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Cellulose dissolution and gelation in NaOH(aq) under controlled CO₂ atmosphere: supramolecular structure and flow properties†

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We investigate the interplay between cellulose crystallization and aggregation with interfibrillar interactions, shear forces, and the local changes in the medium's acidity. The latter is affected by the CO₂ chemisorbed from the surrounding atmosphere, which, combined with shear forces, explain cellulose gelation. Herein, rheology, nuclear magnetic resonance (NMR), small and wide-angle X-ray scattering (SAXS/WAXS), and focused ion beam scanning electron microscopy (FIB-SEM) are combined to unveil the fundamental factors that limit cellulose gelation and maximize its dissolution in NaOH(aq). The obtained solutions are then proposed for developing green and environmentally friendly cellulose-based materials.

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Introduction

The forest products industries are exploring new dissolution and regeneration technologies to achieve high-performance materials with minimal environmental impacts.^{1,2} Industrially, four leading technologies have been used to dissolve cellulose. They include the Viscose and Lyocell methods, which are chemically intensive and present some environmental drawbacks.^{3,4} In this context, new generation Ionic Liquids (ILs) have gained importance and are expected to reach commercial adoption.^{5,6} Other solvent systems include aqueous solutions, such as Bemberg or cuprammonium hydroxide,⁷ and aqueous NaOH, already used in the mercerization process.^{3,4} The latter emerged in 1934 when NaOH(aq) solutions were used to dissolve cellulose in a narrow window of conditions,^{8–10} eventually becoming attractive for cellulose regeneration due to the associated low environmental impact

and cost.^{4,11,12} The dissolution of cellulose in sodium hydroxide solution has been associated with the interactions and hydrogen-bond disruption enabled by sodium and hydroxyl hydrated ions.^{13–16} Such phenomena occur at low temperatures (<−5 °C)^{8–10} and can be enhanced by freezing and thawing.¹⁷ However, sub-zero temperatures are required to improve dissolution and stability. Unfortunately, early gelation has so far inhibited alkali dissolution for large-scale adoption.^{11,14}

Several routes have been proposed to enhance NaOH(aq) solvent dissolution capacity and stability. A recent example includes endoglucanases that hydrolyze cellulose and disrupt the intermolecular hydrogen-bonds, as shown in the BiocelsoTM process.^{4,11,18} The latter includes two additional aspects to improve the solubility and stability of the solution: (1) addition of ZnO, following the work of Davidson *et al.* in 1937 and, (2) freezing (−20 °C) and thawing.^{9,17} Other studies have reported urea and thiourea additives to improve solution stability (several days at room temperature).^{18–28} Recently, Liu *et al.*¹⁵ demonstrated, through molecular dynamic simulations, that urea's dissolving ability is mainly due to the high number density and hydrogen bonding of the molecules around the acetal oxygen atoms of cellulose (O1 and O5), preventing re-aggregation and extending solution stability. Other alternative solvent additives have been proposed,^{14,29} including amphiphilic polymers such as polyethylene glycol (PEG). Yan and Gao³⁰ reported the dissolution of cellulose cotton linters at concentrations up to 13 wt% by using a NaOH(aq) (9 wt%) with 1 wt% PEG-2000. PEG amphiphilicity allowed interactions with the hydrophilic groups of cellulose, screening hydrophobic interactions and leading to cellulose chain entanglement in the aqueous system. The role of hydrophobic interactions has been discussed by Medronho *et al.*,³¹ who used an

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amphiphilic betaine derivative to delay gelation and increase the low critical dissolution temperature, as observed in aqueous NaOH solution.³² However, these types of additives are known to negatively impact the mechanical performance of regenerated cellulose due to the formation of porous structures derived from cellulose instability at the low pH of acid regeneration.^{4,14,30}

To address the need for hydrophobic moieties and to allow for improved processing with aqueous NaOH, the 'hydrophobic effect'³³ is expected to contribute to the gelation of the cellulose–NaOH–H₂O system. Indeed, Sobue *et al.*³² have charted the phase behavior of cellulose under different compositions. Just above the critical –5 °C dissolution/swelling temperature, cellulose is converted from cellulose I to 'Na-Cell-IV' (a hydrated form of cellulose II),^{34,35} allowing for regeneration as a cellulose II polymorph – an overall conversion from parallel to antiparallel chain orientation. Under the critical temperature, where the mixture is in a swollen or solution state, some interactions involving the hydrophobic surfaces of cellulose may lead to eventual antiparallel orientation, affecting the rheology. Thus, incorporating hydrophobic moieties, such as those in polyethylene glycol (PEG), is expected to reduce entanglement and lead to gelation *via* stabilization of the 'hydrophobic' surfaces. While this hypothesis is a reasonable one, one should consider that there may be a combination of other factors at play, both physical and chemical.

The present work introduces an approach to control the physicochemical environment used during cellulose dissolution, considering the freeze/thawing steps. We show the possibility of remarkably enhancing the dissolution of cellulose (tested here with microcrystalline cellulose) in an aqueous alkali solution at a high solids concentration, as high as 12 wt%.

In a CO₂(g)-free atmosphere, the capacity of dissolved cellulose to absorb CO₂ from the surrounding air is increased.^{36,37} Herein, we demonstrate that atmospheric conditions have a critical effect on the rheological behavior of cellulose solutions, a subject that has not been discussed so far. Furthermore, the crystallization and subsequent agglomeration, as evidenced by SAXS/WAXS, are shown to result from the molecular species formed during CO₂(g) chemisorption (NMR and computational methods). Thus, this study reveals fundamental aspects that expand the possibility of NaOH-based systems for cellulose dissolution and regeneration at relevant scales, for instance, in fiber spinning.³⁸

Results and discussion

We first realize the challenges in cellulose dissolution and regeneration due to the instabilities imposed by early gelation or polymer 'jamming' under alkaline conditions.¹⁴ As such, we dissolve cellulose in a CO₂(g)-depleted atmosphere followed by freezing and thawing under centrifugal forces (Fig. S1†). The dissolution and enhanced flow behavior are then confirmed by optical microscopy and rheometry (Fig. 1).

The elastic moduli (G') of the samples (7, 9, and 12 wt% concentration) obtained after thawing are displayed in Fig. 1a, including optical microscopy images taken before and after thawing under centrifugal forces. As observed, the maximum elastic moduli measured at high frequency of cellulose solutions (12% and 9% concentration) plateau at $G' = 1 \times 10^4$ Pa, indicating a gelled system. Moreover, with the increased concentration, the system reached terminal values of elastic modulus, complex and dynamic viscosities (Fig. S2†). The optical images (Fig. 1a) confirm a dissolved gel state at 12 wt% cellulose concentration, indicating a dissolution limit. Furthermore, a 13 wt% cellulose concentration undergoes gelling during dissolution (Fig. S3a†), with additional undissolved cellulose fibers. After freezing and thawing, the amount of undissolved fibers decreases marginally, and the system remains gelled (see Fig. S3b†).

The gelation of alkali-dissolved cellulose has been discussed,³⁹ and time and temperature have been shown to influence molecular entanglement and crystallization.^{16,39}

In this study, the kinetics of cellulose gelation below the linear viscoelastic region was followed by microscopy and rheology (Fig. 1b and S4†) and a master curve for a system with 7 wt% cellulose subjected to 1% strain (10 rad s⁻¹) showed an exponential dependence between the time to gelation (t , min) and temperature (T , °C):³⁹

$$t = 1053 e^{\frac{-T}{8}} \quad (1)$$

Eqn (1) was used to predict the gelation time under the tested conditions. For instance, gelation at 25 °C occurred in ~1 h. Simultaneously, the apparent viscosity was reduced with temperature, accelerating the gelation process. Fig. 1c shows a non-gelated sample that underwent a sudden increase in viscosity at high temperatures (>40 °C) at the onset of gelation. We note that other factors besides time and temperature affect the gelation. This includes the freeze-thawing process,^{9,17} herein enhanced by centrifugation in a planetary movement (Fig. S1 and S5†).

Frozen samples thawed under centrifugal force at room temperature were less viscous than those thawed at rest for *ca.* 5 h (Fig. S5†). Shortening the thawing time delayed gelation, and, consequently, the dissolution capacity was improved after freezing and rapid thawing, as shown by microscopy imaging, Fig. 1a.

The cellulose system was subjected to high shear during centrifugation, eventually aligning cellulose fibrils.^{40–42} The cellulose system under high shear demonstrated shear thinning and birefringence (Fig. 1d), implying uniform and less entangled cellulose chains, impacting gelation stability. Fig. S6† shows that the initial liquid structure of a cellulose suspension is disturbed at high frequencies, recovering a liquid-like behavior (loss modulus, $G'' >$ elastic modulus, G').

The observed effects related to shear strain and oscillatory frequency are ascribed to the occurrence of a pre-gelation stage where interfibrillar interactions start to take place. Therefore, applying high shear stress at high frequency allows



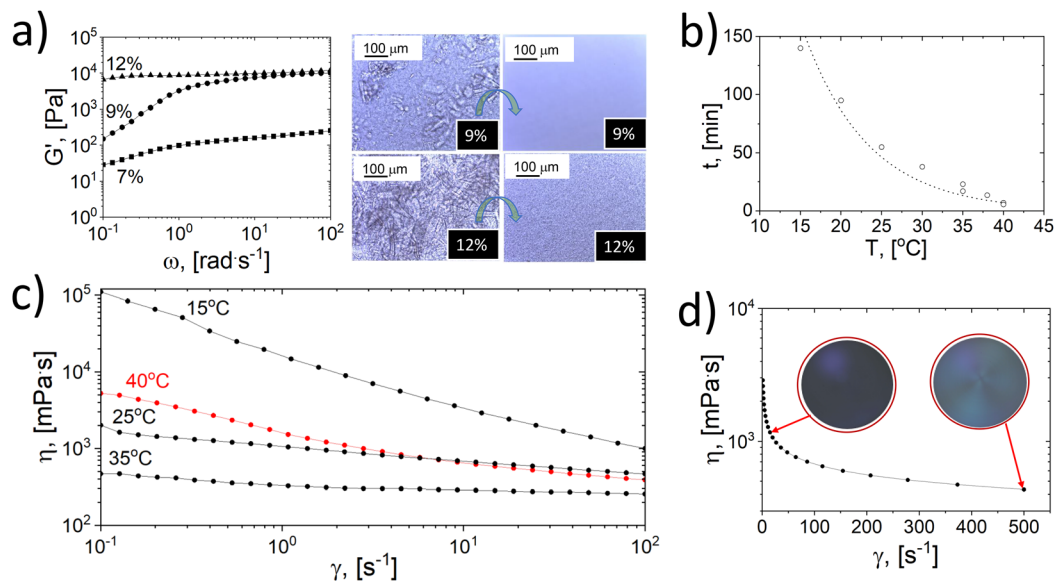


Fig. 1 Gelation and flow properties of cellulose dissolved in NaOH(aq). (a) Effect of concentration on the elastic modulus and the corresponding microscope images before and after centrifugal thawing, the transition is indicated by the green arrow. (b) Master plot (gelation time), (c) viscosity and (d) shear thinning and birefringence (insets) of a cellulose solution at 7 wt% concentration.

the recovery of a liquid-like behavior, destroying the metastable interactions before complete gelation. Hence, time, temperature, and flow forces are essential in gelation phenomena. Importantly, thawing in an open atmosphere led to solutions with a higher viscosity than those thawed in an air-tight environment (Fig. S5[†]). Rapid thawing in open-air conditions significantly affected the gelation process. This is related to the fact that cellulose dissolved in alkali absorbs and reacts with CO₂(g),^{37,43–45} a subject that has not been widely acknowledged in relation to the gelation process. Fig. 2a indicates that

contact of a solution with air during the gelation process (5 days) accelerated the entanglement of cellulose fibrils, increasing the elastic modulus by two orders of magnitude compared to samples prepared in air-tight conditions at room temperature.

The CO₂(g) absorbed in the gelled sample was identified by Raman spectroscopy (see ESI[†]). Fig. 2b includes the main Raman shift band at 1064 cm⁻¹ attributed to the non-degenerated symmetric stretching vibrational mode of carbonate (CO₃)²⁻ ions.^{46–49} It is clear that the band intensity depended on the absorbed CO₂(g). We noted that an aqueous cellulose solution (7 wt% concentration) absorbed up to 17 mgCO₂ per g_{solution} until gelation (see ESI[†]), and exhibited the highest Raman intensity (blue line, Fig. 2b). By contrast, an air-tight sample did not show a Raman signal at this frequency (black line, Fig. 2b).

A sample saturated with CO₂(g) formed a solid-like structured gel (Fig. S7[†]), becoming a rigid solid, which prevented any attempt to assess the flow properties. Moreover, fresh cellulose samples (7 wt%) prepared under conditions to achieve lower CO₂(g) absorption from air, for instance set to 8.2 mgCO₂ per g_{solution} (half the saturation value) were compared after gelation for 12 h in inert and open atmospheres (Fig. 2c and S8[†]). Compared to the samples prepared in sealed containers (12 h, 23 °C), the above gelled systems (12 h, 23 °C, 8.2 mgCO₂ per g_{solution}) showed one and two orders of magnitude higher viscosity, respectively. The elastic modulus revealed that the samples prepared in open-air and with added CO₂(g) formed a stable gel. By contrast, the samples produced in the air-tight container formed a metastable gel with a reversible structure and a liquid-like behavior at high frequency ($\omega > 10$ rad s⁻¹, Fig. S8[†]).

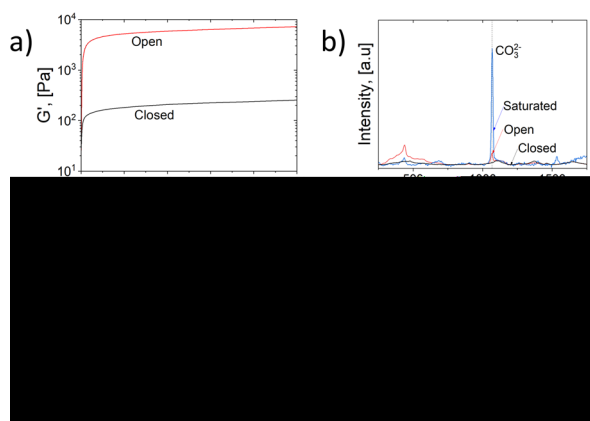


Fig. 2 Gelation of dissolved cellulose during CO₂(g) absorption at 7 wt% cellulose concentration: (a) effect on elastic modulus during contact with open atmosphere at room conditions during five days. (b) Raman identification of carbonate ions formed in the cellulose dissolution samples during gelation in open atmosphere. (c) Effect on viscosity of CO₂(g) absorption compared to gelled samples (12 h, room conditions). (d) CO₂(g) absorption capacity of alkali-dissolved cellulose.



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The formulation of aqueous alkali solvents for cellulose has included the addition of urea/thiourea, which affect the dissolution capacity and temperature/time stability through the formation of urea/thiourea hydroxyl complexes.^{24,25,66} Such molecules might also offer a buffering effect that influences the CO₂(g) absorbed from the atmosphere.

In summary, the holding time, used as a variable to follow the gelation process, is related to the hydrophobic interchain interactions that promote cellulose's crystallization and gelation.¹⁶ Furthermore, according to the present results, a significant contribution to gelation can be assigned to media acidification by CO₂ chemisorption – leading to increased interchain interactions.³⁷ In this case, the shear forces appeared to facilitate the processability of the cellulose system.

Conclusions

The present study reveals that adjusting time-dependent variables (CO₂(g) chemisorption, ionic environment, temperature, and hydrophobic interactions) and processing shear forces allows an elegant control over the gelation phenomena, giving access to the production of cellulose solutions with a wide range of rheological properties, suitable for the preparation of different regenerated cellulose materials.

The present study advances the understanding of cellulose dissolution in alkali media. Further examination is needed to gain a fundamental understanding of the involved interactions and mechanisms.

Author contributions

G. Reyes designed the study, conceived, and drafted the article. A. W. T. King and T. V. Koso performed the NMR experiments and performed the analysis of experimental data. P. A. Penttilä performed the analysis of the WAXS/SAXS experimental data. A. W. T. King carried out the computations and their interpretation. H. Kosonen and O. J. Rojas financed, co-supervised the research, discussed and proofread the manuscript. All authors contributed to writing the manuscript, and all authors read and approved the final version of the manuscript for submission.

Conflicts of interest

There are no conflicts to declare.

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