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1 ORIGINAL PAPER

2 Cationic cellulosic derivatives as flocculants in papermaking

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Author Proof

7 **Abstract** Water-soluble cationic cellulose deriva-
8 tives were synthesized by three different procedures,
9 cationizing bleached hardwood kraft pulp with (3-
10 chloro-2-hydroxypropyl) trimethylammonium chlo-
11 ride. The first procedure involved a previous depoly-
12 merization step with orthophosphoric acid. The
13 second one consisted on dissolving cellulose in
14 NaOH/urea before cationization. For the third proce-
15 dure, the reaction medium was heterogeneous since it
16 was carried out with a part of cellulose with high
17 degree of polymerization. Oppositely to the common
18 methods, cationization occurred under mild condi-
19 tions. Differences among the three derivatives are
20 illustrated by X-ray diffraction patterns of pretreated
21 samples, infrared spectra, and determinations of the
22 degree of substitution, the zeta potential, the charge
23 density and the molecular weight. The performance of
24 these polyelectrolytes for the flocculation of mineral
25 fillers used in papermaking was tested by laser
26 diffraction spectrometry. The flocculant with the
27 highest degree of polymerization and charge origi-
28 nated the best results, particularly when the filler used
29 was kaolin, proving that water-soluble cationic cellu-
30 lose derivatives can aid in the flocculation of fillers
31 used in papermaking. On the contrary, the shortest-
32 chained derivative was not effective. The results were
33 interpreted in terms of the characteristics of the
34 cellulose derivatives flocculants and of the fillers,
35 and neutralization and patching were proposed as the
36 dominant mechanisms.

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Introduction 40

Non-renewable and scarcely biodegradable polymeric 41
aids, such as cationic polyacrylamides (CPAM) or 42
polyethyleneimine (PEI), are often applied in paper 43
mills to achieve good retention of mineral fillers. The 44
particle size of these fillers is generally much smaller 45
than the wire mesh at the forming and drainage section 46
of the paper machine, and thus mechanical retention 47

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48 alone, if no flocculation agents are used, results in high
49 losses (Allen 1985). Cationic polyelectrolytes, besides
50 enhancing retention, improve the drainage behavior
51 and sheet formation, compensating somehow the
52 disruption of fiber bonding caused by fillers (Antunes
53 et al. 2008a).

54 Environmental concerns have led to research into
55 alternative flocculation agents to be used in different
56 fields, dedicating efforts to obtain cleaner and/or
57 cheaper polyelectrolytes from natural and renewable
58 sources. Introducing cationic ammonium groups into
59 polysaccharides has been the answer for many
60 researchers, given their availability and biodegrad-
61 ability. Starch, guar gum, cellulose, dextran and
62 chitosan, among others, have been proved useful
63 (Wood and Mora 1963; Prado and Matulewicz 2014).
64 Nonetheless, while cationic starch and cationic guar
65 gum have found good markets in the manufacturing
66 industries (QY Research 2017), the production of
67 cationic derivatives from the most abundant and
68 available of all polysaccharides, cellulose, remains
69 scarce. Although they are sold as cosmetic ingredients
70 (Kozubal et al. 2014), their potential in the paper
71 industry is being missed.

72 Yan et al. (2009) produced water-soluble cationic
73 cellulose (WSCC) from microcrystalline cellulose to
74 enhance flocculation in wastewater treatments. A
75 similar procedure, i.e., dissolving short-chained cel-
76 lulose in NaOH/urea and then performing cationiza-
77 tion in a homogeneous medium, was followed by Li
78 et al. (2015) aiming at using it as filler modifier. Other
79 authors started from chemically modified cellulose,
80 e.g., cellulose acetate and hydroxyethyl cellulose, as
81 raw materials to obtain WSCC (Liesiene 2010;
82 Liesiene and Kazlauske 2012). Those substrates
83 consisted of alkali-soluble cellulose or modified
84 cellulose with low degrees of polymerization (DP).
85 The resulting cationic derivatives, obtained by means
86 of epoxypropyltrimethylammonium chloride
87 (EPTAC) or (3-chloro-2-hydroxypropyl) trimethy-
88 lammonium chloride (CHPTAC), were not only
89 soluble in aqueous alkaline solutions but also in water.
90 However, solubilizing wood pulp in aqueous media is
91 much tougher. Actually, total dissolution of high-DP
92 **AQ1** α-cellulose may be simply impossible (Qi et al. 2011).

93 Short-chained WSCC may be adequate for floccu-
94 lation by charge neutralization, as long as particles
95 with negative zeta potential at the working pH are
96 involved, but due to its small DP, it is not a good

97 option for flocculation by bridging, which is the
98 primary mechanism of particle aggregation in the first
99 stage of the process. In fact, it was proved that the
100 bridging mechanism dominates when polymers of
101 high molecular weight and medium charge density are
102 used (Rasteiro et al. 2008a).

103 In order to obtain high molecular weight WSCC,
104 solubility in water must be achieved by the introduc-
105 tion of enough ionic groups into high-DP cellulose,
106 such as that from wood. Previous studies report the
107 production of cationic fibers with a degree of substi-
108 tution around 0.2, which can be useful for some
109 applications, but is still too low to promote solubility
110 (Moral et al. 2016).

111 Cellulose-based polyelectrolytes from birch wood
112 pulp were produced by Liimatainen et al. (2011) and
113 Sirviö et al. (2011). Instead of using NaOH and
114 CHPTAC or EPTAC, they performed a previous
115 oxidation step with sodium periodate, and then
116 cationized the substrate with Girard's reagent. They
117 were able to incorporate more than one cationic group
118 per monomer, thus obtaining a very high degree of
119 substitution (and consequently high charge density).
120 In spite of its high DP, this polymer was water-soluble
121 due to its high ionic character. However, to simulta-
122 neously improve retention and drainage in papermak-
123 ing, an agent of medium charge density is more
124 appealing than a highly charged one, as the latter
125 adopts a conformation that favors patching but hinders
126 bridging (Antunes et al. 2008b).

127 In this paper, the syntheses of three different water-
128 soluble cationic cellulosic derivatives from bleached
129 hardwood kraft pulp are reported. The conditions
130 applied, based on a previous kinetic study (Moral et al.
131 2016), are not as harsh as those usually reported in
132 literature (Song et al. 2008; Sirviö et al. 2011; Acharya
133 et al. 2014), since the reaction times are smaller,
134 making the process more feasible. Characterization of
135 the derivatives involved elemental analysis, X-ray
136 diffraction patterns and infrared spectra. Their charge
137 density, viscosity and zeta-potential were measured.
138 Their performance was tested by laser diffraction
139 spectrometry (LDS) with three different mineral fillers:
140 precipitated and ground calcium carbonate (PCC and
141 GCC, respectively), and kaolin, all of them frequently
142 used in paper mills. In fact, LDS has proved to be very
143 useful in assessing the performance of polymeric aids
144 in flocculation (Antunes et al. 2008b; Pinheiro et al.
45 2013; Rasteiro et al. 2008a; Seo et al. 2016). **AQ2**

Materials and methods

Materials

Industrial bleached *Eucalyptus globulus* kraft pulp (BEKP) with a refining degree of 34° SR was used as raw material.

An aqueous solution of the cationizing agent (3-chloro-2-hydroxypropyl) trimethylammonium chloride (60%) (CHPTAC), was purchased from Sigma-Aldrich, and orthophosphoric acid (85%) was bought from Panreac. A cationic polyacrylamide (CPAM) from BASF with MW = 3.7×10^6 g/mol and CD = 1.1 mmol/g (data provided by the supplier), commonly used as retention agent in papermaking, was used for comparison purposes. Two different industrial calcium carbonates and a hydrated aluminum silicate were used as fillers: scalenohedral PCC, rhombohedral GCC and lamellar kaolin, respectively. Their zeta potentials, measured in aqueous suspensions by electrophoretic mobility in a Zetasizer NanoZS (Malvern Instruments) were +9 (pH 10), −28 (pH 10) and −24 mV (pH 6) respectively. The negative values of GCC are due to the presence of anionic polyelectrolytes used to stabilize the GCC dispersions (Vanerek et al. 2000). The fillers also differ in size: their median particle sizes (d_{50}), determined by LDS in a Mastersizer 2000 (Malvern Instruments), were 4.2, 2.0 and 3.5 μm, respectively. NaOH and urea, from Panreac, were also used as solvents.

A representative scheme of the whole experimental procedure, including pretreatments, cationization and separation processes, is depicted in Fig. 1.

Pretreatments

The different polyelectolytes produced are distinguished by the treatment previous to cationization. The cationic celluloses (CC) were labelled by ascending order of degree of polymerization (corresponding to descending order of yield), namely CC1, CC2 and CC3. The materials prior to cationization were named, respectively, C1, C2 and C3.

BEKP was depolymerized with orthophosphoric acid (H_3PO_4): a sample of BEKP, with a moisture content of 66%, was soaked in acid so that H_3PO_4 concentration was 80% and the consistency of the suspension (on a dry basis) was 2%. The acid hydrolysis occurred at room temperature for 2 h, the first hour without stirring and the second one with agitation with a four-blade stirrer at 600 rpm. A gel-like, whitish solution was obtained, similar to a suspension of nanofibrillated cellulose. Apparent dissolution was reverted when the pulp was diluted to 0.5% with distilled water. The suspension was filtered through an 11 μm paper filter, obtaining a powder-like amorphous cellulose (C1). The filtrate was discarded.

A precooled NaOH/urea solution was used to produce C2 and C3. For that, BEKP was diluted to 2% in an aqueous solution containing 6% NaOH and 6% urea, the mole ratio of alkali to anhydroglucose units (AGU) being 12. The suspension was stirred for 1 h at 600 rpm and then filtered through a 11 μm paper filter. The filtrate (lower DP fraction) was named C2, while the fibrous solid retained (higher DP fraction) was labelled as C3.

Cationization

Cationization was performed on the filtration retained fractions (C1 and C3) and on the filtrate (C2) with CHPTAC using a mole ratio to AGU of 3, as shown in Fig. 1. NaOH and urea were also added to C1 and C3 aiming for the same concentration (NaOH 6%, urea 6%, CHPTAC/AGU 3) in all three samples. Cationization lasted only 60 min, by applying gentle mechanical agitation (200 rpm) and maintaining the temperature at 65 °C. The mechanism by which CHPTAC and cellulose are activated with alkali and react is described elsewhere (Moral et al. 2016).

CC1 and CC2 seemed to be completely dissolved in the alkaline media. Since the derivatives are intended to be not only alkali-soluble but also water-soluble, the media were neutralized with hydrochloric acid. While CC2 remained in solution at neutral pH, a part of CC1 (insoluble part) was precipitated, filtered and discarded. Cationization of C3 originated a large amount of undissolved material, which increased even more after the neutralization. In this case, only 20% of the weight of C3 passed through the filter. The three cationic derivatives were soaked in a regenerating medium in which the volume percentage of ethanol was at least 50% (Fig. 1).

The aqueous-alcoholic suspensions were filtered by using a paper filter with an aperture size of 2.5 μm. The filtrates were discarded, although a liquid sample

Fig. 1 Simplified diagram of the experimental procedure used to produce three different cationic cellulose derivatives
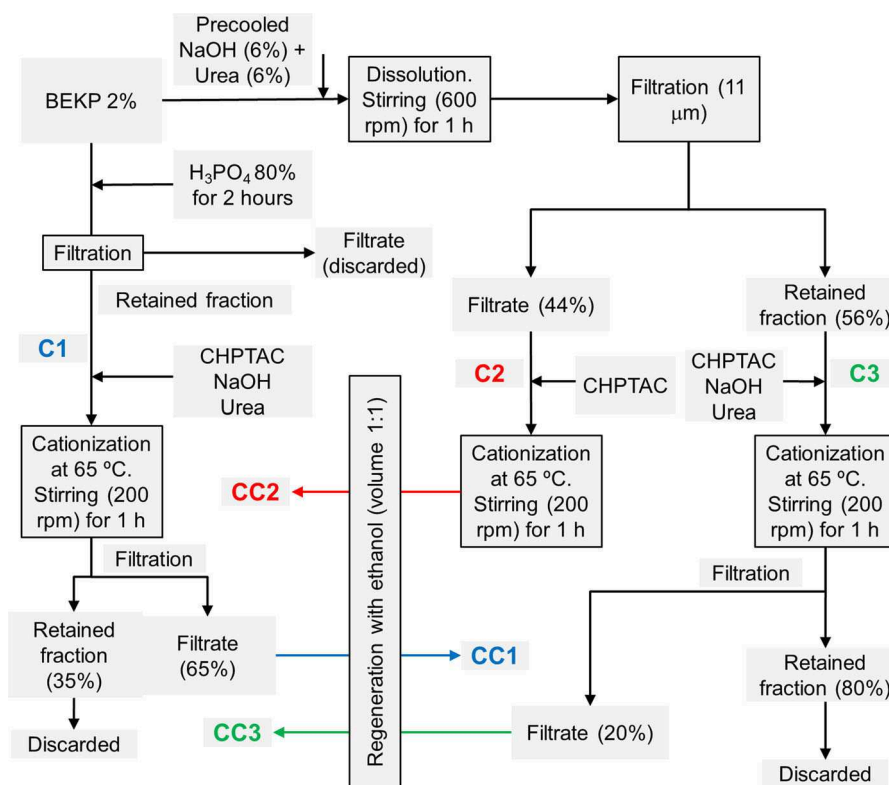
from the CC2 filtration was submitted to mass spectroscopy-gas chromatography (GCMS) to identify any possible by-products. The retained fractions of the filtrations (wet solids) were dried firstly at room temperature for 24 h, and after at 60 °C for 4 h. The solubility in water was confirmed by centrifugation of 1% solutions at $3000 \times g$ for 10 min.

Characterization

The samples were characterized for their degree of polymerization (DP), crystallinity, degree of substitution (DS), charge density (CD), zeta potential, yield and also with FTIR-ATR measurements.

The degree of polymerization of the pretreated samples was determined by dividing the corresponding mean molecular weight (M) by the molecular mass of AGU (162). In turn, the mean molecular weight of the C1, C2 and C3 pretreated cellulose chains was estimated from the limiting viscosity number (mL/g) by using the Mark–Houwink equation with the parameters reported by Eckelt et al. (2011) for cellulose solutions in a copper (II) ethylenediamine solution (Cuen):

$$\eta = 0.0653 M^{0.735} \qquad (1)$$

The limiting viscosity number necessary in Eq. 1 was determined according to the ISO standard 5351-1.

For the crystallinity assessment, aliquots of the pretreated samples C1, C2 and C3 were dialyzed by using a sack from Sigma-Aldrich which ensures retention of compounds whose molecular mass is 12,000 Da or higher, and placed in deionized water for 24 h, in order to remove phosphate salts and other undesired substances. A PANalytical's powder diffractometer with the software X-Pert HighScore provided X-ray diffraction patterns. The original pulp was also analyzed for comparison purposes.

A LECO CNS-2000I elemental analyzer was used to measure the content of carbon, hydrogen and nitrogen. The degree of substitution (DS) was calculated from the ratio of %N to %C (N/C), assuming that only one cationic quaternary ammonium group can be incorporated per anhydroglucose unit (Moral et al. 2016):

$$N/C = \frac{14DS}{144DS + 72 \cdot (1 - DS)} \qquad (2)$$

281 where 14 is the atomic weight of nitrogen, 144 is
282 twelve times the atomic weight of carbon (substituted
283 monomer), and 72 is six times that weight (non-
284 substituted monomer).

285 The charge density (CD) of the cationic derivatives
286 was determined by potentiometric titration in a Charge
287 Analysis System (CAS) from AFG. For that, a small
288 amount of sample (less than 0.1 g) was dissolved in
289 10 mL of deionized water and the solution was titrated
290 with an anionic polyelectrolyte, sodium polyvinylsul-
291 phate (PVSNa, 0.001 N).

292 The zeta potential of 1% (w/w) dispersions in
293 distilled water of the dried CC1, CC2 and CC3 was
294 measured with a Zetasizer Nano ZS device from
295 Malvern Instruments.

296 FT-IR-ATR spectra were recorded by a Bruker
297 Tensor 27 spectrometer with a MKII Golden Gate
298 accessory, setting the resolution to 4 cm^{-1} and the
299 number of scans to 128.

300 Flocculation tests

301 The performance of CC1, CC2 and CC3 as polymeric
302 flocculants was evaluated by LDS in a Mastersizer
303 2000 device from Malvern Instruments, equipped with
304 the Hydro 2000 module. To process the raw scattering
305 patterns, the Mie theory (De Boer et al. 1987), which is
306 rigorous and suitable for small particles (below
307 10 μm), was used considering the refractive index of
308 the mineral fillers as being 1.57 (Wypych 2016).

309 Aqueous suspensions [1% (w/w)] of PCC, GCC and
310 kaolin were submitted to magnetic stirring for 20 min
311 and placed in an ultrasound bath (50 kHz) during
312 15 min in order to disaggregate the particles. For each
313 experiment, 6 mL of the filler suspension were added
314 to the equipment vessel containing 600 mL of distilled
315 water. This was enough to reach an adequate obscu-
316 ration of the He/Ne laser beam. The pump speed was
317 set to 2000 rpm during the measurement of particle
318 size.

319 As for the flocculants, solutions of CPAM, CC1,
320 CC2 and CC3 [0.1% (w/w)] were prepared and stirred.
321 A certain amount of the flocculant in each case (1 mg/
322 g for CPAM, 20 mg/g for the cationic cellulosic
323 derivatives) was added after the stabilization of the
324 filler median size (some initial aggregation occurs
325 spontaneously to a certain degree). Then, the evolution
326 of the median particle size of the fillers together with

327 the added polymer was monitored. Smaller amounts of
328 the WSCC were previously tested (see supplementary
329 information).

Results and discussion 330

Characterization of the pretreated samples 331

332 For the necessary calculations, BEKP was assumed to
333 consist entirely of anhydroglucose units (AGU). This
334 assumption is safe, given the negligible amount of
335 lignin after bleaching, the most probable dissolution of
336 the remaining hemicellulose in the preliminar NaOH/
337 urea treatment and the fact that cationic groups are
338 also incorporated into anhydropentose units
339 (Deutschle et al. 2014).

340 For C1, BEKP was depolymerized with orthophos-
341 phoric acid (H_3PO_4), since this compound works both
342 as a hydrolysis agent, as long as its concentration is
343 higher than 30% (w/w), and as a cellulose activator,
344 causing total amorphization if its concentration is
345 superior to 79 wt% (Vinogradov et al. 2002).

346 For C2 and C3, a precooled NaOH/urea solution
347 was used as solvent due to the influence of urea on
348 hydrophobic interactions of low-DP cellulose (Zang
349 et al. 2002). As mentioned, the NaOH/AGU mole ratio **AQ3**
350 was 12 in order to ensure a good cellulose solvation,
351 since theoretically at least 4 OH^- ions per monomer
352 are necessary in alkaline dissolution (Myasoedova
353 et al. 1991).

354 All samples differ in solubility. As visible in
355 Table 1, the DP of C1 was much inferior to that of
356 BEKP. On the contrary, and as intended, C2 produced
357 from the lower-DP part (soluble in NaOH/urea, at least
358 to a degree in which solvated particles, macroscopi-
359 cally undistinguishable from the solvent, passed
360 through the filter) exhibited a higher value than C1
361 but a smaller value than the original pulp. As for C3, it
362 has the highest mean DP value, superior to that of the
363 original pulp as a result of being obtained from the
364 higher-DP fraction of this pulp.

365 Table 1 also presents the crystallinity index (CI) as
366 calculated from the diffraction patterns shown in
367 Fig. 2a. A linear baseline correction and a Gaussian
368 deconvolution of peaks were carried out with Systat's
369 Peakfit, as exemplified in Fig. 2b for the non-treated
370 BEKP sample. The assignment of Miller indices to the
371 peaks and the notation of these indices are based on the

Table 1 Characteristics of the bleached kraft pulp (BEKP) and of the pretreated cellulose samples

Sample	η (mL/g)	M × 10⁻⁴ (Da)	DP	CI	I(Cell-I/Cell-II)
BEKP	494	18.9	1170	0.813	4.30
C1	132	3.1	194	0.518	1.33
C2	380	13.3	820	0.386	0.36
C3	658	28.0	1703	0.540	0.88

Fig. 2 X-ray diffraction patterns of the bleached kraft pulp (BEKP) and of the pretreated cellulose samples (**a**) deconvolution of the BEKP X-ray diffraction pattern (**b**)
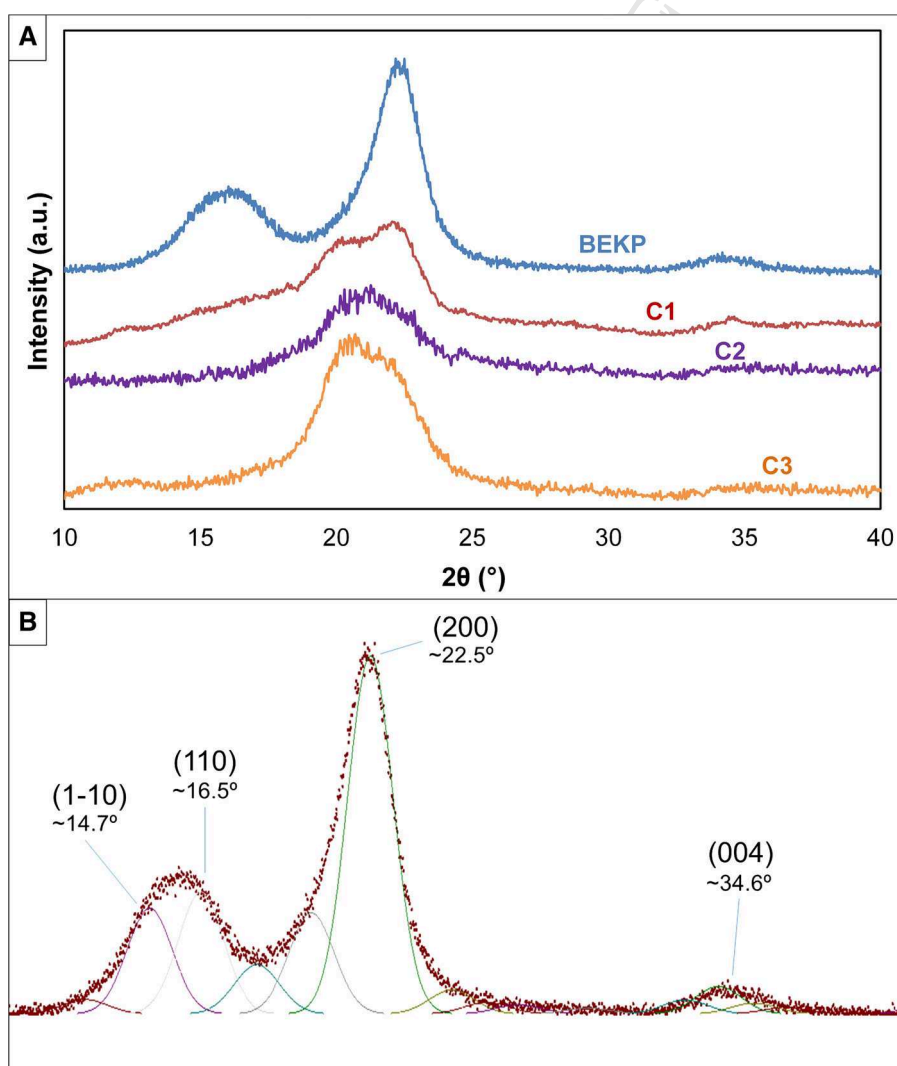
conventions used by French (2014). It is assumed that BEKP, as cellulose from wood, consists fundamentally of cellulose Iβ, while the pretreated samples are mixtures of cellulose Iβ, cellulose II and amorphous cellulose. The crystallinity of the samples was estimated from XRD by identifying the four most prevalent peaks of cellulose I and the cellulose II (110) peak, and dividing their area by the total area (Eq. 3) (Park et al. 2010):

$$CI = \frac{A_{1-10(I\beta)} + A_{110(I\beta)} + A_{200(I\beta)} + A_{110(II)} + A_{004}}{A_{total}}$$

(3)

Both orthophosphoric acid and sodium hydroxide caused a diminishment in *CI*. The lowest crystallinity index corresponded to C2, the only pretreated sample which was totally alkali-soluble.

The diffractogram of BEKP displayed the typical shape of cellulose I (Fig. 2a). Likely, some phosphate groups incorporated into the structure of C1 during the pretreatment remained after dilution and regeneration, since the shape of the corresponding pattern before 21° resembles that of cellulose phosphate esters (Olaru et al. 2007). For C2 and C3, partial amorphization was evident: the peak at 22.5° for the (200) plane of cellulose I became much shorter (C3), or simply indiscernible from the (020) reflection of cellulose II, at 22° (C2). The other peaks became broader, which is a consequence of an increase in the amorphous fraction (Park et al. 2010).

Besides phosphoric acid and inorganic ions, the filtrate of C1, analyzed by GCMS, contained soluble products from the hydrolysis, but not necessarily furanic compounds. The temperature of the pretreatment (20–25 °C) was too low for dehydration.

To elucidate to what extent cellulose I is converted into cellulose II by the pretreatment, the intensity ratio (I(Cell − I/Cell − II)) was calculated with Eq. 4. The numerator contains peaks assigned to cellulose I, while the denominator contains peaks assigned to **AQ4** cellulose II (French 2014; Kolpak et al. 1978). The peak assigned to the (020) plane of cellulose II is omitted because it overlaps with the highest peak of cellulose I. The peak (004) is roughly the same for both cellulose Iβ and cellulose II. It must be stressed that this parameter serves as an indication of the ratio of cellulose I to cellulose II for comparison purposes, but never as an accurate and absolute determination of that ratio.

$$I(Cell - I/Cell - II) = \frac{I_{14.7°} + I_{16.5°} + I_{22.5°} + I_{040}}{I_{12.4°} + I_{20.3°} + I_{040}}$$

(4)

The value corresponding to C1 is not reliable, since the peak (110) of cellulose II (20.1°) may be confused with the most prominent band of cellulose phosphate. As expected, the proportion of cellulose II, more thermodynamically stable, increases with the alkaline treatments (C2, C3), as it also happens, for instance, in cotton mercerization (Poletto et al. 2014). When this alkaline treatment results in apparent dissolution (C2)

and the sample is regenerated with an alcohol, specific peaks of cellulose I cannot be perceived in XRD patterns. C2 may consist completely of cellulose II and amorphous cellulose.

Characterization of the cationic derivatives

The DP values estimated from Eq. 1 for the pre-treated samples were also used for the cationized CC1, CC2 and CC3 samples. In fact, it is legitimate to consider that the DP is not modified with the cationization process, because the temperature is too low for an alkaline hydrolysis to happen at an appreciable extent. For instance, Song et al. (2008) using size exclusion chromatography, showed that the hydrolysis of cellulose during cationization with CHPTAC, NaOH and urea is negligible, even when the reaction took place at 60 °C for 8 h. As can be seen in Table 2, the cellulosic derivative with the highest DP (CC3) was the one presenting, after cationization, the highest degree of substitution, charge density and zeta potential. This is due to the fact that high-DP cellulose needs to have more ionized monomers to become soluble in water, and thus the lowly-substituted parts were rejected. As a drawback, given the mildness of the conditions used in this study, these lowly-substituted parts accounted for the majority of the material. Crystalline and lowly-substituted parts of CC3 could not pass through the filter after neutralizing with HCl.

Table 2 also shows the yield of WSCC from the bleached kraft pulp. It should be noted that CC2 and CC3 share the same pretreatment. 100 g of BEKP could be used to produce 44 g of CC2 and 11 g of CC3 (a total of 55 g of cationic cellulose from one single process), or 60 g of CC1, which is less electrically charged. Sirviö et al. (2011) obtained higher yield values, achieving complete dissolution of high-DP cellulose by producing a polymer with a very high

Table 2 Characteristics of the three cationic cellulosic derivatives

Sample	Yield (%)	DS[a]	CD[a] (mmol/g)	ζ-Potential (mV)
CC1	60	0.33	2.07	+4.5
CC2	44	0.34	2.80	+6.8
CC3	11	0.46	5.01	+16.7

[a] DS and CD mean degree of substitution and charge density, respectively

degree of substitution, but at the cost of a 24 h-long first treatment, a 3 h-long second treatment at 75 °C and then by cationizing with Girard's reagent.

Substitution was in the expected range. Lower degrees of substitution would have implied lack of solubility, while obtaining values close to 1 was impossible under mild conditions. Higher reaction times and higher concentrations of CHPTAC could have improved the yield, but probably not the degree of substitution. Yan et al. (2009) cationizing cellulose with a reagent/AGU molar ratio of 10, achieved DS values of 0.32 and 0.47 by applying reaction times of 6 and 9 h, respectively. These values are in the same range as those presented in Table 2, but their conditions and the use of low-DP cellulose eased solubility and avoided discards of undissolved parts, achieving a yield of 100%.

A gentle process, like the one suggested in this work, can generate samples with degrees of substitution higher than 0.3 at the expense of the yield. If a continuous reactor had been used instead of a batch one, the insoluble fraction could have been recycled, keeping the mild conditions. This would be a feasible alternative to the expensive and time-consuming processes.

The zeta potential of the starting material (fibers from BEKP) in water is slightly negative in a wide pH range and cationization involved a switch towards positive values. As cationic functional groups were incorporated into cellulose, the polymer reached the isoelectric point and then its charge density increased with the degree of substitution. The small difference between the CC1 and CC2 zeta potentials could be deemed not significant. The value found for CC3 suspended in water was much higher. This could be explained by the pretreatments applied in the latter, which decreased the stability of the dissociable groups that have a negative contribution to the surface charge.

All ATR-FTIR spectra, normalized and presented in Fig. 3, showed typical peaks for cellulose in absorption bands at 3330 cm^{-1} (g), related to O–H stretching, and at 2882 cm^{-1} (f), associated with symmetrical stretching of C–H bonds. The intensity of the absorption at 897 cm^{-1} (a), due to C1–H bending and sensitive to a rearrangement of intramolecular hydrogen bonds (Yang et al. 2010), increased with the amorphous fraction of the sample. Particularly for CC2, the derivative with the lowest crystallinity, this peak was almost as high as the one found at

1040 cm^{-1} (b). Bands at 1160 and 1019 cm^{-1} are assigned to C–O–C asymmetric stretching and different vibrations of C–C and C–O bonds, respectively. In the spectra for CC2 and CC3, the decrease in sharpness is evident and these peaks become mere shoulders. The band at 1623 cm^{-1} (e) is due to O–H bending in absorbed water (Granja and Barbosa 2001). Purification after regenerating succeeded to remove urea, since its absorption bands, which would be very prominent between 1700 and 1400 cm^{-1} and between 3500 and 3100 cm^{-1} (Turney et al. 2013), cannot be distinguished.

Spectra of CC1, CC2 and CC3 showed additional peaks at 1427 and 1390 cm^{-1} (d), linked to the quaternary ammonium groups (Sang et al. 2012). Due to the conversion of cellulose I to cellulose II, the spectra of CC2 and CC3 do not possess a peak at 1345 cm^{-1} (Granja and Barbosa 2001). Whether phosphate groups remain in the structure of CC1 is not proved by its spectrum, but their absence is not confirmed either, since the most prominent band of PO$_4$ is given at 1020 cm^{-1}, thus interfering with one of the most noticeable bands in the spectrum of cellulose (Hallac and Ragauskas 2011).

Performance in flocculation tests

The evolution of the median equivalent spherical diameter (d$_{50}$) of the three fillers when in contact with the WSCC is plotted in Fig. 4. On the left side (Figs. 4a–c) the influence of the WSCC addition on the different fillers flocculation is shown. The results were normalized considering the particles median size at the moment of the flocculant addition and the corresponding values are shown in Fig. 4d–f, which provide a better perception of the influence of each polyelectrolyte separately. As stated, CPAM was always used for comparison purposes since it is one of the most common flocculants used in papermaking. Table 3 presents the zeta potential of the suspensions used in the flocculation tests at given pH values.

When kaolin was used, it is evident that CPAM and CC3 promoted a high filler flocculation, with a maximum filler particle size increment close to 6.5 and 7.5 times, respectively. As stated in the literature CPAM is able to flocculate the particles by bridging due to its high molecular weight (Neimo 1999). As for CC3, with a molecular weight one order of magnitude off but a much higher charge density

Fig. 3 Infrared spectra of the original bleached kraft pulp (BEKP) and of the cationic cellulosic derivatives
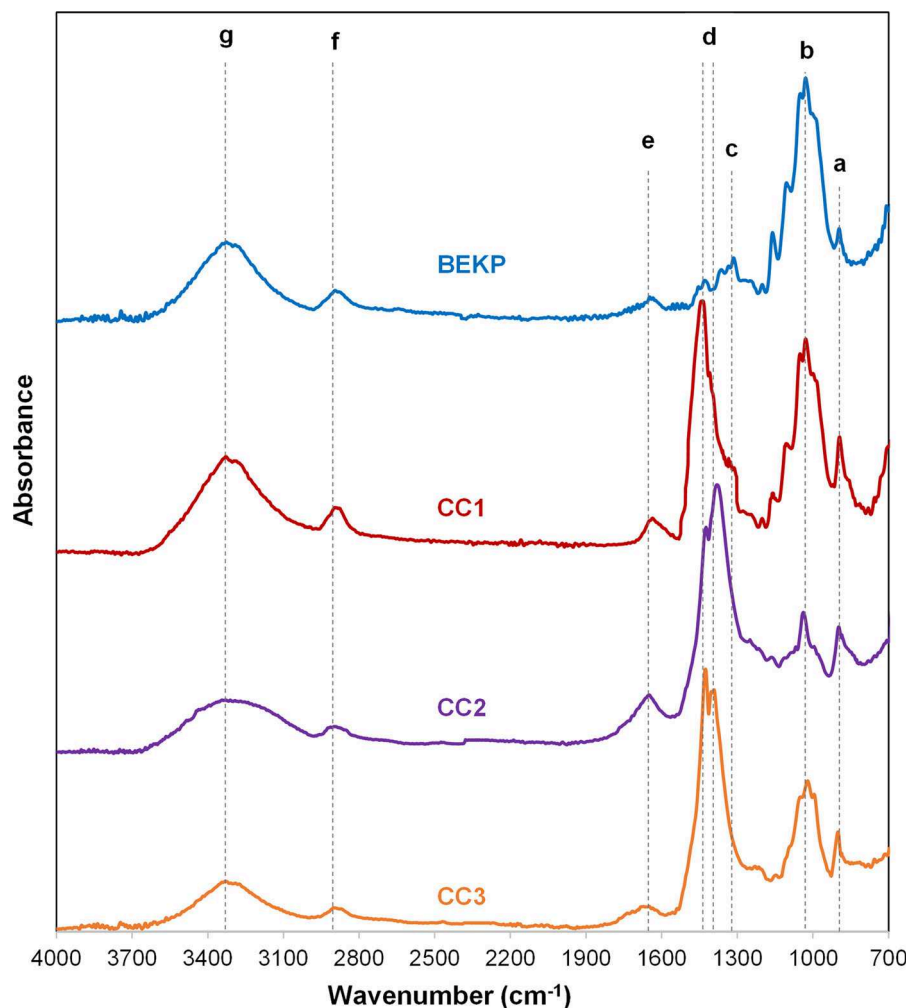
559 (Tables 1, 2), neutralization was most probably the
560 dominant mechanism (Neimo 1999). However, due
561 to the high charge, patching was also likely to occur,
562 which was proven by the good reflocculation ability
563 of the particles after a step of high shear, shown in
564 Fig. 5. According to Rasteiro et al. (2008b), flocs
565 formed by bridging mechanisms do not reflocculate
566 as easily as those formed by patching. In fact, the
567 electrokinetic potential of the kaolin/CC3 mixture
568 was only slightly negative (-7.3 mV), which
569 increases the probability of particle aggregation. In
570 contrast, with CC2 this value was much higher
571 (-27.2 mV) and the flocculation effects were atten-
572 uated, in accordance with the smaller values of the
573 molecular weight and also charge density. CC1 has
574 no influence in filler flocculation, regardless the

575 mineral used, and this is a result of the very small
576 molecular weight, degree of polymerization and also
577 charge density. For this reason, the plot with the
578 normalized values is not presented. This confirms
579 that the pretreatment with ortophosphoric acid was
580 not successful to induce filler flocculation.
581 For GCC similar results are observed with CC2 and
582 CC3, revealing a negligible increment of the particles
583 size. In spite of having also a negative charge, as
584 kaolin, GCC particles are scalenohedral shaped, and
585 not lamellar, and this fact may have hindered the
586 aforementioned flocculating mechanisms. In this case
587 only CPAM seems to be effective.
588 Contrary to kaolin and GCC, PCC has positive
589 charge ($+9$ mV) and therefore the influence of the
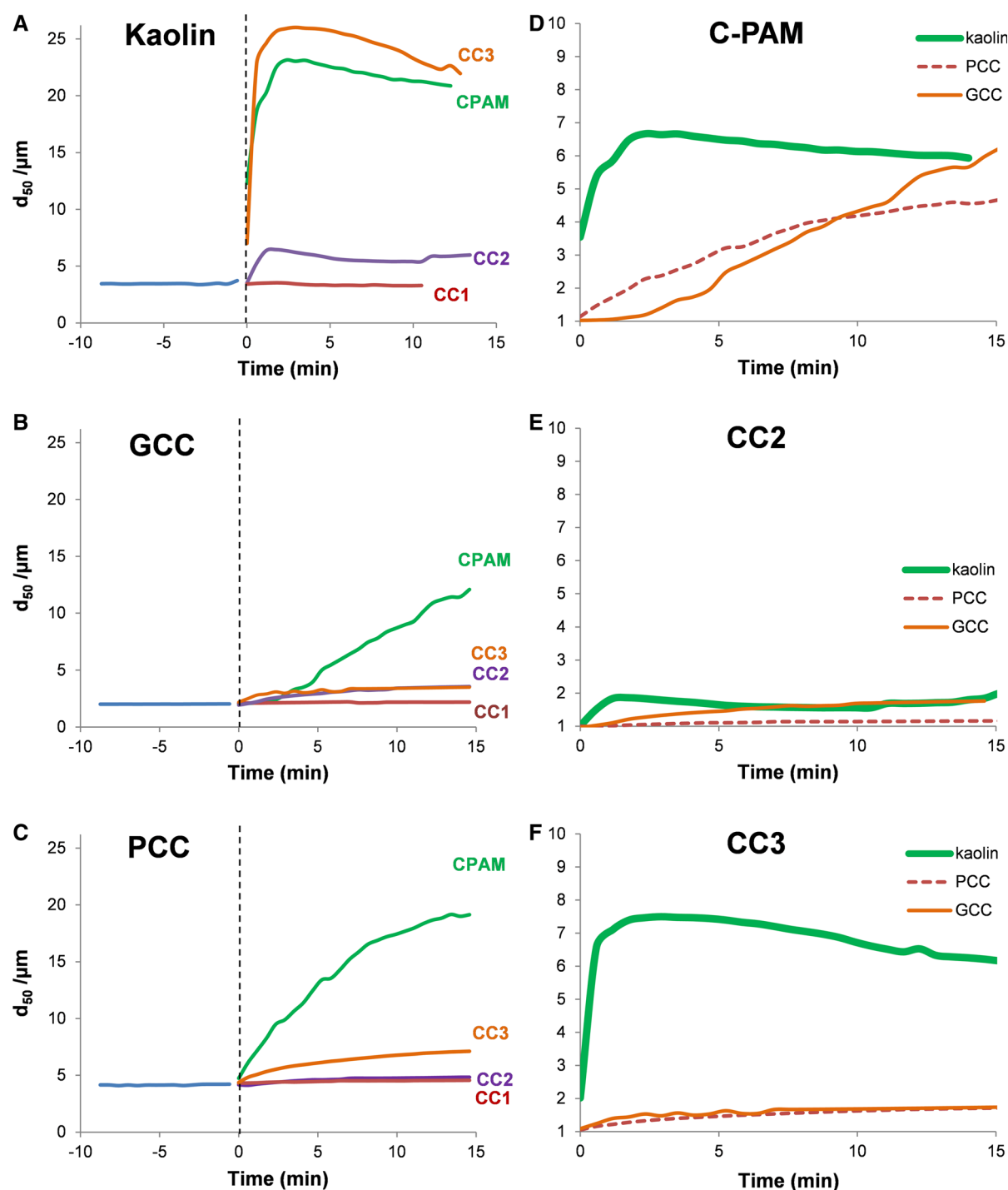590 WSCC on filler flocculation is expectedly different.

Fig. 4 Flocculation kinetics of three mineral fillers with a cationic polyacrylamide (CPAM) and with the cationic cellulosic derivatives (CC1, CC2 and CC3), depending on the choice of filler (**a–c**) and on the choice of flocculation agent (**d–f**)

591 However, similarly to GCC, both CC2 and CC3 don't
592 have significant impact on flocculation. By the con-
593 trary, CPAM has a positive effect on PCC flocculation,

594 by bridging, in agreement with many studies reported
595 in the literature (Rasteiro et al. 2008a; Lourenço et al.
596 2017).

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Table 3 Zeta potential of the suspensions used in the flocculation tests

Filler	WSCC	ζ-Potential (mV)	pH
Kaolin	–	−23.7	5.6
	CC1	−29.5	7.1
	CC2	−27.2	7.0
	CC3	−7.3	7.0
	CPAM	−9.7	7.1
GCC	–	−27.8	10.1
	CC2	−2.7	9.9
	CC3	−11.7	9.8
	CPAM	−18.9	9.9
PCC	–	8.7	10.1
	CC2	0.8	9.9
	CC3	15.4	10.0
	CPAM	7.3	10.1
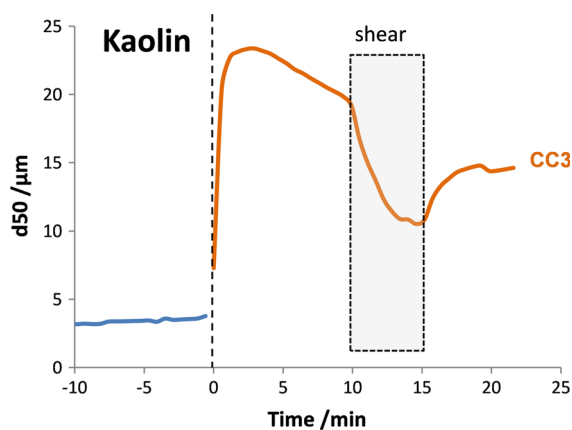
Fig. 5 Reflocculation behavior of kaolin with CC3 after floc rupture

The flocculation process with CPAM is however somewhat distinct for the three fillers studied: with kaolin a fast flocculation occurred, while for GCC it took almost 5 min to double the particle size. It is worth mentioning that CC3 was the polyelectrolyte that promoted the faster kinetics with kaolin. In papermaking a fast flocculation is of utmost importance since the contact time between the stock and the retention agents is as short as possible (usually 30 s or less) (Antunes et al. 2008a) to not disturb the runnability and sheet formation.

It should be noted that a smaller dosage of WSCC (10 mg/g) was tested, and the results showed that flocculation of fillers occurred but in a clearly smaller extent. Those results can be found in the supplementary material of the electronic version of this article.

It is safe to state that by cationizing cellulose it is possible to obtain water soluble derivatives with promising applications as filler flocculant for papermaking. In order to promote an effective flocculation, the WSCC must possess high charge and/or high DP, which in this work was achieved by pretreating cellulose fibers with NaOH and urea, followed by a cationization with CHPTAC, and finally by regenerating the resulting filtrate with ethanol. The obtained dry product, soluble in water, presented a medium degree of polymerization, high charge density and a moderate zeta potential, but the yield of production under mild conditions was quite small (11%). In this work, the best flocculation results were obtained with kaolin due to its higher surface charge and lamellar shape that allowed the WSCC to be adsorbed more easily on its surface.

Conclusions

Three water-soluble cationic derivatives of cellulose, containing at least 30 quaternary ammonium groups per 100 anhydroglucose units and a charge density above 2 mmol/g, were produced with NaOH and CHPTAC under mild conditions, following different pretreatments.

The pretreatment with orthophosphoric acid caused the yield to be the highest, easing solubility by acid hydrolysis and amorphization, but the degree of polymerization (DP) of CC1 was too low to promote a suitable flocculation of filler for papermaking. In fact, by comparing the results with those obtained by applying the other alkaline pretreatment (NaOH/urea), it is possible to conclude that the WSCC whose DP was the highest (CC3) originated the best results in flocculation tests, even better than those for CPAM when the filler used was kaolin. The performance of the derivative with an intermediate DP, CC2, was worse when flocculating PCC and kaolin, but as good with GCC as that of CC3.

When using GCC, the flocculation was faster with CC2 and CC3 than with a conventional CPAM polymer. However, the flocculation tests with PCC only yielded acceptable results with CPAM, most likely due to the high molecular weight of this

polyelectrolyte. Further research could be beneficial if a water-soluble cationic polymer with medium charge density from high-DP cellulose could be obtained.

Supplementary information

The evolution of the median particle size of the fillers with smaller dosages (10 mg/g) of WSCC is provided.

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