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Non-covalently cationized nanocellulose from hemp: Kinetics, key properties, and paper strengthening

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ABSTRACT

Cationic cellulose, despite its long history, has yet to find a place in the paper industry. However, recent research is evaluating the potential of its nanoscale forms. Likewise, the processes of Western manufacturers are optimized for wood pulps, relegating non-wood crops to specific products that, as also proposed by current research, could include nanocellulose. We combined these trends with the existing knowledge of the strong adsorption of poly (diallyldimethylammonium chloride) (polyDADMAC) on cellulosic fibers, which can be deemed a non-covalent kind of cationization. For that, polyDADMAC was first anchored to refined hemp pulps, under conditions that allowed the deprotonation of the primary hydroxyl groups of cellulose. The fiber surface remained positively-charged even after thoroughly washing the samples, owing not only to the small proportions of acidic hemicelluloses and lignin, but also to stable ion-dipole interactions. This non-covalent cationization was found to follow pseudo-second order kinetics, indicating that diffusion through the fiber was the rate-controlling step. PolyDADMAC-containing fibers were then fibrillated by high-pressure homogenization. The surface charge of cationic nanocellulose was greater than that of the starting fibers, as the specific surface area increased. Nonetheless, polyDADMAC caused agglomeration of fibrils to a certain extent. As a drawback, when applied in papermaking, cationic nanocellulose lowered air permeability to a lesser extent than non-cationized nanofibers. As an advantage, the tensile index increased by up to 57% in the absence of any retention agent.

1. Introduction

The cationization of cellulosic fibers has a long and prolific record in the literature, beginning with Wood and Mora's quaternization of cellulose amines *via* excess methyl iodide (Wood and Mora, 1963). Direct cationization with reagents comprising a quaternary ammonium group and a reactive end, such as 2,3-epoxypropyltrimethyl-ammonium chloride (EPTAC), became popular shortly afterwards (Prado and Matulewicz, 2014). However, the requirement of a highly alkaline medium leads to swelling, decrystallization, and depolymerization (Aguado et al., 2019). In different contexts, some works have shown how strongly cationic polyelectrolytes, and more specifically poly-diallyldimethylammonium chloride (polyDADMAC), get adsorbed onto fibers (Shi et al., 2021). This adsorption has often been applied for fiber charge measurement purposes (Serra-Parareda et al., 2021a). In a less explored field, it is also an alternative way of cationization, instead of substituting the most accessible hydroxyl groups by structurally damaging chemical modifications.

Regarding the applications, salt-free electrolyte dyeing of textiles soon became a commonly alleged goal for the cationization of cotton, but it involves important setbacks (Farrell and Hauser, 2013). Likewise, some contributions proposed a partial cationization of fibers to relieve the need for cationic polyelectrolytes in the wet end of paper machines (Aguado et al., 2018), or to strengthen paper (Mayr et al., 2017). Cationic cellulose can also be used to aid retention of fillers and fines in papermaking (Diab et al., 2015) or, following a similar principle (flocculation), for wastewater treatment (Vuoti et al., 2018). Anyway, several decades after the first proposals, cationic cellulose is not used at a large scale either in the textile or the paper industry, as its only commercially successful forms are amphiphilic agents for cosmetics (Cumming et al., 2011).

Seeking another opportunity in the papermaking industry, several publications have pointed at cationic nanocellulose, instead of cationizing the fibers that are obtained after pulping (typically 100–1500 μm in length, 5–50 μm in width). There is enough proof of the interest from a number of papermaking companies in nanocellulose (Balea et al., 2020;

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Sharma et al., 2019). Several legit reasons are given to combine cationization and nanofibrillation. The former is a proper pretreatment for the latter, since it decreases energy consumption during fibrillation (Rol et al., 2019), although causing partial solubilization (Pedrosa et al., 2022). Other advantages are antimicrobial properties (Aderibigbe, 2021), adsorption of water-pollutant anions (Sehaqui et al., 2016), dyeing with anionic pigments (Khatri et al., 2013), stabilization of Pickering emulsions (Silva et al., 2020), and efficient valorization of lignocellulosic waste (Yao et al., 2022). Precisely, nanocellulose production offers another chance for the use of non-wood pulps, which, as of today, constitute a very small fraction of the European paper production (CEPI, 2021). The properties of cellulose nanofibers (CNFs) from hemp, sisal and jute have been described as intermediate between typical CNFs and nanocrystals (Serra-Parareda et al., 2021c).

The approach presented here combines the idea of cationic nanocellulose, along with the use of non-wood crops for that purpose, with the non-covalent pathway for the cationization of cellulose. Unlike cationizing agents with reactive functional groups, such as epoxides or acyl chlorides, polyDADMAC is a highly stable macromolecule. The functionalization by polyelectrolyte adsorption does not require high temperature (on the contrary) or very high pH values that would cause decrystallization, and does not promote any solubilization of the polysaccharide.

Quaternary ammonium groups are not only unreactive toward virtually any electrophile, but also toward most nucleophiles, including deprotonated cellulose (Zhang et al., 2021). However, they are proper anchor points, in adsorption mediated by ionic interactions, to negatively-charged polymers. These include remaining hemicelluloses in chemical pulps, owing to their carboxyl groups, and even cellulose itself if the pH is high enough (Bialik et al., 2016).

All considered, we report a method of production of cationic nanocellulose following non-covalent adsorption of polyDADMAC, whose kinetics and effects on fiber properties are discussed. As it is common practice, the term “nanocellulose” is not strictly restricted here to fibrils in the nanoscale (diameter < 100 nm). Instead it encompasses the microfibers that high-pressure homogenization (HPH) also produces (Serra-Parareda et al., 2021b). Avoiding chemical modifications and excessive energy inputs, our goal is to obtain and apply a suspension of both micro- and nanofibrillated cellulose, frequently considered more feasible than complete nanofibrillation (de Assis et al., 2018). The way we applied this suspension was bulk addition for sheet forming, as in many other studies with CNFs (Sanchez-Salvador et al., 2020), but taking into account that their cationic character relieves the need for any retention agent.

2. Materials and methods

2.1. Materials

The starting material for the production of cellulose nanofibers was a kraft pulp from hemp provided by CELESA (Tortosa, Spain). Its contents of cellulose, hemicellulose, Klason lignin and ashes were determined as 86.5%, 7.1%, 1.4% and 0.6%, respectively, following the common TAPPI standards and useful methods (TAPPI, 2020). This pulp, referred to as ‘hemp pulp’, was received as dry boards. Redispersion in water took place at 3000 rpm for 20 min, in a device that complies to the ISO standard 5263, before use.

Kraftliner and fluting paper were supplied by SAICA (Zaragoza, Spain). Mimicking a typical composition of recycled cardboard, they were mixed in a 65:35 ratio of liner to fluting. The mixture was then dispersed in water, as aforementioned for the hemp pulp. This will be referred to as ‘recycled pulp’.

PolyDADMAC for cationization purposes ($M_W = 107$ kg/mol) was kindly provided by LC Paper (Besalú, Spain). For potentiometric titrations, BTG Instruments (Säffle, Sweden) supplied standard solutions of polyDADMAC, as the cationic polyelectrolyte, and sodium polyethylene sulfonate (PES-Na), as the anionic polyelectrolyte. Copper(II) ethylenediamine (Cuen) and all other reagents were purchased from Sigma-Aldrich.

2.2. Refining and pulp characteristics

With the purpose of evaluating the directs effects of refining on hemp fibers and, more relevantly for this work, its indirect effects on cationization and on the characteristics of CNFs, the hemp pulp had its consistency adjusted to 10 wt% and was beaten in a PFI mill from Metrotec, model NPFI 02 (Lezo, Spain). The number of PFI revolutions (revs.) ranged from 2500 to 10000.

A Schopper-Riegler tester from IDM (San Sebastian, Spain), model 95587 PTI, was used to quantify the loss of freeness in each case, following the ISO standard 5267–1 (ISO, 2011). Likewise, the water retention value (*WRV*) was determined gravimetrically for each degree of refining. Briefly, fiber pads were formed with excess water and then centrifuged at 3000 × *g* for 15 min, in containers with a nitrocellulose membrane (pore size 0.22 μm), and using a Sigma Laborzentrifugen device (Osterode, Germany), model 6K15. The filter cake was then collected, weighted to yield the wet mass (m_W), and oven-dried at 105 °C to measure the dry mass (m_D). *WRV* was thus calculated from the difference between them:

$$\mathrm{WRV} = (m_W - m_D) / m_D \tag{1}$$

Finally, the mean diameter and mean length of unrefined and refined fibers, along with the percentage of fines, were measured by means of a MorFi Compact Analyzer from TechPap (Gières, France).

2.3. Cationization

For each degree of refining, 20 g of pulp (on the basis of dry pulp weight) were suspended in 1 L of water. This suspension was placed into a stainless steel reactor with an electric jacket-mediated temperature control system. Once the temperature reached 65 °C, the reaction medium was alkalized by adding 14.8 g of NaOH to polarize the hydroxyl groups of cellulose. After 30 min and ensuring that the temperature was stable (constant 65 °C), 4 g or 6 g of polyDADMAC were rapidly dissolved in the aqueous alkaline medium. The former case will be referred to as “20%” (i.e., 20 g polyDADMAC per 100 g pulp) and the latter, as “30%”. This proportions were chosen on the basis of previous knowledge (Wallecan and Debon, 2018; Zhang et al., 2016), aiming to approach saturation.

The reaction took place for 5 h, at atmospheric pressure and under sufficient agitation by means of an electric overhead stirrer (3-bladed propeller). Along this time lapse, several samples were taken to evaluate the kinetics in terms of the cationic demand. This property was estimated potentiometrically, carrying out a back titration with a charge detector from BTG Instruments, model Mütek PCD-04. 0.1 g of non-cationized and cationized fibers, on the basis of dry pulp weight, were washed and mixed with 20 mL of deionized water, and then with 50 mL ($V_{PDADMAC}$) of PES-Na 0.001 N ($c_{PES\text{-}Na}$). The fibers of this suspension were forced to sediment in the centrifuge mentioned above, at 10,000 rpm for 20 min. Finally, the supernatant was titrated with polyDADMAC 0.001 N until the isoelectric point (0 mV) was reached. The so-called *cationicity* (Lee et al., 2014), generally identified as a positive charge density (*CD*), could thus be calculated as follows:

$$\mathrm{CD} = (c_{\mathrm{PES\text{-}Na}} \times V_{\mathrm{PES\text{-}Na}}) - (c_{\mathrm{polyDADMAC}} \times V_{\mathrm{polyDADMAC}}) \tag{2}$$

where $c_{PolyDADMAC}$ is the normal concentration of titrating agent, $c_{PES\text{-}Na}$ is the concentration of excess anionic polyelectrolyte, and $V_{PES\text{-}Na}$ is the volume consumed in this titration.

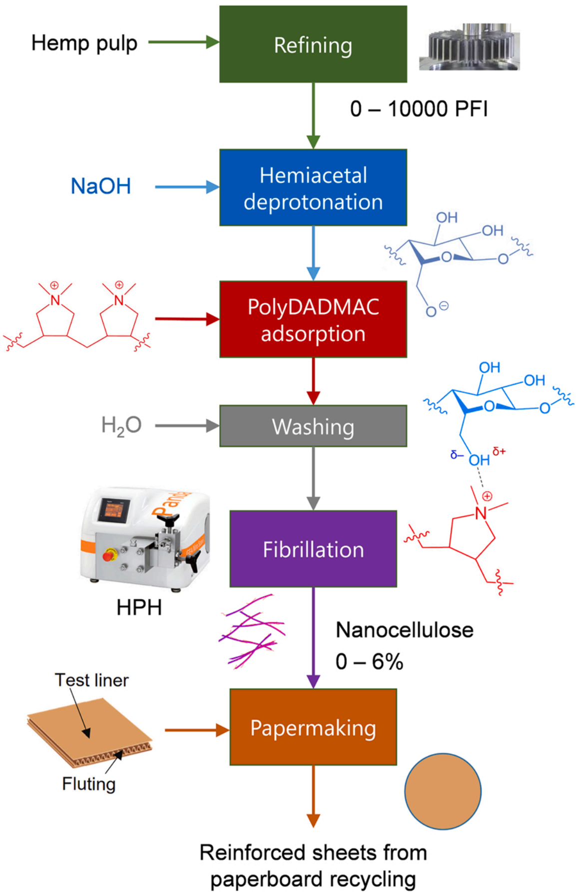

Fig. 1. Simplified diagram of the experimental procedure, including the adsorption of polyDADMAC, the high-pressure homogenization (HPH) and the production of paper with the resulting cationic nanocellulose.

2.4. High-pressure homogenization

PolyDADMAC-cationized fibers were filtered and diluted to a 1% consistency with distilled water. The resulting suspension was submitted 9 times to HPH at increasing pressure: 3 times at 300 bar, 3 times at 600 bar, and 3 times at 900 bar. This was carried out in a laboratory scale homogenizer NS1001 PANDA 2 K-GEA (GEA Niro Soavi, Parma, Italy).

To measure the yield of nanofibrillation, understood as gravimetric yield (Fall et al., 2011; Puangsin et al., 2017), we centrifuged a 0.2 wt% consistency CNF suspension, at 4500 rpm (1254 × *g*) and for 20 min. The sediment was oven-dried at 105 °C and then weighed. Then, the yield was calculated as the weight ratio, always on a dry basis, of the solid stably dispersed in the supernatant to that on the sediment.

To evaluate the transparency of CNF dilute dispersions, they had their transmittance at 600 nm measured in a spectrophotometer from Shimadzu (Duisburg, Germany), model UV-160A.

Likewise, the *CD* of cationic CNFs was measured by performing the same potentiometric that has been described for non-nanoscale fibers.

2.5. Papermaking

30 g of recycled pulp (on the basis of dry pulp weight) were diluted to a consistency of 0.75% with distilled water (<4 μS/cm). Enough nanocellulose, both without polyDADMAC (mechanical CNFs) and with this cationic polyelectrolyte adsorbed on it (c-CNFs), was added so that it constituted 3% or 6% of the total solids weight. Then, the pulp stock, kept on the alkaline side, was stirred for 20 min at 23 °C before filtration. For the control set of sheets, there was no addition of nanocellulose, but the same basis weight (76 ± 2 g m^{-2}) was aimed. In any case, sheets were formed by means of a Rapid-Köthen system from ISP (Oiartzun, Spain), following the ISO standard 5269–2 (ISO, 2011). Drying took place in the same system (i.e., in Rapid-Köthen dryers), at 91 °C and for 10 min. The general experimental procedure, beginning with pulp refining and concluding with this sheet forming process in the Rapid-Köthen system, is presented in Fig. 1.

Before testing, sheets were conditioned at 23 °C and 50% relative humidity, in accordance with ISO 187 (ISO, 2011). Gurley air permeability was determined by measuring the time spent by 100 cm^3 of air to go through the sheet, using a device from ENJO (Altach, Austria) that complies with the ISO standard 5636. Tensile properties were estimated by means of a Universal Testing Machine from Metrotec (Lezo, Spain) and following ISO 1924–2. Mullen burst, Elmendorf tear and Scott bond tests were carried out with three different devices from IDM (San Sebastian, Spain) complying to ISO 2758, ISO 6383–2 and ISO 16260, respectively (ISO, 2011).

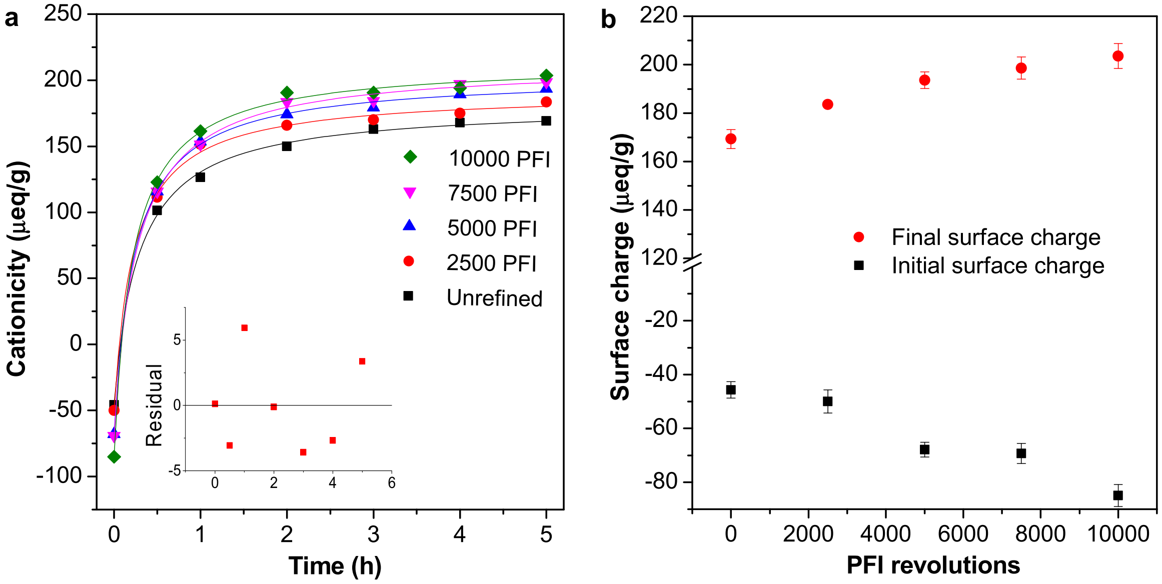

Fig. 2. Kinetic curves of the cationization, showing fitting lines to a pseudo-second order rate equation (a), and highlighting the initial and end values of charge density as functions of the degree of refining (b). Inset figure: distribution of regular errors.

Table 1
Fitting parameters of the pseudo-second order rate equation (Eq. 4), for each number of revolutions (revs.) undertaken during PFI refining.

PFI revs.	CD_0 (μeq/g)	CD_{eq} (μeq/g)	k (g μeq^{-1} h^{-1})	R^2
0	−45 ± 3	227 ± 4	0.015 ± 0.001	0.998
2500	−50 ± 4	241 ± 5	0.018 ± 0.002	0.997
5000	−68 ± 3	271 ± 3	0.016	0.999
7500	−69 ± 4	282 ± 5	0.013 ± 0.001	0.998
10000	−85 ± 4	299 ± 5	0.016 ± 0.001	0.998

2.6. Modeling

Kinetic data, i.e., the results of charge density at different times, were fitted to different rate equations with OriginLab's OriginPro 8.5. One-way and two-way ANOVA analyses, depending on the case, were performed in MS Excel 2016, setting a significance level of $\alpha = 0.05$. The null hypothesis to test the significance of the difference was: *the average of the differences between two sets of values is zero*. Likewise, the null hypothesis when testing the binary interaction of factors was: *the average response for the level of one factor does not depend on the value of the other factor's level.*

To attain a simplified model of the polyDADMAC-covered fiber structure, two assumptions were made. On the one hand, the hydrophobic effect, based on the entropy-driven water exclusion between the methylene groups of polyDADMAC, do not overcome repulsion between like-charged macromolecules, which allows us to neglect multilayer adsorption. On the other hand, due to the limitations to diffusion through the fiber, the measurement of the charge density of fibers by potentiometric titrations roughly corresponds to the surface charge.

3. Results and discussion

3.1. Kinetics of the adsorption of polyDADMAC

Strong ionic interactions were formed between the $–CH_2–O^-$ groups of cellulose in alkaline medium, whose pK_a is lower than that of secondary hydroxyl groups (Bialik et al., 2016), and the quaternary ammonium groups of polyDADMAC. After the washing step and the subsequent reprotonation, the cationic polyelectrolyte was still firmly linked to cellulose *via* ion-dipole forces, and even to the carboxylate groups of hemicellulose by electrostatic interactions. This was confirmed by consistently obtaining a positively-charged sample after rinsing.

The evolution of the charge density with time is depicted in Fig. 2a. Originally, all pulps (unrefined and refined) had negative surface charge. This negative charge increased with the number of PFI revs., due to the higher number of functional groups exposed per gram of pulp. Similarly, during cationization, these increasingly exposed functional groups were available for adsorption of polyDADMAC. In general, as easily visualized in Fig. 2b and as confirmed by the results of ANOVA analyses, for any given time beyond the first 30 min of cationization, the positive influence of refining on cationicity was deemed significant ($p < 10^{-5}$ in all cases).

In what pertains to modeling, it is reasonable to assume that cationization happens preferentially at the surface of fibers, at the fibrils protruding from them, and through the most accessible pores. As no covalent bonds are formed or cleaved during this kind of cationization, the control of the process by any kind of bimolecular substitution kinetics can be discarded. This leaves the modeling of polyDADMAC cationization of cellulose as a case of adsorption kinetics. Eqs. 3, 4, and 5 are adaptations of pseudo-first, pseudo-second and Elovich integrated rate equations (Aguado et al., 2021; Aniagor and Menkiti, 2018; Seema et al., 2018), respectively, in such way that the initial surface charge (CD_0) is taken into account:

$$CD = CD_0 + \frac{CD_{eq}^{\,2} \quad k \quad t}{1 + k \quad t \quad CD_{eq}} \tag{3}$$

Table 2
Evolution of average fiber dimensions and fines content with refining and with the concentration of cationic polyelectrolyte in the medium.

PFI revs.	wt% poly-DADMAC	Fiber length (μm)	Fiber diameter (μm)	Fines (%)
0	0	1007 ± 28	16	41 ± 2
	20	575 ± 47	17	38 ± 2
	30	717 ± 6	17	39.4 ± 0.6
2500	0	768 ± 24	20	40.8 ± 2.7
	20	781 ± 21	17	41.3 ± 0.6
5000	0	743 ± 71	17 ± 1	49 ± 3
	20	633 ± 25	18	50.2 ± 1.0
7500	0	640 ± 16	19	52.9 ± 0.5
	20	681 ± 19	19	52.7 ± 1.1
10,000	0	614 ± 33	19	53.7 ± 0.8
	20	617 ± 26	20	54.1 ± 1.0

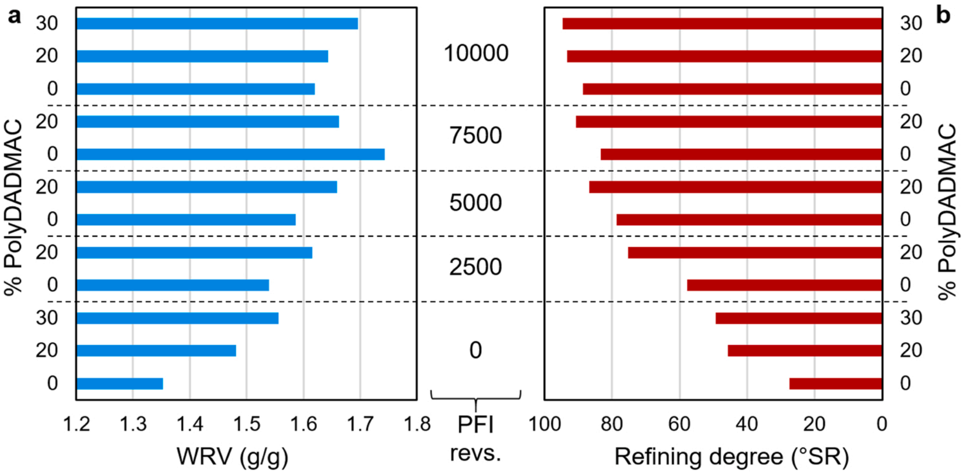

Fig. 3. Combined effect of the number of PFI revolutions (center) and the concentration of polyDADMAC in the aqueous medium to the water retention value (a) and on the Schopper-Riegler degree (b).

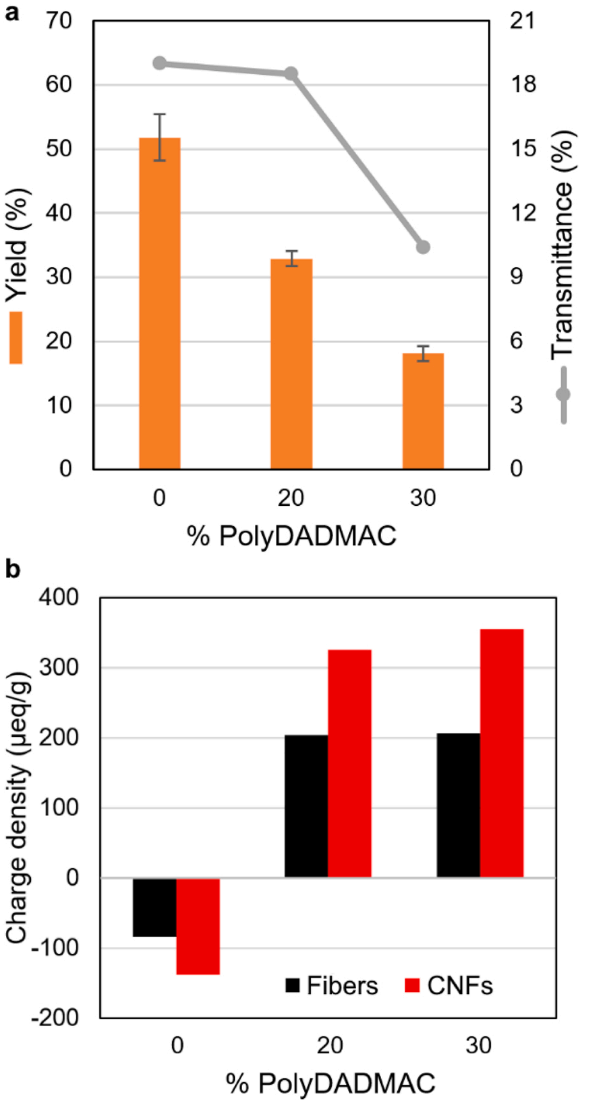

Fig. 4. Effects of the concentration of polyDADMAC during the non-covalent cationization in CNFs: a) diminishment of the percentage of nanofibers that do not settle when centrifuged, and changes in the opacity of the dispersion; b) charge density, compared to the non-nanoscale fibers.

$$CD = CD_0 + CD_{eq}\left(1 - e^{-kt}\right) \tag{4}$$

$$CD = CD_0 + \frac{1}{\beta}\ln \alpha t \tag{5}$$

Fittings to a pseudo-first order equation (Lagengren kinetics, Eq. 3) resulted in correlation coefficients in the range 0.950–0.972 and, more importantly, a non-random distribution of errors. The goodness of the fitting to Elovich kinetics (logarithmic function, Eq. 5) was intermediate, with correlation coefficients between 0.978 and 0.988, and with random distribution of errors only after 2 h of reaction time.

In contrast, as shown in Table 1, correlation to Eq. 4 was excellent. Moreover, Fig. 2 shows, along with the fitting lines, an inset figure representing the regular residuals for the case of 2500 revs., as an example. The absolute value of the average regular residuals was lower than 2 μeq/g for each of the time values. Therefore, it can be concluded that the non-covalent cationization of cellulose with polyDADMAC follows pseudo-second order kinetics. This is not proof of chemisorption, as commonly misunderstood, but rather an indication of diffusion as the rate-controlling stage. This was discussed in depth in an comprehensive review by Hubbe et al. (2019). Indeed, due to the high molecular weight of polyDADMAC, its diffusion through each of the fibers is severely hampered (Serra-Parareda et al., 2021a; Zhang et al., 2016), making it the slowest stage of the sorption process. Still, while the diffusion of non-ionic compounds through cellulose may take more than one day to attain the equilibrium (Aguado et al., 2021), cationic polyelectrolytes quickly reach the saturation point.

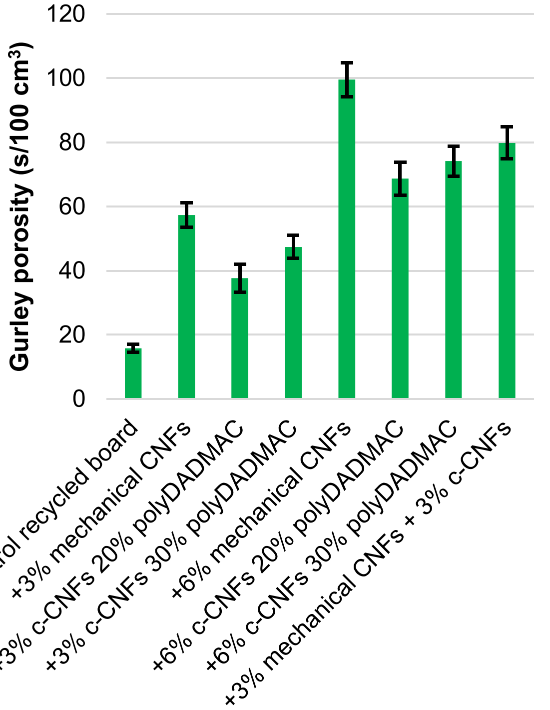

Fig. 5. Results of Gurley's air permeability tests of recycled board sheets, highlighting the effect of non-covalent cationic nanocellulose or mechanical nanocellulose. Error bars comprise twice the standard deviation.

Table 3
Mechanical properties of recycled board sheets, without and with nanocellulose of different kinds. The amplitude of the tolerance intervals equals twice the standard deviation.

	Tensile index (N m g^{-1})	Tear index (N m^2 kg^{-1})	Burst index (kPa m^2 g^{-1})	Scott bond (J m^{-2})
Control recycled board	28 ± 1	7.1 ± 0.8	1.2 ± 0.1	197 ± 8
+ 3% mechanical CNFs	38 ± 4	7.6 ± 0.4	1.55 ± 0.08	256 ± 8
+ 3% c-CNFs 20% polyDADMAC	43 ± 2	7.5 ± 0.5	1.44 ± 0.07	237 ± 11
+ 3% c-CNFs 30% polyDADMAC	44 ± 2	7.1 ± 0.5	1.54 ± 0.08	261 ± 14
+ 6% mechanical CNFs	40 ± 3	8.6 ± 0.3	1.74 ± 0.01	256 ± 16
+ 6% c-CNFs 20% polyDADMAC	36 ± 2	8.1 ± 0.8	1.6 ± 0.2	289 ± 9
+ 6% c-CNFs 30% polyDADMAC	38 ± 5	7.6 ± 0.4	1.7 ± 0.2	285 ± 15
+ 3% mechanical CNFs + 3% c-CNFs	37 ± 5	7.6 ± 0.7	1.6 ± 0.1	289 ± 15

Zhang et al. (2016) compared the time required for the charge to level off with polyDADMAC of different molecular weight: quick if the M_W was 200–350 kDa, much slower if its M_W was 7.5–15 kDa. With an intermediate M_W, we found the corresponding time to be intermediate as well, although the different source of fibers compels us to take this comparison with due caution.

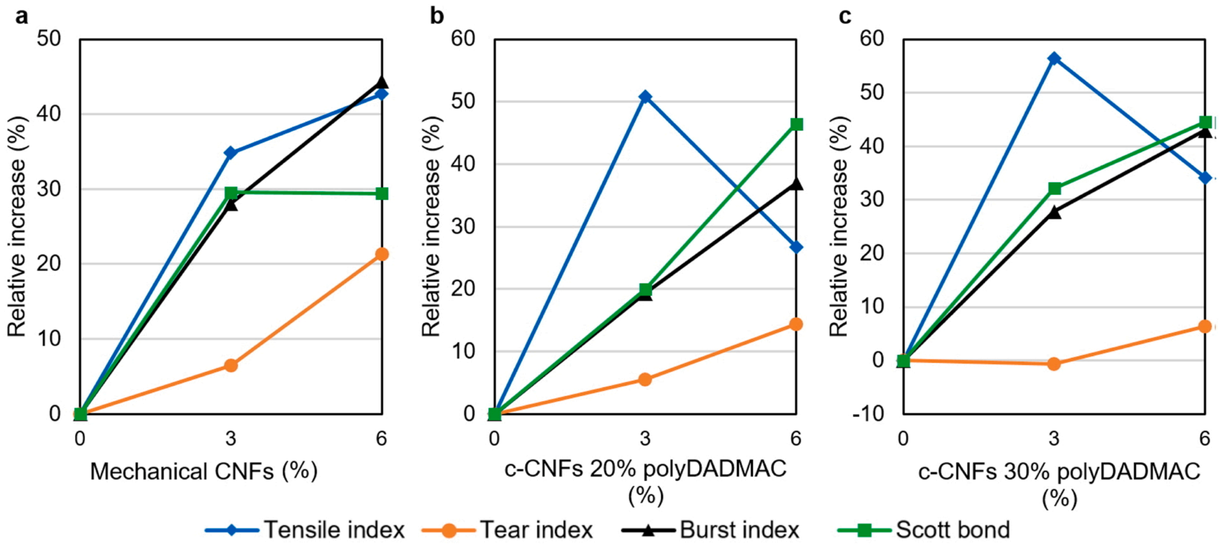

Fig. 6. Mechanical properties of recycled board sheets, as functions of the proportion of nanocellulose in the pulp stock, be it mechanical (a), cationic after adsorption of 20% polyDADMAC (b), or cationic after adsorption of 30% polyDADMAC (c).

3.2. *Influence of the non-covalent cationization on pulp properties*

As it is well-known, refining increases the relative amount of water that fibers can hold, both during fast drainage (freeness tests) or when forcing non-bound water out by centrifugation (Zhao et al., 2016). In other words, the proportions of both unbound and bound water were expected to increase, as confirmed in Fig. 3. Moreover, these graphs for *WRV* (Fig. 3a) and Schopper-Riegler number (Fig. 3b) also show that non-covalent cationization with polyDADMAC resulted, similarly, in more water holding. This was caused by the higher density of hydrophilic functional groups on the fiber surface.

However, the water-holding enhancement effect of cationization was more accentuated on unrefined pulps. We ran a two-way ANOVA factor analysis to check whether the combined effect of refining and polyDADMAC adsorption was significant, resulting in $F = 18.7$ and $p = 1.8 \times 10^{-5}$. Therefore, the null hypothesis for binary interactions can be safely discarded.

The same cannot be said on the combined effect of refining and cationization of fiber dimensions and on the percentage of fines. These properties are displayed in Table 2, where average values are weighted in weight. As expected, refining shortened fibers ($p = 0.04$) and generated fines from them ($p = 0.02$). Nonetheless, the influence of refining on polyDADMAC adsorption was inconclusive ($p > 0.05$ in both cases). Regarding fiber width, there are opposing contributions from fiber wall erosion, on one hand, and an increase in fibers' ability to swell, on the other.

3.3. *How polyDADMAC adsorption impacts the nanocellulose suspension*

After fibrillation by means of HPH, the presence of cationic polyelectrolyte exerted some evident effects on the suspension of cellulosic micro-/nanofibers. PolyDADMAC-induced flocculation outweighed electrostatic repulsion, as shown in Fig. 4a by the diminishment of nanofibrillation yield and transmittance. Being a well-known coagulating and flocculating agent, polyDADMAC chains can act as bridges between nanofibers, thus promoting their aggregation. The increase in size resulted in higher opacity, due to light scattering, and favored sedimentation. This advises against the use of polyDADMAC whenever stable and transparent dispersions of nanocellulose are required.

Fig. 4b shows that, regardless of the sign of the surface charge, its absolute value became greater after homogenization. Two conclusions can be drawn from this: i) the adsorption of polyDADMAC on cellulosic fibers was strong enough not to be disrupted by the HPH; ii) fibrillation exposed surfaces to which polyDADMAC chains had been adsorbed. This supports the notion that adsorption was not limited to the surface, but involved diffusion through the fiber to a significant extent.

3.4. *Enhancement of paper properties*

Fig. 5 shows that the least air-permeable paper was not attained with polyDADMAC-containing nanofibers, but with mechanical CNFs without a cationization pretreatment of any kind. Most likely, the cause is the same as that of the lower transmittance, as polyDADMAC-induced aggregation hampered the homogeneous distribution of CNFs across the sheet and their diffusion through interfiber spaces. Even when c-CNFs obtained with polyDADMAC 30% complemented mechanical nanocellulose (*+3% mechanical CNFs + 3% c-CNFs*), in what we could call a dual system given the latter's slightly negative charge, the sheet was not sealed to a greater degree than when adding *+ 6% mechanical CNFs*. Within non-covalent cationic nanocellulose samples, there is no consistent and significant difference between the different polyDADMAC concentrations, 20% and 30% ($p = 0.75$).

Paper mechanical properties are displayed in Table 3. The burst index, the internal cohesion (Scott bond) and the tensile index were consistently and significantly improved by all kinds of nanocellulose. However, although partially overlapped tolerance intervals do not necessarily imply non-significant differences (MacGregor-Fors and Payton, 2013), most of the differences between mechanical and c-CNFs were non-significant ($p > 0.05$).

Here follows a list of valuable statements drawn after neglecting those non-significant differences. First, a 3% addition of c-CNFs attained a higher tensile index than a 3% addition of mechanical CNFs. Second, combining a 3% addition of c-CNFs (polyDADMAC 30%) with a 3% addition of mechanical CNFs (dual system) attained a lower improvement in the tear index than a direct 6% addition of mechanical CNFs. Third, a 6% addition of c-CNFs attained a higher internal cohesion than a 6% addition of mechanical CNFs.

It is known that nanocellulose, when added to pulps in sheet forming, offers much more surface area for hydrogen bonding and attains a more compact, less porous structure (Li et al., 2021). Overall, this is key to understand why paper is toughened, even though it is not the only factor (Wohlert et al., 2022). While mechanical nanocellulose offers more area, c-CNFs are more strongly bonded to pulp fibers.

In any case, and regardless of the deviation, Fig. 6 highlights the

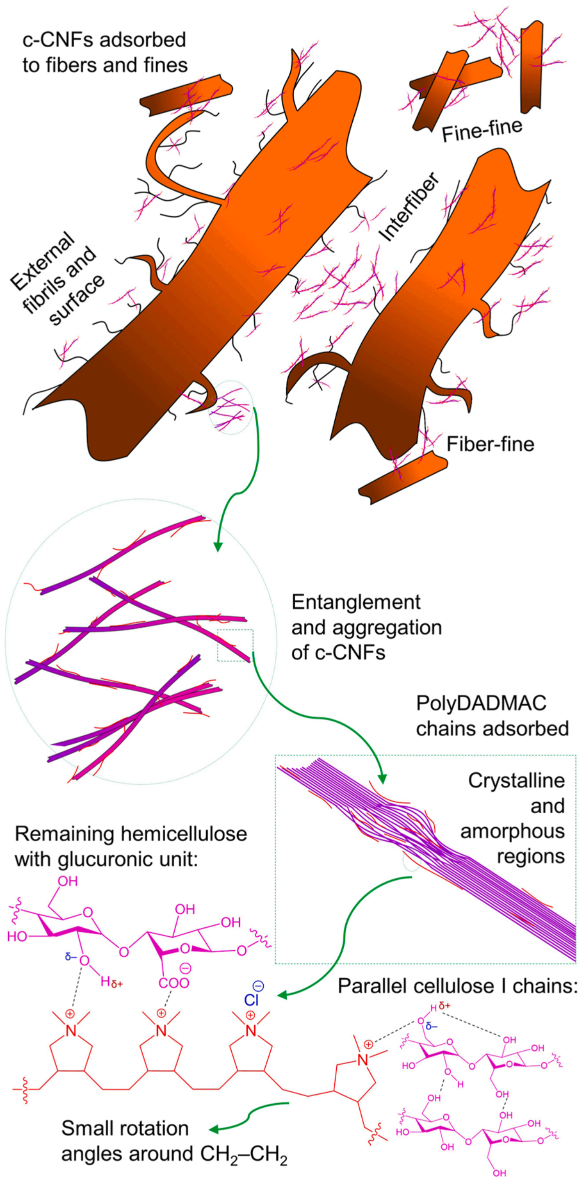

Fig. 7. Interactions between cellulosic fibers, fines, nanocellulose and polyDADMAC at different levels: microscale, nanoscale, and molecular.

trends followed by the mean values for the sake of direct visualization. All in all, the differences between the polyDADMAC-pretreated nanocellulose and the mechanical one were inconsistently positive, negative, or simply non-significant.

3.5. 3.5. Pulp, polyelectrolyte and nanocellulose: schematizing the interactions

The aggregation of c-CNFs, which was evidenced by lower transparency and lower gravimetric yield, did not avoid paper strengthening. We presume that there is a double-edge effect, as the loss of surface area from aggregation was compensated by the favored adsorption on the negatively-charged pulp.

All of this discussion should be combined with our previous elucidations on the relationship concerning polyDADMAC adsorption, the specific surface area and the influence of the pH and the ionic strength (Serra-Parareda et al., 2021a). As estimated therein, the area of the DADMAC monomer is 1.55×10^{17} nm^2 μeq^{-1} and the weight-average end-to-end chain length of the polymer is not greater than 321 nm, corresponding to a rod-like model. Under conditions of low ionic strength and slightly alkaline pH, polyDADMAC can behave as a semi-flexible polymer (Zhang et al., 2019). While the charged ring is planar and stiff, rotation around CH_2–CH_2 bonds is allowed, at least in small angles.

Fig. 7 represents a plausible and simplified model for the adsorption of polyDADMAC onto CNFs and the subsequent interactions with the recycled pulp. Here follows a discussion from bottom to top. The pulp, which has not been submitted to any treatment that could have caused conversion to cellulose II or amorphous cellulose, has its chains arranged in a parallel fashion, at least along the crystalline domains. From the moment that the pH held during adsorption decreases, the reprotonated hydroxyl groups are capable of remain attached to polyDADMAC by ion-dipole interactions, while free monomers grant a positive surface charge. At a higher scale, the same free monomers or even large chain segments promote the coagulation-flocculation of nanofibers. Finally, although aggregated to a certain extent and thus heterogeneously distributed, c-CNFs diffuse through spaces between fibers, between fines, and between fines and fibers, while the adsorbed polyDADMAC chains provide some bridging and anchor points between nanoscale cellulose and fibers/fines.

4. Conclusions

A kraft pulp from hemp, comprising approximately 7% hemicellulose and 1.4% Klason lignin, was successfully cationized without nucleophilic substitution, but *via* polyDADMAC adsorption. The extent of such success depended on the degree of refining, which increased the availability of exposed groups for both ionic and ion-dipole interactions. Charge densities of around 200 μeq/g were reached after 5 h at 23 °C, and in aqueous alkaline media, if the pulp had been refined to 10,000 PFI revs. This so-called non-covalent cationization follows pseudo-second order kinetics, highlighting diffusion through the fiber as the rate-controlling stage.

When the fibers and fines with polyDADMAC were nanofibrillated by means of HPH, the CNFs that were released were consistently more charged than their non-nanoscale precursors, indicating that radial diffusion through the fiber, at least during a time lapse of 5 h, could not be neglected. However, the presence of the cationic polyelectrolyte agglomerated the micro-/nanofibers to a certain extent, resulting in more opaque dispersions and higher proportions of sediment when centrifuging. This was also the cause of a double-edge effect when using this non-covalent cationic nanocellulose as bulk additive in papermaking. For instance, the pretreatment was detrimental to air barrier properties, as the resulting packaging paper was more porous than if mechanical CNFs were used instead. Still, unlike mechanical nanocellulose without a cationization pretreatment, a 3% addition of CNFs that had undergone polyDADMAC adsorption yielded gains in the tensile index of up to 57%. Further research could seek ways of attaining these or greater benefits without the drawback of hampered dispersion.

CRediT authorship contribution statement

Roberto Aguado: Data curation, Investigation, Writing – original draft preparation. **Quim Tarrés**: Investigation, Methodology. **Pere Mutjé**: Formal analysis, Project administration, Resources, Validation. **M. Àngels Pèlach**: Funding acquisition, Project administration, Visualization. **Marc Delgado-Aguilar**: Conceptualization, Supervision, Writing- Reviewing and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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