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Mercerisation of cellulose in aqueous NaOH at low concentrations

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In this study, mercerisation of native cellulose I was achieved in an aqueous sodium hydroxide solution at a concentration of only 1 wt.% NaOH by processing at temperatures below 0°C. This represents a tenfold reduction in the use of NaOH to accomplish this very common transformation. The cellulose sample was a form of hydrolysed cotton with a high crystallinity. The samples were mixed with aqueous sodium hydroxide at various concentrations and stored at -17°C. The samples were then defrosted, neutralised and dried before being analysed by Fourier-transform infrared spectroscopy, wide-angle X-ray diffraction and field-emission scanning electron microscopy. In the route described here, transformation from cellulose I to cellulose II was possible without greatly affecting the crystallinity or the microstructure of the samples.

Introduction

There are two main processes to convert cellulose I to cellulose II: dissolution followed by precipitation and mercerisation. Mercerisation is commonly accomplished by immersing the solid cellulose in sodium hydroxide solutions with or without mechanical tension. This process originally devised by John Mercer in the first half of the 19th century is used in the textile industry in order to help natural fibres gain luster, dyeability and strength. It is also used as an "activation" step prior to the preparation of many commercial products such as cellulose derivatives, regenerated fibres or foams.[1] Additionally, this process is extensively used in research laboratories to produce model cellulose II samples. When cellulose interacts with NaOH at high concentrations, it swells as Na^+ cations penetrate its intracrystalline spaces. As a result, native cellulose, either the one chain triclinic cellulose I_α or the two chain monoclinic cellulose I_β, is transformed to cellulose II. Cellulose II is a two chain monoclinic allomorph. Whereas cellulose I has a parallel chain arrangement, cellulose II has an antiparallel one and the change is irreversible.[2–6] The precise description of this surprising solid-state parallel to antiparallel switch is still under discussion.[3,4,7] An hypothesis relying on close-packed microfibrils of opposed polarity has however emerged in the literature.[8–10] According to this assumption, the alkali-swollen cellulose chains would be progressively liberated from the surface of the microfibrils; they would then be free to comingle and interdigitate in an antiparallel fashion to form cellulose II. However, it is well-known that accessible non-crystalline cellulose chains are also located in the so-called longitudinal amorphous regions.[7,11–13] These regions are never accounted for in the mercerisation models found in the literature, nor does molecular weight reduction.

Independently, it was also demonstrated by fibre diffraction techniques that the transformation occurs through the formation of up to five different Na-cellulose complexes: Na cellulose I, IIa, IIb, III and IV.[3,8,14–16] The four chain monoclinic Na-cellulose I complex is a common intermediary. It is the first allomorph formed when cellulose is exposed to aqueous sodium hydroxide at moderate concentrations (below *ca.* 20 wt.%). In this complex, the sodium cations remain near the surface of the cellulose sheets and they form strong polar bonds with the O(2) and O(6) oxygens, which are known to strongly contribute the intrasheet hydrogen bonds in cellulose I_β.[3,17] I As a result, the cellulose chains are pushed away from their intrasheet neighbours by the intercalated Na^+ ions. The transformation from cellulose I to Na-cellulose I can be monitored by X-ray diffraction. It is usually reflected by a shift from the (200) plane from a distance of 3.9 Å to a distance of 4.4 Å along with a crystallite thinning.[18] The C(1), C(4) and C(6) peaks on the ^{13}C solid-state NMR signal become sharper and unique. This result indicates that the chains are all in a fast interconverting liquid-like conformation as opposed to them belonging to intra-crystalline, surface or amorphous regions in unreacted cellulose.[17,19] However, the chemical shifts of all peaks are distinct from those of cellulose in solution, signifying weak intramolecular hydrogen bonds and confirming Na^+ coordination to the hydroxyl groups at C(2), C(3) and C(6).[17] The last allomorph formed in the course of the transformation is Na-cellulose IV.[3] This one is obtained by washing Na-cellulose I from sodium hydroxide with water or an alcohol and it is the last step before conversion to cellulose II. It has a two chain unit cell with an antiparallel chain conformation and it comprises two intrasheet water molecules which take part in four hydrogen bonds.[3] Its drying results in the stable cellulose II allomorph. In that sense, it is appropriate to call it a cellulose II hydrate.[1,3,14,20] Upon dehydration, the $(1\,\bar{1}\,0)$ peak of Na-cellulose IV shifts from 8.45 to 7.33 Å, whereas the (110) and (020) peaks remain unchanged at 4.4 and 4.0 Å.[20] Consequently, it was assumed that the water molecules in Na-cellulose IV are located between the stacking sheets and that cellulose II crystallization is driven by the stacking of the chains in the direction orthogonal to their hydrophobic surfaces.[4,20]

Mercerisation is strongly dependent on process parameters. It is generally agreed that the NaOH concentration in solution needs to be sufficiently high and exceed 7-8 wt.% for the conversion to be succesful.[11,14,18,21,22] However, water sorption measurements showed that NaOH probably starts interacting with cellulose at concentrations between 5-7 wt.%, depending on the cellulose source and at temperatures near 0°C.[11,22] Mercerisation has also been shown to start at concentrations as low as 6-6.5 wt% for wood celluloses and 8-8.5 wt.% for cotton celluloses, and the completion of the allomorphic swap was also shown to depend strongly on the origin of the substrate.[11,22] Interestingly, it was stated early by Staudinger that NaOH at low temperatures could dissolve cellulose. This dissolution is effective in a narrow temperature-concentration window, the so-called Q-region.[15,17,23] This dissolution process has attracted considerable research interest in the last three decades and it can be used to produce regenerated cellulose products such as textile fibres or sponges.[17,24–26] In fact, a 9.1 wt.% NaOH solution at 4°C can completely solubilise steam exploded wood pulp, and several cellulose sources are dissolved at NaOH concentrations between 8 and 9 wt.% at -20°C.[17,25,27] It was shown that the solubility of cellulose at 4°C is indeed maximum for NaOH concentrations near 10 wt.% and that this solubility decreases steadily with increasing cellulose molecular weight or cellulose concentration in suspension.[17,25,28] Other parameters such as the substrate microstructure, crystallinity, crystalline form, degree of breakdown of the O(3) intramolecular hydrogen bonds, as well as traces of cell wall polysaccharides play a role on the solubility.[17,25,29,30] The temperature is of course a key parameter and solubility decreases with increasing temperatures at positive temperatures.

Several explanations purported to the easy solubility of certain sources have been proposed. As stated above, cellulose can be swollen by the intercalation of Na^+ cations. However, dissolution requires the breakage of intermolecular hydrogen bonds. Cellulose in solution is stabilized by the secondary hydration shell of the Na^+ cations and OH^- anions, and the temperature, size of the cation and its number of hydration shells matter.[17,31] The solubility of cellulose at these temperature could be correlated to the dramatic density distribution change of the large $Na^+(H_2O)_{100}$ clusters at a temperature in the -10°C to 0°C range when compared to higher temperatures, a density drop corresponding to a change of physico-chemical properties.[32] Intramolecular hydrogen bond patterns at O(3) and O(6) can also help explain the solubility difference between cellulose I and II.[17]

In the present work, a presently unexplored concentration-temperature window for mercerisation was examined. This window is in the vicinity of the so-called Q-region but at concentrations that are too low to allow for dissolution. The allomorphic changes were measured using Fourier-transform infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (WAXD). The microstructural changes were visualised using field emission scanning electron microscopy (FE-SEM).

Materials and methods

Materials

Whatman #1 filter paper was used as a cellulose source. These filter papers are made of hydrolysed cotton linters and denoted as “cotton” hereinafter. NaOH pellets (VWR, purity > 99%) were used as received. Filtration was performed over Whatman nylon membranes with 0.45 μm pore size. Distilled water and NaOH were mixed under stirring at room temperature for at least 30 min in proportions of 0.25, 0.5, 1, 2 and 3 wt.% in order to prepare 100 g of solution. One gram of filter paper was then added to the solution and stirred for 1 h with a magnetic stirrer in order to produce a homogeneous suspension. The suspensions were then placed overnight in a freezer at -17°C. They were then left to thaw until they reached room temperature. The treated fibres were filtered over nylon membranes, mixed with 300 ml of water, stirred for a minimum of 2 h and filtered again. The filtration procedure was carried out three times in total, which was found sufficient to reach a neutral pH.

Fourier transform infrared spectroscopy

FTIR measurements were done directly on the air-dried fibre mats with the help of a diamond attenuated total reflectance accessory on a Perkin Elmer Frontier spectrometer. The data was averaged over 16 runs with a resolution of 2 cm^{-1} in the 4000-650 cm^{-1} region and at least three measurements were performed for each sample. Calculations of the total crystallinity index (TCI) was performed from the ratio of the absorption peaks 1372/2900 cm^{-1}.[33,34] The strongest band of the three bands at 2900 cm^{-1} was chosen. All spectra were normalized and averaged from three spectra with the optical spectroscopy software Spekwin32 (F. Menges, Version 1.71.6.1, 2012, http://www.effemm2.de/spekwin/). The classical least square method (CLSM) was also used in order to quantify the extent of transformation from cellulose I to cellulose II depending on the amount of NaOH in solution. As a hypothesis, FP was taken as the cellulose I spectrum, while the sample treated with 3% NaOH was taken as the ideal cellulose II source. Principal component analysis (PCA) was conducted using the Factor 9.2 software using the promin rotation method.[35] The contribution from 4402 participants in the 3800-2650 cm^{-1} and 1700-650 cm^{-1} range was considered and 6 variables were taken into account. The data in the 2650-1700 cm^{-1} wavelength range was discarded since it was only contributing as noise. The components of the rotated loading matrix are reported.

Wide-angle X-ray diffraction

WAXD was performed in transmission on a Pan'alytical X'pert powder diffractometer equipped with a CoKα anode (λ = 1.7903 Å) powered at 40 kV and 40 mA. Programmable anti-scatter slits had a fixed aperture of ¼° whereas the anti-diffusion slits had an aperture of ½°. A 10 mm mask was selected. The detector was a linear Pix'cel 1D detector equipped with 0.04 rad Soller slits. The scan was performed in the 10-50° range in steps of 0.0525°. About 0.3-0.4g of cellulose were compacted in a mortar and pestle in order to reach a satisfying density. The specimens were stacked between two kapton foils. The extent of transformation was also characterised using the CLSM using the same hypothesis as used for the FTIR analysis.

Crystallinity and crystallite width were assessed for the raw materials and for the materials devoid of cellulose I ($c \geq 1$ wt.%) using a peak-fitting procedure similar to the Ruland-Vonk method.[36,37] The Fityk software was used.[38] The routine consisted in normalising the spectra, removing a background, and fitting Pearson VII functions to the more prominent peaks according to admitted crystallographic structures of cellulose I_β and cellulose II.[6,39,40] The crystallinity was calculated as the total peak area. The peak width at half maximum was used to calculate the crystallite width using Scherrer equation in a manner similar to previous works.[36,41] This method is polymer independent and it has the advantage of permitting a straight comparison between the crystallinities of cellulose I and cellulose II.

Field emission scanning electron microscopy

FE-SEM was performed with a field-emission scanning electron microscope Hitachi S-3000N at a partial vacuum of 30 Pa and with an acceleration voltage of 15 kV. The samples were glued on the sample holder using a conductive paste without coating. The images were acquired in the 3D mode.

Results and discussion

Yield and microstructure

All samples were weighted after neutralisation and drying. The yield was generally close to 100 %, a result that contrasts with the results from Rånby (1952) who used cellulose sources that comprised low molecular weight cell wall polysaccharides that could have been dissolved or deacetylated in the NaOH solutions.[22] The fibres initially formed a tight network of interwoven cotton fibres with the usual appearance of cotton fibre 8-19 µm in diameter (Figure 1a). Noticeably, a finer network of microfibres 1-2 µm in diameter was found to be running between fibres. These bundles were not or barely visible on the fibres after treatment, which was probably due to a re-aggregation against the surface of the larger fibres (Figures 1b to f). The morphology of the fibres progressively evolved after NaOH treatment. They were initially thin and straight (Figure 1 b and c) to slightly thicker and twisted (Figures 1 d to f). This change of morphology could be attributed to a swelling in alkali followed by shrinkage in the latter stages of the process. As an example, the fibres obtained after the harshest treatment (c = 3 wt.%) appeared twisted and their diameter became slightly larger with values in the range 14-22 µm (Figure 1f). Their twist was also confirmed by polarised optical microscopy (data not shown). Since the microstructure was very close to that of the starting material, the absence of dissolution is assumed in the rest of the work. Consequently, this process is classified as a mercerisation process.

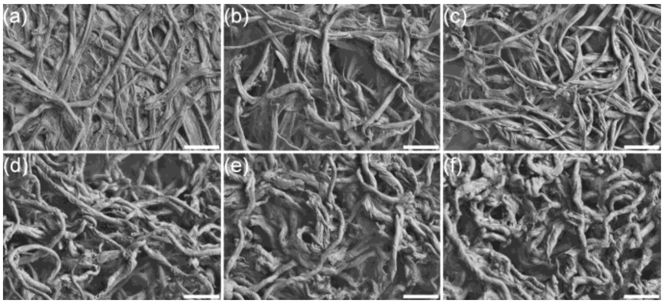

Figure 1. FE-SEM micrographs of the fibres before treatment (a) and after treatment using NaOH concentrations of 0.25 wt.% (b), 0.5 wt.% (c), 1 wt.% (d), 2 wt.% (e) and 3 wt.% (f). Scale bars are 100 µm wide.

Crystalline transformation

The WAXD diffraction results are visible on Figure 2. Initially, the raw cotton material displayed a typical cellulose I pattern with the $(1\bar{1}0)$, (110), (102), (200) and (004) peaks respectively located at $2\theta \sim 17.1°$, 19.2°, 23.7°, 26.4° and 41.4° due to the use of a cobalt source.[22,39,42,43] In contrast, the samples obtained after treatment with c = 1, 2 and 3 wt.% were typical cellulose II diffractograms with $(1\bar{1}0)$, (110) and (020) peak contributions at $2\theta \sim 13.6°$, 23.3° and 25.3°.[5,6,20,22,43] The samples obtained with c = 0.25 wt.% and c = 0.5 wt.% displayed mixed patterns of cellulose I and II. The cellulose II content increased with the initial concentration. The longitudinal order as estimated by the peak (004) was progressively lost as the NaOH concentration increased, indicating further dismantlement of the original crystalline edifice in the **c** axis direction. Diffractograms consistent with Na-cellulose I and Na-cellulose IV were obtained as transformation intermediaries (Figure S1).[4,18,20] In order to assess the sample crystallinity and the crystallite lateral size before and after completion of the transformation, a quick evaluation was performed using a peak fitting procedure (Figures S2 and S3). The results are presented in Table 1. It appeared that the crystallinity was relatively constant and kept in the 20 ±3% range. The lateral crystal size of the cellulose I crystallites in the starting material was calculated to be 69 Å which is consistent with other values reported for cotton crystallites.[44,45] The cellulose II crystallites were more slender with lateral sizes in the 34-41 Å. This thinning is in line with previous results.[18] The classical least square method was also trialled on the WAXD data. It is fairly unusual to use this method on such data to give an estimate of the allomorphic conversion. It was used in the present case as the amorphous background was nearly constant and since the cellulose II crystallite underwent little thickening as the transformation progressed. As a consequence, the diffractograms could be treated as simple mixtures of the two signals. The correlation coefficients were satisfactory and in general R^2 was higher than 96.5%. The crystallographic transition as measured by this method was found to be at least 85% complete after the samples had been treated with concentrations ranging from 1 to 3 wt.% (Table 1).

Table 1. Main results obtained from WAXD and FTIR spectroscopy.

		Cotton filter	**c = 0.25 wt.%**	**c = 0.5 wt.%**	**c = 1 wt.%**	**c = 2 wt.%**	**c = 3 wt.%**
Cellulose I fraction using the classical least square method	**WAXD**	1.00	0.97	0.37	0.02	-0.15	0.00
	FTIR	1.00	0.63	0.11	0.09	0.05	0.00
PCA (first component of the rotated loading matrix)		-0.520	0	0.858	0.977	1.002	1.020
PCA (second component of the rotated loading matrix)		1.513	0.999	0.143	0.023	-0.002	-0.020
Covariance between filter paper FTIR data and others		1	0.994	0.981	0.979	0.979	0.979
Change based on covariance data		0%	29%	90%	100%	100%	100%
TCI (standard deviation in parentheses)		0.831 (0.006)	0.842 (0.006)	0.818 (0.022)	0.847 (0.010)	0.886 (0.005)	0.898 (0.041)
Cellulose lateral crystallite size based on the (200) peak (Å)		69	n.d.	n.d.	34	37	41
Crystallinity as determined by WAXD		19	19	20	20	17	23

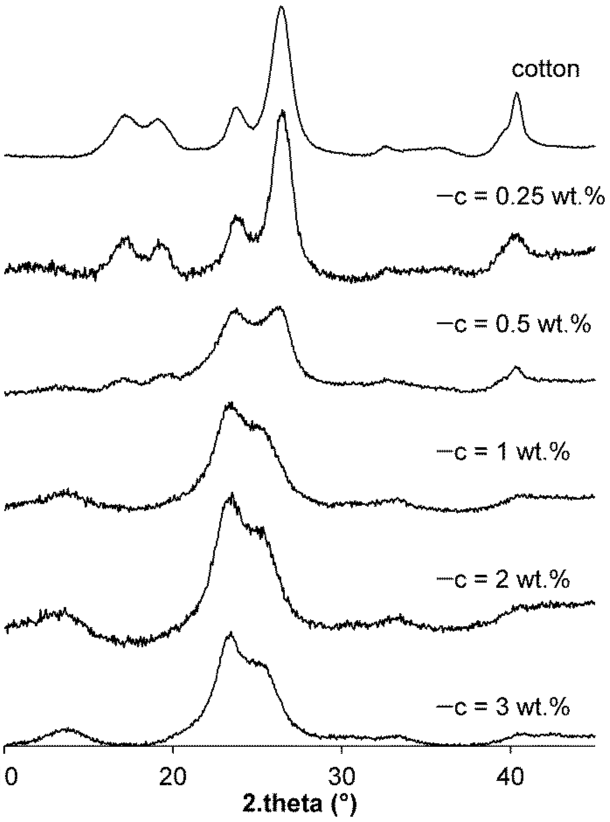

Figure 2. WAXD diffractograms of samples obtained before and after cold NaOH treatment at various concentrations. The spectra were area-normalised and then baseline corrected with a linear baseline for presentation purposes.

Short-range interactions

FTIR was used as a complementary technique. Whereas WAXD is sensitive to crystalline cellulose packing and structures in the 15-70 Å range, FTIR is more sensitive to short-range intermolecular interactions which are typically one order of magnitude smaller. The starting material exhibited a typical cellulose I spectrum. Perhaps the most significant peaks related to the presence of cellulose I are a peak at 3333 cm^{-1} attributed to the O(3)H···O(5) intramolecular hydrogen bond, a local maximum near 3290 cm^{-1} due to the inter-and intramolecular hydrogen bonds at O(6)H, a peak at 2903 cm^{-1} due to –CH stretching and a peak at 1429 cm^{-1} assigned to the in-plane bending of the hydroxyl group on the O(6)H.[33,46,47] These peaks were all visible on the spectrum of the starting material (Figure 3). The transition to cellulose II is well identified since the above-cited local maxima are shifted to 3490 cm^{-1}, 3440 cm^{-1}, 3324 cm^{-1}, 2893 cm^{-1} and 1419 cm^{-1}. This last maxima is noticeably less intense than its counterpart at 1429 cm^{-1} in cellulose I.[33,47–49] Such cellulose II spectra were observed for c = 1 to 3 wt.%. In contrast, the spectra obtained for intermediary NaOH concentrations (c = 0.25 and 0.5 wt.%) were mixed spectra (Figure 3). In a similar way to WAXD, FTIR unambiguously demonstrated a clear transition from cellulose I (filter paper) to cellulose II (c = 1 to 3 wt.%) whereas intermediary concentrations (c = 0.25 and 0.5 wt.%) produced mixtures of cellulose I and cellulose II. The extent of change was also measured quantitatively. A peak amplitude ratio could have been used.[10] However, the CLSM was preferred because it uses all the frequencies simultaneously, providing a greater emphasis on peaks with a higher signal-to-noise ratio.[50]

The CLSM has the other advantage of avoiding a complex peak fitting procedure rendered non-trivial by the multiple overlapped peaks found FTIR spectra of cellulose. The CLSM results indicate that the transformation is over 89% complete when c ≥ 0.5 wt.% (Table 1). This result differs slightly to WAXD wherein FTIR tends to show that the material, as a whole, has undergone more change when scrutinized at the molecular level than at the crystallite level as seen by WAXD. In addition to the CLSM, PCA was also conducted. The first two principal components are reported (Table 1 and Figure S4). The use of these two components explains 99.895 % of the cumulative proportion of variance. The components of the rotated loading value show the clear transition from filter paper to the other materials treated with NaOH and the high similarity between the spectra obtained for c ≥ 1wt.% (Figure 4). PCA also enabled the calculation of the covariance matrix and percentage of change based on this covariance matrix (Table 1). For the sake of simplicity, only the values of the covariance between the filter paper and the other samples are reported. Used as an indicator of change, this covariance shows that the molecular rearrangement induced by the low temperature NaOH treatment is 90% complete at c = 0.5 wt.% and complete for larger values of the concentration in solution, in excellent accordance with the CLSM results. Eventually, a crystallinity index, the TCI, was calculated based on these results and the values are reported in Table 1. The results showed that there was not a statistically significant change in the crystallinity between the start and c = 1 wt.% included. The crystallinity increased very slightly when c reached 2 wt.%.

Discussion

It was thought in the literature that NaOH concentrations below 5 wt.%, and especially below 1 wt.%, do not affect the structure of cellulose I; this was well demonstrated on positive temperatures by FTIR, solid-state nuclear magnetic resonance and WAXD.[11,17,22,23] In boiling conditions, which could be thought as accelerating the conversion, a concentration of 1 wt.% is known to be completely ineffective on the allomorphic transition.[14] Similar results were observed under harsher conditions: 2 wt.% NaOH, 170°C and 10 bars.[51] In contrast to high temperatures, low temperatures seem to be more favourable for mercerisation and this was observed in studies devoted to cellulose dissolution in aqueous NaOH. Indeed, the undissolved cellulose fraction of various cellulose I substrates placed 6-9 wt.% NaOH

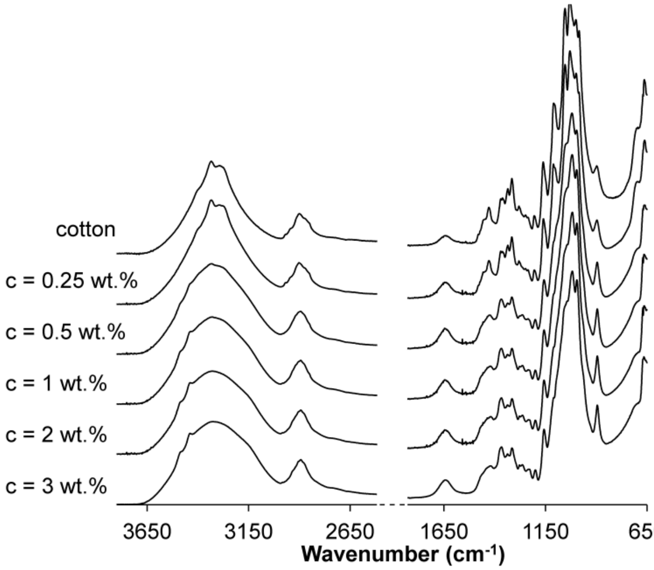

Figure 3. FTIR spectra in absorbance of the samples obtained before and after cold NaOH treatment at various concentrations. The spectra were averaged from three spectra.

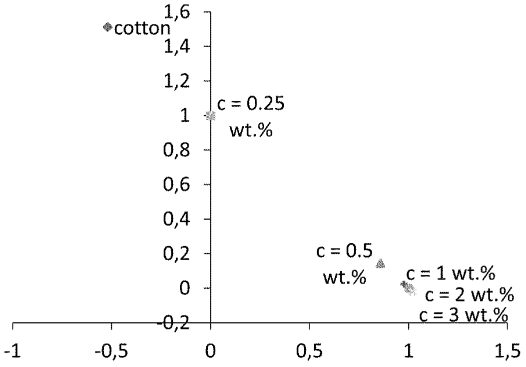

Figure 4. Components of the rotated loading matrix using principal component analysis

solutions at temperatures between -6 to -2°C was completely converted to cellulose II.[17,29] Partial conversion was also observed for the undissolved fraction of cellulose placed in NaOH/urea solutions below *ca.* 0°C.[52] These results strongly point out to the possibility of the formation of Na-cellulose I as an intermediary step on the path to dissolution. It is however not clear whether the formation of Na-cellulose I is necessary for the dissolution to be successful.

In the present work, a low concentration window was explored with the goal of seeing whether it was possible to exploit low temperatures in a simple laboratory setup to convert cellulose I to cellulose II with a lower NaOH concentration. Both WAXD and FTIR demonstrated that the transition from cellulose I to cellulose II was complete at only c = 1 wt.%.

The chemical formula of Na-cellulose I is $C_6H_{10}O_5NaOH\ldots 2H_2O$.[3] This means that under ideal conditions, the conversion of a given weight of cellulose would require only 25% of its mass in NaOH. In this work, the cellulose to NaOH ratio used to achieve complete conversion is ~1. This value is about ten times lower than the NaOH concentrations often used to mercerise cellulose in the literature. The most probable explanation for this particular behaviour might lie in the NaOH:water phase diagram as described elsewhere.[15] It is known that decreasing the temperature below 0°C of aqueous sodium hydroxide at concentrations below 8-10 wt.% results in a biphasic mixture of ice and concentrated aqueous NaOH. Assuming that the migration is total, a temperature of -17°C produces a concentrated aqueous NaOH solution comprising ~13wt.% NaOH.[15] Such a concentration is known to be sufficient to trigger the formation of Na-cellulose I which is most often followed by a transformation to cellulose II.[4,18,20] If this is the mechanism, then the limiting effect of the concentration (c = 0.25 and 0.5 wt.%) can only be explained by an excessive solid (cellulose) to liquid ratio, and this ratio is expected to lie in the 7-8:1 range if one assumes that the lowest concentration able to mercerise cellulose is 7 wt.%.[17,22] The crystallinity results provide additional information. The higher TCI for c = 2 and 3 wt.% could be due to a slower reorganisation of the crystallites upon thawing due to the lower osmotic pressure applied by the more concentrated NaOH solutions. This could be correlated to the slightly larger crystallite sizes measured by WAXD. It is also not possible to completely exclude that some dissolution has already started to take place, thereby granting higher molecular mobility to the polymer chains. These freed chains could then have reorganised in a more ordered manner. Both TCI and crystallite lateral size above c = 1 wt.% correlate with the FE-SEM results that show a seemingly more advanced relaxation of the cell wall constraints through twisting.

Assuming that the most probable mechanism of conversion at low temperature is triggered by a reconcentration of NaOH in the liquid phase at the cellulose substrate surface has large scientific and commercial implications. The first implication of this result is that the phase diagram of cellulose needs to be revisited. The original phase diagram proposed by Sobue *et al.* was built using *in-situ* X-ray diffraction.[23] Consequently, the authors could simply not produce any data in the presently explored concentration-temperature range because of the presence of ice. A putative phase diagram is presented in the supporting information (Figure S5). The second significance of this result is very important in that it shows optimal conditions to conduct mercerisation using low alkali concentrations. The advantage of using a small amount of sodium hydroxide also resides in the simple neutralisation procedure which does not require the additional use of acids such as HCl. Such an acid could induce the formation of solid NaCl aggregates on the surface of the cellulose substrates, which is not desirable from a purity standpoint. Hence, it is expected that this method could have wide applicability in the future, replacing high temperature, high concentration pathways typically relied on for mercerisation.

Conclusions

This work focuses on using low temperatures (-17°C) to convert cellulose I to cellulose II. It is shown that concentrations as low as 1 wt.% (0.25 N) are sufficient to fully convert a cellulose I substrate with a high degree of polymerisation to cellulose II, which is the novelty of this work. This transformation occurs through the formation of Na-cellulose complexes. It is assumed that this conversion is successful due to reconcentration effects of the sodium hydroxide in the liquid phase of the ice-liquid mixture in this concentration-temperature range. This convenient method is expected to be used extensively in the future instead of the usual mercerisation method involving tenfold higher NaOH concentrations. Future work will focus on establishing a precise phase diagram of the working concentration range for this conversion to cellulose II as well as doing *in-situ* observations of the ice growth at the cellulosic substrate surface.

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Notes and references

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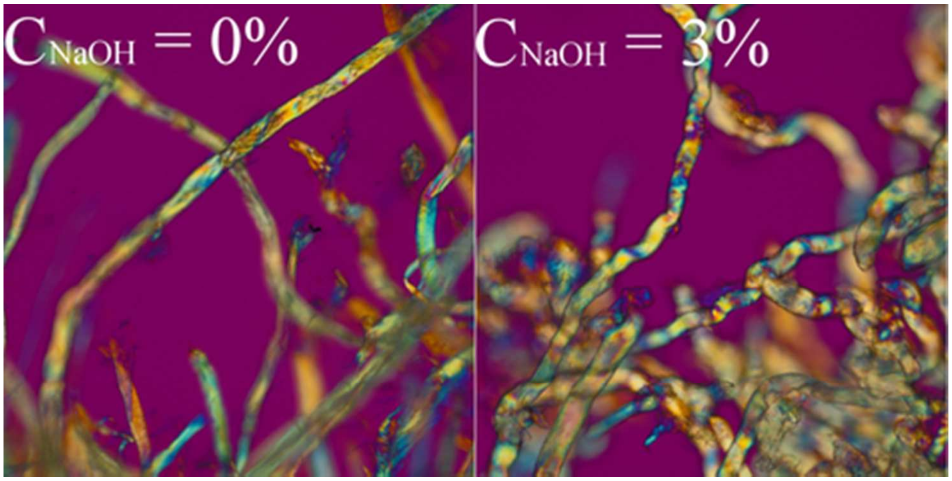
Electronic Supplementary Information (ESI) available: WAXD of the intermediary allomorphs, details on PCA, phase diagram, experiment conducted on MCC. See DOI: 10.1039/b000000x/

1 F. Porro, O. Bédué, H. Chanzy and L. Heux, *Biomacromolecules*, 2007, **8**, 2586–2593.
2 F. J. Kolpak and J. Blackwell, *Macromolecules*, 1976, **9**, 273–278.
3 P. Zugenmaier, *Prog. Polym. Sci.*, 2001, **26**, 1341–1417.
4 Y. Nishiyama, S. Kuga and T. Okano, *J. Wood Sci.*, 2000, **46**, 452–457.
5 P. Langan, Y. Nishiyama and H. Chanzy, *J Am Chem Soc*, 1999, **121**, 9940–9946.
6 P. Langan, Y. Nishiyama and H. Chanzy, *Biomacromolecules*, 2001, **2**, 410–416.
7 A. C. O'Sullivan, *Cellulose*, 1997, **4**, 173–208.
8 T. Okano and A. Sarko, *J. Appl. Polym. Sci.*, 1985, **30**, 325–332.
9 N.-H. Kim, T. Imai, M. Wada and J. Sugiyama, *Biomacromolecules*, 2006, **7**, 274–280.
10 E. Dinand, M. Vignon, H. Chanzy and L. Heux, *Cellulose*, 2002, **9**, 7–18.
11 E. Ott and H. Spurlin, *Cellulose and cellulose derivatives*, Interscience, New York-London, 2nd edn., 1955, vol. 5.
12 O. A. Battista, S. Coppick, J. A. Howsmon, F. F. Morehead and W. A. Sisson, *Ind. Eng. Chem.*, 1956, **48**, 333–335.
13 J. W. . Hearle, in *Fibre structure*, ed. Butterworth, The Textile Institute, London-Manchester, 1963.
14 T. Okano and A. Sarko, *J. Appl. Polym. Sci.*, 1984, **29**, 4175–4182.
15 M. Egal, Ecole des mines de Paris, 2006.
16 H.-P. Fink, H. Dautzenberg, J. Kunze and B. Philipp, *Polymer*, 1986, **27**, 944–948.
17 K. Kamide, *Cellulose and cellulose derivatives*, 2005.
18 J. Schoeck, R. J. Davies, A. Martel and C. Riekel, *Biomacromolecules*, 2007, **8**, 602–610.
19 R. H. Newman and J. A. Hemmingson, *Cellulose*, 1995, **2**, 95–110.
20 K. Kobayashi, S. Kimura, E. Togawa and M. Wada, *Carbohydr. Polym.*, 2011, **83**, 483–488.
21 P. Mansikkamäki, M. Lahtinen and K. Rissanen, *Cellulose*, 2005, **12**, 233–242.
22 B. Rånby, *Acta Scand.*, 1952, **6**, 116–127.
23 H. Sobue, H. Kiessig and K. Hess, *Ztg. Phys. Chem.*, 1939, **B43**, 309–328.
24 C. Chang and L. Zhang, *Carbohydr. Polym.*, 2011, **84**, 40–53.
25 A. Isogai and R. H. Atalla, *Cellulose*, 1998, **5**, 309–319.
26 M. Egal, T. Budtova and P. Navard, *Biomacromolecules*, 2007, **8**, 2282–2287.
27 T. Yamashiki, T. Matsui, M. Saitoh, K. Okajima and K. Kamide, *Br. Polym. J.*, 1990, **22**, 121–128.
28 B. Laszkiewicz, *J. Appl. Polym. Sci.*, 1998, **67**, 1871–1876.
29 N. Le Moigne and P. Navard, *Cellulose*, 2010, **17**, 31–45.
30 5,410,034, 1995.
31 B. Xiong, P. Zhao, P. Cai, L. Zhang, K. Hu and G. Cheng, *Cellulose*, 2013, **20**, 613–621.
32 C. J. Burnham, M. K. Petersen, T. J. F. Day, S. S. Iyengar and G. A. Voth, *J. Chem. Phys.*, 2006, **124**, 024327.
33 M. L. Nelson and R. T. O'Connor, *J. Appl. Polym. Sci.*, 1964, **8**, 1325–1341.
34 F. Carillo, X. Colom, J. J. Suñol and J. Saurina, *Eur. Polym. J.*, 2004, **40**, 2229–2234.
35 U. Lorenzo-Seva and P. J. Ferrando, *Behav. Res. Methods*, 2006, **38**, 88–91.
36 B. Duchemin, A. Thuault, A. Vicente, B. Rigaud, C. Fernandez and S. Eve, *Cellulose*, 2012, **19**, 1837–1854.
37 A. Thygesen, J. Oddershede, H. Lilholt, A. B. Thomsen and K. Ståhl, *Cellulose*, 2005, **12**, 563–576.
38 M. Wojdyr, *J. Appl. Crystallogr.*, 2010, **43**, 1126–1128.
39 Y. Nishiyama, P. Langan and H. Chanzy, *J Am Chem Soc*, 2002, **124**, 9074–9082.
40 A. D. French, *Cellulose*, 2014, **21**, 885–896.
41 B. Duchemin, R. Newman and M. Staiger, *Cellulose*, 2007, **14**, 311–320.
42 L. Segal, M. L. Nelson and C. M. Conrad, *J. Phys. Colloid Chem.*, 1951, **55**, 325–336.
43 A. Isogai, *Macromolecules*, 1989, **22**, 3168–3172.
44 K. Leppänen, S. Andersson, M. Torkkeli, M. Knaapila, N. Kotelnikova and R. Serimaa, *Cellulose*, 2009, **16**, 999–1015.
45 R. H. Newman, *Solid State Nucl. Magn. Reson.*, 1999, **15**, 21–29.
46 Y. Marechal and H. Chanzy, *J. Mol. Struct.*, 2000, **523**, 183–196.
47 H. J. Marrinan and J. Mann, *J. Polym. Sci.*, 1956, **21**, 301–311.
48 M. L. Nelson and R. T. O'Connor, *J. Appl. Polym. Sci.*, 1964, **8**, 1311–1324.
49 X. Colom and F. Carrillo, *Eur. Polym. J.*, 2002, **38**, 2225–2230.
50 J. L. Koenig, *Spectroscopy of Polymers*, Elsevier, 1999.
51 B. Duchemin and M. P. Staiger, *J. Appl. Polym. Sci.*, 2009, **112**, 2710–2715.
52 H. Qi, C. Chang and L. Zhang, *Cellulose*, 2008, **15**, 779–787.



Low NaOH concentrations at low temperatures allow for easy cellulose mercerisation.
39x19mm (300 x 300 DPI)