

Article

Enhancing Flame Resistance of Cellulosic Fibers Using an Ecofriendly Coating

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Abstract: Among the various advanced materials, flame-retardant cellulosic textiles are important as they directly relate to human health and hazards. The use of environmentally friendly flame-retardant coatings is currently one of the major concerns in the textile coating industry. In this work, acrylic acid was grafted onto the surface of cotton using plasma technology to enhance the attachment of acrylate phosphate monomer. Surface analyses, such as scanning electron microscopy (SEM), energy dispersive x-ray (EDX) and attenuated total reflectance Fourier-transform infrared (ATR-FTIR), were carried out to characterize the coating. Textile properties such as wettability and mechanical properties of untreated and treated cotton samples were investigated. A laundering test was also performed to predict the durability of the finishing. The outcomes revealed that acrylic acid-grafted samples treated with acrylate phosphate monomer have good flame-retardant properties.

Keywords: cellulosic; fiber; flame retardant; ecofriendly; cotton; coating



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1. Introduction

Cotton is a natural fiber in which cellulose represents the major component of its chemical structure.

Nowadays, cotton fabrics are widely used in our daily lives due to their remarkable combination of properties: soft to the touch, good moisture vapor transmission and good moisture absorbency [1]. However, being organic in nature, cotton fabrics and other cellulose-based fabrics pose considerable fire risks [2]. Therefore, the flame-retardant finishing of cotton fabrics is important as it is strongly related to the protection of human beings and textile substrates from fire hazards.

In this context, the assessment of the flammability of cotton substrates has been approached by applying suitable flame-retardant finishes that are able to suppress or delay the appearance of a flame or reduce the flame-spread rate [3]. These finishes are applied to textiles by using a variety of agents, including borax and boric acid mixture, nitrogen- and phosphorus-based chemicals, antimony and halogen based chemicals [4].

Coating technology is regarded as the most practical method to impart functional agents to textile substrates [5]. Based on the chemicals used in the coating formulations and also on the desired performance of the coated surfaces, various types of coating techniques are used in textile functionalization, the main types including pad coating, direct or knife coating, sol gel coating, digital coating, electrospinning coating and combined coating [6].

The current textile coating market is dominated by the use of binding agents or binders to fix the chemicals forming the coating layer, which have no affinity for fibers [7].

Numerous chemicals are used as binders. However, in most of them, formaldehyde is used as a crosslinker to apply the resistant coatings that are required by many advanced applications [8]. Formaldehyde is a toxic and carcinogenic chemical that has come under survey [9,10]. In addition, binders can contain solvents that are used as carriers during the manufacturing process. These solvents end up in the environment through waste water and air [11–13]. The major challenge facing textile manufacturers developing coated

textiles is how to rapidly switch to safer chemicals and processes. Recent research on functional coatings on textiles has focused on the use of environmentally friendly technologies and chemicals [6]. In this context, plasma technology was reported as an ecofriendly coating technique.

Plasma is a partially ionized gas composed of various species, such as electrons, negative and positive ions, radicals, excited molecules, neutrals, and UV photons. These different species are useful for textile surface modification. The plasma gas reacts with a small non-polymerizing molecule to achieve surface activation, cleaning, oxidation, modification in surface energy, an increase in surface roughness and etching. Similarly, plasma reacts with a bigger molecule to achieve plasma polymerization, coating, deposition, and creation of nanostructures [14]. These altogether improve the functional value of the textile materials. For fire-retardant coatings, plasma is applied either as a pretreatment, to increase the uptake of flame-retardant chemicals; for graft polymerization of these chemicals; or as a post-treatment to form strong bindings [4]. This technology also has other advantages, such as leaving the characteristics of the textile bulk unaffected, working in the gas phase without the need for water use, reducing processing time and achieving energy saving [15].

The aim of this study was to combine plasma pretreatment and acrylic acid grafting on cotton fabric to enhance the attachment of acrylate phosphate in order to obtain fire-retardant cotton fabric. The acrylic acid finish on cotton highlights a formaldehyde-free route for achieving surface modification of cotton, with high scope for incorporation of much improved physical and mechanical properties [16]. The combination of physical and chemical surface treatments was expected to enhance cellulosic fibers functionality and to contribute to a green and safe production process and end product.

2. Materials and Methods

2.1. Materials

Twill weave cotton fabric with the following specifications was procured commercially: the weight was 280 g m^{-2} and the density was 20 ends cm^{-1} in the warp direction and 14 picks cm^{-1} in the weft direction. The fabric was additionally treated with sodium hydroxide to remove hydrophobic compounds from the fiber surfaces. Analytical grade chemicals purchased from Sigma Aldrich were used for all experiments without further purification: Bis [2-(methacryloyloxy) ethyl] phosphate, molecular weight of 322.25 g/mol, and acrylic acid, molecular weight of 102.13 g/mol. Non-ionic low-sudsing detergent was kindly provided by S2C Company.

2.2. Methods

2.2.1. Plasma Treatment

The cotton samples were treated using an atmospheric pressure plasma jet technology system from Plasmatreat Company (Plasmatreater AS400, Steinhagen, Germany) for surface activation at atmospheric pressure. A high-frequency (23 kHz) pulsed voltage was applied between two tubular electrodes separated by a dielectric material. The PT400 generator delivered a pulse-pause modulated current. The current modulation was controlled by adjusting the plasma cycle time (PCT). With a PCT of 100%, the pulse duration was equal to the pause duration. The main gas flow consisted of dry air, which was introduced through the torch at a pressure of 5 Bar. The torch could be moved in the x- and y-directions to activate surfaces or to deposit films over large surfaces, with a typical velocity and substrate-to-nozzle distance of 5 m/min and 40 mm, respectively. These parameters were fixed after many treatments with various experimental conditions. PCT, frequency and dry air pressure were kept fixed at the standard conditions recommended by the machine constructor to guarantee the long life of the plasma generator. We focused on the variation of the torch velocity as well as the distance between the nozzle and the substrate. For cotton material, when this distance was less than 40 mm, the plasma air blown from the nozzle at 5 bar touched the substrate and induced some burned areas with a brown color.

The optimal torch velocity at a “nozzle/substrate” distance of 40 mm was 5 m/min. For higher velocities, the wettability was not significantly improved and for lower velocities, we encountered the problem of burned areas due to high exposure time to the plasma.

When applied to cellulosic fibers, plasma treatment induces the formation of free radicals on the fibers (Figure 1). These active entities act as initiator agents for chemical reactions that otherwise would not occur on a non-treated fiber.

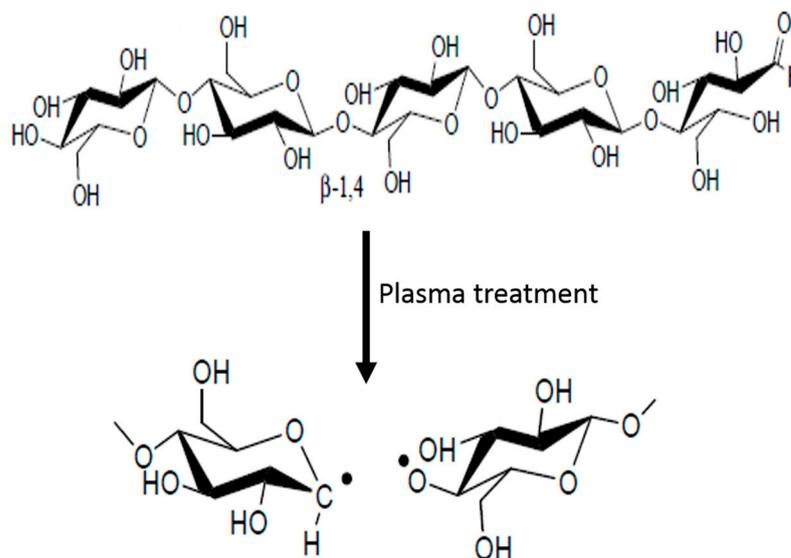


Figure 1. Formation of free carbon and oxygen radicals after cotton plasma treatment.

The literature indicates that the formation of free radicals occurs through ionization or excitation of the cellulosic polymer through electrostatic interaction between the orbital electrons in the polymer and fast-moving electrons induced by plasma. The ionization leads to molecular fragmentation and the formation of free radicals, while excitation leads to dissociation of the polymer to form free radicals [17].

2.2.2. Grafted Polymerization

The samples exposed to air plasma treatment were dipped in acrylic acid aqueous solution (0.5 M) for 4 h at 80 °C. Next, the grafted cotton fabrics were taken out of the solution and washed with 95% ethanol to remove polyacrylic acid homopolymer.

The monomer solution was applied at pH = 7. Under the neutral condition, we achieved optimum monomer grafting and esterification and retained 80% of the initial fabric tenacity [16]. Cellulosic materials degrade upon hydrolysis of glucoside bonds in highly acidic conditions, since the cellulosic chain length (DP) decreases.

2.2.3. Phosphorus Monomer Immobilization Assay

Phosphorus monomer immobilization was performed in an aqueous, heterogeneous mixture with cotton fabrics grafted with polyacrylic acid and monomer (50%) (*w/w*) for 5 min at ambient temperature. Then, a plasma treatment was performed to enable the activation mechanism of the radicals and thus the grafting of the monomer. In addition, the crosslinking and polymerization of the monomer were enabled.

2.3. Characterization and Measurements

2.3.1. Scanning Electron Microscopy

A scanning electron microscope (Model HITACHI TM 3000) was used for morphological characterization of the cotton fiber surface at high magnification. The metallized specimens were analyzed in partial vacuum conditions (0.1–0.15 torr) and under an accelerating voltage of 10 or 15 KV. Scanning electron microscopy with energy dispersive x-ray

(SEM-EDX) analyses were performed to determine the elementary chemical composition or to present the cartography of the distribution of the elements in the form of an image. To increase the SEM image quality, the conductivity of the samples was improved with a nanometric gold film coating. For each treatment, two different samples were used. For each sample, SEM graphs were produced for different areas.

2.3.2. Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy was used to monitor the chemical composition of the surfaces. FTIR spectra were recorded using a commercial ATR-FTIR attachment (Spectrum Two™ FTIR, Perkin Elmer, Waltham, MA, USA). Spectra were recorded between 4000 and 400 cm^{-1} .

2.3.3. Water Contact Angle

The wettability of untreated and treated surfaces was measured using a DSA25 Drop Shape Analyzer. A droplet of 2 μL of ultrapure water was placed on the fabric. The results shown for each sample are the averages of three measurements.

2.3.4. Mechanical Properties

Tensile tests were carried out according to NF EN ISO 13934-2 standards using a Lloyd tensile testing machine (Lloyd LR 5k, Lloyd Instruments Ltd., Largo, FL, USA) at an extension speed of 50 mm/min with 5 kN load cell. Test specimens had dimensions of 75 mm in gauge length with a thickness of 1 mm. Tests were conducted at the warp direction of the fabric and run in triplicate to reduce experimental error. The samples were conditioned before testing.

2.3.5. Flame Retardant Test

The flammability test in vertical configuration was carried out by applying a methane flame for 10 s at the bottom of a fabric specimen (10 cm \times 9 cm). The test was repeated twice for each sample to evaluate burning behavior: time, rate and the final residue. Vertical flammability tests were repeated twice. Photographs showing fabric behaviors were taken and subsequently analyzed with ImageJ software to quantitatively assess the fabric flammability. ImageJ provides a filtered binary image of the targeted area, adjusted near the edges of the sample, and calculates its total area in terms of the number of pixels. The threshold levels were adjusted so that the burned area appeared white in the processed image. ImageJ measures the total surface in all black colored areas in pixels. Therefore, the percentage of the burned area was calculated as the ratio of the total targeted area and the white colored areas.

2.3.6. Evaluation of Laundering Durability

The permanence of flame-retardant treatment after washing was investigated by subjecting flame-retardant fabric to a washing cycle. The treated cotton fabric was washed in Autowash, using the ISO 105-C06 standard method. Laundering involved a washing temperature of 40 $^{\circ}\text{C}$ for 30 min with 150 mL of water containing 0.6 g of non-ionic detergent. Samples were then dried for 10 min at 70 $^{\circ}\text{C}$ [18].

3. Results and Discussion

3.1. Morphological Structure

Figure 2 shows the scanning electron microscopy images for crude cotton as well as samples treated with acrylic acid before and after plasma activation. At 1000 \times magnification, the crude cotton showed a smooth surface with some visible macrofibrils oriented predominantly in the direction of the fiber axis. The surface of the plasma-treated cotton showed a striped and more distinct macrofibrillar structure.

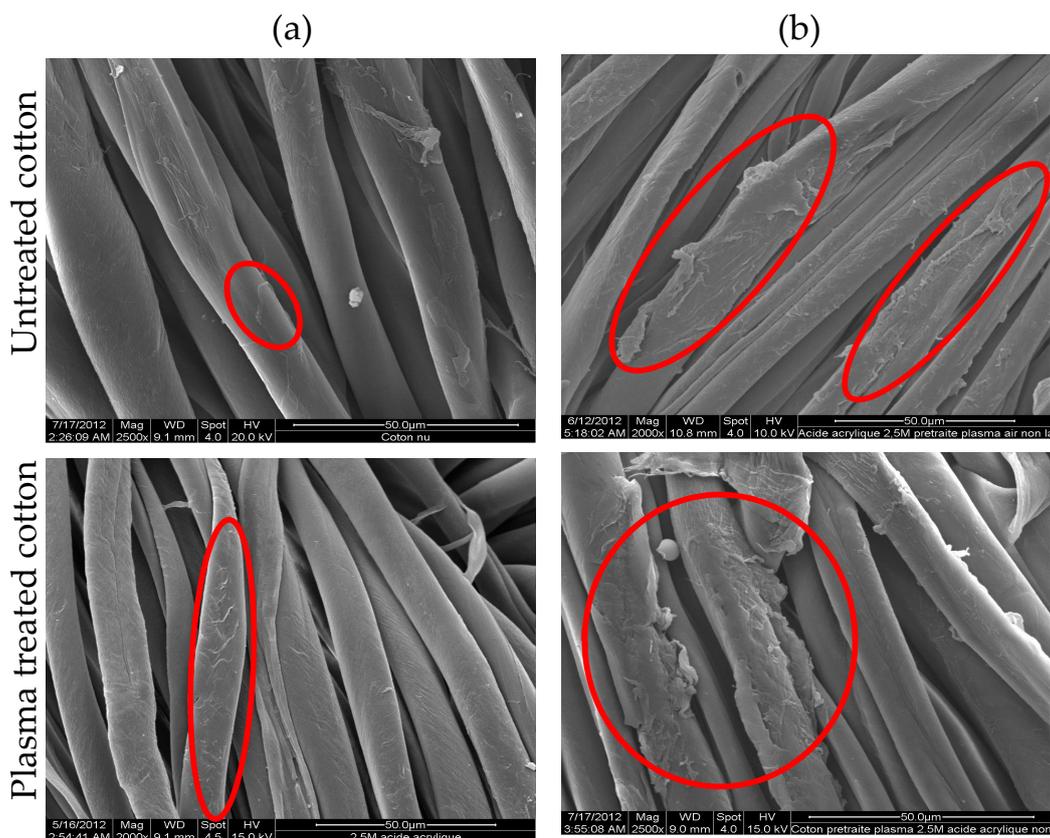


Figure 2. Surface morphology of crude and plasma-treated cotton fabrics (a) before acrylic acid deposition and (b) after acrylic acid deposition.

After treatment with acrylic acid, the plasma-treated fibers clearly showed significant presences of entities on their surfaces which totally covered the fibrillary structure. These results corroborate with those previously presented by Garcia-Torres et al. [19] and prove that the plasma activation was able to graft more acrylic acid onto cotton fibers.

Following phosphorus monomer immobilization (Figure 3a), the fibers clearly showed a grafted coating on their surfaces. A uniform layer appeared on the fibers and in the gaps between individual fibers linking them together. Plasma graft polymerization is an ecological technique capable of simultaneously grafting and polymerizing the monomer onto cotton fabric, forming a polymer layer covalently bonded to the fibers [20].

EDX characterization results show the composition of cellulosic fibers. As shown in Figure 3a, the main constituent elements of flame-retardant fibers were C, O and P elements, indicating that the phosphorus monomer existed on the surface of the treated cotton fabric. The content of the P element was about 4%.

3.2. ATR-FTIR Results

Characterization ATR-FTIR spectra of the cotton surface before and after plasma graft polymerization and monomer immobilization are presented in Figure 4. Spectra of all samples showed characteristic peaks of cellulose. The broad peak at 3291 cm^{-1} was attributed to hydroxyl groups (OH) stretching absorption. The broad stretching vibration of C-H was centered at 2906 cm^{-1} , while C-H bending vibrations were detected at 1434 , 1373 and 1319 cm^{-1} , asymmetric stretching of C-O-C appeared at 1162 cm^{-1} and the vibration involving the C-O stretching appeared at 1058 cm^{-1} and 1027 cm^{-1} [21]. The spectra of surfaces before monomer immobilization did not show a remarkable difference when compared to the untreated sample except for acrylic acid grafting where a new peak appeared at 1715 cm^{-1} (Figure 4b). This peak was attributed to the C=O adsorption band. It indicates that a successfully induced grafting polymerization of acrylic acid was

achieved by plasma activation [22]. The ATR-FTIR was also used to observe the changes of the chemical structure of the cotton fabric after monomer immobilization according to methacrylate functionality and phosphorus content. The FTIR spectrum is shown in Figure 4c. The phosphate structure of the monomer was observed at 1250 cm^{-1} and the bands of both 1029 cm^{-1} and 987 cm^{-1} , which were assigned to stretching vibrations of P=O and P-O-C, respectively, were also observed. The photoreactive methacrylate groups at 1716 , 1166 and 1052 cm^{-1} , corresponding to the vibrations of C=O, C-C-O, and O-C-C, respectively [23], were also detected.

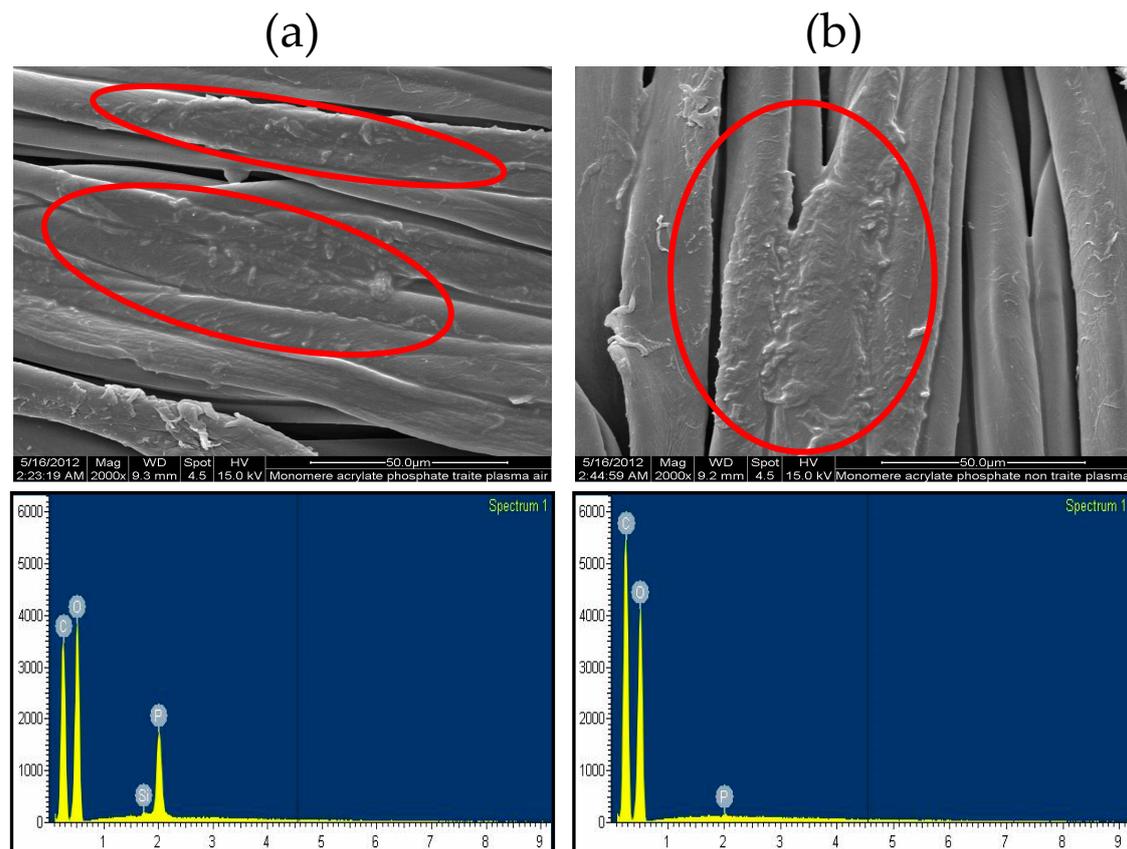


Figure 3. Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) images of flame-retardant cellulosic fibers: (a) before washing and (b) after washing.

3.3. Assessment of the Surface Wettability

The wettability of the cellulose textiles measured as the water contact angle (Figure 5) indicated the hydrophilic behavior of the untreated cotton (UC) and the cotton treated with plasma and acrylic acid (PCA). A contact angle value of 132° indicated the hydrophobic nature of the flame-retardant treatment (flame-retardant coating (FRC)).

The hydrophilicity of the cotton treated with acrylic acid (PCA) was improved. Similar behavior of cellulose surface wettability was reported by Garcia-Torres et al. [19]. Acrylic acid improves the hydrophilicity of cellulosic fibers owing to its high volatility, solubility in water and its bearing of a high ratio of a carboxyl polar group [24].

Side effects associated with the flame-retardant treatment include reduced fabric strength, poorer fabric handle and declined water absorbency. Some of these side effects may be overcome by the use of softeners and wetting agents during the post-treatment process of fabrics [25].

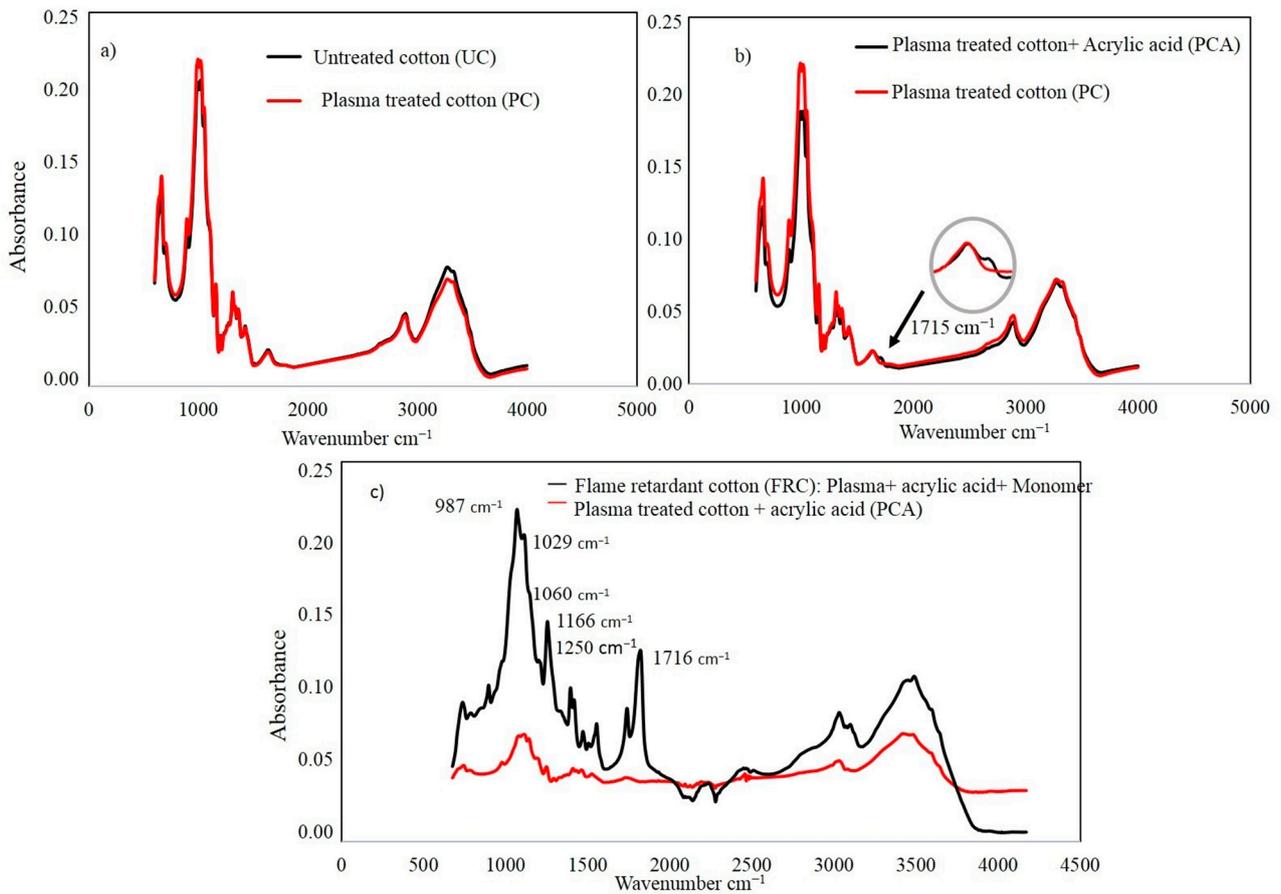


Figure 4. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of untreated and plasma-treated cotton (a) before grafting with acrylic acid, (b) after grafting with acrylic acid and (c) after monomer immobilization.

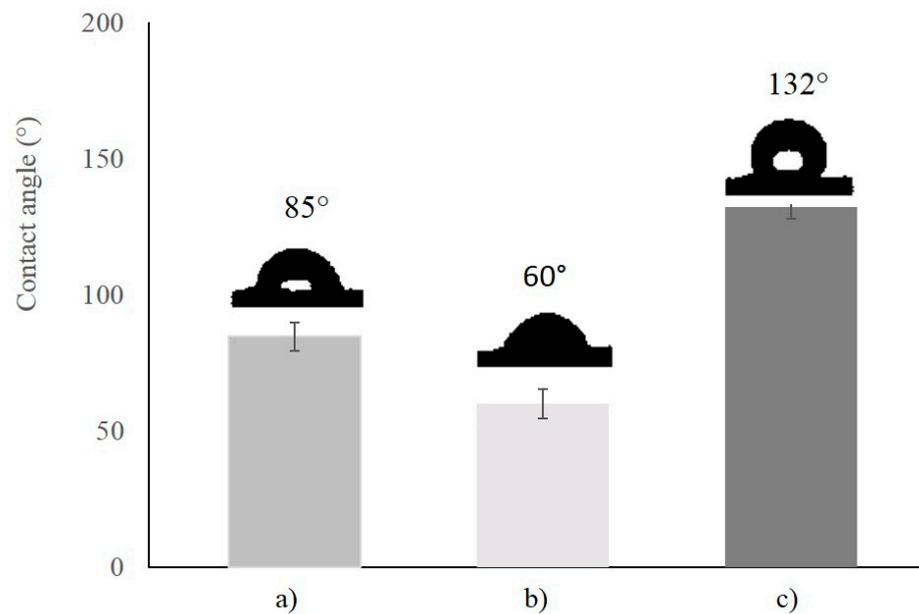


Figure 5. Water contact angles on the cotton surfaces: (a) untreated cotton, (b) plasma-treated cotton after grafting with acrylic acid and (c) treated cotton after immobilization of phosphorus monomer. The results shown are averages of three measurements and the error bar represents the standard deviation.

3.4. Mechanical Properties

It is important to examine the effect of flame-retardant treatment on the mechanical properties of the textiles since they are essential for the material overall function. Tensile strength is one of the most relevant textile mechanical properties. For this reason, tensile strength performance was evaluated after the finishing processes. Figure 6 shows the load–extension curves of untreated and flame-retardant cotton. The tested fabrics failed at the middle of the sample, away from the grips. It can be seen from the curves that the resistance of treated cotton did not change remarkably after flame-retardant finishing. Treated cotton retained about 94% of its initial mechanical properties and the difference was in the error limits. It can be concluded that the coating only occurred on the surface and did not tackle the bulk of cellulosic fibers.

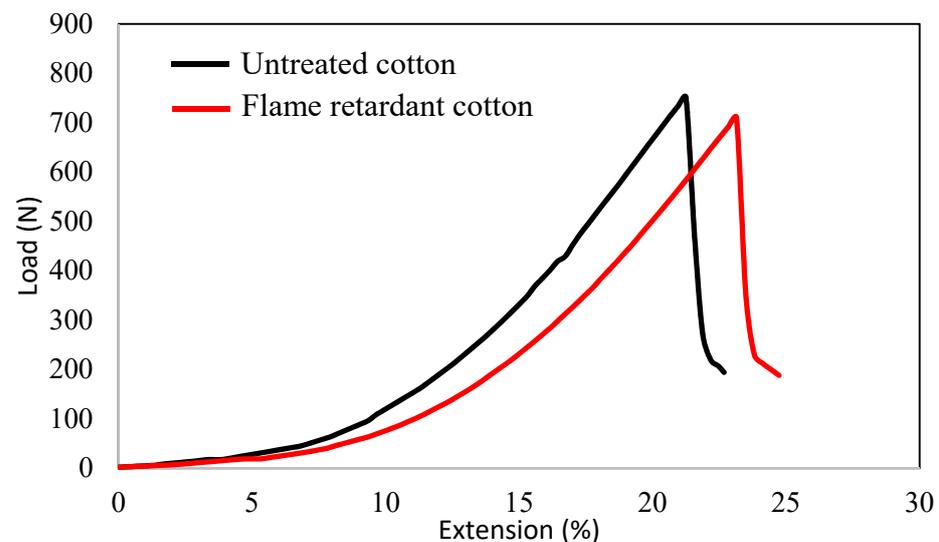


Figure 6. Load–extension curves of cotton fabrics.

For quantitative analyses, we defined two characteristic parameters extracted from the force vs. extension curves: elongation at break and maximum breaking strength (Table 1). The higher the maximum breaking strength value is, the higher the mechanical properties of the cotton fabric are. As shown in Table 1, the maximum breaking strength of untreated cotton was higher than that with the flame-retardant treatment. The difference between these two values was not significant, being lower than 1. The fabric elongation at break did not change remarkably after flame-retardant treatment and the difference between average values was within the error limits.

Table 1. Tensile characteristic parameters.

	Untreated Cotton	Flame-Retardant Cotton
Maximum breaking strength (N)	750 ± 6	710 ± 9
Elongation at break (%)	20 ± 4	23 ± 5

± Standard deviation.

3.5. Flammability

Figure 7 represents the vertical burning behavior of the control and the flame-retardant cotton samples at different intervals of time. It was found that, for the untreated cotton, after removing the ignition source, the flame quickly spread and ignited the whole fabric with no residue remaining. However, for the treated cotton, after removing the ignition source, the flame spreading was slowed down and the char length was less important.

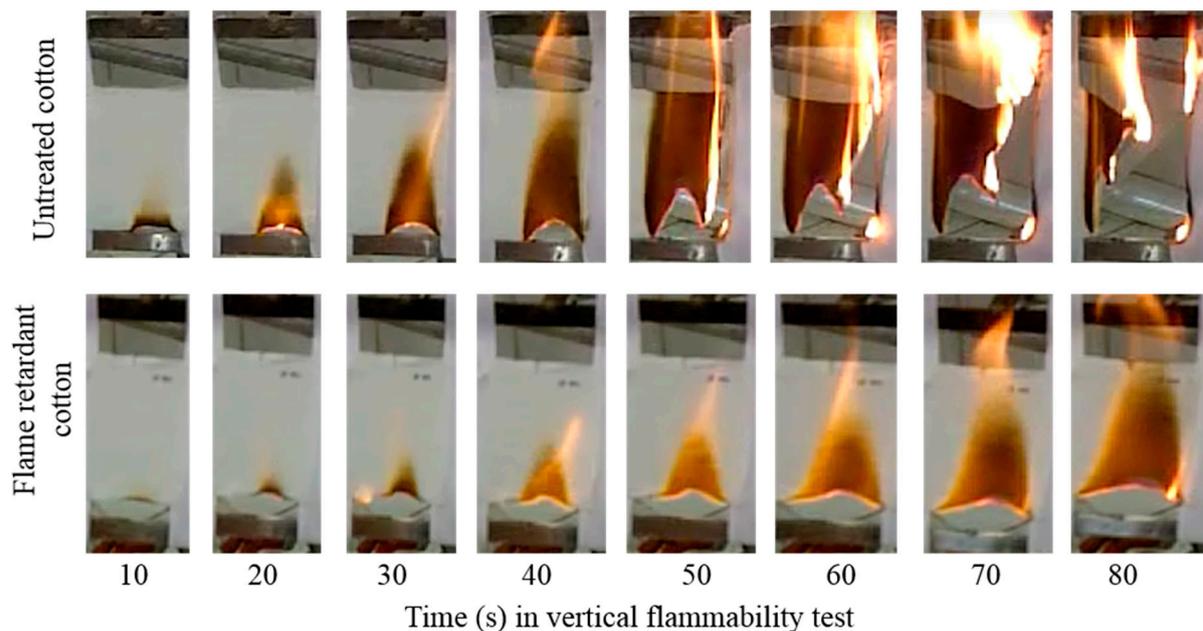


Figure 7. Flammability of untreated and flame-retardant cotton at different intervals of time.

Phosphorus-based chemicals exhibit both condensed phase and gas phase activities. They work in the condensed phase by raising char formation and depriving the gas phase of further volatile decomposition compounds. They also work in the gas phase as flame inhibitors, breaking the cycle of free radical generation [26].

Phosphorus-based chemicals are particularly effective in oxygen-containing polymers, such as cellulose. While heating in the presence of oxygen, the phosphorus decomposes into phosphonic and phosphoric acids which accelerate chain stripping processes and the removal of side groups that react with the phosphorus to become less flammable entities than in a phosphorus-free substrate [27].

It is important to note that, in a real-life situation, the user of the flame-retardant cellulosic material will get a longer time either to extinguish the fire or to escape from the fire zone. In addition, the user will find it easier to escape from fire hazards with slow flame spreading.

Figure 8, showing the output of the image analyzed by ImageJ software, clearly provides evidence of a significant flame-retardant effect on treated cotton fabrics compared to untreated ones. Indeed, the treated samples presented a burned surface of $2.4\% \pm 1.12\%$ after 10 s of exposing the textile to the fire and $44\% \pm 1.8\%$ after 80 s, whereas untreated samples presented a burned surface of $7\% \pm 0.8\%$ after 10 s and $70\% \pm 1.89\%$ after 80 s.

3.6. Laundering Durability

Figure 2b shows the flame-retardant cellulosic fibers after wash and it is obvious that the flame-retardant agent agglomerates are less homogeneous on the surface of the fibers. The content of the P element on the flame-retardant treated cotton fabric surface decreased (0.13%). Most of the product was washed off from the cotton surface.

The significant loss of the flame-retardant coating, resulting from one washing cycle, affected the flame-retardant properties of the washed samples. However, the flame resistance remained slightly better than that of untreated cotton. This is due to the protective non-homogeneous coating that resisted washing.

The obtained results clearly indicate that the coating exhibited low washing fastness.

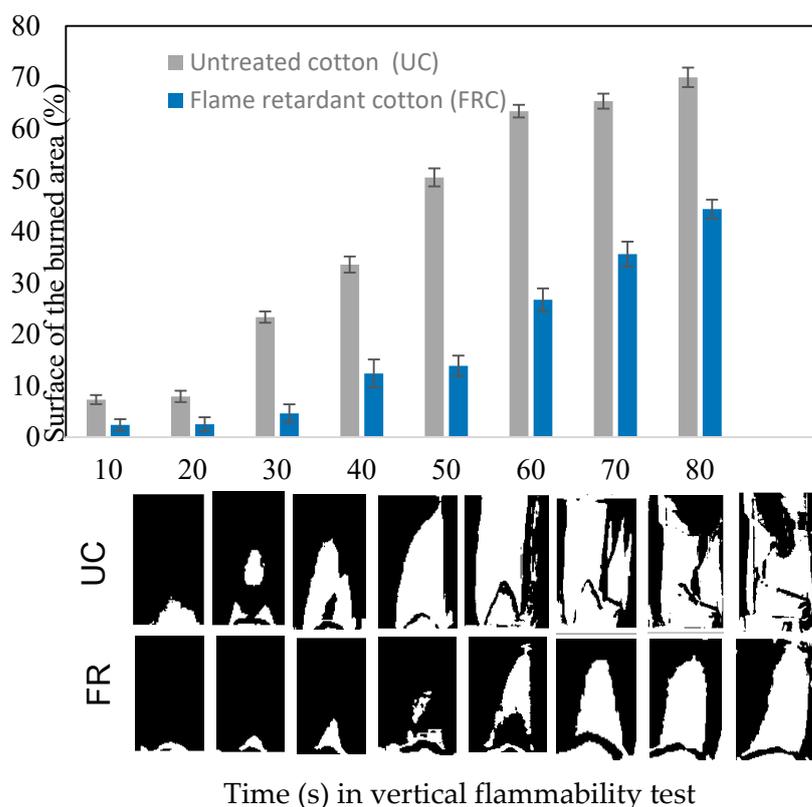


Figure 8. Vertical flammability of untreated cotton (UC) and flame-retardant cotton (FRC). Vertical flammability was quantified by calculating the average percentage \pm (standard deviation) of the surface burned area. ImageJ software was used to calculate the burned area (white area) as well as the total surface area.

4. Conclusions

The goal of the present work was to investigate an ecofriendly flame-retardant treatment for cellulosic fibers. An organic phosphorus monomer was immobilized onto cotton fabrics grafted with polyacrylic acid to improve tethering. Polyacrylic acid was first introduced onto the cellulosic fibers by plasma-induced grafting polymerization. FTIR, SEM, EDX, wettability and mechanical property analysis were conducted to characterize the coated fabric samples. The washing durability was also evaluated.

The important results of the study are summarized as follows:

- The coating showed significant flame-retardant properties compared to untreated fibers.
- The plasma treatment enhanced the graft polymerization of acrylic acid onto cellulosic fibers.
- The coating of cellulosic fabric appeared not to affect the mechanical behavior of the cotton.

Thus, plasma-treated cotton grafted with acrylic acid and linked with phosphorus monomer holds promising potential for firefighting applications. Further experimental investigations are, however, needed to improve the low washing fastness of the coated surfaces.

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