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# Functionalization of Wool Fabric with Phase-Change Materials Microcapsules After Plasma Surface Modification

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**ABSTRACT:** The use of microcapsules has increased in several different areas, namely, textile applications. They have been used as a possible means of introducing new properties, namely, in medical care by antibiotics, skin moisturizers, and other drugs and for thermal comfort. In this study, we examined the influence of dielectric barrier discharge (DBD) plasma treatment on the adhesion of phase-change material (PCM) microcapsules on wool fabric. Several experimental techniques were used to evaluate the wool surface modification after plasma treatment and the influence of the microcapsules' resistance to washing conditions, namely, the determination of the static and dynamic contact angles, surface energy, and adhesion work; X-ray photoelectron spectroscopy; Fourier transform infrared spectroscopy; differential scanning calorimetry; and scanning electron microscopy. Chemical and physical characterization of the wool fiber in the fabric confirmed significant surface modification. The plasma treatment greatly increased the hydrophilicity, surface energy, and adhesion work of the wool fabric; this proved that more microcapsules were adsorbed on the fabric and more microcapsules remained on the fabric surface after the washing procedures. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 2638–2647, 2013

**KEYWORDS:** functionalization of polymers; properties and characterization; textiles

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## INTRODUCTION

In the more developed countries, a growing interest in textiles with new properties and added value has been encouraging the industry to make greater use of microencapsulation processes to impart finishing properties to textiles in a way that is not possible or economically feasible with other technology. Potential applications include fragrances, skin softeners, insect repellents, dyes, vitamins, antibiotics, specific medical applications, phase-change materials (PCMs), and others.[1]

PCMs include materials with the ability to change their physical state within a certain temperature range, absorbing energy during the heating process and releasing it during the reverse cooling process. An insulation effect can be achieved, but the dependency on the temperature and time of use gives it a temporary nature.[2–4] The technology for the incorporation of PCMs into textile structures was developed under a National Aeronautics and Space Administration program in the early 1980s, with the intention of the application of these fabrics to astronaut suits to improve their thermal protection against the extreme temperature fluctuations in outer space.[1,2,4–6]

Wool is one of the most common natural fibers used in the textile industry. Its unique properties make this material very important for use in protection against low temperatures. PCMs interactively respond to each individual physiological condition, absorb, store, and release heat, helping the body to remain comfortable. These materials are responsible for the control within known limits of the body's natural temperature across hot and cold environments and during high and low activity levels. Its application in wool fabrics can add value to these substrates and make them more efficient in extreme weather conditions.

Currently, there are numerous processes for the application of microcapsules into textiles; these include coatings, lamination, padding, melt spinning, bicomponent synthetic fiber extrusion, and foam techniques. However, a major challenge in the area of these innovative textiles is the durability of their properties with repeated use.[2] The conditions of application of the microcapsules in the textile finishing process influence their effectiveness at the functional level. According to Monllor et al.,[7] the impregnation process is more appropriate because of the absence of an affinity between the microcapsules and the substrate. A mechanical procedure, such as impregnation, in which pressure of the roles is necessary, is very adequate for forcing the contact between the microcapsules and the fibers. The polymeric binders also have a significant influence on the microcapsules'

effectiveness. Sánchez et al.[4] showed that different binders contribute to obtain different numbers of microcapsules attached to the textile substrate, and in consequence, the resistances to washing, rubbing, and ironing are affected. Shin et al.[6,8] showed that the heat storage capacity increased when the concentration of microcapsules was higher. Fabrics padded with microcapsules and 3% polyurethane binder retained 40% of their heat storage capacity after five laundering procedures.[6]

The use of microcapsules in textile substrates is already of high importance, and studies have primarily focused on the microcapsules, binders, and application techniques.

In recent years, the surface modification of textile materials by plasma treatment has opened up new possibilities for their functional performance. In fact, plasma technology has been increasingly used in the etching, deposition, and other modifications of various forms of textile materials to improve their surface properties and are expected to achieve very good results, namely, with regard to the conditions for the binding of the microcapsules to the textile substrates.

Plasma treatment effects in textiles have been described and include an increase in the hydrophilic characteristics,[9–18] an improvement of the dyeing properties,[10–12,14,15,18,19] a surface cleaning effect,[17,20,21] antifelting properties,[22,23] the enhancement of adhesion,[16,24–27] and others.

Ghahremanzadeh et al.[28] showed the effect of changes in the wool fiber surface energy and surface charge in shrink-proofing and on the performance properties of thermally adaptable wool fabrics. They found that when the surface energy of the wool increased, the poly(ethylene glycol) (PEG)–dimethylol dihydroxyethylene urea resin finishing presented higher fixation to the fiber and exhibited better durability to washing; this resulted in superior and longer thermal activities. In another study, Cheng et al.[25] investigated the surface modification of wool, polyester, and cotton by atmospheric pressure plasma, with regard to the enhancement of their adhesion to microcapsules, applied by an exhaustion method. They found that more microcapsules adhered to the plasma-treated surfaces compared with the untreated sample surfaces.

The aim of this work was to study the adhesion of PCM microcapsules applied by a padding process in a wool fabric after it was treated with DBD plasma. To analyze the effect of the plasma treatment on the fabric surface and on the microcapsule adhesion, several techniques were used, namely, static and dynamic contact angle measurements, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). Durability tests were performed, and the resistance to washing of the microcapsules in the wool substrates was evaluated.

## EXPERIMENTAL

### Materials

**Wool Fabric.** The textile substrate used was 100% wool plain-weave fabric with 194 g/m$^2$. The raw fabric was scoured with a nonionic detergent (2% owf) at 100°C for 30 min. The thread density was 16 threads/cm in the warp direction and 12 threads/cm in the weft direction.

**Table I.** Plasma Dosages Applied

| Speed (m/min) | *N* | *P* (W) | Dosage (W min/m$^2$) |
|---|---|---|---|
| 4.0 | 1 | 500 | 250 |
| 4.0 | 2 | 500 | 500 |
| 4.0 | 3 | 500 | 750 |
| 4.0 | 4 | 500 | 1000 |
| 4.0 | 5 | 500 | 1250 |

**Microcapsule PCMs.** Microcapsule PCMs (PRETHERMO C-25) produced by Daiwa Chemical Industries Co., Ltd. (Osaka, Japan), were supplied by ATUSMIC Lda (Porto, Portugal). The PRETHERMO C-25 is a melamine microcapsule agent with a higher aliphatic hydrocarbon, which is the thermal storage agent. To bond the PCM microcapsules to the textile substrate, an acrylic binder agent, also supplied by ATUMISC Lda, was applied.

### Methods

**Dielectric Barrier Discharge (DBD) Plasma Treatment.** The textile material was treated in a laboratory prototype, LISBOA, patented[29] by the University of Minho and Softal Electronics. This equipment consists of a metallic electrode coated with ceramic, a metallic counter electrode coated with silicon, an electric generator, and a high-voltage transformer. The fabric passes through the electrodes continuously with air at normal conditions of temperature and pressure. The process parameters, the power of plasma discharge and speed of the fabric, are adjustable.

The plasma dosage is defined by eq. (1):[12]

$$\text{Dosage} = \frac{NP}{vl} \tag{1}$$

where $N$ is the number of passages, $P$ is the power (W), $v$ is the velocity (m/min), and $l$ is the width of treatment (0.5 m).

Different dosages were applied in wool fabric, according to Table I.

**Contact Angle and Surface Free Energy.** Contact angle measurement and calculation of the fiber surface free energy was carried out in a Dataphysics instrument (Filderstadt, Germany) using OCA20 software (Germany). Fifteen measurements were carried out for each sample.

The surface energy ($\gamma$) is considered to be composed of polar and dispersive components. In particular, the polar component results from three different intermolecular forces due to permanent and induced dipoles and hydrogen bonding, whereas the dispersion (nonpolar) component of $\gamma$ is due to instantaneous dipole moments.[30]

The work of adhesion ($W_{\text{Adh}}$), which represents the energy of interaction between the liquid and the solid phases per unit area, is defined by eq. (2).[31] The water contact angle average was used for this calculation:

$$W_{\text{Adh}} = \gamma_l(1 + \cos\theta) \tag{2}$$

where $\theta$ is the water contact angle calculated by goniometer and $l$ means the 'liquid' surface energy.

Table II. Surface Energy Components of the Tested Liquids[32]

| Liquid | $\gamma$ (mJ/m$^2$) | $\gamma^D$ (mJ/m$^2$) | $\gamma^P$ (mJ/m$^2$) |
|---|---|---|---|
| Distilled water | 72.8 | 29.1 | 43.7 |
| PEG 200 | 43.5 | 29.9 | 13.6 |
| Glycerol | 63.4 | 37.4 | 26.0 |

For polar solids or liquids, the total $\gamma$ is a sum of the always existing London dispersion forces ($\gamma^D$) with intermolecular interactions that depend on the chemical nature of the material, compiled as polar forces ($\gamma^P$):[31]

$$\gamma = \gamma^D + \gamma^p \tag{3}$$

The polar and dispersive components of the surface energy ($\gamma^D$ and $\gamma^P$, respectively) were calculated with the Wu method (harmonic mean) by eq. (4):[30]

$$\gamma_{sl} = \gamma_s + \gamma_l - 4\left[\frac{\gamma_s^D\gamma_l^D}{\gamma_s^D + \gamma_l^D} + \frac{\gamma_s^P\gamma_l^P}{\gamma_s^P + \gamma_l^P}\right] \tag{4}$$

For the calculation of the surface energy, three liquids with known surface energies were used (Table II).[32]

**Microcapsule Size Distribution.** Microcapsule dispersion was analyzed in a Malvern Instruments MasterSizer (Worcestershire, U.K.) software version 2.15 to verify the particle size distribution.

**Impregnation of the PCM Microcapsules.** Microcapsules in a water solution were impregnated into the surface of the fabrics, either untreated or treated with DBD plasma, by a padding process in a minifoulard (pressure = 4 bar, $v$ = 6 m/min), and cured in a laboratory oven for 3 min at 140°C. The composition of the padding bath was the following: PCM microcapsules = 160 g/L, binder = 50 g/L, and $MgCl_2$ = 5 g/L. The pH was fixed at 5.

**SEM.** SEM was used to analyze the surface of the wool fabrics before and after plasma treatment and also the fabrics padded with PCM and after the laundering test. The textile samples were coated with a thin layer of gold palladium. The analyses were carried out in an ultra-high-resolution field emission gun SEM instrument (NOVA 200 Nano SEM, FEI Co. Oregon, USA).

**FTIR Spectroscopy.** A Nicolet Avatar 360 FTIR spectrophotometer (Madison, USA) with an attenuated total reflectance accessory was used to record the FTIR spectra of the wool fabric samples. To characterize the PCM microcapsules, the samples were pressed into potassium bromide pellets before the measurement. The IR spectra were collected at a spectral resolution of 16 cm$^{-1}$, with 60 scans, over the range 400–4000 cm$^{-1}$ at room temperature. A background scan with no samples and no pressure was acquired before the spectra of the samples were collected.

**XPS.** XPS analysis was performed with an ESCALAB 200A (VG Scientific, Sussex, U.K.) with PISCES software for data acquisition and analysis. For analysis, an achromatic Al (K$\alpha$) X-ray source operating at 15 kV (300 W) was used, and the spectrometer, calibrated with reference to Ag 3d5/2 (368.27 eV), was operated in Constant Analyzer Energy (CAE) mode with a 20-eV pass energy. Data acquisition was performed at a pressure lower than $1 \times 10^{-6}$ Pa. Spectral analysis was performed with peak fitting with a Gaussian–Lorentzian peak shape and Shirley-type background subtraction (or linear consideration of the data).

**DSC.** A Mettler-Toledo DSC822 instrument (Giessen, Germany) was used to analyze and quantify the PCM energy absorption in the samples with and without DBD plasma treatment before and after the washing test. The DSC thermal analyses were performed under an inert nitrogen atmosphere at a 20 mL/min flow rate, a 10°C/min heating rate, and a temperature range from −10 to 60°C.

**Washing Test.** To test the durability of PCM bonding toward washing, the coated textiles were treated for 1 and 10 cycles in a Linitest C1-20 Original Hanau, Germany, for 30 min at 40°C in accordance with ISO Standard 105-C06 A1S. A solution of ECE detergent type B was prepared with a concentration of 4 g/L. Then, samples of 1.5 g were introduced in a laundry solution bath with a volume of 100 mL with 10 stainless steel balls. When the cycle was finished, the samples were washed twice with distilled water. After that, the samples were dried under ambient conditions.

## RESULTS AND DISCUSSION

### Effect of DBD Plasma Discharge on the Wool Fabric

**Static and Dynamic Contact Angles.** Many researchers have successfully used plasma technology to improve the wettability and hydrophilicity properties.[9,15,16,18,20] The contact angle technique is used to evaluate these properties, although the provided information is not complete with regard to the wetting characteristics of textile materials. It is difficult to measure the contact angle in textiles because of the absorbency and porosity of these materials and their irregular structure. In such cases, a wicking or dynamic contact angle can be used to provide information about the wetting properties of the textiles.

The surface properties of the wool fabric were analyzed by static and dynamic contact angle measurements to evaluate the effect of different plasma dosages. The static contact angle for the wool fabric without plasma treatment was 160.8°; this is considered hydrophobic. Table III shows the variation of the contact angles with water drop on the wool fabric with different dosages applied. The contact angle measurements showed a decrease after DBD plasma treatment, which corresponded to a higher hydrophilicity. These results suggested that the surface of the plasma-treated wool samples changed significantly because of chemical etching, which tends to create oxidized species on the surface of wool fibers.[33]

A low plasma discharge dosage was enough to change the fiber surface from hydrophobic to hydrophilic. With plasma activation of the wool fabric, it was possible to considerably improve the water adsorption velocity. When a dosage of 1250 W min/

Table III. Static Contact Angles of the Wool Fabric

| Dosage (W min/m$^2$) | | | | | |
|---|---|---|---|---|---|
| Untreated | 250 | 500 | 750 | 1000 | 1250 |
|  |  |  |  |  |  |

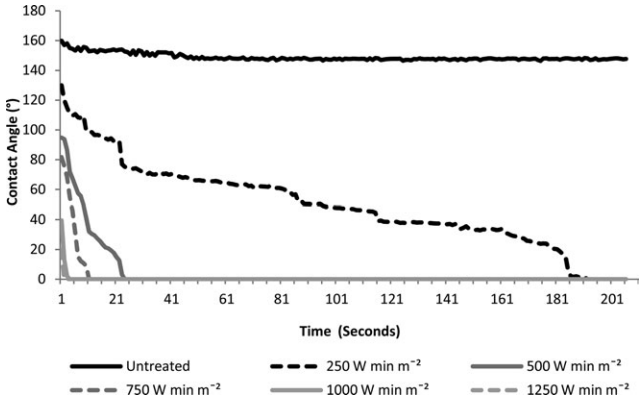


**Figure 1.** Dynamic contact angles of the wool fabric with different plasma dosages.

$m^2$ was applied, the absorption of the water droplet was almost instantaneous (Figure 1). Similar results have been reported in literature for different synthetic and natural fibers, with mention of modifications in accessible polar groups at the surface and the creation of microporosity as the main reason for this decrease.[11,12,25,34,35]

**Surface Free Energy.** DBD plasma is very effective for increasing the surface energy of textiles, not only by chemical conversion of the surface but often simply through a plasma cleaning process. In the cleaning process, inert and oxygen plasmas are used. The plasma is able to remove, via ablation, organic contaminants, either natural or added, on the materials and to increase the surface energy and improve the wettability of the substrate.[20,21]

With water, PEG, and glycerol contact angle values, the total surface energy ($\gamma$), dispersive component ($\gamma^D$), and polar component ($\gamma^P$) were calculated, and the results are shown in Table IV. The total surface energy significantly increased after DBD plasma treatment. Initially, the dispersive and polar components of the wool fabric without treatment were 4.4 and 0.0 mJ/$m^2$, respectively. For the dosage of 1250 W min/$m^2$, the dispersive component decreased until it reached 0.5 mJ/$m^2$, and the polar component had a huge increase, up to 53.0 mJ/$m^2$.

The results were similar to the ones published by Dai et al.,[36] where oxygen plasma treatment was responsible for an increase in the specific surface energy from approximately −4 to 60 mJ/$m^2$.

These results could be explained by the partial decomposition of the hydrophobic layer after DBD plasma treatment, which was caused by the etching process and the formation of new polar groups on the wool fiber surface.[33,37]

**SEM.** Figure 2(a,b) illustrates the SEM micrographs obtained from the surface of the untreated wool fabric and that treated with DBD plasma. The SEM images of the untreated wool fiber in Figure 2(a) show a smooth fiber surface, in which the escarpments are prominent and well defined. Despite a slight change in the appearance of the wool fiber after it was treated with a plasma dosage of 1250 W min/$m^2$, this difference, in terms of roughness, was not significant when compared with the untreated fiber.

**XPS.** XPS surface analysis was used to evaluate the superficial chemical changes (depth ≈ 10 nm) after plasma treatment. The surface composition of the wool fiber without treatment was found to be quite similar to that reported in literature.[33] The outermost part of the epicuticle membrane was covered with a fatty acid monolayer containing a high concentration of carbon. Beneath the fatty acid monolayer was a protein layer containing some nitrogen and sulfur-forming disulfide bonds. The detected sulfur was also from thioester linkages between the fatty acid and protein layers. Most oxygen was attributed to amide bonds and other hydrophilic groups.[33,37,38]

According to Table V and Figure 3, after plasma treatment, the changes in the carbon and oxygen concentrations were quite significant, with a decrease in the carbon concentration and an increase in the oxygen concentration. The O/C atomic ratio increased significantly from 0.17 to 0.26 after DBD plasma modification of the wool fabric; this was due to the oxidation of the hydrocarbon chains, which enhanced the level of oxygen-based functional groups on the surface. The amount of N1s did not vary greatly after the plasma treatment. The content of sulfur after the DBD plasma treatment decreased slightly. The increase in the O content was also attributed to the oxidation of S atoms present in the wool fiber. Another explanation was that the DBD treatment may have etched away the cuticle, which contained a large number of disulfide bonds (S—S).[33]

For further analyses, the C1s and O1s spectrum were deconvoluted with XPSPEAK software, as revealed in Figure 4(a–d). According to the literature,[39] the carbon-containing groups on the wool fiber surface are C—C/C—H (≈284.8 eV), CN/CS (≈285.6 eV), C—O (≈286.5 eV), and O—C=O (≈288.1 eV). The oxygen-containing groups are C=O/C—OH (≈531.4 eV),

**Table IV.** Contact Angle (Standard Deviation), Surface Energy, and $W_{Adh}$ Values

| Sample | $\theta_{Water}$ (°) | $\theta_{PEG}$ (°) | $\theta_{Glycerol}$ (°) | $\gamma$ (mJ/$m^2$) | $\gamma^D$ (mJ/$m^2$) | $\gamma^P$ (mJ/$m^2$) | $W_{Adh}$ (mJ/$m^2$) |
|---|---|---|---|---|---|---|---|
| Untreated | 160.8 (0.5) | 132.6 (5.9) | 151.8 (4.5) | 4.4 | 4.4 | 0.0 | 4.1 |
| 250 W min/$m^2$ | 130.7 (14.0) | 60.9 (4.0) | 151.2 (5.5) | 10.5 | 10.0 | 0.5 | 25.3 |
| 500 W min/$m^2$ | 95.5 (7.8) | 54.7 (5.7) | 141.8 (9.9) | 15.4 | 9.0 | 6.3 | 65.8 |
| 750 W min/$m^2$ | 81.2 (9.9) | 51.3 (3.1) | 133.4 (7.2) | 21.4 | 5.5 | 15.8 | 83.9 |
| 1000 W min/$m^2$ | 38.7 (7.6) | 47.1 (5.2) | 130.5 (5.7) | 30.5 | 5.0 | 25.5 | 129.6 |
| 1250 W min/$m^2$ | 20.5 (9.0) | 45.5 (4.9) | 129.3 (4.5) | 53.4 | 0.5 | 53.0 | 141.3 |

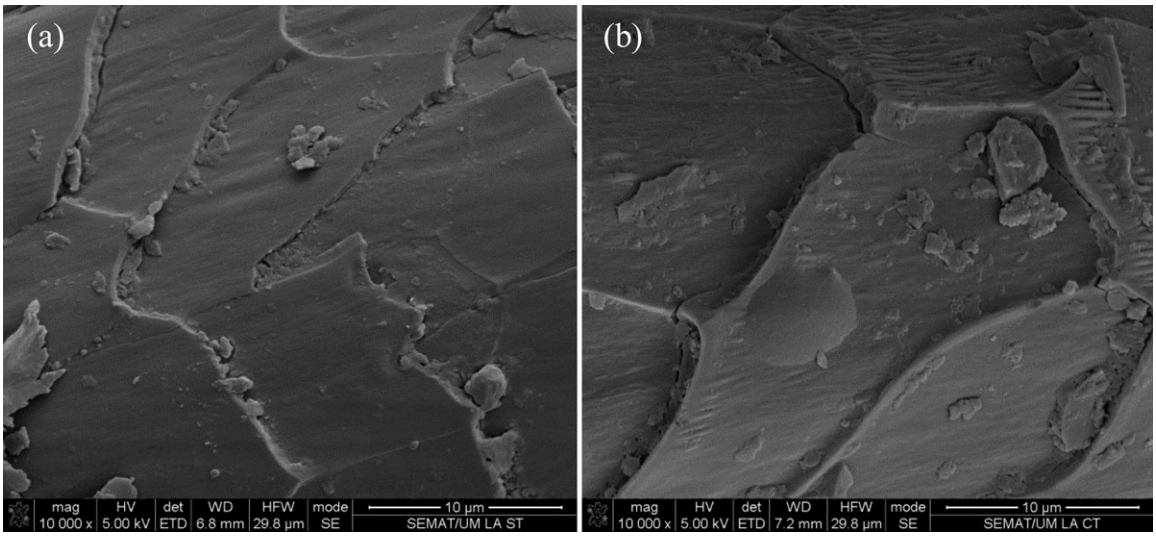


**Figure 2.** SEM micrographs obtained with secondary electrons of the (a) untreated and (b) DBD plasma-treated wool fabric with a dosage of 1250 W min/m$^2$.

**Table V.** Elemental Composition in Percentage, Atomic Ratios, and Deconvolution of $C_{1S}$ Spectra for the Untreated and Plasma-Treated (1250 W min/m$^2$) Wool Fabric

| | Atomic composition (%) | | | | Atomic ratio | | | Relative chemical bond area of $C_{1S}$ (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | C | O | N | S | O/C | S/C | N/C | C—C/C—H (284.8 eV) | C—N/C—S (285.6 eV) | C=O (286.5 eV) | O—C=O (288.1 eV) |
| Untreated | 77.00 | 13.50 | 6.74 | 2.75 | 0.17 | 0.04 | 0.08 | 57.33 | 20.90 | 14.42 | 7.35 |
| DBD treated | 73.32 | 19.18 | 5.32 | 2.18 | 0.26 | 0.03 | 0.07 | 51.46 | 21.01 | 16.94 | 10.59 |

sulfates/O—C=O (≈532.3 eV), and nitrates (≈533.2 eV). The concentration of aliphatic carbon decreased. The more oxygen-containing chemical functionalities, such as hydroxyl and carboxyl groups, were introduced on the wool fiber surface with air plasma treatment, which essentially contributed to an improvement in the wettability of the wool fabric. This could be explained by the oxidation of the aliphatic carbon (C—C) and of the C—N groups. An increase in carboxylic acid after the DBD plasma treatment was a consequence of the oxidation of hydrocarbon chains located on the wool surface; this was in accordance with the amount of covalently bonded surface lipids present in the wool fiber.[40–42] The relative chemical bond area of C1S in percentage is also shown in Table V.

The results indicate that the DBD plasma treatment had a double effect on the wool surface. First, the hydrophobic lipid layer on the exterior of the wool fiber was oxidized and partially removed. Because the exocuticle, that is, the layer of the surface itself (epicuticle), was highly crosslinked via disulfide bridges, DBD treatment had a strong effect of oxidizing the disulfide bonds [Figure 4(c,d)] and so reducing the crosslinking density.[43]

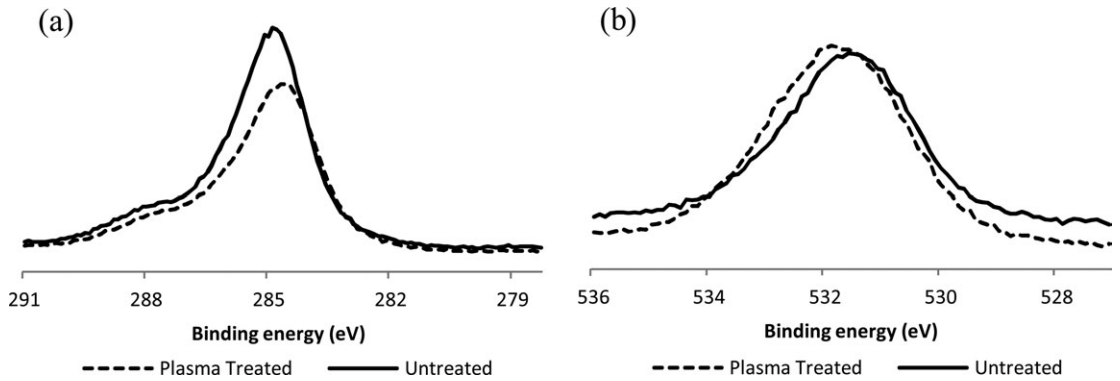


**Figure 3.** Photoemission spectra of the wool fibers before and after DBD plasma treatment (1250 W min/m$^2$): (a) $C_{1s}$ and (b) $O_{1s}$.

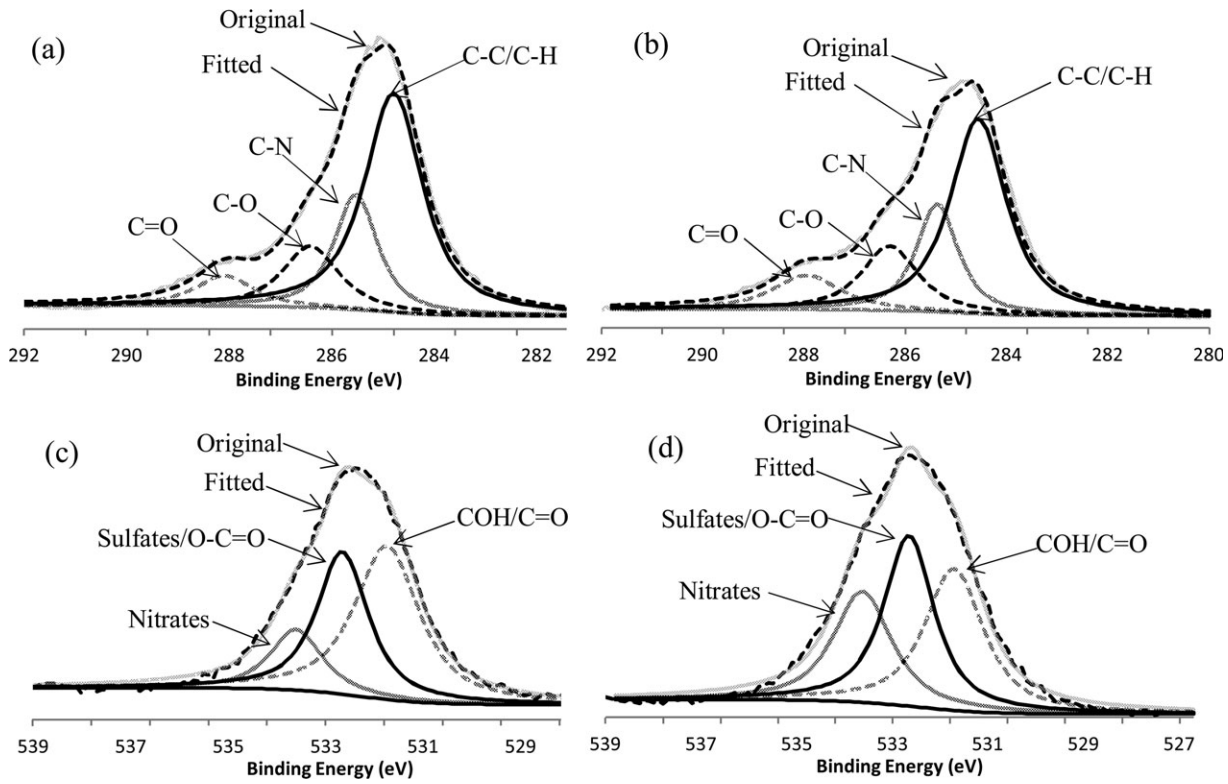


**Figure 4.** Deconvoluted XPS $C_{1S}$ and $O_{1S}$ core level spectra of (a,c) untreated wool fibers and (b,d) plasma-treated (1250 W min/$m^2$) wool fibers.

### PCM Microcapsule Size Distribution

A broad size distribution was observed in the dispersed microcapsules, with sizes ranging from 1 to 110 $\mu$m [Figure 5(a)]. The average diameter of the microcapsules was 47.0 $\mu$m. The larger particle size observed could be attributed to aggregates of smaller microcapsules or to nonuniform mixing during the reaction. To characterize the shape and surface topography of the microcapsules, SEM was also performed. Figure 5(b) illustrates the microcapsules fixed on the wool fiber. Three different sizes of microcapsules can be observed in Figure 5 (40.4, 12.5, and 17.3 $\mu$m).

### Effect of the DBD Plasma Discharge on PCM Microcapsule Adhesion

**SEM.** SEM was used to evaluate the morphology of the samples of wool fibers without and with plasma treatment finished with PCM microcapsules. As shown in Figure 6(a,b), several PCM microcapsules were fixed on the surface of the fabrics; we noticed that the surface modification of the wool substrate caused by DBD plasma treatment [Figure 6(b)] permitted the fixation of more microcapsules compared with the untreated sample [Figure 6(a)].

Plasma treatment increased the wettability/hydrophilicity of the wool fibers and caused a better adsorption of the reactants (crosslinker and PCMs) and more effective absorbance at the surface.

After one washing cycle, the number of microcapsules decreased in the samples without plasma treatment; on the contrary, we observed that in the samples pretreated with plasma, the presence of a high quantity of the crosslinker was responsible for the PCM fixation [Figure 6(c,d)].

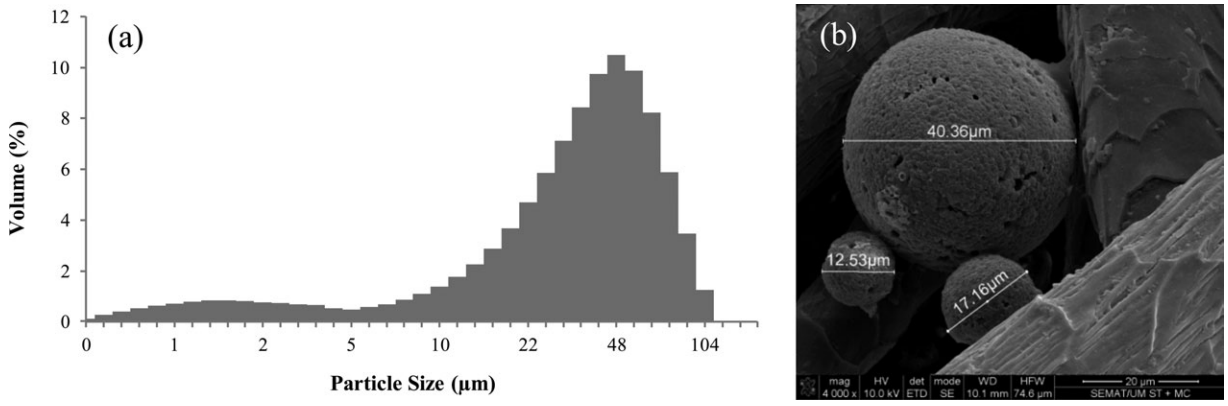


**Figure 5.** PCM microcapsule size distribution and SEM micrograph.

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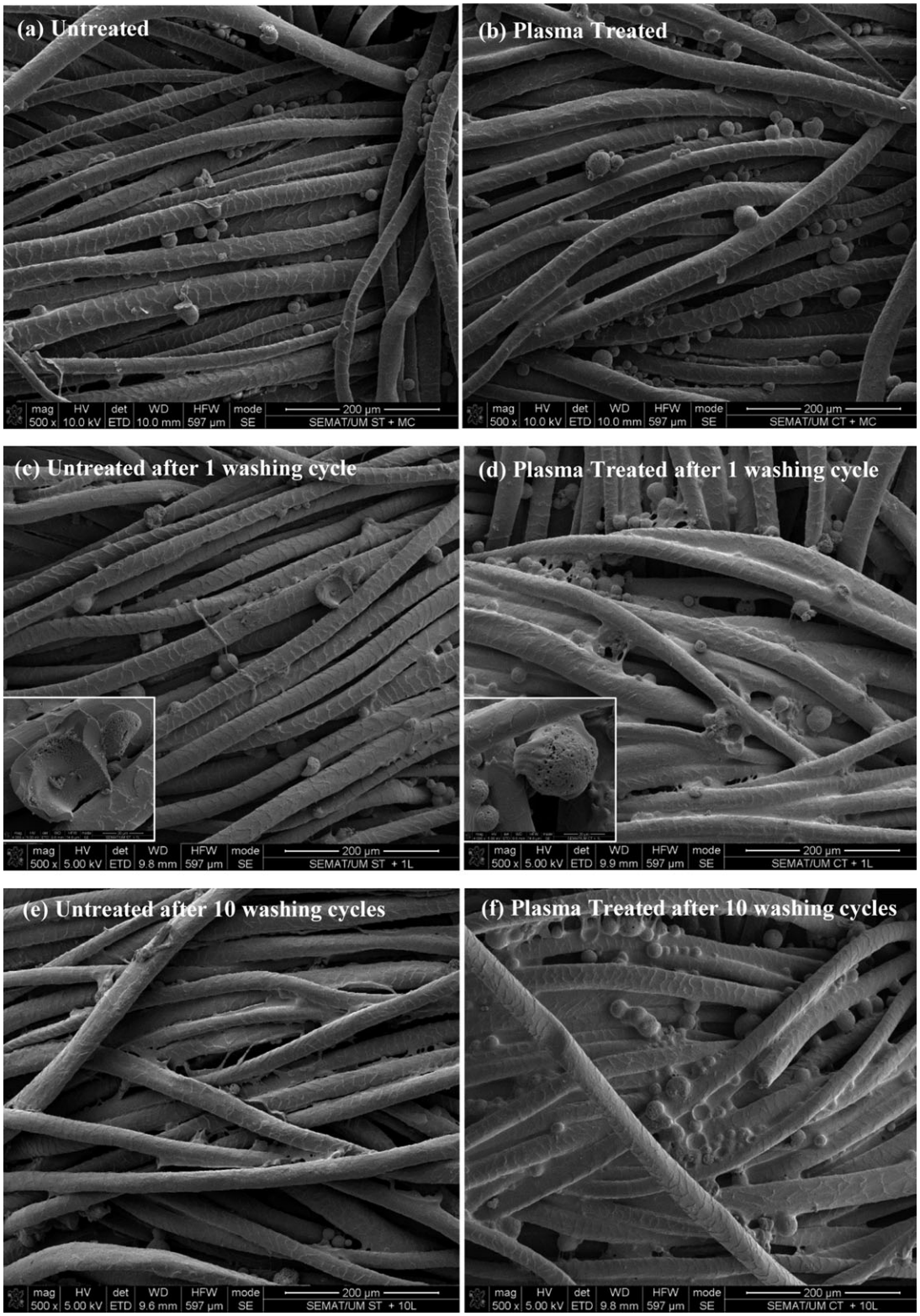


**Figure 6.** SEM micrographs obtained with secondary electrons (SE) of the untreated and plasma-treated (1250 W min/m$^2$) wool fabric with PCM microcapsules before and after washing fastness test.

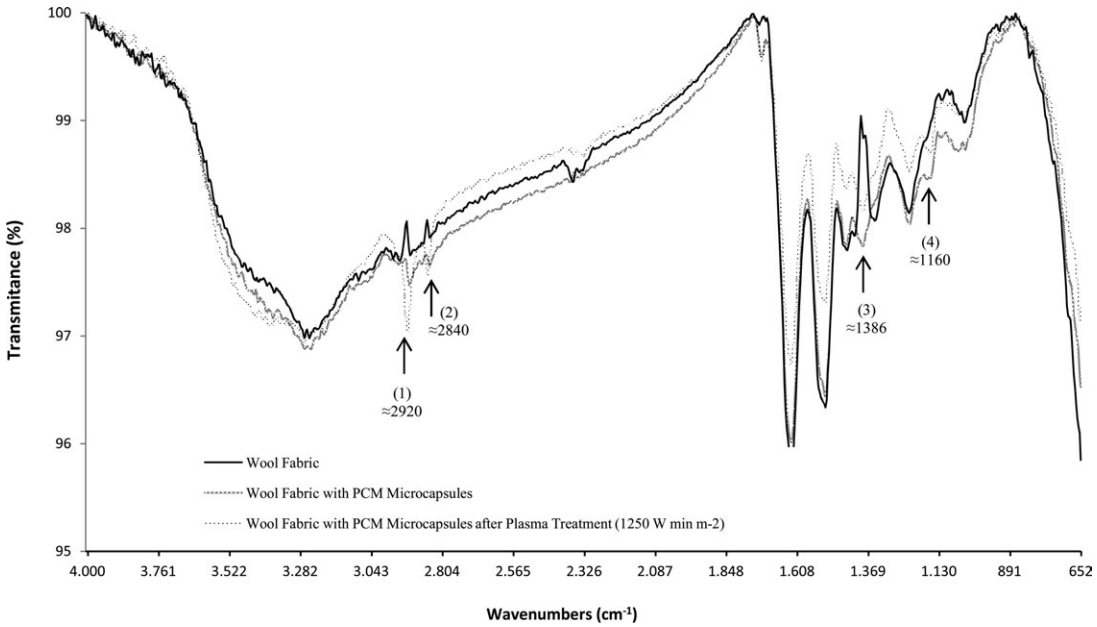


**Figure 7.** FTIR spectra of wool fabric, wool fabric with PCM microcapsules, and wool fabric with PCM microcapsules after DBD plasma treatment.

After 10 washing cycles, it was possible to see that some microcapsules were removed in the sample treated with DBD plasma, although the majority was still fixed to the fabric [Figure 6(f)] compared with the untreated wool [Figure 6(e)].

The results could be explained by previous studies,[9,25,20,23,25] which demonstrated that wool fabric becomes more hydrophilic and the work of adhesion is increased after plasma treatment. The polar functional groups formed by means of plasma treatment make the external substances attach more easily to the wool substrate.[25]

Another explanation for the major effects of the plasma treatment adhesion enhancement results from overlap effects: the removal of the organic contamination of weak boundary layers by cleaning or ablation and the creation of chemical groups by surface oxidation, as shown by the XPS results, which could interfere with strong interaction bonding between the wool fiber and the binder used.

**FTIR Spectroscopy.** Figure 7 shows FTIR spectra of the following samples: the wool fabric (control), wool fabric with PCM microcapsules, and plasma-treated wool fabric with PCM microcapsules. In Figure 8, the FTIR spectra of the melamine PCM microcapsules are presented. The appearance of four characteristic peaks of the melamine microcapsules after their

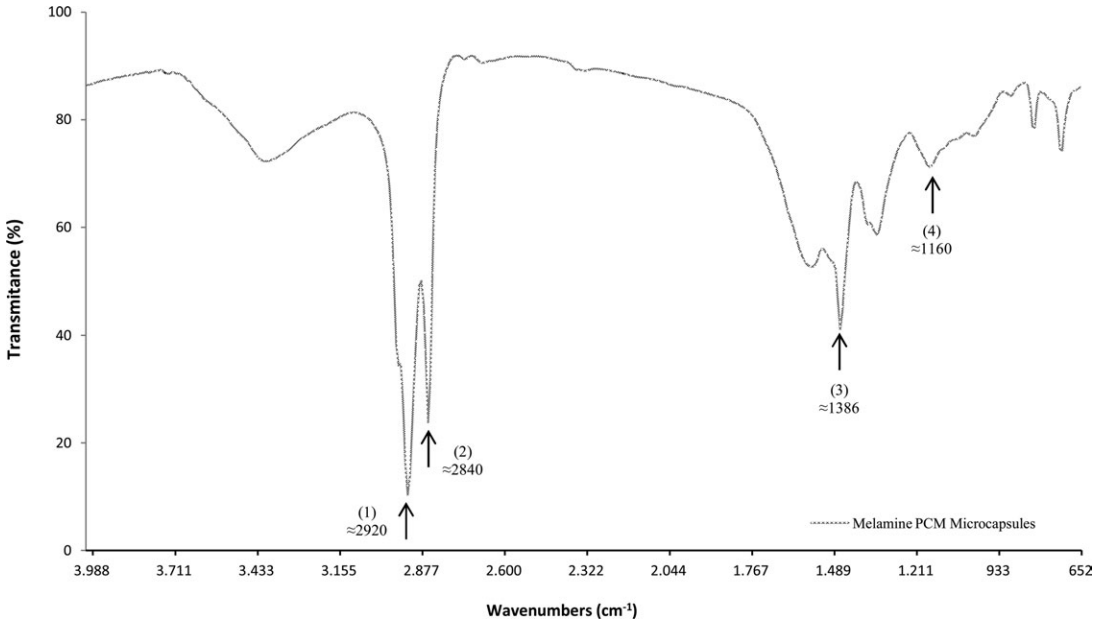


**Figure 8.** FTIR spectra of the melamine PCM microcapsules.

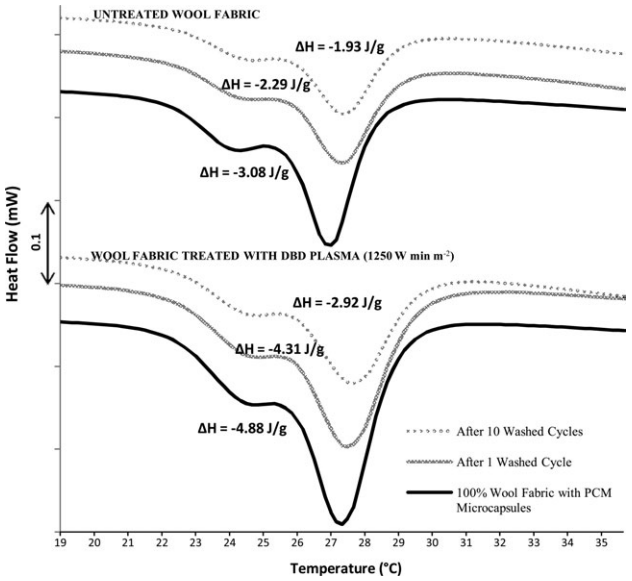


**Figure 9.** DSC thermograms of the untreated and plasma-treated wool fabric with PCM microcapsules before and after the washing test ($\Delta H$ = enthalpy).

application was noticed. The peaks were N—H stretching vibrations at about 2920 $cm^{-1}$, C—H stretching vibrations at about 2840 and 1386 $cm^{-1}$, and C—O stretching vibrations at about 1160 $cm^{-1}$.

These four peaks were slightly higher for the sample treated with plasma; this proved that more microcapsules were adhered to the DBD-plasma-treated wool.

**DSC.** Figure 9 shows the differences obtained in the energy storage capacity of the coated textiles by comparison of the samples with and without plasma treatment before and after the washing tests. By means of enthalpy (Joules per gram), the evaluation of the amount of PCM microcapsules that were fixed to the fiber was done.

An increase in the energy storage capacity in the samples treated with plasma was observed; this confirmed that plasma treatment increased the adsorption capacity with regard to the PCM microcapsules. Figure 9 also shows the DSC curves of the untreated and DBD-plasma-treated 100% wool fabric padded with PCM microcapsules and the same samples after 1 and 10 washing cycles.

As could be verified, the adhesion of the PCM microcapsules in the plasma-treated-wool increased considerably. In the untreated wool, the enthalpy decreased 25.7% after 1 washing cycle, whereas in the DBD-treated wool, the enthalpy only decreased 11.7%. After 10 washing cycles, the enthalpy of the treated sample (−2.92 J/g) was approximately the same as that of the sample without treatment before the washing test (−3.08 J/g).

## CONCLUSIONS

Microcapsules have been used in textiles for a long time; however, their adhesion to textile fibers is not well known, and most cases are not very adequate with regard to common use. Microcapsulated products are relatively expensive, and the final products must respond to client demand. For this reason, it is important that they be able to remain fixed on the fabric, withstanding many washes and rubbing action. Wool fabric was treated with DBD plasma discharge to modify the surface and promote the adhesion of microencapsulated PCMs. The plasma treatment caused a decrease in the static and dynamic contact angles and an increase in the surface energy of the wool substrate. XPS analysis showed that the DBD treatment increased the amount of oxygen on the surface of the substrate, created more polar groups, and improved the hydrophilicity/wettability of the wool fiber. The work of adhesion was higher after plasma modification.

All of these modifications of the wool fiber after plasma treatment led to a remarkable increase in microcapsule adhesion to the fabric during finishing as compared to the untreated samples. When DBD treatment was applied to the wool fabric, the microcapsules were successfully fixed on the surface of the fiber, even after several washing cycles. DBD plasma treatment can be considered as an excellent solution for promoting the functional performance of textile products finished with PCM microcapsules, achieving more durable properties, and so contributing to the sustainability of innovative textiles.

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