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Grafting of Amine Functions on Cellulose Acetate Fibers by Branched Polyethylenimine Coating

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Abstract:

The aim of this study is to functionalize cellulose acetate (CA) fibers with an amine function by the adsorption of branched polyethylenimine (bPEI) into the fiber surface. The adsorption was carried out by immersing CA tow in branched bPEI solution and washing off with water to remove any non-adsorbed bPEI. The mass increase and X-ray Photoelectron Spectroscopy (XPS) quantified the amount of bPEI adsorbed on the surface of the CA fibers. The effects of the coating duration, bPEI molecular mass, bPEI concentration, bPEI solvent and plasma treatment on the amount of the bPEI adsorbed and the amine density on the surface of the CA fibers have been investigated and reported here. The surface morphology of bPEI-treated CA fibers, compared to one of native CA fibers, was investigated by both Electron Probe Micro-Analyzer (EPMA) coupled with X-ray mapping, which is an important tool to analyze surface chemical composition, and Scanning Electron Microscopy (SEM), in order to illustrate the

morphology of the CA fibers after bPEI adsorption as well as the plasma effect on adsorption process. The evaluation of bPEI coated-CA fibers for the adsorption aldehydes was carried out by exposing them to formaldehyde vapor generated from a formaldehyde solution. The adsorption mechanism was investigated by Cross Polarization - Magic Angle Spinning ^{13}C Carbon Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR) which proved that the aldehydes are chemically attached to the surface of CA fibers in the form of hemiaminals. Finally, the shelf life of plasma-treated CA fibers coated with bPEI was studied and reported.

Keywords: cellulose acetate, branched polyethylenimine, volatile aldehydes, selective adsorption, low pressure cold plasma, XPS, solid state NMR.

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1. Introduction

Esophageal cancer, Chronic Pulmonary Obliteration and Cardiovascular Disease are the main illness causes by cigarette smoke [1-3]. As a consequence of the health impacts of cigarette smoke, the tobacco industries are currently investigating techniques to reducing exposure to harmful components of cigarette smoke [4, 5]. Cigarette smoke contains a number of hazardous components, among them aldehyde compounds including formaldehyde, which has not only an acrid smell but also allergenic effects [6, 7]. As a way to reduce the harmfulness of this substance, the activated carbon is widely used conventionally [8-12]. Nevertheless, by using such material as a physical adsorbent, not only aldehydes are reduced, but also other components that bring flavors into the cigarette smoke, decreasing the taste effect of the cigarette smoke; therefore, the feeling of satisfaction of smoking is inhibited. For that reason, the development of a selective method to adsorb aldehyde compounds from mainstream cigarette smoke is one of the main objectives of the tobacco industry.

Research and development of cigarette filters, which have a high degree of selectivity for particular smoke constituents, has been conducted for many years. For the removal of semi-volatile and gaseous smoke constituents, selectivity is achieved by chemical rather than physical means. Recently, an assessment of the chemisorption ability has been carried out to remove highly volatile aldehyde and HCN from mainstream cigarette smoke, using a weakly basic macroporous resin of polystyrene crosslinked with divinylbenzene (Diaion™ CR20) with a surface functionalized with amine functions as an additive in the cigarette filter [13]. In this study, it has been shown that Diaion™ CR20 is a highly selective and effective adsorbent for formaldehyde, acetaldehyde and HCN from mainstream cigarette smoke. The reduction of these components is more significant than that achieved by activated carbon [13]. This result also indicates that chemisorption can be an effective way for the removal of certain toxic vapours from cigarette smoke [13]. Furthermore, other technological approaches for reducing

emissions cigarette smoke toxicants have been newly reported, such as “split-tipping approach to enhance mainstream smoke air dilution [14]; or by loading charcoal in cigarette filters in order to reduce strongly the levels of carbonyls compounds, such as formaldehyde and acrolein in main stream cigarette smoke [15]; or by incorporation of cupric (II) ions, which have an excellent HCN complexation property and into carboxymethyl cellulose/cellulose acetate (CMC/CA) porous composite microspheres, which were developed by a combination of emulsion-solvent evaporation and an in situ ionic crosslinking method [16].

Polyethylenimine (bPEI) is a branched chain polymer which has a huge number of amine groups and has been extensively used to modify cellulosic surfaces, in environmental areas for chelating heavy metal ions [17-19], for selectively adsorbing endotoxins from protein solutions [20] and for developing drug delivery systems [21, 22]. Different aspects of adsorption of cationic polyelectrolytes onto cellulosic material have been explored. The adsorption process is being explained by a cation exchanging reaction [23-25] or by charge compensation [26]. Hydrogen-van der Waals bonding [27, 28] and the mechanical confinement have also been demonstrated to have a substantial impact on the retention of cationic polyelectrolytes. As reported by Lindström the following processes occur during adsorption: i) movement of polyelectrolytes from solution to the fiber surface (the definition of the available fiber surface depends on the molecular weight of the polyelectrolyte), ii) immobilization of the polyelectrolyte on the fiber surface, iii) reformation of the polyelectrolyte on the fiber surface. The general conception, at present, is that the polyelectrolytes are colliding with fibers either by Brownian motion [29] or by turbulent motion [30, 31]. Numerous studies have been conducted in order to modeling the kinetics of polyelectrolyte adsorption on cellulosic fibers [23, 29-33]. All of these approaches have used a Langmuir model to describing the kinetics. Kindler et al. [34] have introduced a stationary

layer around the fibers in order to use a mass transfer model, while Van de Ven [29] and Wägberg [23, 30, 31] have used a Brownian collision or turbulent collision model, where the fibers are considered as rigid spheres, which collide with spherical polyelectrolyte molecules or by polyelectrolyte diffusion in the cellulosic fibers [33].

The adsorption of bPEI into cellulosic derivatives have been widely explored by different physical-chemistry methods for different applications in recent years (for a review see [26], [35-41]). The adsorption of a low and a high molecular mass polyethyleneimine (bPEI) as cationic polyelectrolyte polymer onto cellulose fibers in aqueous media has been also investigated [42]. In these studies it has been shown that the low molecular mass bPEI penetration into the porous wall of the fibers is easier than the high molecular mass bPEI for which the adsorption in the inner pores is negligible [42].

Cellulose acetate (CA) is a generic name that describes a wide variety of materials that differ in their degree of substitution (DS), which is the average number of acetyl groups per anhydroglucose unit (AGU). While the DS of CAs can theoretically range from 0 to 3, commercially available CAs have a DS between 0.8 and 2.9 [43]. The physical characteristics of CAs are dependent on their DS [44]. This is consistent, given the differences between hydroxyl (OH) and acetyl (OAc) groups. Hydroxyl groups occupy a small volume, are polar, and can act as both donors and acceptors in hydrogen bonding. OAc groups are bulky, weakly polar, and can only behave as hydrogen bond acceptors, which gives CA materials a large network of polar interactions consisting of hydrogen bonds and dipole-dipole interactions, and is expected to have a significant influence on their final properties[45]. The characteristics of CAs, which are affected by the OH/OAc ratio, also cover their solubility [46]. The physical properties of CA illustrate the chain conformational behavior and their intermolecular interactions. Materials made of CAs are typically semi crystalline: chemically homogeneous linkages of underivatized or fully derivatized monomers can be locally organized into a

crystalline state, whereas heterogeneous linkages, consisting of randomly substituted monomers along the chain, are amorphous [47, 48]. The introduction of acetyl groups at random along the cellulose chain causes a sharp increase in sorption as the crystallinity is destroyed. Over a wide range of degrees of substitution (0.8 - 2.2) the sorption decreases linearly as the proportion of acetyl groups increases. Finally, at very high degrees of substitution, the sorption decreases much more rapidly as the units can now crystallize in the cellulose triacetate lattice [49]. Most of adsorption or modification studies, have been focused on cellulose and its derivatives, however, only few such studies have been reported on cellulose acetate systems [50-54].

In order to find an alternative to Diaion™ CR20 as adsorbent in the cigarette filter, we investigated the effect of grafting amine functions on the cellulose acetate fibers on the reduction of the aldehyde compounds in the cigarette smoke [55]. The grafting of amine functions was performed using N₂/H₂ and NH₃/He high pressure cold plasma [55]. The modified fibers were characterized mainly by XPS analyses, which showed the presence of amine functions on the fiber surfaces. Unfortunately, the density of the grafted amine functions was low and insufficient to adsorb the aldehyde compounds generated in the cigarette mainstream smoke. Taking advantage of the high density of amine functions present on the branched bPEI, in this work we investigated the immobilisation of branched bPEI on the CA fibers by adsorption method using aqueous or alcoholic solutions of bPEI. This work is motivated in one hand to reduce certain gas phase constituents in the mainstream smoke of a cigarette during smoking, and in the other hand to develop a process, which does not involve expensive or time-consuming manufacturing, and/or processing steps. X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Electron Probe Micro-Analyser (EPMA) have characterized the modified CA fibers. The effect of treatment of the CA fibers by an Argon low-pressure cold plasma on the bPEI adsorption was studied.

The effect of the modified CA-bPEI on the adsorption behavior of formaldehyde and the adsorption mechanism was monitored by CP-MAS ^{13}C NMR spectroscopy in the solid state. Finally, the ageing of plasma-treated CA-bPEI fibers was also investigated by XPS determining the variation of the amine density on the CA fibers over 60 days.

2. Materials and methods

2.1 Materials

Branched polyethylenimine (bPEI) were purchased from two different suppliers: (i) Sigma-Aldrich (Saint-Quentin Fallavier, France): pure bPEI, M_n 600, M_w 800; 50% in water (w/w), M_n 1200, M_w 1300; and (ii) Alfa Aesar: pure bPEI, M_w 1200. All these polymers were used as received. The sample from Sigma-Aldrich bPEI 50% water (w/w), M_n 1200, M_w 1300, has been lyophilized in the laboratory. All solvents (acetone, ethanol and dichloromethane) were reagent-grade and used without any further purification. All solutions were prepared using ultrapure water purified with a MilliQTM Academic system (Merck Millipore, Burlington, Massachusetts, United States). Formaldehyde 37% in water and ^{13}C formaldehyde 20% in water was purchased from Aldrich (Saint-Quentin Fallavier, France) and Eurisotop (Saint-Aubin, France) respectively, and used as received. Cellulose acetate tow with a degree of substitution of 2.5 was provided by British American Tobacco (Southampton, UK).

2.2 Cellulose Acetate (CA) tow drying and weighting

Before any manipulation (coating with bPEI, plasma treatment and morphology study) the cellulose acetate tow samples were dried in an oven (Memmert, model 100-800, Schwabach, Germany) at 45 °C for 24 h to remove any absorbed traces of water. Samples were immediately put into a Petri dish, which placed in a sealed bag, which prevents the

reabsorption of air moisture, by the dry tow. These steps are critical to determine the exact mass of the CA tow. Dried CA tow samples (before bPEI coating and plasma treatment) were slightly stretched, and weighed in a sealed bag to avoid any contact with air moisture as described above. All the masses were measured with a precision balance (Mettler Toledo model XA105, accuracy 0.01/0.1 mg, Greifensee, Switzerland) with an accuracy of 0.01 mg.

2.3 Coating of CA fibers with bPEI

In a typical experiment, dried CA tow (500 - 900 mg) was introduced into a closed Petri dish and suspended in a solution (20 ml) of bPEI of defined concentration under constant and slow stirring (30 rpm) with orbital platform shaker (Heidolph, Unimax 2010, Schwabach, Germany) for a specified period of time. The treated tow was subsequently washed 3 times with deionized water (20 ml) from a Milli-Q station (Merck Millipore, Billerica, MA, USA) to remove any residual bPEI and then ambient air-dried in the fume cupboard for 2 h followed by drying in an oven at 45 °C for 2 days. The grafting yield of bPEI on the CA fibers was estimated using the following equation:

$$\text{Grafting yields (\%)} = 100 \times (\text{dry mass of grafted CA tow} - \text{dry mass of initial native CA tow}) / (\text{dry mass of initial native CA tow}).$$

2.4 Cold plasma treatment

In this work, a low pressure capacitive coupled discharge (CCP) plasma (Europlasma, Bruges, Belgium) operating at the radio frequency of 13.56 MHz was used. The aluminum reactor chamber was depressurized with a roughing pump of 80 m³. h⁻¹ (Edwards, Genevilliers, France) combined with a turbomolecular pump of 1250 l/s (Pfeiffer Vacuum HiPace 1200C, Annecy, France), allowing to reach a pressure base below 10⁻⁶ mbar. The

reactive gas was then introduced into the chamber. When the pressure became constant, the generator was switched on and adjusted to a certain power value, resulting in a continuous glow discharge between the parallel plates. Samples to be treated were placed in the center of the discharge. Argon plasma was used as the process gas for the study. For the experiments that are presented here, the plasma creation process was performed under the following conditions: Plasma power = 500 W, flow rate = 1000 sccm (standard cubic centimeter per minute) and the maximum power of the radio frequency plasma device was 600 W.

2.5 Formaldehyde adsorption tests

The bPEI coated-CA tow samples were exposed to gaseous ^{13}C -labelled formaldehyde obtained by bubbling Argon in a commercial solution of ^{13}C -labelled formaldehyde in water (37%) for 24 hours. After formaldehyde adsorption, the samples were investigated by CP-MAS ^{13}C NMR spectroscopy.

2.6 Characterizations

2.6.1 X-Ray Photoelectron Spectroscopy (XPS)

The characterization of the modified surfaces was performed by X-ray photoelectron spectroscopy (XPS). XPS analyses were performed using a Kratos AXIS Ultra DLD (Kratos Analytical, Manchester, UK). Samples were excited using the Al $K\alpha$ monochromatic source (1486.7 eV) at 150 W (10 mA, 15 kV) and photoelectrons were transferred to the 165-mm radius hemispherical analyzer using a combined magnetic and electrostatic lens system (hybrid mode) providing 500-meV energy resolution. Analyses were carried out at the normal of the sample surface and the analysis area was $700 \times 300 \mu\text{m}$. The base pressure of the analysis chamber remained below 5.10^{-9} Torr during the acquisition. The narrow scans

(centerlines) were recorded using a pass energy of 40 eV and a jump of 0.1 eV, the wide scans using a pass energy of 160 eV and a jump of 1 eV, respectively. The XPS spectra shown were performed with charge correction. The charge correction was performed using the C1s centerline, fixing the "hydrocarbon" (C-H/C-C) signal at 285.0 eV. The samples were inserted using a target with 2 mm diameter holes. The nature of the cellulose acetate wick samples (glass wool type) made the acquisition of XPS spectra very complicated. Using the small 2 mm hole allows the X-ray beams to be focused on the sample surface and charge compensation was achieved by using simultaneous bombardment of low energy ions and low energy electrons on the sample surface. This target was used with the monochromatic source for all measurements. Each measurement was repeated three times and the average value was recorded. The mean free path of the photoelectrons, which depends on their kinetic energy, directly gives the detection depth. For a photoelectron energy of 1486.7 eV, the estimated mean free path for an organic material λ is about 0.5 nm [56]. Thus, for an angle θ of 85 °, the analyzed depth of the sample is about 0.13 nm. XPS data for polyethylene imine is given according to the literature [57].

2.6.2 Morphology

The morphologies of the untreated CA fibers and coated bPEI- CA fibers were observed using a field emission gun scanning electron microscope (FEG-SEM), Hitachi (Tokyo, Japan) S4700, at an accelerating voltage of 6 kV and a current of 15 mA. Images were taken at various magnifications to ensure representative imaging of the samples. To analyze the chemical composition of the samples, Electron Probe Microscopy Analyses (EPMA) were carried out on a CAMECA SX100 (Gennevilliers, France). The samples were mainly analyzed in cross sections. Cross sections were embedded into epoxy resin, polished (up to 1/4 μm) and carbon coated with a Bal-Tec SCD005 sputter coater (Los Angeles, California,

USA). Nitrogen X-ray mapping were carried out at 15 kV and 40 nA. Images are color coded; from red for a high concentration of the analyzed element, to black for a low concentration of the analyzed element

2.6.3 Nuclear Magnetic Resonance (NMR)

CP-MAS (solid state) NMR spectra were acquired on a Bruker Advance 400 MHz Spectrometer (Wissembourg, France). ^{13}C NMR spectra were obtained at 100.6117 MHz frequency. More than 10, 000 scans were accumulated except for native CA tow for which only 1024 scans were performed.

3. Results and Discussion

3.1. Optimization of the coating of branched polyethylenimine on cellulose acetate fibers

3.1.1 CA tow pre-treatment

In order to determine the amount of bPEI adsorbed on the CA tow based on mass variation, we have tried our best to avoid variation due to adsorbed water. Before coating, CA tow samples were dried, weighed and then kept under inert atmosphere. After the coating, the same drying process was repeated before weighing the samples. Firstly, we determined the optimum conditions to dry the tow. A native CA tow was dried in an oven at 45 °C for time intervals 24, 48, 72, 96 hours and one week. A mass loss of native CA tow from 3.5 to 4% was observed during the first 24 h. The mass variation reached a plateau at 4.2% (SD \pm 0.1%, number of samples= 12) after 48 hours. The mass loss observed after one week of drying was 4.3% that is similar to the one observed after 48 hours. This indicates that drying the CA tow

for 48 hours is sufficient to remove the residual water in our experimental conditions. To determine the influence of immersing CA tow in water, a CA tow sample was dried as described above and its mass was determined (W_0) then immersed in water for 30 minutes and then dried again under the same conditions described above. The mass of the CA tow determined after drying (W_1) was the same as the original mass after drying before water immersion (W_0). These results ascertain that the drying process used during this study is sufficient to remove all the residual water from the CA tow and any mass variation observed after bPEI coating will be due to the amount of bPEI adsorbed on CA fibers and not to the water absorption. Therefore, for all the experiments carried out during this study: the CA tow samples were dried in an oven at 45 °C for 48 h and weighed in a sealed bag, to avoid any contact with air moisture before bPEI solution treatment.

3.1.2 Coating of CA fibers with polyethylenimine (bPEI)

At the beginning of this study, we carried out some feasibility experiments to determine the optimum conditions for the coating procedure. A first experiment using 20% bPEI in water was performed on CA tow using a glass bottle and slow stirring (30 rpm) with orbital platform shaker for the coating step. Nevertheless, after the treatment the tow morphology was deteriorated. For this reason, we decided to use a closed Petri dish (traditionally used for electrophoresis gel staining) for the coating under slow stirring (30 rpm) with orbital platform shaker. We were delighted that this protocol allowed optimum conditions preserving the morphology of the CA tow for further analyses.

In order to optimize the adsorption of bPEI on CA fibers, five parameters were studied: (i) coating duration; (ii) bPEI concentration; (iii) bPEI solvent; (iv) bPEI molecular weight and (v) plasma treatment. The characterization of the bPEI-coated CA fibers was monitored by

XPS analyses for the density of the amine functions on the fibre surface. The amount of bPEI coated on the CA fibres was determined by determining the mass of CA tow after coating and drying. All the results are given in Tables 1 and 2.

Figure 1 and Table 1 about here

3.1.2.a Effect of coating duration

As in our previous work [55], the coating of bPEI on CA fibers was monitored essentially by XPS analyses. The XPS survey spectra permitted us to follow the surface chemical modifications through the atomic content variations. Typical XPS spectra are shown in Figure 1 for untreated CA fibers and bPEI-coated CA fibers during 5 minutes with 5 and 20% of bPEI in water solution. The peak around 400 eV attributed to N1s is clearly visible in the case of bPEI-coated CA fibers [55]. The small peak observed in the same region in the case of the untreated CA fibers is due to contamination. Contamination most likely happened during sample handling and/or during the tow production.

In order to optimize the adsorption of bPEI on CA fibers, the influence of the immersion duration of the CA tow in the bPEI solution on the amount of the bPEI adsorbed was studied. The coating was performed for 2, 5, 30, and 60 min (Table 1, entries a, b, c and d). After coating, the tow was washed 3 times with water to remove any non-adsorbed bPEI. The treated CA tow samples were dried as described above and weighed in a sealed bag to avoid any mass increase due to air moisture absorption. The mass increase results showed that increasing the coating time from 2 to 60 minutes did not affect the amount of the bPEI adsorbed on the CA fibers (Table 1, entries a, b, c and d) within the measurement error. Dried treated CA tows were characterized by XPS. Table 1 shows that the Nitrogen atomic concentration does not change significantly with the increase in coating time from 2 to 60

minutes as expected from the mass measurements. The Nitrogen-Carbon ratios were the same for all the coating durations except for 60 minutes, which was decreased by 0.02 within the XPS analysis error. The XPS results in combination with the mass increase results confirm that the coating duration does not affect the amount of the adsorption of bPEI on CA fibers under the experimental conditions used. In view of these results, we used only 5 minutes as immersion time (2 minutes is too short for reproducibility) for the all experiments carried out afterward.

3.1.2.b Effect of the bPEI concentration

The influence of the bPEI concentration on the density of the grafted amines on the CA fibers surface was also investigated. The coating of CA tow with bPEI was carried out using bPEI (Mw 1200) of different concentrations; 5, 10 and 20% in water. The coating time was limited to 5 minutes. The samples were dried, weighed and analysed by XPS as before. Table 1 (entries b, e and f), gives the elemental composition of the CA tow versus the concentration of bPEI and the mass increase after coating. The mass increase results do not show any variation within the different bPEI concentrations. The Nitrogen atomic concentration (%) also remains relatively constant while increasing the concentration of bPEI. These results show that the bPEI polymer even for the 5% w/w solution saturated the CA fibers surface. As no increase is observed, we can conclude that the bPEI layer does not continue to grow after the CA tow is fully recovered. This indicates that the use of bPEI with 5% concentration is sufficient for our coating the CA fibers.

3.1.2.c Effect of bPEI solvent

The solvent effect on bPEI adsorption was explored using 5% (w/w) bPEI in water and ethanol with an immersion time of 5 minutes. The mass increase results show that the amount

of bPEI adsorbed is similar in both cases (Table 1, entries b and g) however, the results of the XPS analysis surprisingly showed a decrease in the amount of Nitrogen on the CA fibers surface when water was substituted by ethanol. Branched Polyethyleneimine (bPEI) is a weak polybase, whose charge density depends on pH. In a recent paper, Mavrantzas et al studied the conformation of bPEI in function of pH [58]. In their model pKa values of primary, secondary, and tertiary amines of the branched PEI chain were assigned as 10.5, 7.5–8.5, and 5.0, respectively in agreement with earlier studies [59, 60]. Under acidic pH conditions, all amine groups in the bPEI chains were fully protonated. Under neutral pH conditions, primary amines were considered fully protonated, secondary amines were considered alternatively protonated, and tertiary amines were considered unprotonated. On the other hand, under basic pH conditions, all amine groups in the bPEI chains were unprotonated; therefore, none of the amino groups in bPEI was protonated [58]. In our case, since in this work the solutions were carried out in water or EtOH and the pH of a weak base is dependent on both pKa values and the bPEI concentration, we assume that the pH values of the 5-20% solutions in both water or EtOH solutions is around pH = 11. So, the adsorption of bPEI on the neutral surface of cellulose acetate tow is achieved through the Van der Waals type interactions. A mechanism is proposed for the adsorption process in which the doublet of the nitrogen atoms in bPEI acts as donor to the carbonyl oxygen atom of the acetyl group and for the hydroxyl group of the cellulose acetate fiber. The interactions between the bPEI and the surface of cellulose acetate fibers is more pronounced in aqueous medium than in the alcoholic solution, as shown by the XPS decreased nitrogen percentage on the CA fibers surface in the case of ethanol as a solvent.

3.1.2.d Effect of bPEI molecular weight

The study of the effect of bPEI molecular weight was also studied. Experiments were conducted with a concentration of 5% (w/w) and treatment time of 5 min with branched bPEI of different molecular weights using H₂O as a solvent. The results of the XPS analysis (Table 2) showed a decrease in the amount of Nitrogen on the fiber surface when the coating was performed with a low bPEI molecular weight whereas the mass increase is not affected. This behavior has been reported by J. Petlicki and T.G.M. Van de Ven [42], who have shown that the kinetics of adsorption of low-molecular-weight bPEI on cellulose fibres is significantly different from that of high-molecular-weight bPEI. Indeed, the adsorption of high molecular weight bPEI occurs in two distinct steps: first, adsorption on the outer surface of the fiber and, second, on the inner pores of the cellulose fiber. The second step is about 100 times slower, in that each molecule must diffuse through a channel in the fiber wall to enter the internal fibers, which may account for the significantly higher proportion of available amino groups in higher molecular weight CA fibers. However, the adsorption of low molecular weight bPEI proceeds differently. Again, the outer surface is supposed to be covered first, but the amount adsorbed on the outer surface is only a small fraction of the total amount that can be adsorbed. The majority of the low molecular weight bPEI molecule chains fill the roughened area and end up inside the inner surface of the fiber wall. Thus, the kinetics of low-molecular-weight bPEI is primarily governed by the rate at which the chains can diffuse into the pores of the fiber wall. It should be noted that since the amounts of bPEI that can be adsorbed onto pulp fibers are highly dependent on the experimental conditions (molecular weight, ionic strength, pH, bPEI concentration, pulp consistency, time), it is not surprising to find a number of different isotherms in the literature for bPEI adsorption onto cellulose fibers [42].

Table 2 here

3.1.2.e Effect of plasma treatment on the coating

Between the various approaches to fiber surface modification [61], the low-temperature plasma modification technique is one of the most promising, since it affects a very thin layer near the surface. Many investigations have demonstrated that plasma modification can enhance polymer coating surface properties, which are of importance in several industrial applications [62-64]. Cold Argon (Ar) and atmospheric plasma treatments have been used to modify the structure of cellulose triacetate and cellulose acetate for a variety of applications [65-68]. Depending on the plasma parameters, these treatments cleave covalent bonds, leading to oxidation and degradation of cellulose. The bombardment of high energetic ions on the fiber surface causes modification of the rough topography and etching with the loss of mechanical strength. The modulus and tenacity of the cellulosic fibers were also decreased after plasma treatment. A recently reported work on Argon Plasma Oxidized Cellulose [69] has provided a comprehensive understanding of this phenomenon. Both XPS and FTIR have revealed that the oxidation of the fibers and therefore increase in the content of polar groups in the surface layers of the studied materials and the ablation of the material were proportional to the exposure time of the plasma discharge. The tendency to water absorption was enhanced by the presence of hydrophilic polar groups. Longer the modification time, the higher the water absorption rate. The pH values indicated that the plasma treated is more acidic due to the greater content of hydroxyl and carboxyl groups.. Inspired from the different results mentioned above and the assumptions that Argon plasma treatment can create the new functional groups on CA fiber surface and could increase the absorption of water, which could improve the adsorption of the branched (bPEI) polymer in CA fibers. Therefore, we

conducted several tests on CA tow fibers either before or after coating with bPEI to determine if the Argon (Ar) plasma treatment is efficient and can improve the grafting of amine functions on the cellulose acetate fibers. For this, the effect of Ar plasma treatment on the coating has been investigated in two different ways: (i) direct Ar plasma treatment of coated (bPEI) on CA tow and (ii) Argon plasma treatment of native CA tow followed by coating with 5% bPEI (M_w 1200) solution in aqueous media.

For all experiments, the coating and post-coating conditions described above were used. The Ar plasma conditions were: power = 500 W, flow 1000 sccm and treatment time 300 s. Table 3 shows the mass variation and atomic composition of the bPEI-coated CA, bPEI-coated CA/plasma-treated and plasma-treated CA followed by coating with bPEI, compared to the native CA fibers. The mass variation results show that treating the native CA with Ar plasma results in a very small decrease of the CA fibers' mass (Table 3). This indicates that etching of the CA fibers surface was caused by the Ar plasma treatment confirmed by the morphology study (see next section). In addition, the mass increase observed when Ar plasma treatment has been applied on bPEI-coated CA fibers was relatively lower in comparison to that observed for bPEI coated CA fibers (Table 3). Again, this indicates that an etching of the fibers' surface has been caused by the Ar plasma treatment. Similarly, to the mass increase, the Nitrogen composition determined by XPS was relatively lower in the case of CA fibers on which Ar plasma treatment was performed in comparison to untreated bPEI-coated CA fibers (Table 3). Indeed, the Nitrogen content determined for CA/plasma/bPEI and CA/bPEI/plasma was 7.8 and 11.3% respectively in comparison to the untreated bPEI-coated CA with 19.1% of Nitrogen content (Table 3). Such a result was not expected, since the plasma treatment should normally create the polar functional groups on the surface layer of the CA fibers in order to improve the intermolecular interactions based on H-bonds and Van der Waals forces. In our case, the Argon plasma treatment causes ablation of the treated materials. The ablation

pathway could be generated by the effect that the Argon plasma must transfer energy to the CA fiber surfaces. Energy transfer may occur by one of the two mechanisms: either by (i) direct energy transfer, i.e., by the inelastic collisions of high energy particles with the atoms of the modified CA fiber or by (ii) radiative energy transfer process [70].

Table 3 here

Another interesting observation during these experiments was that, when bPEI-coated CA fibers were treated with Ar plasma, a weak but noticeable yellow fluorescence color of the fibers was observed. This emission does not appear in the starting materials before the Ar plasma treatments, in contrast to the case of Ar plasma-treated CA followed by bPEI coating. This phenomenon could be assigned to fluorophores produced in a chemical reaction between the carbonyl groups of cellulose acetate and amine functions of bPEI polymer. We also propose that imines (or Schiff bases), formed in the reaction of bPEI amine groups with CA carbonyl groups during the Ar plasma treatment are responsible for the appearance of the yellowing coloration. A similar fluorescence in the case of cellulosic materials was reported in the literature [71-74].

3.2. Fiber Surface Morphology

In order to investigate the morphology variation of the fiber surface, a comparison between native and treated fibers' surface morphology was carried out using Electron Microprobe Micro-Analyser (EPMA) coupled with Scanning Electron Microscopy (SEM) and X-ray mappings for the detection of the nitrogen element. Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) was also used to investigate the fibers' surface morphology.

3.2.1 Electron Probe Micro-Analyser (EPMA)

The total surface area is very important for the application for which the CA tow is designed. Therefore, the conservation of the fiber structure after coating is essential in order to preserve the same original total surface area. In order to investigate the effect of the bPEI coating on the tow structure (fiber entanglement and gluing), the bPEI-coated CA tow samples were examined by Scanning Electron Microscopy and compared to the native CA tow. Figure 2 shows micrographs of native CA tow, CA coated with bPEI using water as solvent and CA coated with bPEI using EtOH as solvent. High bPEI concentration (20%) was used to confirm whether fiber gluing would happen or not. The results obtained (Figure 2 panel a vs b) show that the CA tow maintains its original structure, and no gluing layer has been observed between the fibers. No significant difference was seen when EtOH (Figure 2 panel c) substituted water.

Figures 2 here

Additionally, EPMA coupled with X-ray mappings is an important tool to analyze the surface composition of the CA fibers. In this study, the focus was on the Nitrogen element to confirm the presence of amine functions on the surface. The mappings are color coded in black and the color chosen for the element (in our case, the colour of the nitrogen) is between green-yellow; with black characterizing the absence of the element and the chosen colour the presence of the element.

The results obtained are given in Figure 3 and show a neat difference between the surface of native CA and bPEI-coated CA fibers (Figure 3, a and b). The X-ray mapping profiles clearly show the presence of Nitrogen on the fibers' surface, which indicates the presence of amine

functions. The results obtained in the case where water has been substituted by ethanol show a similar image and profile with less contrast on the presence of nitrogen element (Figure 3, c). These results are in good agreement with the XPS results given in the previous section (See Table 1, entries b and g).

Figures 3 here

3.2.2 Field Electron Gun - Scanning electron microscopy (FEG-SEM)

In order to investigate the coating and plasma treatment effects on the CA fibers, FEG-SEM analyses were performed on native and treated CA fibers. The results show clearly the surface change after the bPEI coating (Figure 4, panels a and b). Figure 4, panel b indicates that the coating layer is quite homogenous and the surface roughness became more important in comparison to the untreated fibers (Figure 4, panel a). The results obtained for bPEI-coated CA fibers displayed in Figure 4, panel b followed by Ar plasma treatment shows the etching effect and the loss of the surface roughness (Figure 4, panel c). This explains the lower density of the Nitrogen determined by XPS analyses for these samples (Table 3). From these morphology results, it can be concluded that the plasma treatment has a negative effect on the coating of bPEI on the CA fibers. In fact, when the plasma treatment is carried out after the coating, it causes an etching of the surface, which results in a loss of coating layer thickness (Figure 4, panel c). Based on the etching effect, it can also be concluded that the plasma treatment of native CA tow results in a smooth fiber surface which prevents coating adhesion and thus can explain the lower Nitrogen density for the plasma-treated CA fibers followed by bPEI coating (Table 3).

Figure 4 here

3.3. Solid state NMR characterization of bPEI coated CA fibers

In order to evaluate the adsorption of aldehydes by the bPEI-coated CA tow produced in this study, a test with formaldehyde was performed. Solid-state NMR analysis provides a tool to understand the mechanism of the adsorption of the aldehydes on the surface of the bPEI-coated CA fibers. This test was carried out by exposing the bPEI-coated CA tow to the ^{13}C -labelled formaldehyde vapor. CP-MAS ^{13}C NMR analyses were carried out for native CA, bPEI-coated CA and bPEI-coated CA after exposure to formaldehyde vapor. The CP-MAS ^{13}C NMR spectra are shown in Figure 5. The assignments of different ^{13}C signals in the case of native CA (Figure 5, a) have been attributed according to the literature data [75]. The spectrum of bPEI coated CA (Figure 5, b) shows signals resulting from the bPEI coating in the area of 52 - 40 ppm. The different signals and their chemical shifts correspond closely to those published by Holycross et al. for ^{13}C NMR of branched bPEI in CDCl_3 [73]. The spectrum obtained after exposure to ^{13}C -labelled formaldehyde vapor (Figure 5, c) shows the disappearance of bPEI signals around 52 - 40 ppm and new signals appearing around 90 ppm, attributed to the bPEI/formaldehyde reaction, whereas the signal of the CA tow remained unchanged, proving that a reaction occurred between the bPEI coating and gaseous formaldehyde.

Figure 5 Here

It has been established that adsorption of the aldehydes by the amino compounds results from a reaction between carbonyl and amine groups. The mechanism of the reaction is described in detail elsewhere [76-78]. While the earlier literature described the reaction in solution for use in organic synthesis, the same process has been suggested for capture of aldehydes [79, 80], even though some modifications may occur due to the attachment of the amine to a surface, inhibiting the freedom of rotation and translation found in solution (Scheme 1).

The most probable mechanism of reaction of an aldehyde with a primary amine is given in the literature [81], in which the nitrogen free pair of the amine attacks the carbonyl carbon, then undergoes proton exchange to form an unstable hemiaminal intermediate, and finally the imine is formed by dehydration from the hemiaminal. The reaction steps are reversible and the reaction is driven to imine formation by removal of water (Scheme 1).

In the present study, from the CP-MAS ^{13}C NMR spectrum, it can be deduced that the trapped formaldehyde species are mainly in the hemiaminal state (around 90 ppm) since no imine form was detected around 160 ppm [81]. Hemiamines are often considered unstable compounds that are susceptible to conversion to the initial imine or amine, but in this case we assume that the species on the bPEI-coated CA cable remained in the stable hemiamine state, which may be due to the excess water in the formaldehyde solution [81]. The other peaks that appeared around 90 ppm could be attributed to unreacted formaldehyde derivatives, such as poly(acetals) or trioxanes, due to the presence of formaldehyde in large excess over the available amine functions on the surface of the CA fibers [81, 82].

Scheme 1 here

3.4. Surface functionalization stability of bPEI coated CA fibers

It was reported in the literature that the principal mechanisms occurring during ageing are chemical reactions with the storage medium and relaxation of side groups and chain segments in the surface region [82]. Numerous works have related the aging study of previously plasma-treated polymers in view of getting a good understanding of the time evolutions of the surface amine groups. For instance, Williams et al. have investigated the mechanisms and kinetics of the aging process of polytetrafluoroethylene (PTFE) samples maintained either in phosphate-buffered saline (PBS) or in air for periods of up to 1 month after O₂, Ar, N₂ and NH₃ plasma treatment [83]. The authors observed, after periods up to 1 month, an ageing in PBS on N₂-treated or NH₃-treated surfaces; replacement of nitrogen by oxygen occurs rapidly in the first 20 min of storage whereas fluorine depletion is more gradual, and all reactions proceed more slowly thereafter.

In our work, the stability of amine groups on the treated CA tow was monitored by XPS. Treated CA tow samples were kept in air at room temperature for 60 days without humidity control. XPS analyses results showed that in the case of bPEI-coated CA fibers, the density of amines on the CA fibers surface was practically the same over the 60 days of storage under the conditions mentioned (Table 4). In the case where plasma treatment was employed, the density of amines on the CA fibers surface was almost stable after 25 days of storage. Only 5.4 and 5.1% of amine were lost during storage for the bPEI-coated CA followed by Ar plasma treatment and Ar plasma-treated CA followed by bPEI coating, respectively. After 2 months of storage, the loss of amines became important where 19.6% of amine was lost in the case of bPEI-coated CA followed by Ar plasma treatment; whereas only 12.8% of amine was lost for Ar plasma-treated CA followed by bPEI, coating under the same conditions (Table 4). From these results, we can conclude that the plasma treatment has a negative impact on the

stability of the amine groups grafted on the CA fibers. It seems that this negative effect is more significant when the Ar plasma treatment was carried out after the coating (Table 4).

On the other hand, and based on an investigation by J. Martinez Urreaga et al. [73] it was demonstrated of short wavelength UV radiation effect on celluloses treated with different amino compounds in aqueous solutions of different pH with polyethylenimine (PEI), hexamethylenetetramine (HMTA), and ethylene diamine (EDA), and air-irradiated with low-pressure Mercury Vapor Lamp for various time durations. Photo yellowing has been determined by classical colorimetry and degradation processes and products have also been identified by diffuse reflectance spectroscopy (FTIR and UV-visible). Degradation processes have been compared with those obtained in the same materials by thermal processes. Cellulose treated with EDA and PEI shows intense photo yellowing, which is dependent on the pH of the treatment solution. Color alterations in these materials are well correlated to the presence the imine groups and disappearance of the amino groups, ascertained by FTIR determinations. HMTA-treated cellulose, however, undergoing intense thermal yellowing, shows only insignificant photo jaunting. These results were attributed to the presence of colored Schiff bases produced upon condensation between the amino and carbonyl groups.

Table 4 here

4. Conclusions

The surface of cellulose acetate (CA) fibers was successfully modified by polymer coating using branched polyethylenimine (bPEI). XPS was used to quantify the amine functions grafted on the surface of the CA fibers. The optimum coating conditions, were studied and it turns out that, under the experimental conditions applied in this work, the amount of bPEI

adsorbed on the CA fibers surface is: (i) Not affected by the coating time and bPEI concentration; (ii) Slightly affected by bPEI molecular weight and bPEI solvent; and (iii) Highly affected by the Ar plasma treatment either before or after bPEI coating.

The presence of amine functions on the surface of the CA fibers was also confirmed by studying the surface morphology before and after bPEI treatment on CA fibers, using EPMA (Electron Probe Micro-Analyzer) coupled with X-ray mapping in both H₂O and EtOH as solvents. The X-ray mapping profiles clearly show the presence of Nitrogen on the fibers' surface, which indicates the presence of amine functions but less in case of EtOH. These profiles are in good agreement with the XPS results. The fiber surface morphology results obtained from FEG-SEM (field emission gun scanning electron microscopy) analyses show that the CA tow maintains its original structure, and no gluing layer was observed between the fibers, and indicates that the negative effect of the Ar plasma on the density of the amine functions probably due to etching. Solid-state ¹³C NMR analyses confirm that aldehyde compounds in the gas phase can be adsorbed onto bPEI-coated fibers. The adsorption process is a chemisorption and the hemiaminal form is the stable amine resulted from the reaction between the formaldehyde and the amine functions on the surface of the CA fibers.

Finally, the shelf-life tests carried out on bPEI-coated CA tow shows that the coating is stable over the 60 days of storage. However, plasma-treated CA tow samples show that the density of the amine functions on the CA fibers was almost stable during the first 25 days of storage, and after 60 days, the degradation became more significant especially when the plasma treatment was performed after bPEI coating.

The evaluation of the bPEI-coated CA tow as a cigarette filter for the reduction of aldehyde compounds and HCN from the cigarette smoke was carried out at British American Tobacco (BAT), Southampton, UK. The results are BAT's intellectual property and will be published in a forthcoming paper.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Author Statement

KB performed the majority of the experiments and of the spectra recording. CJ conducted the plasma experiments. YL initiated the experiments and planning their execution an. CR supervised the organic chemistry experiments. AM designed the experiments and performed the interpretation of raw data. AM, YL, CR wrote, edited and revised the manuscript. All authors read and approved the manuscript.

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.

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Figures and captions

Figure Captions

Fig. 1. XPS survey of (a) untreated CA fibers, (b) coated with 5% of bPEI (c) coated with 20% of bPEI in water solution during 5 minutes of treatment.

Fig. 2. SEM micrographs of untreated and treated cellulose acetate fibers: (a) Dried native CA tow, (b) bPEI (Mw 1200) coated CA tow in H₂O, t = 5min; (c) bPEI (Mw 1200) coated CA tow in Absolute EtOH, t = 5 min

Fig. 3. EPMA X-ray mappings of Nitrogen in untreated and treated CA tow samples: (a) Untreated CA tow, (b) bPEI (Mw 1200, 5% in H₂O) coated CA tow, (c) bPEI (Mw 1200, 5% in EtOH) coated CA tow. Corresponding profiles are included.

Fig. 4. SEM micrographs of native and treated CA fibers: (a) Native CA, (b) bPEI coated CA tow, (c) bPEI coated CA tow followed by Ar plasma treatment. bPEI (Mw 1200, 5% in H₂O)

Fig. 5. CP-MAS ¹³C NMR spectra for (a) Native CA tow; (b) bPEI coated CA tow; (c) bPEI coated CA tow after exposure to gaseous ¹³C-formaldehyde.

Scheme1. Reaction Scheme between an Aldehyde and an Amine during Aldehyde Adsorption according to reference [73]

Tables

Table 1

Effects of coating duration and bPEI concentration on the adsorption of bPEI on the CA fibers. Mass increase and element concentrations determined by XPS on the surface of the different CA tows coated with branched bPEI (M_w 1200) in H₂O.

Table 2

Effect of bPEI molecular weight on the adsorption of bPEI on the CA fibers. Mass increase and element Concentrations determined by XPS on the surface of the different CA tows coated with branched PET of different molecular weights. Coating time: 5 minutes and polymer solution in water.

Table 3

Effect of plasma treatment on the coating of CA fibers with bPEI. Mass variation and Element concentrations determined by XPS on the surface layer of the different CA tow samples.

Table 4

Element concentration of C, O and N determined by XPS on the surface layer of the different treated CA tows at different time intervals.

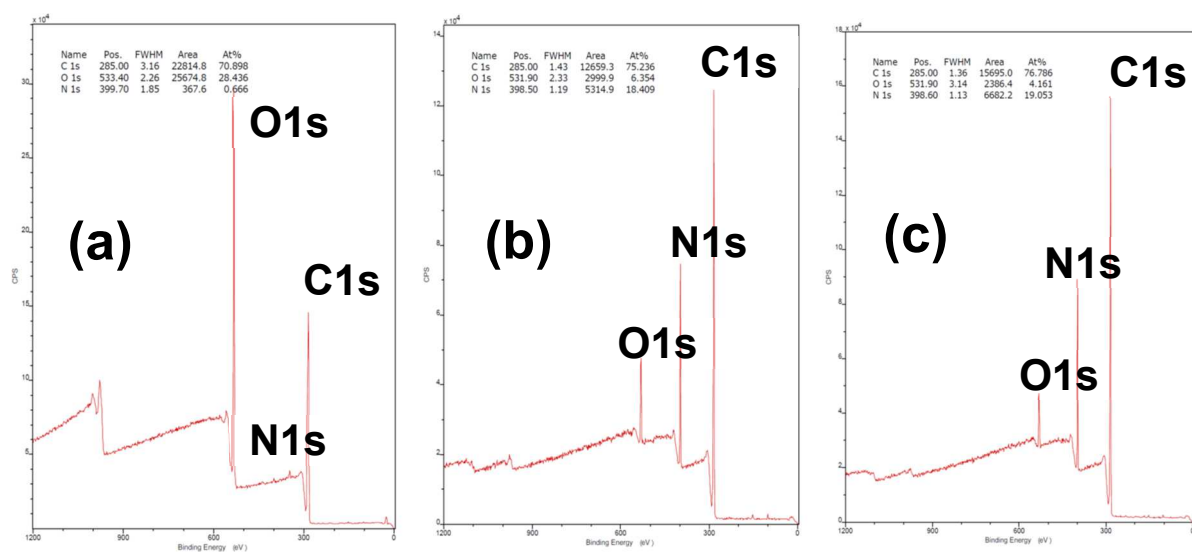


Figure 1.

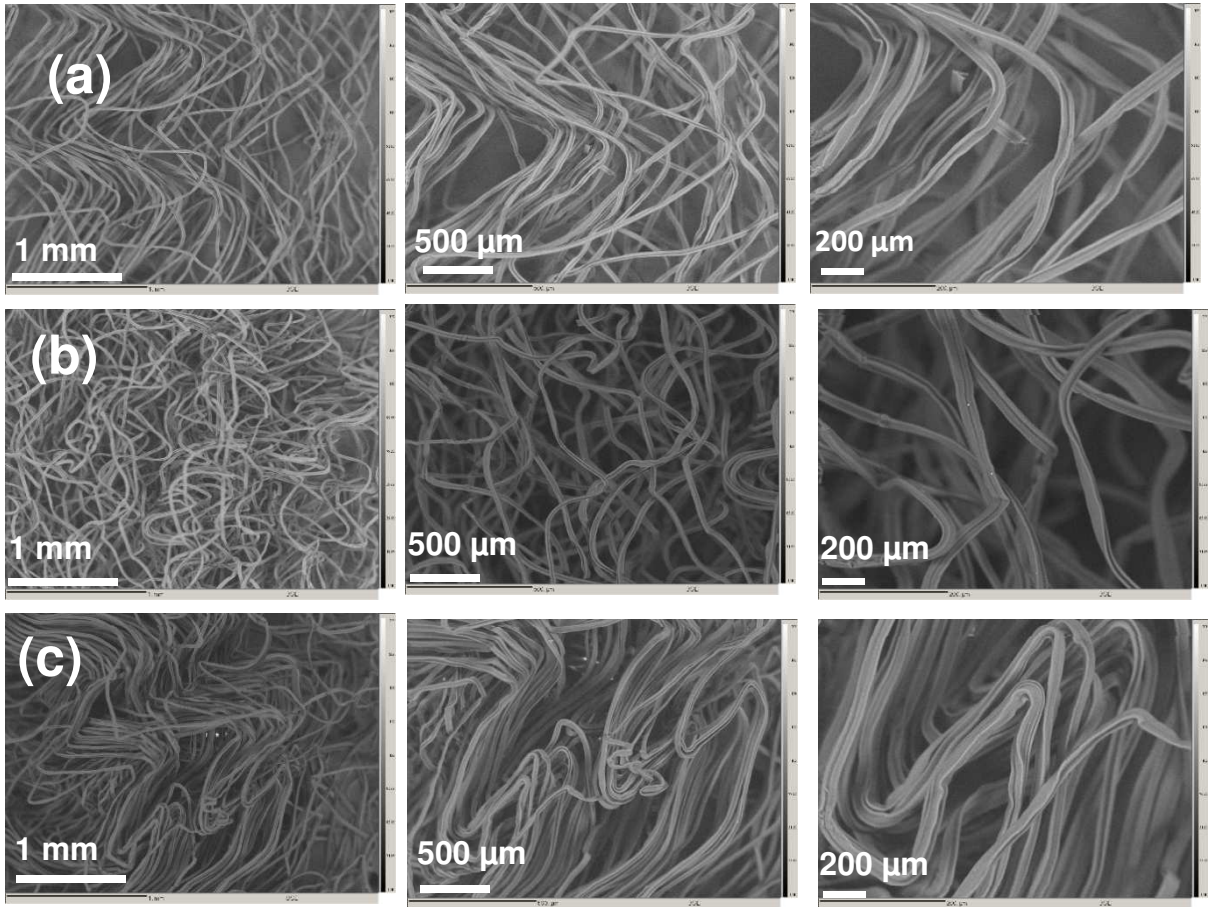


Figure 2.

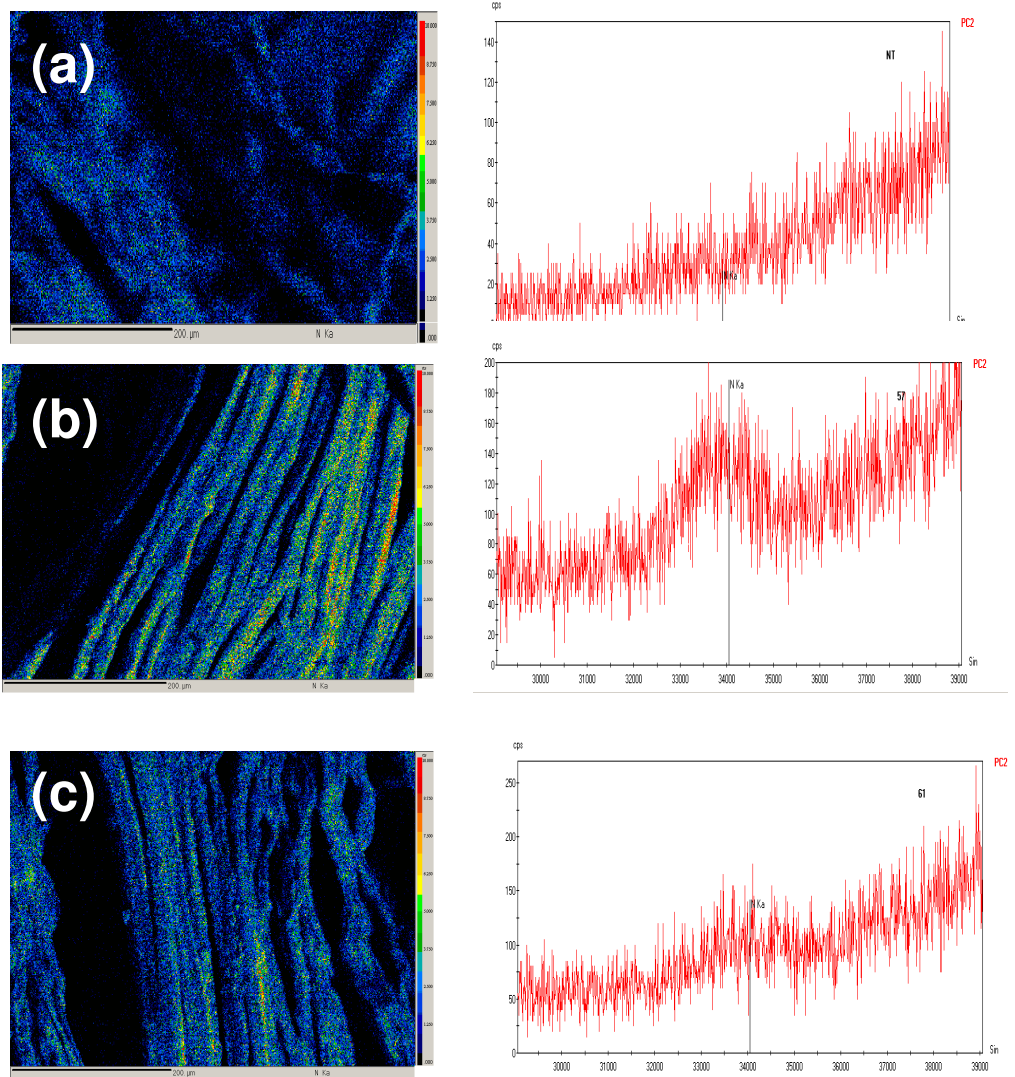


Figure 3.

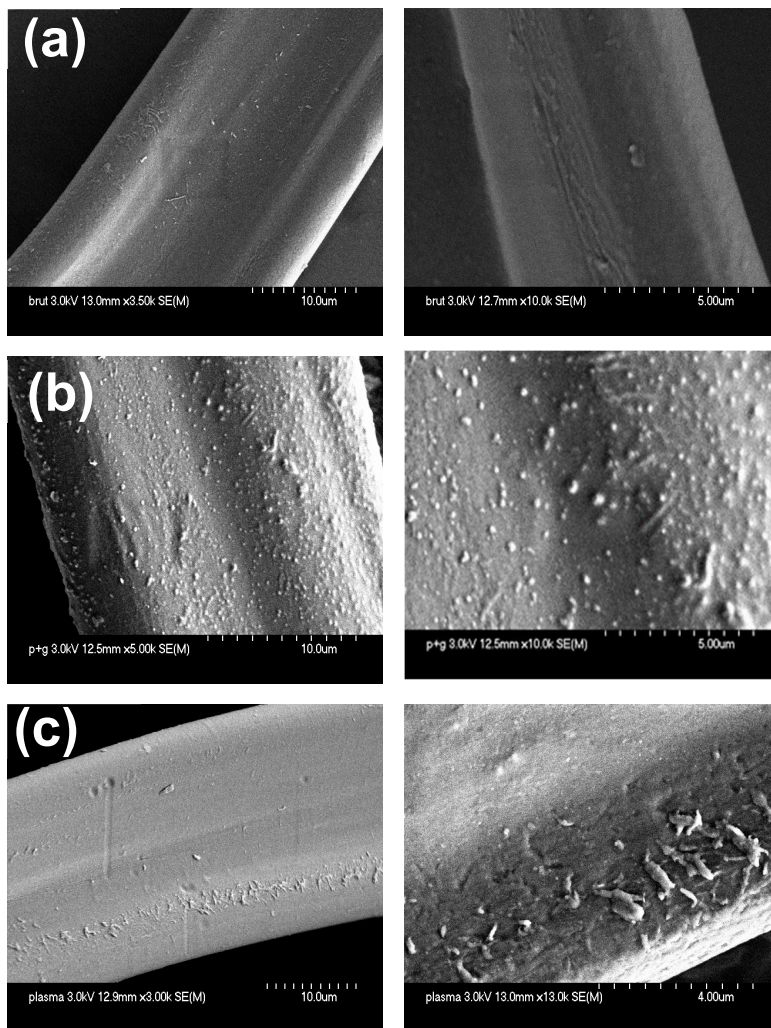


Figure 4.

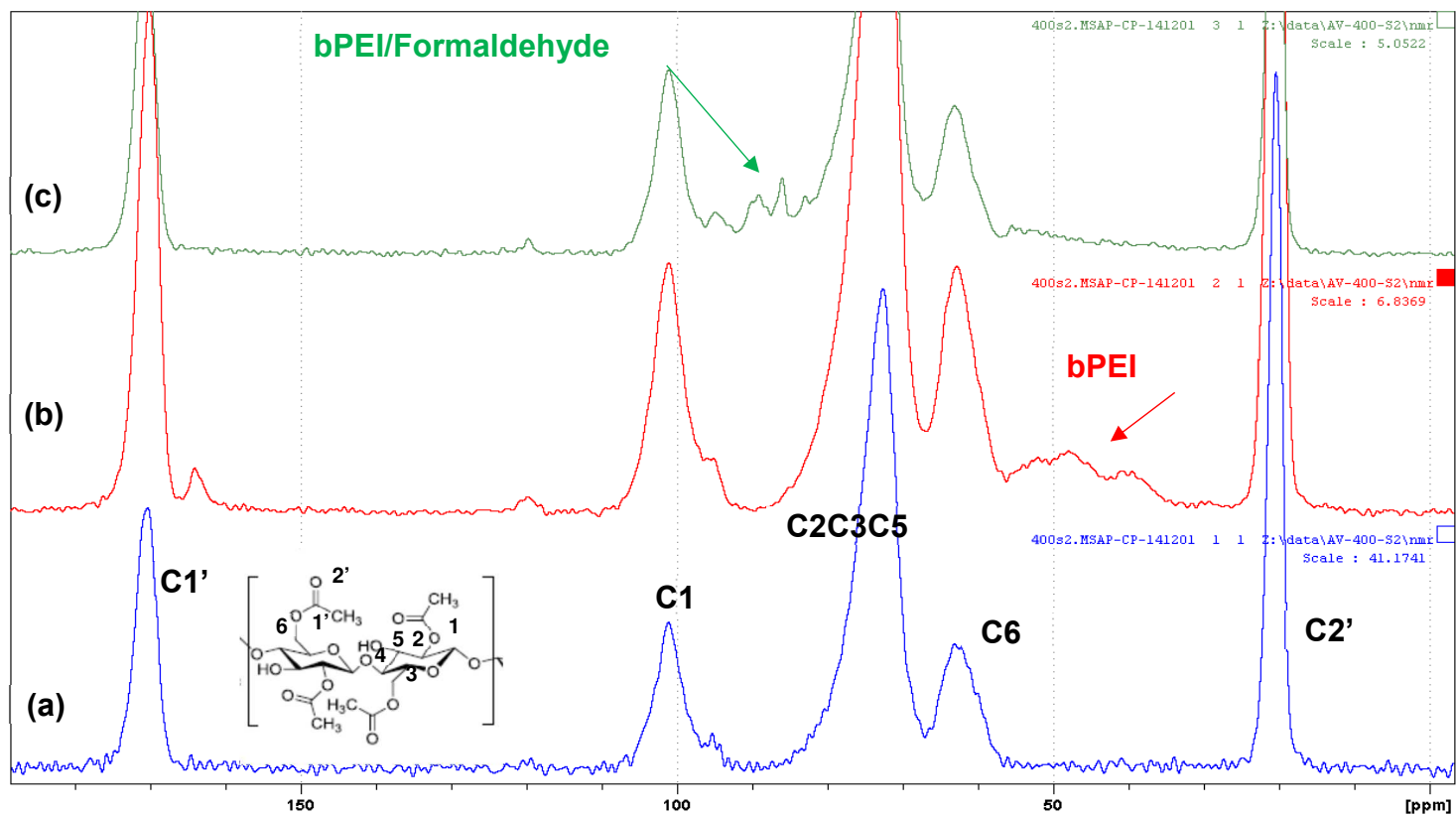
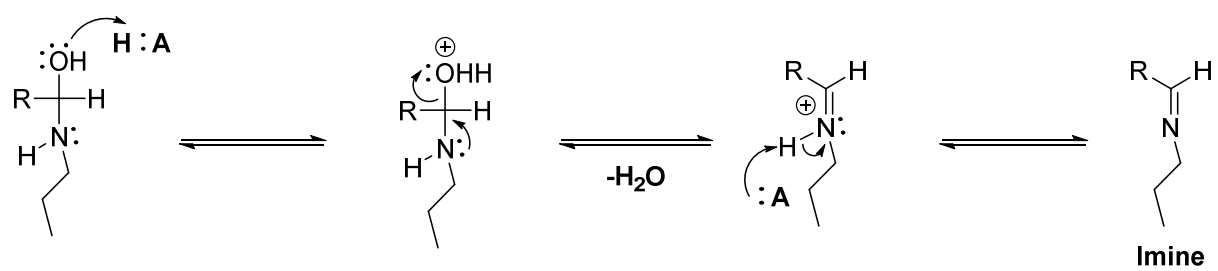
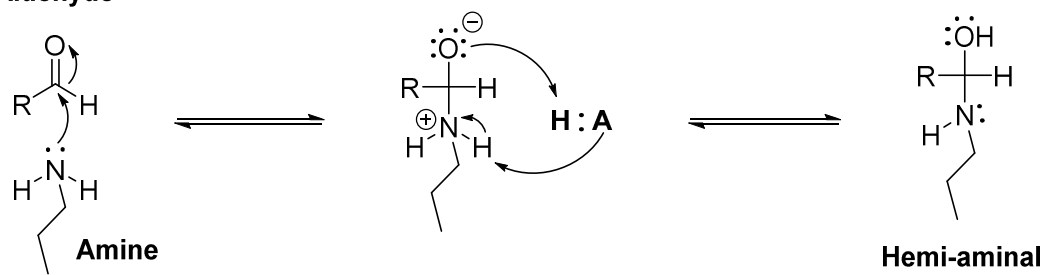


Figure 5.

Aldehyde



Scheme1.

Table 1

Effects of coating duration and bPEI concentration on the adsorption of bPEI on the CA fibers. Mass increase and element concentrations determined by XPS on the surface of the different CA tows coated with branched bPEI (M_w 1200) in H₂O.

Samples	Coating time (min)	bPEI concentration (w/w)%	Mass increase (%)	Element composition (Atomic %)			Atomic ratios		
				C(1s) 285 eV	O(1s) 533 eV	N(1s) 400 eV	O/C ratio	N/C ratio	N/O ratio
Native CA				70.9	28.4	0.66	0.4	0.01	0.03
a	2	5	5.2	75.6	5.2	19.2	0.07	0.25	3.57
b	5	5	5.3	75.2	6.3	18.4	0.08	0.24	3.00
c	30	5	5.4	76.3	4.6	19.1	0.06	0.25	4.17
d	60	5	5.2	78.1	4.0	17.9	0.05	0.23	4.60
e	5	10	5.3	75.7	5.8	18.6	0.07	0.25	3.57
f	5	20	5.5	76.8	4.2	19.1	0.05	0.25	5.00
g*	5	5	5.4	71.3	14.1	14.6	0.20	0.20	1.00

* EtOH as solvent

Table 2

Effect of bPEI molecular weight on the adsorption of bPEI on the CA fibers. Mass increase and element concentrations determined by XPS on the surface of the different CA tows coated with branched bPEI of different molecular weights. Coating time: 5 minutes and polymer solution in water.

Samples	bPEI Mw (g/mol)	Mass increase (%)	Element composition (Atomic %)			O/C ratio	N/C ratio	N/ O ratio
			C(1s) 285 eV	O(1s) 533 eV	N(1s) 400 eV			
a	800	5.2	73.9	10.9	15.5	0.15	0.21	1.40
b	1200	5.4	75.2	6.3	18.4	0.08	0.24	3.00

Table 3

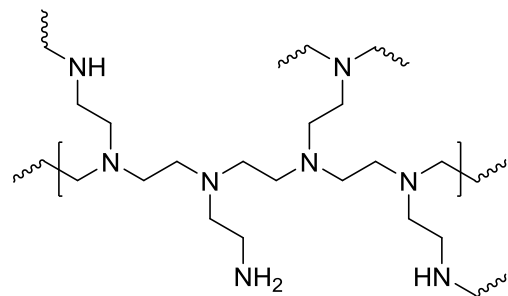
Effect of plasma treatment on the coating of CA fibers with bPEI. Mass variation and Element concentrations determined by the XPS on the surface layer of the different CA tow samples.

Treatment	Mass variation (%)	Element composition (Atomic %)			Atomic ratios		
		C(1s) 285 eV	O(1s) 533 eV	N(1S) 400 eV	O/C ratio	N/C ratio	N/O ratio
None	0.0	75.9	23.3		0.31	0.00	0.00
Ar plasma	-0.2	74.7	25.3		0.33	0.00-	0.00
bPEI coating	+5.3	76.3	4.6	19.1	0.05	0.25	5.00
bPEI Coating/Ar plasma	+3.8	75.2	13.5	11.3	0.18	0.15	0.83
Ar plasma/bPEI coating	+3.2	78.7	13.6	7.8	0.17	0.11	0.65

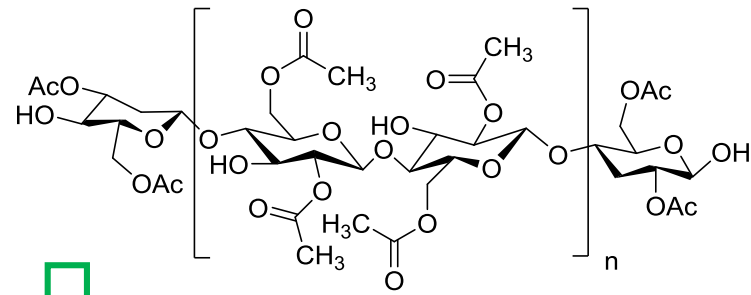
Table 4

Element concentration of C, O and N determined by the XPS in the surface layer of the different treated CA tows at different time intervals.

Samples	Post treatment time (days)	Element composition (Atomic %)			Atomic ratio		
		C(1s)	O(1s)	N(1S)	O/C ratio	N/C ratio	N/O ratio
		285 eV	533 eV	400 eV			
CA/bPEI coating	0	76.3	4.6	19.0	0.06	0.25	4.17
	25	75.4	4.8	18.5	0.06	0.25	4.17
	60	75.2	5.1	17.8	0.07	0.24	3.43
CA/bPEI coating/Ar plasma	0	74,3	8.6	11,2	0.11	0.15	1.36
	25	78.1	9.3	10.6	0.12	0.14	1.17
	60	77.1	10.9	9.0	0.14	0.12	0.86
CA/Ar plasma/bPEI coating	0	78.7	13,6	7.8	0.17	0.10	0.59
	25	79.0	14.1	7.4	0.18	0.09	0.50
	60	81.9	15.7	6.8	0.19	0.08	0.42



20% branched PEI in H₂O or EtOH



Cellulose Acetate

