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# Impact of Water in the Casting of Cellulosic Film from Ionic Liquid Solutions

DOI: 10.5604/12303666.1152718

## Abstract

*This study addresses in detail the role of water in the consecutive steps of film forming: cellulose dissolution, regeneration and drying, and its impact on the mechanical properties of the cellulose film. Prehydrolysis kraft (PHK) pulp was subjected to hydrothermal treatment (HT) prior to its dissolution in 1-ethyl-3-methylimidazolium acetate [emim]OAc. After the treatment, the DP of the pulp was 440 and the polydispersity index was as low as 3.1. HT-pretreated pulp was dissolved in [emim]OAc with a water content of 2, 7, 14 and 21 wt%. The pulp dissolution was completed within 15 min regardless of the water content in the solvent. The rheological behavior, one of the key properties in film formation, was determined at varied temperature and cellulose concentration. Cellulose films were prepared from solutions with cellulose concentrations of 8, 12 and 16 wt% at a temperature of 90 °C. The impact of water on the macromolecular, morphological and mechanical properties of the transparent films prepared was thoroughly studied. With a very low polydispersity of the cellulose chain, the films prepared revealed high strength ranging from 87 to 106.5 MPa at elongation from 10 to 50% in conditioned state.*

**Key words:** transparent cellulose film, water, cellulose hydrothermal treatment, ionic liquid (IL), morphological properties, mechanical properties.

## Introduction

The production of cellulosic films from ionic liquid (IL) solutions offers environment-friendly, safe and low-energy access to renewable materials for various applications in which high mechanical strength and transparency is demanded [1].

Several ionic liquids (ILs) have been identified as good solvents for a number of biopolymers like cellulose, chitin, starch and proteins, producing solutions suitable for the spinning of fibres and casting of films [2 - 7]. In particular, the high solubility of (bio) polymers in ILs is advantageous in terms of cost and energy efficiency [8, 9].

The archetypal cellulose dissolving IL [emim]OAc is low-viscous, non-toxic and non-corrosive, which renders the solvent attractive for cellulose processing at low temperatures, such as fibre spinning [2]. IL-based technology is safer when

compared with the Lyocell process, and moreover it offers the possibility to prepare fibres with a broad palette of properties.

In a previous study, films were cast from solutions of cotton cellulose in [emim]OAc employing varied coagulation baths: demi water, aqueous isopropanol, methanol and aqueous methanol [1, 10].

The properties of the polymer solutions are crucial for fibre or film formation. It is known that a prolonged thermal impact (above 100 °C) on cellulose/ILs solutions causes a considerable decrease in cellulose DP [11 - 13]. Basic compounds such as methylimidazole and pyridine or molecular co-solvents like DMSO in the amount of 5 to 20% can impede cellulose degradation [3].

Several protocols have been proposed for the dissolution of cellulose in ILs like [emim]OAc and [bmim]Cl at temperature ranges of 70 - 120 °C and 1 - 20 wt% of cellulose concentration [14].

Co-solvents such as toluene, 1,4-dimethylbenzene, 2-propenenitril, and water all affect the cellulose solution similarly, lowering its viscosity by as much as 50% [15].

Impurities and water exert a strong impact upon the solution viscosity of ILs solutions.

The rheology of a 1% solution of Avicel microcrystalline cellulose (DP = 170) in [emim]OAc with a water content up to 20 wt% [16] deserves attention. At a water content below 15 wt%, the cellulose/[emim]OAc /water solution reveals features of a Newtonian fluid over a wide range of the shear rate, while with a 15 - 18 wt% water content, a dilution effect is observed, caused by the incomplete dissolution of the cellulose. A small amount of the water in [emim]OAc affects the dissolvability of cellulose favourably [17]. Microcrystalline cellulose (MCC) is less sensitive to water content than eucalyptus or spruce dissolving pulp. In [emim]OAc the dissolution is rapid and homogeneous; swelling of the heterogeneous fibres does not occur [17].

It has been documented in an earlier research [1] that hydrothermally treated (HT) cellulose is particularly suited for the casting of films from IL solutions. The HT of wood pulp changes its properties in a favorable manner; in particular, the polydispersity index (PDI) can be decreased and the degree of polymerization can be tailored to a desired value [18 - 22]. HT cellulose could be dissolved faster at a relatively high cellulose concentration.

The aim of the work herein was to investigate the impact of residual water in HT cellulose on the solubility in [emim]OAc, on the properties of the solution and on the mechanical properties of the film prepared. Three series of solutions

with a cellulose concentration of 8, 12 and 16 wt% were prepared for this purpose. The water content in the cellulose was varied as follows: 2, 7, 14 and 21 wt%, and molecular and morphological changes were traced (see **Table 1**). Further goals of this study were to explain the phenomenon of opalescence that is observed in the course of film drying, and to monitor the degree of polymerization throughout the cellulose processing.

## Experimental

### Materials

The following materials were used:

- [Emim]OAc, 1-ethyl-3-methylimidazolium acetate, C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: 90%, Refractive index: 1.499. The material was purchased from BASF, Germany.
- Ethyl alcohol made by Avantor Performance Materials Poland S.A. (formerly POCH S.A.).
- Dissolving pulp Alicell Super, called PHK in short, supplied by Western Pulp, Canada, Applications: rayon filament, cellophane; pulp characteristics: alpha cellulose - 93.5%, brightness- ISO > 91% acc. to ISO 2470:1999, intrinsic viscosity: 570 ml/g, R10: 91.8%.

### Methods

#### Hydrothermal pretreatment of the cellulose pulp

PHK dissolving pulp was subjected to hydrothermal treatment as described in detail earlier [20]. The pulp was processed at 161 °C for 30 minutes, washed afterwards with demineralized water and dried to a water content of 2, 7, 14 and 21%, respectively. The HT cellulose ob-

**Table 1.** Symbols and characterisation of samples; \*) – recovered [emim]OAc.

Symbol of sample	Cellulose concentration	Water content in cellulose
	wt%	wt%
RCF 20	8 (series I)	7
RCF 21		14
RCF 22		21
RCF 23	12 (series II)	2
RCF 24		7
RCF 25		14
RCF 26	16 (series III)	21
RCF 27		2
RCF 28		7
RCF 29	16 (series III)	14
RCF 30		21
RCF 31		2
RCF 24 *)	12	7

tained, characterized by a degree of polymerisation (DP) of 440 and polydispersity index (PDI) of 3.1, was used as a cellulose substrate to prepare cellulose/IL solutions.

#### Preparation of cellulose/IL solutions

Three series of solutions were prepared with HT cellulose concentrations of 8, 12 and 16 wt%. The water content in the HT cellulose was varied systematically: 2, 7, 14 and 21%. The cellulose was wetted with the IL at 20 °C and the suspension obtained was heated up to 90 °C for 15 minutes. To ensure complete dissolution, the temperature was kept for a further 60 minutes. The solution obtained was deaerated by storing it at 80 °C. After the deaeration, the solutions were used for film casting without additional filtration. The deaeration time was adjusted to the viscosity of the solutions. The first solution series (8 wt%) was used for film casting after 24 hours, the second series (12 wt%) after 48 hours and the third one (16 wt%) after 72 hours.

#### Casting of the cellulose film

The cellulose-[emim]OAc solution was heated to 80 °C, poured onto a heated metal surface, distributed by means of a simple casting device equipped with a knife at a defined distance of 0.6 mm to remove any surplus of the solution, and then put into a regeneration bath consisting of a 80/20 mix of ethanol/water at 20 °C. The immersion time in the coagulation bath was typically 6 minutes. The film was then placed into a demineralized water wash bath at 90 °C for 3 hours and next in another demineralized water bath at 60 °C for 1 hour. The film samples were finally kept for 24 hours in demineralized water at ambient temperature before being dried at 50 °C.

### Analytical methods

#### Assessment of solutions by means of a microscope

A Biolar ZPO, Poland, optical microscope equipped with an advanced image analysis system (MultiScan V. 14.02) was used to take images of the cellulose/IL solutions and films.

#### Assessment of cellulose film by SEM/ESEM

Images of the cross-section and surface of the cellulose films were obtained using a scanning electron microscope: SEM/ESEM, Quanta 200, FEI Co. USA. The images were recorded under a high

vacuum using a standard Everhart-Thornley detector at a voltage of 25 kV. The software analySIS Docu (Soft Imaging System Co.) was used to process the images.

#### Rheology measurements

A Brookfield rheometer R/S-CPS+ with Rheo3000 V1.2 software (USA) was used to assess the shear viscosity of the cellulose-(water)-IL solutions. For the steady shear experiments, the cone/plate geometry (radius of the metering cone R = 12.5 mm, inclination angle  $\alpha = 1^\circ$ ) was chosen. Measurements were conducted at temperatures of 50, 70 and 90 °C, with an accuracy of 0.1 °C.

A typical analysis sequence comprised 3 phases: I: linear increase in the shear rate from 1 to 100 s<sup>-1</sup>, II: constant rate of 100 s<sup>-1</sup>, III: linear decrease from 100 to 1 s<sup>-1</sup>.

The Carreau-Yasudy [23, 24] model was used to calculate the zero shear viscosity:

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\eta_0 - \eta_{\infty}) \left[ 1 + (\dot{\gamma}\lambda)^a \right]^{\frac{n-1}{a}}$$

with:  $\eta_0$  - zero shear viscosity (low Newtonian viscosity),  $\eta_{\infty}$  - upper Newtonian viscosity,  $n$ ,  $\alpha$ ,  $\lambda$  - material constants, - shear rate.

Typically  $\eta_{\infty}$  of polymer solutions is non-significant ( $\eta_{\infty} \approx 0$ ) and the equation reduces to a 4-parameter equation.

#### Mechanical properties of the cellulose films

The mechanical properties of the cellulose films were assessed using an Instron 5544 (USA) tensile tester in accordance with Standards PN-ISO 4593:1999 and 93:1999 PN-EN ISO 527-3:1998 at a relative humidity of  $64 \pm 4\%$  and temperature of  $20 \pm 2$  °C.

Film samples of  $50 \times 15$  mm size were stretched at a rate of 10 mm/min and 1 mm/min, respectively, to determine the tensile strength and elasticity modulus.

#### Molecular mass distribution of cellulose

The molecular mass distribution (MMD) was determined by gel permeation chromatography (GPC/SEC). The function of mass distribution (MMD), average molecular mass ( $\bar{M}_n$ ,  $\bar{M}_w$ ) and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) were determined as described elsewhere [25]. The results were calculated by the universal calibra-

tion method: a and K parameters in the Mark-Houwink equation took the following values:  $a = 0.65$ ,  $K = 17.3 \times 10^{-3}$  ml/g for the PEO/PEG standards, and  $a = 1.0$ ,  $K = 12.78 \times 10^{-3}$  ml/g for cellulose [1, 26, 27].

### Polymerization degree in the cellulose film

The degree of polymerization of the cellulose films was determined according to the ISO 5351:2010 standard.

### FT-IR spectra of cellulose films

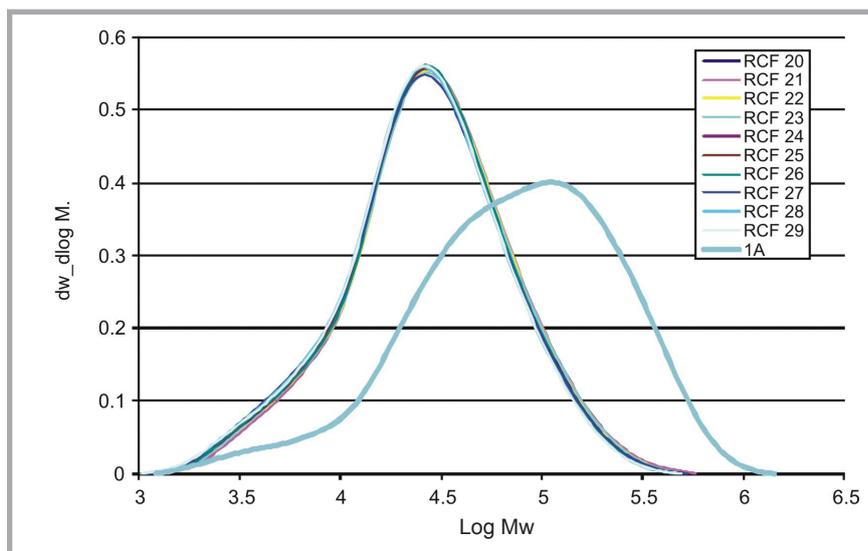
The spectrophotometric IR spectrum was recorded using a Genesis Series FTIR™, Unicam Co (USA), equipped with the specialized software WinFIRST of ATI Mattson Co, USA, with a reading accuracy of  $\pm 1$  cm<sup>-1</sup>. Tablets with 1 mg of the material tested in 300 mg of KBr were prepared. Operational parameters of the device: measurement range: 4000 - 500 cm<sup>-1</sup>, resolution: 4.0, number of scans collected for background and samples: 16.

## Results and discussion

### GPC examination of cellulose throughout the process

The effect of hydrothermal treatment on the MMD is shown in **Figure 1** and **Table 2**. The decrease in DP is reflected by a shift of the HT cellulose MMD towards lower molecular mass values. Also a slight decrease in the polydispersity index from 3.7 to 3.1 is observed. This is due to the removal of low molecular mass compounds which are probably degraded to soluble carbohydrate oligomers.

**Figure 1** also shows the degradation occurring during dissolution and casting. All film samples show a slight reduction in cellulose DP and polydispersity. Despite the general overlap of the MMD curves, there is a clear difference arising from the preparation procedure. In par-



**Figure 1.** Molecular mass distribution of PHK and HT cellulose film.

**Table 2.** Characteristics of molecular mass distribution of PHK cellulose and HT cellulose.

Parameter	Symbol of PHK cellulose	
	1 A commercial	1 A HT
Mn, kDa	35.20	33.21
Mw, kDa	130.20	103.27
Polydispersity PDI (Mw/Mn)	3.7	3.1
DP	804	628

ticular, the storage of the solution at an elevated temperature influences the molecular mass, as shown in **Table 3**, where series I, II, and III correspond to different deaeration times. The Mw averages decrease to 42.0, 40.0 and 39.0 kDa in series I, II and III, respectively. The effects of the thermal impact on cellulose dissolved in ionic liquids have been investigated in detail earlier and are in accordance with the results presented herein [13].

Moist (never-dried) film samples with different water contents of 1.0, 10 and 88% were prepared to examine the influence of water in the cellulose films on the results of the MMD analysis. The results presented in **Table 4** confirm that water had no significant influence, as all three

samples showed a consistent average molecular mass and PDI values.

### Microscopic analysis of the solutions prepared for film casting

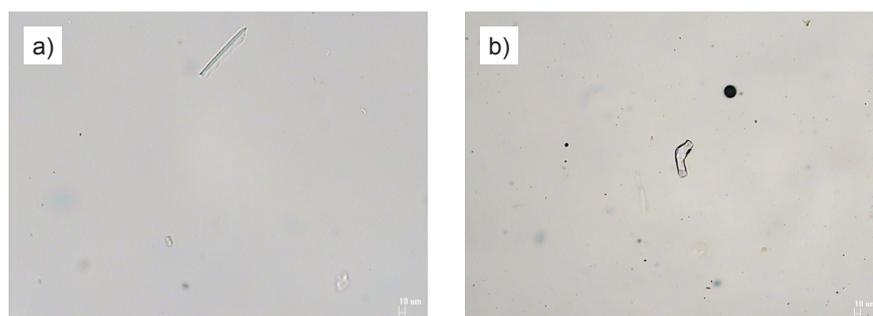
HT cellulose samples with different water contents of 2, 7, 14 and 21 wt% were dissolved in [emim]OAc to prepare a first series of the solutions with a total cellulose concentration of 8 wt%. Regardless of the water content, all cellulose samples dissolved quickly and completely, and the subsequent deaeration proceeded without problems (**Figure 2**). The solutions were then assessed by optical microscopy. No undissolved cellulose fibres were visible in the solution. By increasing the cellulose concentration, tiny particles with a diameter below 0.01 mm emerged in the

**Table 3.** MMD characteristics of cast cellulose films.

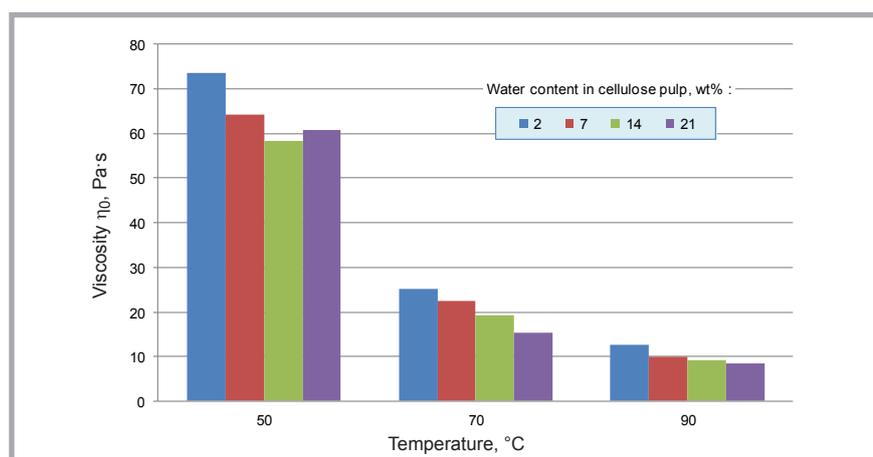
Parameter	Symbol of cellulose film									
	RCF 20	RCF 21	RCF 22	RCF 23	RCF 24	RCF 25	RCF 26	RCF 27	RCF 28	RCF 29
	Serie I			Serie II				Serie III		
Mp, kDa	27.06	27.50	27.50	26.85	26.21	26.39	26.71	26.21	25.74	26.06
Mn, kDa	16.92	17.70	17.10	17.07	16.51	16.67	16.70	15.99	15.82	15.83
Mw, kDa	41.56	43.39	42.22	42.25	40.24	40.51	40.51	40.44	39.01	39.09
Mz, kDa	88.24	95.52	89.85	90.21	84.86	84.88	84.33	87.15	81.32	81.66
M <sub>z+1</sub> , kDa	155.14	174.40	156.02	156.79	147.04	145.98	145.40	152.84	139.38	141.41
Mv, kDa	41.56	43.39	42.22	42.25	40.24	40.51	40.51	40.44	39.01	39.09
Polydispersity PDI (Mw/Mn)	2.46	2.45	2.47	2.48	2.44	2.43	2.43	2.53	2.47	2.47

**Table 4.** Molecular mass distribution properties of cellulose films with different moisture content.

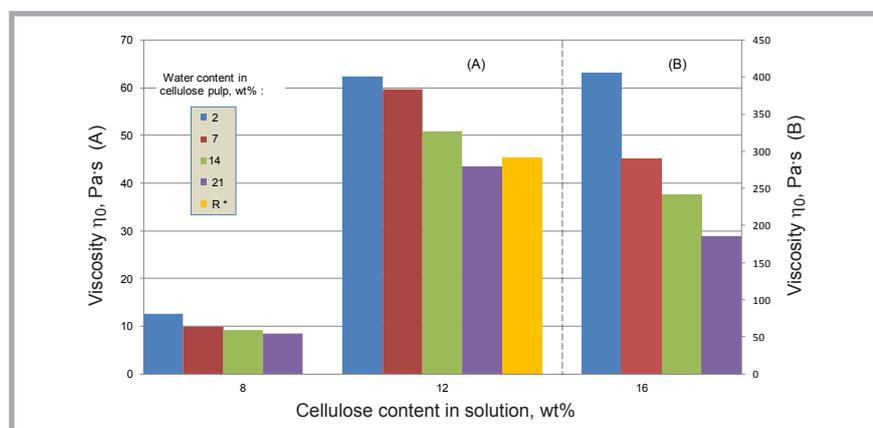
Parameter \ Moisture, wt%	88.0	10.0	1.0
Mp, kDa	26.56	26.56	26.85
Mn, kDa	16.59	16.41	17.07
Mw, kDa	41.72	41.77	42.25
Mz, kDa	90.70	92.52	90.21
M <sub>z+1</sub> , kDa	161.50	169.65	156.79
Mv, kDa	41.73	41.77	42.25
Polydispersity PDI (Mw/Mn)	2.52	2.55	2.48



**Figure 2.** Microscopic images of cellulose-[emim]OAc solutions 15 minutes after dissolution: a) cellulose concentration 12 wt%, water content in cellulose 21%, b) cellulose concentration 16 wt%, water content in cellulose 21%.



**Figure 3.** Impact of temperature and water content in HT cellulose on the zero shear viscosity  $\eta_0$  of the RCF solutions with 8 wt% cellulose concentration.



**Figure 4.** Impact of water content in the RCF solution on the zero shear viscosity  $\eta_0$ . Cellulose content in the solution: 8, 12, 16 wt%, at 90 °C. R\* - a recovered IL was used for dissolution (water content in the solvent - 9 wt%, moisture of cellulose - 7%).

solutions. These are probably process-related pulp impurities. The solutions were not filtered prior to film casting.

In the second series, solutions with a cellulose concentration of 12 wt% were prepared following the same protocol but with the deaeration time extended to one day. No undissolved cellulose fibres were visible in the solution.

In the third series, solutions with a cellulose concentration of 16 wt% were prepared following the same protocol but with the deaeration time extended to one day. The prolonged thermal impact had a clear effect on the colour of the solutions, which showed intensive hues. The amount of undissolved cellulose particles in series III solutions was higher than in the preceding ones.

#### Impact of water on the viscosity of the HT cellulose-[emim]OAc solution

Figure 3 illustrates the impact of temperature and residual water content in the HT cellulose on the zero shear viscosity  $\eta_0$  of the respective RCF solutions with 8 wt% cellulose concentration. An increase in the solution temperature from 50 to 90 °C causes a noticeable 6-fold drop of  $\eta_0$  (Figure 3). Generally in all series at constant temperature, a decrease of  $\eta_0$  is observed as the cellulose water content increases. This general trend was observed for the entire concentration range from 8 to 16 wt% studied herein (Table 5, Figure 4). An exception was observed at 50 °C and 21 wt% of the residual water content, where a small increase in  $\eta_0$  was recorded. This could be attributed to incipient gel formation.

The method of hysteresis loop was employed in the rheological investigations. The hysteresis loop is not equivalent to the phenomenon of thixotropy since it may emerge also in the course of examining viscoelastic materials [28, 29]. Descriptions can be found in technical literature concerning the viscoelastic properties of cellulose/IL systems. The method commonly employed in the examination of viscoelastic properties consists in dynamic oscillation shearing. Both thixotropy and viscoelasticity feature the time-instability of a substance. Measurements of the surface ( $S_H$ ) of the hysteresis loop of the flow curves of the HT cellulose-[emim]OAc solutions were used to characterize the instability.

**Table 5.** Parameters determined with the 4-parametric Carreau-Yasuda equation and surface of hysteresis loop  $S_H$ . \*) – recovered [emim]OAc.

Symbol of sample	Cellulose concentration, wt%	Water content in cellulose, wt%	Water content in solution, wt%	Temp., °C	Computed parameters in Carreau-Yasuda equation					Surface of hysteresis loop $S_H$ , Pa·s <sup>-1</sup>
					$\eta_0$ Pa·s	$\lambda$ s	a	n	R <sup>2</sup>	
RCF 20	8 (series I)	7	0.56	50	64.34	0.07	1.09	0.49	0.9997	6,953
		7	0.56	70	22.39	0.06	2.10	0.70	0.9988	2,096
		7	0.56	90	9.85	0.03	1.73	0.73	0.9846	759
RCF 21		14	1.12	50	58.29	0.07	1.01	0.52	0.9998	5,797
		14	1.12	70	19.18	0.05	2.49	0.71	0.9980	1,626
		14	1.12	90	9.18	0.04	2.01	0.78	0.9975	402
RCF 22		21	1.68	50	60.71	0.07	0.82	0.49	0.9999	5,273
		21	1.68	70	15.41	0.05	2.75	0.74	0.9987	960
		21	1.68	90	8.49	0.03	1.50	0.73	0.9887	236
RCF 23	2	0.16	50	73.51	0.07	0.81	0.44	0.9999	7,942	
	2	0.16	70	25.22	0.04	1.55	0.61	0.9985	2,627	
	2	0.16	90	12.68	0.03	1.36	0.69	0.9958	867	
RCF 24	12 (series II)	7	0.84	70	158.45	0.02	0.70	0.00	0.9984	100,836
		7	0.84	90	59.69	0.04	1.04	0.52	0.9988	6,120
RCF 25		14	1.68	70	134.50	0.02	0.76	0.12	0.9976	41,959
		14	1.68	90	50.92	0.06	1.60	0.64	0.9980	3,288
RCF 26		21	2.52	70	107.33	0.03	0.91	0.25	0.9982	33,740
		21	2.52	90	43.49	0.06	1.46	0.67	0.9965	1,214
RCF 27		2	0.24	90	62.32	0.04	1.31	0.51	0.9881	7,509
RCF 28		7	1.12	90	289.89	0.04	0.96	0.00	0.9946	185,465
RCF 29		14	2.24	90	241.19	0.04	1.11	0.00	0.9935	151,557
RCF 30		21	3.36	90	185.02	0.03	0.89	0.00	0.9956	123,521
RCF 31		2	0.32	90	406.09	0.06	1.26	0.00	0.9886	275,269
RCF 24 *)		12	7	8.74	90	45.51	0.06	1.25	0.66	0.9988

A three-parameters Carreau equation is mostly employed to compute  $\eta_0$ . It is derived from *Equation 1* assuming that  $\eta_{\infty} = 0$  and  $\alpha = 2$  [21]. The prime disadvantage of this and many other rheological models is that the fit is rather poor at low shear rates in the transition zone between the Newtonian- and power-law regime [21]. The Carreau-Yasuda model was developed to overcome this problem. Values calculated from the 3-parameter Carreau equation are typically lower in comparison to those computed from the Carreau-Yasuda equation. The high R<sup>2</sup> values (*Table 5*) indicate that the model equation fits well with the experimental data. Material constant  $n$  equals zero for highly viscous cellulose solutions with a concentration of 16 wt%.

The influence of the water content in the cellulose pulp on the zero shear viscosity  $\eta_0$  of RCF solutions with different cellulose concentrations of 8, 12, 14 and 16 wt% at 90 °C is shown in *Figure 4*. HT cellulose samples were prepared with water contents of 2, 7, 14 and 21 wt%. Evidently the amount of water in the system increases as the cellulose concentration rises. In the HT cellulose/IL solutions with a cellulose concentration of 8, 12 and 16 wt%, the amount of water in the resulting solution was 0.16 - 1.68, 0.24 - 2.52

and 0.32 - 3.36 wt%, respectively. For all cellulose/IL solutions (concentration: 8 - 16%, solution water content 0.16 - 3.36 wt%) the same trend was observed: an increase in the moisture in the cellulose used for the preparation of the IL solutions caused a decrease of  $\eta_0$ . This is in accordance with literature reports concerning the investigated range of water introduced to the solution [15]. Water contained in the solvent affects the dissolution. With native [emim]OAc, the dissolution is rapid and homogeneous without any swelling of heterogeneous elemental cellulose fibres.

*Table 5* shows that with an increase in  $\eta_0$ , the surface  $S_H$  of the hysteresis loop grows, which is particularly distinct in the cellulose solution series with 16 wt% concentration of high  $\eta_0$  viscosities in the range of 180 - 400 Pa·s. When the cellulose concentration in the solution rose from 12 to 16 wt% at 90 °C and given the water content,  $\eta_0$  increased by 4.3 to 6.5 times and the surface of the hysteresis loop was 30 to 100 times larger. The enormous increase in the hysteresis loop surface, indicating general time-dependent rheological instability, may have been caused by the observed augmentation of viscoelastic features of the solutions with acellulose concentration of 16 wt% in

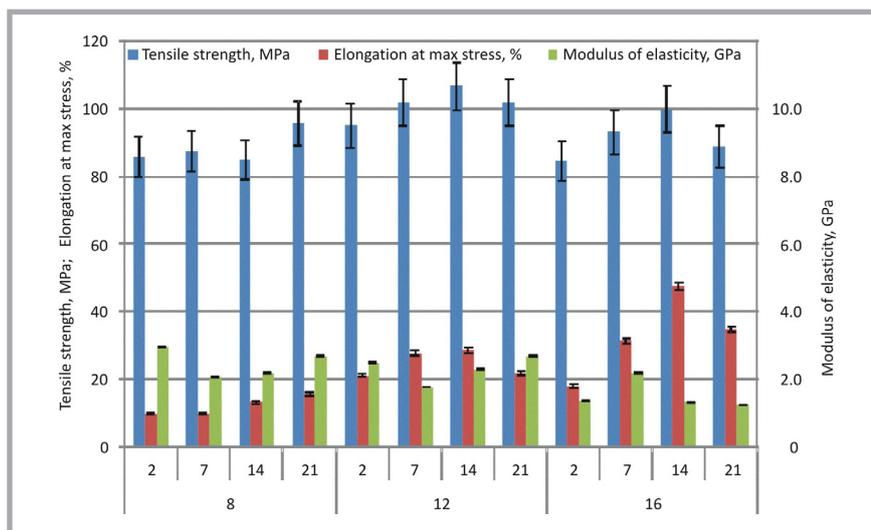
[emim]OAc. This is in accordance with a previous report [30].

The solution marked RCF 24\* was prepared using recovered [emim]OAc with a 9% residual water content and HT cellulose with a water content of 7% which resulted in a total water content of 8.68% (*Table 5*) in the solution. In comparison to the reference solution RCF 24 made from native IL, the resultant  $\eta_0$  viscosity was lower, which is in accordance with other results concerning the impact of water on the viscosity of the [emim]OAc solutions. The  $\eta_0$  viscosity values in solutions RCF 24\* and RCF 26 (*Table 5*) are close to each other, in which the water content in the solutions amounted to 8.68% and 2.52%, respectively.

#### Impact of water in the HT cellulose-[emim]OAc solution on the mechanical properties of the film

The influence of residual water introduced to the solution via cellulose on the mechanical properties of the resulting films is shown in *Figure 5*.

Cellulose films with a tensile strength of 87 - 106.5 MPa and elongation to break of 10 - 50% could be prepared from HT cellulose/IL/water solutions by coagula-



**Figure 5.** Impact of water content in the HT cellulose-[emim]OAc solution on the mechanical properties of the respective films. Concentration of cellulose in the solution: 8, 12 and 16 wt%.

**Table 6.** Impact of water in the film upon DP standard dissolving conditions; \*- film dried to 2% moisture, then immersed in water for 24 hours and dried again.

Symbol of cellulose film	Cellulose concentration in solutions, wt%	Moisture of cellulose film, %	Dissolving in CED, ISO 5351	Viscosity, ml/g	DP	
RCF 20	8 (series I)	87	yes	193	245	
		1.5	yes/no	nd	nd	
		1.8	no	nd	nd	
		10	yes	193	245	
		22*	no*	nd	nd	
		46			197	250
		72			199	253
		86			197	250
RCF 22			80		182	230
RCF 23			75		182	230
ECF 24	12 (series II)	60	yes	177	223	
RCF 25		50		182	230	
RCF 26		70		186	235	
RCF 27		72		186	235	
RCF 28		77		186	235	
RCF 29	16 (series III)	60		179	225	
RCF 30		53		190	240	
RCF 31		50		188	238	

tion in an EtOH/water mixture (80/20). The cellulose concentration in the solution shows an influence on the elongation of the film prepared. An increase in elongation was observed as the cellulose concentration became higher, which may be related to small amounts of residual IL acting as a plasticizer in the film because the washing was less efficient. The highest elongation of 50% was found in films made from a solution with a cellulose concentration of 16 wt% and cellulose water content of 14%. The highest tensile strength was found in films cast from solutions with 12 wt% cellulose and cellulose water content of 14%, while lowest tensile strength appeared when the

cellulose water content was 2% (series I and II). The increase in cellulose concentration in the solution to 16 wt% led to an increase in viscosity, which necessitated the extension of the deaeration-annealing time. This caused a decrease in the cellulose molecular mass and, consequently, a drop in the film tensile strength. Moreover the casting of film from the high viscosity solutions results in a thicker film. In the films (series III) a differentiation of the tensile strength can be seen in dependence on the amount of water in the cellulose (relationship similar to series II). The moisture of the cellulose undoubtedly exerts an influence upon the film's mechanical properties.

### Assessment of the degree of polymerization DP in the film

The DP of the coagulated cellulose was estimated by measuring the intrinsic viscosity, which provides quick access to the average DP.

It was found that the final cellulose films with moisture below 10% do not dissolve in CED. On the other hand the dissolution proceeds with undried films and those with moisture above 10%. Thus it was necessary to use never-dried films to assess the DP of the films. Films with low moisture and those dried to 2% and next immersed in water for 24 h are insoluble in CED. This phenomenon is associated with the hornification of cellulose [31]. It was shown previously that residual water did not influence the intrinsic viscosity measurement. The results of the measurements are summarized in **Table 6**.

### FT-IR spectra of cellulose films

FT-IR spectra for cellulose films formed from solutions with various water concentrations are presented in **Figure 6**. There are substantial differences of absorbance at various wavelengths, for example at 900  $\text{cm}^{-1}$ , which responds to the amorphous cellulose structure. Changes can be seen in the range of 1100 to 1500  $\text{cm}^{-1}$ , but only 1300 - 1500  $\text{cm}^{-1}$  can be used for interpretation of structural changes of cellulose [32]. Changes in intensities are observed for bonds 1448 and 1376  $\text{cm}^{-1}$ . At around 1625  $\text{cm}^{-1}$ , due to the bending motions of water molecules, as seen in **Figure 6**. Some changes in the intensities of bonds in the 3200 - 3500  $\text{cm}^{-1}$  region are observed. This broad band contains information about inter and intramolecular hydrogen bonds.

### Impact of drying conditions on film transparency

Films cast from HT cellulose-[emim]OAc solutions are partially opalescent when wet, and get transparent during drying. The films were dried by spreading on a polished steel sheet heated up to 50  $^{\circ}\text{C}$ . It was observed that opaque regions appeared on the film where it did not adhere evenly to the heating surface. Such spots turned white and opaque in contrast to the remaining transparent film surface. Air bubbles emerged in spots where steam accumulated, supposedly causing the opalescence. **Figure 7** presents SEM images of the cellulose films during drying.

At 100× magnification a round surface (opaque) is seen on the film. Morphological differences on the film surface are better discernible at 1000× magnification, showing an opaque fragment, less uniform and somewhat water-etched. Light penetrating the surface is refracted or dissipated, giving the opalescence effect. Thus the transparency of the final films can be tuned by adjusting the drying conditions.

### Impact of cellulose concentration in the solution on film morphology

The films prepared from different solutions are characterized by good uniformity of thickness, surface smoothness, tenacity and elongation. At 10,000× magnification, SEM images reveal scarce tiny objects on the film surface, mainly in the sample marked RCF 24 (Series II), while in another sample no such objects appear; but a surface texture can be observed (Figure 8).

A uniform thickness is observed in the cross-sections of the films from series III. On the other hand, micro-ruptures appear in the cross-sections, probably caused by the film forming conditions employed.

Films from series III are smooth, uniform and thicker than those from the preceding series. They also show the highest elongation - up to 50%.

Films made from a solution of HT cellulose with a 12 wt% concentration and DP of 440 are characterized by the highest tensile strength of 106.5 MPa.

### Conclusions

The study presented in this article focused on the role of water in cellulose solutions prepared for film casting. Prior to dissolution, the pulp cellulose was subjected to hydrothermal treatment (HT). This pre-treated cellulose shows enhanced

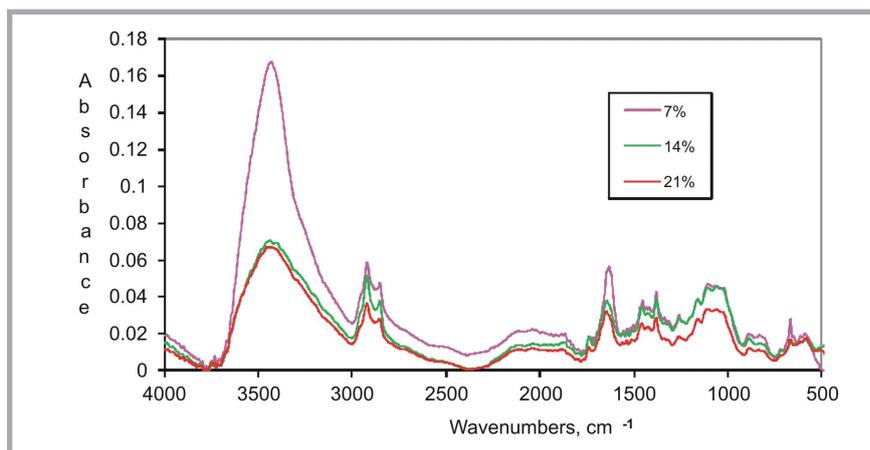


Figure 6. FT-IR spectra of cellulose film made from solutions with 16 wt% of the total HT cellulose content and cellulose water content of 7, 14 and 21%.

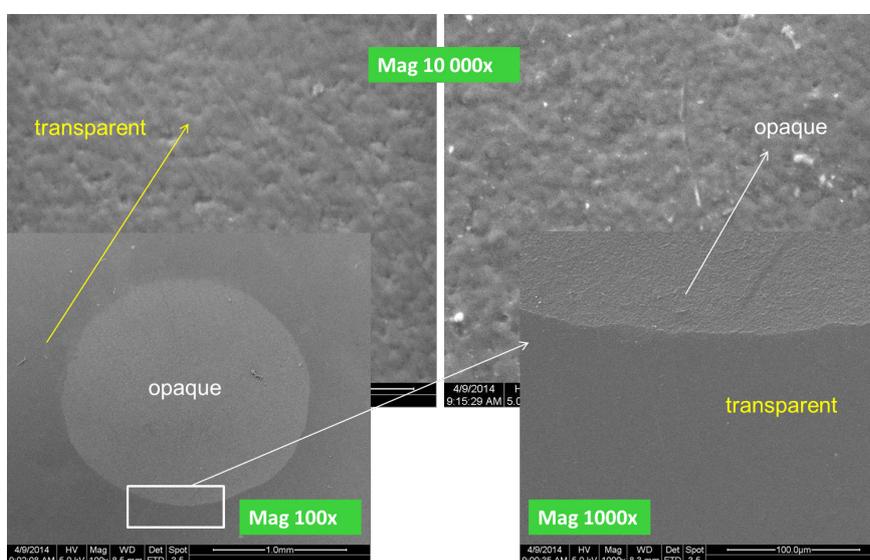


Figure 7. SEM of film surface cast from HT cellulose-[emim]OAc solution.

performance in preparing films than regular untreated material. The presence of water in cellulose-IL solutions is, in practice, unavoidable. Commercial ionic liquid (IL) used in the experiments might contain only small, insignificant amounts of water, but IL recovered from the process for reuse may hold some inherent moisture. The prime source of water that enters into the system is cellulose. Com-

mercial pulps and intermediate cellulose materials on an industrial scale always contain water and the use of a perfectly dewatered material is unimaginable. It appeared that a certain amount of water in the solution for casting does not impede the process of preparing cellulose solutions. However, the water does have an impact on the mechanical properties of the film prepared. It appeared that

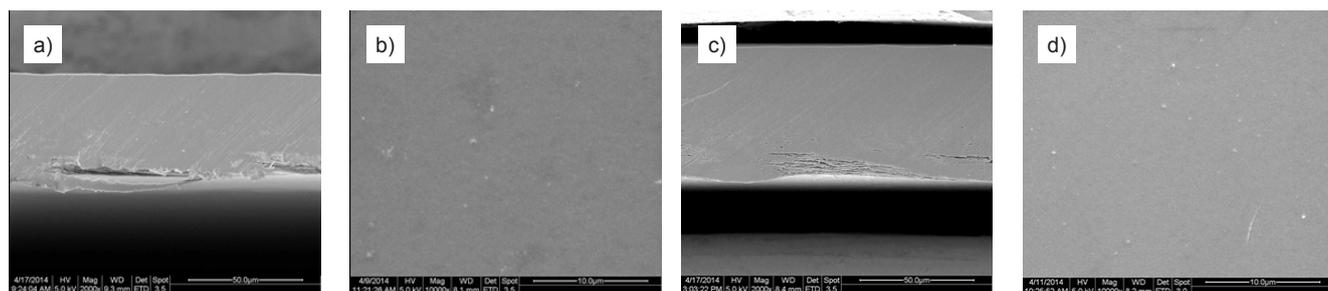


Figure 8. SEM: a) RCF 24 (Series II) cross-section, b) RCF 24 (Series II) surface, c) RCF 31 (Series III) cross-section, d) RCF 31 (Series III) surface.

the best results for mechanical strength parameters such as tensile strength and elongation can be achieved with a small amount of water in the solutions prepared for casting.

Enumerated below are detailed conclusions.

1. The increase in cellulose water content from 2 to 21% used for preparation of solutions with cellulose concentrations of 8, 12 and 16 wt% in [emim]OAc results in a drop in the zero shear viscosity  $\eta_0$ .
2. The Increase in cellulose water content from 2 to 21% used for preparation of solutions with cellulose concentrations of 8, 12 and 16 wt% in [emim]OAc causes a change in the mechanical properties of the film prepared. Films with highest tensile strength and elongation were made from cellulose with a 7 and 14% water content.
3. Films with the highest tensile strength of 106.5 MPa were prepared from solutions at 12 wt% concentration of cellulose. The cellulose water content was 14%.
4. Films with the highest elongation of 50% were prepared from solutions at 16 wt% cellulose concentration. The cellulose water content was 14%.
5. Cellulose films never-dried and such of moisture above 10% cast from ILs are soluble in CED, whereas those of moisture below 10%, as well as those next re-wetted are not soluble in CED.
6. Drying conditions showed an impact upon the uniformity of the film surface and its transparency.



## Acknowledgments

We would like to express our gratitude to the Wood Wisdom-Net Research Programme and ERA-NET Bioenergy, Formas, Akzo Nobel, Andritz, Metsä Fibre, Organo Click, Solvay Rhodia, SP Processum, and Stora-Enso for their financial support.

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Received 24.04.2013 Reviewed 22.05.2015