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Polymer Degradation and Stability 220 (2024) 110646

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.journals.elsevier.com/polymer-degradation-and-stability

Cellulose nanocrystals polyelectrolyte complexes as flame retardant treatment for cotton fabrics

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ARTICLE INFO

Keywords:
Cellulose nanocrystals
Cotton
Flame retardancy
Polyelectrolyte complexes

ABSTRACT

In this work, polyelectrolyte complexes (PECs) are employed as an efficient way for the deposition of functional flame retardant coatings based on cellulose nanocrystals (CNCs). To this aim, CNCs have been combined with branched polyethyleneimine (BPEI) obtaining gel-like PECs to be deposited on cotton by an easy doctor-blading approach. The morphology of the coated fabrics was investigated by scanning electron microscopy. The thermal stability was evaluated by thermogravimetric analyses while the achieved flame retardant properties were assessed by horizontal flammability tests. The deposition of the CNCs/BPEI PECs produces a homogeneous coating capable of self-extinguishing the flame with only 8 % of weight added to the fabric. Post combustion residue investigations highlighted how these CNCs/BPEI PECs can produce a swelled charred barrier consisting of polyaromatic structures embedded within an amorphous carbon. The results reported in this paper open up to a practical and industrially viable strategy for the exploitation of CNCs in the field of flame retardant coatings.

1. Introduction

Sustainability is the key concept that should drive the choice of raw materials sources for the development of technology. Indeed, the ever-increasing need for a circular economy based on the use of sustainable, reusable, and recyclable resources is pushing both research and industry to explore new strategies for the production of functional materials. Among the plethora of biological derived polymers, cellulose is the most common amphiphilic polymer available on Earth, with an annual production in the order of tens of Gtons/year [1]. Cellulose finds broad applications from building materials to clothes, from paper industry to packaging and pharmaceuticals. Cellulose displays a hierarchical architecture that results in peculiar chemo-physical and structural characteristics. In particular, the elementary nanoscaled crystalline building blocks of cellulose (the cellulose nanocrystals, CNC) are a lively research topic. CNCs are the rigid part of the elementary fibrils that, once assembled into larger bunches, form the microfibrils that compose the cell walls of plants [2]. The most common method to extract CNCs is via a chemical oxidation of the raw cellulosic material in order to completely solubilize the more reactive amorphous domains and maintain the less reactive crystalline domains, while also introducing surface charges [3]. CNCs are always elongated crystals of few nm in lateral size and submicron length. Their high aspect ratio and the electrostatic charge brought by their surface impart interesting self-assembly and film-forming capability [4]. Notably, CNCs display impressive properties such as high transparency, high crystallinity, high strength and Young's modulus, ease of functionalization, high gas barrier and interesting char forming abilities [5–7]. Due to this unique set of properties, CNCs have been widely applied for the development of bulk materials and membranes produced through water-based processes [8–10]. Of particular interest is the use of the Layer-by-Layer (LbL) assembly for the production of nanostructured functional coatings and thin films [11–13].

The LbL is an attractive approach for the water-based assembly of green components through the consecutive adsorption of oppositely charged polyelectrolytes or nanoparticles which anchor one to the other forming multilayer films [14–16]. Through the years, LbL has been employed for the deposition of CNCs-based assemblies characterized by strong mechanical properties, high gas barrier properties, and electrical conductivity [17,18]. In recent years, LbL has been also successfully applied for the deposition of flame retardant (FR) coatings on different kind of substrates such as fibers, textiles, foams and thin films [19–21].

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https://doi.org/10.1016/j.polymdegradstab.2023.110646
Received 16 November 2023; Received in revised form 21 December 2023; Accepted 23 December 2023
Available online 24 December 2023

The application of LbL to this field has been driven by the need to replace conventional and potentially dangerous FR chemicals with novel, high performing and green solutions [22–24]. Within this context the use of bio-sourced coating constituents, such as CNCs, is of great academic and societal interest. To this aim, a recent attempt has been performed by LbL assembling tannic acid modified Mxene and P-N functionalized CNCs on cotton fabrics [25]. A 20 bi-layers coating was found able to increase the limiting oxygen index to 32 % and effectively reduce heat and smoke release rates. The same assembly also showed electromagnetic interference shielding characteristics. Unfortunately, despite the promising results achieved, the need to use washing baths to avoid cross contamination, the production of large amount of waste solutions and the time-consuming nature of the procedure represents unsurmountable constraints that prevent the further development of LbL at the industrial level.

Recently, the use of polyelectrolyte complexes (PECs) has been proposed as a possible solution to overcome such limitations [26]. Moving from the same chemical fundamental of LbL, PECs can be formed as either soluble or coacervate phase in water solutions by mixing oppositely charged polyelectrolytes and nanoparticles under controlled conditions (e.g. concentration, pH, ionic strength etc.) [27,28]. In this way, it is possible to achieve a single deposition bath characterized by either high concentration or gel-like behavior and thus capable of depositing functional coatings with fewer deposition steps with respect to LbL [29]. Up to now, this approach has been successfully applied to both natural and synthetic fabrics [30–34]. For example, it has been demonstrated that the one pot deposition of a branched polyethylene-imine (BPEI)/poly (sodium)phosphate PEC was sufficient for conferring self-extinguishing properties to cotton [32]. Similar results were achieved by chitosan/phytic acid and chitosan/montmorillonite complexes when deposited on wool and acrylic fabrics, respectively [33,34].

In this work, we report the use of CNCs-based PECs for the deposition of FR coatings on cotton fabrics. This approach, to the best of the authors' knowledge, has never been attempted before and could possibly lead to an industrially viable route for the deposition of functional CNCs-based coatings. To this aim, BPEI has been selected as cationic counterpart to anionic CNCs for the production of PECs to be applied by a simple doctor blade coating on cotton fabrics (Fig. 1).

In the PECs composition the BPEI acts as continuous polyelectrolyte matrix gluing the CNCs together. This latter favorable char-forming ability is hypothesized to contribute to the build up of a protective barrier during combustion [7]. The coating morphology on cotton fabrics was investigated by scanning electron microscopy. The thermal stability and flammability of treated fabrics were studied by thermogravimetric analyses and horizontal flammability tests, respectively. Post combustion residues have been imaged by SEM and analyzed by Raman spectroscopy. Preliminary leaching tests have also been performed in order to investigate the coating durability.

2. Materials and method

2.1. CNC synthesis and characterization

Cellulose nanocrystals (CNC) with carboxylic functionalities bearing a negative charge at pH > 4 were produced from Northern Bleached Softwood Kraft pulp Celeste 85 kindly provided by SCA (Sundswall, Sweden), following a modified procedure from the literature [35]. Briefly, 10 g of the cellulose pulp were dispersed in deionized water and 160 mg of 2,2,6,6-Tetramethyl-1-piperidinyloxy, free radical (TEMPO), (Alfa Aesar, Germany) and 1 g of sodium bromide (Sigma, Germany) were added. 35 mL of sodium hypochlorite (10 % active chlorine) were added in one step. After this addition the pH was 11.9 and was maintained about 10.5 by addition of NaOH 1 M as far as the reaction proceeded at RT under stirring. After 5 h the oxidized pulp was left to sediment, the supernatant was removed and repeated washings with plenty of deionized water were performed until the pH was 6.5. The oxidized pulp was sonicated by a Bandelin Sonoplus HD2200 sonicator, 200 W (Germany) equipped with a 13 mm tip for 4 min at 80 % power delivered in aliquots of 35 mL suspension volume and finally vacuum filtered over a cellulose acetate 5 μm filter (Sartorius, Germany) to remove course residues or contaminations. The desired final CNC concentration was obtained by a rotary evaporator (Heidolph, Germany).

2.2. PECs preparation and deposition on cotton

0.3 wt% solution of BPEI (250k Mn, pure from Sigma Aldrich) was poured under stirring in CNC 0.3wt% suspension using either a 1:1 or 1:2 v/v BPEI/CNC ratio. After ~15 min the formation of a light-yellow gel indicated that complexation occurred (see digital images in Fig. 1). The solid concentration in the achieved gels was 0.3wt%. This value is employed to calculate the amount of gel for that is needed in order to achieve a target weight gain of 10wt% on the fabric. Cotton fabrics (density 400 g/m^2, purchased from Fratelli Ballesio S.r.l. Torino, Italy) were washed with ultrapure water and dried in oven and then ironed in order to remove wrinkles and achieve a flat substrate for the subsequent deposition. Half of the needed BPEI/CNC gel was deposited on the fabric by means of a manual blade coating procedure. During the coating the gel is evenly spread on the surface of the cotton by means of a spatula (Fig. 1). The same procedure was then repeated on the other fabric surface. The so coated fabrics were then dried in a ventilated oven at 40 °C for one night.

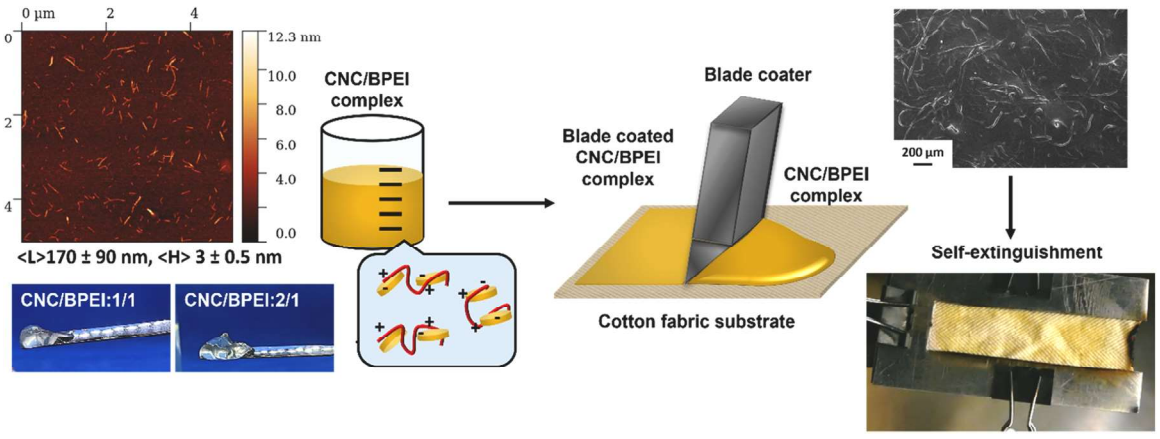

Fig. 1. Scheme of the work: AFM topography of obtained CNC and CNC/BPEI preparation procedure and deposition with flammability test.

2.3. Characterization

The morphological characterization of the CNCs was accomplished by Atomic Force Microscopy (AFM). To perform AFM measurements, a uniform distribution of individual CNC was obtained by dropping of a dilute suspension (concentration < 1μg/mL) of the negatively charged nanocrystals over a positively charged substrate. To this purpose, silicon substrates were carefully washed and inserted into a reaction vessel (Vol = 250 mL) containing 200 mL of aminopropyl triethoxy silane (APTES) which was connected to a vacuum pump. The gas phase silanization reaction lasted for 2 min.

The AFM images were acquired by an NT-MDT NTEGRA instrument in tapping mode acquisition (tip spring constant = 40 N/m) and analyzed by Gwyddion2.59 software [36]. Conductometric titrations of the carboxyl groups was performed by a Delta Ohm 2256 instrument (Padova, Italy). The samples were brought to pH 2.8 by addition of HCl then the solution was titrated by 0.5 M NaOH. The carboxyl content per weight of CNCs (mmoles g-1) was calculated as:

$$[COOH] = \frac{C \cdot V}{m}$$

where C is the concentration of the NaOH solution, and m is the mass of CNCs. V is the volume of the NaOH solution added to reach complete ionization of carboxyl groups. Zeta potential of CNCs were obtained by the LitesizerTM 500 particle analyser setting the temperature at 25 °C. The Smoulocowski model was used to convert the mobilities into zeta potential values. The morphology of coated fabrics and post combustion residues was imaged by SEM (Zeiss Evo 15, Jena, Germany) operating at 5 kV. Samples were positioned on conductive tapes and gold sputtered before the measurements. Attenuated Total Reflectance Fourier Transform Infrared (ATR-IR) spectra were collected at room temperature in the 4000–700 cm^{-1} range (16 scans and 4 cm^{-1} resolution) by a spectrophotometer (Frontier, Perkin Elmer, Italy) equipped with a Ge crystal. The thermal stability was evaluated by TGA (Discovery, TA analysis). The samples (10 +/- 1 mg) were placed in alumina pans and subjected to an isothermal treatment for 30 min at 100 °C in order to remove moisture, the temperature was then increased to 700 °C at 10 °C/min. The test was performed in both N_2 and technical air atmosphere. In the following T_{onset} is defined as the temperature corresponding to a 10 % weight loss. The reaction to flame exposure was tested by horizontal flammability test. A 2 cm pre-mixed blue methane flame was applied two times for 6 s to the short side of a sample (17×68 mm) tilted by 45° along its axis. The test was repeated at least 3 times for each formulation. During the test, parameters such as after-flame time (defined as the time for which flame persists after the ignition source has been removed on the basis of ISO 13,943, expressed in s), the occurrence of afterglow and the final residue (%) were recorded. Raman spectra of post combustion residues were collected on an InVia Raman Microscope (Renishaw, New Mills, UK argon laser source 514 nm) coupled with a Leica DM 2500 optical microscope. D and G band were fitted by Gaussian-Lorentzian functions. Treated fabrics after flammability test were cut by 15 mm in order to remove the portion damaged by the applied flame. A preliminary leaching test was performed by dipping the treated fabrics in deionized water under magnetic stirring for 10 min at 23 °C. Samples were dried in oven for 1 night at 40 °C before further functional characterization.

3. Results and discussion

3.1. Synthesis and CNC characterization

The CNC were characterized in terms of particle shape, size and polydispersity by AFM while the hydrated size and the possible aggregation was tested by DLS in aqueous suspensions (Fig. S1).

A representative AFM image is shown in Fig. 1. A statistical analysis of the size performed on a data set of 900 CNCs indicated a length of 170 ± 90 nm and a height of 3 ± 0.5 nm (Fig. S1). The colloidal stability of the CNC suspension was confirmed also by their zeta potential value of -25 ± 1 mV at 25 °C and by a carboxyl group content per CNC mass of 2.11 ± 0.06 mmoles/g. The prepared CNC were then used as nanoparticles in the preparation of PECs gels with BPEI and then applied to cotton.

3.2. Coating morphology on cotton

The $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v and $CNC_{0.3}/BPEI_{0.3}$ 1:1 v/v coated cotton fabrics were characterized by means of SEM and FTIR in ATR mode. Fig. 2 shows SEM micrographs of unmodified and coated cotton while Fig. S2 collects the acquired spectra. Neat cotton shows the typical morphology of natural fabrics with yarns made of fibers of irregular shapes. The deposition of both PECs formulations yields coherent and homogeneous coatings that continuously cover the fabric structures. High magnification micrographs show how the coating acts as a glue compacting the low-adhered fibers on the surface thus increasing the friction between the underlying interwoven fibers. Indeed, the treated cotton fabrics appear stiffer than the untreated ones as pointed out by a practical test performed by wrapping the untreated and treated fabrics over a glass vial (Fig. S3). Neat cotton and $CNC_{0.3}/BPEI_{0.3}$ 1:1 v/v can bend following the glass curvature while $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v produces visible edges. This behavior is ascribed to the presence of CNCs films from which are notoriously stiff and brittle. Conversely, the highly branched structure of BPEI favors ductility and this compound might acts as a soft component conferring flexibility to the PECs [37]. Indeed, in the case of PECs prepared with high CNC amount (i.e., $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v) some cracks of the coating layer are noticeable by SEM thus suggesting a stiffer behavior. This phenomenon could be also related to the removal of the equilibrium water from the coating during SEM observations, which is known to have an impact on the plasticity of PECs [38]. Despite the formation of the above-mentioned cracks, both coatings show a good adhesion to the substrate due to the polar affinity between cotton hydroxyls group and the CNC/BPEI PECs. ATR-IR spectra confirm the deposition of PECs encompassing both the selected components. Indeed, the characteristic signals of CNC and BPEI functional groups are easily detected at 1600 cm^{-1} (asymmetric COO^- stretching and asymmetric NH_3^+ bending), 1490 cm^{-1} (symmetric NH_3^+ bending) and 1400 cm^{-1} (symmetric COO^- stretching) [39].

3.3. Thermal stability

The thermal and thermo-oxidative stability of neat and coated fabrics were evaluated by TGA in nitrogen and technical air, respectively. The TG plots are reported in Fig. 3 while Table S1 collects the related parameters. In inert atmosphere, cotton displays a well-known decomposition step mainly resulting from the depolymerization of the cellulose glycosyl units to volatile products (mostly levoglucosan). The same units also undergo a competing dehydration reaction towards the production of a thermally stable char (10 % of the initial mass) [40,41]. The presence of the PECs leads to an early decomposition as supported by a reduced T_{onset}. This can be ascribed to the presence of CNCs acidic functionalities that can favors the cellulose dehydration pathway thus producing an increase in the final residue at 700 °C (see Table S1) [42–44]. This residue can be ascribed to the inherent char forming characteristics of CNCs coupled with the coexistence of amino and carboxylic acid functionalizations within the deposited PECs, which have been recently demonstrated to be effective char-formers in polyaminoacids [42,44]. In air, the presence of oxygen modifies the first decomposition step by increasing char formation as a consequence of the oxidative dehydrogenation of anhydrocellulose and also adds a second weight- loss step where such char is oxidized to water and carbon dioxide. [40]As already observed in nitrogen, coated fabrics show an anticipation in T_{onset} with an increase of the char formed within 300–400 °C.

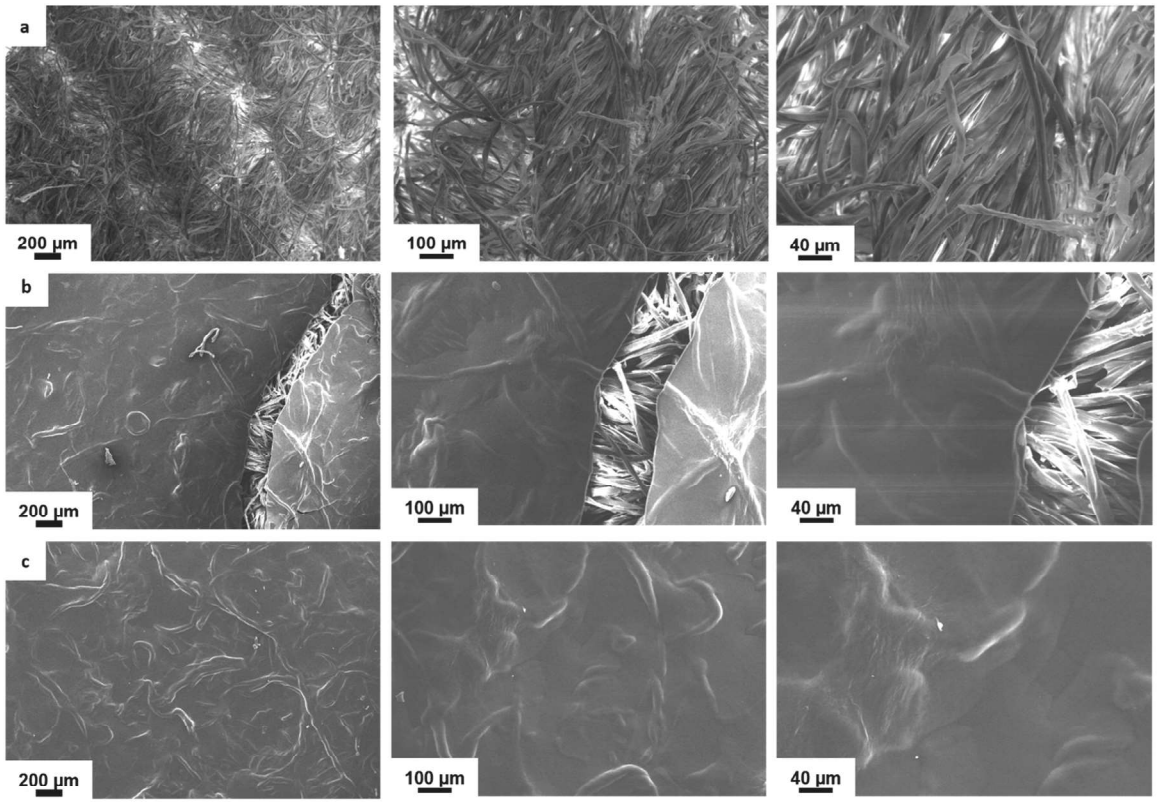

Fig. 2. Morphology of cotton substrate (a), $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v (b) and $CNC_{0.3}/BPEI_{0.3}$ 1:1 v/v (c).

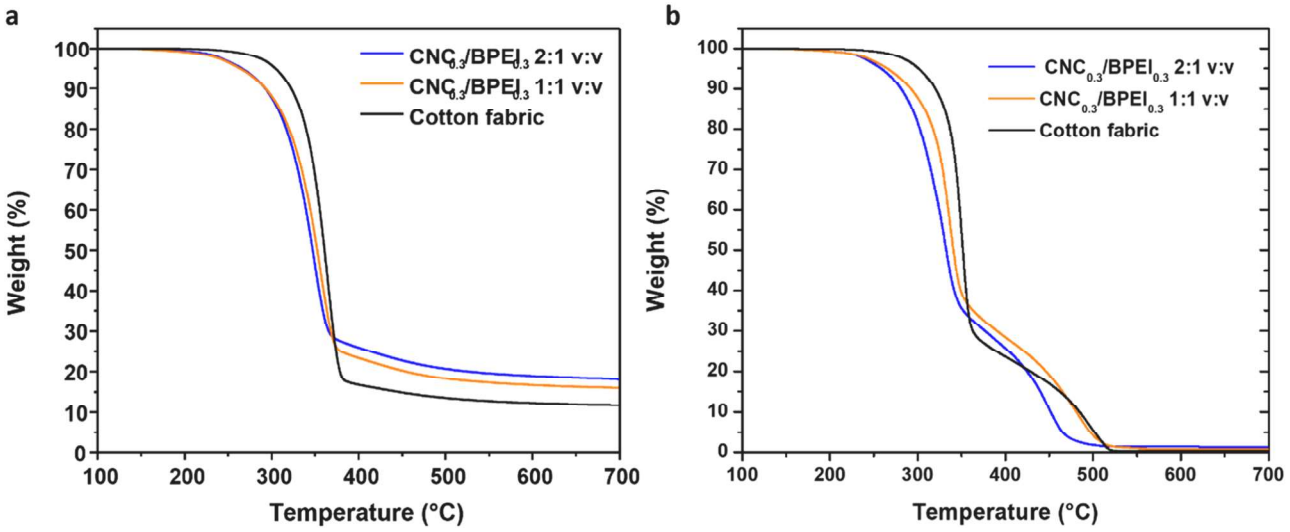

Fig. 3. TG plots of neat cotton and cotton treated by CNC0.3/BPEI0.3 2:1 v/v and CNC0.3/BPEI0.3 1:1 v/v in N_2 and air atmospheres.

The produced char is then oxidized within 450–500 °C. Interestingly, samples coated with $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v display an anticipation of this last step, thus suggesting that the produced charred structures are more prone to oxidation.

3.4. Flammability

Flammability tests in horizontal configuration were conducted in order to assess the reaction of the treated samples towards a flame contact and their propensity to start a fire. Fig. 4 collects the images of the samples during the test and a comparison with the literature background, while Table S2 summarizes the parameters measured during the tests. During the test, neat cotton ignites after 2–3 s of flame application and the flames spread to the entire length of the sample. After the flame extinguishes, the residual portion of the sample is completely consumed by the afterglow phenomenon, which is typical of cotton fabrics. By contrast, $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v immediately extinguishes the flame after the igniter removal. Simultaneously, a char layer is formed, and the after-glowing is confined to the portion of cotton fabric directly exposed to the flame. The formed char impedes the after-glowing extension thus protecting the rest of the sample (Table S2). The same behavior is displayed by $CNC_{0.3}/BPEI_{0.3}$ 1:1 v/v. A comparison with the literature background highlights how these CNC/BPEI PECs can rival with other water-based FR systems encompassing phosphorous-based compounds

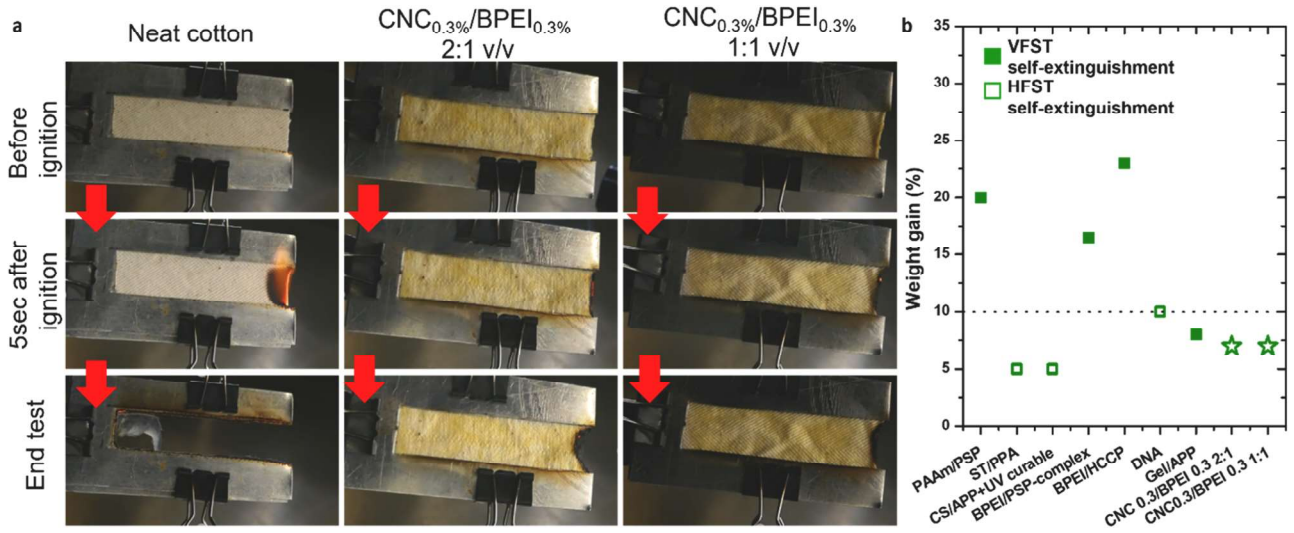

Fig. 4. Flammability test (a) of $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v and $CNC_{0.3}/BPEI_{0.3}$ 1:1 v/v and comparison with literature exploiting PEC and LbL assembly deposited on cotton fabric (b) [32] ,[45–50].

(Fig. 4b).

3.5. Post-combustion residue analysis

The residues collected after flammability tests have been analyzed by means of SEM and Raman spectroscopy (Fig. 5). Collected SEM micrographs, performed at the portion of the fabric that was directly exposed to the methane flame, show how the CNC/BPEI PECs were capable of producing a stable charred residue characterized by a swelled morphology. Indeed, as pointed out by high magnification micrographs, intumescent-like structures can be easily detected on both samples. These structures efficiently protected the underlaying cotton from the flame while also preventing the spread of the afterglow phenomenon after the flame extinguished. This is also evidenced by the presence of nearly undamaged fibers that are clearly visible underneath the coating. The formation of intumescent like-structures for systems bearing carboxylic acids and amine functionalities is also supported by the literature background [42,44]. Raman spectra performed on the charred portion of the residues clearly evidence peaks at 1350 cm^{-1} and 1580 cm^{-1} known as the D and G bands commonly correlated to sp[2] carbons in graphene related materials and pyrolysis products [51,52]. The presence of a well-defined G band and a rather broad D band suggests the formation of disordered carbonaceous structures embedding polyaromatic clusters [53]. The former can be ascribed to the char produced from amide crosslinked BPEI due to the NH_3^+/ COO^- bonds in the deposited PECs while the latter are likely resulting from CNCs thermal decomposition towards graphitic-like structures [54,55]. During flammability tests, the produced protective barrier limits the release of combustible decomposition products from the underlaying cotton towards the flame while also providing favorable thermal insulation. This considerably limits the release of volatiles fueling the flame to the point where combustion cannot be sustained anymore, and the flame extinguishes.

3.6. Preliminary leaching test

A preliminary leaching test was performed by exposing the coated samples to deionized water under magnetic stirring in order to evaluate possible changes in coating morphology and functional properties. Fig. 6 collects SEM micrographs and images from flammability tests performed on fabrics after the leaching test. Both $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v and $CNC_{0.3}/BPEI_{0.3}$ 1:1 v/v coatings seem to be almost unaffected. Indeed, the collected SEM micrographs display a morphology similar to what was already observed for the as prepared samples (compare Fig. 6 with

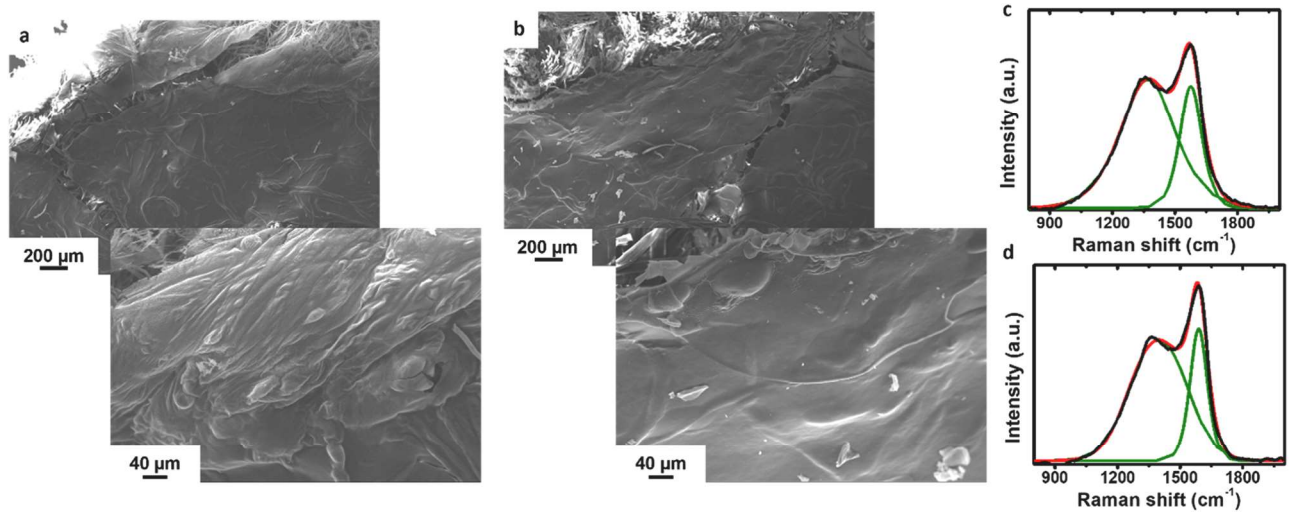

Fig. 5. SEM post combustion analysis with Raman of $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v (a and c) and $CNC_{0.3}/BPEI_{0.3}$ 1:1 v/v (b and d).

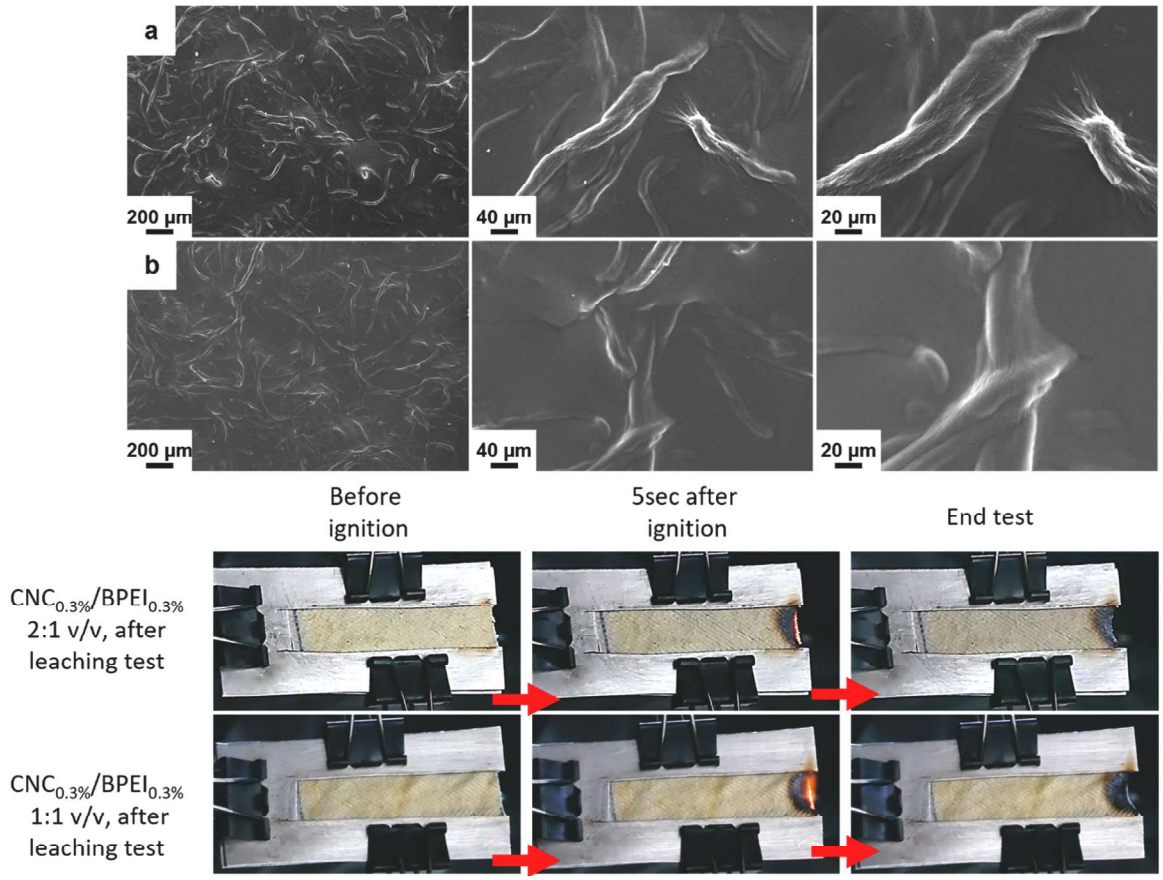

Fig. 6. Durability study: morphology by SEM and flammability results of $CNC_{0.3}/BPEI_{0.3}$ 2:1 v/v and $CNC_{0.3}/BPEI_{0.3}$ 1:1 v/v.

Fig. 2). During flammability tests, the samples self-extinguish the flame right after the removal of the methane igniter. The formation of a charred region capable of confining the after-glowing phenomenon within the portion of the fabric exposed to the flame is also clearly observable. Post-combustion characterization of the residue collected after flammability tests was performed by SEM and Raman spectroscopy (Fig. 7).

SEM micrographs reveal the formation of a compact charred layer where intumescent-like micron-scale bubbles can be easily detected at higher magnifications. As previously observed, such charred structures are capable of protecting the underlying cotton fibers that appear to be undamaged. Raman spectra still confirm the formation of amorphous carbonaceous structures embedding polyaromatic clusters. These results clearly point out that these PECs can maintain the desired FR properties after the performed leaching test thus displaying a somewhat inherent durability even without a post-crosslinking treatment. This phenomenon can be ascribed to the presence of BPEI, which has been often correlated with improved coating stability due to its strong adhesion to the substrate [56].

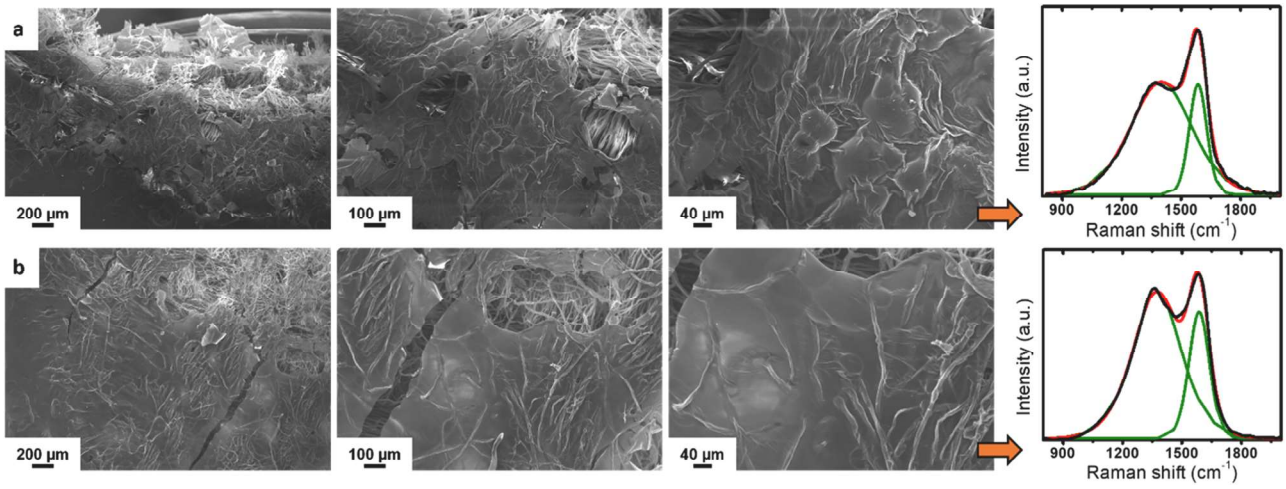

Fig. 7. SEM micrographs and Raman spectra characterization of post-combustion residues collected from CNC0.3/BPEI0.3 2:1 v/v (a) and CNC0.3/BPEI0.3 1:1 v/v after leaching test (b).

4. Conclusions

In order to improve the flame retardancy of cotton, an easy to manipulate polyelectrolyte complexes hydrogel was prepared by mixing negatively charged cellulose nanocrystals and branched polyethyleneimine and then blade coated to cotton fabrics. The morphology of the deposited PECs was investigated by SEM, highlighting the formation of a continuous and compact coating on the fabric surface. A nearly instantaneous self-extinguishing behavior after the removal of the igniting source was observed for PECs treated fabrics during horizontal flammability tests. The afterglow phenomenon, typical of cotton, was considerably reduced by the presence of the coating. Post combustion residue investigation, performed by SEM, highlighted how the deposited PECs are capable of producing a protective carbonaceous structure characterized by expanded micro-intumescent bubbles. Raman spectroscopy provided complementary results pointing out the formation of thermally stable polyaromatic structures embedded within an amorphous carbon. Such structures act as a protective barrier limiting the amount of combustible volatiles fueling the flame, eventually leading to a self-extinguishing behavior. The durability of the FR performances of the deposited coating to leaching was also preliminary evaluated. After the leaching test, fabrics displayed nearly unmodified FR behavior, thus suggesting a certain degree of durability. The approach proposed in this paper provides a novel route to the practical exploitation of CNCs in the field of water-based FR treatments. Future works might be focused on the development of different PECs compositions in order to target specific flame retardancy or improved durability while also addressing other important functional properties such as breathability and wearability.

Supplementary material

AFM statistical analysis of CNC suspension, FT-IR in ATR mode of neat and treated cotton fabrics, practical demonstration of stiffness of neat and treated fabrics, TGA data of neat and treated fabrics, flammability data of neat and treated fabrics are supplied as Supplementary material.

CRediT authorship contribution statement

Lorenza Maddalena: Conceptualization, Data curation, Formal analysis, Investigation, Writing – original draft. **Johanna Mae Indias:** Data curation, Investigation. **Paolo Bettotti:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Resources, Supervision, Writing – original draft. **Marina Scarpa:** Conceptualization, Funding acquisition, Investigation, Resources, Supervision, Writing – original draft. **Federico Carosio:** Conceptualization, Funding acquisition, Resources, Supervision, Writing – review & 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.

Acknowledgments

The authors thank D. Pezzini for SEM acquisitions. This work was supported by the Italian Ministry of University (MIUR) call PRIN 2017 with the project PANACEA [grant number 2017LEPH3M].

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2023.110646.

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