2002, imidazolium based ionic liquids were found to dissolve cellulose.¹⁵ Since then, several studies of dissolution in this type of media have been reported. Several

Table I. Data on Spin Dopes Prepared for wet Spinning. The Total Content of Cellulose (Microcrystalline Cellulose + Dissolving Pulp) was 10 wt % in all Solutions

Sample	% MCC out of total cellulose	Average DP _w
1	100	330
2	75	583
3	60	734
4	40	936
5	20	1138
6	15	1189
7	5	1290
8	0	1340

Abbreviation: MCC, microcrystalline cellulose.

imidazolium based ionic liquids have been used as solvents for preparing spin dopes used to produce regenerated fibers, and the resulting material may show mechanical properties in the same range as the commercially used solvent NMMO.¹⁶ One of the most efficient ionic liquids for dissolving cellulose seems to be the 1-ethyl-3-methyl imidazolium acetate, BASF, Ludwigshafen, Germany (EMIMAc), which has been reported to dissolve cellulose up to at least 25 wt %.¹⁷

Fibers spun from dissolved cellulose may exhibit different mechanical properties depending on solution state of the cellulose, influencing the degree of orientation of the polymer.¹⁸ The draw ratio, that is, the intensity of stretching that the newly formed fiber is subjected to, will also affect the degree of orientation and thereby the mechanical properties of the fiber.¹⁹ The spin dope must also have certain viscoelastic properties to exhibit spinnability, for example, the ability to form threads without breakage.¹⁹ The precipitation, or coagulation, of cellulose into a nonsolvent will affect the mechanical properties of the fiber. For example, a mild precipitation in the viscose process will give a regenerated fiber with a higher wet modulus.²⁰ In the original viscose process, the molecular weight of the pulp is significantly decreased in an aging step. This is done to decrease the viscosity of the dope and facilitate processing. This study investigates the effect of degree of polymerization (degree of polymerization (DP)_w) on the properties of spin dopes and nondrawn wet spun regenerated cellulose fibers from dopes of mixed cellulose sources.

EXPERIMENTAL

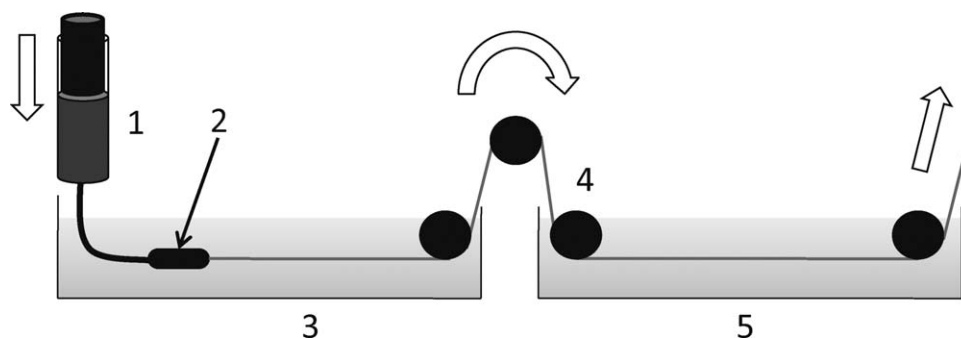
Materials

Two kinds of cellulose were used to prepare the spin dopes. Microcrystalline cellulose, Avicel PH-101, Fluka, Wallingstown, Ireland, with an average DP_w of 330, was purchased from Sigma Aldrich. Bleached Kraft dissolving pulp from eucalypt, with an average DP_w of 1340, was provided by Bahia Pulp S.A., Camaçari, Brazil. The pulp sheets were cut in smaller pieces, milled, and sieved to a particle size of <1 mm in diameter. All cellulose samples were dried at 60°C for at least eight hours before use. The solvent 1-ethyl-3-methyl imidazolium acetate ≥ 90%, produced by badische anilin und soda fabrik, was used without further purification. Karl Fisher titration indicated a water content of approximately 0.3% in the ionic liquid.

Preparation of Spin Dopes and Cellulose Fibers

The cellulose solutions were prepared by first heating the solvent to 70°C and then adding dry cellulose under vigorous stirring to disperse the cellulose particles in the solvent. The total amount of cellulose in each sample was 10 wt %. The samples were left to dissolve for at least 12 h at 70°C without stirring, to avoid mixing in of air. The average DP_w of the cellulose in the spin dopes was manipulated by varying the ratio of microcrystalline cellulose and pulp in the samples according to Table I. In a typical dissolving trial, an approximate solution volume of 65 mL was prepared.

The spin dope was transferred to a preheated stainless steel cylinder and multifilament fiber was produced with simple lab scale wet spinning equipment. A model of the equipment can be seen in Scheme 1. Both spin dope and cylinder were heated to 70°C. The spin dope was filtered using 140 μm stainless steel filters and the spinneret was equipped with 120 circular orifices of 80 μm diameter. The flow rate of spin dope was controlled by a pump and kept at 2.3 mL·min⁻¹. The choice of coagulation medium has a strong impact in the rate of coagulation, which leads to different properties of the fiber. In this case, the spinning setup limited the alternatives to efficient coagulants that could solidify the cellulose fast enough so that an actual fiber could be collected at the end of the fiber line. From an industrial point of view, where complete recovery of solvents is ideal, an uncomplicated coagulation medium is obviously preferred. Hence, coagulation took place in pure tap water, heated



Scheme 1. Lab scale multifilament wet spinning setup: (1) Stainless steel pressurized extruder with a piston; (2) Spinneret with integrated filter; (3) Coagulation bath (4) Godets; (5) Washing bath.

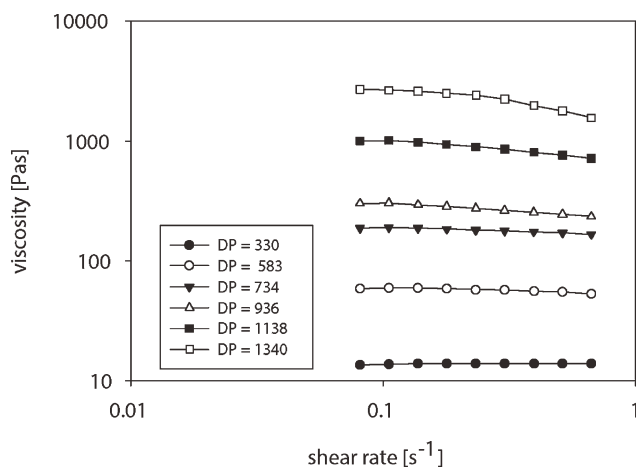


Figure 1. Viscosity as a function of shear rate for spin dopes with cellulose of different average DP.

to approximately 80°C and the fresh fibers were washed in a second bath of heated water (approximately 80°C) before rolled up on Bakelite rollers and were left to dry at ambient temperature before characterization. To avoid any effects of drawing on the mechanical properties of the fibers, the winding speed was approximately the same as the speed of the godets taking the fiber from the coagulation bath to the washing bath, that is, 2.1 m·min⁻¹.

Characterization

DP_w was estimated for dissolving pulp and microcrystalline cellulose Avicel PH-101 by size exclusion chromatography by dissolution in DMAc and 8% LiCl and subsequent dilution with DMAc to a final LiCl concentration of 0.5% and a cellulose concentration of 0.4 mg·ml⁻¹. The samples were separated by molecular weight on a set of three columns, PLgel Mixed A (300 × 7.5 mm) with a guard column (Polymer Laboratories) and analyzed using a refractive index detector HP 1047 (Hewlett-Packard). Temperature of the columns was set to 80°C and flow rate was 1.0 mL·min⁻¹. Calibration was done using narrow polystyrene standards with molecular weights ranging from 5120 to 6120,000 Da. The average DP_w of the cellulose mixes was calculated from these data.

Rheological properties of the spin dopes were characterized using a Bohlin instruments CS50 rheometer equipped with a 4°/4 mm cone and plate measuring system at 50°C for both oscillatory and rotational measurements.

The surface and the cross section of the spun fibers were examined using scanning electron microscopy (Leo Ultra 55 FEG Scanning Microscope). Small pieces of fiber was prepared and sputtered with gold under vacuum before inspection.

The linear density was estimated by assuming that the fibers were uniform over their whole length, by weighting a known length, at least three meters, of the dried fiber. Tensile testing and elongation of fibers was performed in a controlled environment to avoid effects of differences in relative humidity between experiments. The conditions in the testing facility were set to 50 ± 2 % relative humidity and 23 ± 1°C and the fibers were pre-

conditioned for several hours before measurements took place. The fibers were mounted in a 100 mm gap on a Zwick Roell 2.5Z tensile tester and pulled at a speed of 1.7 mm·s⁻¹ until the point of break. For the wet tensile measurements, the fibers were immersed in deionized water for 300 s before testing, to allow full wetting of the structure. The fibers were immediately clamped in the tensile tester and pulled. In all data points values of linear density are provided with fiber in dry state.

RESULTS AND DISCUSSION

Characterization of Spin Dopes

A polymer solution is expected to exhibit a non-Newtonian viscous behavior, and cellulose in an ionic liquid is no exception.²¹ However, an extensive Newtonian plateau can be observed for low shear rates and/or concentrations.^{22,23} Steady state viscosity measurements on spin dopes demonstrated a dramatic increase in viscosity with increasing DP_w, see Figure 1. Shear thinning behavior can be seen for all spin dopes except the one with lowest DP in this interval.

In this case, the equipment did not provide reliable measurements at sufficiently low shear rates to find the true zero shear viscosity of spin dopes with higher DP, as the shear thinning onset was already passed in the measured interval. This can be observed in Figure 1. The trend is clear, nonetheless. As expected, the viscosity of the spin dope is power law dependent of average DP. In these measurements there will be no sign of the molecular weight distribution, only the average molecular weight is important. This is one of the reasons why viscometry itself is not sufficient to characterize a polymer solution, as many properties of the final product may well be directly dependant on the distribution of polymer weight.

It can be noted by studying Figures 1 and 2 that the Cox Merz rule, which suggests that $\eta(\dot{\gamma})$ and $\eta^*(\omega)$ are superimposable, could not be applied in this case. The failure of the Cox Merz rule in other polymer systems has been suggested to originate from polymer–polymer interactions such as hydrogen bonding between polymers.²⁴

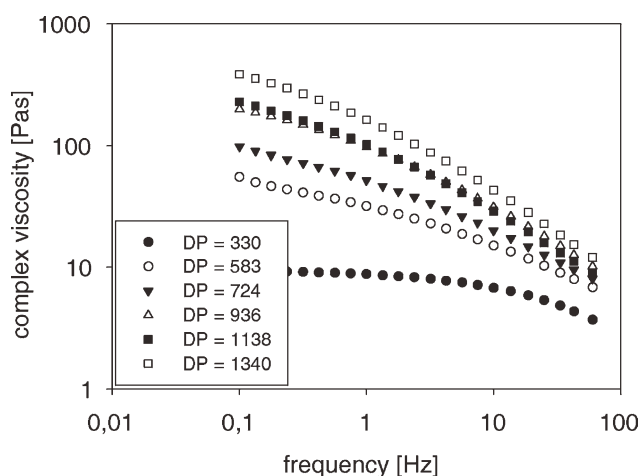


Figure 2. Complex viscosity as a function of frequency for spin dopes of different DP at 50°C.

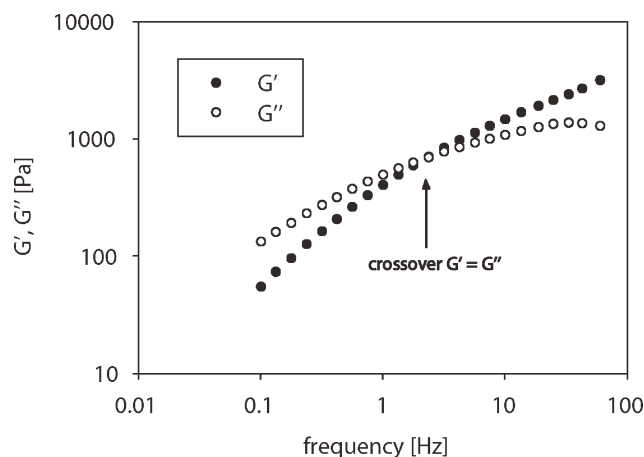


Figure 3. Relationship between elastic and viscous moduli during a frequency sweep for sample 5 with average DP of ≈ 1100 at 50°C .

Solvent quality is important for solution viscosity, as the viscosity and polymer–solvent interactions are directly linked. This is shown for example in the Mark Houwink relation. In the case of ionic liquids, which all are hygroscopic, one main concern is water impurities. According to early publications in the field of ionic liquids as solvents for cellulose even water impurities as low as 1% imply significant problems in the polymer dissolution process, a reason being competing hydrogen bonding.¹⁵ Although the solvent quality of the ionic liquid used in this study was stated only $\geq 90\%$, only a very small water content (0.3 %) was detected by Karl Fisher titration. However, there might be other impurities such as imidazole derivatives and inorganic material not accounted for affecting the solvent quality and thereby also the rheological behavior.

The magnitude of and relationship between elastic and viscous moduli will provide more information about the polymer interaction. As long as the viscous modulus G'' is larger than the elastic modulus G' the system is considered a fluid, while the opposite is true for a semisolid such as a gel. For viscoelastic materials, such as polymer melts and polymer solutions, a cross over point is expected at some frequency. The frequency at which the cross over takes place indicates entanglement frequency, or degree of physical or chemical crosslinking of the polymers in solution.²⁵ A typical response of a viscoelastic material (spin dope) under a frequency sweep is shown in Figure 3, where 20 wt % of the polymer is microcrystalline cellulose. At a frequency around 4 Hz the elastic modulus exceeds the viscous modulus.

A similar shape of the moduli curves are seen in all samples, but the magnitude and relative positions, that is, the cross over points differ between the samples with different average DP. A summary of this can be overviewed in Table II.

If closer attention is paid to the crossover points, a peculiar relation can be seen. There seems to be two different processes in play, both giving rise to a linear response in the crossover point in relation to the average DP of the spin dope, but in two different regimes. This is clearly shown in Figure 4.

Table II. Main Rheological Results from Evaluation of the Spinning Dopes. G' , G'' are Presented at 1 Hz

Sample	Average DP _w	G' [Pa]	G'' [Pa]	Cross over point [Hz]
1	330	4.30	54.9	54.5
2	583	72.1	185	36.6
3	734	153	285	21.4
4	936	358	494	4.42
5	1138	404	494	2.26
6	1189	563	681	2.18
7	1290	638	703	1.88
8	1340	689	751	1.40

For polymers of low DP_w, the slope is significantly steeper, meaning that the change in viscoelastic behavior is large. In the second regime on the other hand, even large differences in average DP does not affect the relation between the viscous and elastic moduli to a large extent, even though the magnitudes of both moduli and viscosity increases with increasing DP. The double linear regime effect is likely to be attributed to the fact that there are two distinctly different types of cellulose present in the samples, and the behavior of one type dominates at each regime. This behavior may be advantageous in process optimization.

Characterization of Fibers

A representative scanning electron micrograph of spun fiber is presented in Figure 5. The fibers were broken to reveal the interior surface and the micrographs revealed a smooth surface and a homogeneous cross section with no voids or obvious sign of a visible skin-core structure. The diameter of the single filaments was estimated to *circa* 20 μm .

Density of fibers can be calculated given the titer and the fiber diameter. Assuming a perfect spinning procedure and no losses, the titer for the fiber bundle can be divided by 120 to get the individual titer of each single filament. Information on fibril diameters is also given by electron micrographs.

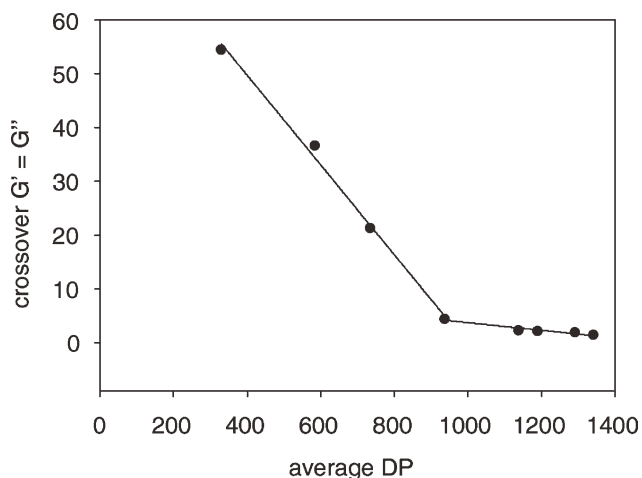


Figure 4. Crossover point $G' = G''$ as a function of DP at 50°C .

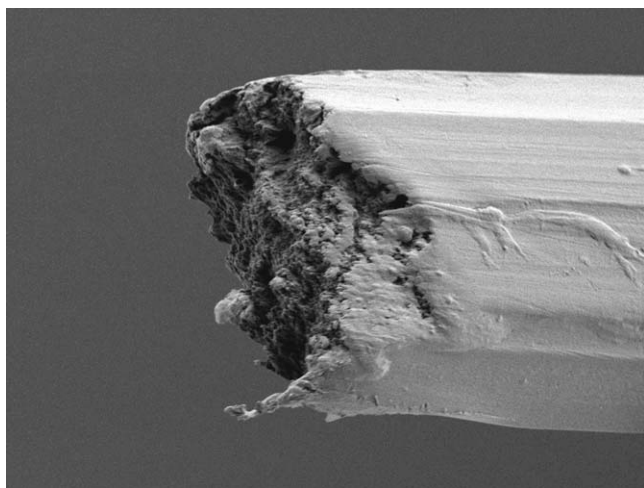


Figure 5. Scanning electron micrograph of regenerated fiber.

$$\rho = \frac{10^2 \text{ titer}}{3\pi d^2} \quad (1)$$

where the density ρ is shown in grams per cubic centimeter, the titer is expressed in tex (grams per 1000 meter, measured on the fiber bundle) and diameter is given in microns, approximated for individual filaments. According to this, the density should be around $1 \text{ g}\cdot\text{cm}^{-3}$ meaning that the cellulose is loosely packed in the fibrils. Without drawing, an amorphous structure of the cellulose fibers can be expected, and the low density can be related to this. As no visible voids are seen in micrographs, the overall structure seems loose but homogeneous. Linear density (titer) of the fibers varied between around 40 to around 70 (see Table III).

Tensile testing showed a strong correlation between average DP_w and mechanical properties of the fibers. A comparison between dry and wet fibers is provided in Figure 6. In this case, water acts as a softener and clearly has a huge effect on most properties. Only elongation seems rather unaffected by the wetting procedure, whereas the stiffness drops to almost a tenth of the

Table III. Data on the Regenerated Cellulose Fibers with Different Average DP

Sample	Average DP_w	Titer [$\text{g}\cdot 1000 \text{ m}^{-1}$]	Density [$\text{g}\cdot\text{cm}^{-3}$]
1	330	69.6	1.18
2	583	53.4	1.17
3	734	37.9	1.00
4	936	41.6	0.91
5	1138	51.6	1.13
6	1189	40.1	1.06
7	1290	49.2	0.83
8	1340	44.8	0.83

dry values. Error bars in the graphs from tensile testing indicate the variation within each fiber, whereas the trends may look a bit skewed and the results not entirely consistent. This might be due to the spinning equipment. During the spinning trials, efforts were made to keep all relevant parameters (i.e., temperature, speed) stable, but due to the elementary setup this could not always be done to full satisfaction.

Elongation in dry state does not seem to be significantly affected by cellulose DP_w in this case. However, in the wet state, a tendency can be seen, with increase in elongation in fibers of higher DP_w . Tenacity, or strength, of the fibers is clearly affected by both wetting and average DP_w . In the case of the dry fiber, it doubles its tenacity when comparing the fiber with lowest molecular weight to the fibers with highest molecular weight. In the case of the wet fiber, the strength increases fivefold when increasing the DP_w from 330 to 1340, as can be seen in Figure 6. Compared with regenerated cellulose fibers described in literature, the mechanical properties of these fibers are not satisfactory, previous results on regenerated fiber tenacity was reported to be well over $25 \text{ cN}/\text{tex}$.^{16,26} There are several reasons behind this. One reason is the mixing in of microcrystalline cellulose, which normally has too low DP for conventional fiber spinning. Another reason is the spinning set up; usually the air gap spinning is chosen for regeneration of cellulose from ionic liquid

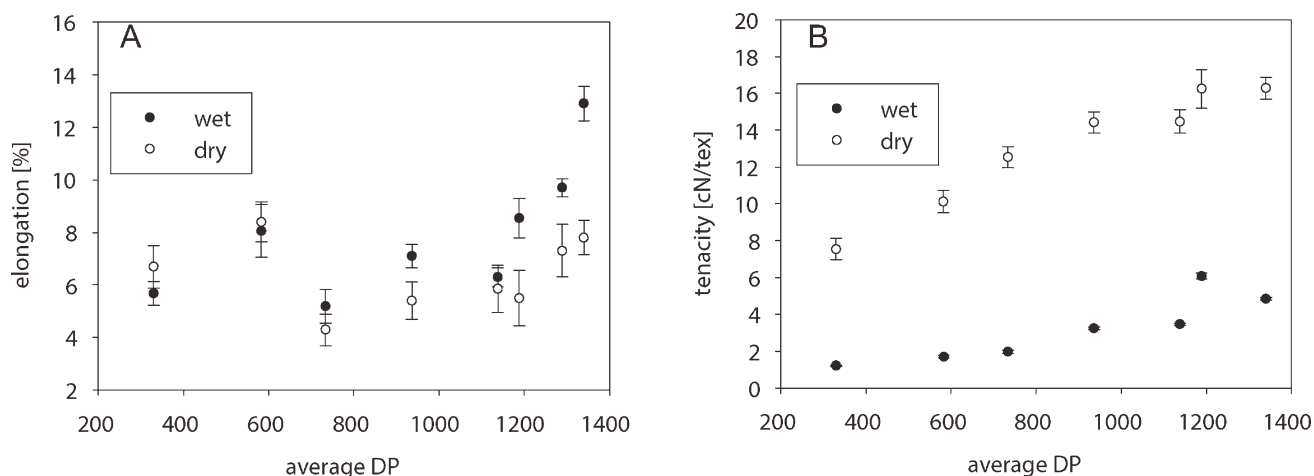


Figure 6. Mechanical properties of the regenerated cellulose fibers in dry and wet state as a function of average DP: (A) elongation (B) tenacity.

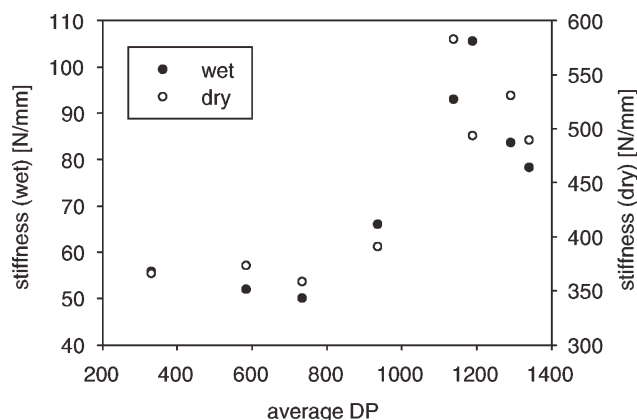


Figure 7. Stiffness or Young's modulus/elastic modulus, of the regenerated cellulose fibers as a function of average DP for wet and dry fibers.

solutions. High cellulose concentration is expected to result in fibers with better mechanical properties, and only 10 wt % was used in these trials. Finally, fibers are typically aligned and their mechanical properties improved by drawing. Here fibers were analyzed in undrawn condition.

Stiffness, expressed as the elastic modulus of fibers is presented in Figure 7 and is defined as the reversible, or elastic, portion of the deformation of a material. As is clearly shown, stiffness is double for both wet and dry fibers when increasing DP_w from 330 to 1340. However, adding water to the fiber will inevitably reduce the stiffness by almost a decade, again proving the water to be a powerful softener, at least for this amorphous type of cellulose. For all information on mechanical properties it is important to understand that the tensile testing setup and especially the rate of deformation may have an effect on the data why the results presented herein are to be compared only amongst themselves or data tested in a similar fashion. Trends are of course always applicable, but magnitude of data might differ depending on equipment and test parameters.

Interestingly, fibers with different potential final properties can be prepared by adjusting the DP_w within a broad range, all in which viscosity still is manageable when using the ionic liquid EMIMAc as a solvent. Depending on final use the mechanical properties of the fiber will be very relevant, and using a solvent with the capacity to dissolve cellulose of high DP_w while maintaining a truly dissolved state with moderate viscosity can be one way to tweak these.

CONCLUSIONS

A series of 10 wt % cellulose solutions in EMIMAc was prepared from microcrystalline cellulose and/or pulp. The average DP_w of the cellulose in the solutions ranged from 330 to 1340. The viscosity of the solutions increased with DP_w and the cross-over of elastic and viscous modulus were found to vary linear in two different regimes at different DP intervals. Wet spinning of the cellulose into hot water without drawing generated fibers of different mechanical qualities, not necessarily linear with respect to average DP_w . Elongation did not seem affected to the

same extent as tenacity and stiffness, which both increased steep with increased DP_w of the polymers in the tested fibers.

ACKNOWLEDGMENTS

Södra Research Foundation is gratefully acknowledged for financial support. The authors thank Dr. Maria Sedin at Forest Products and Chemical Engineering, Chalmers, and Johannes Thunberg, Organic Chemistry, Chalmers, for assistance during rheology and microscopy, respectively. They also thank Eugenio Ferrario and Artimplant AB for providing equipment and assistance during fiber spinning, and to Södra Innovation, Väröbacka, Sweden, for providing the tensile testing equipment.

REFERENCES

- Liebert, T. In *Cellulose Solvents: For Analysis, Shaping and Chemical Modification*; Tim F. Liebert, Thomas J. Heinze and Kevin J. Edgar, Eds., American Chemical Society: **2010**; pp 3–54.
- Cross, C. F.; Bevan, E. J.; Beadle, C. *Brit. Pat. 8700*, **1892**.
- Klemm, D.; Heublein, B.; Fink, H. -P.; Bohn, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 3358.
- Rentto, M. E. 2011, Press release. Available at: http://www.cisionwire.com/neo-industrial-plc-g/r/avilon-develops-environmental-friendly-cleantech-innovation_e200454, accessed April **2012**. Accessed April 12 2012.
- Graenacher, C.; Sallmann, R. US Pat. 2179181, **1939**.
- Boerstael, H.; Koenders Bernardus, M.; Westerink, J. B. *WO 9606208*, **1996**.
- Yan, L.; Gao, Z. *Cellulose* **2008**, *15*, 789.
- Zhang, L.; Ruan, D.; Zhou, J. *Ind. Eng. Chem. Res.* **2001**, *40*, 5923.
- Isogai, A.; Atalla, R. H. *Cellulose* **1998**, *5*, 309.
- Saalwächter, K.; Burchard, W.; Klüfers, P.; Kettenbach, G.; Mayer, P.; Klemm, D.; Dugarmaa, S. *Macromolecules* **2000**, *33*, 4094.
- Rosenau, T.; Potthast, A.; Milacher, W.; Adorjan, I.; Hofinger, A.; Kosma, P. *Cellulose* **2005**, *12*, 197.
- Rosenau, T.; Potthast, A.; Sixta, H.; Kosma, P. *Prog. Polym. Sci.* **2001**, *26*, 1763.
- Adorjan, I.; Potthast, A.; Rosenau, T.; Sixta, H.; Kosma, P. *Cellulose* **2005**, *12*, 51.
- Wendler, F.; Graneß, G.; Heinze, T. *Cellulose* **2005**, *12*, 411.
- Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.
- Kosan, B.; Michels, C.; Meister, F. *Cellulose* **2008**, *15*, 59.
- Kosan, B.; Schwikal, K.; Meister, F. *Cellulose* **2010**, *17*, 495.
- Boerstael, H.; Maatman, H.; Westerink, J. B.; Koenders, B. M. *Polymer* **2001**, *42*, 7371.
- Ziabicki, A. *Fundamentals of Fibre Formation*; Wiley: Bath, **1976**.

20. Kotek, R. *Handbook of Fiber Chemistry*, 3rd ed; CRC Press: Boca Raton, FL, **2006**.
21. Budtova, T.; Egal, M.; Gavillon, R.; Gericke, M.; Heinze, T.; Liebert, T.; Roy, C.; Schluffer, K.; Navard, P. In *Cellulose Solvents: For Analysis, Shaping and Chemical Modification*; American Chemical Society: Washington, DC, **2010**; pp 179–196.
22. Gericke, M.; Schluffer, K.; Liebert, T.; Heinze, T.; Budtova, T. *Biomacromolecules* **2009**, *10*, 1188.
23. Sescousse, R.; Le, K. A.; Ries, M. E.; Budtova, T. *J. Phys. Chem. B* **2010**, *114*, 7222.
24. Kulicke, W. M.; Porter, R. S. *Rheol. Acta* **1980**, *19*, 601.
25. Xu, S.; Zhang, J.; He, A.; Li, J.; Zhang, H.; Han, C. C. *Polymer* **2008**, *49*, 2911.
26. Laus, G.; Benvoglio, G.; Schottenberger, H.; Kahlenberg, V.; Kopacka, H.; Röder, T.; Sixta, H. *Lenzinger Ber.* **2005**, *84*, 71.