

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

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ABSTRACT: Cellulose was electrospun with various concentrations of ionic liquid and cosolvent. Three different cosolvents were used in this study; dimethylacetamide (DMAc), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO). The cosolvents were added to modify the viscosity, electrical conductivity, and surface tension of the solutions. The solubility of cellulose in ionic liquids is highly affected by changes in solvent properties on the molecular level in the binary solvent systems. The difference in molecular structure of the cosolvents and the interactions between

cosolvent and ionic liquid can explain the difference in dissolution power of the cosolvents. Scanning electron microscope (SEM) was used to characterize electrospun cellulose fibers. For the systems tested the importance of having a rather high viscosity and high surface tension, and some degree of shear thinning to produce fibers is shown. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1901–1909, 2012

Key words: cellulose; ionic liquid; electrospinning; dissolution; nanofibers

INTRODUCTION

The manufacture of nanofibers by means of electrospinning has attracted a lot of interest during the last 15 years.^{1–3} A multitude of applications of nanofibers, related to their specific properties, has been proposed. Examples being reinforcement material,⁴ filtration,⁵ protective clothing,⁶ and sensor devices.⁷ Utilizing wood-based cellulose as a source for fiber manufacture is becoming increasingly attractive and the importance of wood-based cellulose fibers is expected to further increase due to the environmental impacts associated with cotton production, depletion of fossil carbon, and a positive effect on greenhouse gas generation.^{8–10} Thus, there is a lot of interest in using cellulose as raw material for electrospun nanofibers. However, this task has turned out to be quite difficult due to the limited solubility of cellulose in volatile solvents suitable for electrospinning and the challenging chain dynamics of the cellulose molecule (chain stiffness) in solution. In

fact, all known solvents for cellulose appear to be nonvolatile and forms strong interactions with the cellulose molecule rendering the usual solidification mechanism in electrospinning by simple drying difficult, if not impossible. Precipitation from solution seems to be the only feasible solidification mechanism for cellulose nanofibers. Electrospinning of cellulose without any chemical reaction in various solvent systems have been studied and reported, including *N*-methylmorpholine *N*-oxide/water (NMMO/water),^{11–13} NaOH/urea,¹⁴ lithium chloride/dimethylacetamide (LiCl/DMAc),^{12,15,16} and ionic liquids.^{17–20}

Ionic liquids have been found to have outstanding dissolving properties of cellulose.^{21–25} Ionic liquids are salts with relatively low melting points, thus forming stable liquids at temperatures below 100°C.^{26–28} Some of the most frequently used ionic liquids for dissolution of cellulose are the imidazolium-based ionic liquids. Their properties are determined by their chemical composition and they have been used in regeneration of cellulose into gels, fibers, and films.^{29–32} However, regarding electrospinning of cellulose fibers from ionic liquids there are very few articles wherein a thoroughly investigation of the process parameters has been investigated.

The main challenge of preparing nanofibers from any polymer solution by electrospinning is to find the appropriate conditions that will allow for the

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formation of a stable Taylor cone³³ so that continuous fiber spinning can occur. There are three main groups of electrospinning parameters that affect fiber formation. These groups are: process parameters (e.g., applied voltage, solution flow rate, and spinning distance),³⁴ solution parameters (e.g., concentration, viscosity, polymer molecular weight, surface tension, and conductivity),³⁵ and ambient conditions (e.g., temperature and humidity).³⁶

Cellulose is a linear polysaccharide consisting of repeated D-glucose units which forms strong inter- and intramolecular hydrogen bonds. Using cellulose and ionic liquids makes the electrospinning process more challenging due to the rigidity of cellulose chains³⁷ and the lack of vapor pressure characteristic of ionic liquids.^{23,38} To approach the challenge of electrospinning cellulose from ionic liquids we have used the conditions of a published procedure as a starting point for our experiments.²⁰ The paper of Xu et al.²⁰ concluded that the fiber morphology was mainly determined by the collection and solidification method used. They also reported the effect of relative humidity on fiber productivity.

Our article reports on the electrospinning of cellulose from 1-ethyl-3-methylimidazolium acetate (EmimAc) as well as solvent systems where a viscosity and surface tension modifying cosolvent was included. Hence, we investigate the relations of spinnability and fiber formation to rheological properties, surface tension, and electrical conductivity of the solutions. A cosolvent e.g., dimethylacetamide (DMAc), dimethyl formamide (DMF), or dimethyl sulfoxide (DMSO) was added to the solution to lower viscosity and surface tension without any cellulose precipitation. If the surface tension of the solutions is very high, it would hinder the electric field from deforming the droplet at the end of the needle, i.e., the Taylor cone, into an elongated fiber. In the literature, dimethyl sulfoxide (DMSO) has been added as a cosolvent to lower the viscosity, increase the conductivity, and to lower the surface tension of the cellulose/ionic liquid solutions.²⁰

EXPERIMENTAL

Materials

Ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate (EmimAc) $\geq 90\%$, dimethyl sulfoxide (DMSO) $\geq 99.5\%$, dimethylacetamide (DMAc) 99.8%, and dimethyl formamide (DMF) $\geq 99.5\%$ was purchased from Sigma–Aldrich. All chemicals were used without further purification.

Dissolving pulp from Domsjö AB, Sweden, was used. According to the supplier the viscosity was 530 ml/g and the degree of polymerization (DP) was 750. Size-exclusion chromatography (SEC) was

TABLE I
Solutions Prepared for Electrospinning

Sample	Amount pulp in samples (wt %)	Cosolvent	Cosolvent in solvent mixture (wt %)	EmimAc in solvent mixture (wt %)
1A	2.5	DMF	90	10
2A	2.5	DMF	70	30
3A	2.5	DMF	50	50
4A	2.5	DMF	30	70
5A	2.5	DMF	10	90
1B	2.5	DMAc	90	10
2B	2.5	DMAc	70	30
3B	2.5	DMAc	50	50
4B	2.5	DMAc	30	70
5B	2.5	DMAc	10	90
1C	2.5	DMSO	90	10
2C	2.5	DMSO	70	30
3C	2.5	DMSO	50	50
4C	2.5	DMSO	30	70
5C	2.5	DMSO	10	90
ABC0	2.5	–	0	100

done by Institute of Biopolymers and Chemical Fibres (IBWCh) in Poland, following the method of Ekmanis³⁹ using polystyrene as external standard, M_n and M_w were estimated to be 74,057 and 335,045 g mol⁻¹, respectively. The column used was 1 × Plgel guard 20 μ m + 3 × MixedA 20 μ m, 7.5 mm × 300 mm (Polymer Laboratories, Shropshire, UK) with a HP 1047 differential refractometer (Hewlett Packard, Palo Alto, CA). Temperature of the column was 80°C, DMAc/0.5% LiCl was used as eluent, flow rate was 1.0 mL min⁻¹, and injection volume was 100 μ L.

Methods

Sample preparation

All solutions were prepared using the same procedure. Pulp sheets were cut in small quadratic pieces, about 1 mm in size. The pulp pieces were then dried in an oven at 80°C for 12 h before use. Appropriate amount of cosolvent (DMAc, DMF, or DMSO) according to Table I was added to the pulp. The pulp absorbed the cosolvent, during roughly 1 min, and then the ionic liquid (EmimAc) was added to the mixture. The mixture of pulp, cosolvent, and EmimAc was then stirred at 80°C for 12 h in a sealed container, which generated a clear and homogenous solution. The reason for first adding cosolvent to the pulp followed by ionic liquid was to enhance the ionic liquid diffusion rate into the pulp. It was found that by using this method, the dissolution process was simplified and less time consuming. The clear and homogenous solution was then subjected to electrospinning for 1 h. Tests were performed in triplets.

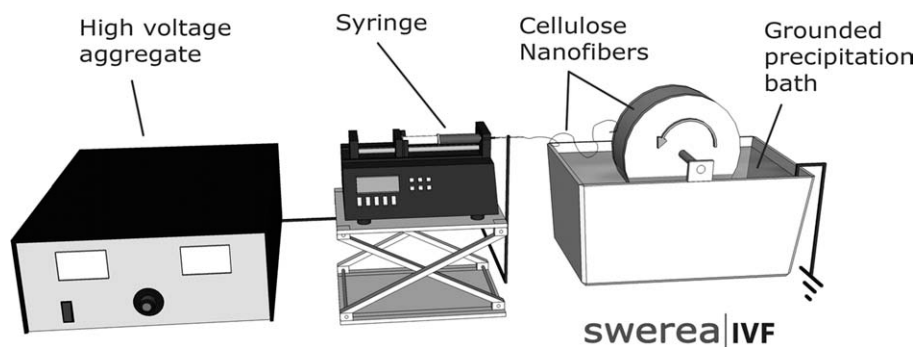


Figure 1 Electrospinning equipment.

Electrospinning

The electrospinning setup is shown in Figure 1 and 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 (with a diameter of 10 cm) covered with an aluminum foil. The collector was partly submerged in a water bath to achieve precipitation of the cellulose solution into solid polymer fibers.

Electrospinning was performed using a syringe capped with a blunt needle (0.6 mm i.d.) which was filled with the appropriate 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 to the collector was set to 10 cm. Solution flow rate was set at 0.3 mL h⁻¹ and the collector had a rotational speed of 25 rpm. To control surrounding atmosphere, the electrospinning equipment was set up in a room with constant relative humidity (RH 65%) and temperature (20°C). The study was conducted with one type of cellulose (dissolving pulp) and at one constant cellulose concentration (2.5 wt %). Studies on celluloses with different molecular weight distributions are under way.

Characterization

Viscosity measurements using shear stress sweeps were performed on 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. Steady state shear viscosity was measured at shear stresses in the range 0.24–370 Pa. A scanning electron microscope (SEM), JEOL JSM-5300 (JEOL, Tokyo, Japan) was used at a voltage of 10 kV to study the fiber morphology. To perform the SEM analysis, the fiber samples were first subjected to gold sputtering to avoid electrostatic charging of the samples. The micrographs were taken at 1000× magnification. Surface tension was measured using the

pendant drop technique. The instrument used was a VCA Video Contact Angle System 2500 (AST, Billerica, MA). The needle size used was 25 gauge (0.2540 mm i.d.) and the focus of the camera was calibrated with methanol. The software VCAOptimaXC 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. Conductivity was measured with a CON 5/TDS 5 Conductivity meter (Eutech Instruments, Singapore/Oakton Instruments, Vernon Hills, IL). The conductivity meter was calibrated before use with conductivity standards of 12,880 and 1413 $\mu\text{S cm}^{-1}$ from Hanna Instruments, USA.

RESULTS AND DISCUSSION

Cellulose dissolution

All spinning solutions had a cellulose concentration of 2.5 wt %. The highest amount of cosolvent in solutions prepared for spinning experiments was solvent composition of 10 wt % EmimAc and 90 wt % cosolvent (DMAc, DMF, or DMSO). The molar ratio of EmimAc to cellulosic Anhydrous Glucose Unit (AGU) was 3.79 : 1 in these solutions which is in the range of the highest cellulose concentration in EmimAc reported without cosolvent in fiber spinning.²¹ DMAc and DMF were not used for electrospinning at a cosolvent composition of 90 wt %, samples 1A and 1B, since they did not form a clear homogenous solution. The molar ratios of EmimAc to cosolvent in these turbid samples were 1 : 20.9 (DMF) and 1 : 17.6 (DMAc), respectively. However, DMSO could form solutions at a cosolvent composition of 90 wt % corresponding to a molar ratio of EmimAc to DMSO of 1 : 19.6. Because the molar ratio between ionic liquid and cosolvent were approximately the same, it implies that the cosolvent affect the ionic liquids interaction with cellulose and thus the solubility of cellulose. It is known from the literature that the solubility of cellulose in ionic liquids is highly affected by changes in solvent

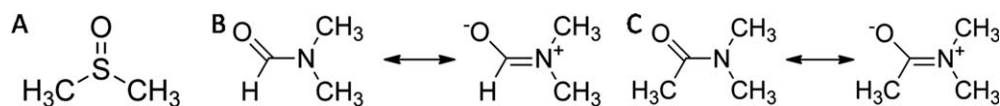


Figure 2 Molecular structure of (A) DMSO, resonance forms of (B) DMF and (C) DMAc.

properties on the molecular level, like hydrogen bonding, electrostatic interaction, and van der Waals bonding in binary solvent systems.²³ For example, the presence of small amounts of moisture greatly reduces the solubility of cellulose in 1-*n*-butyl-3-methylimidazolium chloride (BmimCl).²³

From an NMR study by Remsing et al. it was proposed that ionic liquid rich clusters or ion pairs persist in EmimCl highly diluted in DMSO.⁴⁰ The data revealed that the interactions between the C₄mim⁺ and Cl⁻ ions strengthen as the DMSO content of the solutions increases, and ionic liquid rich clusters persist in this solvent even at concentrations below 10 wt % of ionic liquid. From a study by Attri et al. wherein the interactions between DMF and ionic liquid, where the thermophysical properties, densities, and ultrasonic sound velocities were studied, it was found that the interactions between ionic liquid molecules and DMF increased as the concentration of ionic liquid decreased.⁴¹ These studies show that there is stronger interaction between ionic liquid and DMF as compared to the interaction between ionic liquid and DMSO. This implies that the interaction between cellulose and ionic liquid is more affected upon cosolvation with DMF than with DMSO. As a consequence the solubility of cellulose in ionic liquid is more affected upon addition of a cosolvent that can have strong interaction with the ionic liquid. Both DMF and DMAc have a molecular

structure that allows a resonance form with a negative pole on the oxygen atom that can act as a hydrogen bond acceptor (see Fig. 2). Furthermore, the lack of H-donor ability ($a = 0$)⁴² and low H-bond basicity in DMSO compared to EmimAc also suggests that DMSO does not disrupt interionic interactions.^{40,43} This could explain the wider solubility range when using DMSO as cosolvent compared to DMF and DMAc.

Rheological behavior

The steady state shear viscosity of the solutions as a function of shear rate is given in Figures 3–5. Each sample was analyzed in triplicate and the mean values of the triplicates were plotted. All measurements were performed in constant stress mode (0.24–370 Pa). Consequently the plotted curves cover different ranges of shear rate.

Cellulose dissolved in EmimAc with DMAc as cosolvent

In Figure 3, the viscosity as a function of shear rate is given for samples based on EmimAc and DMAc, at different ratios. It is evident that the viscosity of the samples increases with the EmimAc content. At 30 wt % EmimAc, the viscosity is around 0.1 Pa·s whereas at 90 wt % EmimAc, the viscosity reaches

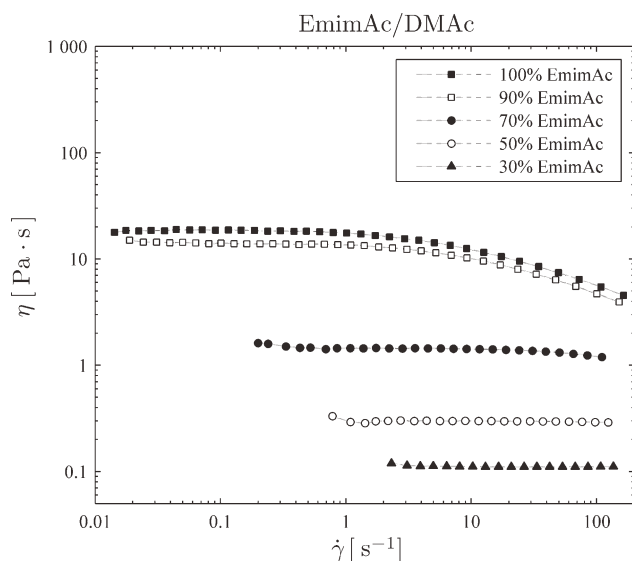


Figure 3 Viscosity as a function of shear rate on cellulose dissolved in EmimAc with DMAc as cosolvent at different ratios.

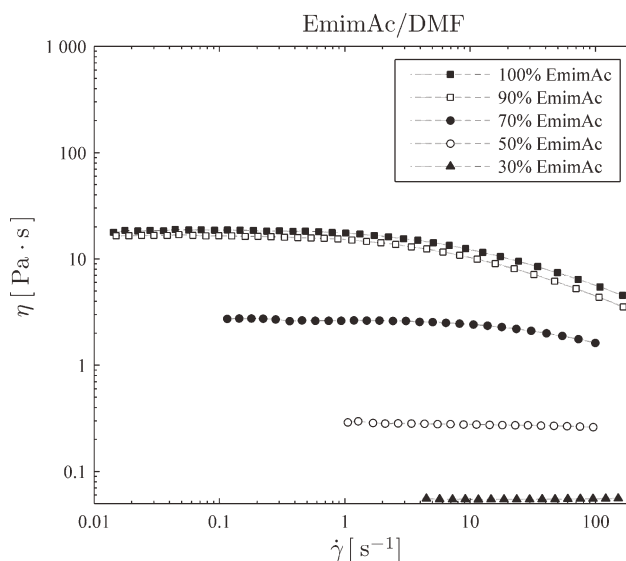


Figure 4 Viscosity as a function of shear rate on cellulose dissolved in EmimAc with DMF as cosolvent at different ratios.

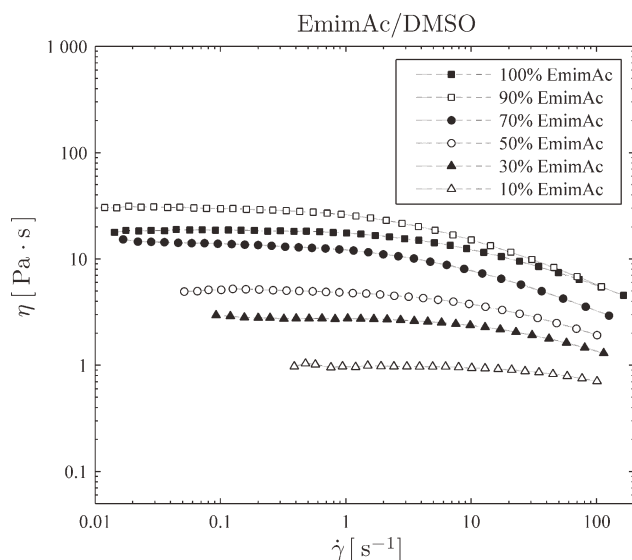


Figure 5 Viscosity as a function of shear rate on cellulose dissolved in EmimAc with DMSO as cosolvent at different ratios.

values of 15 Pas. This is fully in line with expectations, as the cellulose solubilizing component of the solvent system is EmimAc. 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 cosolvent, the reduced solubility will force the cellulose molecules to adapt a conformation with a lower gyration radius. Consequently, the viscosity of the system is reduced. A shear thinning behavior is noted from the curves, 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 EmimAc/DMAc solutions with the highest cellulose solubility and thereby largest gyration radii and random coil flexibility show the greatest shear thinning tendency.

Gericke et al. studied rheological properties of different celluloses (microcrystalline cellulose, spruce sulfite pulp, and bacterial cellulose) dissolved in EmimAc.⁴⁴ At room temperature, indications on a Mark-Houwink exponent in the range 0.4–0.5 were obtained indicating EmimAc being a theta (good) solvent for cellulose. They further found that the critical overlap concentration, c^* , was an increasing function of temperature in the interval 0–100°C. Intrinsic viscosity strongly decreased (decreasing radius of gyration) with increasing temperature. For microcrystalline cellulose (DP 300) c^* increased from 0.7 to 2.6%. The corresponding figures for bacterial cellulose (DP 4420) were 0.24–0.5%. c^* indicate the critical concentration were viscosity as a function of polymer concentration turns, from being a linear

increasing function, into a power law. At this point the molecular coils (radius of gyration is a measure of the coil dimension) start to overlap and are thought to form inter molecular entanglements strongly affecting the viscosity of the solution.⁴⁵ Shear thinning can be interpreted as a result of a decreasing entanglement density as a result of shear. In analogy with the effect of increasing temperature (EmimAc becomes a poorer solvent with increasing temperature) it seems reasonable to assume that an increasing amount of cosolvent has a similar effect on the critical overlap concentration in our case. Because our cellulose concentration is 2.5% it may well be that the cosolvent shifts c^* to values higher than 2.5%, that is, we may go from semi dilute into the dilute regime where entanglements are lacking. It can be speculated that the existence of entanglements between cellulose molecules in the solution is important for the spinability as is the case for a number of other polymers in good solvents.⁴⁶ According to Shenoy et al. complete (no beaded fibers and drops) and stable fiber formation occurs at ≥ 2.5 entanglements per molecule chain.

Cellulose dissolved in EmimAc with DMF as cosolvent

In Figure 4, the viscosity as a function of shear rate is given for samples based on EmimAc and DMF, at different ratios. Also for this system, the viscosity of the samples increases with the EmimAc content. At 30 wt % EmimAc, the viscosity is low, around 0.06 Pas whereas at 90 wt % EmimAc, the viscosity reaches values of 17 Pas. As for the DMAc system described above, this is to be expected. Also for the DMF-based system, a shear thinning behavior is noted from the curves with the highest fractions of EmimAc. When comparing Figures 3 and 4, it is evident that the DMF-based system and the DMAc-based system are very similar. However, slightly lower viscosity values are noted at a low EmimAc concentration for the DMF-system whereas the opposite behavior rules at higher concentrations of EmimAc.

Cellulose dissolved in EmimAc with DMSO as cosolvent

In Figure 5, the viscosity as a function of shear rate is given for samples based on EmimAc and DMSO, at different ratios. For this system, like the DMAc and DMF-based systems, the viscosity of the samples at high EmimAc fractions is higher than at low EmimAc fractions. Also for the DMSO-based systems, a shear thinning behavior is noted from the curves. In comparison with corresponding systems based on DMAc and DMF, higher viscosity values

are noted for the DMSO-based system (compare Figs. 3–5). Both the higher viscosity and the more pronounced shear thinning in the samples with high EmimAc content can be explained by the same reasoning as above regarding polymer coil radius and flexibility for the DMF/DMAc-based systems. What is not explained by this though is the fact that the sample dissolved in 90 wt % EmimAc and 10 wt % DMSO exhibit a higher viscosity than the sample dissolved in 100 wt % EmimAc. However, one possible explanation can be made by linking this behavior to the discussion in the Cellulose Dissolution section regarding the wider dissolution range of the DMSO system. In that section, it is argued that ionic liquid rich clusters could explain why the sample dissolved in 90 wt % DMSO and 10 wt % EmimAc still produces a clear solution. One could imagine this reluctance to interactions between DMSO and EmimAc to lead to local variations in solvent concentrations, i.e., while the binary solvent system is not strictly phase separated; there may be local regions which are richer than 90 wt % in EmimAc, and others which are richer than 10 wt % in DMSO. If this is true, the cellulose would prefer to be present in the EmimAc-rich regions. Because these regions would not make up the whole sample volume, the local cellulose concentration in the EmimAc rich regions should be higher than the overall concentration of 2.5%. Furthermore, as the solvent system contains 90 wt % EmimAc, the EmimAc-rich regions could be viewed as the continuous phase of the system. Thereby, the bulk viscosity would be dictated, e.g., increased, by the increased cellulose concentration in the continuous, EmimAc-rich regions. The reduced viscosity in more DMSO rich samples would then be attributed to an increased significance of the effect of coil radius reduction as already discussed.

Surface tension

The surface tension as a function of molar fraction EmimAc is given in the figure below for samples based on the different cosolvents (Fig. 6). Each sample was analyzed in triplicate and the mean values of the triplicates were plotted.

For all three solvent systems the surface tension decreases with decreased molar fraction EmimAc. It can be seen from Figure 6 that by using DMF or DMAc as cosolvent the surface tension of the spinning dope decreases to a larger extent than by using DMSO as cosolvent. For the DMSO-based system the surface tension decreases from 45 mN m⁻¹ at 1 molar fraction EmimAc to 42.5 mN m⁻¹ at 0.05 molar fraction EmimAc. For the DMF-based system the surface tension decreases to 35 mN m⁻¹ at 0.15 molar fraction EmimAc and for the DMAc-based system to 33.5 mN m⁻¹ at 0.18 molar fraction

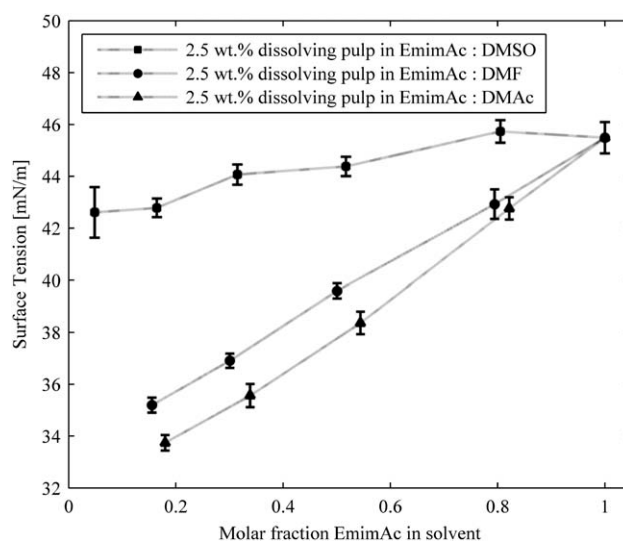


Figure 6 Mean values of surface tension measurements. Error bars represents standard deviation. Lines are only a guide to the eye.

EmimAc. The DMSO-based system has the highest surface tension regardless of molar fraction EmimAc. The differences in surface tension reduction between the different cosolvents are simply related to the different surface tensions of the pure cosolvents. Reported surface tension values of the pure cosolvents used are as follows:

- DMSO: 43.36 mN m⁻¹ at 20°C⁴⁷
- DMF: 36.73 mN m⁻¹ at 20°C⁴⁸
- DMAc: 36.3 mN m⁻¹ at 20°C⁴⁹

It is clearly seen that these literature values correspond to the curves plotted in Figure 6, both with regards to the approximate values at highest cosolvent fraction and the internal order of the curves.

Conductivity

The conductivity as a function of molar fraction EmimAc is given in the figure below for samples based on the different cosolvents (Fig. 7). Each sample was analyzed in triplicate and the mean values of the triplicates were plotted.

It can be seen from Figure 7 that all three solvent systems appear to have a maximum conductivity depending on molar fraction EmimAc. For solutions containing DMF the peak is around 0.3 molar fraction EmimAc, for solutions containing DMAc the peak is around 0.35 molar fraction EmimAc, and for solutions containing DMSO the peak is around 0.18 molar fraction EmimAc. Solutions containing DMF exhibit highest electrical conductivity and solutions containing DMAc lowest regardless of molar fraction EmimAc. It is difficult to explain both the presence of the conductivity maxima and the order

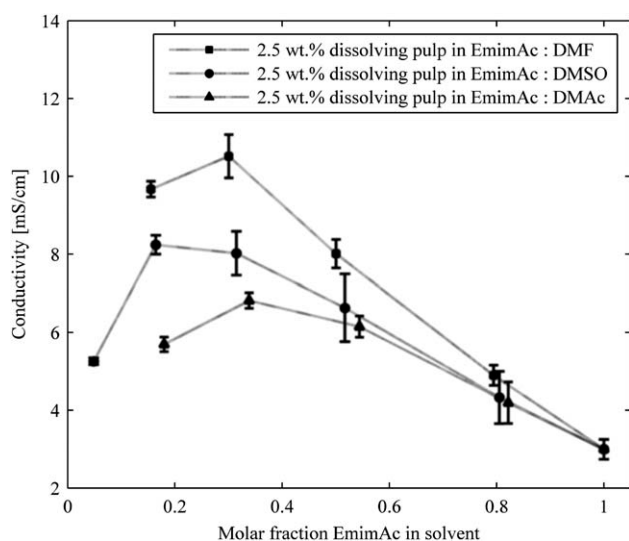


Figure 7 Mean values of conductivity measurements. Error bars represents standard deviation. Lines are only a guide to the eye.

of the curves. It is particularly interesting to point out that the DMSO-based system, which stands out in all of our prior results fall in-between the DMF- and the DMAc-based systems when it comes to conductivity. One can only conclude that all systems exhibit similar values of conductivity and that they all show a conductivity maximum in the lower region of EmimAc fraction.

SEM

SEM pictures were taken of all samples (see Table II) and classified according to fibers formed. Fiber formation was ranked from +: no fibers formed to +++: fiber formation. Examples of the different classes are shown in Figure 8.

From Table II it is clear that the DMSO-based system is the best fiber forming system. It is also evident from all three systems that a fairly high content of EmimAc is desired for forming fibers. But not too high, considering that pure EmimAc (sample ABC0) did not give the best fiber formation. For the DMAc-based system and the DMF-based system the best fiber formation were at 90 wt % EmimAc. For the DMSO-based system the best fiber formation were between 50 and 70 wt % EmimAc. The fact that DMSO turns out to be the best cosolvent out of the three studied is most likely related to the different dissolution power of the EmimAc/DMSO system as opposed to the other two, as discussed above. In the system using DMSO as cosolvent, the dissolved cellulose will probably adapt a conformation, entanglements and/or radius of gyration more suitable for fiber formation compared to the corresponding amount of DMF or DMAc.

Both the DMAc-based system and the DMF-based system forms fibers at zero shear viscosities above 10 Pas and these viscosity curves all show a shear thinning behavior. The DMSO-based system forms fibers at viscosities above 5 Pas and with a shear thinning behavior. It is apparent that a certain degree of viscosity in all three systems is needed to achieve good fiber formation. The reason that a lower zero shear bulk viscosity can form fibers in the DMSO-based system could be the presence of local variations in solvent and polymer concentration. Regions of increased cellulose concentration and hence, locally increased viscosity, may aid fiber formation. It is difficult to say whether shear thinning is beneficial in itself for fiber formation. However, one could imagine that a higher viscosity at low shear rates could be beneficial for the formation of a stable Taylor cone, while a lower viscosity at the high deformation rates present in the jet ejected from the Taylor cone could be preferable. In fact, by plotting the degree of shear thinning (reduction in viscosity over the measured stress interval divided by zero shear viscosity) versus zero shear viscosity, (Fig. 9), the region with the most pronounced shear thinning proves to be where the best fiber formation occurs. Unfortunately, the dependence of shear thinning behavior cannot be completely decoupled from initial viscosity as the best fiber forming samples, i.e., those with the most pronounced shear thinning behavior, are also those with the highest zero shear viscosities.

Fibers could be electrospun from solutions with a surface tension greater than 42 mN m^{-1} , regardless of molar fraction EmimAc and cosolvent. This indicates, which would not be surprising, that a certain

TABLE II
Fibre Formation

Sample	Cosolvent (wt %)	Fibre formation test 1	Fibre formation test 2	Fibre formation test 3
1A	90 wt % DMF	–	–	–
2A	70 wt % DMF	+	+	+
3A	50 wt % DMF	+	+	+
4A	30 wt % DMF	+	++	+++
5A	10 wt % DMF	+++	+++	+++
1B	90 wt % DMAc	–	–	–
2B	70 wt % DMAc	+	+	+
3B	50 wt % DMAc	+	+	+
4B	30 wt % DMAc	+	+	+
5B	10 wt % DMAc	++	++	+++
1C	90 wt % DMSO	+	+	+++
2C	70 wt % DMSO	+++	+	+++
3C	50 wt % DMSO	+++	+++	+++
4C	30 wt % DMSO	+++	+++	+++
5C	10 wt % DMSO	+++	++	+++
ABC0	0 wt %	+++	++	++

–: could not be electrospun; +: no fibre formation; ++: fibre formation tendencies; +++: fibre formation.

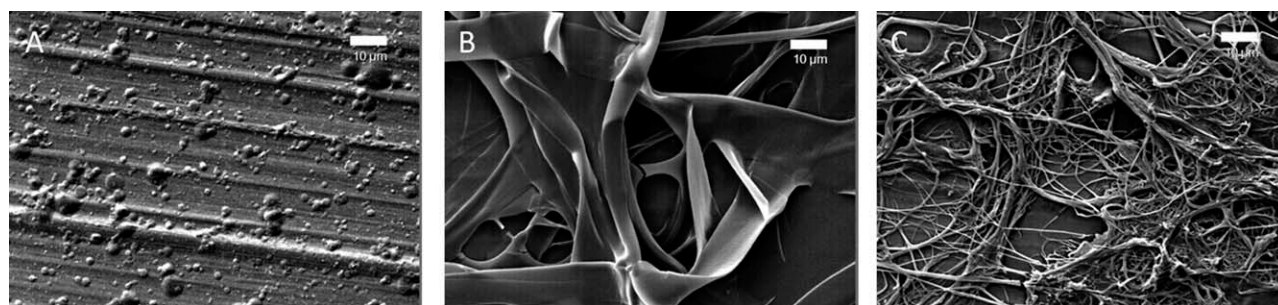


Figure 8 SEM images of electrospun cellulose fibers (A) example of classification +: no fiber formation (see Table II); (B) example of classification ++: tendencies to form fibers; (C) example of classification +++: fiber formation.

degree of surface tension is beneficial for fiber formation. As for shear thinning, the dependence of surface tension cannot be fully decoupled from viscosity; most of the fiber-forming samples with the highest surface tensions have relatively high zero shear viscosities.

From the results presented herein, no clear correlation between fiber forming ability and conductivity could be made. By studying Figure 7 and Table II it is seen that solutions with conductivity values between 3 and 11 mS cm⁻¹ (i.e., in the whole range investigated in this article) could produce fibers. However, the conductivity range studied here is not exceptionally large. It is likely that a conductivity dependence on fiber formation would have been seen if a wider range of conductivities had been investigated.

CONCLUSIONS

The processing parameters when electrospinning cellulose from ionic liquids with a cosolvent; DMF, DMAc, or DMSO, was studied to relate solution parameters (e.g., viscosity, surface tension, and conductivity) to spinability and fiber formation. Regardless of which co-solvent used it is shown that a

certain degree of viscosity and surface tension is needed to form fibers. The DMSO-based system exhibited higher viscosity values compared to the DMAc- and DMF-based systems and formed fibers at a broader interval of EmimAc fractions. Hence, it is spinable at lower content of EmimAc than the DMAc- and DMF-based systems. The surface tension of the solvent mixtures is less affected when using DMSO as cosolvent in comparison to the other two cosolvents. There could be no clear connections drawn between spinability and conductivity. Interestingly, the solutions with the most pronounced shear thinning behavior, i.e., the DMSO-based system, are also the best fiber forming solutions. The system with DMSO as cosolvent was found to give the best fiber formation, which is linked to the solubility of cellulose in ionic liquids with different cosolvents. 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 cosolvent (DMAc or DMF) compared to interaction between ionic liquid and DMSO.

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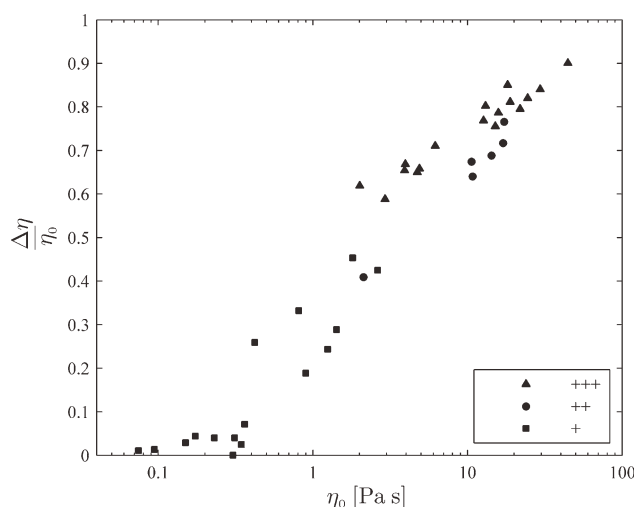


Figure 9 Shear thinning.

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