Cellulose gelation in NaOH solutions is due to cellulose crystallization.

Ana Pereira[‡], Hugo Duarte[±], Pegah Nosrati[φ], Marta Gubitosi[φ], Luigi Gentile[φ], Anabela Romano[‡], Bruno Medronho[‡, *] and Ulf Olsson[φ]

[‡]Faculty of Sciences and Technology (MeditBio), Ed. 8, University of Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

[φ]Division of Physical Chemistry, Department of Chemistry, Lund University, P.O. Box 124, 221 00 Lund, Sweden

[±]Department of Chemistry "Ugo Schiff", Università di Firenze & CSGI, Via della Lastruccia 31, 50019, Sesto Fiorentino, Firenze, Italy.

*Corresponding author: bfmedronho@ualg.pt

Abstract

Cellulose gelation in 2 M NaOH aqueous solution was followed by time resolved turbidity and rheology measurements. The kinetics of gelation is observed to change from several hours down to few seconds when the temperature is increased from 25 to 30 °C, consistent with earlier work. The increase of turbidity upon gelation demonstrates the formation of larger cellulose aggregates, while wide angle X-ray scattering data confirms the gradual formation of crystalline domains. This suggests that the gelation can be understood as cellulose precipitation/crystallization where an effectively cross linked network and gelation results from that cellulose chains may participate in more than one crystallite.

Keywords: cellulose; gelation; NaOH; crystallites, WAXS

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Introduction

Cellulose processing for new advanced materials is a rather challenging issue since dissolution is often an initial required step and far from being trivial [2-4]. The list of efficient solvent systems is limited, and current discussion is still not unanimous on the relevant solvent key features or interactions that drive dissolution [5-10]. Nevertheless, once dissolved, the cellulose solutions are typically metastable and thus sensitive to aging or pH and temperature changes, which may induce gelation-regeneration of the cellulose dopes [1, 11, 12]. Such gelation-regeneration phenomenon is not only interesting from a fundamental point of view but of major importance for the development of, for instance, cellulose-based films or fibers [13]. Among the solvent systems available, aqueous NaOH is a common solvent for cellulose dissolution particularly due to the fact that it is inexpensive and of low toxicity [14]. Recently, it was observed that microcrystalline Cellulose (MCC) can be dispersed in NaOH at concentration lower than 1 wt% and samples are stable for up to two months in room temperature. However, a fully molecularly dissolved state was not observed. [15]. Generally, the conditions for dissolution in NaOH(aq) must be rigorously controlled: dissolution occurs within a narrow temperature (i.e. sub-zero) and concentration (ca. 1.5-2.5 M) ranges [16]. The reason for this can be understood from the opposite dependences of the solubility on the NaOH concentration of neutral cellulose and its sodium salt [9].

It is well established that the cellulose solution stability is strongly temperature dependent. Roy et al., performed time resolved rheological measurements of the linear viscoelastic properties of cellulose solutions in 2.2 M NaOH(aq) in the temperature range 15-35 ºC [1]. It was found that the estimated gelation time, t_{gel}, obtained from the storage and loss moduli crossover, decreased essentially exponentially with increasing temperature. Nevertheless, the reason for such gelation was not clarified, and has since not yet been fully explained [1, 14]. Thus, in order better understand this gelation phenomenon on the molecular level, wide angle X-ray diffraction experiments at different temperatures that report on the association of cellulose molecules have been performed. In addition, time resolved turbidity data and rheology experiments are presented to further characterize the cellulose aggregation and characterize the gelation, respectively.

Material and methods

Materials. The microcrystalline cellulose, Avicel PH101, Lot: 61113C, Box 00083, was purchased from Sigma-Alrich. The sodium hydroxide, 97% pure, anhydrous pellets, was

purchased from Merck, Darmstadt, Germany. The water used was purified in-house using a MILLIPORE Milli-Q Gradient A10, Millipore, Molsheim, France.

Sample preparation. A solution of 2.0 M NaOH was prepared as stock solution by dissolving NaOH pellets in Milli-Q water. The stock solution was pre-cooled in an ice bath and microcrystalline cellulose (MCC) was then slowly added to the solution under vigorous stirring using a magnet stirrer. The dispersion was left to stir in the ice bath until becoming a semi-transparent, homogeneous dispersion (> 5 minutes). Afterwards, the solution was left in a freezer (-20 ºC) for 20 minutes. Once the sample had undergone the freezing step, it was thaw at room temperature by first letting it stir in an ice bath for 10 minutes followed by stir without any temperature control for an additional 20 minutes. After the final stirring, the samples were ready and kept at room temperature.

Wide-Angle X-ray Scattering (WAXS). Wide-angle X-ray scattering measurements were performed using the SAXSLab Ganesha 300XL instrument (SAXSLAB ApS, Skovlunde, Denmark), a pinhole collimated system equipped with a Genix 3D X-ray source (Xenocs SA, Sassenage, France). Data were collected with the detector placed at a sample-to-detector positions that yields to the WAXS region between 0.5 and 2.5 Å^{-1}. The sample was sealed in the capillary (1.5 mm diameter) and measured just after preparation and after 9 and 144 hours at 45 C. During the experiments the temperature was controlled by an external recirculating water bath with an accuracy of 0.2 ºC and fixed to 25 ºC. The two-dimensional (2D) scattering pattern was recorded using a 2D 300 k Pilatus detector (Dectris Ltd., Baden, Switzerland) and radially averaged using SAXSGui software to obtain I(q). The measured scattering curves were corrected for solvent scattering.

Rheology. Rheological measurements have been carried out using an Anton Paar Physica MCR 301 stress controlled rheometer (Anton Paar, Germany) with direct strain oscillation for real-time strain control equipped with a Couette cylinder geometry (cup diameter: 28.929mm, bob diameter: 26.673mm, bob length: 39.997mm). The temperature was controlled using a water circulator apparatus (±0.2 °C). To prevent evaporation, an appropriate solvent trap was used. All investigated samples were firstly loaded in the rheometer at 10 ºC since the gelation process is rather slow at low temperatures and subsequently the target temperature was settled to an higher value between 25 and 30 ºC.

Turbidity measurements. The absorbance of cellulose solutions was measured at 800, 825, and 850 nm on an UV/vis spectrometer (Specorde 200 Plus, Analytic Jena). None of the

chemical species in the solution show any absorption at these wavelengths. Hence, the measured absorbance is solely due to scattering and can be used to calculate the turbidity as $-(1/L)\ln(T)$, where T is the average transmission from the three wavelengths and L is the optical path length of the cuvette.

Results and Discussion

In the present work, the alkali system is revisited, and the influence of temperature on the gelation kinetics of 4 wt% cellulose in 2 M NaOH(aq) was studied by means of time-resolved dynamic experiments from 25 to 30 °C (Figure 1). As it can be observed in the insert of Figure 1, the sample initially behaves as a viscous fluid with the loss modulus G'' higher than the storage modulus *G'*. *G'* evolves much faster than *G''* until their crossover is observed (i.e. the gel point, t_{gel}, is defined as the time when *G' = G''*). It is striking that t_{gel} changes from several hours at room temperature to a couple of minutes for temperatures around 30 °C or above. The data in Figure 1 are very similar to the results of Roy *et al.,* who studied 5 wt. % cellulose in 2.2 M NaOH(aq) [1], and basically confirms their work.
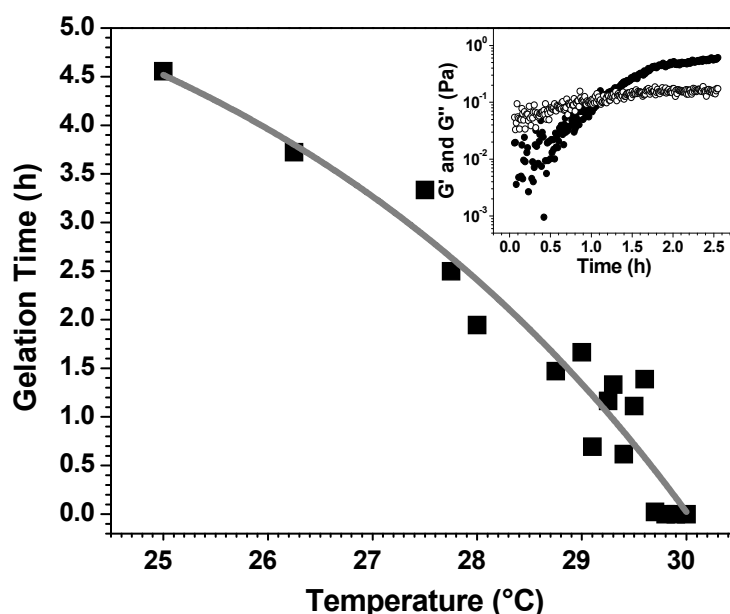

Figure 1: Gelation time, t_{gel}, of 4 wt% MCC in 2.0 M NaOH as a function of temperature. The solid line is a guide to the eyes. The inset shows an example of the time evolution of *G'* (full circles) and *G''* (empty circles) at 29.5 °C. Qualitative similar profiles are generally observed for all temperatures. The time-resolved oscillatory measurements were performed at a constant angular frequency of 1 rad/s and strain of 0.1% (within the linear viscoelastic regime).

Recent SAXS measurements have shown that cellulose aggregation increases with increasing temperature, as shown by an increased scattering intensity at lower q values [15]. Variations in light scattering can also be followed by turbidity experiments. In Figure 2a, a time resolved turbidity study is reported where the temperature was alternating between 25 and 45 °C, changing the temperature every 2 hours. As can be seen, the turbidity remains essentially constant when the temperature is 25 °C, while it increases with time at 45 °C. This shows that at 45 °C there is gradual increase in cellulose aggregation, but no such increase is observed at 25 °C on the time scale of 2 hours. The fact that the turbidity and the complex viscosity is retained when lowering the temperature from 45 to 25 °C indicates that the aggregation is irreversible and that at 25 °C the solutions are only kinetically stable.
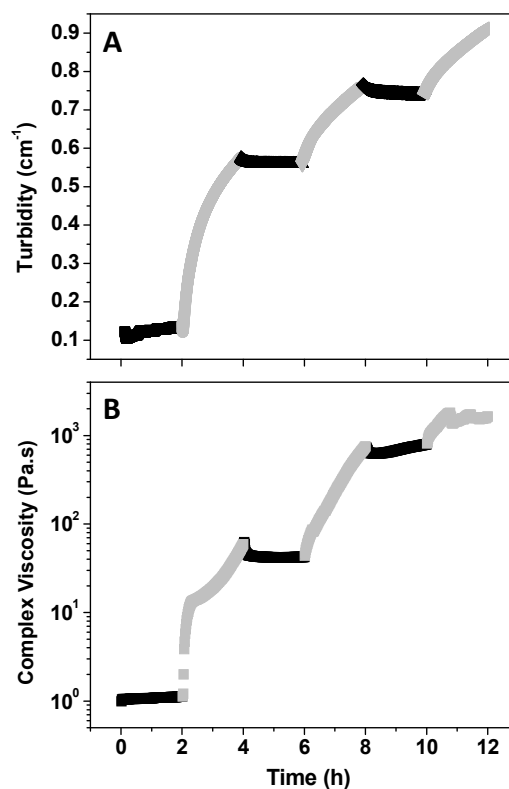

Figure 2: Alternating 25 °C (black symbols) and 45 °C (grey symbols) temperature experiments of turbidity (a) and complex viscosity (b) for 4 wt. % MCC in NaOH(aq). Samples were kept at 2 hours at each temperature before changing to the other temperature.

In Figure 2b, the time evolution of the complex viscosity, following the temperature cycling as in the turbidity experiments, is presented. As can be seen, the viscosity data essentially follow the turbidity data. At 45 °C the viscosity gradually increases with time while

it essentially remains constant when the temperature is 25 °C. The data in Figures 2a and 2b clearly demonstrate (i) the coupling between the sample viscosity and the aggregation state of cellulose, (ii) the irreversibility of the aggregation process, and (iii) the significant difference in aggregation kinetics between 25 and 45 °C. The irreversibility was also noted by Roy *et al.* [8].

The irreversibility is further illustrated in Figure 3. Here, the evolution of *G´* and *G"* are continuously monitored during a temperature ramp, at a constant heating rate (1 ºC/min) and angular frequency of 1 rad/s. During heating from 10 to 25 ºC, the sample behaves as a liquid-like solution with *G"* > *G´*. At about 26 ºC, *G´* and *G"*, cross and *G'* increases strongly with increasing temperature. When the temperature is reversed from 40 to 10 ºC only minor changes are observed in respect to the final stage at 40 ºC achieved with the first ramp test.
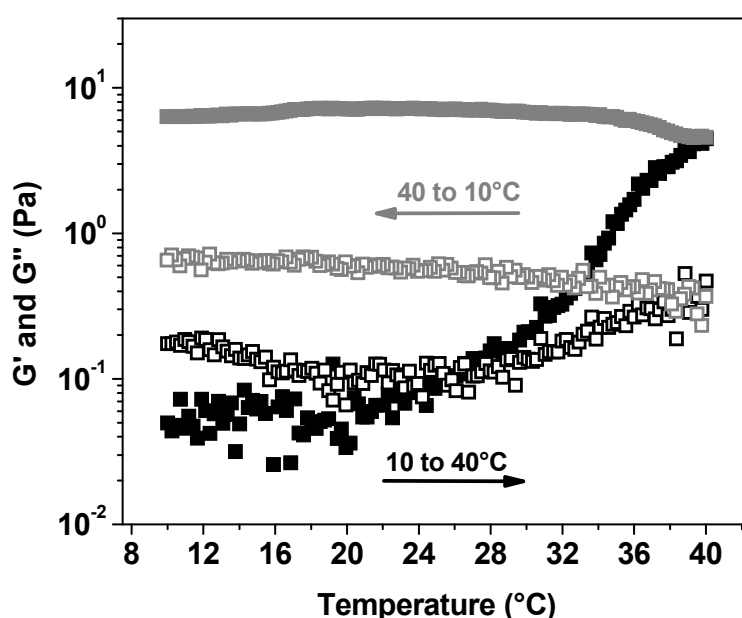

Figure 3: Temperature sweeps for 4 wt% MCC in NaOH(aq) from 10-40ºC (black squares) and from 40-10 ºC (grey squares). The elastic and viscous moduli are represented by the filled and empty symbols, respectively. The test was performed at a constant frequency of 1 rad/s and strain of 0.1%. The heating and cooling rates were kept constant at 1 °C/min. As can be seen, the 40 °C values are conserved as the sample is cooled back to 10 °C demonstrating that the gelation is irreversible.

To further characterize the aggregation of cellulose at elevated temperatures, a sample was stored at 45 °C and a wide angle X-ray scattering (WAXS) experiments was performed directly after preparation, and then also after 9 and 144 days. The solvent subtracted WAXS patterns

are presented in Figure 4a. As can be seen, there is a weak diffraction peak at q=1.4 Å^{-1} that grows in intensity with time. At longer times, a second peak at q=1.55 Å^{-1} is also observed. The observed diffraction we attribute to the precipitation of crystalline cellulose, presumably partly as sodium salt due to the high pH. The two reflections can be indexed to the 110 and 020 reflections of Na Cellulose IV crystals or Cellulose II [17]. The results are consistent with those of Isobe et al. who studied cellulose precipitation from alkali-urea solutions [12].

Precipitation of cellulose II has been recently suggested to occur in another strong alkaline system, 40 wt% tetrabutylammonium hydroxide [18]. Cellulose II is a more stable crystalline form compared to native Cellulose I and therefore dissolving Cellulose I (MCC) may result in a supersaturated state with respect to cellulose II that (slowly) precipitates. Thus, it is here suggested that the observed gelation is due to the precipitation and crystallization of cellulose. A cartoon on the hypothetical gel structure is shown in Figure 4b where cellulose chains may participate in more than one crystallite to form the 3D cross linked network. Polymer crystallization is a complex process, possibly involving multiple kinetically trapped states [19]. In the nucleation and growth process, the long chain molecules may belong in more than one crystallite. The crystallites may thus compete for the same molecule and, moreover, such crystallites can act as effective cross-linkers. Gelation is in fact a general feature of polymer crystallization. Gelation associated with polymer crystallization has been studied extensively for e.g. poly(vinyl alcohol), PVA[20-23].
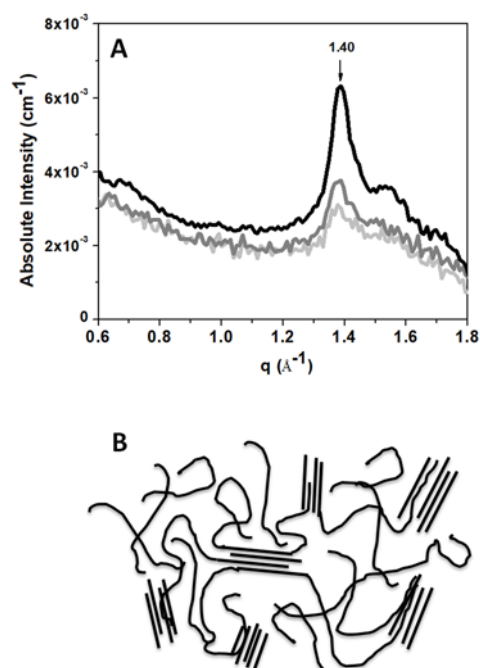

Figure 4: a) WAXS- patterns of freshly prepared (light grey line), aged for 9h (dark grey line) and aged 144h (black line) 4 wt.% of MCC in

NaOH(aq) solutions at 45 ºC. The arrow highlights the evolution of the main diffraction peak at q=1.4 Å^{-1}.b) Carton illustrating the gel structure obtained from the cellulose crosslinking where the crystallites are suggested to work as junctions points.

Conclusions

Cellulose gelation in 2M NaOH(aq) has been studied by time resolved rheology, turbidity and wide angle X-ray scattering. In agreement with Roy et al. [1], we find that the gelation kinetics is strongly temperature dependent, increasing rapidly with increasing temperature. Wide angle X-ray scattering data reveals the formation of crystalline domains, as the sample gels, and we conclude that the gelation in fact is due to the crystallization and precipitation of cellulose. We also note that this kind of gelation is a common feature of polymer crystallization from solution.

Acknowledgments

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