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Structural modifications of cellulose samples after dissolution into various solvent systems

Jérémy Rebière^{1,2} · Maëlie Heuls^{1,3,4} · Patrice Castignolles⁴ · Marianne Gaborieau^{3,4} · Antoine Rouilly¹ · Frédéric Violleau² · Vanessa Durrieu¹

Abstract This work deals with the modifications resulting from the dissolution of four commercial cellulosic samples, with different crystallinity rates and degrees of polymerization (DPs), in four solvent systems, known and used to dissolve cellulose. The dissolution conditions were optimized for the 16 various systems and followed by turbidity measurements. After regeneration, the samples were analyzed by thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), and X-ray diffractometry (XRD) to study their modification. Viscosimetry measurements were used to evaluate the potential decrease of the DP after dissolution. The observed structural modifications established that, for low DP, all the solvent systems were efficient in dissolving the cellulose without altering the DP, except BMIM [Cl], which provoked a decrease of up to 40 % and a decrease of around 20 % of the degradation temperature (onset temperature, T_0). For high molecular weight (MW) celluloses, DMSO/TBAF was the only system to allow a complete dissolution without

any molar mass loss and degradation temperature modification.

Keywords Cellulose · Dissolution · Underivatizing solvent · Structural effects · Crystallinity index · Degree of polymerization

Introduction

Cellulose is the most abundant natural polymer on earth, consisting of a chain of D-glucopyranoside units, usually named anhydroglucose units (AGUs), β -(1 \rightarrow 4) linked. Products derived from cellulose have many applications in paper, chemical, and energy industries. Cellulose contains one proximal 4-OH-group, one hemiacetal at the terminal AGU (so-called reducing end), and three hydroxyl groups per AGU. The numerous hydroxyl groups give cellulose a good hydrogen bonding ability. The hydrogen bond network governs many aspects of the properties and chemical behavior of cellulose [1, 2], but Van der Waals interactions and electronic effects have also a major role [3]. Cellulose is a semi-crystalline polymer, and the ratio of crystalline and amorphous regions affects its swellability, its solubility, and its physical properties. As most natural and synthetic polymers, cellulose presents some variability in its chain length. This variability is described by the molar mass distribution (MMD) of the material. Cellulose samples come from various natural origins and different processes of extraction and purification, all of which govern their MMD. The main technique used for the MMD determination of cellulose is size exclusion chromatography (SEC) also previously called gel permeation chromatography (GPC). To be characterized with these analytical techniques, cellulose needs to be dissolved in a solvent system. Unfortunately, cellulose is insoluble in water and most

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organic solvents under conventional conditions. However, for more than 30 years, many solvent mixtures have been studied for the dissolution/decrystallization and modification of cellulose. These mixtures can be classified into two categories: (1) the derivatizing solvents used to modify and to affect the chemical and physical structure of cellulose chains, and (2) the non-derivatizing solvents known to help the dissolution of the cellulose chains without chemical modification of the structure. In both cases, the preservation of the structure and degree of polymerization (DP) of cellulose during the dissolution is an actual challenge [4]. Additionally, as cellulose need to be dissolved to be analyzed, it is extremely difficult to precisely know cellulose structure in its native state, especially regarding chain length, and finally to understand precisely the effect of the dissolution.

Different non-derivatizing multi-component systems have been used, most of them consisting of dissolved salts in organic or aqueous solutions, as *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) [5–8], dimethylsulfoxide/tetra-*N*-butylammonium fluoride (DMSO/TBAF) [9, 10], dimethylsulfoxide/diethylamide/sulfur-dioxide (DMSO/DEA/SO₂) [11], aqueous solutions like *N*-methylmorpholine-*N*-oxide (NMMO)/H₂O [12, 13], calcium thiocyanate (Ca(SCN)₂)/H₂O [14] or sodium hydroxide (NaOH)/urea/H₂O systems [1, 15, 16] or ionic liquid systems such as butyl-methylimidazolium chloride (BMIM [Cl]) [17] or acetate (BMIM [OAc]) [18], or methyltripropylammonium levulinate (TriC₃ [Lev]) [19].

In all these works, the aim of the dissolution was either to facilitate cellulose chemical modification through homogeneous conditions, and in this case the DP preservation is not a priority, or to characterize cellulose MMD (e.g., for pulp and paper applications or biorefinery purposes) of specific samples of various crystallinity and origin. In the latter case, if the dissolution involves some modification of the chain integrity, then the measurement becomes meaningless. Therefore, it appeared interesting to study specifically the influence of several solvents systems on various cellulose samples of different crystallinity rates and DP.

This work describes the effects of four solvent systems on four different cellulose samples. Dissolution and regeneration conditions were compared between solvent systems cautiously selected: (1) DMAc/LiCl mainly used to determine the MMD analysis by size exclusion chromatography (SEC) [20–22]; (2) the DMSO/DEA/SO₂, known for 50 years to render crystalline cellulose amorphous, making following treatments more efficient [23]; (3) BMIM [Cl], studied as a pre-treatment of cellulosic samples [24]; and finally, (4) the DMSO/TBAF, generally used to functionalized cellulose samples [25]. The four cellulose samples differed in both their crystalline rate and DP: Avicel and cotton fibers known to have low DP, and on the contrary α -cellulose and Vitacel chosen for their high DP. Cellulosic samples were analyzed before and after dissolution and regeneration by scanning

electron microscopy (SEM), thermogravimetric analysis (TGA), X-ray diffractometry (XRD), solid-state NMR spectroscopy, and viscometry in order to highlight the modifications induced by the dissolution process.

Materials and methods

Materials

Dimethyl sulfoxide (DMSO, 99.7 %, anhydrous), *N,N*-dimethylacetamide (DMAc, 99.8 %), bis(ethylenediamine)copper(II) hydroxide solution (CED solution, 1 M in copper, molar ratio of ethylenediamine/copper of 2:1), diethylamine (DEA, 99.5 %), tetrabutylammonium fluoride trihydrate (TBAF, 97 %), lithium chloride (LiCl, 99 %), and ethanol (96 %) were purchased from Sigma-Aldrich (Steinheim, Germany), acetone (99 %) from Carlo Erba Reagent (Molsheim, France), sulfur dioxide gas (SO₂) from Air Liquide (Toulouse, France), and 1-butyl-3-imidazolium chloride (BMIM [Cl], 98 %) from Solvionic (Toulouse, France).

A single batch of each of four different samples of cellulose has been studied with differing crystallinity index (CrI) and average of DP (Table 1). Avicel (PH-101, Ph Eur, cellulose microcrystalline, batch no. BCBK2051V), α -cellulose (powder, batch no. BCBH3503V), and cotton fibers (cotton linters, medium fibers, batch no. MKBQ8042V) were purchased from Fluka, Sigma Aldrich (Steinheim, Germany), and Vitacel (L600/30, Ph Eur, powdered cellulose, batch no. 7120891215 X) from JRS Pharma (Rosenberg, Germany).

Dissolution methods

General principle

The dissolution of the cellulose samples can be divided into three steps:

1. *Pre-drying*: (at 103 °C for 2 h) to decrease sample moisture content which can hinder the dissolution;
2. *Swelling*: to expand fiber volume in order to enhance solvent penetration under mild heating (except for ionic liquid BMIM [Cl] solvent system);
3. *Dissolving*: to solubilize the cellulose, under specific operating conditions (Table 2);

Three additional steps have been necessary to regenerate the dissolved cellulose samples:

4. *Regenerating*: to allow the precipitation of the dissolved sample by adding hot non-cellulose-solvent;

Table 1 Characterization of cellulosic samples in terms of crystallinity index (CrI) and degree of polymerization (DP and DP_v): comparison between supplier's and experimental data

Cellulosic samples	Supplier's data			Experimental data	
	CrI range (%)	DP range	DP batch value	CrI (%)	DP _v
Avicel	70–90	150–350	217	78	226 ± 9
Cotton fibers	60–80	190–250	nc	64	271 ± 7
Vitacel	40–60	440–2250	1079	42	1072 ± 27
α-Cellulose	50–70	700–1200	nc	50	1209 ± 38

nc not communicated

5. *Washing-filtering* (several times): to remove all solvent residues and obtain the purest regenerated sample possible into hot non-solvent, under air drying (Table 3);
6. *Post-drying*: to eliminate all solvent residues, under air drying.

Dissolution

For each cellulose sample, a total dry weight of 1.0 g of cellulose was solubilized in round-bottomed flasks in the four different systems. Specific conditions have been carried out for each solvent system according to the literature: (1) BMIM [Cl] Ionic Liquid (IL) [26, 27], (2) DMSO/TBAF (D/T) [9], (3) DMSO/DEA/SO₂ (D/S) [11], and (4) DMAc/LiCl (D/L) [28].

Optimal dissolution conditions, particularly in terms of time and temperature, have been selected for each sample (Table 2) to avoid the degradation of the cellulose sample [18, 29]. The equilibrium of the dissolution process was determined as obtaining clear liquids were obtained; it was then confirmed by turbidity measurements.

For BMIM [Cl] (IL): 100.0 g of BMIM [Cl] was mixed at 110 °C under continuous magnetic stirring, during 30 min, wherein the cellulose was added gradually and heated at 110 °C. Below 110 °C, the viscosity of the ionic liquid affects the efficiency of the dissolution, and above 110 °C, a strong coloration of the liquid was observed. This coloration indicates a degradation of the cellulose-solvent system. Only the

reaction time can be modified and varied for the different celluloses dissolved.

For DMSO/TBAF (D/T): the cellulose sample and 20.0 g of DMSO were placed under continuous magnetic stirring for 2 h at 60 °C to open the fibers. Then 70.0 g of DMSO/TBAF solution (11:1; w/w ratio) was added under the same stirring for 30 min. According to the kind of cellulose, the reaction temperature varied between 60 and 100 °C.

For DMSO/DEA/SO₂ (D/S): the cellulose sample was placed into 40.0 g of liquid DMSO for 2 h at room temperature (RT) under continuous magnetic stirring to open the fibers. Meanwhile, a DMSO/SO₂ solution was prepared through bubbling of SO₂ in the DMSO solution. From this DMSO/SO₂ solution, a volume corresponding to 1.19 g of SO₂ was added to the cellulose-DMSO swelled mixture, followed by 1.35 g of DEA. This final solution was left under stirring at RT to avoid the evaporation of the SO₂ in solution. Reaction time varied according to the cellulose to be dissolved.

For DMAc/LiCl (D/L): the cellulose was successively washed and filtered with distilled water, ethanol, and finally DMAc to open the fibers. Under continuous magnetic stirring, washed cellulose was mixed with 100.0 g of DMAc for 30 min at 150 °C. After cooling the solution to 100 °C, 8.0 g of LiCl was added and left to stir at RT to avoid the degradation of the cellulose-solvent unit. The reaction time was then adapted according the cellulose dissolved.

The optimized experimental conditions are summed up in Table 2.

Table 2 Dissolution experimental conditions: optimal time (*t*) and temperature (*T*), for each solvent and cellulose sample

Cellulosic samples	Experimental conditions	IL	D/T	D/S	D/L
Avicel	<i>t</i> (h)	3.0	0.5	0.3	24.0
	<i>T</i> (°C)	110	60	RT	RT
Cotton fibers	<i>t</i> (h)	0.5	0.5	0.3	24.0
	<i>T</i> (°C)	110	60	RT	RT
Vitacel	<i>t</i> (h)	0.5	0.5	4.0	24.0
	<i>T</i> (°C)	110	70	RT	RT
α-Cellulose	<i>t</i> (h)	4.0	0.5	1.0	48.0
	<i>T</i> (°C)	110	100	RT	RT

RT room temperature

Regeneration and wash

For the regeneration of the dissolved cellulose samples, non-solvents of cellulose, called non-cellulose-solvents, such as distilled water, ethanol, or acetone [30, 31], were used. Hot non-cellulose-solvent was necessary to increase the miscibility with the dissolution solvent to regenerate the dissolved cellulose with the least amount of residual solvent in the regenerated fibers. Three solution volumes of non-solvent were necessary. After 1.5 h under magnetic stirring, filtration was used to retrieve the regenerated samples, after which 100.0 mL of non-solvent was used to wash the regenerated sample. Four successive washing/filtering steps, 1 h each, were carried out to obtain white and

Table 3 Regeneration and successive washing (W.1) experimental conditions of cellulose samples according to the dissolution solvent system

Experimental steps	Experimental conditions	IL	D/T	D/S	D/L
Regeneration	Solvent	Water	Water	Ethanol	Water
	T (°C)	80	70	50	70
W.1	Solvent		Water/ethanol	(50:50 v/v)	
	T (°C)	75	70	50	70
W.2	Solvent		Ethanol		
	T (°C)	60			60
W.3	Solvent		Ethanol/acetone	(50:50 v/v)	
	T (°C)	50	50	50	70
W.3	Solvent		Acetone		
	T (°C)	RT	RT	RT	RT

RT room temperature

pure regenerated celluloses. Regeneration conditions are summed up in Table 3. The regenerated cellulose samples were dried in air at room temperature until a stable mass was obtained.

Instrumental analysis

Turbidity measurements

Turbidity measurements were carried out in triplicates with a nephelometer 2100P turbidimeter 46500-00 (Hach Company, Loveland, CO, USA) featuring a scattered light detector perpendicular to the light beam. The correlation between transmitted and scattered light allows the determination of the presence of non-dissolved particles bigger than the wavelength of the incident light (860 nm) in a solution with precision. The units of turbidity from a calibrated nephelometer are called nephelometric turbidity units (NTU). Calibration was done between 1 and 1000 NTU. Then 20.0 mL of the solution was stabilized for 30 min at optimized dissolution temperatures (see Table 2) before measurements.

Thermal degradation by thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out to characterize the thermal decomposition of untreated and regenerated samples. The thermal stability data were obtained on a TGA/DSC, SDT Q600 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). The temperature was increased under atmospheric air from 25 to 130 °C at a heating rate of 10 °C/min, then up to 600 °C at a heating rate of 5 °C/min. In the literature, two specific temperatures are used to evaluate the degradation of a polymer: the onset temperature (T_o , °C) and the midpoint temperature (T_m , °C). T_o was determined at the intersection of the tangent to the main degradation threshold with the baseline of the differential thermogravimetric (DTG) curve. T_m was defined as the middle temperature of the apex degradation of DTG curve or the inflection point on the analytical thermogravimetric (ATG) curve. T_o and T_m were

directly determined by the Mettler Toledo software via the DTG curve. In this study, only T_o was determined in duplicate.

Structural observation by scanning electron microscopy (SEM)

Electron micrographs of different samples were performed with a Jeol 6510 LV Scanning Electron Microscope (SEM) without pre-treatment. Only $\times 200$ micrographs were shown in the conditions: direct observation; BEC; WD: 9–10 mm; SS60; 68–70PA.

Crystallinity index (CrI) measurements by x-ray diffraction (XRD)

XRD was performed using a Bruker D8 Advance Powder X-ray Diffractometer with $\text{CuK}\alpha$ radiation (Bruker, Germany). Scans of cellulosic samples were obtained from 5 to 40° (2θ) and 0.02°/15 s per step.

Some methodologies exist to determine the crystallinity rate as explained by Park et al. [32]. According to their findings, the deconvolution method (DM) was preferred to determine CrI over the older and simplistic peak height method that does not take into account the different diffractograms of cellulose types I and II. The deconvolution was carried out with the software Topas (Bruker, Germany). For the untreated celluloses, after subtraction of the background (recorded separately), the XRD diffractogram was deconvoluted into Gaussian crystalline peaks (at 15, 16, 21, 22, and 35°) and a broader Gaussian amorphous peak centered around 20 to 22° [33]. The crystallinity index (CrI) was obtained by dividing the sum of the crystalline peak areas with the sum of all peak areas.

Solid-state ^{13}C NMR spectroscopy

The ^{13}C cross-polarization (CP) NMR spectra were recorded under magic-angle spinning (MAS) on a Bruker Avance III 300 spectrometer operating at a 300 MHz Larmor frequency

for ^{13}C . A commercial double resonance probe supporting MAS rotors with a 7 mm outer diameter was used at a spinning frequency of 5 kHz. The ^{13}C CP-MAS NMR spectra were recorded with a 2-ms contact time, a 1-s relaxation delay, and 5120 scans. The ^1H and ^{13}C pulses were calibrated with glycine. The ^{13}C chemical shift scale was calibrated using the most intense cellulose signal at 76 ppm [34].

Viscometry measurements

In order to evaluate whether the modification of the samples occurred upon dissolution and regeneration, the values of the intrinsic viscosity of the commercial and the regenerated cellulose samples in CED solution were determined according to ASTM D-1795 [35] and their viscometric-average degree of polymerization (DP_v) were calculated. Measurements were done with a glass capillary-type viscometer 150 Cannon-Fenske (Cannon Instrument Company, State College, PA, USA). In a 50.0-mL flask, a sufficient mass (200–300 mg) of the cellulose sample was mixed in 25.0 mL of distilled water under shaking overnight at room temperature. When the fibers seemed totally swelled, 25.0 mL of CED solution was added and the mixture was shaken overnight at room temperature. After complete dissolution, 10.0 mL of the solution was analyzed. All the measurements were done manually, using a chronometer and visual observation, and repeated at least four times (two dissolutions and two measurements for each dissolution).

Statistical analysis

The turbidity, onset temperature T_o , and DP of each cellulose solution were measured two to three times non-consecutively. The values reported are the average of the multiple analyses with the corresponding average error value. The results obtained were treated by Minitab Release 17 statistical package and analyzed by one-way analysis of variance with a confidence level of 0.95 and Tukey-Kramer multiple mean comparisons. In Tables 4, 5, and 6, the results which do not have

the same exponent letter for one of the parameters are significantly different for this parameter.

Results and discussion

Characterization of cellulosic commercial samples

CrI and DP_v of commercial samples were evaluated by XRD deconvolution method and the ASTM D-1795 standard [35], respectively. The results are summed up in Table 1 and compared with the supplier's data.

DP_v obtained for the commercial samples were in accordance with the supplier's data values, confirming the suitability of the method. CrI values obtained were close to the supplier's data and similar to the values found in the literature [36].

Avicel and cotton fibers were then considered as low MW samples while α -cellulose and Vitacel were of higher DP. As expected, Vitacel was the more amorphous sample and Avicel the more crystalline.

Dissolution processes

The penetration of the solvent into cellulose fibers depends directly on the nature and the polarity of the solvent. Most solvents have the ability to dissolve the cellulose by breaking the hydrogen bond network. They penetrate into the crystal lattice to achieve the dissociation of the assembly chains. For each solvent, the experimental conditions (summed up in Table 2) have been optimized in order to have the smoothest conditions (i.e., minimal temperature and time), involving slight differences from one sample to another. In all cases, dissolution was considered complete when solutions were limpid. Turbidity measurements were used afterwards to confirm the dissolution (Table 4).

For all samples, the difference between solutions and pure solvent turbidity values was lower than 50 NTU. According to Mazza et al. [37], all the samples could then be considered as dissolved.

Table 4 Turbidity values (in NTU) of pure solvent systems and cellulose solutions

Solutions	Solvent system			
	IL	D/T	D/S	D/L
Pure solvent	0.70a ± 0.00	13.20a ± 0.27	1.23a ± 0.06	13.67a ± 0.31
Avicel	1.80a ± 0.10	11.43a ± 0.15	30.77b ± 2.48	15.40a ± 0.10
Cotton fibers	2.30b ± 0.44	9.56b ± 0.06	2.27a ± 0.06	17.03a ± 0.15
Vitacel	2.47b ± 0.23	13.67a ± 0.06	0.60a ± 0.00	23.40b ± 0.10
α -Cellulose	3.30c ± 1.08	7.03c ± 0.15	40.10c ± 0.36	46.33c ± 6.15

Different letters in the same column indicate a statistical difference between the mean values ($P < 0.05$)

Table 5 Onset temperature T_0 (°C) of thermal degradation obtained from DTG curves, for untreated and regenerated celluloses

Cellulosic samples	Untreated	Solvent system			
		IL	D/T	D/S	D/L
Avicel	301.5a ± 3.2	271.5b ± 0.8	321.2a ± 0.2	247.8d ± 0.3	260.3c ± 3.5
Cotton fibers	312.3a ± 1.5	295.9a ± 0.9	313.5a ± 9.3	295.2a ± 5.9	261.2b ± 0.8
Vitacel	304.4a ± 1.2	262.0c ± 1.4	306.9a ± 5.8	274.7b ± 6.7	283.6b ± 4.5
α-Cellulose	311.7a ± 3.0	262.1c ± 1.1	306.2a ± 2.8	276.4b ± 3.7	233.5d ± 1.8

Different letters in the same line indicate a statistical difference between the mean values ($P < 0.05$)

For D/S and D/L solvent systems, temperature was fixed at RT to avoid the evaporation of SO₂ gas [38] or cellulose degradation [29, 39], respectively. On the contrary, a significant heating was necessary to decrease the viscosity of IL solvent system and thus improve the dissolution. A too high temperature could lead to a brown coloration suggesting some degradation occurred. Thus, the optimal temperature was fixed at 110 °C. For the D/T solvent system, the dissolution time did not appear as limiting and was fixed at 30 min. The temperature was then adapted for each cellulosic sample (from 60 to 100 °C).

However, some differences could be observed, depending on the cellulosic samples, in relation with their MW and crystallinity. Among the low MW samples, cotton fibers were easily dissolved in the four solvent systems, with the softest conditions (Table 2). Avicel was also dissolved by all solvents, but turbidity value in D/S was 30 times higher than the pure solvent system value (Table 4), suggesting that its high CrI (Table 1) is an obstacle to its dissolution, even if this solvent is well known for the amorphization of cellulose [11, 40].

The high MW samples were correctly dissolved in IL and D/T systems according to the turbidity values. In D/L system, the measurements (Table 4) demonstrated a significant influence of the cellulosic chain length, suggesting this system only dissolved low molar mass celluloses (Avicel and cotton fibers) and just swelled the high molar mass celluloses (α-cellulose and Vitacel) even if clear solutions were observed for all the cellulosic samples. Clear solutions despite incomplete dissolution have also been observed in the case of some high amylose starches in DMSO [41]. This difficult dissolution had also been observed for lignocellulose in D/L by Kotelnikova et al. [42].

As a conclusion, D/T and IL seemed to be the most appropriate systems to dissolve all the four cellulose samples. However, for IL, cellulose crystallinity seemed to affect the dissolution, as for each category of MW, the sample with the highest CrI required the longest dissolution time.

Cellulose structural modifications

Thermal stability

In the literature, the TGA measurements revealed three steps of the decomposition process [43]: drying (40–150 °C), removal of organic volatile matters (215–350 °C), and combustion of carbonaceous char (350–690 °C). Han et al. [44] have demonstrated that variations of the decomposition temperature occurred on cellulose samples after dissolution through BMIM [Cl] and regeneration as compared to commercial samples. The small weight loss, up to 6–8 %, observed in the low temperatures (less than 125 °C) for all the samples, corresponded to the evaporation of the natural absorbed water. In this work, only the onset temperature T_0 (Table 5) was studied to identify the modifications of the cellulose structure due to the dissolution.

All the T_0 obtained comprised between 233 and 321 °C, corresponding to the temperature range referred as the active pyrolysis zone of primary and secondary alcohol groups, and identified as the beginning of the decomposition of the cellulose. The thermal degradation zone of cellulose was identified between 290 and 350 °C [45, 46]. According to their studies, 302 °C is the onset temperature reference of the cellulose pyrolysis. T_0 lower than 290 °C meant that OH groups were easily degraded, revealing an increased access to these chemical functions,

Table 6 DP_v values for untreated and regenerated celluloses

Cellulosic samples	Untreated	Solvent system			
		IL	D/T	D/S	D/L
Avicel	226a ± 9	164e ± 5	295b ± 7	192d ± 2	248b ± 6
Cotton fibers	271a ± 7	145c ± 4	274a ± 7	239a ± 5	270a ± 7
Vitacel	1072a ± 27	403e ± 6	1206a ± 13	470d ± 10	645c ± 12
α-Cellulose	1209a ± 38	421c ± 7	1172a ± 15	558b ± 6	550b ± 10

Different letters in the same line indicate a statistical difference between the mean values ($P < 0.05$)

probably due to the alteration of the crystalline and organized structure. This loss of thermal stability could be related to a significant loss of structural and therefore mechanical cohesion. Degradation temperatures close to 280 °C (amorphous cellulose degradation) indicated the amorphization of the native crystalline structure, and thermal degradation close to 250 °C (cellobiose degradation) and 215 °C (D-glucose degradation) indicated the degradation of the cellulosic chain structure [47].

Some differences of T_0 values were observed between untreated and regenerated cellulose samples (Table 5). With D/L solvent system, a significant decrease of T_0 was observed for all the samples. All T_0 comprised between 250 and 290 °C, meaning that the degradation of the crystalline structure occurred during the dissolution/regeneration except for α -cellulose, with a decrease up to 25 % and a T_0 of 233.5 °C close to the cellobiose unit one.

For D/S solvent system, the regenerated cotton fiber T_0 was not significantly different from the value of the untreated sample. High MW samples seemed to have been slightly degraded and maybe only amorphized (T_0 comprised between 275 and 295 °C), while Avicel, the sample with the highest CrI, measured T_0 was beneath 250 °C.

With IL solvent system, all regenerated samples could be considered as amorphous cellulose, except cotton fibers with T_0 close to the native cellulose sample.

Amazingly, no significant change of T_0 was observed for the D/T system, whatever the samples. D/T seemed to be the only solvent system able to dissolve the four cellulose samples without significant modifications of their thermal properties.

Fibers structure by SEM

SEM allowed the visualization of the four cellulose fibers and their modifications after dissolution/regeneration. The untreated cellulose fibers were mostly rod-shaped. The transverse dimensions of particles of the commercial celluloses fibers (Fig. 1) varied from 15 to 25 μm , and their longitudinal dimensions varied in a larger extent, from a few hundred micrometers to several thousand micrometers. The surface structure of the fibers was not strictly ordered. The SEM of α -cellulose on Fig. 1a and Avicel on Fig. 1b illustrated the modifications observed after the dissolution/regeneration, and some observations were made from the other two cellulose types. Morphological elements of the samples regenerated were modified differently depending on the solvent system used. Regenerated fibers seemed to be less organized than native fibers and formed agglomerates for low DP regenerated cellulose samples (Fig. 1b) and in case of D/L and IL for the high DP regenerated cellulosic samples (Fig. 1a). Original fiber organization disappeared completely. For the high DP regenerated cellulose samples (Fig. 1a), after the dissolution and regeneration through D/T and D/S, some fragments of native fibers subsisted.

Regardless of the cellulose sample and the solvent system used in the dissolution, the micrographs at higher magnifications (not included) showed that all the regenerated fibers were thinner (around 0.5–1 μm with D/S and D/L, and 1.5–3 μm with D/T) than the native cellulose fibers, except after dissolution into IL. D/S, D/L, and D/T solvent systems seemed to separate and open the fibers, breaking some intermolecular bonds between the samples. Nevertheless, these macroscopic observations are difficult to relate to the chemical integrity (DP) of the polymeric chain. The reduction of the fibers thickness did not necessarily involve degradation of the chain length.

XRD and solid-state NMR structural analysis

XRD diffractograms were used to study how the dissolution through these different solvent systems affected the cellulosic samples. As expected [33, 48], the dissolution treatment modified the crystalline structure form of cellulose, from type I (native) to type II (post-swelling and dissolution) in most cases (Fig. 2). The amorphous and crystalline peaks changed with the crystalline structure, making these peaks difficult to define and accurate CrI values difficult to determine [49].

Regarding α -cellulose, the crystallinity of the form I untreated sample was measured using the main crystalline peak at 22.5° [50], identified by the Cell.I line on Fig. 2. After the dissolution/regeneration process in D/T, D/L, and IL, the main crystalline peak was shifted to 21.7°, corresponding to the main crystalline peak of cellulose form II (Cell.II line on Fig. 2), demonstrating the crystalline form change. It was accompanied by the shift of the less intense crystalline peak from 15 to 12°, also indicative of the transformation to type II cellulose [33]. This phenomenon was observed after the dissolution through all solvent systems and for the four cellulose samples, except for α -cellulose and Avicel into D/S solvent system. After regeneration from the D/S solvent, only a fraction of Avicel and a small fraction of α -cellulose were converted to cellulose type II. The incomplete change or almost absence of change of the crystalline form, added to the high turbidity values obtained (Table 4), could be related to a swelling phenomenon.

The retention of the cellulose I crystalline structure in α -cellulose after regeneration in the D/S solvent system was confirmed by solid-state ^{13}C NMR spectroscopy (Fig. 3). A small fraction of the cellulose type I was converted to amorphous cellulose, as shown by the slight decrease of signals at 90, 73, and 66 ppm and the slight increase of the signals at 84 and 64 ppm [34]. The fraction of cellulose type II formed was too small to be detected in this experiment.

The regeneration in each solvent system resulted in a decrease in intensity of the crystallinity peaks on the XRD diffractograms, as mentioned by Ahn et al. [51]. The dissolution with D/T, D/L, and IL degraded the crystalline structure

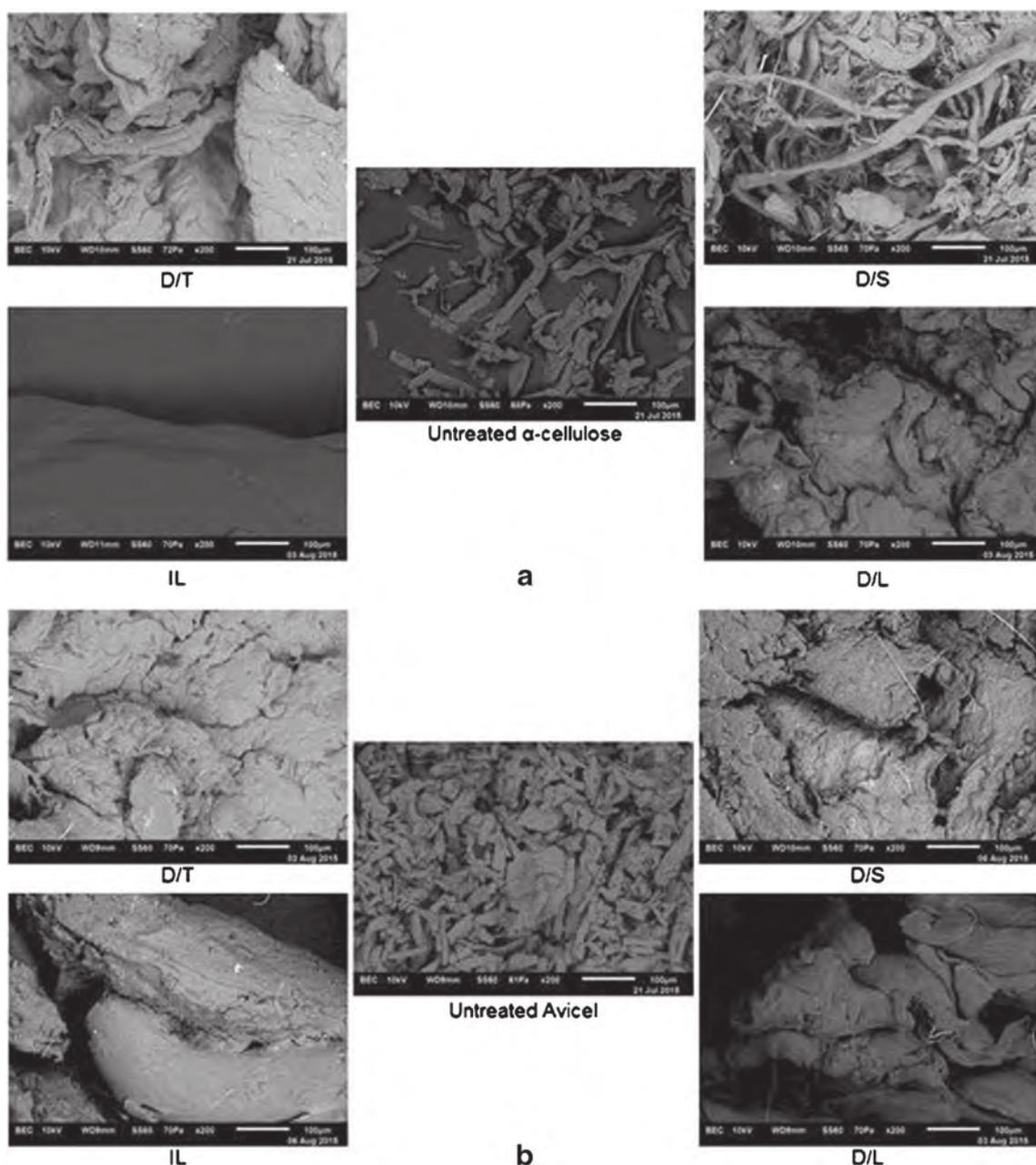


Fig. 1 SEM micrographs of α -cellulose (a) and Avicel (b), untreated and regenerated after dissolution through the different solvent systems ($\times 200$ with $\rightarrow 100 \mu\text{m}$)

of all samples to such an extent that they were almost amorphized. On the contrary, the dissolution through D/S solvent system allowed the retention of a large fraction of the organized structure. With the four solvent systems, overall crystallinity was clearly decreased.

DP_v measurements

The DP_v measurements of all the studied systems (four cellulose samples and four solvent systems) are presented and compared to the values of non-dissolved cellulose samples in

Table 6. The viscosimetric method using dissolution in cuproethylenediamine [35] is not ideal but is recognized to give a good approximation of the cellulose DP, excluding the effect of hemicellulosic polymers, and allowing a fair comparison of the effects of various treatments [52].

The dissolution of the cellulose samples affected the DP_v of these samples. The use of IL decreased significantly the DP_v values: by between 50 and 70 % in the case of low molar mass samples (cotton fibers and Avicel) and by 30 to 40 % for the high molar mass samples (Vitacel and α -cellulose), suggesting IL degraded cellulose, as showed by Ahn et al. [51].

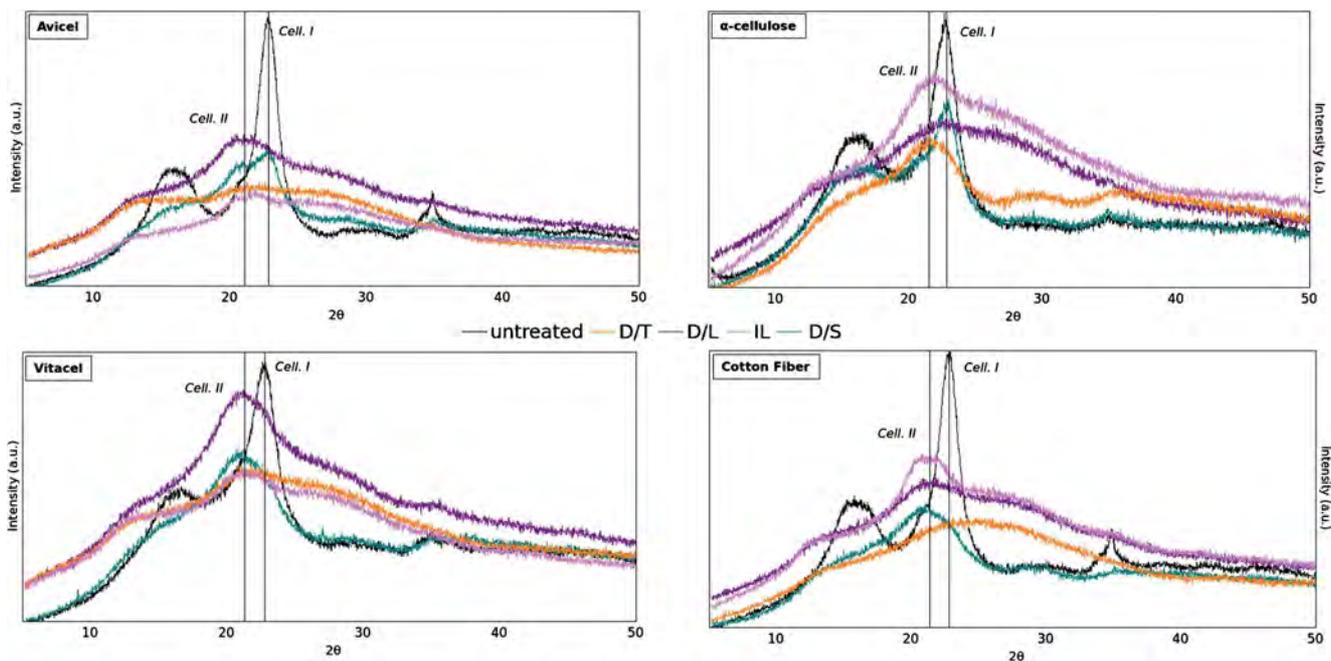


Fig. 2 XRD diffractograms showing different crystallinity forms between the different commercial and regenerated cellulose samples

Similarly, the use of D/S solvent system reduced the DP_v values by half for the high DP cellulose samples and by nearly 20 % for the low DP cellulose samples. This system known to amorphize cellulose samples also induced a significant decrease of the DP_v . The D/L solvent system, used for molar mass characterization by size exclusion chromatography (SEC) [53], did not modify the low DP samples, but decreased by almost half the DP of high molar mass samples. Finally, the use of D/T solvent system did not significantly affect the chain length of the samples. However, the DP_v values were slightly higher than for the untreated samples, and that might be due to the formation of aggregates over the dissolution.

Discussion

In this study, we have tried to find the optimal conditions for the dissolution of different cellulosic samples (low or high DP, various crystallinity rate) in four different solvents, the classical D/L and three others (D/S, IL, D/T) chosen for their relative innocuity, and to evaluate the influence of the dissolution/regeneration process on cellulose properties (crystallinity and DP_v). Obviously, the conditions of dissolution (temperature and time) and of regeneration (antisolvent and temperature) varied according to the sample/solvent couple and impacted cellulose modification, but as these conditions were necessary for the dissolution, it is still worthy to study the ability of each solvent to dissolve the various kinds of cellulose and the impact of the dissolution on cellulose integrity, especially on its MW. This is particularly important in the quest for an alternative solvent for the SEC analysis of cellulose.

From the results presented above, basic conclusions would be that some solvents, such as D/S, dissolve correctly only one kind of cellulose (cotton fibers). Others, such as D/L, dissolve more efficiently low DP samples independently of their crystallinity. Finally, D/T and IL were able to dissolve all types of cellulose.

However, as the operating conditions to reach the dissolution were different and as the dissolution mechanisms are also variable depending of the solvent nature [4], the effects of these dissolutions need to be discussed.

The mechanism of dissolution of cellulose in D/S (DMSO/DEA/SO₂) has been described in the 1980s [11] and D/S is, among the non-derivatizing and non-aqueous solvents, supposed to be one of the more versatile [54]. Dissolution in D/S is obtained at room temperature (Table 2), took more time

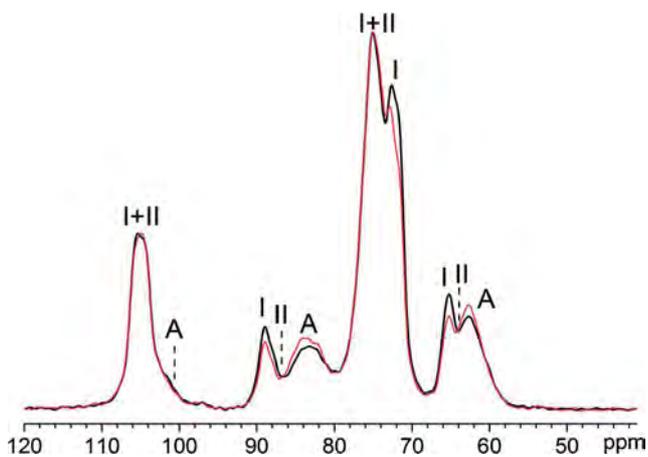


Fig. 3 Solid-state ¹³C CP-MAS NMR spectra of α-cellulose untreated (black) and after regeneration on the D/S solvent system (red). I, II, and A indicate signals characteristics of cellulose type I, cellulose type II, and amorphous cellulose, respectively

for the high MW samples (i.e., α -cellulose and Vitacel) and seemed less efficient with highly crystalline samples (i.e., α -cellulose and Avicel) according to turbidity values (Table 4) and to the persistence of Cellulose I crystalline structure after regeneration (Fig. 2). Finally, looking at the TGA and DP_v results (Tables 5 and 6), it degraded all samples significantly, except the cotton fibers. The cellulose from these fibers is the purest sample of cellulose as it did not undergo classical extraction treatments of hemicelluloses and lignin, supporting the idea that the complex between the -OH of cellulose, SO₂, and amine in DMSO is really specific to native cellulose [11]. For the other samples, the presence of impurities and/or the modifications of the cellulosic arrangement during the extraction and purification process seem to hinder the formation of this complex and subsequently to involve a marked degradation of their chain integrity either during the dissolution or the regeneration.

The use of ionic liquids is extremely trendy especially regarding carbohydrate samples. The choice of BMIM [Cl] was guided by the fact that it was supposed to dissolve microcrystalline cellulose, cotton linters, and bacterial cellulose with very high DP, up to 2500 [55]. During our experiments, even after many trials, solubilization required a high temperature of 110 °C while in the literature for the same kind of process, a temperature of 85 °C seemed to be high enough [56]. In these conditions, Avicel and α -cellulose were more difficult to solubilize, with longer dissolution times, probably because of high crystallinity and high MW, respectively (Table 1). However, all solubilizations were achieved satisfactorily (Table 4). The dissolution by IL caused the degradation of all cellulosic chains, as observed on T_o (Table 5), and the DP decrease was more important as the original DP of the cellulose sample increased (Table 6). Dissolution in BMIM [Cl] is promising as it dissolved all the samples, but the operating conditions (e.g., time, temperature, protective atmosphere...) are difficult to manage and can cause important degradation of the cellulosic chains.

Organic solvents in presence of organic salts (i.e., D/T and D/L) are also common media to dissolve cellulose. DMAc/LiCl is the usual solvent for the gel permeation analysis of cellulose and is supposed to be used in a future standard protocol [22]. The mechanism of dissolution is still under discussion but relates essentially to the complexation of the solvent either with the highly oxophilic cation or directly with the cellulosic hydroxyl groups, leaving the chloride ions free to form hydrogen bonds with the carbohydrate chains destroying the inner organization of the cellulosic pattern [57]. In our study, dissolution of the cellulosic samples in D/L occurred in 24 to 48 h at room temperature (Table 1) but was more efficient for the low MW samples (Table 4). After regeneration, all traces of native Cellulose I crystalline structure disappeared (Fig. 2), but the process provoked a strong decrease of T_o for all samples (Table 5) and of the DP_v value, especially for the samples with high molar mass. The loss of DP_v reached 39 and 54 % for Vitacel and α -

cellulose, respectively, questioning the ability of such solvent system to dissolve high MW cellulosic samples.

DMSO/TBAF is another well-known cellulose-dissolving solvent system, for which the mechanism is mainly based on the capacity of the fluoride ion to disrupt the hydrogen bond network within the cellulose, thanks to a strong ion-dipole interaction with cellulosic hydroxyl groups, and helped by the good solvation of the bulky cation by the DMSO [57]. The dissolution in D/T did not affect significantly the physical structure of the cellulose samples; neither T_o nor DP_v were decreased (Tables 5 and 6). And that was even true in the case of α -cellulose, which required a higher temperature of dissolution of 100 °C (Table 2). With this solvent system, short times of dissolution are necessary, the dissolutions are really effective for all the samples, and after regeneration the sample integrity is preserved.

According to our experiments, DMSO/TBAF seems to be the ideal candidate to dissolve various kinds of cellulosic samples and might be tested in the future as solvent for SEC analysis. However, alternative methods to monitor and quantify the dissolution could shed another light on the dissolution of cellulose, such as the real-time quantitative NMR previously applied to starch [58].

Conclusions

In this work, the dissolutions of four different types of cellulose in four different solvent systems DMAc/LiCl, DMSO/DEA/SO₂, BMIM [Cl], and DMSO/TBAF, known as underivatizing, were achieved. Each solvent system affected differently the cellulose structure.

Depending on the solvent used to solubilize the samples, some degradation could be observed. All systems seemed to degrade the cellulosic fibers. DMAc/LiCl achieved the dissolution of the low DP cellulose samples (i.e., Avicel and cotton fibers) but hardly that of the samples of higher molar mass (i.e., Vitacel and α -cellulose). DMSO/DEA/SO₂ dissolved properly without degradation of only the cotton fibers, but reduced consequently the DP of high DP cellulose samples. Into IL and DMSO/TBAF solvent systems, the dissolutions were achieved regardless of the kind of cellulose samples employed. However, with the operating conditions used, IL system degraded all celluloses, as observed with the decrease of the temperature of degradation and of the DP_v values by almost 50 %. Finally, DMSO/TBAF seemed to be the less degrading system: DP_v values of regenerated celluloses were similar to those of untreated celluloses. Considering the crystallinity modification, Avicel and cotton fibers regenerated from D/T were almost completely amorphous whereas α -cellulose and Vitacel regenerated from D/T do not exhibit pronounced crystalline signal. This solvent system appeared to be a promising non-derivatizing solvent both for reactivity but also as an elution solvent for the determination of the molar mass distribution.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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