

Exploring the possibilities of non-covalently cationized nanocellulose for papermaking

Roberto Aguado (✉ roberto.aguado@udg.edu)

University of Girona. C/ Maria Aurèlia Capmany

Quim Tarrés

University of Girona. C/ Maria Aurèlia Capmany

Pere Mutjé

University of Girona. C/ Maria Aurèlia Capmany

M. Àngels Pèlach

University of Girona. C/ Maria Aurèlia Capmany

Marc Delgado-Aguilar

University of Girona. C/ Maria Aurèlia Capmany

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Abstract

As cationic cellulose, despite its long history, has yet to find a place in the paper industry, recent research is assessing the potential of its nanoscale forms. We combined this trend 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 kraft pulps from hemp, under conditions that allowed the deprotonation of the hemiacetal groups of cellulose. Conveniently, a highly positively-charged fiber surface remained 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 is the rate-controlling step. PolyDADMAC-containing fibers were then fibrillated by high-pressure homogenization. Far from promoting desorption, cationic nanocellulose had greater surface charge than the starting fibers, as the specific surface area increased. Nonetheless, polyDADMAC caused agglomeration of fibrils to a certain extent, resulting in, besides loss of transparency, higher permeability when applied in papermaking by bulk addition. As an advantage, the tensile index increased by up to 57% in the absence of any retention agent.

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 followed shortly afterwards, 2,3-epoxypropyltrimethyl-ammonium chloride (EPTAC) arising as the most popular choice (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 polydiallyldimethylammonium chloride (polyDADMAC), get adsorbed onto fibers (Lamminmäki et al. 2011; Wallecan and Debon 2018). This adsorption, which has often been applied for fiber charge measurement purposes (Serra-Parareda et al. 2021a), 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). Soluble cationic cellulose can also be used as flocculants in papermaking (Aguado et al. 2017) or, following the same principle, 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, nor it is in wastewater treatment plants, 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 targeting the typical fibers that are obtained after pulping (generally 100–1500 μm in length, 5–50 μm in width). Indeed, there is enough proof of the interest from a number of papermaking companies in nanocellulose, the existence of commercially available products standing as the most evident demonstration (Sharma et al. 2019; Balea et al. 2020). Several legit reasons are given to combine cationization and nanofibrillation. The former is a unique pretreatment for the latter, although causing partial solubilization (Pedrosa et al. 2022). In the context of apparel usage, the optical density of cellulose nanofibers (CNFs) after dyeing with reactive pigments has been found to be enhanced (Khatri et al. 2013). Other advantages are antimicrobial properties (Aderibigbe 2021), adsorption of water-pollutant anions (Sehaqui et al. 2016), stabilization of Pickering emulsions (Silva et al. 2020), and efficient valorization of lignocellulosic waste (Yao et al. 2022).

The approach presented here combines the idea of cationic nanocellulose, exposed above, 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. Still, other alleged advantages, such as the antimicrobial properties and the fixation of anionic agents, are maintained.

Quaternary ammonium groups are not only unreactive towards virtually any electrophile, but also towards most nucleophiles, including partially deprotonated cellulose (Zhang et al. 2021). However, they are proper anchor points, in adsorption mediated by stable ionic interactions, to negatively-charged polymers. It is known that strongly alkaline media ($\text{pH} > 12$), not necessarily high enough to disrupt crystallinity, favor the dissociation of hemiacetal groups, turning cellulose into an anionic polyelectrolyte (Bialik et al. 2016). Conveniently, a slightly alkaline medium ($\text{pH} > 9$) suffices to grant both the dissociation of the remaining carboxyl groups and the polarization of hydroxyl groups in general. In the latter case, the oxygen atom of the $-\text{OH}$ group holds a partial negative charge, something that has long been exploited for ion-dipole interactions. This is why papermakers successfully rely on cationic polyelectrolytes in the wet end of the paper machine (Aguado et al. 2017).

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), but it encompasses the microfibrils 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 as 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.

Experimental

Materials

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, at 3,000 rpm for 20 min, in a device that complies to the ISO standard 5263, before use. This will be referred to as “recycled pulp”.

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 market pulp, referred to as “hemp pulp”, was received as dry boards and redispersed as described above for the recycled pulp.

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

Refining and pulp characteristics

With the purpose of evaluating the direct 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 2,500 to 10,000.

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 3000g 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:

$$WRV = (m_w - m_D) / m_D \quad (1)$$

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).

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, aiming to polarize the hydroxyl groups of cellulose. After 30 min, and ensuring the temperature is 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%”.

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-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:

$$CD = (C_{PES-Na} \times V_{PES-Na}) - (C_{polyDADMAC} \times V_{polyDADMAC}) \quad (2)$$

where $C_{PolyDADMAC}$, C_{PES-Na} is the normal concentration of titrating agent, 0.001 N, and V_{PES-Na} , V_{PES-Na} is the volume consumed in this titration.

High-pressure homogenization

PolyDADMAC-cationized fibers were filtered and diluted to a 1% consistency with distilled water. The resulting suspension were submitted 9 times to high-pressure homogenization (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 2K-GEA (GEA Niro Soavi, Parma, Italy).

To estimate the yield of nanofibrillation, we centrifuged a 0.2 wt.% consistency CNF suspension, at 4500 rpm ($1254 \times g$) and for 20 min. The sediment, consisting of non-nanoscale fibers or fibrils, was oven-dried at 105°C and then weighed. Therefore, 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.

Papermaking

30 g of recycled pulp (on the basis of dry pulp weight) were diluted to a consistency of 0.75% with distilled water ($< 4 \mu\text{S}/\text{cm}$). 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 ($76 \pm 2 \text{ g m}^{-2}$) 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).

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, three assumptions were made. First, hydrophobic interactions between the methylene groups of polyDADMAC and the pulp are neglected, on the basis of them being weaker than electrostatic forces. Second, and on the same basis, repulsion between like-charged macromolecules allows us to neglect multilayer adsorption. Third, due to the limitations to diffusion through the fiber, the charge density of fibers, as determined by potentiometric titrations, roughly corresponds to the surface charge.

Results And Discussion

Kinetics of the adsorption of polyDADMAC

Strong ionic interactions were formed between the deprotonated hemiacetal groups ($-\text{CH}_2-\text{O}^-$) of cellulose, as the secondary hydroxyl groups are not expected to become dissociated at the pH of the

adsorption process (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 linking to cellulose *via* ion-dipole forces, and even to the remaining carboxylate groups of acidic hemicelluloses. This was confirmed by consistently obtaining a positively-charged sample after adsorption during at least 30 min and rinsing.

The evolution of the charge density with time is depicted in Fig. 2a. Originally, all pulps (unrefined and refined) had negative surface charge, due to the polarized hydroxyl groups and the carboxyl groups of the remaining glucuronic acid of hemicellulose units. This negative charge increased with the number of PFI revs., due to the higher number of functional groups exposed per gram of pulp. Likewise, during cationization, these increasingly exposed functional groups were available for adsorption of polyDADMAC. In general, as easily visualized from 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 undone 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 (Aniagor and Menkiti 2018; Seema et al. 2018; Aguado et al. 2021), respectively, in such way that the initial surface charge is taken into account:

$$CD = CD_0 + \frac{CD_{eq}^2 kt}{1 + ktCD_{eq}}$$

3

$$CD = CD_0 + CD_{eq} (1 - e^{-kt})$$

4

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

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 $\mu\text{eq/g}$ 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 impressive review from Hubbe et al. (Hubbe et al. 2019). Indeed, due to the high molecular weight of polyDADMAC, its diffusion through each of the fibers is severely hampered (Zhang et al. 2016; Serra-Parareda et al. 2021a), 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.

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.

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 ($\mu\text{eq/g}$)	CD_{eq} ($\mu\text{eq/g}$)	k ($\text{g } \mu\text{eq}^{-1} \text{ h}^{-1}$)	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

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, likewise, in more water holding. Indeed, the surface of the fibers became covered by ionic, and thus hydrophilic, functional groups.

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 ($p = 0.02$). However, the influence of polyDADMAC adsorption was inconclusive ($p > 0.05$ in both cases). Regarding fiber width, refining does have well-known effects, but the sum of forces eroding the fiber wall and an increase in fibers' ability to swell makes the outcome difficult to predict.

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 \pm 28	16	41 \pm 2
	20	575 \pm 47	17	38 \pm 2
	30	717 \pm 6	17	39.4 \pm 0.6
2500	0	768 \pm 24	20	40.8 \pm 2.7
	20	781 \pm 21	17	41.3 \pm 0.6
5000	0	743 \pm 71	17 \pm 1	49 \pm 3
	20	633 \pm 25	18	50.2 \pm 1.0
7500	0	640 \pm 16	19	52.9 \pm 0.5
	20	681 \pm 19	19	52.7 \pm 1.1
10000	0	614 \pm 33	19	53.7 \pm 0.8
	20	617 \pm 26	20	54.1 \pm 1.0

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. Figure 4a shows the effects of polyDADMAC adsorption to different levels on the nanofibrillation of fibers that had been refined to 10000 PFI revs. CNF suspensions became more easily precipitable, which was not easily predictable considering the opposing effects of electrostatic repulsion between polyDADMAC-coated nanofibers and polyDADMAC-induced aggregation. The latter outweighed the former, as shown by the diminishment of nanofibrillation yield and transmittance. In other words, the weight ratio of fibrils that sedimented by centrifugation increased with the amount of polyDADMAC.

Being a well-known coagulating and flocculating agent, polyDADMAC chains can act as bridges between nanofibers, thus increasing their effective size. Not only was phase separation promoted, but also, within the stably dispersed phase (supernatant), the increase in size resulted in higher opacity due to light scattering. This can be a drawback in applications that require stable and transparent dispersions of nanoscale cellulose, but it should not be a problem if microscale (rather than nanoscale) particles are tolerated or desired.

Figure 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 that were not accessible to the polyelectrolyte of opposite charge for potentiometric titrations (PES-Na), but where polyDADMAC, at least its shortest chains, had diffused through.

The use of non-covalent cationic nanocellulose for paper strengthening

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. Therefore, before dealing with the effects on paper strength themselves, it is worth observing Fig. 5, which 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 cationic CNFs, or between c-CNFs obtained with different polyelectrolyte concentrations, 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.

In any case, and regardless of the deviation, Fig. 6 highlights the 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. It may be suggested that the negative effects from polyelectrolyte-induced agglutination were somehow compensated by the favored nanofiber-fiber interaction.

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 m² kg⁻¹)	Burst index (kPa m² 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

Pulp, polyelectrolyte and nanocellulose: schematizing the interactions

In light of all the results, we can draw some conclusions about the hypotheses tested and, not less importantly, new hypothesis to be considered in future research. The former include the aggregation of micro-/nanofibers that was evidenced by lower transparency and greater proportion of sediment after centrifugation. The latter involve the double-edge effect of c-CNFs in paper strengthening, as we presumed that the loss of surface area due to aggregation accounted for a negative influence, while the favored adsorption on the pulp exerted a positive contribution.

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 $1.55 \times 10^{17} \text{ nm}^2 \mu\text{eq}^{-1}$ 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 $\text{CH}_2\text{-CH}_2$ bonds is allowed, at least in small angles.

Figure 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 hemiacetal groups and even some secondary 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.

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 around 200 $\mu\text{eq/g}$ 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 for 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 tensile index gains up to 57%. Further research could seek ways of attaining these or greater benefits without the drawback of hampered dispersion.

Declarations

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Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Availability of data and materials

The authors made all data public in the repository of the University of Girona.

Code availability

Not applicable.

Author contributions

All authors made substantial contributions to the conception of the work, the acquisition and interpretation of data, and writing. The first draft of the manuscript was written by Roberto Aguado and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Ethics approval

Not applicable. No studies involving humans and/or animals.

Consent to participate

Not applicable. No studies involving humans and/or animals.

Consent for publication

Not applicable. No studies involving humans and/or animals.

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Figures

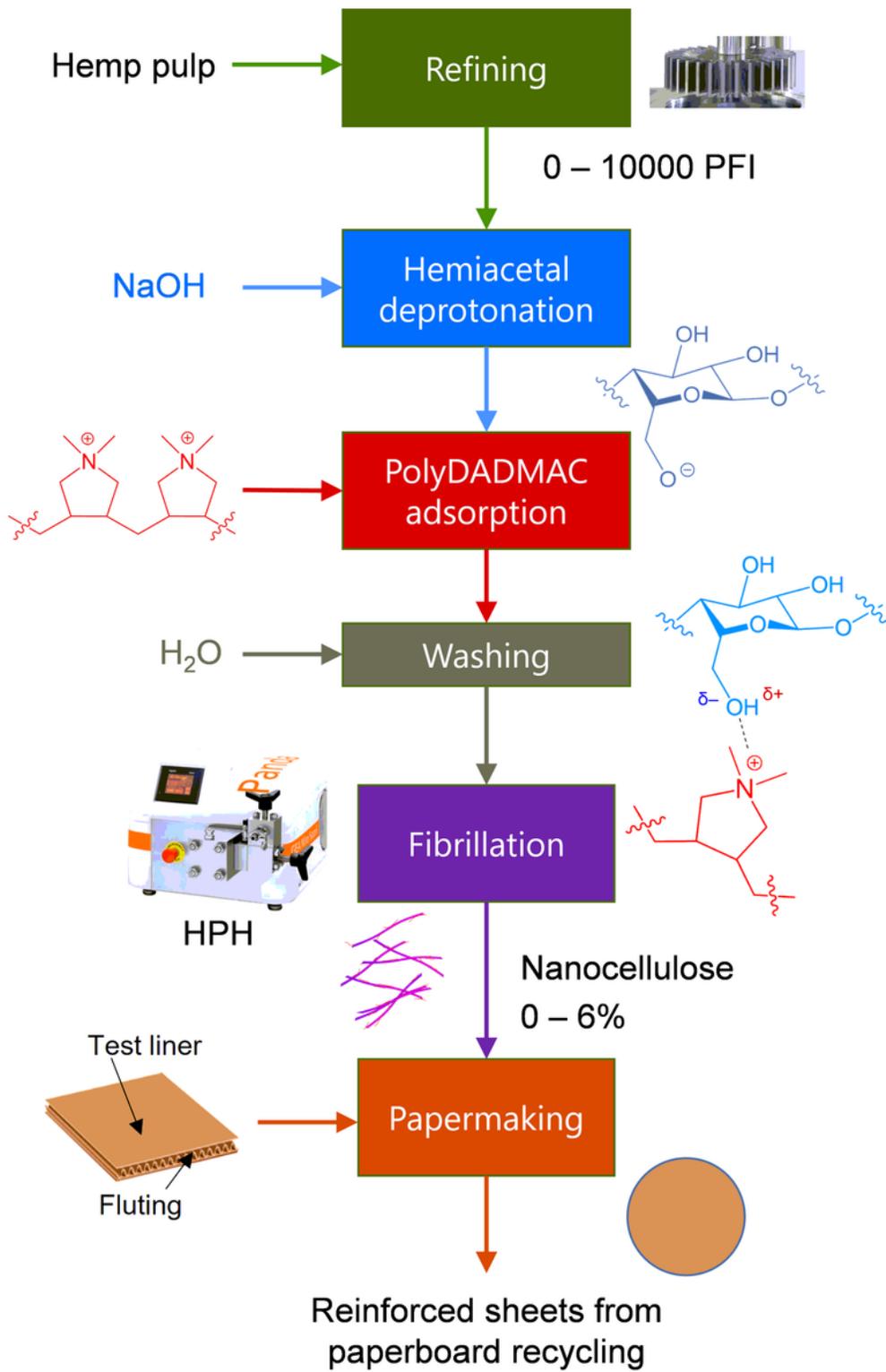


Figure 1

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

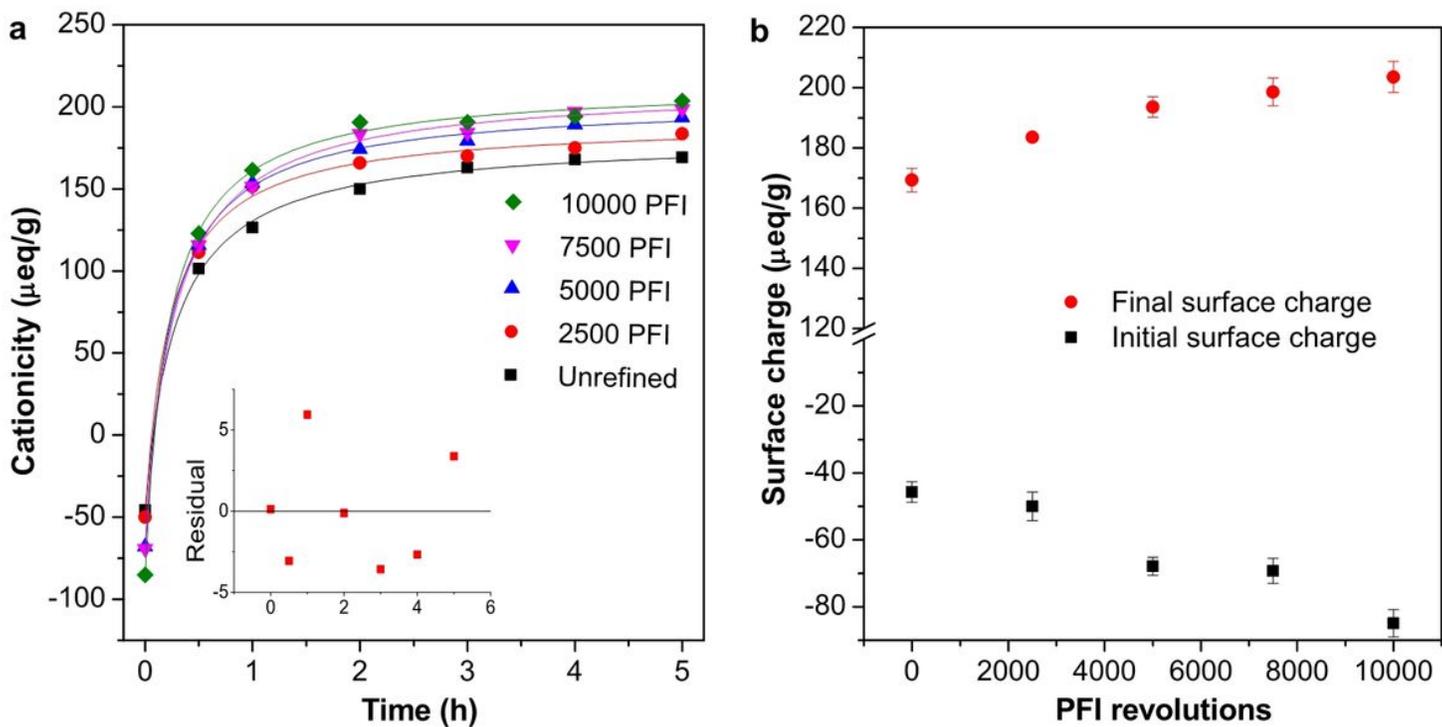


Figure 2

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

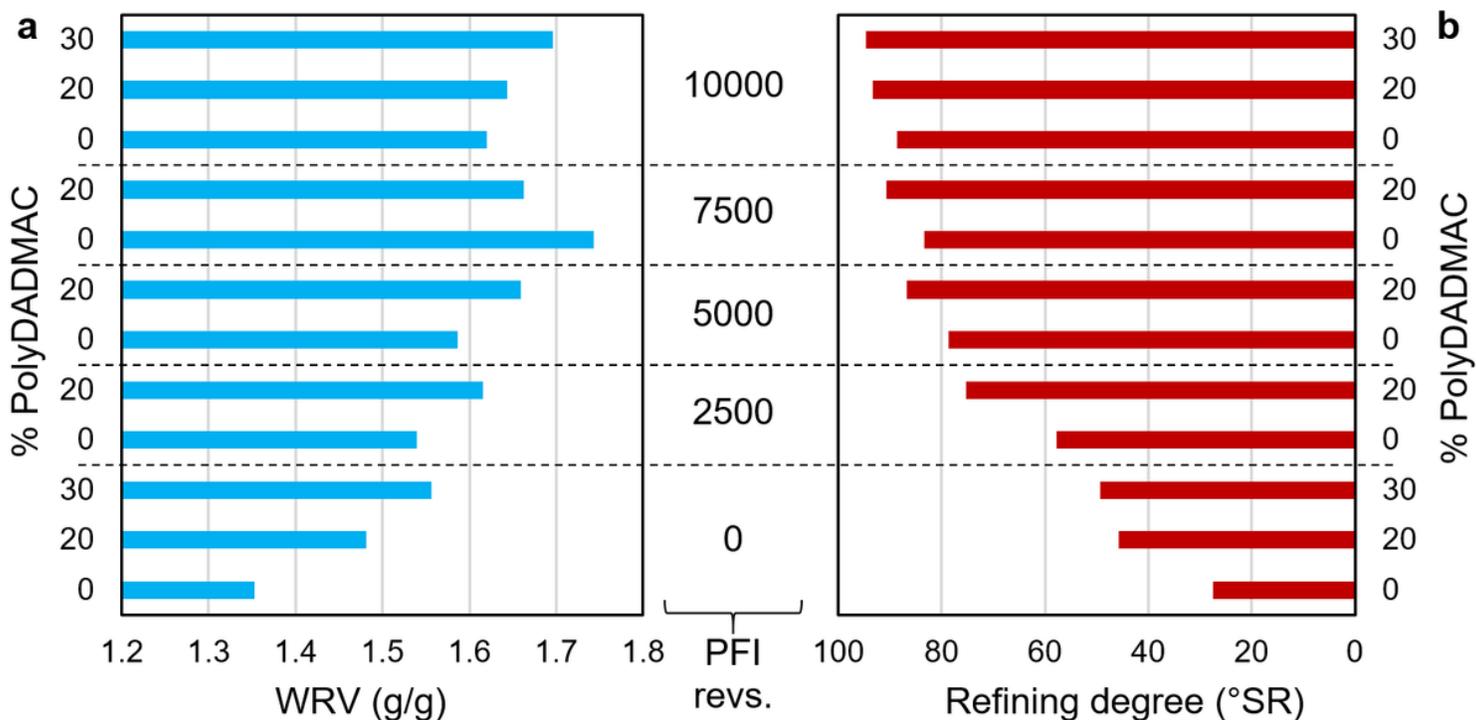


Figure 3

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)

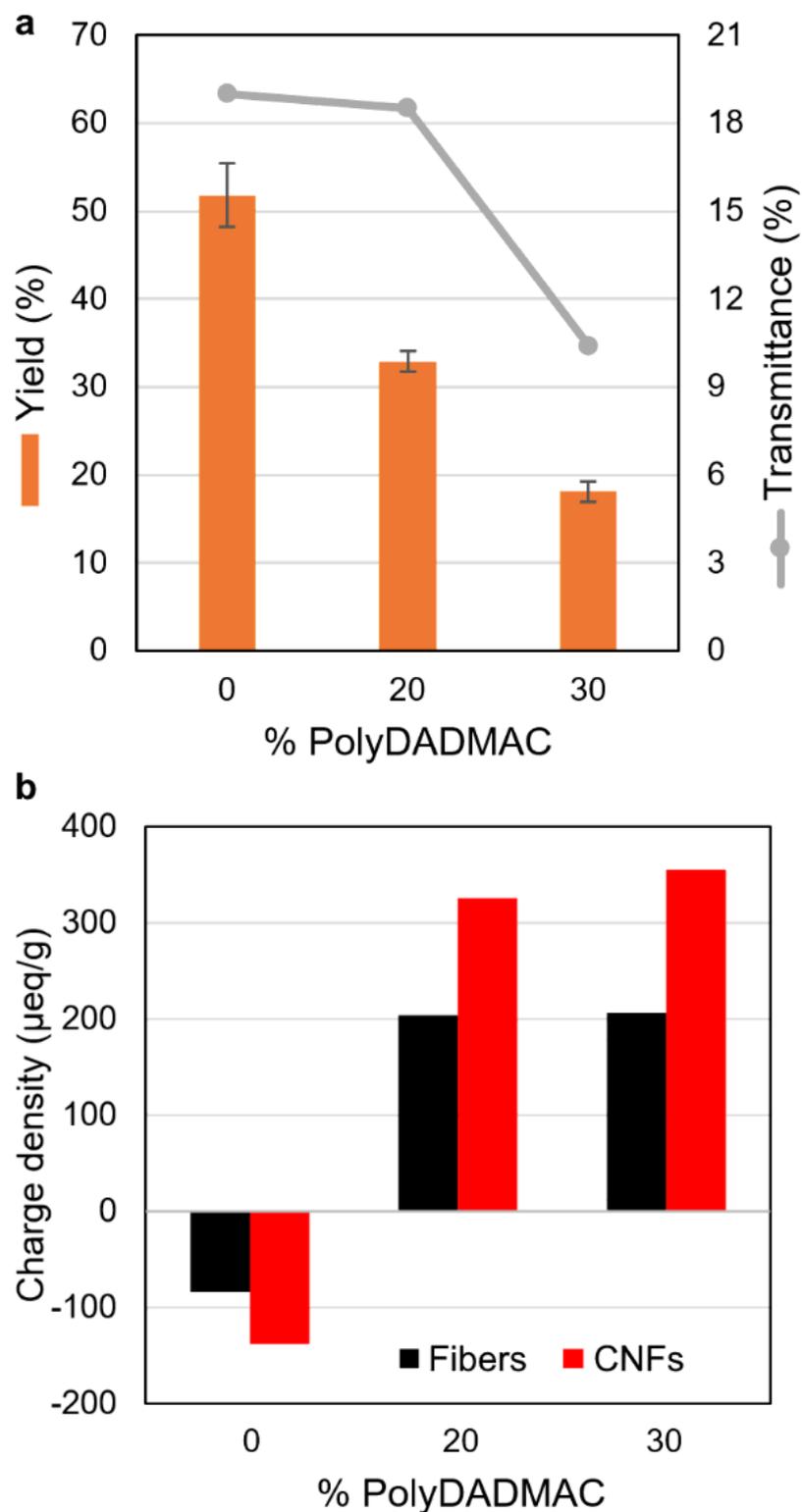


Figure 4

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

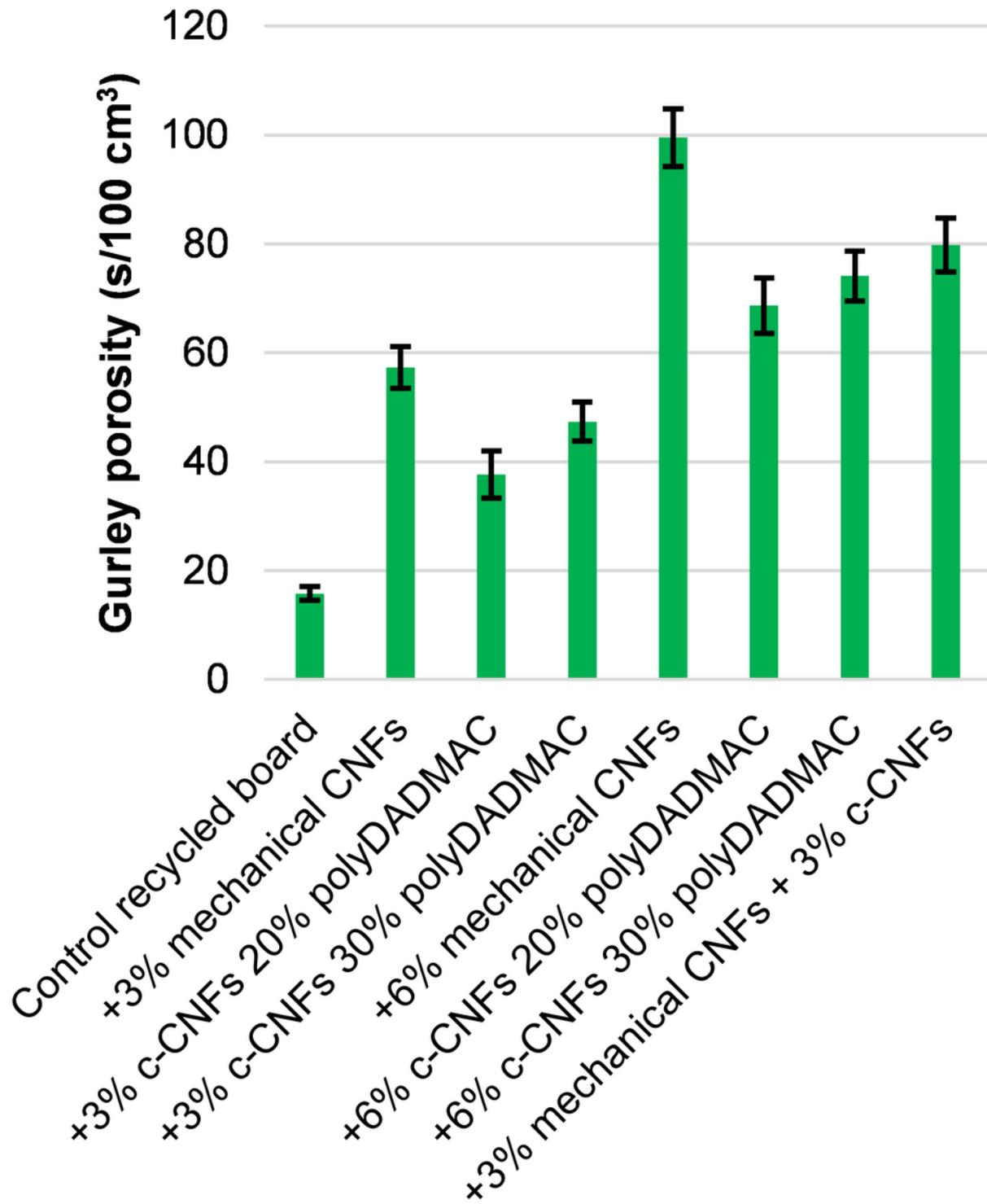


Figure 5

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

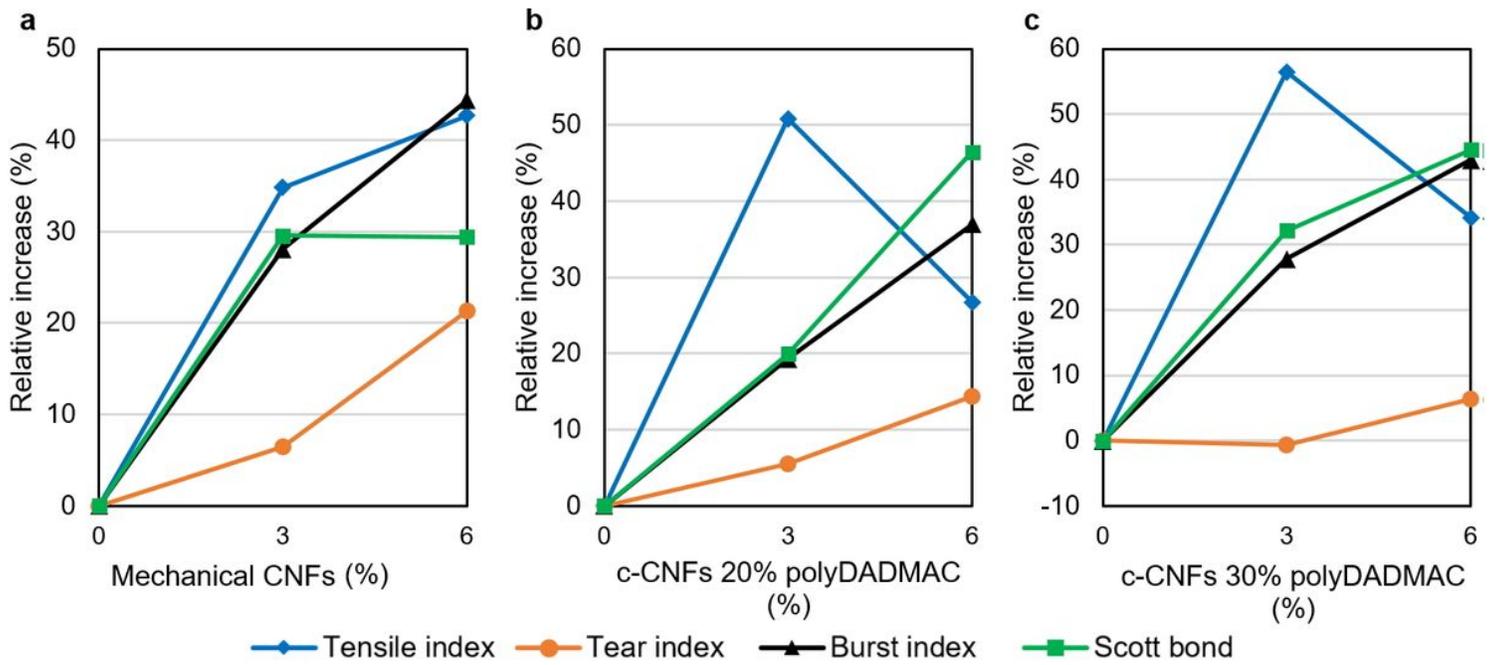


Figure 6

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)

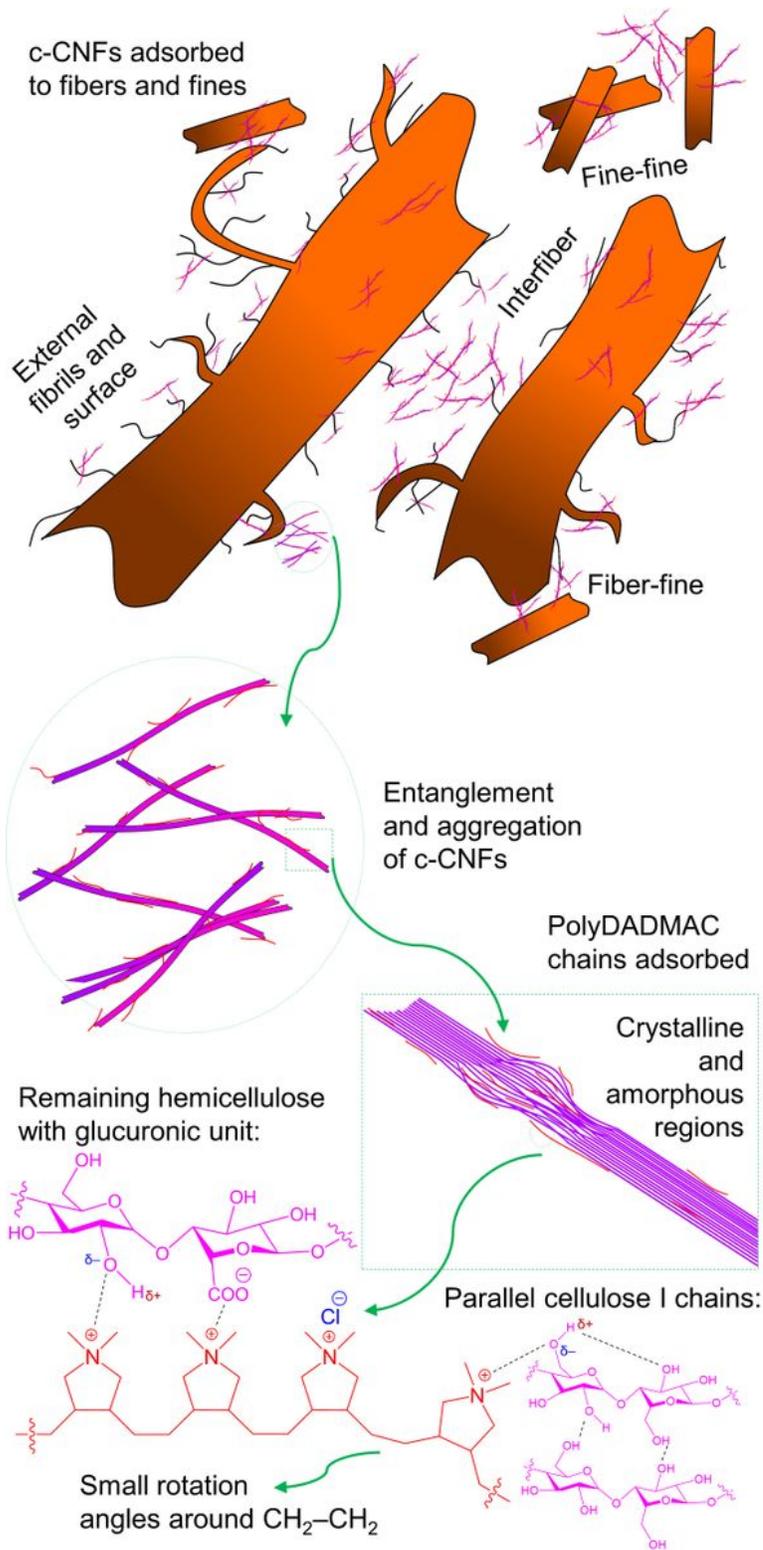


Figure 7

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