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Influence of water on swelling and dissolution of cellulose in 1-ethyl-3-methylimidazolium acetate

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ABSTRACT

In this study the effect of residual coagulation medium (water) on cellulose dissolution in an ionic liquid is discussed. Solubility of dissolving grade pulp; HWP and SWP, and microcrystalline cellulose in binary solvents, mixtures of 1-ethyl-3-methyl-imidazolium acetate and water, was investigated by turbidity measurements, light microscopy, rheometry, and CP/MAS ^{13}C-NMR spectroscopy. The viscoelastic properties of the cellulose solutions imply that residual water affect the cellulose dissolution. However, it is not obvious that this always necessarily poses serious drawbacks for the solution properties or that the effects are as severe as previously believed. Turbidity measurements, viscosity data and crystallinity of the regenerated cellulose correlated well and an increased conversion to cellulose II was found at low water and cellulose contents with an apparent maximum of conversion at 2–5 wt% water. At high water content, above 10 wt%, dissolution and conversion was largely inhibited.

1. Introduction

Native cellulose is an immensely important material for mankind, used in a variety of forms for everything from paper and clothes to building material (O'Sullivan, 1997). With the ability to regenerate cellulose into other forms, new products with other properties could be developed. However, regeneration of cellulose has long been struggling with the use of inefficient or environmentally hazardous solvents (Kim, Kim, Kwak, Ko, & Kwon, 2006). With cellulose as the basis for large scale production of man-made textile fibers, it is of growing interest to develop new, as well as to understand and improve existing, methods for its dissolution and coagulation to regenerated materials. Lately an increasing number of studies have been presented in this field (Budtova et al., 2010; Hauru, Hummel, King, Kilpeläinen, & Sixta, 2012; Spinu, Dos Santos, Le Moigne, & Navard, 2011). Ionic liquids (ILs), organic salts with low melting points, can be used for direct dissolution of biomass, which is an important finding since most other solvents fail to dissolve biomass in general and cellulose in particular (Lindman, Karlström, & Stigsson, 2010; Sun et al., 2009; Swatloski, Spear, Holbrey, & Rogers, 2002). Despite a tendency to react with cellulose (Ebner, Schiehser, Potthast, & Rosenau, 2008; Liebert, 2008), 1-ethyl-3-methyl-imidazolium acetate (EMIMAc) is still one of the most popular ionic liquids for cellulose dissolution.

Regenerated cellulose can be produced from native cellulose by dissolution followed by precipitation. A conversion to regenerated cellulose means a change in the crystalline structure, from cellulose I_α or I_β in native cellulose to cellulose II in regenerated cellulose. This conversion can also be achieved by swelling or mercerization. When producing regenerated cellulose via a direct dissolution route, native cellulose is dissolved and the solvent is thereafter substituted with a coagulation medium, often water. The regenerated cellulose is removed and collected in a desired shape while the water/solvent-mixture is separated and recycled. A large part of water can be removed from the ionic liquid by e.g. partial phase separation using K_3PO_4 to bind water before the enriched ionic liquid phase can be collected and further purified by energy consuming evaporation of the water (Gutowski et al., 2003). Efficient recycling strategy is a key issue to minimize solvent consumption and environmental impact. However due to the hygroscopic nature of ionic liquids and the relatively high boiling point of water, this step would mean high energy costs in a large scale application. Understanding the effect of remaining water in the ionic liquid is therefore fundamental working with separation of water and ionic liquid.

By changing solvent or solvent properties, the properties of the regenerated cellulose can be altered, ranging from a rigid and crystalline state to a softer amorphous material (Cheng et al., 2012;

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Fink, Weigel, Purz, & Ganster, 2001). There are important applications where a more accessible amorphous system is more favorable than a rigid crystalline structure. One example is the conversion from cellulose to glucose using enzymatic degradation. It has been reported that this conversion is enhanced when pretreating the system with a solvent system which produces a more accessible amorphous cellulose e.g. DMSO/EMIMAc (Cheng et al., 2012). If an end-product benefits from a crystalline structure, impurities in the solvent could drastically decrease the value, or alter the properties, of the product (Ward, 1950). Due to the hygroscopic nature of ionic liquids, water impurities could be an issue. According to early publications in the field of ionic liquids as solvents for cellulose even water impurities as low as 1 wt% imply significant problems in the polymer dissolution process, a reason suggested being competing hydrogen bonding (Swatloski et al., 2002). It is well known that controlled water content is important in cellulose dissolution, also in other solvent systems such as N-methylmorpholine-N-oxide (NMMO). For that system the addition of water first enables polymer dissolution at low amounts, but inhibits dissolution when exceeding 2 moles of water per mol NMMO (Maia, Peguy, & Perez, 1981; Wachsmann & Diamantoglou, 1997). Recently, ionic liquid solutions with a water content of up to 15 wt% was reported to dissolve cellulose at low (1 wt%) concentration (Le, Sescousse, & Budtova, 2012). It was shown that the properties of the cellulose–solvent system were greatly affected; cellulose aggregation and reduced viscosity were effects of the increased amount of water. However, the cellulose was still in dissolved state up to high concentrations of water, as indicated by optical microscopy. The solvent viscosity and the cellulose–solvent interactions are directly linked; hence the nature of the solvent is of crucial importance as described by the well-known Mark Houwink relation (McNaught & Wilkinson, 1997).

Appropriate solvent parameters to allow for dissolution has been discussed terms of polarizability and the so called Kamlet Taft parameters describing hydrogen bonding abilities (Kamlet & Taft, 1976; Taft & Kamlet, 1976). These are measured on liquids using dyes such as 4-nitroaniline, *N*,*N*-diethyl-4-nitroaniline, and Reichardt's dye (Doherty, Mora-Pale, Foley, Linhardt, & Dordick, 2010; Hauru et al., 2012). This has been done for several ILs such as EMIMAc and also for mixtures of ILs and molecular liquids, including water. It should be noted that caution in general must be taken when discussing solvent parameters for mixed solvents using above investigations since undefined effects regarding dye interaction with the different components may interfere (Hauru et al., 2012). Cellulose is soluble in certain intervals of solvent basicity or hydrogen bond acceptor ability, β, between 0.8 and 1.2, and "net-basicity", β–α, between 0.35 and 0.9, were α is the acidity or hydrogen bond donor ability of the solvent. According to these data, cellulose should be soluble in EMIMAc/water mixtures up to a water content of around 10–15 wt%. Empirical methods have confirmed a limit of 10–15 wt% water in EMIMAc for low concentrations of microcrystalline cellulose (Le et al., 2012).

The aim of the present work is to increase the understanding of the consequences of residual water in EMIMAc in cellulose processing. In this study dissolution behavior of cellulose were analyzed for turbidity, rheological properties and morphology using microscopy when increasing cellulose concentration, from 2 to 10 wt%, and with addition of up to 10 wt% of water to the solvent. Three materials with different degrees of polymerization were analyzed, one microcrystalline cellulose (MCC), one hardwood pulp (HWP) and one softwood pulp (SWP). Due to its degree of polymerization and resulting limited solubility, the regenerated HWP was most interesting for crystallinity index measurements exploring transition from cellulose I to cellulose II.

2. Materials and methods

Microcrystalline cellulose, Avicel PH-101 (MCC, $M_w = 53470$, $M_n = 24235$) was purchased from Sigma–Aldrich. Bleached Kraft dissolving pulp from Eucalypt (HWP, $M_w = 217142$, $M_n = 73394$) was provided by Bahia Pulp S.A. and sulfite dissolving pulp from Norway spruce (SWP, $M_w = 457745$, $M_n = 114703$) was provided by Borregaard. Degree of polymerization was estimated by size exclusion chromatography in DMAc/LiCl using polystyrene standards. For native HWP crystallinity index was 65%, determined by XRD calibrated solid state NMR (see Section 2.4). Pulp sheets were milled and sieved to a particle size of ≤1 mm in diameter. 1-Ethyl-3-methyl-imidazolium acetate, EMIMAc, (LOT STBC9122V) was purchased from Sigma–Aldrich and used as received. Volumetric Karl Fischer titration (Metrohm 905 Titrando) confirmed 0.46 wt% water content in the ionic liquid.

2.1. Preparation of cellulose solvent and solutions

The binary solvents solvent were prepared as bulk solutions and used throughout the analyses. Deionized water and IL was mixed to give 2, 5, 8, 10, and 15 wt% water, respectively. Actual water content was determined and adjusted using volumetric Karl Fischer titration. Cellulose was dried overnight at 70 °C and the resulting moisture content was determined gravimetrically to 3 wt% or less. Cellulose was then added to the solvent by dry weight, stirred vigorously and dissolved at 50 °C during 5 h in closed containers to avoid any changes in water concentration.

2.2. Characterization of cellulose solutions

Viscoelastic data were collected on a Bohlin Instruments CS50 rheometer equipped with a 4°/4 mm cone and plate measuring system. A closed container equilibrated at 48 °C was used for all samples in both oscillatory and rotational measurements. This temperature was chosen for practical reasons; it was sufficiently cold to give low viscosities for most low viscosity samples, and sufficiently warm to avoid a rigid material for the high viscosity samples.

Apparent absorbance was measured at 800, 825, and 849 nm, respectively on a UV/vis spectrophotometer (Agilent 8453, G1103A). Turbidity τ was calculated according to:

$$\tau = \frac{A}{L}\ln(10) \tag{1.1}$$

where A is the absorbance and L cuvette length. The reported turbidity was given as an average of values at the chosen wavelengths. These three wavelengths were chosen as there is no residual absorption from the sample in this interval and all detected apparent absorbance was then only a result of particle light scattering, turbidity. The linear agreement, of Beer–Lambert law, for absorbance measurements holds for $A \leq 1.5$, which translates to turbidity around $\tau = 3.5$. Above this threshold, all results are to be treated qualitatively rather than quantitatively. A calibration curve was constructed using deionized water and microcrystalline cellulose in order to estimate the amount of non-dissolved cellulose in the sample. The relationship between turbidity of samples and amount of undissolved material was according to the calibration curve $\tau = 0.9061\,a$, where a is the amount of non-dissolved MCC in the sample, expressed in mg/g with a coefficient of determination (R^2) exceeding 0.999. By knowing the amount of non-dissolved cellulose in a real sample and the amount of added cellulose, the calibration curve can be used to estimate the degree of dissolution.

Micrographs of cellulose solutions were captured on a Zeiss Discovery V12 light microscope using a Canon Powershot G9 mounted on a Zeiss universal digital camera adapter d30 M37/52 × 0.75.

2.3. Cellulose films

Cellulose films of approximately 1 mm thickness were prepared by coagulating cellulose solutions between two flat surfaces in deionized water. The films were washed thoroughly several times in water to remove residual solvent. The films were then stored in never-dried condition in deionized water until NMR characterization.

2.4. Characterization of cellulose films

All NMR experiments were performed on a Varian Inova-600 operating at 14.7 T and equipped with a 3.2 mm solid-state probe. Measurements were conducted at 298 K with a MAS spinning rate of 15 kHz. In this study, the ambition was to record quantitative information from the signal intensity in the CP/MAS spectrum. An array of spectra, with different cross-polarization times, was recorded in order to investigate the intensities of signals corresponding to amorphous and crystalline parts of the sample. This experimental approach was based on work by Larsson, Wickholm, and Iversen (1997). It was found that the normalized signal intensity of crystalline cellulose was equal to that of the amorphous cellulose when using cross-polarization contact times between 500 and 2000 μs. A contact time of 1200 μs was chosen for all samples. Additional acquisition parameters for the CP/MAS ^{13}C-NMR measurements included a 2.9 and 4.0 μs ^{1}H and ^{13}C 90° pulse, respectively, 35 ms acquisition time with proton decoupling, 5 s recycle delay, and 4096 acquisitions for each spectrum.

The solid-state NMR spectra were processed by MestreNova 7.0.3 software. For all spectra zero-filling with 8192 points, phase correction and a first order polynomial baseline correction were used in the processing. Conventional apodization of 30 Hz was applied to remove noise without decreasing apparent signal resolution.

Two reference samples, one consisting of cellulose I and one consisting of cellulose II, were used as standards for crystallinity index determinations of the samples in this study. The crystalline amounts in the two reference samples were determined using XRD peak height method described by Park, Baker, Himmel, Parilla, and Johnson (2010), to be 67% cellulose I and 80% cellulose II, respectively. Solid-state NMR spectra of the two reference samples were then acquired and normalized, and two regions with regard to the chemical shift were chosen, 65.5–65.7 ppm and 107.5–107.7 ppm. These signal regions originate from cellulose I and cellulose II, respectively. Samples with unknown crystallinity index were then analyzed over the same regions. By comparing the obtained integral values with those acquired from the reference samples the crystallinity index, CI, for the two allomorphs could be calculated. Overlapping signals in semi-dissolved HWP made crystallinity index determination samples using XRD impossible. However, using this method, solid-state NMR calibrated with XRD, the resulting crystallinity values corresponded to those that would have been obtained by XRD.

3. Results and discussion

3.1. Apparent solubility of cellulose

Solubility of the three different types of cellulose was investigated using turbidity and light microscopy. Turbidity for samples as a function of cellulose content and water content in the EMIMAc solvent is found in Table 1. Cellulose pulp at this concentration range, of 2–10 wt%, is well known to be soluble in pure EMIMAc (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Zavrel, Bross, Funke, Büchs, & Spiess, 2009), why samples of water content 0 wt% were omitted in the turbidity study. The samples of 15 wt% water, on the other hand, were non-uniform and clearly not dissolved for any of the cellulose types, why turbidity measurements were omitted also in this case. The results show a distinct difference between the different types of cellulose materials. Dissolution of Avicel MCC, constituting of smaller particles and with a low degree of polymerization, was less sensitive to water compared to the two pulps. The turbidity measurements did not show any substantial difference between the two dissolving pulps.

From the linear relationship of the turbidity calibration curve it can be calculated that all MCC samples with small amounts of water and/or cellulose, are to more than 99%, dissolved. The least dissolved sample is not surprisingly 10 wt% MCC in EMIMAc with 10 wt% water, which, according to the calibration curve is dissolved to 94.2%. The MCC calibration curve should not be used quantitatively for the pulp samples since the fibers are not likely to scatter light in the same concentration dependence as the MCC particles.

Light microscopy images of samples with 2 wt% of each type of cellulose dissolved in water-containing EMIMAc can be found in Fig. 1. For samples with 2 and 5 wt% water content, available as Supplementary data, no macroscopically non-dissolved cellulose was visible. For the two pulps with 8 wt% water content the impact of water in the solvent can be seen with a few non-dissolved fibers clearly visible for the SWP and barely visible for the HWP. At 10 wt% water both pulps have a significant amount of non-dissolved cellulose. For MCC no particles can be seen even at this water concentration. However, as the cellulose concentration increases, non-dissolved material starts to appear even in the MCC samples in accordance to turbidity data shown in Table 1. For the samples in EMIMAc with 15 wt% water, there is a significant amount of non-dissolved material in all three samples. Light microscopy images of all cellulose contents are available as Supplementary data.

The so called Kamlet Taft parameters α and β, describing a solvent's hydrogen bond donor/acceptor properties, are suggested to be key parameters for predicting solvents for cellulose (Hauru et al., 2012). According to a "solubility window" constructed by assessing a range of different cellulose solvents and non-solvents, cellulose should be soluble in EMIMAc with 10–15 wt% added water. As seen in Fig. 1 and Table 1 MCC in low concentration is indeed soluble in EMIMAc solvent with at least 10 wt% water. However, at 10 wt% MCC content, the critical amount of water included in the solvent is decreased to between 5 and 8 wt%, lower than those predicted by the Kamlet Taft parameters. For the two dissolving pulp samples, it can be seen in Table 1 that the turbidity of 2 wt% pulp solutions starts to increase already at around 8 wt% water content. This is not an effect of bubble formation but confirmed as residual particles in the micrographs shown in Fig. 1, where small amounts of non-dissolved fiber are found in both pulp samples at a water content of 8 wt%. At 10 wt% water content there is a lot of non-dissolved material. For the more concentrated solutions, there is even lower tolerance of water, less than 5 wt%, confirmed also in micrographs. All micrographs can be accessed in Supplementary data.

As seen in Table 2, for solutions with a cellulose concentration of 2 wt%, the corresponding stoichiometry for anhydrous EMIMAc is almost 47 mol IL/mol anhydroglucose unit (AGU). For a cellulose concentration of 10 wt% the corresponding stoichiometry is 8.5 mol IL/mol AGU, and cellulose is still dissolved. For solutions with 8 wt% water content and 8 wt% cellulose concentration the stoichiometry corresponds to 10.1 mol IL/mol AGU, thereby exceeding a ratio that should dissolve cellulose. However, Fig. 1 shows non-dissolved fibers for samples containing ≥8 wt% water. This can be explained by the assumption that some of the ions of the IL are solvated by the water molecules and inaccessible for cellulose. The acetate anion interacts stronger with cellulose than with water (Liu, Sale, Holmes, Simmons, & Singh, 2010); yet there will be competing hydrogen bond formation between IL and water,

Table 1
Turbidity as a function of water content and cellulose concentration, for SWP, HWP and MCC, respectively. Samples that are not completely dissolved are indicated in colors of increasing red intensity.

↓ water content (wt%)	SWP concentration (wt%) → 2	5	8	10	HWP concentration (wt%) → 2	5	8	10	MCC concentration (wt%) → 2	5	8	10
2	0.17	0.21	0.75	0.21	0.14	0.14	0.27	0.71	0.00	0.00	0.12	0.07
5	0.30	0.10	0.84	1.45	0.13	0.24	0.53	1.34	0.00	0.00	0.09	0.34
8	0.04	0.44	2.71	4.15	0.16	0.78	2.83	5.00	0.05	0.02	0.07	1.59
10	3.51	2.43	6.36	6.55	3.41	5.66	6.49	6.72	0.05	0.06	2.52	5.27

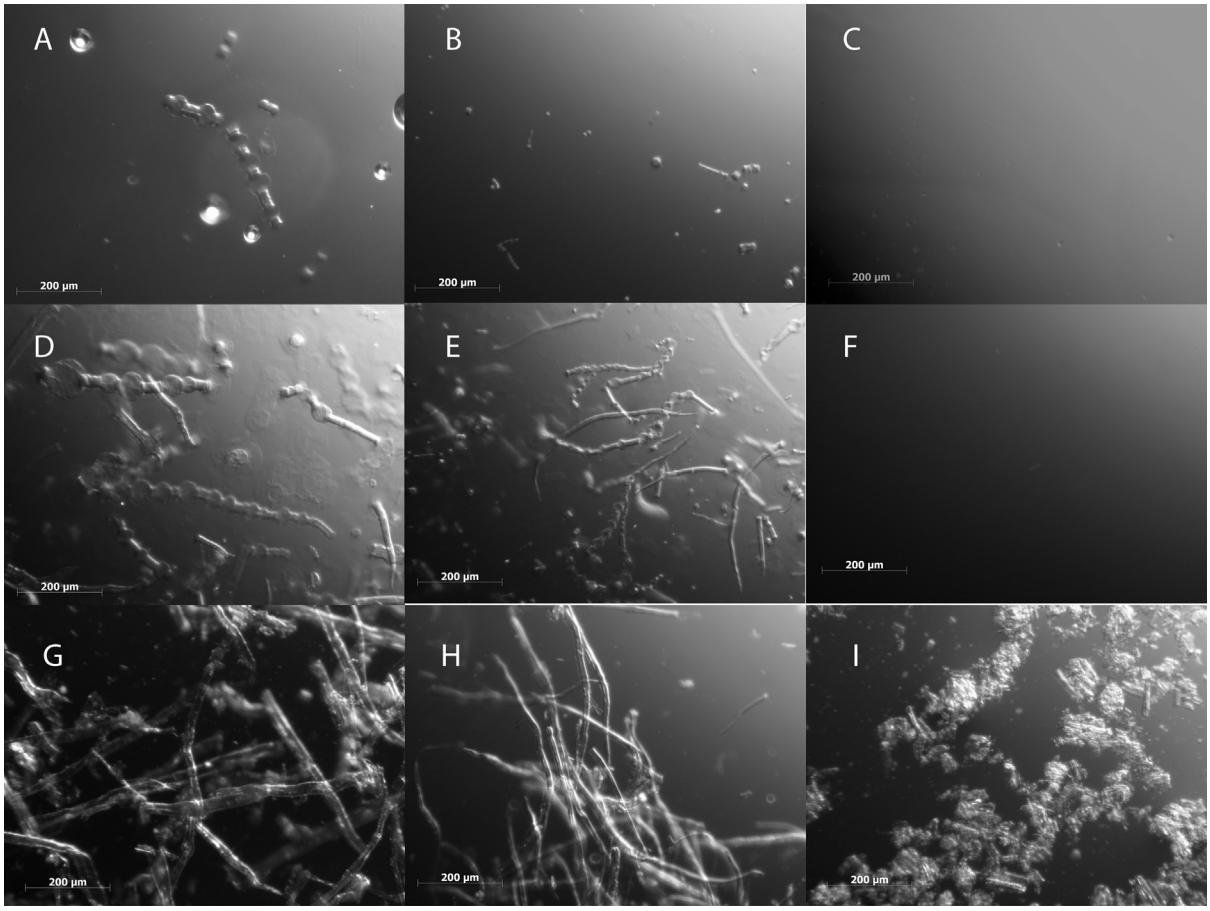

Fig. 1. Top row; micrographs of 2 wt% cellulose, SWP (A), HWP (B) and MCC (C), in EMIMAc containing 8 wt% water. A few non-dissolved fibers undergoing heterogeneous swelling, i.e. ballooning can be noted in the pulps, whereas MCC is completely dissolved. Center row: 2 wt% cellulose, SWP (D), HWP (E) and MCC (F) in EMIMAc containing 10 wt% water. A significant amount of non-dissolved but swollen fiber is found in the pulp samples while MCC is completely dissolved. Lower row: 2 wt% cellulose, SWP (G), HWP (H) and MCC (I) in EMIMAc containing 15 wt% water. Cellulose is to a large extent undissolved and any swelling of fiber is homogeneous; no balloons are formed.

Table 2
Molar ratio AGU/EMIMAc/water for samples in this study.

Water content (wt%)	Cellulose concentration (wt%) → 2			5			8			10		
	AGU	EMIMAc	H_2O	AGU	EMIMAc	H_2O	AGU	EMIMAc	H_2O	AGU	EMIMAc	H_2O
0	1	46.6	0	1	18.1	0	1	10.9	0	1	8.6	0
2	1	45.7	8.8	1	17.7	3.4	1	10.7	2.1	1	8.4	1.6
5	1	44.3	22.1	1	17.2	8.6	1	10.4	5.2	1	8.1	4.1
8	1	42.9	35.3	1	16.6	13.7	1	10.1	8.3	1	7.9	6.5
10	1	42.0	44.1	1	16.3	17.1	1	9.9	10.4	1	7.7	8.1
15	1	39.6	66.2	1	15.4	26.7	1	9.3	15.4	1	7.3	12.2

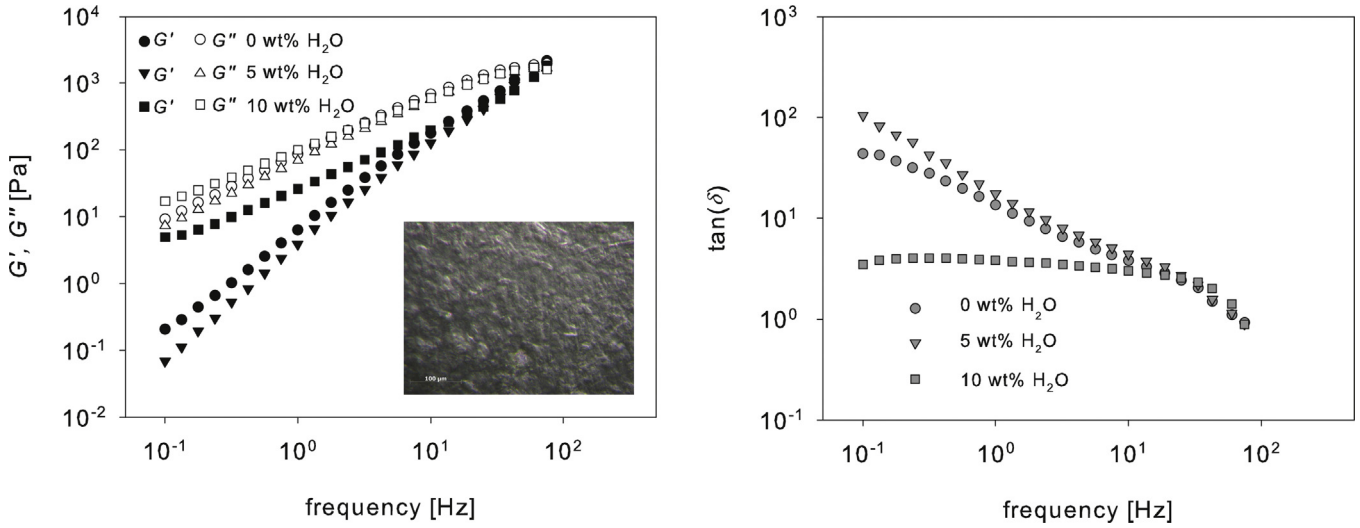

Fig. 2. Frequency dependence of storage moduli G', loss moduli G'' and the loss tangent tan(≏) for 10 wt% MCC solutions. Insert shows a micrograph of 10 wt% MCC (M_w = 53470, M_n = 24235) in EMIMAc with 10 wt% water.

especially when water is in molar excess. A reasonable assumption is that each acetate anion interacts with two water molecules (Shi, Damodaran, Nulwala, & Luebke, 2012). The amount of free IL is then reduced to 3.6 mol IL/mol AGU which could lead to incomplete dissolution. As found, the amount of IL needed for dissolution is influenced also by the degree of polymerization (DP) of the cellulose. It can be concluded that a water concentration which is acceptable for dilute cellulose solutions may well not be acceptable at higher polymer concentrations or for cellulose of other DP. When discussing the ability of a solvent to dissolve cellulose, the concentration of the latter must also be taken into consideration.

As noted in Fig. 1, water present in the solvent does not only affect the amount of cellulose that is soluble in EMIMAc, it also affects how the dissolution occurs. In neat EMIMAc, dissolution is instantaneous and homogeneous – without any sign of heterogeneous fiber swelling. In hydrated samples, the dissolution is accompanied by a swelling process known as ballooning. The ballooning effect is known in less powerful solvents and has been studied in e.g. NaOH(aq), NMMO and some ionic liquids (Cuissinat & Navard, 2006a, 2006b; Cuissinat, Navard, & Heinze, 2008). This effect is unique to fibrous materials and is for that reason not visible in the MCC samples at any time. In general, five different modes of dissolution can describe cellulose behavior in different solvents, as described earlier for both cotton and wood based fibers (Cuissinat & Navard, 2006a):

Mode 1: Fast dissolution by disintegration into rod-like fragments.
Mode 2: Large swelling by ballooning, and then dissolution of the whole fiber.
Mode 3: Large swelling by ballooning, and partial dissolution of the fiber, still keeping its fiber shape.
Mode 4: Homogeneous swelling, and no dissolution of any part of the fiber.
Mode 5: No swelling and no dissolution (case of a non-solvent).

As expected, a non-solvent (here water) added to the solvent, will shift the dissolution mode of cellulose in the ionic liquid from mode 1 to mode 2 and then at higher non-solvent concentrations to mode 3 as seen in the samples containing 8 and 10 wt% water in Fig. 1. Finally, with enough of non-solvent added, the system will enter mode 4, as seen in the samples containing 15 wt% water. Mode 2 is still acceptable from a processing point of view, but any higher dissolving mode would cause detrimental effects to e.g. a fiber spinning line due to residual non-dissolved material.

3.2. Dynamic viscoelasticity of cellulose solutions

To probe the dynamic properties of the cellulose solutions with various water content in the solvent, frequency sweeps were performed over three decades (0.1–100 s^{-1}) at 48 ± 0.1 °C. These experiments can reveal information about the state of solution of the system. For example, the critical gel point of a polymeric system can be defined in terms of loss tangent (tan(≏) = $G''/G' \approx 1$), which at the gel point is independent of frequency and the storage and loss moduli overlap (Winter & Chambon, 1986). In Fig. 2, the storage and loss modules as well as tan(≏) for MCC samples at a cellulose concentration of 10 wt% can be seen. A gradual build-up of a gel-like behavior can be seen as the moduli lose their frequency dependence going from 0 to 10 wt% water in the solvent. For MCC in neat EMIMAc and up to 5 wt% water there is clear and unambiguous frequency dependence over the entire frequency span. An indication of increased frequency dependence for 5 wt% water compared to the reference solution without water can be noticed, although this difference is very small. It seems that at 5% water in the solvent, MCC is fully soluble with minor rheological differences. It is also clear that tan(≏) approaches a plateau at low frequencies for the 10 wt% water solution which, as mentioned, is defining for network structures/gels (Song, Niu, Wang, & Zhang, 2011). According to the insert in Fig. 2 showing the micrograph of 10 wt% MCC in EMIMAc with 10 wt% water, the cellulose is not fully dissolved at these conditions. To explain the gel like behavior then, we consider that apparent yield stress due to fillers in a polymer melt is similar to the behavior of a high viscosity fluid at sufficiently low frequencies (Oxfall et al., 2012; Vermant, Ceccia, Dolgovskij, Maffettone, & Macosko, 2007; Vlasveld, de Jong, Bersee, Gotsis, & Picken, 2005). Thus the data could be explained by either gel-formation, or the non-dissolved MCC particles acting as filler in a dissolved cellulose system, or a combination.

In Fig. 3, a similar tendency can be noticed for 10 wt% HWP solutions, although not as clear as in the case of MCC. The data overlap almost completely, especially for 0% water and 5% water, and all samples appear to be close to the critical gel point. The DP of the HWP is much higher than that of the MCC, which might explain why the cellulose seems gel-like even without added water in the solvent; high DP polymers are entangled even at lower concentrations.

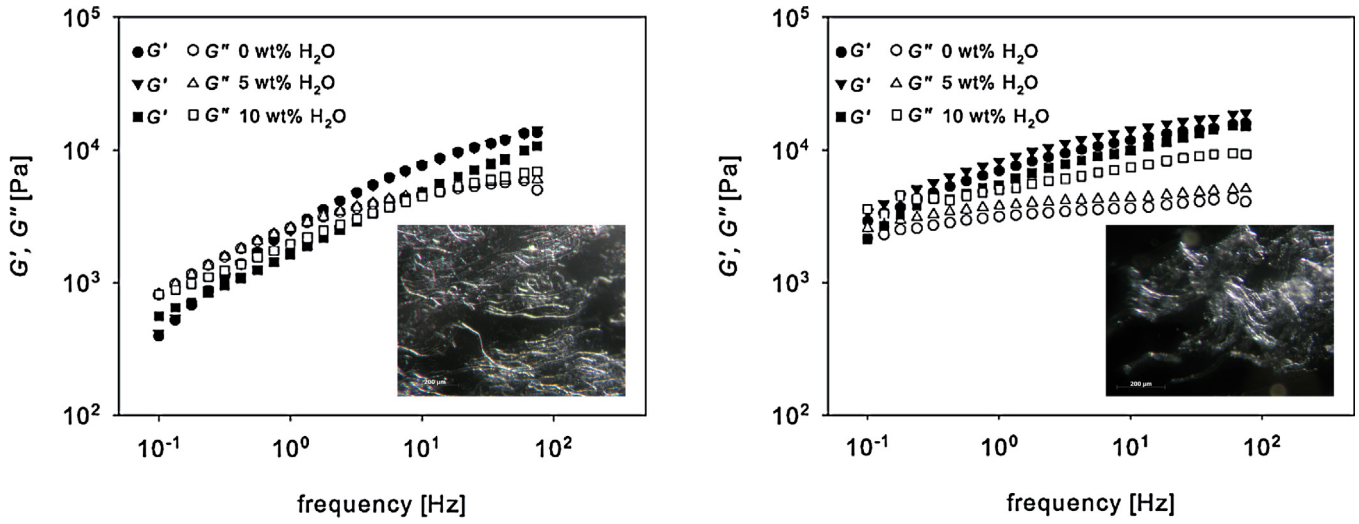

Fig. 3. Storage moduli and loss moduli for 10 wt% HWP (M_w = 217142, M_n = 73394) (left) and SWP (M_w = 457745, M_n = 114703)(right) solutions in EMIMAc with water content ranging from 0 to 10 wt%. Inserts show micrographs of 10 wt% pulp in EMIMAc with 10 wt% water.

Moduli for HWP samples are less frequency dependent than for the MCC samples for all water concentrations but at 10 wt% water in the solvent data deviates from the behavior of the other samples in the HWP series. Micrographs as shown in inserts in Fig. 3 reveal a lot of non-dissolved material in the 10 wt% water sample, which might explain the deviation in these data.

For SWP most samples overlap but the gel-like behavior is more pronounced than for the HWP samples, which is explained by the even higher DP for this pulp. As for HWP, the storage modulus of the sample with 10 wt% water falls below the other two. This is contrary to the effect of water in the MCC samples, and might be an effect of the even lower solubility of the pulps in hydrated solvent. For MCC, most of the cellulose is still dissolved at this water content. For the pulps the increased water content might lead to phase separation and/or insufficient amount of cellulose being dissolved to form a polymer network of similar strength as for 5 wt% water.

The gel point of MCC in neat EMIMAc was found at a cellulose concentration of 12.5 wt% by Song and coworkers, who also discovered a liquid crystalline phase at even higher concentrations. As shown in Fig. 4, the apparent gel-point of cellulose in EMIMAc can be reached not only by increasing cellulose loading but can also, at a sufficient cellulose concentration, be reached by increasing water content in the solvent. At 2 and 5 wt% cellulose there is no real difference between the HWP samples in neat EMIMAc and those in EMIMAc containing 10 wt% water. For 8 wt% HWP, the sample in pure EMIMAc shows a solution-like behavior, with a pronounced frequency dependence of tan(≏). However, for the 8 wt% HWP sample in EMIMAc with 10 wt% water, we see a plateau at low frequencies, indicating a gel-like network structure.

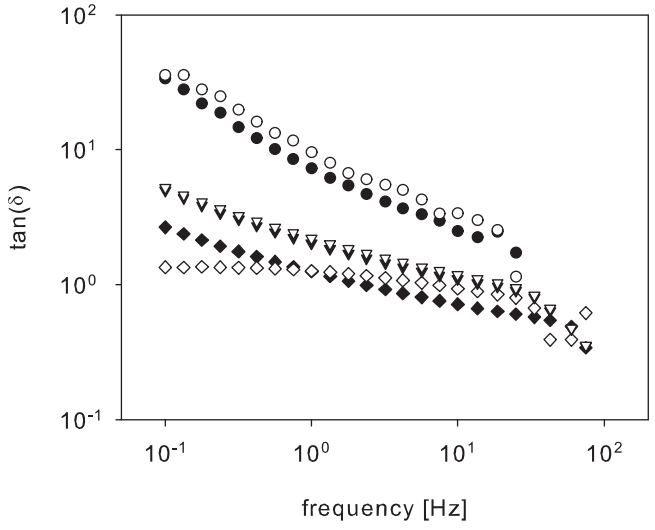

Fig. 4. Effect of cellulose concentration and water content on gelation in terms of tan(≏) for HWP samples.

As indicated by turbidity data in Table 1, and confirmed by micrographs in Fig. 1, samples with 2–8 wt% HWP and SWP are not completely dissolved in the solvent containing 10 wt% water. Small differences in rheology for the first two samples are revealed in Fig. 4 which could be explained by an introduction of several different effects as water content increases. For example, more water will lead to decreased overall solvent viscosity and possibly an increased mobility of dissolved cellulose below the overlap concentration of the polymer. It will also lead to a decreased number of accessible IL leading to a decreased solubility of cellulose, resulting in some cellulose not in perfect solution and fewer polymers involved in entanglements, hence a decreased viscosity/rigidity of the system. At the same time, non-dissolved particles can act as fillers which instead leads to increased viscosity/rigidity, at least at higher cellulose concentrations. Furthermore, if we assume some dynamic effects, like rearrangements of IL–cellulose–water interactions over time it can be expected that dissolved cellulose may re-aggregate chain-to-chain at higher water contents, i.e. without an IL surplus. This may lead to a sort of physically cross-linked gel like structure and increased viscosity/rigidity. Hence, from rheology alone there is not enough information to reveal what type of system we are dealing with.

A decrease in viscosity for slightly hydrated solvent (5 wt% water) is noted in Fig. 5 for MCC samples with a cellulose concentration of 10 wt%. This was also noticed for other cellulose types and concentrations (not shown). A decreased solubility power of the solvent should indeed be reflected in a more contracted polymer conformation, leading to a lower viscosity. The same decreasing viscosity effect was noticed by Le and coworkers for 1 wt% cellulose in water and EMIMAc and was then explained by a polymer chain aggregation due to a decreased solvent preference for the polymer in the presence of water (Le et al., 2012).

At 10 wt% water content (Fig. 5), we see the gel-like/network structure effect once more. This sample displays a non-Newtonian

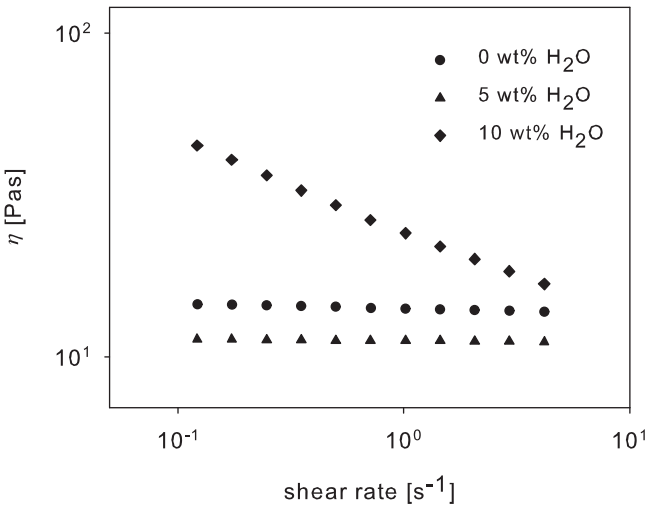

Fig. 5. Rotational viscometry showing apparent viscosity η of 10 wt% MCC solutions in EMIMAc with 0, 5, and 10 wt% water, respectively.

behavior and no Newtonian plateau is visible. Instead, the curve corresponds to that of a particle filled polymer melt, or in this case a solution (Kataoka, Kitano, Sasahara, & Nishijima, 1978).

3.3. Crystallinity of regenerated cellulose samples

The crystallinity index (CI) of all HWP samples obtained using CP/MAS ^{13}C NMR is summarized in Table 3. High conversion from cellulose I to cellulose II can be found at low initial cellulose content and low amount of water in the ionic liquid, indicating complete dissolution. From molecular dynamic simulations it has been concluded that the hydroxymethyl group of the C-6 in the AGU is in the trans-gauche (tg) position for cellulose I (Nishiyama, Langan, & Chanzy, 2002) and in the gauche-trans (gt) position for cellulose II (Langan, Nishiyama, & Chanzy, 2001). The difference in conformation results in two different crystalline structures where cellulose II is the most stable one. Corresponding simulations of cellulose in the presence of EMIMAc show that the hydroxymethyl group had the same conformation, gt, as in the cellulose II crystalline structure (Liu et al., 2012) and the conversion to a cellulose II crystalline structure could therefore be favored in the presence of EMIMAc.

In this work the relative CI-values were acquired using solid-state NMR and the errors were estimated to be ±4%. According to previous studies, CI values should not be interpreted as absolute since results may vary considerably depending on the method used (Park et al., 2010). However, for analyzing trends in a series analyzed under identical conditions, it serves well for internal comparisons.

There is an apparent maximum conversion for cellulose contents at around 2–5 wt% water contents in the ionic liquid. Previously it has been found that when using other ILs as solvents for cellulose even small amounts of water in the ionic liquid (1 wt%) significantly weakened its dissolution ability (Swatloski et al., 2002). The present work indicates that with EMIMAc as solvent for cellulose, an increased mobility of the ionic liquid due to the addition of a small amount of water instead aids dissolution. Since the hydrogen bonds between cellulose and IL are stronger than the water-IL hydrogen bonds (Hauru et al., 2012; Liu et al., 2010), the cellulose–IL interaction is still preferred. With the addition of a larger amount of water, a decrease in the conversion to cellulose II can be seen.

For samples with more than 8 wt% of starting material a significant amount of amorphous material was detected in the product. This corresponded to molar ratios less than 10 EMIMAc per AGU, as can be seen in Table 2. The high amount of amorphous material in samples with high cellulose content can be explained by the high degree of entanglement, partly "locked" by parts of cellulose deprived of solvent ions and prone to aggregation. At higher water content aggregation should be more likely to occur since more solvent ions are withdrawn from the polymer. Furthermore, Liu et al. found that cellulose modeled in water had the hydroxymethyl group in the gg position, a position that could inhibit the formation of cellulose II and promote the formation of an amorphous structure (Liu et al., 2012). At high water content and high cellulose content, residues of remaining cellulose I is detected in the product and for samples with more than 15 wt% water only cellulose I is present and no conversion to cellulose II can be seen. When comparing CI-values with the molar ratios depicted in Table 2 it can be seen that the threshold corresponds to a molar ratio 1:1 of water and EMIMAc. It should however be noticed that there is still conversion from cellulose I to amorphous material, since the crystallinity index of native pulp exceeds that of all samples treated with EMIMAc/water. This means that the ionic liquid is able to at least partly dissolve/swell crystalline cellulose I even for high content of water but the conversion to cellulose II is largely inhibited. This is in line with the swelling type of Mode 4 in the model of dissolution proposed by Cuissinat, described above (Cuissinat & Navard, 2006a).

A correlation is noted when comparing data from turbidity data and viscosity data with the crystallinity index of the regenerated cellulose from HWP solutions in Table 3. For samples that have been highly dissolved, i.e. samples with low water- and cellulose content, low viscosity is found and a maximum conversion cellulose

Table 3
Results for crystallinity index measurements from CP/MAS ^{13}C NMR of HWP, (a) CI for cellulose II, (b) CI for cellulose I, (c) fraction of amorphous cellulose. Cellulose I crystallinity index for native HWP was 0.65. Increasing intensity of color describes an increased relative amount of cellulose II, cellulose I and amorphous material, respectively.

	(a) CI for cellulose II				(b) CI for cellulose I				(c) amorphous fraction			
	HWP concentration (wt%) →				HWP concentration (wt%) →				HWP concentration (wt%) →			
← water content (wt%)	2	5	8	10	2	5	8	10	2	5	8	10
0	0.70	0.47	0.25	0.29	0.00	0.00	0.03	0.02	0.30	0.53	0.72	0.69
2	0.70	0.57	0.30	0.25	0.01	0.01	0.01	0.03	0.29	0.42	0.69	0.72
5	0.68	0.56	0.31	0.23	0.00	0.04	0.01	0.03	0.32	0.40	0.68	0.74
8	0.63	0.34	0.18	0.13	-0.03	0.01	0.02	0.07	0.37	0.65	0.80	0.80
10	0.40	0.33	0.17	0.09	0.04	0.07	0.14	0.15	0.56	0.60	0.69	0.76
15	0.02	0.00	0.00	0.00	0.46	0.53	0.55	0.58	0.52	0.47	0.45	0.42

II can be seen. A small trend both in viscosity and CI-measurements indicate that the EMIMAc benefits from a small amount of water for the conversion to cellulose II.

4. Conclusions

In this study the influence of water in EMIMAc during dissolution of three different cellulose samples was investigated using light microscopy, rheometry and solid-state NMR. It was shown that the transition where EMIMAc is no longer an excellent solvent but merely a swelling agent is not sudden, and that a certain amount of water can actually be accepted or even in some cases preferable. The amount of cellulose which is soluble in EMIMAc was concluded to be influenced by DP, cellulose concentration and amount of water present in the IL. Light microscopy shows that pulp swelling occurred by ballooning in water contents between 5 and 15 wt%.

In general, low amount of cellulose and low amount of water yielded regenerated cellulose of high crystallinity. The same samples were found to be well dissolved, according to light microscopy and turbidity measurements. This means that complete dissolution facilitates not only destruction of the native cellulose I structure, but also the re-crystallization to cellulose II. At the same time, an apparent *maximum conversion* to cellulose II was noted at 2–5 wt% water content in the solvent, which correlates to viscosity measurements that show a minimum at the same water content. This is interpreted as an effect of improved mobility of the cellulose chains in the solvent with small amounts of water; since the solvent viscosity is lower but the excess of EMIMAc ions is still large enough to completely dissolve the cellulose.

At 10 wt% water, corresponding to a molar ratio EMIMAc/water of 1:1, some solutions reached an apparent critical gel-point. However, part of this behavior is likely to be explained by undissolved material acting as filler. Here, it was evident that rheology does not reveal all information and must be used in combination with other methods.

Increasing the water content over 10 wt% inhibited dissolution severely and which hindered conversion from cellulose I to cellulose II. Light microscopy revealed non-dissolved material at a water content of 15 wt%, for all concentrations and DPs of cellulose.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.08.042.

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