FUNCTIONALIZATION OF TEXTILE MATERIALS BY DOUBLE BARRIER DISCHARGE PLASMA

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Abstract: *The pre-treatment of textile materials by non-thermal plasma technologies can offer many advantages over conventional chemical processes used to surface modification. This technology doesn't involve the use of water and chemical reagents, resulting in a more eco-friendly and economical process. In this study air atmospheric pressure plasma treatment at normal ambient conditions was applied in various textile materials, namely: polyamide, polyester, acrylics and wool.*
The pre-treated textile materials were characterized using advanced instrumental techniques including X-ray photoelectronic spectroscopy (XPS), differential scanning calorimetry (DSC) atomic force microscopy (AFM) and scanning electron microscopy (SEM). Wettability analysis with different liquids was conducted to study static contact angle as well as surface energy and adhesion work of the plasma-treated fibrous materials. Chemical and physical characterization of the fabric confirmed significant surface alteration. Surface modification concerning the improvement of adhesion regarding a functionalizing substance, i.e. phase change materials (PCM) microcapsules was also investigated.
Keywords: *plasma treatment, wettability, textile, surface modification, PCM*

1. Introduction

Recently, there has been an increase in the number of new textile products with one or more functionalities. In fact, around the world, the growing interest in textiles with new properties and high added value has been encouraging the industry to make greater use of several techniques that allow imparting new types of finishes and innovative properties to textiles materials.

Potential applications in textile substrates include fragrances, insect repellents, thermo chromic pigments, dyes, vitamins, antibiotics, specific medical applications, phase change materials, among others, using for instance, microencapsulation process. The central issue for the applications of microcapsules in textiles is a system that is easy to apply, does not negatively affect textile properties and allows normal care procedures of garments or home textiles [1].

Although research studies concerning the application of microcapsules to textile substrates are increasingly attracting interest, they primarily focused the microcapsules, binders and application techniques. Few studies are directed to the textile substrates modifications, which can highly improve microcapsules performance. This fact is very important since the microencapsulated materials are relatively expensive and in most part of the cases their adhesion behaviour on fibers is not very resistant to use.

In recent years, surface modification of textile materials by plasma treatment has opened up new possibilities in this field. In fact, plasma technology has increasingly been used in etching, deposition, or other modifications of various forms of textile materials to improve surface properties [2].

A cursory survey of the literature will reveal that plasmas are being used for wide range of applications related to textile surface modifications. Plasma is an ionized gas in a neutral state with an equal density of positive and negative charges. This state is defined as the fourth state of the matter and it can be achieved in an ample range of temperatures and pressures. Besides charged particles, plasmas also contain neutral atoms and molecules, excited atoms and molecules, radical and UV photons [4], independent of the gases used [3].

A non-thermal (or cold or low temperature) plasma is a partially ionized gas with electron temperatures much higher than ion temperatures. The high-energy electrons and low-energy molecular species can initiate reactions in the plasma volume without excessive heat and avoiding substrate degradation. Non-thermal plasmas are particularly suited to apply to textile processing because most textile materials are heat sensitive polymers [2, 3].

There are quite different available plasma methods. In the present work the dielectric barrier discharge (DBD) was employed. DBD is a type of cold plasma generated by a high electric discharge in atmospheric conditions. It consists of two parallel electrodes separated by narrow gap. In order to prevent arcs and short circuit between the electrodes, one or both electrodes are covered with suitable dielectric materials.

Various methods are used to characterize the polymer surfaces and evaluate the wettability performance of the polymers before and after plasma treatment. The most common among them utilizes liquid–solid contact angle measurements [5].

The purpose of this research has been the calculation of the energy of interaction (work of adhesion) in systems consisting of untreated and plasma-treated fabrics, as also as of the effect on the resistance of PCM microcapsules binding to the fibers. The experiments were conducted to determine the nature and magnitude of the fabric´s surface energy components acting in the wettability performance and their dependence on treatment conditions and dosage. In order to analyse the effect of plasmatic treatment on the fabrics and related PCM microcapsules adhesion, several techniques are used, namely contact angle measurements, XPS, DSC, AFM and SEM micrograph. The padded samples undergone washing fastness tests in order to evaluate the practical effect of the plasmatic reinforcement of PCM bonding to textile substrates.

2. Materials and Method

2.1 Fabrics and Microcapsules

The textile substrates used in this study were part of a multifiber fabric (ISO 105-F10) consisting of polyamide (PA), polyester (PET), acrylic (PAC) and wool (WO) fabrics.

The PCM utilized was a melamine microcapsule agent (PRETHERMO C-25) which consists primarily of the higher aliphatic hydrocarbon, which is the thermal storage agent. In order to bond the PCM microcapsules to the textile substrate, an acrylic binder agent labelled as IMP was applied. These products were kindly supplied by ATUSMIC (Portugal).

2.2 Plasma Treatment

The fabrics were treated in a laboratorial DBD plasma prototype machine. This equipment consists of a metal electrode coated with ceramic and a metal 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, with adjustable power and speed. Plasmatic dosage is defined by the equation 1 [6]:

$$\text{Dosage} = \frac{N \cdot P}{v \cdot l} \qquad (1)$$

Where, N = number of passages, P = power (W), v = speed ($m.min^{-1}$), and l = width of treatment (0.5 m).

Different dosages were applied according to following parameters: Speed: 4.0 $m.min^{-1}$; Power: 600 W; Number of passages: 1, 2, 3, 4, 5 and 6. Thus, the dosages applied to the samples were respectively 300, 600, 900, 1200, 1500, 1800 $kW.min.m^{-2}$.

2.3 Surface Energy and Work of Adhesion

Contact angles measurement and calculation of the fibers surface free energy was carried out in Dataphysics equipment using OCA20 software.
The work adhesion (W_{Adh}) equation (2), which represents the energy of interaction between the liquid and the solid phases per unit area, was calculated by means of water contact angle evaluation [7].

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

The polar (Y^D) and dispersive (Y^P) components of the surface energy (Y) were calculated using the Wu method (harmonic-mean) [8]. Since it is necessary at least two liquids for the calculation of surface energy, three liquids with known surface energy and surface energy components were used in this study, namely: distilled water (Y: 72.8; Y^D: 29.1; Y^P: 43.7), polyethylene glycol 200 (PEG) (Y: 43.5; Y^D: 29.9; Y^P: 13.6), and glycerol (Y: 63.4; Y^D: 37.4; Y^P: 26.0) [9].

2.4 Chemical and Morphological Characterization

The surface chemical composition of all the fabrics before and after plasma modification was determined by X-Ray photoelectronic spectroscopy using the VG Scientific ESCALAB 200A equipment. Surfaces of the plasma treated and the PCM coated samples were observed with an ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company. Atomic force microscopy (AFM) was used to verify surface topography and roughness of untreated and plasma treated samples. AFM analyses were performed with a multimode AFM microscope with a Nanoscope® IIIa ADCS controller (Veeco Metrology Group).

2.5 PCMs Microcapsules Application and Differential Scanning Calorimetry analysis

Microcapsules in a water solution were applied to the surface of the fabrics by padding process in a mini-foulard (pressure of 4 bar, velocity of 6 $m.min^{-1}$), and cured in a laboratory oven for 3 minutes at 140 ºC. The recipe of the solution was the following: PCM microcapsules - 160 $g.L^{-1}$; binder - 50 $g.L^{-1}$; and $MgCl_2$ - 5 $g.L^{-1}$. The pH was fixed at 5. Mettler Toledo DSC822 equipment was used in order to analyse and quantify the PCM energy absorption of the sample with and without DBD treatment before and after washing test.

3. Results and Discussions

3.1 Wettability, Surface Energy and Work of Adhesion

Wettability of textiles is affected by chemical changes acting as functionalization means induced by plasma treatment. The table 1 shows the results of contact angle average of fifteen measurements performed for each sample studied with three different liquids. As can be seen the water contact angles of the plasma treated fabrics decrease with increasing dosage as compared to the control samples.

Table 1: Solid surface energy γsv and its dispersive, γ^d and polar, γ^p components in $mJ.m^{-2}$

Samples		θ_{Water} (°)	θ_{PEG} (°)	$\theta_{Glycerol}$ (°)	γ ($mJ.m^{-2}$)	γ^D ($mJ.m^{-2}$)	γ^P ($mJ.m^{-2}$)	W_{Adh} ($mJ.m^{-2}$)
PA	Untreated	145.9	83.8	152.6	6.60	6.40	0.23	12.50
	300 $W.min.m^{-2}$	139.8	67.8	123.0	10.50	10.00	0.50	17.20
	600 $W.min.m^{-2}$	135.5	59.4	118.9	14.61	14.61	0.00	20.90
	900 $W.min.m^{-2}$	116.7	44.0	116.8	20.50	20.00	0.50	40.10
	1200 $W.min.m^{-2}$	80.3	38.7	117.3	23.17	9.84	13.33	85.10
	1500 $W.min.m^{-2}$	73.3	36.7	115.8	27.00	7.84	19.16	93.70
	1800 $W.min.m^{-2}$	62.0	35.4	112.7	36.77	5.27	31.50	106.97
PES	Untreated	162.4	65.0	138.9	10,50	10.00	0.50	3.40
	300 $W.min.m^{-2}$	23.6	49.6	122.6	35.50	10.00	25.50	139.50
	600 $W.min.m^{-2}$	20.5	47.0	102.8	118.09	0.16	117.93	141.00
	900 $W.min.m^{-2}$	10.0	37.1	104.9	119.15	0.65	118.50	144.50
	1200 $W.min.m^{-2}$	4.3	33.3	104.8	117.96	0.93	117.03	145.40
	1500 $W.min.m^{-2}$	0.0	31.3	104.1	116.01	1.17	114.84	145.60
	1800 $W.min.m^{-2}$	0.0	33.3	105.0	119.01	0.88	118.13	145.60
PAC	Untreated	23.4	74.6	119.9	35.50	10.00	25.50	139.60
	300 $W.min.m^{-2}$	0.0	45.8	94.8	133.51	0.80	132.71	145.60
	600 $W.min.m^{-2}$	0.0	45.5	87.7	127.60	1.75	125.85	145.60
	900 $W.min.m^{-2}$	0.0	31.4	87.5	107.70	3.37	101.33	145.60
	1200 $W.min.m^{-2}$	0.0	27.7	94.5	107.52	2.71	104.81	145.60
	1500 $W.min.m^{-2}$	0.0	27.2	97.0	108.23	2.41	105.82	145.60
	1800 $W.min.m^{-2}$	0.0	32.9	94.0	112.67	2.30	110.37	145.60
WO	Untreated	166.2	132.3	159.5	3.89	3.89	0.00	2.10
	300 $W.min.m^{-2}$	113.6	54.0	135.1	15.50	15.00	0.50	43.70
	600 $W.min.m^{-2}$	81.7	47.0	120.9	22.23	7.99	14.24	83.30

	900 W.min.m^{-2}	64.0	34.6	115.5	34.33	5.52	28.81	104.70
	1200 W.min.m^{-2}	45.0	28.3	117.6	56.63	2.53	54.10	124.30
	1500 W.min.m^{-2}	35.2	27.5	123.6	73.20	0.93	72.27	132.30
	1800 W.min.m^{-2}	0.0	29.3	100.2	111.82	1.81	110.01	145.60

It is noted that plasma treatment increases the total energy surface Y. The dispersive term does not depend on the plasma conditions whereas the polar term increases significantly after DBD plasma treatment [7].
Table 1 also clearly shows that there is a pronounced rise in the work of adhesion over a short dosage of plasma treatment and then steadily increases with more intense plasma conditions.

3.2 Chemical characterization

The chemical composition of the external polyamide, polyester, acrylic and wool fibres surface of untreated and DBD plasma-treated were analysed by the XPS technique. Characteristic changes of the elemental surface composition of plasma-treated fibers can be observed in Table 2.

Table 2: Elementar composition (%) e atomic ratio for the untreated and treated (1800 W.min.m^{-2}) samples.

Samples		Atomic Composition [%]				Atomic Ratio		
		C_{1s}	O_{1s}	N_{1s}	S_{1s}	O/C	N/C	S/C
Polyamide	Untreated	74.67	17.75	7.58	-	0.24	0.10	-
	Treated	70.25	19.83	9.92	-	0.28	0.14	-
Polyester	Untreated	74.67	25.29	0	-	0.34	0.00	
	Treated	64.17	35.42	0.41	-	0.55	0.01	
Acrylic	Untreated	79.51	11.84	8.65	-	0.15	0.11	-
	Treated	72.37	16.95	10.68	-	0.23	0.15	-
Wool	Untreated	77.00	13.50	6.74	2.75	0.17	0.08	0.04
	Treated	73.32	19.18	5.32	2.18	0.26	0.07	0.03

Atomic composition (%) of the C_{1s} decreases, whereas the O_{1s} peak rises by increasing the plasma dosage for all the fibers. The increase in the O/C atomic ratio implies a rise in the level of oxygen-based functional groups in the surface when the plasma treatment is applied. The nitrogen content (N_{1S}) increment regarding the polyester, polyamide and acrylic fibers shows that nitrogen related chemical reactions were involved because N_2 gas exists in atmospheric pressure plasma.
The results obtained in contact angle, surface energy and XPS analyses showed a marked increasing effect of the functional polar groups with plasmatic discharge treatment in textile materials, which influences positively the wettability of materials. Similar results are reported in the literature to different textiles materials [7,8,10].

3.3 Morphological characterization

Figure 1 shows the SEM micrographs of the polyester and wool samples before and after DBD plasma treatment (1800 W.min.m^{-2}). The roughness was found to increase with the plasma treatment.

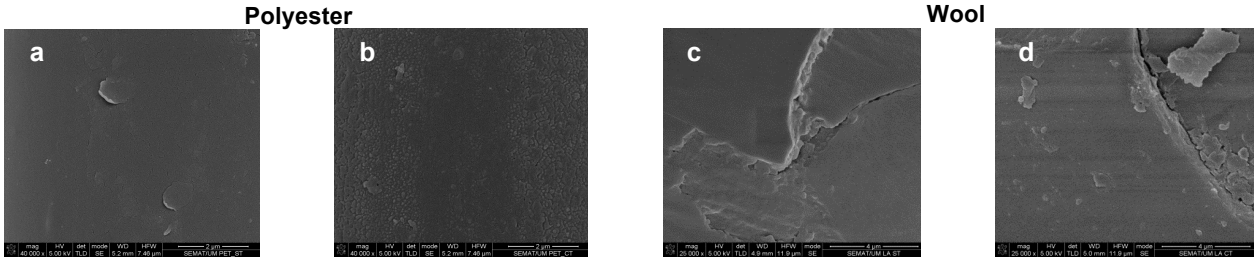

Figure 1: SEM images of polyester and wool fabrics before (a) (c) and after plasma treatment (b) (d) respectively.

According to the literature most of non-polymerizable gases (namely Ar, O_2, N_2, He) are apparently effective on etching [11-12]. The figure 2 shows the roughness obtained before and after DBD plasma treatment in PET fabric by atomic force microscopy technique.

Figure 2: AFM images of polyester fabrics before (a) and after plasma treatment (1800 W.min.m^{-2}) (b)

Plasma treatments of the fibers create a rougher surface, which may allows the formation of more contact points between the fiber and the coating by means of physical interaction, favouring the adhesion between coating agents and the fibers [13].

3.4 Differential Scanning Calorimetry

Table 3 shows the difference obtained in energy storage capacity of the coated PET, WO and PA textiles when compared the samples with (1800 W.min.m^{-2}) and without plasma treatment before and after washing tests. By means of enthalpy (J.g^{-1}) evaluation is possible to verify the amount of PCM microcapsules that are fixed to the fiber.

Table 3: Entalpy (J.g^{-1}) results of the samples untreated (UN) and plasma treated (T) before and after (*) 10 washing cycles.

Samples	PET				WO				PA			
	UN	T	UN*	T*	UN	T	UN*	T*	UN	T	UN*	T*
ΔH (J.g^{-1})	-2.71	-3.30	-2.43	-3.25	-3.24	-5.44	-2.22	-4.59	-2.78	-3.74	-2.26	-2.63
Peak (ºC)	26.7	26.7	26.7	26.8	26.4	26.4	26.5	26.6	26.3	26.3	26.3	26.6

An increase in energy storage capacity in the samples treated with dosage of 1800 W.min.m^{-2} can be observed, which confirms that plasma treatment increases the adsorption capacity of the textiles towards PCM microcapsules. As can be verified, the adhesion of the PCM microcapsules in treated fabrics considerably increases. For instance, while in the untreated wool, enthalpy has decreased 31.1 % after 10 wash cycles, in DBD treated wool the enthalpy only decreases 15.6 %. After 10 washing cycles, the enthalpy of the treated sample (-4.59 J.g^{-1}) is approximately 30 % of the value concerning the sample without treatment before washing test (-3.24 J.g^{-1}).
Figure 3 shows the SEM images of untreated and DBD plasma treated wool fabric, padded with PCM microcapsules, and the same samples after ten washing cycles. It is possible to observe that several PCM microcapsules are fixed on the surface of the fabrics. Plasma treatment increases the wettabilitity/hydrophilicity of fabrics causing a better adsorption of the reactants (cross linker and PCM) and more effective bonding at the surface. After washing cycles, the number of microcapsules has decreased in the samples without treatment and the presence of the cross linker in the sample pre-treated with plasma is noticed.

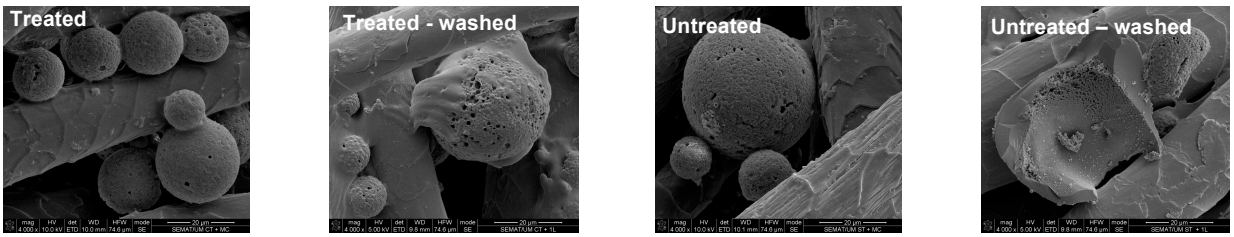

Figure 3: SEM images of PCM microcapsules fixed on wool fabrics with and without plasma treatment before and after 10 washing cycles

The results confirm that SEM analysis is in total accordance with DSC analysis previously shown.

4. Conclusions

Polyamide, polyester, acrylic and wool fabrics were treated with a DBD plasma technique to modify their surface energy in order to increase the adhesion of PCMs microcapsules coatings. Plasma treatment has caused the decrease of the contact angle and an increase of the hydrophilicity due to an increase of the surface energy of the fibres. These modifications are caused by the generation of functional polar groups demonstrated by the increase of chemical groups with O and N atoms, as shown by XPS measurements. In addition, the increased roughness of the fabrics after plasma treatment as verified by AFM and SEM measurements can be a promoter of surface adhesion. The DSC results showed a significant increase in the amount of PCMs microcapsules fixed in the fabrics pre-treated before and after washing cycles. The plasma treatment creates micro-roughness on the surface of the fibres, resulting in a better mechanical interlocking fibres-microcapsules, and also functional groups, leading to chemical interfacial bonding between the fibre and the binder. The plasma treatment can be used to produce different surface states for distinct and desired textile attributes. Plasma can be considered as an environmentally-sound technology, an energy-efficient approach to textile finishing. The importance of cost-competitive atmospheric plasma treatment emphasizes its explosive increase in interest and use in industrial, particularly in the field of promoting adhesion for textile coating applications.

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