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Effect of Urea Concentration on the Viscosity and Thermal Stability of Aqueous NaOH/Urea Cellulose Solutions

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Aqueous solutions of sodium hydroxide (NaOH) and urea are a known and versatile solvent for cellulose. The dissolution of cellulose occurs at subambient temperatures through the formation of a cellulose-NaOH-urea "inclusion complex" (IC). NaOH and urea form a hydrate layer around the cellulose chains preventing chain agglomeration. Urea is known to stabilize the solution but its direct role is unknown. Using viscometry and quartz crystal microbalance with dissipation monitoring (QCM-D) it could be shown that the addition of urea reduced the solutions viscosity of the tested solutions by almost 40% and also increased the gelation temperature from approximately 40°C to 90°C. Both effects could also be observed in the presence of additional cellulose powder serving as a physical cross-linker. Using Fourier transform infrared (FTIR) spectroscopy during heating, it could be shown that a direct interaction occurs between urea and the cellulose molecules, reducing their ability to form hydrogen bonds with neighbouring chains.

1. Introduction

Cellulose is a biocompatible, sustainable biopolymer with a wide range of existing and potential future uses in industry [1]. Textiles and paper are common uses for cellulose but it also has applications in hydrogel form as a chromatography medium [2] and potential as a scaffold material for tissue engineering [3]. Unlike many other polymers, cellulose cannot be melted or cured and thus must be dissolved and regenerated during processing [4]. The dissolution of cellulose has been achieved using a number of solvent systems but many require the use of harsh solvents or toxic chemicals [5, 6]. However, as described by Cai and Zhang, cellulose can be dissolved using 7 wt% NaOH and 12 wt% urea in an aqueous solution at low temperatures [7]. NaOH/urea is inexpensive compared with the recently favoured ionic liquids and its low toxicity makes it an attractive alternative to the traditional viscose process [8].

The dissolution of cellulose becomes thermodynamically favourable at low temperatures through the formation of a cellulose-NaOH-urea "inclusion complex" (IC), where the NaOH and urea surround the cellulose chains in a hydrate layer to form a "wormlike" structure [9]. Urea is thought to help stabilize the solution by accumulating around the hydrophobic regions of cellulose through van der Waals forces [10]. Isobe et al. similarly stated that "urea prevents hydrophobic mutual association of cellulose" [11]. After the IC is formed, it provides a barrier to cellulose-cellulose interactions, although the imperfect nature of the shell does allow some aggregates to form [12].

The precise role of urea in this complex is debated, with Cai et al. proposing that only NaOH hydrates directly interact with the cellulose, while the urea hydrates form a shielding layer around the NaOH [9]. Based on nuclear magnetic resonance (NMR) studies, Xiong et al. suggested that urea does not have strong direct interactions with cellulose but does interact with the hydrophobic regions through van der Waals forces [10]. Isobe et al. also proposed that urea interacts with the hydrophobic regions of the dissolved cellulose in alkali

solutions, based on X-ray diffractometry [11]. In contrast, others such as Lu et al. and Song et al. claim that the urea does interact directly with the cellulose to form hydrogen bonds, based on dynamic light scattering and 13C CP/MAS NMR studies, respectively [12, 13]. Previous research agrees that urea alone is not sufficient to solubilize cellulose but is useful in aiding the dissolution of cellulose in alkali solutions [14].

The solvation power of NaOH/urea is limited to 5-6% cellulose and the cellulose solution has a relatively high viscosity, which is thought to be caused by intermolecular interactions between the cellulose chains and chain entanglement [2, 15]. Additionally, despite the formation of the IC, the cellulose-NaOH-urea solution is considered metastable, as the aggregation of the cellulose chains leads to irreversible sol-gel transformation over time. Gelation can also be triggered by heating, as the enhanced thermal motion of the cellulose causes random association and entanglement of the chains [11, 13]. The sol-gel transition temperature varies with cellulose concentration because increased concentration leads to more frequent cellulose-cellulose interactions [16].

Undissolved cellulose particles can be added to the solution, acting as a physical cross-linking agent during the sol-gel transition [17]. Upon solvent removal, the dissolved portion of cellulose is regenerated around the suspended particles, creating a so-called all-cellulose composite hydrogel, leading to a material with strongly improved mechanical properties [18]. As mechanical properties of unreinforced cellulose gels made from NaOH/urea solutions are comparatively low, this can be seen as a crucial step to widen the application potential of this new class of biomaterials [19]. However, the addition of cellulose particles also leads to an increase of the viscosity of the solution, mainly through increased intermolecular interactions between dissolved cellulose and the suspended particles and is therefore likely to influence the stability of the cellulose solution. In addition, unlike in the case of thermoplastic polymers, an increase in processing temperature does not lead to a reduction in viscosity but to the sol-gel transition, resulting in a high level of cellulose-cellulose interactions and an increase in viscosity [6]. Furthermore, the addition of water to the solvent system will lead to cellulose coagulation or precipitation, eliminating the possibility of using a simple dilution process to control the solution viscosity [20].

Although the formation of the IC and especially the role of urea in it has attracted some interest in recent years, most work has been carried out at subambient temperatures to study the solution properties and little is known about the role of the IC and urea during the sol-gel transformation at elevated temperatures. Qin et al. reported that a small increase in the urea concentration can strengthen the IC and prevent aggregation [21]. However, it is not clear how much cellulose was dissolved in the mixture of NaOH, urea, and water and the highest temperature tested in their experiments was 10°C, which is much lower than the gelling temperatures reported by Cai and Zhang [16]. It therefore remains unclear whether additional urea can prevent destruction of the IC at higher temperatures, thereby hindering gelling and stabilizing the solution.

Viscosity measurements are key to monitoring the gelation process with time. Rheometers have been used to study the sol-gel transition of cellulose solutions and determine the storage and loss moduli of the resulting hydrogels. Quartz crystal microbalance with dissipation monitoring (QCM-D) is an alternative tool for rheological measurements that offers the advantage of being nondestructive. The QCM-D records data for multiple harmonic oscillations of a liquid film placed on a quartz crystal. Small changes in the rheological properties of the sample lead to measurable changes in the crystal's resonance frequency and the rate at which vibrational energy is dissipated by the system. Energy dissipation and frequency changes allow modeling the experimental data to extract values for several sample parameters, including viscosity [22, 23].

To better understand the role of urea in cellulose solutions and the sol-gel transition we investigated the effect of increasing urea concentration on the viscosity of cellulose solutions and the rate of gelation during heating. Viscosity measurements were carried out using both a standard viscometer and QCM-D to extract information on rheology during gel formation as well as the shear-induced disruption of the molecular organization of cellulose gels. Fourier transform infrared (FTIR) spectroscopy was also used to investigate the molecular changes occurring during formation of the cellulose gels at high temperatures and with varying urea concentration.

All investigations were carried out on regular cellulose solutions as well as solutions with suspended cellulose particles acting as an additional physical cross-linker. It is hypothesized that the additional physical cross-linker will help understand the interplay between urea and cellulose in the solutions.

2. Experimental

2.1. Materials.
Sigmacell cellulose powder, Type 20 (average particle diameter 20 μm), and urea (ACS grade) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide (purity 97%) in pellet form was purchased from Thermo Fisher Scientific (Waltham, MA, USA). All chemicals were used as received.

2.2. Preparation of Cellulose Solutions.
A solution of 12 wt% urea and 7 wt% NaOH in distilled water was prepared and cooled to −12°C. 5 wt% cellulose powder was added to the solution and stirred for approximately 60 seconds at 300–400 rpm. The mixture was kept overnight at −12°C and then stirred vigorously at 1000–1200 rpm using an overhead stirrer (IKA Eurostar overhead stirrer, IKA Works GmbH & Co. KG, Staufen, Germany) for approximately 5 min until the cellulose particles were no longer visible. The solution was immersed in a bath of glycol and water (ratio 1 : 4) to keep the solution temperature constant at −12°C for the entire preparation time.

The solution was then centrifuged for 2 minutes at ∼ 56.3 g using a MSE Centaur centrifuge (MSE Ltd, London, UK) to remove any remaining cellulose agglomerates and was then stored at 1-2°C until further use. The final cellulose concentration was found to be 4.98 ± 0.2 wt%. This solution is referred to as standard solution (SS).

Supplementary cellulose powder was added in the cold saturated cellulose solution to produce a solution containing suspended cellulose particles (SPS), with the suspended cellulose equal to 50 wt% of the amount of dissolved cellulose. The suspension was made homogeneous by vigorous stirring at 1000 rpm using the overhead stirrer, using a glycol bath to maintain the low temperature and prevent agglomeration of cellulose chains and/or ICs.

Multiples of 6 wt% urea were added to either SS or SPS to generate solutions with a range of concentrations from 6 to 30%, referred to as SS, SS-6U, SS-12U, SS-18U, SS-24U, and SS-30U and their corresponding counterparts for SPS solutions.

2.3. Characterization. A Haake rotational viscometer and MV1 spindle with associated computer system was used to measure the rotational velocity of the spindle, force applied, and solution temperature.

Each sample of SS was measured at 1°C, at shear rates between 1 and 1000 s^{-1} at twenty exponentially spaced points. The samples of SPS were tested similarly but their higher viscosities limited measurements to shear rates between 1 and 370 s^{-1} in the instrument.

The effect of extra urea on the gelation behaviour of SS and SPS was tested by placing samples in the viscometer at 1°C and heating them to 100°C over the course of 50 min at a shear rate of 50 s^{-1}. 30 wt% added urea was used for SS and 24 wt% added urea for SPS.

To calculate values for the zero shear viscosity, additional viscosity measurements were carried out using a QCM-D instrument (Q-Sense E4, Biolin Scientific Holding AB, Stockholm, Sweden) equipped with the Q-Sense Open Flow module. The quartz sensor was gold-coated, with a native resonant frequency of 4.95 MHz ± 50 kHz. Data was recorded for overtones 1–13 using the QSoft 401 software (v 2.5.8.527, Biolin Scientific). Baseline data of the sensor in air was recorded for approximately 120 seconds, followed by pipetting 100 μL of sample onto the sensor and data recording for an additional 300–420 seconds. Measurements were conducted at 20°C. The data was analysed using QTools software (v 3.012.518, Biolin Scientific). The Voigt model was applied to extract values for the solution zero-shear viscosity for overtones 5, 7, and 9. Three samples were measured for each formulation. Samples of SS and SS with added urea (SS-6U to SS-24U) were measured and compared with samples of the solvent (7% NaOH/12% urea/81% water) and solvent with the same portions of urea added (6–24%).

FTIR was carried out using a Bruker Vertex 70 spectrometer and OPUS operating software (Bruker Optics, Lower Hutt, New Zealand). The wavenumber range scanned was 4000–630 cm^{-1}; 128 scans of 4 cm^{-1} resolution were signal-averaged and stored. A mercury cadmium telluride (MCT) detector was used and cooled in liquid N$_2$. Attenuated total reflectance (ATR) mode was used and data recorded as an absorbance spectrum. Every measurement included 128 scans. Each sample was held inside a custom-made stainless steel chamber that was connected to a Watlow series 989 temperature controller (Watlow, Christchurch, New Zealand). The samples were heated from 25 to 85°C in 5°C intervals at
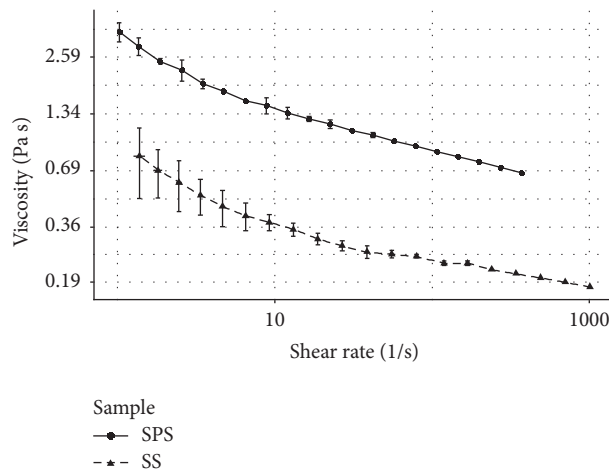

FIGURE 1: Comparison of the viscosity of unmodified SS and SPS solutions over a range of shear rates. $T = 1$°C.

a heating rate of approximately 10°C/min. The samples were allowed to stabilize for 60 seconds before a measurement was carried out. Thirteen additional measurements were taken at 85°C at three-minute intervals to assure a full sol-gel transition for all measured samples.

3. Results and Discussion

3.1. Differences between SS and SPS. Both SS and SPS showed strong shear thinning and SPS was significantly more viscous than SS at all shear rates (Figure 1). The presence of suspended particles will increase the viscosity of a solution because the solid particles increase friction as the solutions are sheared. Additionally, intermolecular interactions between suspended and dissolved cellulose will contribute to an increase in viscosity. These interactions will decrease the mobility of the cellulose chains in solution and lead to stronger and stiffer cellulose structures upon regeneration, such as hydrogels or films [24, 25].

3.2. The Effect of Added Urea on SS and SPS Viscosity. The effect of the amount of added urea was measured for SS and SPS solutions containing urea ranging from 0–30% for SS and 0–24 wt% for SPS. Values were compared for five ranges of applied shear (8-9, 55–57, 107–118, 240–270, and 340–370 s^{-1}). A clear linear reduction in the viscosity with urea content can be seen at all applied shear rates and for both types of solution, apart from SS-30U (Figure 2).

Urea is known to form crystals in aqueous solutions, if oversaturated [26, 27], and could be observed in samples containing added urea after prolonged storage times at subambient temperatures (~4°C). Crystal growth can spread through nuclei produced from small clusters of just 10–20 molecules [28]. It is therefore reasonable to surmise that some of the urea in the SS-30U sample had crystallized at low shear rates but was redissolved by the higher shear forces present at higher shear rates, leading to the observed reduction in viscosity with increasing shear rate. We therefore conclude that SS-30U had a urea concentration above the critical

SS

SPS

Shear rate range (s^{-1})

- 8-9   + 240–270
- ▲ 55–75   ⊠ 340–370
- ■ 107–118

(a)

Shear rate range (s^{-1})

- 8-9   + 240–270
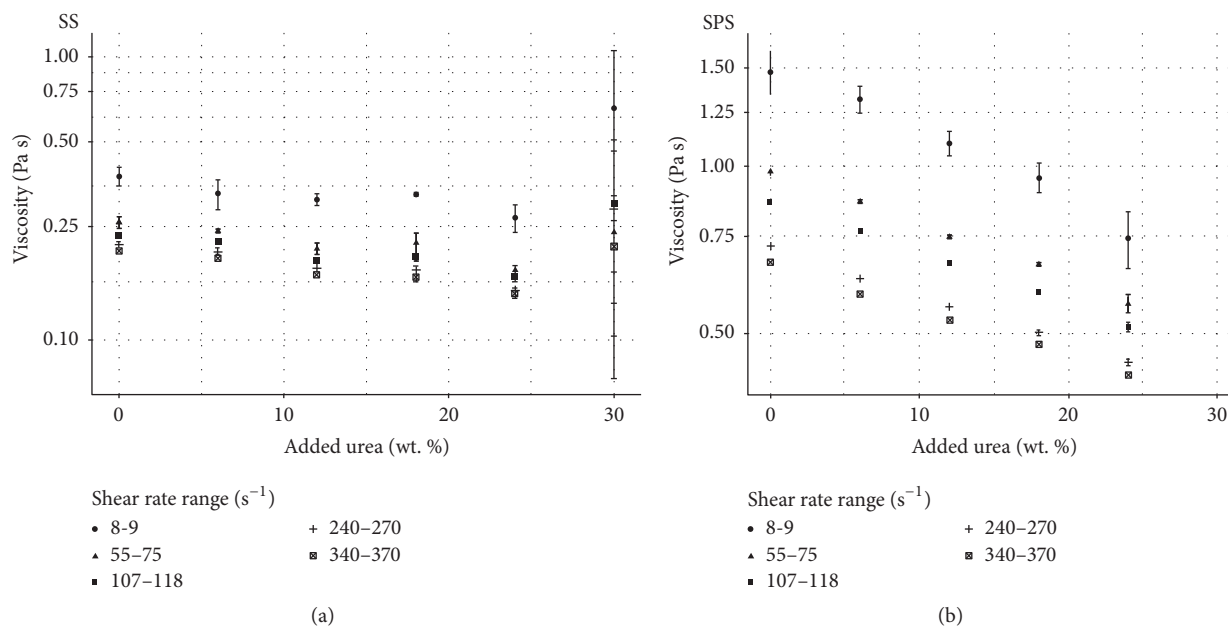- ▲ 55–75   ⊠ 340–370
- ■ 107–118

(b)

FIGURE 2: Measured viscosity of SS (a) and SPS (b) with added amounts of urea measured at different shear rates. A decrease in viscosity with increasing urea content was observed for all samples, at all tested shear rates, apart from SS-30U. $T = 1°$C.
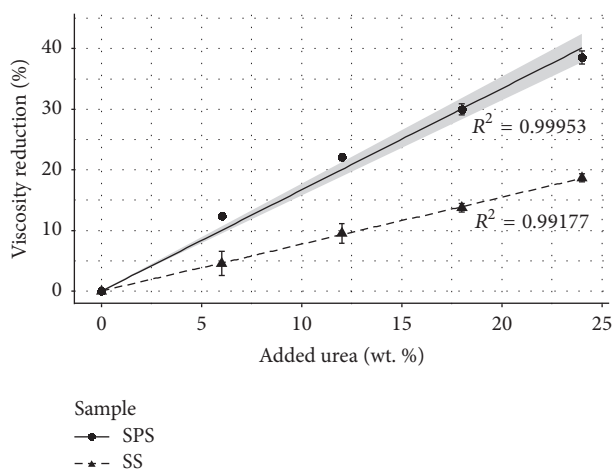

Sample
—●— SPS
- ▲ - SS

FIGURE 3: Reduction in viscosity of SS and SPS samples, shown at example of shear rates of 164 and 146 s^{-1}, respectively. A linear fit for each is also shown, with corresponding R^2 values at a confidence level of 95%, represented by the grey regions. $T = 1°$C.

concentration for the viscosity reduction effect of urea at low shear rates and temperatures.

Because the SS-30U appears to be oversaturated at 1°C, it was neglected in the analysis below. For all other tested samples, the viscosity reduction can be described by a simple linear fit. Regardless of the applied shear rate, the addition of urea decreased the viscosity of samples by up to 31% for SS and by up to 60% for SPS (Figure 3).

The magnitude of the effect of added urea viscosity indicates that urea directly interacts with cellulose. While the formation of the IC does minimize intermolecular cellulose

interactions, the "imperfect urea shell" still allows hydrogen bonds to form between cellulose chains at high cellulose concentrations, at increased temperatures, or during prolonged storage [12]. The increased urea concentrations in solution in our samples may have reduced the imperfections in the urea shell. As previously mentioned, urea is thought to accumulate on the hydrophobic regions of the cellulose, thus preventing its reassociation [10]. As observed by Song et al., not all of the urea in solution is involved in the formation of the IC but, rather, a fraction of it appears to exist in free form [13]. Therefore, part of the urea is present in solution as free hydrates, while the remaining urea is present as hydrates associated with the IC. The two forms of urea hydrate may exist in equilibrium with one another so that the presence of excess urea in solution will displace the equilibrium towards the inclusion of urea in the IC, thus strengthening the shielding of the cellulose chains.

The urea seems to have a significantly stronger effect on SPS than on SS. This difference may arise from the added urea effectively blocking interactions between the dissolved and suspended cellulose. Song et al. found indications that there is "limited or no interaction between urea and cellulose without dissolution," but shielding the dissolved cellulose should still reduce the cellulose-cellulose interactions [13]. There is also a possibility that the added urea helped to dissolve some of the suspended cellulose, although this is unlikely because the additional urea was mixed at 1°C (or higher) and cellulose is known to be most soluble in this solvent at −12°C [29].

The rheometric measurements were confirmed by QCM-D measurements. The addition of urea to the SS clearly had a viscosity reducing effect, while there was no change in solvent viscosity (Figure 4). The observed values were slightly higher than those recorded using the viscometer,
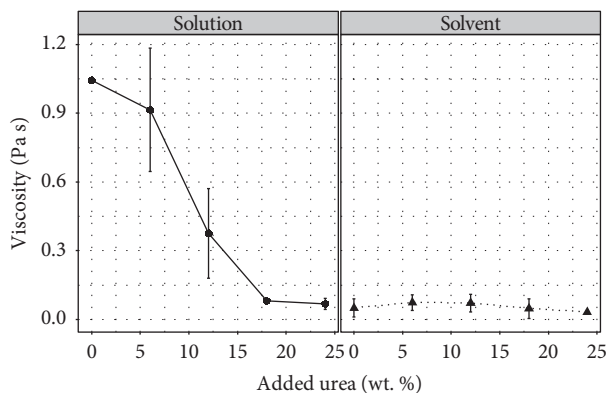
FIGURE 4: Modeled viscosity of SS compared with the solvent containing added amounts of urea, as determined by QCM-D. The viscosity of the cellulose solutions clearly decreased with urea addition, while there was no effect on the solvent viscosity. $T = 20°C$.

FIGURE 5: Effects of 30 wt% added urea on SS gelation and 24 wt% added urea on SPS gelation.

which seems counterintuitive, as one might expect a decrease in viscosity to accompany the higher temperature used during QCM-D experiments compared with that for the viscometer measurements. However, the values displayed in Figure 4 are merely a representation of the applied model calculating a *de facto* zero-shear viscosity and therefore can be considered reasonable.

However, the linear decrease in viscosity seen in Figure 3 is not apparent in Figure 4, and the viscosity values appear instead to plateau somewhere around 18 to 24% of added urea. As stated above, it is known that excess urea exists as free urea hydrates in cellulose solutions. We therefore assume that, without the influence of the physical shearing of the viscometer, the added urea formed urea hydrate clusters in the solution over time in the QCM-D, eventually leading to crystallization. The unstable system is represented by the high variation in calculated viscosity for 6 and 12% added urea. Viscosity reduction at higher urea concentrations (18 and 24%) under steady state was inhibited and the repulsion of individual cellulose chains was therefore not further reduced. The lack of physical stirring might also aid to explain the large observed deviations, as samples might show small inconsistency in urea distributions which can result in differences in measurements. Furthermore, QCM measurements can be sensitive to relative humidity and corresponding moisture uptake and release of the tested sample [30]. Since the measurements were conducted in an open cell module, it cannot be ruled that small changes in water content could contribute the deviation of the results.

3.3. Thermal Stability Testing. Increased solution stability is desirable for industrial applications, because Lu et al.'s and the authors' own (unpublished) observations show that cellulose in the NaOH-urea-water solvent begins to gel over time, even when stored below ambient temperature [12].

The effect of urea on the thermal stability of the two solutions was tested by ramping up the sample temperature in the rotational viscometer at a shear rate of $50\,\mathrm{s}^{-1}$ from 1°C until significant gelling occurred, represented by an increase
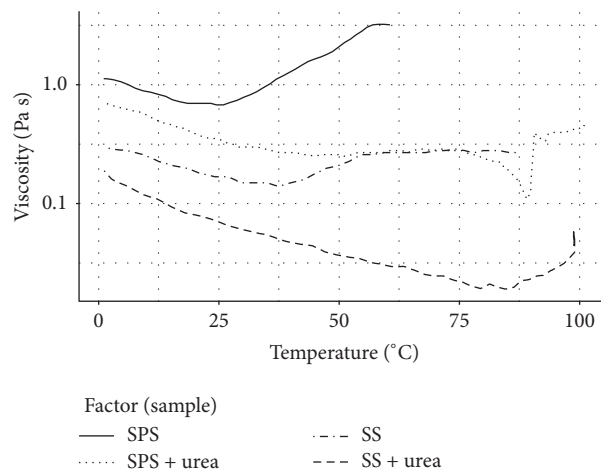
in viscosity. Both SS and SPS were tested, first unmodified and then with the highest used concentration of urea (30 wt% and 24 wt% added, resp.). The trend in viscosity with temperature presented in Figure 5 is consistent for all samples, with a marked initial viscosity reduction with temperature, followed by a viscosity increase at the gelation point. Based on these results, it is apparent that over a relatively short time frame, the viscosity reduction caused by increased temperature had a greater effect on the viscosity than early gelation at low to moderate temperatures, as expected for water based polymer solutions [31]. However, at moderate to high temperatures, formation of the hydrogel network dominated, resulting in an overall viscosity increase. Additionally, it can be hypothesized that greater amounts of urea are made available to stabilize the IC because the solvation of urea increases with temperature [27].

The QCM-D results for SS and SPS confirm earlier observations made based on the viscometer data that solutions with added urea are more stable and showed a reduced viscosity. Figure 5 clearly shows that while the viscosity increase caused by gelation was dominant from approximately 40°C for unmodified SS, the viscosity of SS-30U did not begin to increase until nearly 90°C. Also, SPS gelation began at 26°C, while gelation of SPS-24U did not become noticeable until the sample was heated over 55°C. This increased stability corresponds well with the results of Chang et al., who found that solutions with lower urea concentrations had reduced transparency and stability, as well as with the observations of Isobe et al., who found that the addition of urea leads to increased thermal stability of the solution [25, 32]. Both sets of results, viscometry and QCM-D, support the notion that urea decreases cellulose-cellulose interactions; yet it remains unclear if this occurs directly or indirectly [12, 13]. Regardless, the constant shear applied in our experiments during heating led to mechanical breakup of the gel, apparent from the gradual increase in viscosity with increasing temperature, in contrast to the expected rapid increase upon phase transition usually observed during temperature-induced gelation [33].
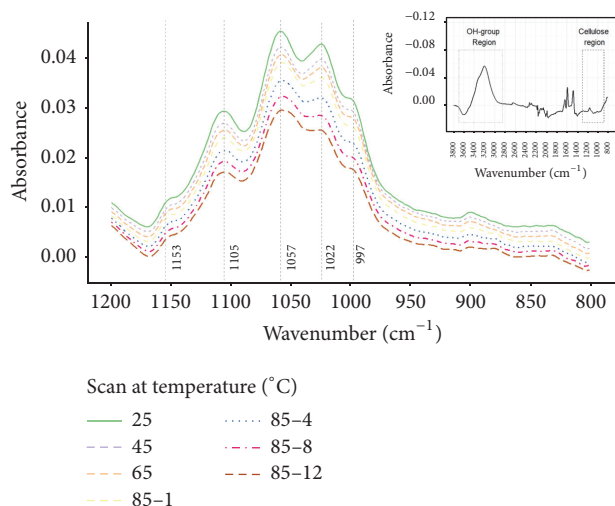
FIGURE 6: Spectral evolution of the cellulose absorptions in the fingerprint region for the gelling of SPS, shown for scans selected at different temperatures and different stages at 85°C. The background signal from NaOH/urea solvent without cellulose at the same experimental stage was subtracted. The spectra are offset by 0.001 absorbance units for clarity. Bands for relevant peaks are marked by vertical lines.

The applied shear also led to obvious wall-slip effects, shown in the SPS sample with added urea by a large drop in viscosity 85°C that was rapidly recovered.

3.4. FTIR Analysis. A direct observation of the molecular behaviour of the solutions was undertaken using FTIR to quantify the gelling behaviour during heating. The analysis of the solutions' spectra revealed distinct changes in the cellulose region ranging from 1200 to approximately $900 \, \text{cm}^{-1}$, that is, the fingerprint region where most of the vibrations of the bonds in the glucopyranoside rings of the cellulose molecules are present (Figure 6). In particular, peaks were apparent at 1153, 1105, 1057, 1022, and 997 cm^{-1}, corresponding to νCOC at the β-glycosidic linkage, ring stretching vibrations, νCC and νCO, respectively.

The absorbance of the characteristic peaks was calculated using a local baseline connecting the two adjacent valleys and normalized between 1 (beginning of experiment) and 0 (end of experiment) to facilitate comparisons between the different experimental conditions tested. The progress of the normalized absorbance during each experiment shows a clear decrease, indicating a clear conformational change in the cellulose bonds caused by gelation. As an example, the absorbance peak at 1057 cm^{-1} for the SPS samples at different urea concentrations displays different trends. A steeper decrease can be observed in the absence of added urea, and there was a delayed decrease when the urea concentration in the solution was increased, suggesting urea had a strong influence on gel formation (Figure 7). Similar qualitative behaviours were observed for the other absorbance trends at the other cellulose peaks (data not shown). Thus, we believe
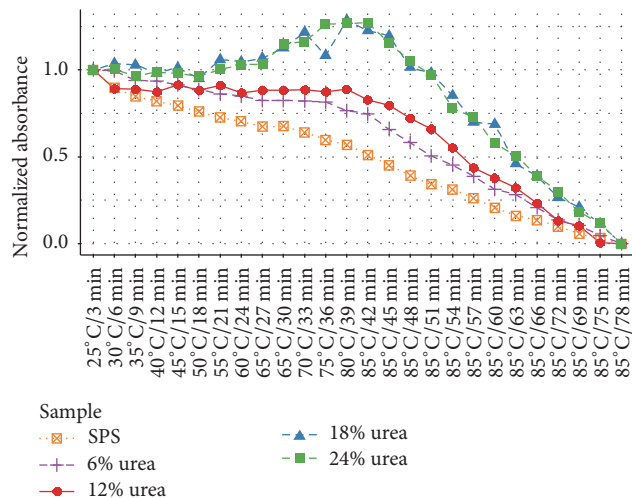

FIGURE 7: Trends in normalized absorbance for the 1057 cm^{-1} peak in the SPS experiments. The normalization was carried out to obtain 1 and 0 at the beginning and the end of the experiment, respectively.
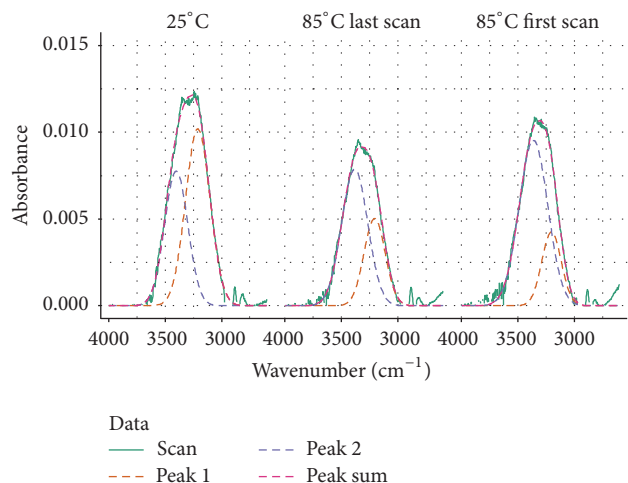

FIGURE 8: Absorbance profile in the OH stretching region during gelation of SS with 6% added urea. Background was SSb with 6% added urea at the same experimental stage. The dashed curves show the two Gaussian peaks used to deconvolute the OH peak of cellulose.

that a direct interaction between urea and cellulose does exist in the solution.

The analysis of the OH stretching region of the spectrum (3800–3000 cm^{-1}) also reveals that urea had a clear effect on the overall molecular interactions between solvent and cellulose governed by hydrogen-boding (Figure 8). It is worth noticing that the NaOH-urea-water solvent and the dissolved and the dispersed cellulose constitute a chemical environment extremely rich of OH groups, which in turn produce a varied array of hydrogen bonds. The multitude of stretching vibrations related to the OH groups will respond in concert to the temperature change and the gelation process, resulting in a complex IR spectrum. In an attempt to extract significant information from the νOH band, its spectral evolution was
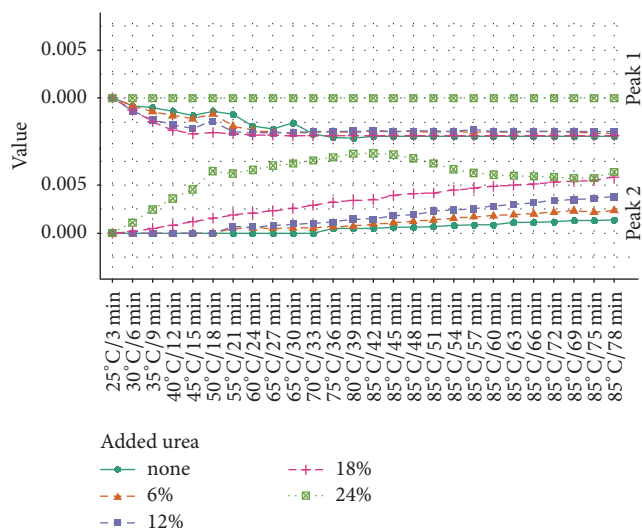
FIGURE 9: Trend in peak heights for the two Gaussian peaks used to deconvolute the absorbance profile in the OH stretching region for the SS samples at different urea concentrations. Peaks 1 and 2 are centred at 3205 and 3376 cm^{-1}, respectively.

deconvoluted using two Gaussian profiles centred at approximately 3205 and 3376 cm^{-1}, referred to below as Peak 1 and Peak 2, respectively. Further deconvolution was not felt necessary because of the inherent complexity of the spectrum, which would inevitably lead to an overfitting exercise with a number of peaks with questionable physical meaning. Interestingly, this region in the IR spectrum has been associated with the inter- and intramolecular bonding of cellulose chains [34–36]; therefore it must be also sensitive to changes in the hydrogen-bonding state of the cellulose molecules. This is particularly relevant during gelation, where a large structural rearrangement of the hydrogen bonds in the system takes place as the cellulose chains associate to form the hydrogel network. In particular, interchain hydrogen bonding and intrachain hydrogen bonding have been reported in the same region as Peak 1 and Peak 2, respectively [37, 38]. The development of the absorbance for the two Gaussian peaks showed two opposing trends. While Peak 2 increased in absorbance during gelation, the intensity of Peak 1 diminished.

When tracing Peaks 1 and 2 individually for the tested formulations, the influence of urea on their behaviour becomes obvious (Figure 9). Peak 1 shows a pronounced reduction in amplitude with increasing urea content and the rate of reduction in peak height becomes more marked as the urea content increases. The opposite trend is seen for Peak 2 (Figure 9) and the increase in Peak 2 height becomes more pronounced with increasing urea content. In a similar but mirrored fashion to Peak 1, the slope of the trend increased with urea content. In addition, lower concentrations of urea caused the onset of this peak to appear at later experimental stages. Overall, the data shows strong absorbance changes related to the νOH bonds, reflecting a lower propensity to form hydrogen bonds with vicinal chains and thus a stabilization of inter- and intramolecular bonding with increasing urea content. Based

on these results, a mode of action of urea on the gel formation and gel structure can be proposed and may help to explain how the added urea prevents gel formation upon heating. If intermolecular bonding is hampered, while intramolecular bonding is promoted, the cellulose chains will not be able to form a strong network with one another, and the resulting gel will become weaker with increasing urea content in the solution. As stated by Cai and Zhang, the cellulose chains are surrounded by the IC, preventing cellulose agglomeration, but the IC breaks down upon heating [11, 16]. We postulate that the additional urea helps to form less defective IC complexes, which surround the cellulose chains and act as a more efficient shield and thus prevent intermolecular bonding of the cellulose. The added urea raises the gelling temperature because more thermal energy is required to break the ICs surrounding the cellulose chains to enable the sol-gel transition.

4. Conclusions

Urea was shown to be an effective viscosity reducing agent for NaOH/urea-based cellulose solutions. For cellulose solutions containing added (suspended) cellulose powder, the viscosity reduction was more pronounced than when the same quantities of urea were added to the standard solution. Added urea can also partially suppress the gelation behaviour of those solutions at elevated temperatures and can increase the gelation point, essentially improving the solution stability.

FTIR analysis indicated that a direct interaction occurs between urea and cellulose for solutions containing excess urea. Urea may play two distinct roles, one stabilizing the inclusion complex and the other preventing hydrogen bond formation between neighbouring cellulose chains, explaining both the reduction in viscosity and the suppression of gelation.

Competing Interests

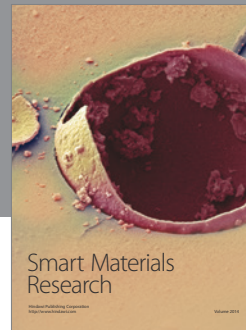The authors declare that they have no competing interests.

Acknowledgments

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