

DOI: 10.1002/macp.((insert number))

Full Paper

Dissolution capacity of novel cellulose solvents based on triethyloctylammonium chloride

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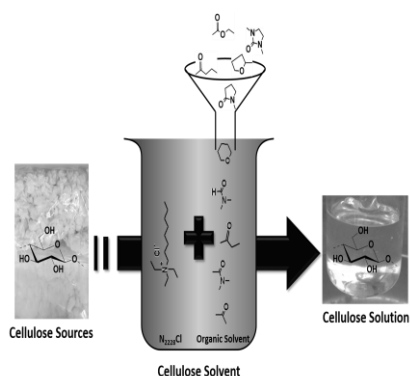
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Dissolution of cellulose from various sources (microcrystalline cellulose and different dissolving grade pulp fibers) is investigated in solvent systems based on triethyl(n-octyl)ammonium chloride (N₂₂₂₈Cl). Clear cellulose solutions are obtained with N₂₂₂₈Cl in a variety of solvents, e.g., dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc) and acetone. It is possible to prepare clear cellulose solutions from pulp fibers with concentrations up to 15 wt%. However, it is found that the cellulose is degraded, especially when neat (i.e., molten) N₂₂₂₈Cl is used as solvent. The present work includes comprehensive rheological characterization of the cellulose solutions, both with shear- and extensional rheology. In most cases, the viscosity values are low (complex viscosities below 100 Pas for 5-

10 wt% dissolved cellulose), and the solutions show more Newtonian- than viscoelastic behavior.



1. Introduction

The unique properties of cellulose make it useful for a variety of applications and products, e.g., paper, board, textiles, and nonwoven fabrics. Moreover, derivatives of cellulose play an important role in a broad range of industrial applications.^[1] However, the processing of cellulose is challenging since the biopolymer does not dissolve in water or in common organic solvents. Dissolution of (semi-crystalline) cellulose requires that the solvent disrupts the relatively strong inter- and intramolecular hydrogen bonds within its structure, as well as the interactions between the hydrophobic faces of its anhydroglucose units (AGU).^[2-6] Different solvents for cellulose can be categorized into derivatizing or non-derivatizing solvents, depending on the change of the molecular structure of the polysaccharide.^[7-9] Non-derivatizing solvents such as *N,N*-dimethylacetamide (DMAc) in combination with lithium chloride, as well as recently proposed ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BMIMCl) or 1-ethyl-3-methylimidazolium acetate (EMIMAc), are commonly used for homogeneous derivatization of cellulose.^[10-12] For processing of cellulose into fibers, the non-derivatizing solvent *N*-methylmorpholine-*N*-oxide (NMMO) is prominent and has reached commercial success, i.e., the Lyocell process.^[13, 14] However, a limitation of this solvent is its thermal instability.^[15] Further investigations into dissolution and shaping of cellulose are currently

ongoing in order to develop the next generation of efficient cellulose solvents. Noteworthy examples include fiber spinning of cellulose from solvents such as aqueous alkali in combination with urea^[16], and thiourea^[17] or novel ionic liquids.^[18]

An interesting class of new solvents of cellulose is based on alkylammonium electrolytes. Alkylammonium fluorides, such as tetra(n-butyl)ammonium fluoride trihydrate, TBAF*3H₂O, in combination with dimethyl sulfoxide (DMSO), has been established as media for homogeneous derivatization of cellulose.^[19] Recently, it has also been shown that the electrolyte triethyl(n-octyl)ammonium chloride (N₂₂₂₈Cl) has an exceptional ability to dissolve cellulose.^[20] The fact that its solution in acetone dissolves cellulose is relevant, because this ketone is normally used as a cellulose precipitation agent.^[21] Additionally, solutions of this electrolyte in acetone or DMAc were recently employed as reaction media for cellulose derivatization.^[22]

The aim of the current study was to investigate the dissolution of cellulose in a system consisting of N₂₂₂₈Cl together with a variety of different organic solvents, including DMSO or DMAc. The long-term goal is to obtain solutions that can be used for cellulose processing, such as fiber spinning or solution blowing into nonwoven materials. Different cellulose sources were investigated with varying average degrees of polymerization (DP). Moreover, the concentration of cellulose in the solutions was varied. The effect of the dissolution was controlled visually by cross-polarized microscopy, an extensively employed method for controlling the state of dissolution in cellulose chemistry.^[23-25] The resulting biopolymer solutions were characterized with regard to both shear- and elongational viscosity. In addition, cellulose degradation during the dissolution was studied as a function of dissolution time and temperature.

2. Experimental Section

2.1. Material

Microcrystalline cellulose (MCC, Avicel PH-101, Fluka, DP_v (ISO-5351) = 135) was used for lab-scale dissolution studies with various organic solvents. Additionally, three different types of dissolving grade pulps were investigated. A Buckeye pulp (**P1**) with a reduced DP (acid hydrolysis, final average $DP_v = 288$), a “Purple grade” pulp achieved through a pre-hydrolysis kraft process received from Södra ($DP_v = 534$, **P2**), and a dissolving grade Domsjö sulfite pulp ($DP_v = 582$, **P3**). Bacterial cellulose was obtained from fzmb GmbH, Bad Langensalza, Germany (average DP = 6500). The cellulose was dried at 100°C for 2 h prior to use. triethyl(n-octyl)ammonium chloride ($N_{2228}Cl$) was purchased from Orgentis Chemicals (m.p. 81°C) and was dried at 60°C over potassium hydroxide for 2 h prior to use. Acetone (VWR), 2-butanone (VWR), 3-pentanone (Sigma Aldrich), benzonitrile (Sigma Aldrich), tetrahydropyran 99% (Acros), 2-methyltetrahydrofuran >99% (Acros), acetonitrile (VWR), tetramethylurea (TCI), 1,3-dimethyl-2-imidazolidinone 98% (Acros), dimethylpropylenurea (Sigma Aldrich), *N*-methylpyrrole >99% (Acros), *tert*-butyl methyl ether (VWR), sulfolane (VWR), *N,N*-diethylacetamide 99% (Alfa Aesaer), *N,N*-diethylformamide 99% (Acros), *N*-methylpyrrolidone 99% (Acros), *N,N*-dimethylformamide 99.8% (Acros) DMAc 99.5% (Acros) and DMSO >99.7% (Acros) were used as received.

2.2. Methods

2.2.1. Preparation of Cellulose Solutions

Cellulose dissolution in $N_{2228}Cl$ applying DMSO or DMAc as co-solvent (**S1**)

Depending on the required concentrations, dry cellulose (**MCC**, **P1**, **P2** and **P3**) and $N_{2228}Cl$ were weighed into a glass reactor provided with a mechanical stirrer. The mixture was heated to 120°C, with manual mixing to achieve a good mixing of the polymer and the electrolyte. After melting of $N_{2228}Cl$, the stirrer was turned on and the mixture was stirred for 1 h at 120°C. Subsequently, the mixture was allowed to cool slowly. During the cooling process, the

corresponding volume of DMSO or DMAc was added to the clear melt. The obtained clear solutions were used for further investigations.

Cellulose dissolution in N₂₂₂₈Cl/organic solvent applied as a binary solvent mixture (S2)

Dry cellulose (MCC or **P1**), N₂₂₂₈Cl and a chosen organic solvent (1,3-dimethyl-2-imidazolidinone, (DMI), *N,N*-dimethylformamide, (DMF), *N*-methylpyrrolidone, (NMP), sulfolane, 1-methylimidazole, *N,N*-dimethylpropyleneurea, benzonitrile, *N*-methylpyrrole, tetramethylurea, *N,N*-diethylformamide, *N,N*-diethylacetamide, DMSO, or DMAc), were mixed together in the required amounts prior to the dissolution process. To achieve a clear cellulose solution, the mixture was stirred for 2 h at 60°C, and then left at room temperature overnight under stirring. In the same manner, the ¹³C-NMR sample was prepared employing acetone-*d*₆.

MCC dissolution with N₂₂₂₈Cl and volatile organic solvents (S3)

For volatile organic solvents, the cellulose solution was prepared by adding cellulose, N₂₂₂₈Cl and the organic solvent together at the beginning of the dissolution procedure and heating it to 85°C for 2 h. In order to achieve a clear cellulose solution, it was necessary to remove a part of the organic solvent, leading to increase of the electrolyte concentration in the mixture. Once a clear solution was observed, the temperature was decreased and the previous removed solvent was added back to the solution, thus achieving a clear cellulose solution with the desired concentration. Depending on the chosen solvent, different temperatures for distillation were employed (see “distillation temperatures” in **Table 1**). In the same manner, the ¹³C-NMR sample was prepared employing acetone-*d*₆.

Dissolution of cellulose in pure N₂₂₂₈Cl using laboratory-scale kneader

Two experiments were performed. In the first, a 15 wt% cellulose solution of **P1** was prepared. The pulp (36 g) was suspended in water (194 g) and subsequently N₂₂₂₈Cl (195.5 g) was added to yield N₂₂₂₈Cl/H₂O, 50/50, mass basis. The pulp suspension was placed in the kneader (Haake, Rheocord 90) and the dissolution process was carried out by water removal under constant shear

and reduced pressure (91 → 115°C mass temperature, 750 → 10 mbar, 5 → 10 rpm). After a total evaporation time of 70 min, the cellulose solution in N₂₂₂₈Cl still contained fiber fragments. An increase of the temperature to 125°C for few minutes led to a strong decrease in torque moment. The temperature was then reduced to 118°C, and an after-dissolution time followed (60 min, 118°C, 10 mbar, 10 rpm).

For the second experiment, a 15 wt% cellulose solution of **P2** was prepared in pure N₂₂₂₈Cl, with an additional adjustment of the pH-value. A pulp suspension was prepared as given above, followed by addition of the electrolyte to give N₂₂₂₈Cl/H₂O, 50/50, mass basis, and the pH-level of the suspension was adjusted to 10.5 with 10% NaOH aqueous solution. After carrying out the dissolution as given above (70 minutes; water removal 98 → 115°C, 750 → 10 mbar, 5 → 10 rpm), the temperature was increased to 125°C during 10 minutes, and then reduced to 118°C, followed by an after-dissolution step (60 min, 118°C, 10 mbar, 10 rpm).

2.2.2. Characterization of Cellulose Solutions

All prepared solutions (N₂₂₂₈Cl/ organic solvent) were controlled visually by placing samples of the solutions between cross-polarized glass plates and examine them for the presence of undissolved fragments in an optical microscope (Carl Zeiss, Axioskop 40).

Prior to capillary breakup extensional rheometry (CaBER) measurements, the air/solution surface tensions and the densities of the solutions were measured. Surface tensions were measured on a Krüss tensiometer at 25°C and the values were taken after 1800 sec applying Du Noüy ring method. The densities of the solutions were measured by using a glass pycnometer (2 mL) at 23°C.

¹³C-NMR measurements were performed on a Bruker Avance 250 MHz at room temperature with 10240 scans applying 120 mg sample per mL solvent.

2.2.3. Rheological Characterization

Initial shear rheology measurements of cellulose solutions in N₂₂₂₈Cl/DMSO (molar ratio; 1/3.2) were performed with a plate-plate Haake Mars II rheometer. Viscosity was plotted as a function of shear rate for various temperatures. A small amount of low-viscosity paraffin oil was added around the solutions for sample protection prior to the measurements.

More extensive shear rheological characterization (applying 5 wt%-solutions), were carried out with rotation rheometer “Haake Rheostress 100” using cylinder double slit measuring equipment (DG41) in oscillation mode (frequency sweep) at 25, 40 and 60°C. For the samples of higher cellulose concentration, the measurements were carried out with a Haake Mars rotation rheometer using a cone-plate measuring equipment C60/4° in oscillation mode at three different temperatures; 25, 40 and 60°C. The following calculations of the master curves and weighted relaxation time spectra were done at a reference temperature of 25°C. For the 15 wt% cellulose solutions prepared in the lab-scale kneader, the rheological characterization of the solutions was also performed with rotation rheometer (Haake Mars). For the **P1** sample, a cone-plate measuring equipment (C60/4°) in oscillation mode (frequency sweep) at 75, 85 and 95°C was used, and for the **P2** sample (with pH-level adjustment) a plate-plate measuring equipment (PP60, 1 mm gap) in oscillation mode at 95, 85, 110 and 125°C was used. The solids contents of the solutions were determined gravimetrically by means of weighing of precipitated cellulose films, after washing and drying.

For the extensional rheology, a CaBER instrument (Haake) inflict an axial stretching deformation on a discrete cylindrical volume of test fluid placed between circular parallel plates, which gives a close approximation of shear-free uniaxial extensional flow. The CaBER measurements in this study were carried out for the determination of the extensional properties at room temperature (24°C) using 6 mm-plates, and a Newtonian fit was carried out for the evaluation.

2.2.4. Cellulose Degradation

For the intrinsic viscosimetry measurements (DP-values), the regenerated cellulose samples were dissolved in either copper (II) ethylenediamine solutions (Cuen, Merck) and measured according to DIN 54270, or they were dissolved in Cuoxam ($[\text{Cu}^{\text{II}}(\text{NH}_3)_4](\text{OH})_2$) and measured according to an internal institute standard of TITK.^[26] For this purpose the intrinsic viscosity in Cuoxam $[\eta]_{\text{Cuoxam}}$ (mL g^{-1}) was detected by the means of an automatic measuring capillary viscometer (Schott AVS 360). The $\text{DP}_{\text{Cuoxam}}$ was calculated according to the equation:

$$\text{DP}_{\text{Cuoxam}} = 2 \cdot [\eta]_{\text{Cuoxam}}$$

3. Results and Discussion

The finding that N_{2228}Cl is able to dissolve cellulose (MCC) in combination with acetone was surprising; especially considering that acetone usually is used as precipitation agent in polysaccharide chemistry.^[21] Thus, it was decided to study further organic solvents in combination with N_{2228}Cl regarding their cellulose dissolution capabilities. Previously, only dissolution of MCC in $\text{N}_{2228}\text{Cl}/\text{solvent}$ was examined. Consequently, the effect of N_{2228}Cl on the dissolution(s) of celluloses with higher DP was also investigated in this study.

3.1. Dissolution of Microcrystalline Cellulose in N_{2228}Cl applying Different Organic Solvents

The first set of experiments was focused on the dissolution of MCC in solutions of N_{2228}Cl in organic solvents. Thus, different solvent classes (e.g. ketones, ethers, and esters) were examined. The choice of the solvents was based on their solvatochromic parameters, e.g., those published by Catalán.^[27] These parameters include Lewis acidity (SA), Lewis basicity (SB), dipolarity (SD) and polarizability (SP). **Table 1** shows the dissolution of MCC in $\text{N}_{2228}\text{Cl}/\text{organic solvent}$, along with the corresponding solvent descriptors.

It was observed that solutions of N_{2228}Cl in solvents that cause appreciable cellulose swelling, e.g., DMF, DMSO, and NMP dissolve cellulose under mild conditions (2 h, 60 °C).^[28] On the

other hand, cellulose dissolution in $N_{2228}Cl$ together with solvents that are not efficient in cellulose swelling, like 2-butanone, 2-methyltetrahydrofuran, tetrahydropyran, ethyl acetate and 3-pentanone required a different experimental protocol, namely, the electrolyte concentration in the mixture was increased by partial distillation of the volatile solvent, as shown for (**S3**). Consequently, cellulose dissolution in $N_{2228}Cl$ /solvent may be related to the ability of the (pure) organic solvents to swell cellulose.

In order to demonstrate that cellulose dissolution is non-derivatizing, i.e., occurs without formation of a cellulose derivative, we employed ^{13}C -NMR spectroscopy to examine its solutions in $N_{2228}Cl$ /acetone- d_6 and $N_{2228}Cl$ /DMSO- d_6 (**Figure 1**). In parts A and B of Figure 1, the signals appearing between 5 and 60 ppm are due to the $N_{2228}Cl$ and the respective deuterated solvents; the signals for the AGU appear between 60 to 105 ppm. For the dissolution in $N_{2228}Cl$ /acetone- d_6 (Figure 1A), the AGU signals appears at 60.9 (C6), 71.6 - 81.9 (C2 - C5) and 103.2 ppm, in agreement with ^{13}C NMR results of Kostag et.al. in the same solvent system,^[21] and of glucose oligomers in 1-(n-butyl)-3-methylimidazolium chloride/DMSO- d_6 ^[29] In Figure 1B, the AGU signals appears at 59.9 (C6), 72.1 - 81.3 (C2 - C5) and 102.5 ppm. In summary, our ^{13}C -NMR spectra indicate that the solvent system based on $N_{2228}Cl$ belongs to the group of non-derivatizing solvents.

Furthermore, the results summarized in Table 1 show that all solvents used, possess a very low or a zero value for the acidity (SA) while the values for polarizability (SP) and dipolarity (SD) are comparatively high, which is typical for dipolar aprotic solvents. As already described by Hauru et al. ; the basicity (SB) of the solvent has the biggest impact towards dissolving cellulose.^[30] If the value for the basicity is low, e.g., acetonitrile and benzonitrile, the systems were not able to generate translucent cellulose solutions. This might lead to the conclusion that the nitriles did not dissolve cellulose due to their low basicity value. However, it should be noted that this approach is just an approximation and cannot fully predict the interaction of solvent, electrolyte, and cellulose. Hence, even if the values for the basicity for

N,N-diethylformamide and *N,N*-diethylacetamide are relatively high, it was not possible to achieve a clear cellulose solution in these systems. For tetrahydropyran, 2-methyltetrahydrofuran, and ethyl acetate, solidification of the solution occurred if the temperature was decreased. All other solvent mixtures remained liquid at room temperature.

3.2. Investigation of Cellulose Solutions in N₂₂₂₈Cl/DMSO or N₂₂₂₈Cl/DMAc

3.2.1. Lab-scale Experiments

Thus far, N₂₂₂₈Cl/organic solvent was investigated as solvent for MCC only. In this part, the same solvent systems were examined regarding the dissolution of dissolving grade pulps and thus for samples with higher average DP compared to MCC. Three different dissolving grade pulps with varying DP were studied (**P1**, DP_v = 288; **P2**, DP_v = 534, and **P3**, DP_v = 582). Two different solvents systems were investigated, namely N₂₂₂₈Cl/DMAc and N₂₂₂₈Cl/DMSO.

DMSO is well described in literature as a co-solvent for ionic liquids but has not previously been used together with N₂₂₂₈Cl. Additionally, cellulose was dissolved in N₂₂₂₈Cl/solvent by two methods: the dipolar aprotic solvent was added as “diluent” to the solution of cellulose in molten electrolyte (**S1**), or the binary mixture (electrolyte/solvent) was employed directly as solvent (**S2**). The influence of both dissolution methods (**S1** or **S2**) on the final solution was also part of the investigation. The first set of experiments was focused on the concentrations that could be reached depending on the cellulose source applied in N₂₂₂₈Cl/DMSO (**Table 2**).

For all pulps investigated, clear cellulose solutions were achieved, as verified by cross-polarized microscopy (**Figure 2A + 2B** and **Figure 4A**). As can be seen in Figure 2, solutions of the pulps **P2** and **P3** exhibits no remaining fragments (Figure 2A, B), whereas the solution of 7.5 wt% **P1** sample possesses a few undissolved fragments (Figure 2C). The monitored solutions summarized in Table 2 showed better dissolution capabilities if DMSO was employed as co-solvent after the preparation as a melt (**S1**, e.g. entry 2), whereas samples prepared by applying procedure **S2** did not lead to clear cellulose solutions (entries 4 and 6). Although the temperature

was increased from 60 to 120°C, some undissolved fragments could still be observed by microscope evaluation (**Figure 3**). Thus, the dissolution procedure had a significant influence on the successful dissolution of the cellulose samples examined.

It was found that a molar ratio of 1 to 3.2 for N₂₂₂₈Cl/DMSO is an optimum ratio; decreasing the ratio of electrolyte/DMSO led to turbid cellulose solutions (Table 2, entries 7 - 9). For the dissolving grade pulps with higher DP (**P2** and **P3**), the maximum concentrations were in the range 5-7.5 wt%. As expected, cellulose with lower DP is more soluble in this solvent.

In order to probe the effect of the organic solvent, some solutions of cellulose with different concentrations were also prepared in N₂₂₂₈Cl/DMAc (Table 2, entries 7, 8). The samples were compared in the microscope to check if there were still fiber fragments left (**Figure 4**). Comparison of the microscopic images shows that both solvents were useful for dissolving the **P1** pulp. Examining the 5 wt% cellulose concentration, the pulp is completely dissolved in the presence of DMSO, i.e., there are no undissolved fragments (Figure 4A). For DMAc, some very small undissolved parts were detected (Figure 4B).

The samples described in Table 2 were prepared in a scale of 10 – 15 g of cellulose. For the rheological characterization, higher amounts of the cellulose solutions were required. Thus, upscaling was carried out (up to 70 g of pulp) and the most promising solutions (as high cellulose concentration as possible without any undissolved fragments) were studied (**Table 3**).

The solvent system N₂₂₂₈Cl/DMSO with a molar ratio of 1 to 3.2 was selected.

The quality of the solutions was examined by cross-polarized microscopy indicating that the upscaling did not affect the dissolution itself.

3.2.2. Dissolution in Lab-scale Kneader

The first dissolution in the kneader was carried out with **P1** pulp to obtain a 15 wt% cellulose solution without addition of organic solvent, i.e., neat, molten N₂₂₂₈Cl was used as solvent. The microscope view of the dissolved cellulose revealed a good dissolution, no undissolved fiber

fragments were detected (**Figure 5**). A preparation of an appropriate film for the determination of the solids content of the solution was very difficult and the values determined of the cellulose concentration were 13.7 wt% and 12.8 wt%. This was significantly lower than the expected 15 wt%, and there was an unusually large difference between the duplicates. The reason is most likely cellulose degradation, which makes it impossible to achieve a complete cellulose precipitation. Cellulose degradation during the dissolution process was shown by a large decrease in DP_{Cuoxam} ; the precipitated cellulose showed a DP-value of 48 compared to the starting the DP of 288 (corresponding to a cellulose degradation of 83%). Thus, the dissolution conditions affected cellulose degradation strongly, most likely due to the chloride anion and potential Hofmann degradation (of the electrolyte). Similar results have been found for ionic liquids with imidazolium cations and chloride anions, if no adjustment of pH-value was done. However, an adjustment of the pH-value of the aqueous solutions of imidazolium chlorides permits cellulose dissolution without significant losses of DP.^[31] Thus, a second experiment with adjusted pH-value was carried out (pulp **P2**, 15 wt%). The prepared solution was clear and did not contain any undissolved fragments; however, it crystallized extremely quickly. Even a storage temperature of 85°C led to formation of small crystals (**Figure 6**).

The results of the solids content for the solution gave a value of 15.2 wt%, very close to the intended 15 wt%. However, the adjustment of the pH-level did not result in the desired prevention of cellulose degradation; the DP_{Cuoxam} of the cellulose went from 534 prior to dissolution to 142 after dissolution and regeneration (corresponding to 73% degradation). Thus, it seems that the dissolution of the pulp fibers in the solvent system is dependent on the cellulose degradation, and the degradation could not be avoided under the conditions employed.

3.3. Rheological Characterization of Cellulose Solutions

The dissolution of cellulose in a solvent, and the rheological properties of these solutions are of great importance for further processing of the cellulose solution into fibers and nonwoven

materials. Melts and solutions of polymers generally show a shear thinning behavior. Thus, a graph for viscosity plotted against shear rate for these fluids show a Newtonian plateau with a constant zero-shear viscosity (η_0) at low shear rates. Thereafter, there is an onset of shear thinning and the viscosity drops. In the oscillatory experiment at low frequencies; a perfect elastic material should show stress in phase with the oscillating strain. However, in viscoelastic materials the stress will be out-of-phase with the strain. Thus, the stress can be divided into two components; the storage modulus, which corresponds to the elastic part and the loss modulus, corresponding to the viscous part. During a gelation process, the elastic response gets stronger than the viscous response and the solution display a gel-like behavior.

The results of the rheological characterization of the 15 wt% solution of the pulp **P1** prepared in the lab-scale kneader showed low viscosity values, which is realistic considering the low DP-value. The complex viscosities determined were 38 Pas at 75°C, 16 Pas at 85°C and 7 Pas at 95°C, and the solution showed a Newtonian behavior (**Figure 7**). Measurements at lower temperatures were not possible due to very rapid solidification.

Also for the 15 wt% solution of the **P2** pulp with adjusted pH-level, the viscosity values were relatively low (**Figure 8**). Due to crystallization of the solution, it was not possible to measure at low temperatures and the measurement at 95°C was carried out prior to the measurement at 85°C. The complex viscosities determined was 560 Pas at 85°C, 200 Pas at 95°C, 53 Pas at 100°C and 14 Pas at 125°C, and the solution showed a Newtonian behavior at the higher temperature.

3.3.1. Comparison of celluloses from different sources

The different dissolving grade pulps were dissolved according to method **S1** to solutions containing 5 wt% cellulose and a molar ratio of N₂₂₂₈Cl/DMSO of 1/3.2. The samples were measured at three different temperatures (20, 40, and 60°C, see **Figure 9**). Pulp **P3** showed the

highest viscosity (η_0 of ca 32 Pas at room temperature) followed by the pulp **P2** and finally the pulp **P1**, which is reasonable considering the different DP-values. However, the difference between the **P3** and **P2** pulps is somewhat larger than expected (difference in DP between these two pulps is not very large). Solutions of pulp **P1** showed a Newtonian fluid behavior at higher temperatures (40-60°C) and only shear thinning at very high shear rate at 20°C. Solutions of **P2** possess Newtonian plateaus at all temperatures studied, with a η_0 of about 10 Pas at room temperature, and shear thinning with different onsets depending on temperature. Solutions of **P3** showed less clear behavior, especially at 20°C and 40°C, where there are no Newtonian plateaus. It is likely that this solution behaves like a gel at lower temperatures, due to the solution state of this sample.

Samples prepared with the same method of dissolution and possessing the same cellulose concentration were also studied by means of shear rheology and CaBER-measurements (sample **15-17** in Table 3). However, due to very low viscosities of the solutions, calculation of master curves and relaxation time spectra was not possible. The solutions hardly showed elastic properties, and a determination of storage moduli did not result in reliable results. Thus, the data of the complex viscosities are presented only (**Figure 10**). The results shown in Figure 10 indicate Newtonian behavior in most cases; only the complex viscosities of sample **16 (P2)** showed a small dependence on the angular velocity at 25 and 40°C, and in the case of **P3** (sample **17**) at 25°C. The complex viscosities of the solutions were below 10 Pas for all the samples, even at room temperature.

CaBER measurements were carried out for the determination of the extensional properties at room temperature (24°C) using 6 mm plates. For evaluation, Newtonian fits were carried out. **Table 4** contains the determined breakup times, calculated shear viscosities and extensional viscosities. Normalized diameters of the samples versus time are shown in **Figure 11**. The breakup curves are linear rather than exponentially decreasing, indicating Newtonian rather than viscoelastic fluids (for elastic fluids, the diameter decays exponentially). The breakup

times are relatively short, most likely due to low amount of chain overlap. Sample **16 (P2)** shows a higher extensional viscosity value and breakup time. Additionally, sample **17 (P3)** possessed lower viscosity values than expected, most likely due to incomplete cellulose dissolution or re-precipitation of cellulose fibers. That is, the measured values are of a solution with a de facto lower cellulose concentration. Values, which are more reasonable, would be in the same range as for sample **16 (P2)**. Since the samples showed low viscosities and Newtonian behavior, further samples with higher cellulose concentrations were subsequently investigated. However, for the CaBER measurements of these samples (**18-21**, Table 3), there were uncertainties due to some undissolved fiber fragments in the solutions, and the samples were considered not suitable for further evaluation.

3.3.2. Comparison: Different Cellulose Concentrations

A series of samples using pulp **P1** and applying different concentrations (N₂₂₂₈Cl/DMSO, 1/3.2) prepared according to **S1** were characterized with shear rheology at three different temperatures (20, 40, and 60°C, **Figure 12**). The samples with low concentrations (2-5 wt%) showed Newtonian fluid behavior with η_0 below 5 Pas at room temperature. Shear thinning was observed for the samples with higher cellulose concentrations (7.5-10 wt%) at higher shear rates, and the η_0 are low for all samples. Unfortunately, the microscope images of the samples with concentrations of 7.5-10 wt% cellulose showed undissolved fiber fragments, resulting in uncertainties in the evaluation of the results.

Furthermore, the four additional samples with higher cellulose concentrations of the different dissolving grade pulps (sample **18-21** in Table 3) were also measured at three different temperatures (25, 40, and 60°C) and the calculated master curves, including the complex viscosities, and weighted relaxation spectra, were made at a reference temperature of 25°C (**Figure 13**). It can be seen that the complex viscosities were significantly higher by increasing the cellulose concentration. For the dissolving pulps with 7.5 wt% of cellulose, the complex

viscosities were in the range of 25-60 Pas, compared to the previous values, all below 10 Pas. Shear-thinning behavior was also more clearly seen at higher angular velocities for these samples. However, the complex viscosities were still relatively low. This fact in addition to the solution state of the samples made them not suitable for conventional fiber spinning. The storage and loss modulus, shown in the master curves, indicate that there is no crossing of the storage modulus curve with the loss modulus curve, i.e., there is no indication of gel-like behavior for any of the samples. Due to the low viscosities of the solutions of **P1** (**19**, Table 3) and 5 wt% **P3** (**20**, Table 3); measurements at 60°C were not possible. Thus, in these cases, the master curves and relaxation spectra were calculated for 25 and 40°C only. The differences in viscosity between the samples of different dissolving grade pulps could be due to several reasons, including the molecular weight distributions of the pulps, different cellulose degradation during dissolution or various solution states, leading to better or worse pulp dissolution.

3.3.3. Other Factors influencing the Rheological Properties of the Cellulose Solutions

Some measurements were also conducted to compare different ratio of electrolyte to DMSO. All samples were from pulp **P1** with 5 wt% and were measured at 20°C. It could be expected that samples with a higher amount of DMSO would show a lower viscosity, which was found. However, these samples (entries **9-11**, Table 2) contained appreciable amounts of undissolved fiber fragments, which would influence the total dissolved cellulose concentration and consequently the viscosity, which made it difficult to draw any further conclusions from these results.

Measurements of samples prepared in different ways were also conducted; either from melt (**S1**) or by addition of all ingredients at the beginning (adding N₂₂₂₈Cl, DMSO and cellulose together and keeping the temperature at 60°C for 6 hours or 120°C for 1 hour (based on **S2**)). The samples were made from pulp **P1** and had a concentration of 5 wt%. The shear rheology

measured at 20, 40, and 60°C show, for samples from the melt, clear Newtonian plateaus. They show an almost constant η_0 for the higher temperatures (ca. 0.4 Pas for 60°C and ca. 0.9 Pas for 40°C, **Figure 14**). However, the other two samples do not demonstrate Newtonian plateaus; instead the viscosity is constantly lower at increasing shear rates, which indicates gel-like behavior.

3.4. Cellulose Degradation

Variations in color of the solutions prepared in different ways, i.e., as melt (**S1**) compared to solutions obtained by mixing the components (**S2**) raised the question of cellulose degradation during the dissolution. **Figure 15** shows two cellulose solutions, prepared with method **S1** (flask on the right side) or **S2** (left side). Regeneration of cellulose and the subsequent dissolution with Cuen allows determination of the obtained DS values by viscosimetry. The degradation of the cellulose during dissolution was investigated by preparing samples in different ways and measuring the DP_{Cuen} of the regenerated cellulose after dissolution. The results are presented in **Table 5**.

To exclude influences of residues of lignin and hemicelluloses on the color changes, an experiment was additionally conducted with dissolution of pure bacterial cellulose (BC). The BC and the electrolyte were mixed and heated to 120°C and dramatic color changes were observed, especially after longer time.

The degradation of cellulose is most severe by dissolution in neat $N_{2228}Cl$, which was also found for dissolution in the kneader. In this case, the cellulose DP_{Cuoxam} of cellulose decreased from DP 288 initially to 48 after dissolution for pulp **P1**, and from 534 to 142 for pulp **P2** with adjusted pH-value (pH 10.5). Different reasons for the severe degradation are conceivable. In case of the dissolution with adjusted pH-value applying NaOH, it could occur oxidative alkaline degradation. However, it is more likely, that the electrolyte itself underwent Hofmann elimination and consequently led to degradation of cellulose, such observations were already

described for quaternary ammonium salts by Casarano et al.^[32] After investigation of heating of pure N₂₂₂₈Cl, it was found that the solvent itself also changed color at elevated temperatures, see **Figure 16**. As shown in Figure 16, increasing the temperature to 120°C and the long treatment of the solution at these conditions led to a change in color. It can be assumed that Hofmann elimination took place and the resulting products generated the observed change in color. It should also be considered that a relatively small amount of impurities can cause a change in color, which especially can be observed during homogeneously modification reactions of cellulose.

4. Conclusions

Cellulose dissolves in N₂₂₂₈Cl in combination with DMSO, DMAc, acetone, DMF, 2-butanone, NMP, 1-methylimidazole, ethyl acetate, 2-methyltetrahydrofuran, tetrahydropyran, 1,3-dimethyl-2-imidazolidinone or 3-pentanone, yielding clear solutions. The amount of cellulose that can be dissolved depends on both the biopolymer (e.g., its DP) and the protocol of dissolution. For dissolving grade pulps, concentrations up to 7.5 wt% cellulose were obtained and even higher cellulose concentration (10-15 wt%) can be reached with pulps of lower DP, or when a pure melt of N₂₂₂₈Cl is used. The procedure to dissolve the cellulose is crucial for the completeness of the dissolution. A melt of N₂₂₂₈Cl results in less undissolved material, while at the same time, there is more intense degradation of cellulose and the solutions become somewhat colored. For the studied conditions, the complex viscosities of the solutions of dissolving grade pulps were low (2-7 Pas for 5 wt% cellulose concentrations at 25°C and ca. 25-60 Pas for 7.5 wt% solutions), and the results of CaBER-measurements showed that the solutions had a Newtonian fluid behavior. Thus far, the investigated solutions are not suitable for conventional fiber spinning processes due to the solution states and the low viscosities. Further studies will be carried out to investigate the suitability of N₂₂₂₈Cl as a cellulose solvent to form nonwoven cellulosic materials with a solution blowing technique. Current

investigations are also conducted using cellulose solutions based on N₂₂₂₈Cl as reaction media for homogeneous derivatization.

Acknowledgements: K. Jedvert gratefully acknowledges the Swedish Research Council Formas for financial support. O. A. El Seoud thanks the Brazilian agencies FAPESP for financial support (2014/22136-4) and CNPq for research productivity fellowship (307022/2014-5).

Received: Month XX, XXXX; Revised: Month XX, XXXX; Published online:

((For PPP, use “Accepted: Month XX, XXXX” instead of “Published online”)); DOI: 10.1002/marc.((insert number)) ((or ppap., mabi., macp., mame., mren., mats.))

Keywords: cellulose dissolution, quaternary ammonium salts, rheology, degradation

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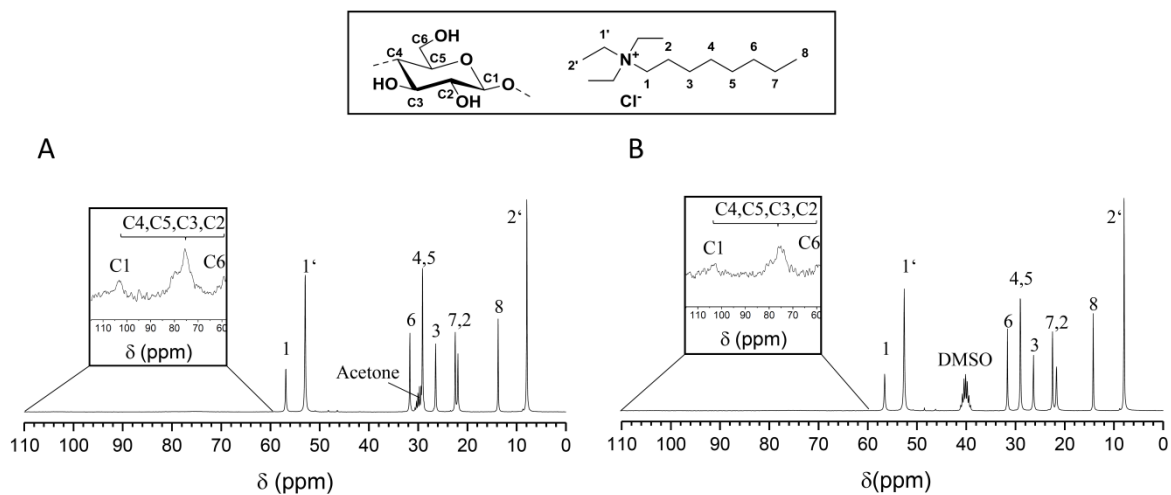


Figure 1: ^{13}C -NMR spectra of cellulose dissolved in $\text{N}_{2228}\text{Cl}/\text{acetone-}d_6$ (A), and in $\text{N}_{2228}\text{Cl}/\text{DMSO-}d_6$ (B)



Figure 2. Images of cellulose solutions of (A) 5 wt% P2, (B) 5 wt% P3 and (C) 7.5 wt% P1, obtained by cross-polarized microscopy.

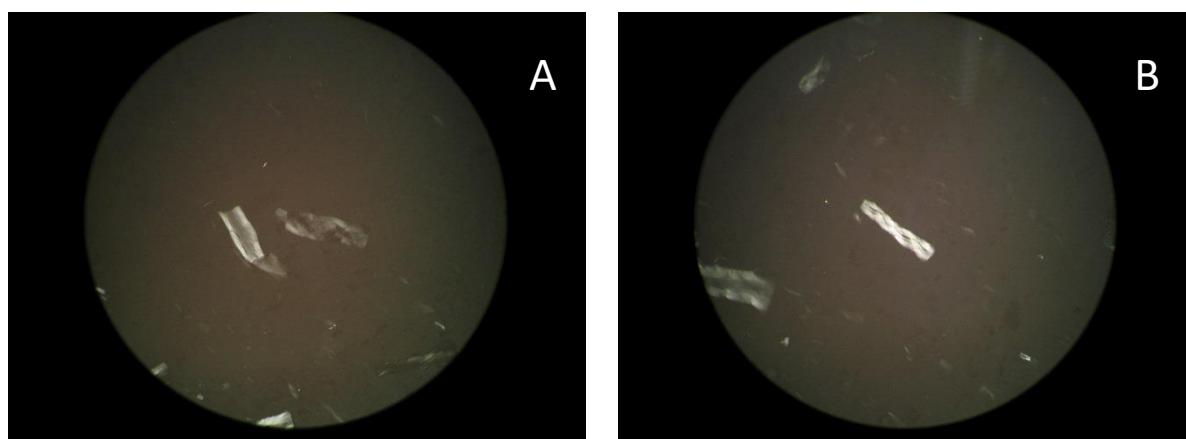


Figure 3. Microscopic images of no. 4 and 6. Applying approach S2 both solutions contained some undissolved fragments. Increasing the temperature from 60°C (A) to 120°C (B) did not improve the dissolution behavior.

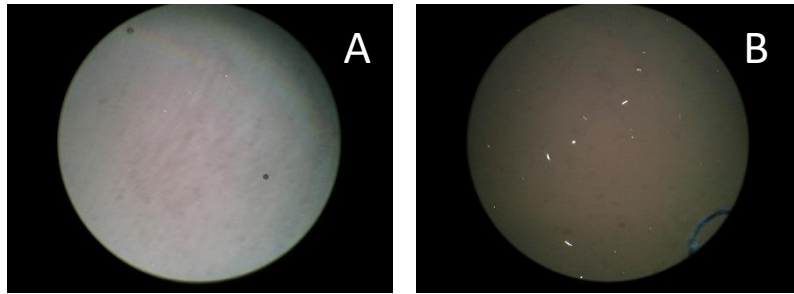


Figure 4. Comparison of two 5 wt% **P1** samples dissolved in different solvent systems. On the left hand side is demonstrated the sample that was dissolved in $N_{2228}Cl/DMSO$ (A). The solution on the right side was dissolved in $N_{2228}Cl/DMAc$ (B).



Figure 5: Microscope image of the prepared cellulose dope (15 wt%, pulp P1, polarized light, 10x objective)

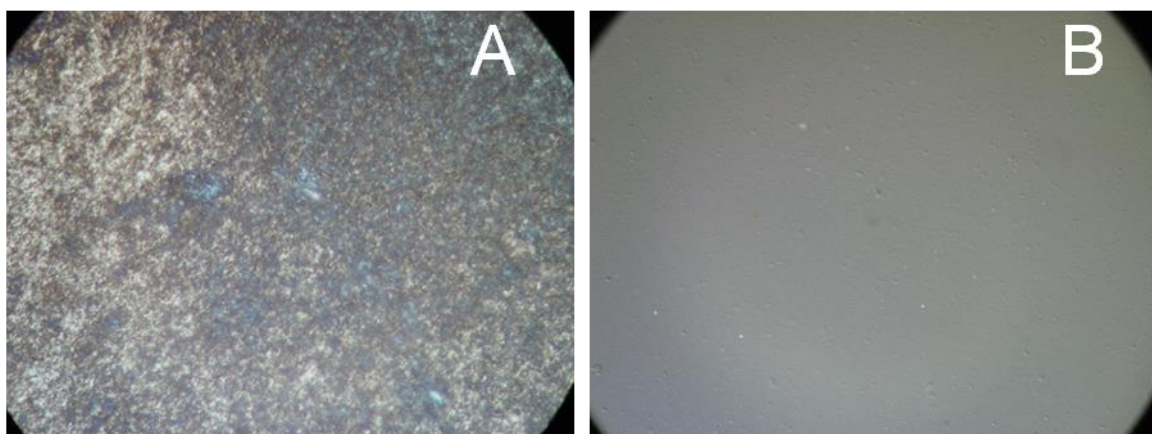


Figure 6: Microscope images of the prepared cellulose dope (15 wt%, pulp P2, adjusted pH-value, polarized light, 10x objective) after storage at different temperatures; (A) Storage at $85^{\circ}C$, (B) Storage at $95^{\circ}C$.

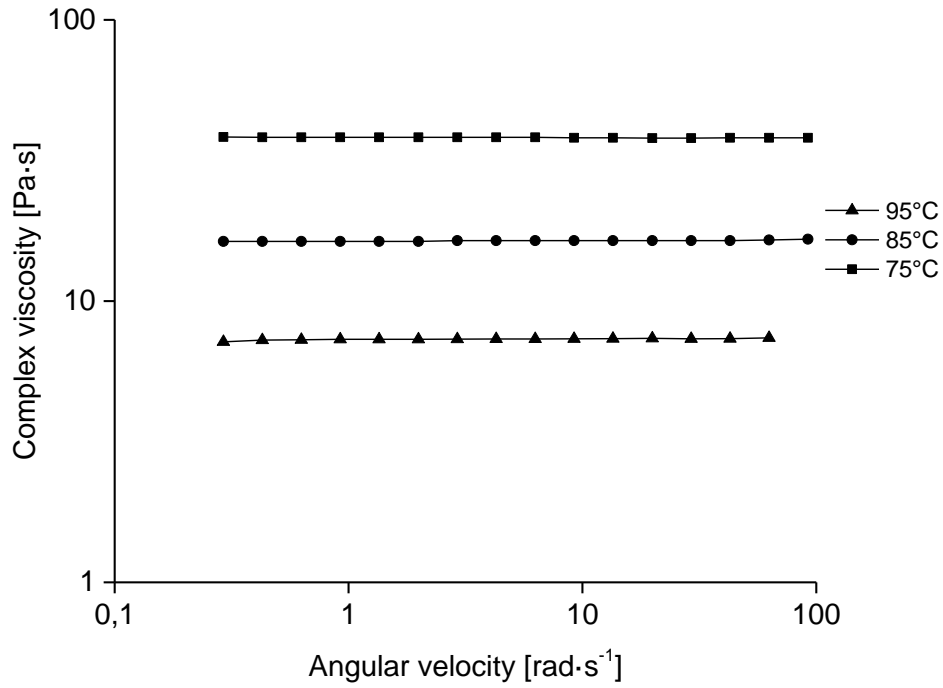


Figure 7. Frequency sweeps of 15 wt% solution of **P1** pulp prepared in lab-scale kneader, measured at 75, 85 and 95°C.

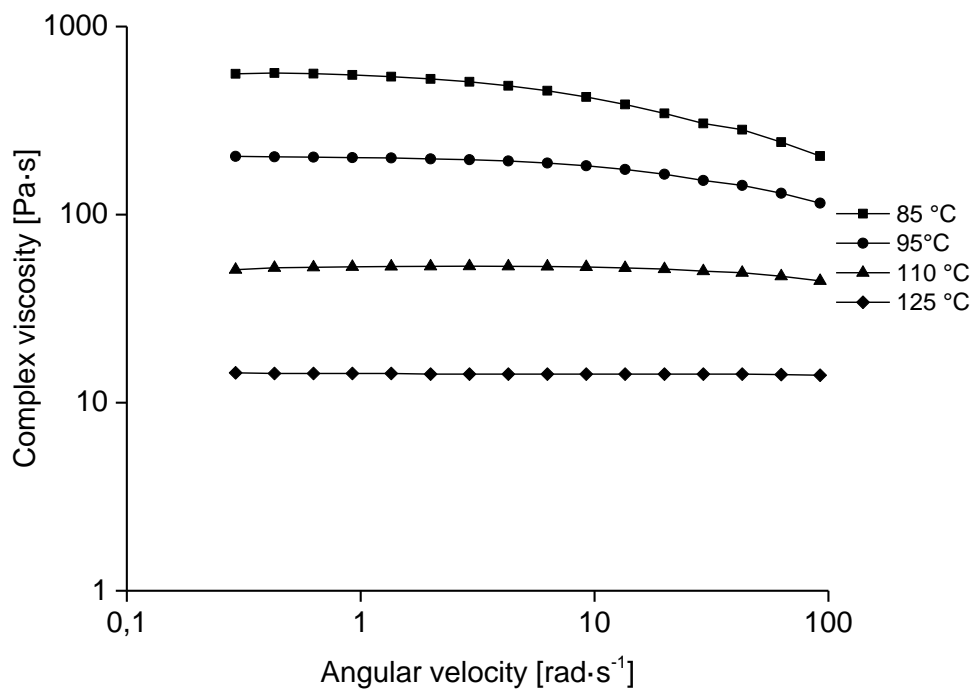


Figure 8. Frequency sweeps of 15 wt% solution of **P2** pulp and adjusted pH-level, prepared in lab-scale kneader, measured at 85, 95, 110 and 125°C.

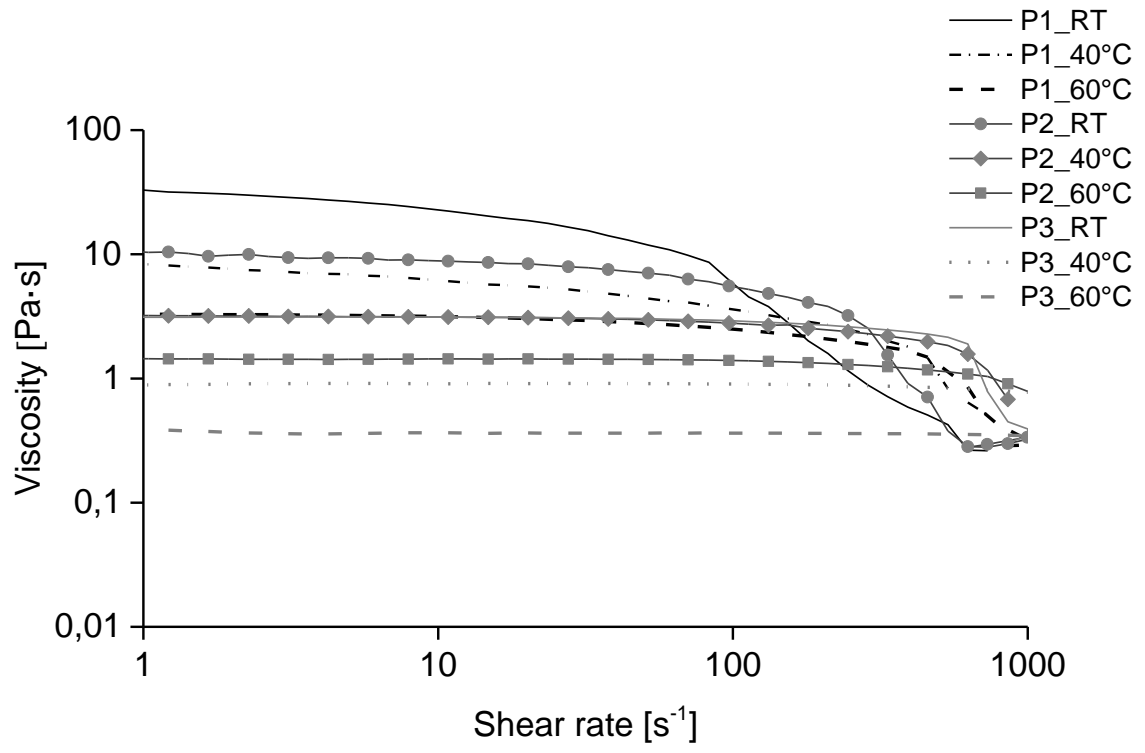


Figure 9. Viscosity as a function of shear rate for samples from different pulps, measurements were run at three different temperatures (20, 40, and 60°C).

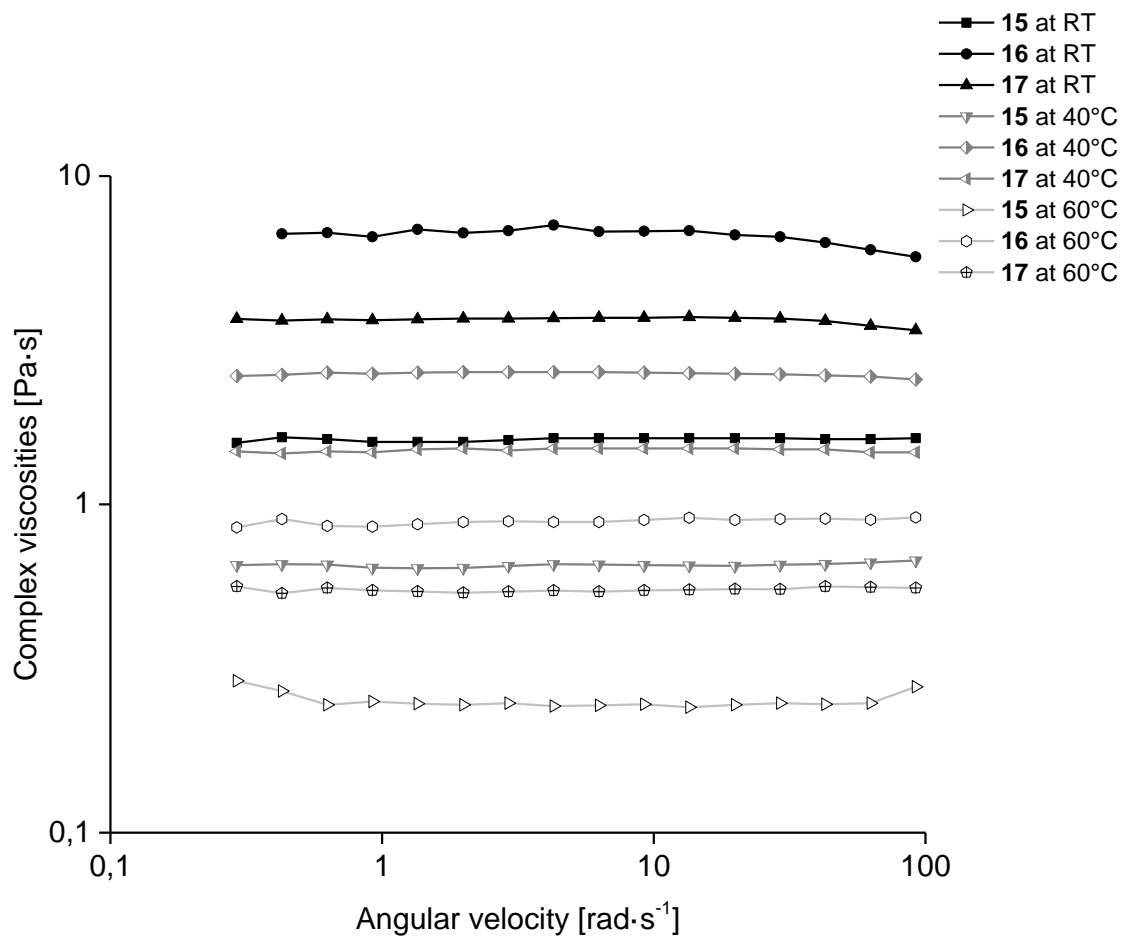


Figure 10. Complex viscosities of investigated solutions depending on the angular velocity at measuring temperatures 25, 40, and 60°C.

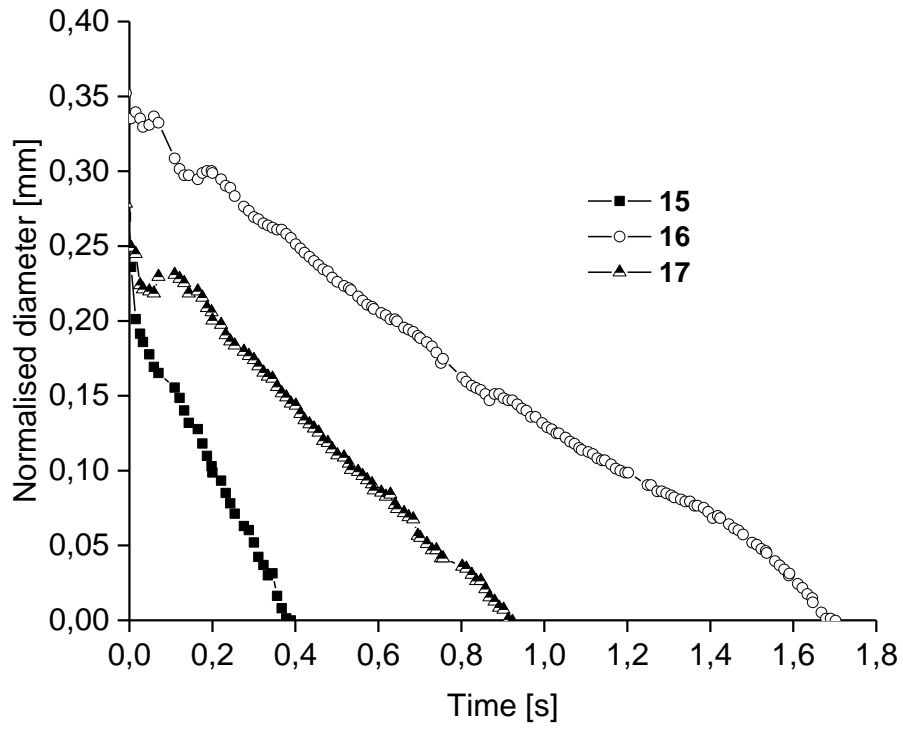


Figure 11. Graph of breakup curves (normalized diameter vs. time) from CaBER measurements for the 5 wt% samples (samples **15-17**, Table 4).

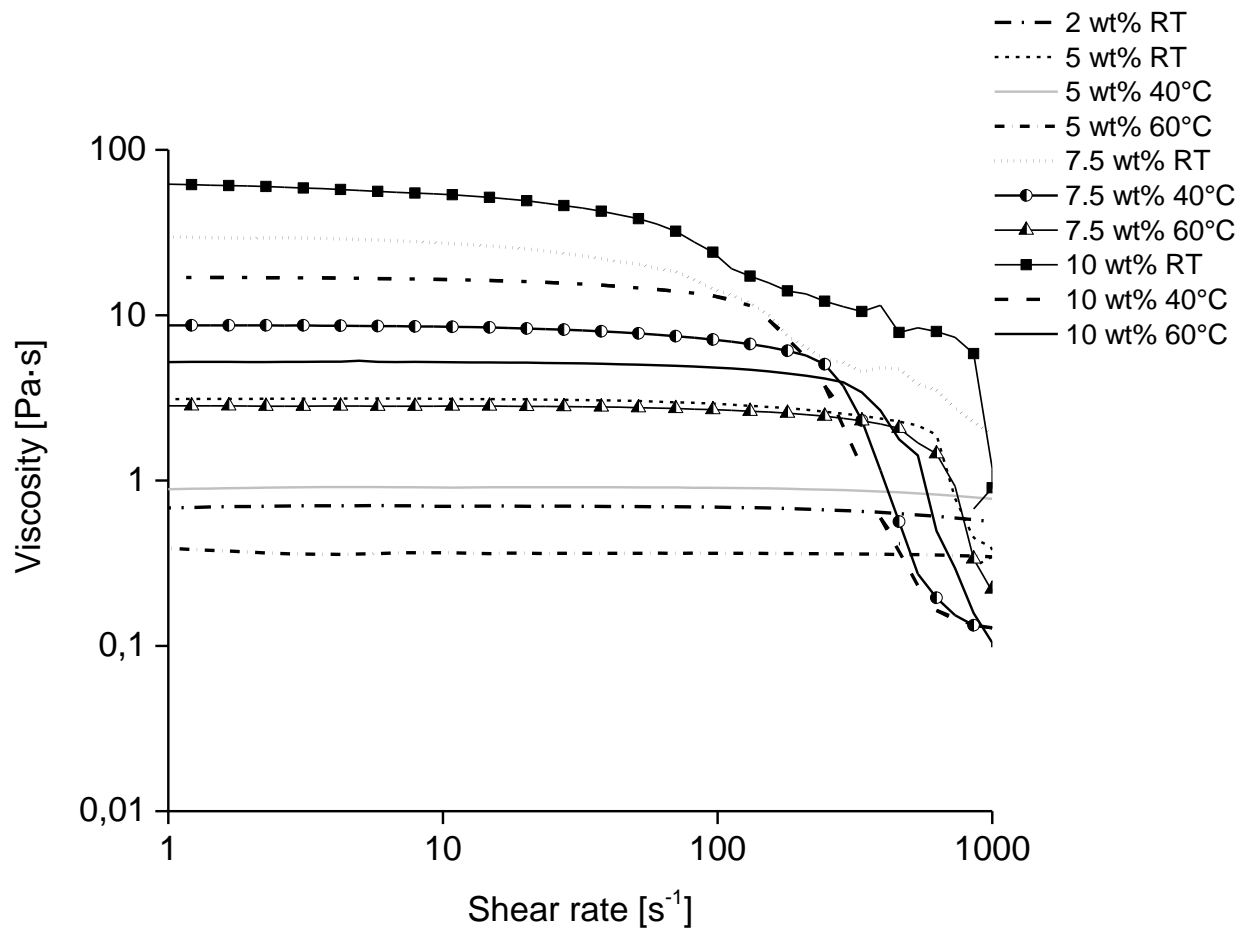


Figure 12. Viscosity as a function of shear rate for samples (pulp **P1**) with varying cellulose concentration.

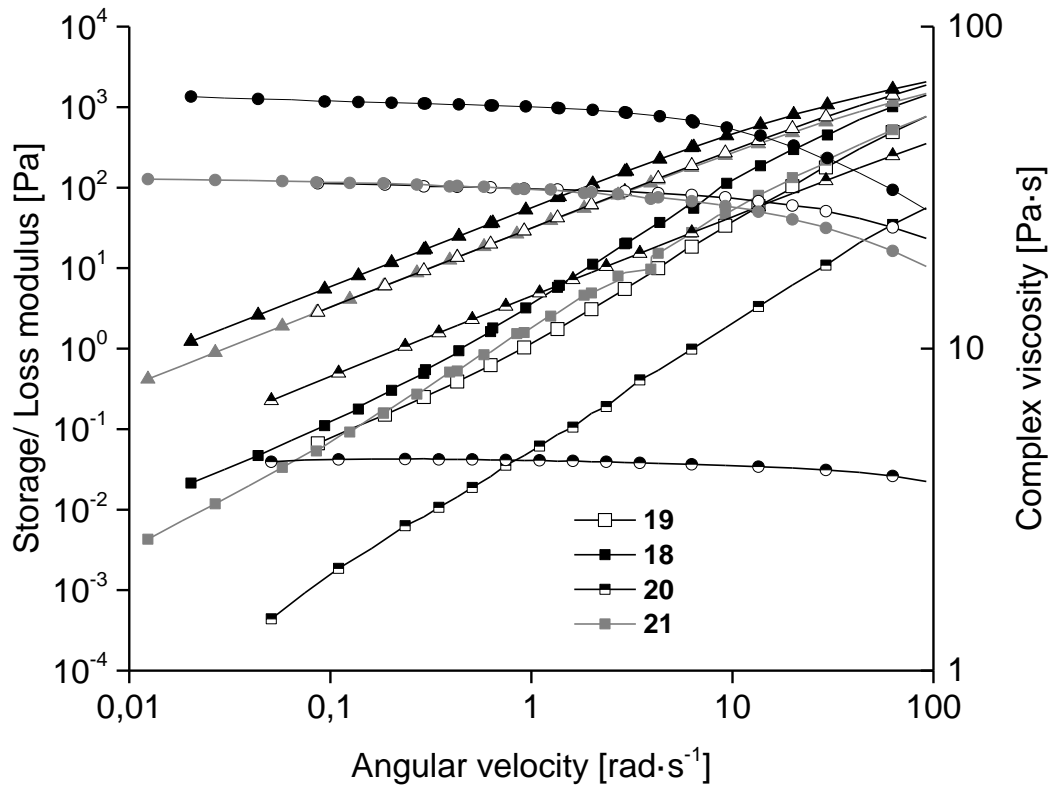


Figure 13. Master curves (reference temperature 25°C) of samples with higher cellulose concentration (samples **18-21** in Table 3). The triangles show the storage moduli, the squares represent the loss moduli and the open circles show the complex viscosities (axis on right-hand side).

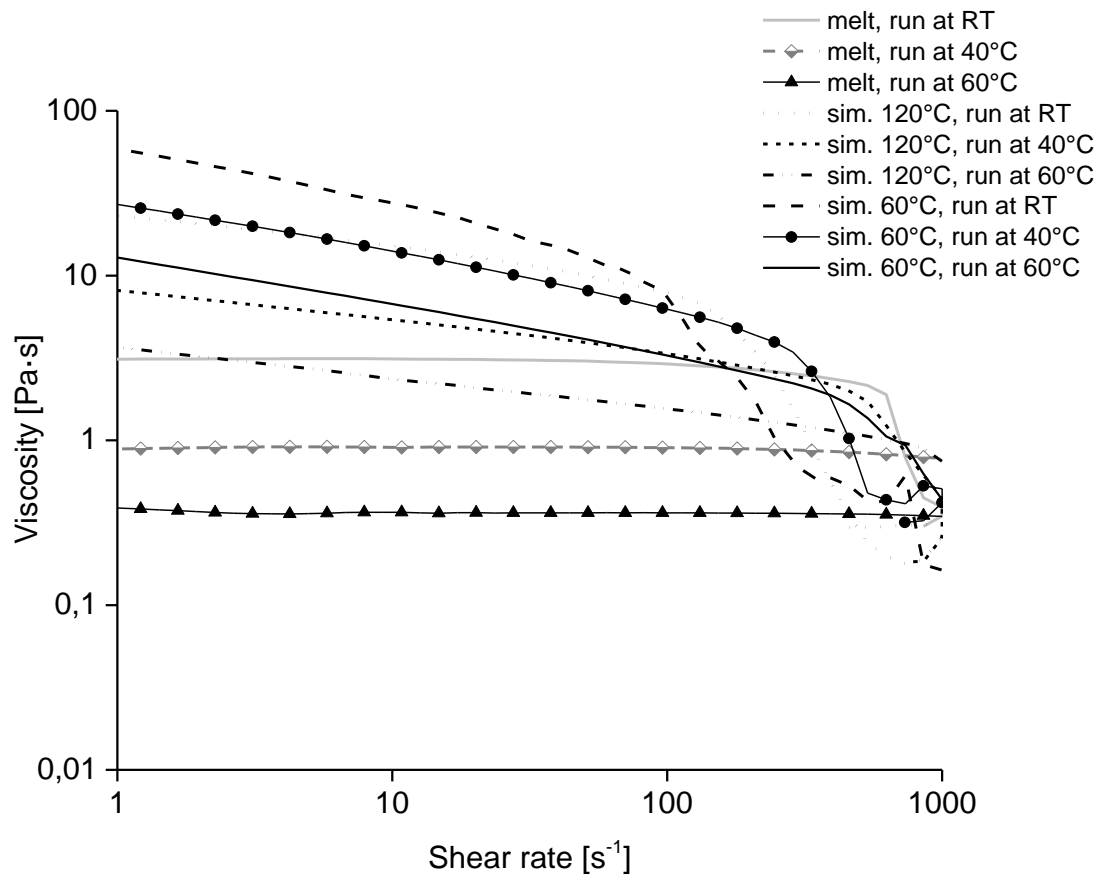


Figure 14. Viscosity as a function of shear rate for samples of a 5 wt% cellulose concentration (P1) prepared at different ways; from melt, added sim. and kept at 60°C for 6 hours, added sim. and kept at 120°C for 1 hour.

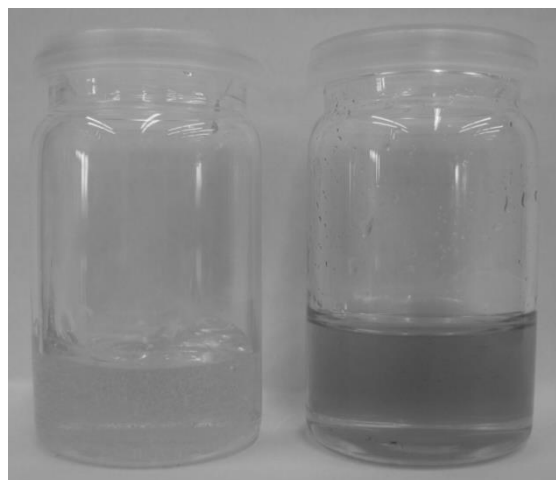


Figure 15. Comparison of two 5 wt%-solutions. To the left (sample **4**, Table 2), preparation based on procedure **S2** stirred for 6 hours at 60°C, and to the right (sample **2**, Table 2) was prepared following procedure **S1**.

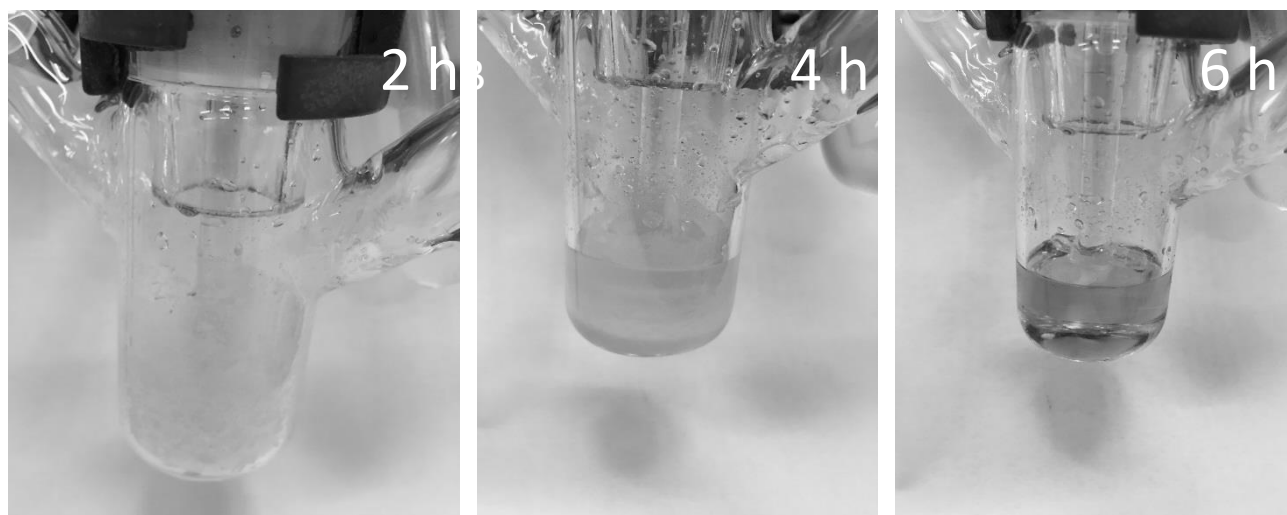


Figure 16. The images demonstrate the color change of pure $N_{2228}Cl$ during a time span of 6 h. In the first two hours, the salt was treated at 70°C (left), the following two hours; it was heated to 100°C (middle). The last two hours $N_{2228}Cl$ was stirred at 120°C (right).

Table 1. Dissolution of MCC in presence of N₂₂₂₈Cl/organic solvent and solvent descriptors

No.	Solvent	SA	SB	SD	SP	Solution System	Cellulose dissolution ^{a)}
1	<i>N,N</i> -dimethylacetamide (DMAc)	0.028	0.65	0.99	0.76	S2	+
2	dimethyl sulfoxide (DMSO)	0.072	0.65	1.00	0.83	S2	+
3	<i>N,N</i> -dimethylformamide (DMF)	0.031	0.61	0.98	0.76	S2	+
4	acetone	0.000	0.48	0.91	0.65	S3 (85°C)	+
5	2-butanone	0.000	0.52	0.87	0.67	S3 (130°C)	+
6	1-methyl-2-pyrrolidinone (NMP)	0.024	0.61	0.96	0.81	S2	+
7	sulfolane	0.052	0.37	0.90	0.83	S2	-
8	1-methylimidazole	0.069	0.66	0.96	0.83	S2	+
9	acetonitrile	0.044	0.29	0.97	0.65	S3 (85°C)	-
10	tetrahydrofuran	0.000	0.59	0.63	0.71	S3 (85°C)	-
11	<i>N,N'</i> -dimethylpropyleneurea	-	-	-	-	S2	-
12	benzonitrile	0.047	0.28	0.85	0.85	S2	-
13	ethyl acetate	0.000	0.54	0.60	0.66	S3 (105°C)	+
14	2-methyltetrahydrofuran	0.000	0.58	0.77	0.70	S3 (100°C)	+
15	<i>N</i> -methylpyrrole	-	-	-	-	S2	-
16	tetrahydropyran	-	-	-	-	S3 (120°C)	+
17	<i>N,N</i> -diethylformamide	0.000	0.61	0.94	0.75	S2	-
18	<i>N,N</i> -diethylacetamide	0.028	0.65	0.99	0.74	S2	-
19	1,3-dimethyl-2-imidazolidinone	-	-	-	-	S2	+
20	<i>tert</i> -butyl methyl ether	0.000	0.51	0.42	0.62	S3 (85°C)	-
21	tetramethylurea	0.000	0.62	0.88	0.78	S2	-
22	3-pentanone	0.000	0.56	0.69	0.79	S3 (130°C)	+

a) – All dissolution experiments were carried out with 0.5 g cellulose and 4.75 g organic solvent.

The signs represent; +: clear solution, -: dissolution of cellulose was not possible.

Table 2. Dissolution of different dissolving pulps in the system N₂₂₂₈Cl/DMSO or N₂₂₂₈Cl/DMAc

No.	Type of pulp	Cellulose concentration [wt%]	Molar ratio N ₂₂₂₈ Cl: OS ^{a)}	OS ^{a)}	Preparation of solution	Dissolution
1	P1	2	1:3.2	DMSO	S1	+
2	P1	5	1:3.2	DMSO	S1	+
3	P1	7.5	1:3.2	DMSO	S1	(+)
4	P1	5	1:3.2	DMSO	S2 ^{b)}	-
5	P1	10	1:3.2	DMSO	S1	(+)
6	P1	5	1:3.2	DMSO	S2 ^{c)}	-
7	P1	5	1:2.9	DMAc	S1	+
8	P1	10	1:2.9	DMAc	S1	(+)
9	P1	5	1:12.8	DMSO	S1	-
10	P1	5	1:9.5	DMSO	S1	-
11	P1	5	1:4.8	DMSO	S1	-
11	P3	2	1:3.2	DMSO	S1	+
12	P3	5	1:3.2	DMSO	S1	+
13	P2	5	1:3.2	DMSO	S1	+
14	P2	7.5	1:3.2	DMSO	S1	+

a) - OS: organic solvent

b) - Solution was prepared at 60°C

c) - Solution was prepared at 120°C

+ clear solution; (+) few undissolved fiber fragments left; - no dissolution

Table 3. Solutions of cellulose prepared in N₂₂₂₈Cl/DMSO for rheological characterization.

(molar ratio of N₂₂₂₈Cl/DMSO: 1 to 3.2).

No.	Type of pulp	Cellulose concentration [wt%]
15	P1	5.0
16	P2	5.0
17	P3	5.0
18	P2	7.5
19	P1	10.0
20	P3	5.0
21	P3	7.5

Table 4. Solution properties of 5 wt% samples, including the capillary break-up extensional rheology (CaBER) results.

Sample no.	Type of pulp	DP of cell.	Surface tension [mN m⁻¹]	Solution density [g cm⁻³]	Breakup time [sec]	Shear visc. [Pas]	Extensional visc. [Pas]
15	P1	290	36.4	1.0382	0.38	1.36	4.08
16	P2	560	34.2	1.0350	1.70	4.37	13.1
17	P3	580	26.5	1.0358	0.92	2.12	6.35

Table 5. Degree of polymerisation (DP_{Cuen}) of cellulose dissolved in and regenerated (DP of starting cellulose 288)

Medium	Dissolution			Regenerated Cellulose
	Procedure	Temperature	Time	DP_{Cuen}
$N_{2228}Cl/DMSO$	S2	60°C	6 h	238
$N_{2228}Cl/DMSO$	S2	120°C	6 h	151
$N_{2228}Cl/DMSO$	S1	120°C/ RT ^{a)}	1 h / 23 h	125

a) – RT: room temperature

Cellulose dissolution and characterization is performed in novel solvent systems based on triethyl(n-octyl)ammonium chloride ($N_{2228}Cl$). The findings show that it is possible to achieve clear solutions in a variety of organic solvents combined with $N_{2228}Cl$. Cellulose concentrations up to 15 wt% is achieved also for pulp fibers. However, cellulose degradation occurs during dissolution and mechanisms for this are discussed.

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Dissolution capacity of novel cellulose solvents based on triethyloctylammonium chloride

