ORIGINAL RESEARCH

The relevance of the pretreatment on the chemical modification of cellulosic fibers

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Abstract Cationized fibers and other kinds of chemically modified fibers impart many advantages in papermaking, but unfeasibly long reaction times are necessary to attain acceptable degrees of substitution, due to the low reactivity of bleached kraft pulps. In this work, different aqueous pretreatments were tested in order to activate cellulose towards a 60 min-long etherification with a quaternary ammonium reagent. Severe decrystallization treatments, namely alkalization with NaOH 20%, NaOH/urea or FeTNa, conducted to the best reactivity results (substitution from 2 to 10%), but the fiber properties were harshly affected. Pretreatments involving H_3PO_4 at different concentrations were also performed, with distinct results, from unnoticeable effects at 20% to amorphization and excessive depolymerization at 80%. Finally, aqueous ammonium thiocyanate was tested as activator and had little effect on fibers, although the addition of ammonia resulted in high degrees of substitution, while maintaining the pulps' capability to retain inter-fiber water and cellulose I as the prevalent allomorph.

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Graphical abstract
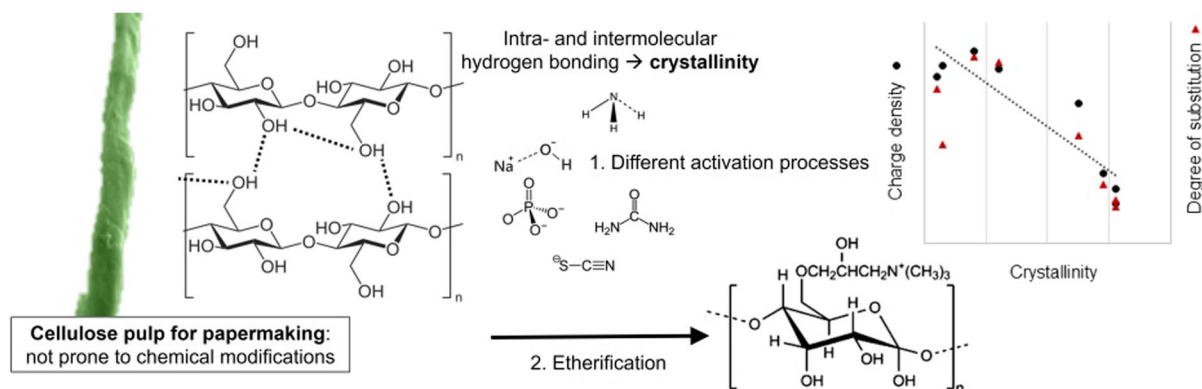
Introduction

Despite the usefulness of many cellulose derivatives, the conditions required currently by heterogeneous etherifications make a fiber functionalization stage impractical in a pulp or paper mill. Modified starches are widely used as wet-end additives, but fibers are always essentially composed of native cellulose, even though they could also attain interesting functionalities. For instance, inserting cationic functional groups, commonly quaternary ammonium, into the structure of cellulose fibers and/or fines can compensate their negative charge density (Sood et al. 2010), improve the internal bond strength of paper (Montplaisir et al. 2006), diminish the dependence on poorly biodegradable polymeric aids (Aguado et al. 2017), and decrease drainage time during sheet forming (Mayr et al. 2017). Sehaqui et al. (2016) produced cationic cellulose nanofibers with quaternary ammonium groups, and proved their usefulness in water treatment processes, as they could retain fluoride, nitrate, and other anions. Antimicrobial properties have also been shown, with death rates of 98% or even higher for *Candida oleophila* (Littunen et al. 2016). This chemical reaction, commonly known as cationization, is an etherification of some hydroxyl groups of cellulose in, most frequently, an aqueous alkaline medium (Prado and Matulewicz 2014).

The biggest hindrance to be overcome is the high crystallinity and thermodynamic stability of cellulose in pulps for papermaking. Mayr et al. (2017) obtained a degree of substitution of only 0.034 after treating fines with a quaternary ammonium epoxide for 15 h. Most likely, the best conversion values result from oxidation followed by Girard's reagent T (Sirviö et al. 2014), but etherifications are still more common in the literature, also more common than crosslinking (Gruber et al. 1996). Furthermore, our work aims to study the effects of pretreatments not only for cationization, but also for a broad variety of chemical modifications on cellulose. Previous kinetic studies of cellulose etherification have suggested that the reaction takes place quickly in activated regions of fibers, but very slowly in stable regions (Hedlund and Germgård 2007). In a recent article, the authors have proved that the cationization of cellulose fibers showed similar kinetics (Aguado et al. 2018), as the degree of substitution stabilized after a certain time, and further functionalization could be obtained if prior activation of fibers was performed.

Cellulose polymorphism is due to the intramolecular and intermolecular hydrogen bonding system. Cellulose in fibers from wood and plants is essentially cellulose Iβ, a form with a certain crystal structure that was described in detail by Nishiyama et al. (2002). Some treatments may affect hydrogen bonding between hydroxyl groups, thus decreasing crystallinity or converting an allomorph into another. Decrystallization, i.e., the creation of amorphous domains, is one of the ways of activating cellulose for functionalization, since it increases the entropy of the polymer. Other ways involve swelling and

ionization. Alternatively, if the reaction desired is especially difficult, an easier nucleophilic substitution can be performed beforehand, as it is easier to transform already modified cellulose (Heinze 2004).

Although certain organic polar liquids and molten salts can be used to activate cellulose (Fischer 2004), this work focuses on aqueous pretreatments, as the subsequent functionalization is carried out in an aqueous solution. In order to obtain cationic fibers with high strength, the cellulose activator must swell the fibers, but not dissolve them. Generally speaking, cellulose solvents can be used as activators if the conditions are milder than those used for dissolution. In fact, some sort of activation is always the first stage of dissolution in aqueous media (Zhang et al. 2009).

In this paper, the objective is to compare four different activating pretreatments under a total of 26 sets of experimental conditions, in order to test their influence on cellulose fibers and to improve the results of the following reaction. Then, cationization is carried out under mild conditions. Despite keeping the focus on cationization, the findings could be extrapolated to other etherifications of polysaccharides. The selection of cellulose activators include sodium hydroxide, more widely used than any other in previous studies, but also some agents used in the literature to dissolve this polymer: orthophosphoric acid (H_3PO_4) (Vinogradov et al. 2002), FeTNa (Vu Mahn et al. 2010), ammonium thiocyanate (NH_4SCN) with or without ammonia (Mahmud-Ali and Bechtold 2015), and several combinations with urea (Jin et al. 2007). It is hypothesized that chemical modifications of wood pulp by etherification can yield satisfactory results with a short reaction time, as long as a pretreatment that produces the proper structural changes in cellulose has been applied.

Materials and methods

Pulp and reagents

All pretreatments and reactions took place on a bleached kraft pulp from *Eucalyptus globulus* (BEKP), also used in a previous work of ours (Aguado et al. 2017). The Schopper–Riegler freeness was 18 °SR. Its composition, determined by following the common TAPPI methods, resulted in 82% α-cellulose (T429 cm-10), 0.4% ashes (T211 om-02), 0% acid-

insoluble lignin (T122 om-15), kappa number of 1 (T236 om-99). The average molecular weight (M, Da) of the cellulose pulp, estimated from the limiting viscosity number (η, mL/g) measured in a copper(II) ethylenediamine solution (Cuen) as defined in ISO 5351, by applying the Mark-Howink equation (Eq. 1) with the parameters for cellulose reported by Eckelt et al. (2011), was found to be 189 kDa.

$$\eta = 0.0653\,M^{0.735} \tag{1}$$

An aqueous solution of orthophosphoric acid (H_3PO_4, 85%), urea pearls, sodium tartrate dihydrate and iron trichloride ($FeCl_3$) were purchased from Panreac (Barcelona). A solution of (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC) with a mass concentration of 60% was obtained from Sigma-Aldrich (Madrid).

BEKP fibers were disintegrated in water at 3000 rpm (disintegrator from Lorentzen and Wettre), in accordance to ISO 5263. The consistency was adjusted to 10% and the pulp was stored at temperatures below 10 °C.

To synthetize FeT, an iron(III)-tartrate complex, 20 g of $FeCl_3$ and 96 g of sodium tartrate dihydrate were dissolved in 200 mL of distilled water, adding sulphuric acid to adjust the pH to 4. The dissolution was submitted to gentle stirring (200 rpm) for 30 min. By pouring it into 300 mL of acetone, the coordination compound immediately precipitated as a yellow powder. The solid and the liquid were separated by filtration. FeT became FeTNa in a NaOH solution (El-Wakil and Hassan 2008).

The experimental procedure, including the characterization of both the pretreated fibers and the functionalized fibers, is schematized in Fig. 1.

Pretreatments

All the pretreatment processes, which involved the reagents listed in Fig. 1 at different concentrations, took place at constant temperature and with a 3-bladed stirrer (600 rpm), by means of an Agimatic-E plate (Selecta) with a PID device including a Pt-100 probe from Sensotherm. The pulp was soaked in the activation solutions at a liquid-to-solid ratio of 20.

It should be pointed out that the pretreatments with NaOH/urea required adding the urea pearls to a precooled NaOH solution. Otherwise, the exothermic
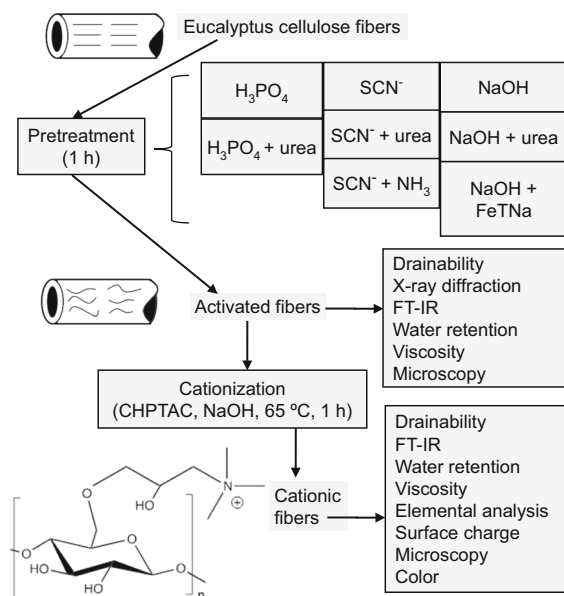
Fig. 1 Simplified diagram of experimentation

dissolution of the alkali would have prompted the hydrolysis of urea. Treatments with NaOH at 60 °C were disregarded, since this activation is known to work better at low temperature (Jin et al. 2007).

After 60 min of agitation and heating, the suspensions were diluted in water to a pulp consistency of 1%. Then, they were vacuum-filtered through an 11 μm paper filter. The solids were weighted to determine the yield towards non-solubilized fibers. A small portion (less than 2%) of the solid fraction was used to measure the moisture content by drying at 105 °C (ISO 638). The filtrate was poured into ethanol, with an ethanol-to-water ratio of 1, to regenerate dissolved cellulose, if any. The previous solid fraction was also poured into the suspension to ensure that the swelling effects of ethanol were the same for all pretreatments. This suspension was filtered again and left to dry at room temperature for 24 h.

Cationization

Etherification of cellulose with CHPTAC was carried out under mild conditions. Assuming that BEKP consisted solely of anhydroglucose units (AGU), it was soaked in a CHPTAC/NaOH aqueous solution so that the CHPTAC/AGU mole ratio was 1.6 and the NaOH/CHPTAC mole ratio was 1.2.

In all cases, the temperature was kept at 65 °C for 60 min., with a pulp consistency of 3%. Afterwards, the suspension was neutralized with diluted HCl and poured into ethanol to regenerate cationic cellulose in solution. Fibers were retained on a Whatman filter (11 μm), washed with distilled water, and allowed to reach equilibrium moisture at approximately 23 °C.

The percentage of nitrogen (%N) in the cationic fibers was determined by combustion with LECO's elemental analyzer CNS-2000I. The degree of substitution (DS) was estimated from Eq. 2 (Aguado et al. 2018). A Charge Analysis System device from AFG was used to measure the surface charge density (CD). Since the equipment is designed for liquids, a back titration method was used instead of a direct one. For that, a small sample of cationized pulp was soaked in excess of an anionic polyelectrolyte, sodium polyethylenlsulphate (PESNa, 1.8 meq/L). The liquid was titrated with a cationic polyelectrolyte, polydiallyldimethylammonium chloride (PDADMAC, 2.2 meq/L). The endpoint of the potentiometric titration was the isoelectric point (0 mV). Inversely, to measure the charge density of BEKP, a sample was soaked in PDADMAC and the titrant was PESNa.

$$DS = 162\%N/(1401 - 152\%N) \qquad (2)$$

Observation of structural changes

Representative samples of pretreated pulps, once dried, were submitted to a PANalytical's powder X-ray diffractometer using X'Pert software. Gaussian deconvolutions of the diffraction patterns and integrations of the peaks were performed with Systat's Peakfit software. The crystallinity index (CI) was calculated as follows:

$$CI = \left(A_{1-10(I\beta)} + A_{110(I\beta)} + A_{200(I\beta)} + A_{110(II)} \right. \\ \left. + A_{020(II)} + A_{004} \right)/A_{TOTAL} \qquad (3)$$

In Eq. 3, A is the area under each of the Gaussian peaks resulting from integration. Miller indices $1-10(I\beta)$, $110(I\beta)$, $200(I\beta)$, $110(II)$, $020(II)$ and 004 correspond to the characteristic peaks of cellulose Iβ, II or, in the case of plane 004, both crystalline allomorphs (French 2014).

The limiting viscosity number (η) was measured for both the pretreated and the cationized pulps. Pulp viscosity was measured by following the ISO standard

5351. Briefly, a sample was completely dissolved in Cuen and the time taken to flow through a Cannon–Fenske capillary viscometer was compared to that of the blank solution. Then, Eq. 1 was used to estimate the average molecular weight, which was divided by the molecular weight of AGU, 162, to calculate the degree of polymerization (DP) of the pretreated samples.

Certain pretreated and cationic samples were chosen, along with BEKP, to obtain ATR-FTIR spectra by using a Bruker Tensor 27 spectrometer. Scans were carried out from 3800 to 800 cm^{-1}, with a resolution of 4 cm^{-1}. Furthermore, some visible light absorption spectra were produced by means of a Varian Cary 50 UV–Vis spectrophotometer, from 400 to 750 nm.

Analysis of fiber properties

The Schopper–Riegler freeness was measured in a DFR-05 device from Mütek, by using a 70 mesh screen (212 μm of aperture size). The measurement was performed in a suspension of 2 g of pretreated pulp in 1 L of demineralized water with the "Freeness" settings.

The pulps were also observed by scanning electron microscopy (SEM from JEOL, model JM-6400). Vacuum-dried fibers were distributed on a cylindrical slide, which was coated with gold.

Water retention value (WRV) was determined in accordance with the SCAN-C method 62:00, as the ratio (w/w) of water retained by a test pad of fibers after centrifugation (3000 g, 15 min) to the dry pad. The test pad was formed by filtration of the samples dilute suspensions on a 100 μm filter paper. It must be noted that the WRV calculated by following this method is notoriously lower than that measured by the TAPPI useful method 256 (900 g for 30 min).

Results

Direct effects of pretreatments

Table 1 shows WRV, the Schopper–Riegler number, the limiting viscosity, the average degree of polymerization and the yield for each set of experimental conditions. Calculations were performed assuming that the pretreatments are not derivatizing. Since water

is a swelling agent itself, the original pulp treated with water alone (numbered 0 in Table 1) was submitted to the same mechanical treatments as the rest of the cases. This way, the focus can be put on chemical activation.

By using the pretreatments involving H_3PO_4 at high concentrations (Table 1, sample codes 11 and 12), NaOH 20% (code 14), NaOH/urea (codes 15, 16) or NH_4SCN 60% (code 26), fibers swelled far more than when they were soaked in water alone (code 0), as can be observed from the water retention value. However, WRV decreased from 1.6 to 1.1 g/g after a treatment with FeT 10% and NaOH 6% (code 20), but it must be taken into account that fibers suffered drastic structural changes. They formed a dark green gel as soon as stirring started and most of them were regenerated upon dilution, but they kept an orange-to-red color after neutralization and rinsing. *Supplementary material* shows that Fe atoms were somehow inserted into the structure of cellulose, even when FeT concentration was 2.5%.

WRV indicates the capability of the fibers to retain intra-fiber water while the Schopper–Riegler number (Table 1) shows the capability to retain inter-fiber water when a fast filtration process occurs. Yield values below 100% may not only indicate the dissolution of cellulose or its hydrolysis towards sugars, but also the dissolution and hydrolysis of hemicellulose, generally less stable. Regarding viscosity, it must be taken into account that the repeatability reported in the corresponding TAPPI standard (T230 om-13) is 4%, and thus, slight differences in this measurement can be simply due to random error.

Figure 2 displays SEM images for the original pulp that had been treated with water alone (Fig. 2a, d and g), and for pretreatments that have been numbered in Table 1 as 10 (Fig. 2b), 14 (Fig. 2c), 23 (Fig. 2e), 16 (Fig. 2f), 25 (Fig. 2h) and 18 (Fig. 2i), at different magnification values. Considering that the pulp pad was prepared in the same way for all samples, treatments with H3PO4 60% or with NaOH resulted in less packed density and less ease to form fiber bundles (Fig. 2b, c). In particular, the alkaline treatments resulted in clear external fibrillation (Fig. 2c, f and i).

Partial amorphization of fibers can be estimated from the X-ray diffraction patterns in Fig. 3. The Miller indices for the most notorious crystalline peaks are shown, and the crystallinity index (CI) was

Table 1 Conditions and general results for the different pretreatments

Code	Activation agent	T (°C)	WRV (g/g)	Schopper–Riegler (°SR)	η (mL/g)	Average DP	Yield (%)
0	Water	23	1.6	18	491	1159	100
1	H₃PO₄ (aq.) 20% w/w	30	1.5	18	478	1118	100
2	H₃PO₄ (aq.) 20% w/w	60	1.6	18	502	1195	99
3	H₃PO₄ (aq.) 40% w/w	30	1.7	15	481	1127	94
4	H₃PO₄ (aq.) 40% w/w	60	1.8	16	482	1130	90
5	H₃PO₄ (aq.) 40% w/w + Urea 2.5% w/w	30	1.8	15	490	1156	92
6	H₃PO₄ (aq.) 40% w/w + Urea 2.5% w/w	60	1.8	15	461	1064	90
7	H₃PO₄ (aq.) 60% w/w	30	1.7	13	413	916	84
8	H₃PO₄ (aq.) 60% w/w	60	1.9	12	340	703	82
9	H₃PO₄ (aq.) 60% w/w + Urea 2.5% w/w	30	1.9	13	405	892	83
10	H₃PO₄ (aq.) 60% w/w + Urea 2.5% w/w	60	2.0	12	352	737	80
11	H₃PO₄ (aq.) 80% w/w	30	2.4	< 10	210	365	73
12	H₃PO₄ (aq.) 80% w/w	60	2.2	< 10	147	225	60
13	NaOH (aq.) 10% w/w	23	1.9	16	461	1064	87
14	NaOH (aq.) 20% w/w	23	2.2	12	495	1172	79
15	NaOH (aq.) 10% w/w + Urea 2.5% w/w	23	2.1	14	511	1224	75
16	NaOH (aq.) 20% w/w + Urea 2.5% w/w	23	2.3	11	475	1108	69
17	NaOH (aq.) 10% w/w + FeT 2.5% w/w	23	1.9	11	422	943	82
18	NaOH (aq.) 20% w/w + FeT 2.5% w/w	23	1.9	10	367	780	77
19	FeT 10% w/w in NaOH (aq.) 3% w/w	23	1.5	< 10	309	617	79
20	FeT 10% w/w in NaOH (aq.) 6% w/w	23	1.1	<10	231	416	70
21	NH₄SCN (aq.) 45% w/w	30	1.6	18	465	1077	98
22	NH₄SCN (aq.) 45% w/w	60	1.8	19	476	1111	89
23	NH₄SCN (aq.) 45% w/w + Urea 2.5% w/w	30	1.7	18	488	1150	96
24	NH₄SCN (aq.) 45% w/w + Urea 2.5% w/w	60	1.8	17	520	1253	82
25	NH₄SCN 45% w/w in NH₃ (aq.) 25% w/w	30	1.9	18	506	1208	84
26	NH₄SCN 60% w/w in NH₃ (aq.) 25% w/w	30	2.1	18	517	1244	85

calculated with Eq. 2. The CI for H₃PO₄ 80% could be overestimated since the peak assigned to the (110) reflection of cellulose II may be actually due to the presence of cellulose phosphate.

FTIR spectra in Fig. 4 are presented mainly to check whether or not pretreatments were derivatizing. Except for the cationized sample, the shape of all spectra resembles native cellulose. The absorbance at 897 cm⁻¹ (a) can be assigned to C1–H bending and is sensitive to the supramolecular order of the polymer. The most prominent peak of cellulose is found at 1040 cm⁻¹ (b), related to C–O–C stretching, and it is possible to distinguish multiple peaks at bands

assigned to different vibrations of the C–C bonds (c). The band at 1623 cm⁻¹ (d) is related to the O–H bonds in absorbed water. The peaks found at 2282 cm⁻¹ (e) and 3300 cm⁻¹ (f) can be associated to stretching of C–H and O–H bonds in cellulose, respectively. Besides these ones, the spectrum of cationic cellulose has notorious peaks at 1427 and 1390 cm⁻¹ (g), due to the quaternary ammonium group (Aguado et al. 2017).

Influence of the pretreatments on cationization

Table 2, which contains the charge density (CD) and the DS of all samples, is an indication of the reactivity
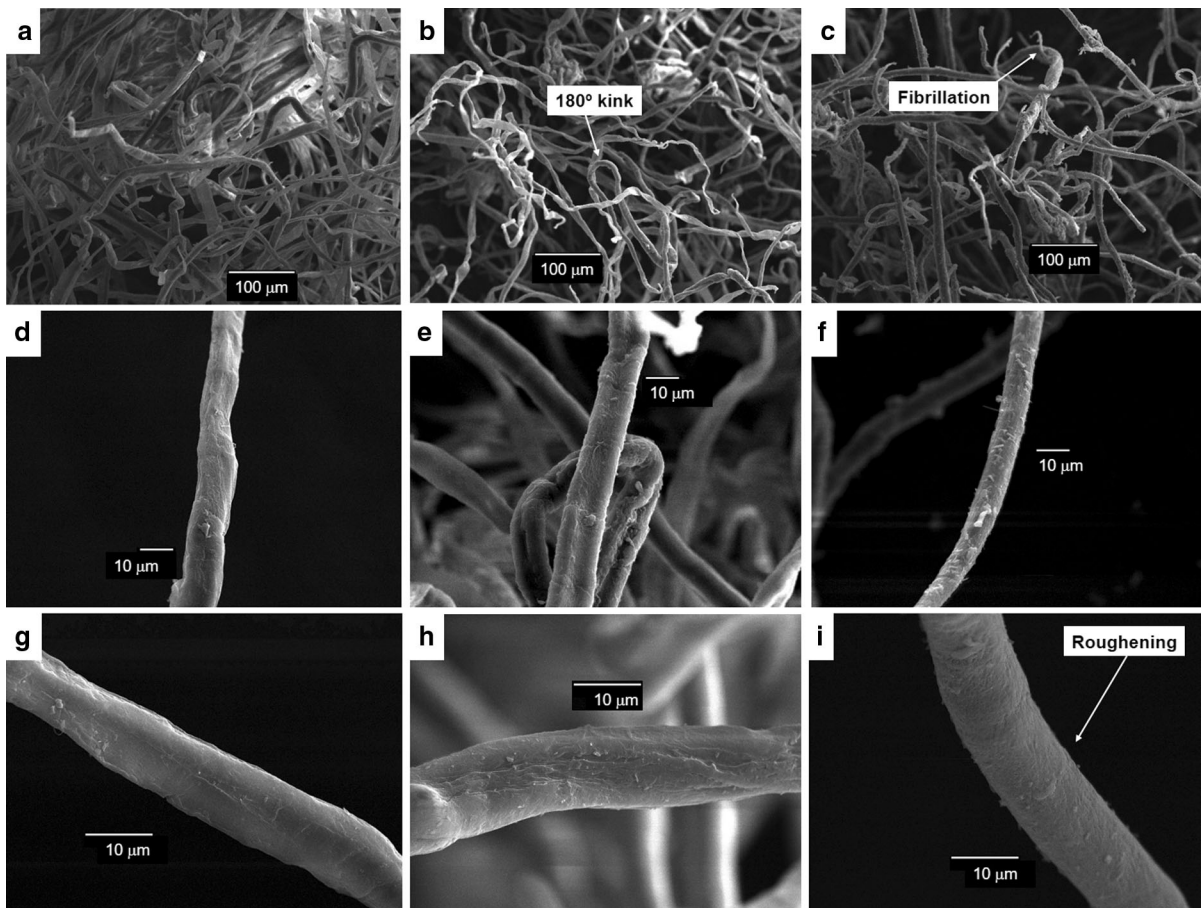
Fig. 2 Micrographs at × 200 of pulp (**a**), pulp treated with H_3PO_4 (**b**), and pulp treated with NaOH (**c**). Micrographs at × 1000 of pulp (**d**), pulp treated with SCN^- (**e**), and pulp treated with NaOH and urea (**f**). Micrographs at × 200 of pulp (**g**), pulp treated with SCN^- and NH_3 (**h**), and pulp treated with FeTNa (**i**)

provided by each pretreatment. If there is a discrepancy between DS and CD, the latter is preferred to indicate the extent of cationization, because the former may carry overestimation due to the presence of cationized hemicellulose or underestimation due to heavier atoms (iron, phosphorus).

A scan at visible light wavelengths was motivated by the observation of yellowing in NaOH-treated samples, and it was confirmed that the absorbance of blue light ($\sim$ 400–500 nm) increased. To show that this yellowing is not a necessary consequence of cationization, the absorbance values at 457 nm are displayed for other samples in Table 3. Since absorbance could increase by simply using thicker samples, it should be noted that this information is only valuable when compared with the original pulp.

Table 3 also contains the WRV, the η and the Schopper–Riegler number of selected cationic samples. The increase in viscosity is not only due to the increase in the molecular mass by the attachment of quaternary ammonium groups, but also to the change in the polymer conformation (*a* in Eq. 1) (Harding 1997).

Discussion

Orthophosphoric acid treatments

A mild swelling agent only affects the amorphous portion of the fiber. Only with strong swelling agents, like H_3PO_4 80%, the crystalline structure of the fiber was disrupted. This was the only concentration that

Fig. 3 X-ray diffraction patterns of representative treatments, indicating the Miller indices of the most important planes and the CI (calculated by the area method) at the right side of each spectrum
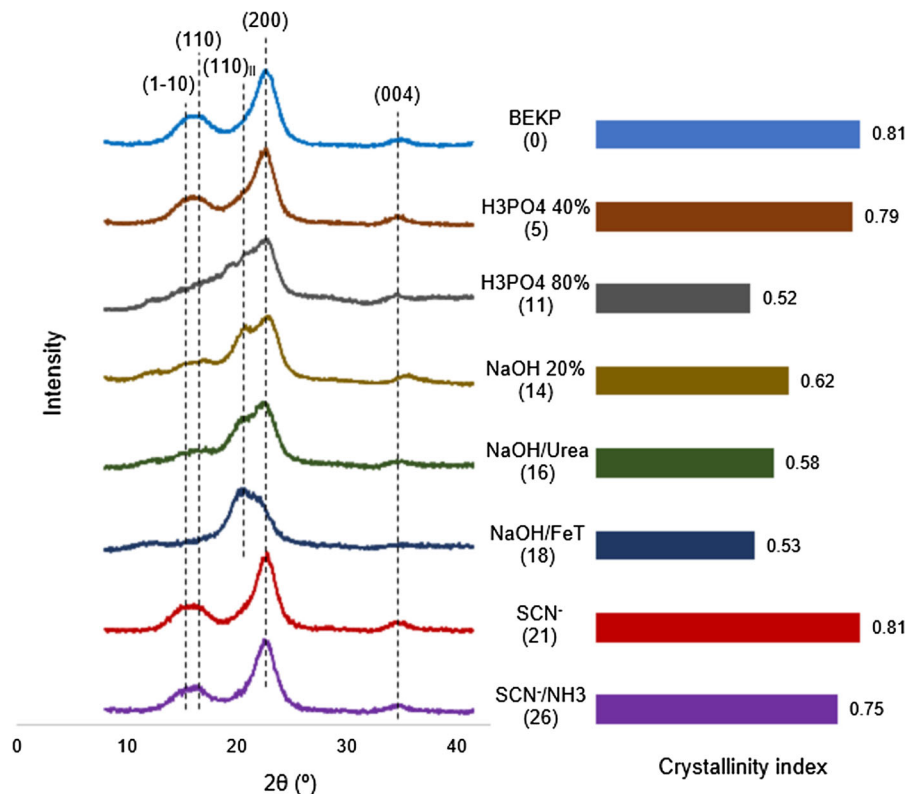
activated cellulose towards high DS and CD values (Table 2). Figure 5 relates those variables to decrystallization.

A mechanism for the phosphate decrystallization of cellulose was proposed by Zhang et al. (2009): first, cellulose is esterified towards cellulose phosphate. This reaction is reversible. Then, water molecules compete with hydroxyl groups from cellulose to form hydrogen bonds with other cellulose chains. As a by-reaction, hydrolysis of β-glycosidic bonds occurs, particularly at high temperature. If it stays aqueous and below 100 °C, cellulose phosphate is easily converted back to free phosphoric acid and amorphous cellulose.

The by-reaction aforementioned, cellulose depolymerization, always happens when treated with any strong mineral acid or even with concentrated weak acids. If conditions are too mild to hydrolyze the crystalline regions, only the amorphous fraction is attacked and solubilized, resulting in chains of highly-crystalline cellulose (Wei et al. 1996). The particularity of phosphoric acid is that it decreases the CI of

cellulose. At the same time, it is a decrystallization agent and a depolymerization agent.

In fact, only the pretreatments involving H_3PO_4 60% or 80% (Table 1, codes 7–12) led to significant depolymerization of cellulose. The low yields obtained with H_3PO_4 40% may be due to the hydrolysis and solubilization of hemicellulose. As for the temperature effect, an increase of 30 °C led to a decrease in the DP of ca. 500 (samples 8 and 12 with H_3PO_4 80%). As a consequence of high temperatures and high acid concentrations, fiber–fiber interactions were much affected and the Schopper–Riegler number could not even be quantified.

The addition of urea showed little effect on activation, unlike in the pretreatments with NaOH or thiocyanate. Even though urea has been reported to have a positive influence on phosphorylation, it also inhibits the inverse reaction towards regenerated phosphoric acid and amorphous cellulose (Ghanadpour et al. 2015).

Diffraction patterns in Fig. 3 also support the notion that phosphorylation was reversed in the aqueous media when H_3PO_4 concentration was 40%,
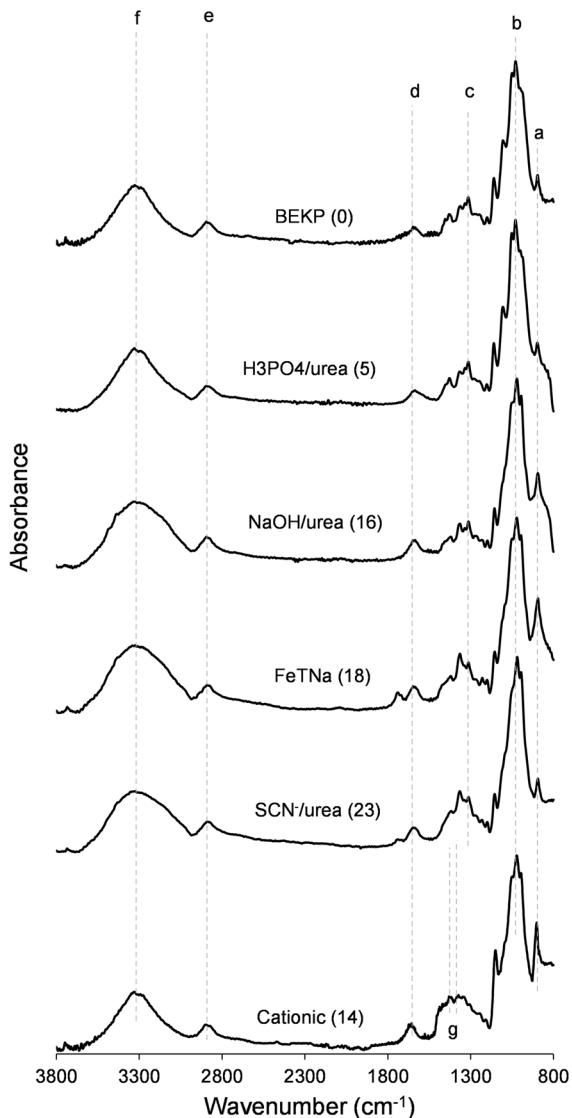
Fig. 4 FTIR spectra of the original pulp, the pulp after some representative pretreatments, and the pulp after a NaOH/urea treatment followed by cationization

Table 2 Cationicity of the 27 cationized samples, including the original pulp (0) and the 26 pretreated pulps

Code	DS	CD (meq/g)
0	0.020	0.081
1	0.025	0.084
2	0.029	0.126
3	0.030	0.150
4	0.036	0.164
5	0.032	0.142
6	0.035	0.163
7	0.032	0.185
8	0.036	0.218
9	0.030	0.205
10	0.037	0.218
11	0.084[a]	0.340
12	0.057[a]	0.277
13	0.082	0.283
14	0.099	0.355
15	0.089	0.286
16	0.101	0.391
17	0.050[a]	0.242
18	0.053[a]	0.363
19	0.037[a]	0.355
20	0.065[a]	0.382
21	0.024	0.111
22	0.029	0.156
23	0.030	0.154
24	0.030	0.168
25	0.052	0.290
26	0.059	0.284

[a]Possibly underestimated

but the shape of the pattern for H_3PO_4 80% between 17° and 20° resembles that of lowly-substituted cellulose phosphate (Wan Daud et al. 2011). This retention of some phosphate groups is undesirable because of its negative CD.

NaOH and NaOH/urea treatments

The most obvious effect undergone by fibers in aqueous, strongly alkaline solutions was swelling. Swelling produces internal stresses that, in these cases,

break intermolecular bonds irreversibly, and thus the degree of supramolecular order decreases (Fig. 3). Each fiber became able to retain more water, as shown by WRV (Table 1) and by the peak associated to absorbed water in FTIR spectra (Fig. 4b, d). At the same time, the surface area of the fiber increased, as external fibrillation is clear in Fig 2c, f.

The use of NaOH to increase reactivity of cellulose is already well-known (Okano and Sarco 1985). This conventional method proved better for cationization (Table 2) than any of the non-alkaline pretreatments. By adding urea, decrystallization increased (Figs. 3 and 5), fibers swelled more, and even higher DS and CD values were reached by functionalization. Nonetheless, Jin et al. (2007) showed that an aqueous

Table 3 Properties of certain cationized samples, compared to those of the original pulp

Code	WRV (g/g)	Schopper–Riegler (°SR)	η (mL/g)	A_{457}
0 (before cationization)	1.6	18	491	0.134
0	1.9	18	510	0.135
5	1.9	16	504	0.132
14	2.8	15	617	0.144
16	3.1	14	592	0.149
18	2.8	14	464	0.230
21	1.9	18	496	0.136
26	2.4	19	560	0.139
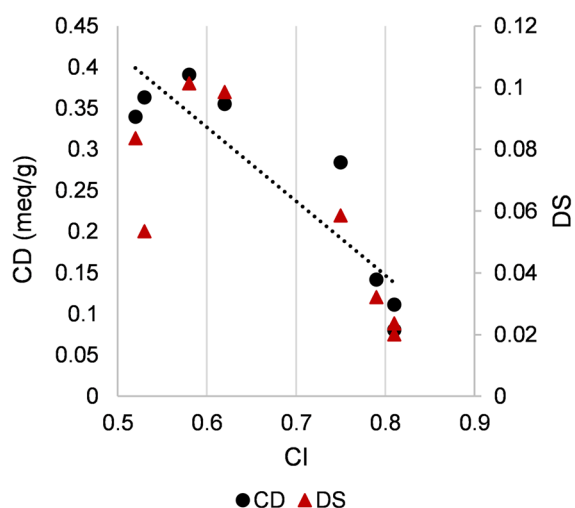
Fig. 5 Influence of the extent of the decrystallization on the reactivity towards cationization, expressed as the degree of substitution (DS) and as the charge density (CD)

solution of urea alone barely amorphizes cellulose. The role of urea in cellulose dissolution is still not clear and different explanations have been suggested, e.g., that urea hydrates become bonded to the NaOH hydrates complexed with cellulose, as many studies show no direct interaction between urea and cellulose (Budtova and Navard 2016).

However, these alkaline pretreatments have important drawbacks if these functionalized fibers are meant to be used to form sheets of acceptable strength. Upon treatment with NaOH or NaOH/urea, cellulose Iβ was partially converted into amorphous cellulose and into cellulose II (Fig. 3). Cellulose II keeps the fiber structure, but it is mechanically inferior to cellulose Iβ. The low Schopper–Riegler numbers, particularly in contrast to the high WRV, show that inter-fiber water is easily removed by fast filtration. These weakening ways to activate cellulose are undoubtedly useful

when aiming at soluble derivatives, but not for applications in which strength is required. Drainability improved after cationization (Table 3), but SR numbers are still far from the original pulp and this would hinder sheet forming.

Yellowing of cationized samples was another undesired side-effect (Table 3). While this was only caused by cationization following alkaline pretreatments, the pretreatments themselves (at room temperature) did not produce any change in color. However, decrystallization likely made cellulose more sensitive to heat-induced oxidation during cationization. In fact, it has been reported that etherifying nanocellulose with quaternary ammonium groups at 120 °C results in a brown product (Ho et al. 2011).

Treatments with FeTNa

It has been verified that samples treated with H_3PO_4 20–60% did not retain phosphate groups, no carbamate groups were appreciated in the FTIR spectra of urea-treated samples (Fig. 4), and cellulose was not esterified towards cellulose thiocyanate with NH_4SCN (Figs. 3 and 4). However, regardless the concentration, Fe(III) remained bound to cellulose after dilution, neutralization, and rinsing with distilled water, hot water and different organic solvents. Such binding was not expected, as in previous works FeTNa is regarded as a non-derivatizing solvent system (El-Wakil and Hassan 2008), although the complex was both prepared and applied in different ways.

It can be proposed that, in the first place, cellulose undergoes swelling and activated in the alkaline medium, being then attacked by FeT. The dipolar bonds between the central Fe atom and the –OH of tartaric acid groups are replaced by dipolar bonds between Fe and the different –OH groups of

anhydroglucose units. Unlike urea, FeTNa interacts with cellulose in terms of chemical bonds, but this interaction was not expected to be stable. Besides binding to cellulose and making it less crystalline, the attack by the iron complex promotes the switch from cellulose I to cellulose II (Figs. 3 and 4). In fact, the lack of cellulose I, a case in which the peak for the (200) plane simply becomes unappreciable, was observed in only one of the X-ray diffraction patterns, corresponding to 20% NaOH and only 2.5% FeT.

During the treatments with FeT 10% (Table 1, codes 19 and 20), fibers were rapidly attacked and disintegrated. The harsh decrease in pulp viscosity (Table 1) is not only due to depolymerization, which undoubtedly happened to a lesser extent, but also to the new conformation of polymer chains when fibers were regenerated (lower M and a parameters of Eq. 1).

Their capability to retain inter-fiber water is very low, as indicated by the Schopper–Riegler number (Table 1). Due to their weakness, these fibers are not suitable for papermaking. Nonetheless, a high charge density was obtained after cationization (Table 2), which may be useful for other applications.

Ammonium thiocyanate treatments

NH$_4$SCN did not swell wood pulp fibers to a high degree and, as cellulose activator, its performance was clearly worse than that of NaOH and 40–60% phosphoric acid. Accordingly, the structural changes inflicted to cellulose were very slight, with no appreciable depolymerization (Table 1) and little decrystallization (Figs. 3 and 4), but fibers preserved their strength.

The big size of the NH$_4^+$ ion in the aqueous solutions of NH$_4$SCN was probably the main cause for these drawbacks. The influence of the cation has been explained by Mahmud-Ali and Bechtold (2015), who achieved high degrees of fiber swelling with NaSCN/urea. According to them, replacing some water molecules by urea in this complex system resulted in better activation, which was expected because the latter can prevent cellulose chains from aggregation by steric effects.

In contrast to aqueous systems, it is known that cold solutions of NH$_4$SCN in anhydrous ammonia can even dissolve high-DP cellulose fibers (Hudson et al. 1983). In this work, aqueous NH$_3$ was used to avoid dissolution. The presence of NH$_3$ molecules eased the dissolution of NH$_4$SCN in the medium by increasing the saturation concentration, caused fiber swelling by themselves, and partially replaced water in the complex bonding systems. As a result, cationic fibers that had undergone these treatments (Table 1, codes 25 and 26) achieved values of substitution and charge density in the medium range (Table 2), but keeping most cellulose I, high DP, low yellowness and high Schopper–Riegler numbers (Table 3). The viscosity values obtained (Table 1), higher than that of the original pulp (491 mL/g), mean that the chemical agent could have selectively dissolved hemicellulose or low-DP cellulose.

Conclusions

- Bleached wood pulp was etherified with (3-chloro-2-hydroxypropyl)trimethylammonium chloride, attaining degrees of substitution as low as 0.02 when no pretreatment was applied.
- Alkalization with NaOH was used to activate cellulose, resulting in relatively high degrees of substitution (0.1) and charge density values once cationized. Besides, the addition of urea enhanced the effect of NaOH, namely swelling, dissolution, and decrystallization. However, fibers became less capable of retaining inter-fiber water upon sheet forming, and also less white when cationized.
- An iron(III)-tartrate complex promoted both decrystallization and conversion of cellulose I into cellulose II, but the fibers were severely weakened.
- Alternative pretreatments consisting on orthophosphoric acid and ammonium thiocyanate were tested. It was found that the former needed a high concentration (80%) to activate cellulose towards degrees of substitution above 0.05, and fibers were unusable for papermaking due to the severe treatments. Ammonium thiocyanate was ineffective unless mixed with aqueous ammonia, which resulted in good fibers activation while keeping good drainability.

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