

Chemical Treatments for Improving Adhesion Between Electrospun Nanofibers and Fabrics

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ABSTRACT: Nanofiber-coated fabrics have potential uses in filters and protective clothing. One major challenge is to ensure good adhesion of nanofibers to the fabrics achieving satisfactory durability against abrasion for practical use. This work is aimed to study adhesion mechanisms and their improvement between nanofibers and textile substrates; to achieve this goal cotton fabrics were treated with an alkali solution, while nylon fabrics were treated with ethanol. Adhesion of polyamide-6 electrospun nanofiber layer to fabrics was evaluated by means of a peeling test. Treated fabrics showed improved bonding towards nanofibers: adhesion energy was $\sim 0.58 \text{ J m}^{-2}$ for both untreated fabrics, and after treatments increased to 0.93 and 0.86 J m^{-2} for cotton and nylon ones, respectively. Optical observations revealed that nanofibers deposited on fabrics are mainly linked to external protruding fibers (i.e., fabric hairiness). Therefore, surface hairiness seems to be the critical factor limiting adhesion. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39766.

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INTRODUCTION

Electrospinning is recognized as the main method and the most versatile way to produce polymer-based nanofibers. In electrospinning process, nanofibers are produced by repulsive electrostatic forces acting on a polymer fluid (e.g., polymer solution). The most simple electrospinning setup consists of a pump that pushes the polymer solution to a capillary, a collector on which nanofibers are deposited and an electric power supply that generates the electrostatic field between the capillary and the collector. As the electrostatic repulsive forces exceed the surface tension of the polymer fluid, a drop at the capillary tip is stretched into a cone (so-called “Taylor cone”) and a stream of fluid is ejected from the vertex of the cone towards the collector. The formation of a single unbroken filament is ensured by polymer chain entanglements of the polymer solution. Despite the huge scientific knowledge developed in the field about nanofiber formation within an electric field,^{1–6} some issues have to be faced for reaching real industrial applications, namely increase of nanofiber throughput, continuous collection of nanofiber layers and adhesion of electrospun nanofibers to substrates. For applications such as clothing,⁷ filtration,^{8–11} and protective devices^{12–15} electrospun nanofibers have to be deposited on a substrate (usually a textile material such as woven or non-woven fabrics). The substrate has the function to give mechanical properties allowing further processing, such as pleating in filter production or sewing

in protective clothing. The most simple way to deposit nanofibers on a substrate is to place the substrate between the jet source and the collector. Unfortunately, textiles being dielectric materials can interfere with electrospinning process.^{11,16} On the other hand, nanofibers have to be stuck to the substrate with an adequate strength. The enhancement of adhesion between nanofiber layers and textile substrates promoted by plasma treatments has been recently investigated.^{17,18}

In this study, chemical treatments will be investigated for improving adhesion on plain fabrics composed of staple fibers. Notwithstanding adhesion has been improved by the proposed treatments, a limiting factor for adhesion enhancement has been identified for textile substrates.

EXPERIMENTAL

Materials

Cotton and nylon fabrics were plain-weave fabrics both composed of staple fibers and supplied by Testfabrics (USA). The cotton fabric was a Bleached Desized Cotton Print Cloth Style 400 with a weight of 102 g m^{-2} . The nylon fabric was a Spun Nylon 66 DuPont Type 200 Woven Fabric with a weight of 124 g m^{-2} . Sodium hydroxide (NaOH, BioXtra, $\geq 98\%$) and ethanol (EtOH, ACS reagent grade $\geq 99.5\%$) were supplied by Sigma-Aldrich (Italy), and used as reagents for treatments of the fabrics. Commercial fiber grade polyamide-6 (PA6, $2.2 \times 10^4 \text{ g mol}^{-1}$) was

dissolved in pure formic acid (reagent grade $\geq 95\%$ by Sigma-Aldrich) at concentration of 15% w/w at room temperature using a magnetic stirrer overnight (about 16 h). The PA6 solution was used in electrospinning for the production of nanofibers.

Chemical Treatments

Alkali treatments are often used in textile industry to remove waxes from the cotton fiber surface and to modify cellulose-based fibers, in particular cotton (e.g., mercerization). Alkali treatments are also often used in the improvement of adhesion in coating processes and composites. In this study, cotton fabrics were treated with a water solution of NaOH (2% w/v) for 1 h. Liquor ratio was 80 : 1 and temperature was 70°C. Subsequently, the samples were rinsed in cold water, squeezed and dried in an oven at 50°C for 2 h. The samples were labeled as "Cotton + NaOH".

In a previous work,¹⁹ nylon fabrics were treated with EtOH before polypyrrole deposition. It was demonstrated that polypyrrole layer was strongly linked to the treated fibers surface. In this study, nylon fabrics were immersed in flasks containing ethanol (80% v/v) and demineralized water. The liquor ratio was 80 : 1. The treatment was carried out at 70°C and lasted 1 h. Subsequently, the samples were rinsed in cold water, squeezed and dried in an oven at 50°C for 2 h. The samples were labeled as "Nylon + EtOH".

Both the fabrics were conditioned at 20°C and 65% R.H. for at least 24 h after treatments, and were measured and weighted.

Fabrics and Nanofibers Characterization

Mechanical properties of the fabrics before and after the treatments were measured by means of an Instron 5500R dynamometer on specimens of 5 cm \times 15 cm, according to ISO 13934-1. Measurements were taken on warp directions. The maximum force (expressed in N) and elongation at break were recorded and averaged.

FTIR spectra were recorded using a Thermo Nicolet Nexus spectrometer, by Attenuated Total Reflection (ATR) technique with Smart Endurance accessory (diamond crystal ZnSe focusing element), in the range from 4000 to 550 cm^{-1} with 100 scans and 4 cm^{-1} of band resolution. Omnic 6.2 software (by Thermo Electron) was used to perform ATR baseline correction and smoothing (9 points) of the spectra, then FTIR spectra were elaborated with Origin[®] 8.1 software (by OriginLab).

Scanning electron microscopy (SEM) investigations were performed using a LEO (Leica Electron Optics) 435 VP SEM, with an acceleration voltage of 15 kV at about 30 mm working distance. The fabric and nanofiber samples were sputter-coated with a 20 nm-thick gold layer in rarefied argon (20 Pa), using an Emitech K550 Sputter Coater, with a current of 20 mA for 180 s, in order to improve the image quality.

Finally, wettability of treated and untreated fabrics was measured using a Drop Shape Analysis System DSA from Krüss GmbH. The water absorption time was obtained by placing 10 μL of deionized water, using a computer-aided micro-liter syringe, on the flat fabric surface and measuring the time required for the drop to be completely absorbed by the fabric.

For each sample, at least 10 measurements were taken and average absorbance time values were calculated.

Electrospinning of Nanofiber on Fabrics

The fabrics were cut in square of 15 cm by side and stuck to the stainless steel collector with adhesive tape. The polymer solution was electrospun using a typical single-jet electrospinning setup illustrated elsewhere.¹⁸ Electrospinning conditions were the following: +25 kV voltage to the metal tip (collector was grounded); 20 cm of tip-to-collector distance; solution flow-rate was 0.06 mL h^{-1} ; metal tip internal diameter was 0.2 mm; temperature was $27 \pm 2^\circ\text{C}$ and relative humidity was $50 \pm 4\%$; 20 min duration of nanofiber deposition (which correspond to a nanofiber layer weight of $0.92 \pm 0.18 \text{ g m}^{-2}$ at this condition).

Peeling Tests and Optical Observations

Adhesion strength between the electrospun nanofiber layer and fabric substrates was evaluated using a peeling test method. Nanofiber-coated fabrics were cut in strips (2 cm \times 15 cm). An adhesive tape was stuck to the nanofiber layer at the free end in order to facilitate proper peeling and avoid grip slippage. The strips were clamped to the two free ends (i.e., nanofiber layer and fabric). The first was held by the movable clamp of the instrument, while the latter was held by the stationary clamp. An Instron 5500R dynamometer equipped with a 10 N load cell was used to register strain–stress curves to separate the nanofiber layer from the fabric surface at a constant rate of 50 mm min^{-1} . Figure 1 shows pictures during the execution of a peeling test. The adhesion strength (expressed in J m^{-2} , as ratio between energy and surface) was calculated as average value of eight test specimens. Student's *t*-test was used to statically compare the values of two samples. When the *P*-value is less than the significance level of 0.01, the null hypothesis will be rejected and the result will be statistically significant. Prior to testing, the nanofiber-coated fabric samples were conditioned at 20°C and of 65% R.H. for at least 24 h.

After peeling tests the samples (i.e., nanofibers layer and fabric surfaces) were observed by means of a Wild M8 Stereomicroscope (Swiss) equipped with a JVC SuperLoLux video-camera.

RESULTS AND DISCUSSION

Tensile Properties of Fabrics

Tensile properties of fabrics were measured before and after the proposed chemical treatments (Table I). In the case of cotton, it was observed a notable loss (about 60 N) in tensile strength after the NaOH treatment. Therefore, the chemical treatment damaged to some extent the fibers. In contrast, the elongations at break slightly increased, as sign that the fabrics become more soft and flexible. However, the residual mechanical properties do not impede to employ the fabrics in practical applications.

Interestingly, on nylon fabric mechanical properties were found to increase after the EtOH treatment. The fact that the load at the break increased in Nylon + EtOH, as compared to the untreated nylon fabrics, could be attributed to a contraction in the sample size. It was observed that Nylon + EtOH experienced a change in dimensions in the order of about 1 cm in both warp and weft directions, which means a shrinking of

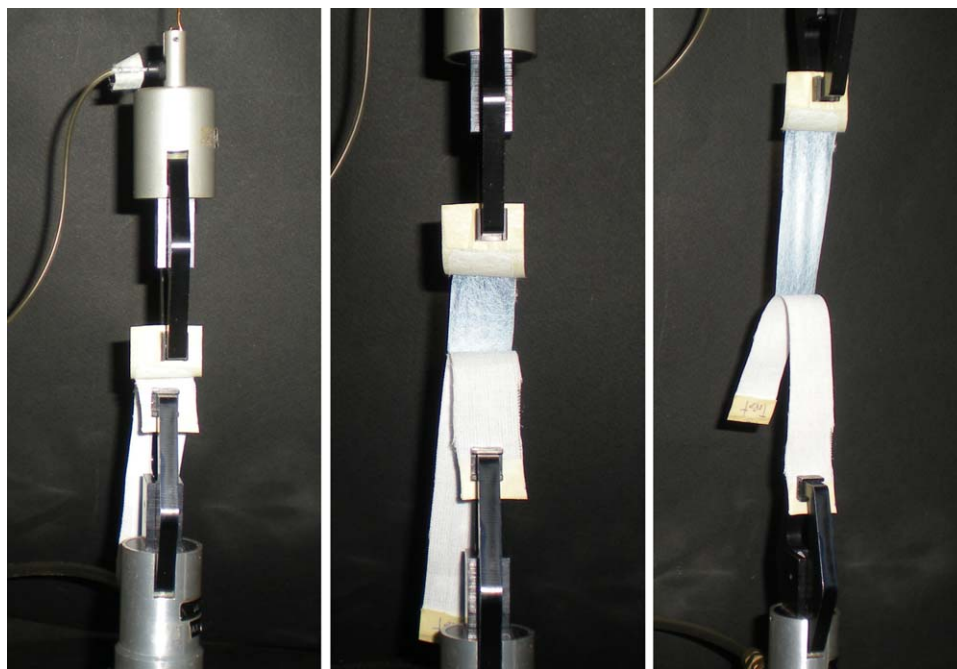


Figure 1. Pictures of the peeling tests. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

6–7%. On the other hand, the weight of the samples did not change. Therefore, the shrinking induced by the treatment in EtOH could justify the increase in both tensile strength and elongation.

FTIR Analysis

ATR FTIR is a powerful tool for investigating surface treatments because the infrared beam analyses only a thin layer (i.e., 1–2 μm) of the fiber surface. The main spectral changes observed on cotton fabrics related to the alkali treatment are reported in Figure 2. Changed spectral features were observed in the region from 2800 to 2950 cm^{-1} (a) attributed to CH_2 stretching. Such absorption bands are usually originated from wax substances on the cotton fiber surface (cuticle).²⁰ It is supposed that the alkali treatment removed waxes naturally present on the primary cell wall of the fibers or used for the production of the fabric, such as sizing compounds. This could explain the improvement in wettability observed on Cotton + NaOH.

Other slight changes were observed in the range 3310–3360 cm^{-1} (b) related to absorption bands of OH-stretching vibrations involved in intra-molecular hydrogen bonds of cellulose.^{21,22} It seems that the treatment altered to some extent the arrange-

ment of O(3)H...O(5) intra-chain hydrogen bonds. In particular, untreated cotton is characterized by two peaks at 3341 and 3326 cm^{-1} , while a single peak centered at 3335 cm^{-1} was observed after alkali treatment.

The most significant change observed in the FTIR spectra of nylon fabrics before and after EtOH treatment falls in the region from 1400 to 1500 cm^{-1} (Figure 3), which corresponds to absorptions due to CH_2 scissoring vibrations. In this region, nylon 66 exhibits four distinguishable peaks at about 1470, 1460, 1440 (weak), and 1415 cm^{-1} .^{23–25} The peaks at 1470 and 1415 cm^{-1} were assigned to methylene scissoring modes in *trans* planar chain conformation adjacent to NH and CO groups,

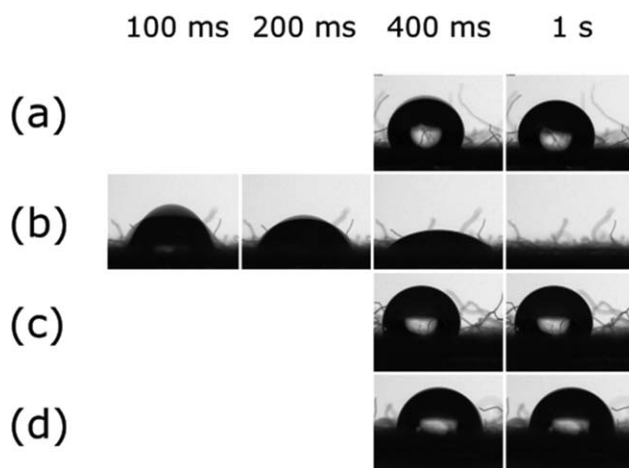


Figure 2. ATR FTIR spectra of cotton (a) in the region from 2800 to 2950 cm^{-1} (CH_2 asymmetric stretching), and (b) in the region from 3310 to 3360 cm^{-1} (OH stretching of cellulose).

Table I. Tensile Properties of Fabrics Before and After the Treatments

Sample	Load at the break (N)	Elongation at the break (%)
Cotton	388 ± 22	9.2 ± 0.5
Cotton+NaOH	330 ± 15	10.9 ± 0.4
Nylon	752 ± 29	32.5 ± 1.1
Nylon+EtOH	903 ± 59	43.9 ± 1.3

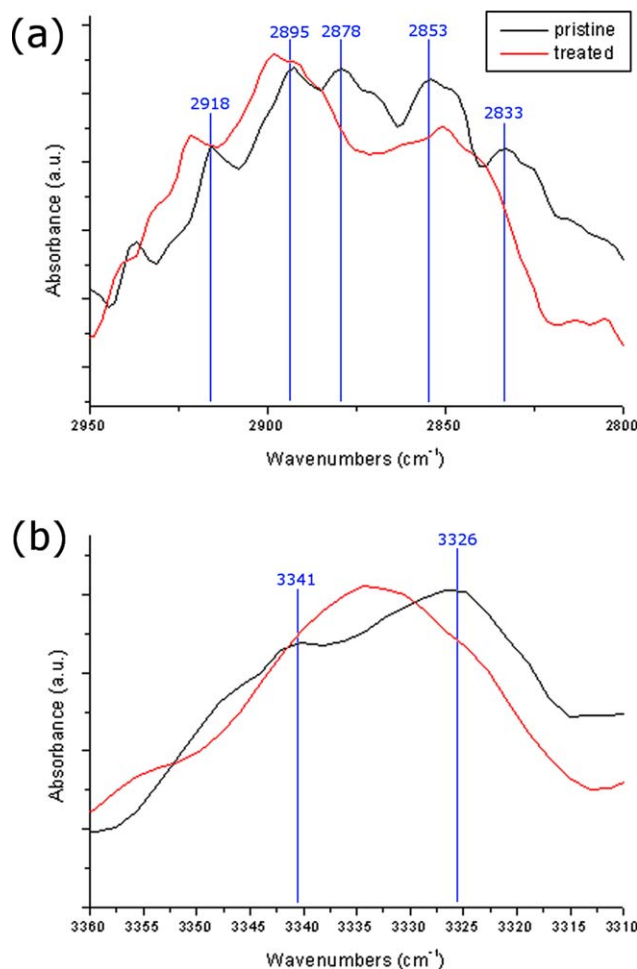


Figure 3. ATR FTIR spectra of nylon in the region from 1410 to 1480 cm^{-1} (CH_2 scissoring). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. The NH-vicinal peak at 1470 cm^{-1} and the CO-vicinal peak at 1415 cm^{-1} results in the weak peak at 1440 cm^{-1} when *trans* conformation is lost. Finally, the peak at 1460 cm^{-1} is attributed to non-amide vicinal methylene scissoring. After the treatment with EtOH, a slight decrease in intensity of the peak at 1460 cm^{-1} is observed, this could be a sign of the existence of conformationally disordered methylene sequences with enhanced motion²⁴ and could explain the hydrophilic behavior of the fabrics after treatments (see below).

Wettability of Fabrics. It can be difficult to compare wettability of hydrophilic fabrics by using contact angle measurements due to large errors of these measurements when the water drops are quickly absorbed by the fabric. In the present investigation, water drop absorption time evaluation was used as a robust method for comparing hydrophilic behavior changes induced by the treatments. Drop absorption time was determined for all the fabrics prior and after subjecting them to chemical modifications, as well as contact angle, when possible. In particular, contact angle cannot be measured on treated cotton (Cotton + NaOH) because of the short lasting time of the drops on the fabrics. Water droplets on fabric surfaces were videoed during the wettability tests using a high-speed camera; pictures are

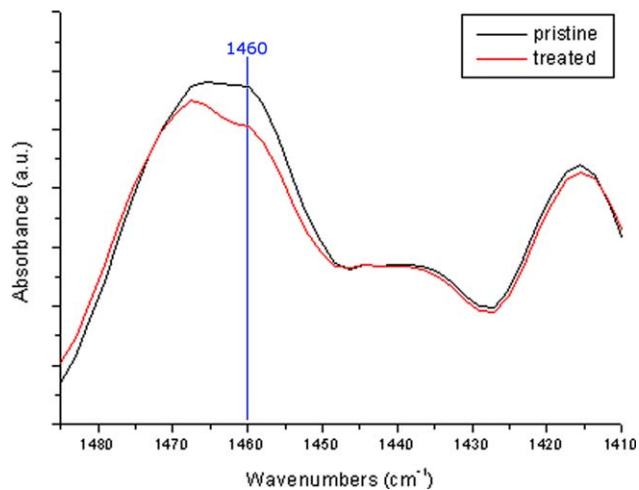


Figure 4. Pictures of water drop absorption process at different times, namely 100, 200, 400 ms, and 1 s, on the fabrics: (a) untreated cotton; (b) Cotton + NaOH; (c) untreated nylon; (d) Nylon + EtOH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported in Figure 4 at different times for comparison. The results are reported in Table II.

SEM Observations. Figure 5 reports pictures by SEM of untreated and treated fabrics. No significant changes in surface morphology and roughness can be observed before and after treatments by means of SEM. In particular, cotton fibers showed the typical wrinkled surface (a), while nylon fibers have a quite smooth fiber surface, even if some small hollows can be observed (c). The fiber surface morphologies of both cotton and nylon do not change after the treatments (b, d).

Electrospun nanofibers were characterized by SEM analysis in order to check nanofiber morphology and range of fiber size. SEM pictures are reported in Figure 6, as examples. Electrospun nanofibers have diameters in the range of 120–200 nm. Shape and regularity do not change when nanofibers are electrospun on the different substrates. Therefore, the nature of the fabric has no influence on the electrospun nanofiber morphology at this electrospinning condition.

Peeling Test. Peeling test results are reported in Table III. The adhesion values of untreated cotton and nylon fabrics are nearly closed. Therefore, it seems that for such kind of substrates (i.e., fabrics composed of staple fibers) the chemical affinity of nanofibers towards fiber surfaces is not the main parameter for having adhesion to electrospun nanofibers, in the opposite case it

Table II. Water Drop Absorption Times and Contact Angles Before and After the Treatments

Sample	Drop absorption time	Contact angle ($^{\circ}$)
Cotton	$6.4 \pm 1.4 \text{ s}$	120 ± 8
Cotton+NaOH	$0.43 \pm 0.12 \text{ s}$	-
Nylon	>10 min	132 ± 5
Nylon+EtOH	$8.2 \pm 2.5 \text{ s}$	115 ± 9

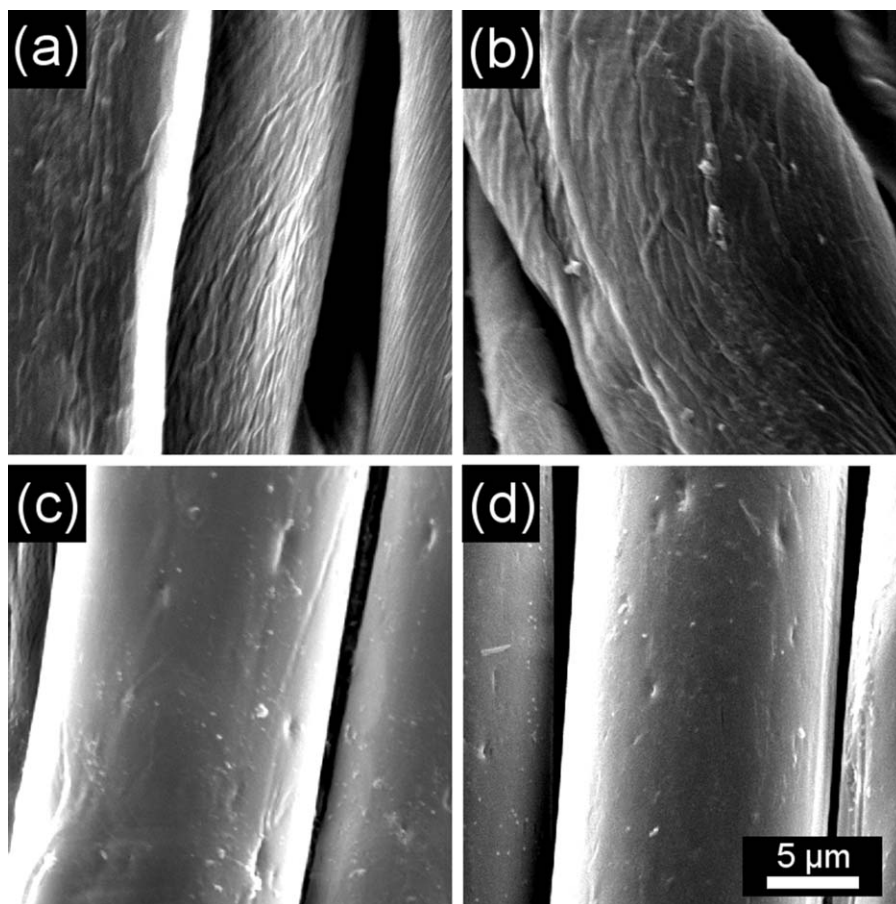


Figure 5. SEM pictures of the fiber surfaces: (a) untreated cotton; (b) Cotton + NaOH; (c) untreated nylon; (d) Nylon + EtOH. All pictures have the same magnification.

should be observed a difference in nanofibers adhesion between cotton and nylon fabrics. Moreover, also the fiber surface of cotton and nylon seemed not have influence on adhesion, as observed in Figure 5 (a) and (c).

On the other hand, it can be seen that the chemical treatments (alkali for cotton and ethanol for nylon) improved notably the adhesion energy between nanofibers and fabrics. In particular, there was a gain of about 60% in adhesion energy for Cotton + NaOH and 51% for Nylon + EtOH compared to untreated fabrics. The student's *t*-test was used for assessing whether the means of two groups (i.e., adhesion on untreated and treated fabrics) are statistically different from each other. A threshold significance value of 0.01 was fixed. All *t*-test values are less than 0.01, suggesting that the adhesion improvements promoted by the treatments are statistically significant.

Finally, the measured values and the adhesion improvements observed are similar to those reported in literature using plasma treatments on fabrics composed of staple fibers.¹⁷ In contrast, using other kind of substrates (e.g., non-woven) the improvement in adhesion promoted by plasma treatments could be slightly higher.¹⁸ This could be an evidence that probably there is a limiting adhesion factor that depends on the physical structure of the substrates, other than chemical affinity.

Stereomicroscope Observations. After peeling tests, both nanofibers layers and fabric surfaces were observed by means of an optical stereomicroscope in order to collect information to understand the mechanism of the bonding between nanofiber layer and fabrics. Interestingly, it was observed that the nanofiber layer is mostly linked with protruding fibers. The picture (a) in Figure 7 clearly shows the signs of the fabric hairiness (visible in the picture (b) in Figure 7) marked on the nanofiber layer.

On the other hand, Figure 7(c) shows a small fragment of nanofiber layer stuck to a protruding fiber of the fabric after peeling tests. It could be assumed that the electrospun nanofibers were actually linked to few anchor points on the fabric surface. Therefore, surface hairiness seems to be the most critical limit for considerably improving adhesion on fabric composed of staple fibers, even if improvements can be promoted by treatments.

CONCLUSION

Cotton fabrics were treated with an alkali solution, while nylon fabrics were treated with ethanol. Polyamide-6 nanofiber layers were electrospun on untreated and treated fabrics. Adhesion of nanofibers to the fabrics was characterized by means of a peeling test. Both treatments improved bonding of nanofibers towards fabrics, in particular adhesion energy increased by 60

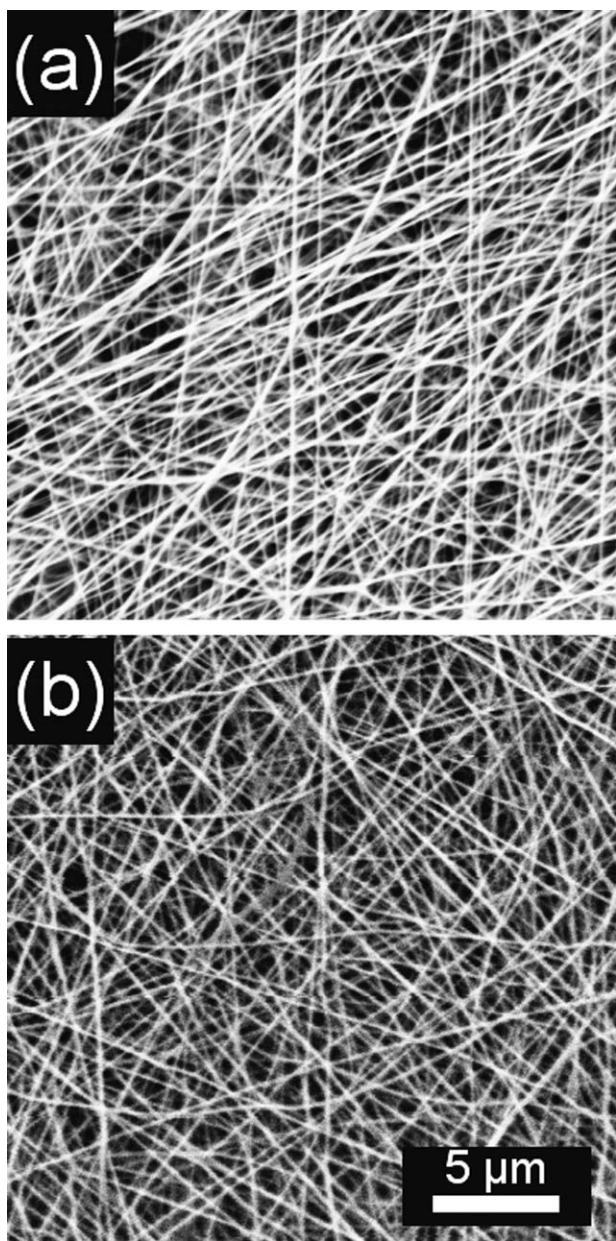


Figure 6. SEM pictures of the electrospun PA6 nanofibers (a) on cotton and (b) on nylon. All pictures have the same magnification.

and 51% on alkali-treated cotton fabrics and ethanol-treated nylon-66 fabrics, respectively. Nevertheless, for practical applications, adhesion should be at least one order of magnitude greater than the values obtained in this study and cited references.^{17,18}

Table III. Peeling Test Results

Sample	Adhesion energy (J m^{-2})	<i>P</i> -value
Cotton	0.58 ± 0.23	<0.01
Cotton+NaOH	0.93 ± 0.39	<0.01
Nylon	0.57 ± 0.15	<0.01
Nylon+EtOH	0.86 ± 0.15	<0.01

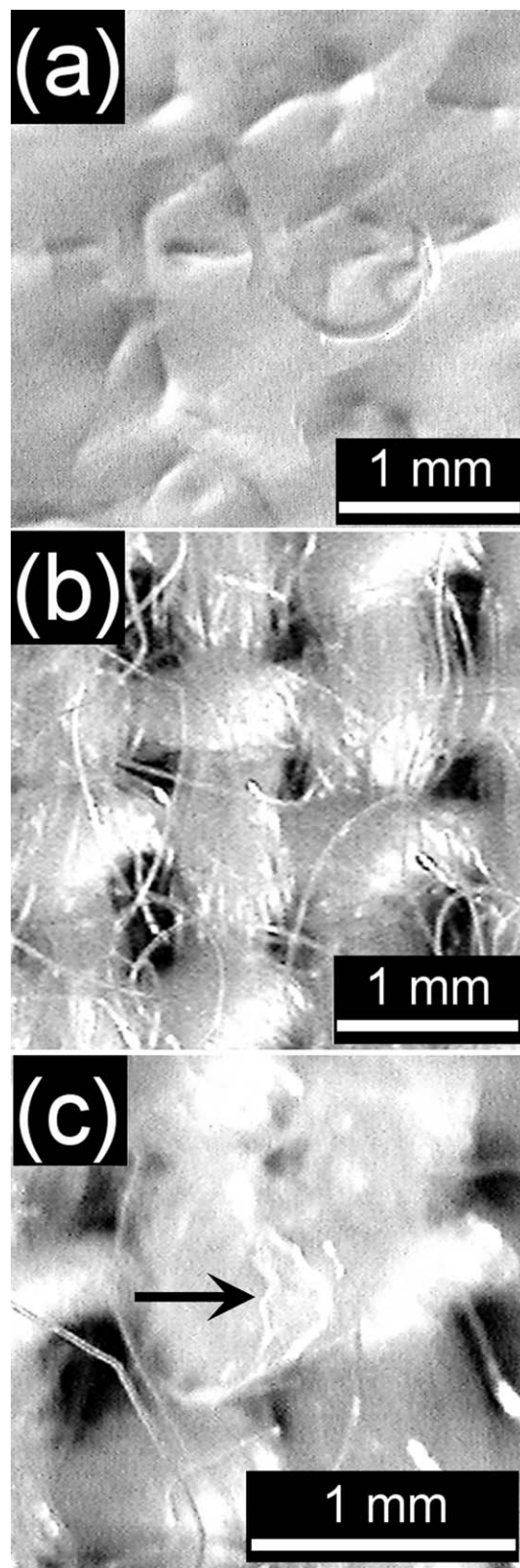


Figure 7. (a) Picture of the nanofiber layer after peeling test. (b) Picture of the hairiness of the nylon fabric surface. (c) Picture of the nylon fabric surface after peeling test with a small fragment of nanofiber layer (indicated by the arrow) stuck to a protruding fiber.

The treatments increased the wettability (i.e., decrease in both water absorption times and contact angles) of the fabrics and produced slight chemical conformational changes, but did not modified the fiber surface morphologies. However, considering both cotton and nylon fabrics there is no a clear correlation between adhesion energies and absorption times.

Optical microscopy observations on both nanofiber layer and fabric after peeling tests suggested that on staple fabrics the electrospun nanofibers were actually linked to few anchor points (i.e., protruding fiber) on the fabric surface. Therefore, surface hairiness of fabrics seems to be a critical limit for considerably improving adhesion, even if improvements can be promoted by the treatments.

Staple fabrics have an intrinsic structural factor that limits the improvement achieved by the treatments (i.e., hairiness). Simple treatments were used in order to draw attention to that. It seems that not all textile materials (such as fabrics) are suitable substrates for electrospun nanofibers.

Therefore, further works shall be focused to assess adhesive behavior of fabrics with low hairiness using, for instance, fabrics composed of continuous filaments or monofilaments.

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