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Enhancement of Poly(Ethylene Terephtalate) Adsorption Using a Green Process

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***Abstract*— This paper deals to the enhancement of the polyester woven's hydrophilicity using a green process. Firstly, we have functionalized the polyester surface by air atmospheric plasma using a Dielectric Barrier Discharge DBD system. The results of the water contact angle (°) and capillarity (%) demonstrate the improvement of the hydrophilicility of polyethylene terephtalate surface. The durability of hydrophilicity improvement was investigated by grafting Sericin on the plasma treated polyester surface. Besides, the zeta potential measurements and X-ray Photoelectron Spectroscopy (XPS) analysis were performed to confirm the hydrophilic character imparted to the polyethylene terephtalate surface by the introduction of polar groups after air atmospheric plasma treatment and Sericin grafting. The morphologies of samples fabrics were studied by a scanning electron microscopy (SEM).**

***Index Terms*—Air atmospheric plasma, Durability, Hydrophilicity, Sericin.**

I. Introduction

Generally, the problems connected with textile hydrophobicity reducing are usually solved by chemical modifications of textile surfaces. For decades, many researches focused on the cold plasma as a new technology of the surface materials and textiles modification [1]. Mostly, plasma treatment was used for the enhancement of the surface hydrophilicity and above all of the man-made textiles [2]-[3] such as polyester which is known by its poor wetting behavior in aqueous liquids. Leroux et al. [4] have showed that after an air atmospheric plasma treatment of the Poly (ethylene terephtalate) fabrics under 60 kJ power treatment, the water contact angle decrease from 80° to 40-50° and the capillarity increase until 80% independently of fabric structure. Besides, Flor et al. [5] have demonstrated using XPS analysis that the improvement of hydrophilicity is due to the incorporation of the amine and carboxylic groups on the PET surface treated using air radio frequency plasma. Therefore, the reactive plasma particles; such as ions, electrons, excited atoms and photons; provide the breaking of covalent bonds by the collision phenomenon [6] to create free radicals and functional groups on the treated surface. The wettability enhancement of polymeric surfaces can be obtained easily by plasma treatment in oxygen containing gas. However, after exposure to air, the wettability is not durable due to the ageing process [7]. For the textile applications of wettability enhancement, increased durability has been obtained using plasma graft polymerization techniques. The monomers used in plasma graft polymerization for wettability enhancement are acrylic acid [8]-[9]-[12], nitro compounds [10], 2-hydroxyethyl methacrylate (HEMA) [11]-[12], methyl methacrylate (MMA) [11] and acrylonitrile [13]. Besides, surface plasma activation can be followed by adhesion of resin matrix [14] or coating of polymers. In our study, we have immobilized the plasma functional groups by Sericin crosslinking. Sericin is a gummy water-soluble protein helding Fibroin fibers derived from silkworm Bombyx mori. It constitutes about 20-30% of total cocoon weight [15]. In fact, Sericin is mostly rejected as a silk processing's wastewater [16]. Therefore, many researchers were working on extracting and recovering Sericin from wastewaters to reduce their environmental impact and mainly to benefit from its various physico-chemical properties [17]- [18]. Principally, Sericin is characterized by excellent moisture-absorbing and desorbing properties which are mainly attributed to the amount of hydrophilic amino acids of Sericin protein as it is shown in Tables 1. Therefore, Sericin has various applications in diversified fields such as cosmetics, medical [19], moisturizers etc [16].

Name of amino acids	% of total Sericin weight [20]	Nature
Glycine	10.70	Hydrophobic
Alanine	4.30	Hydrophobic
Valine	3.80	Hydrophobic
Leucine	1.70	Hydrophobic
Isoleucine	1.30	Hydrophobic
Methionine	0.50	Hydrophobic
Phenylalanine	1.60	Hydrophobic
Cystine	0.30	Hydrophobic
Proline	1.20	Hydrophilic
Tyrosine	4.60	Hydrophilic
Tryptophane	0.56	Hydrophilic
Serine	27.30	Hydrophilic
Threonine	7.50	Hydrophilic
Aspartic acid	18.80	Hydrophilic
Glutamic acid	7.20	Hydrophilic
Arginine	4.90	Hydrophilic
Lysine	2.10	Hydrophilic
Histidine	1.70	Hydrophilic

Table. 1. Different amino acids present in Sericin from degumming solution.

As a protein, Sericin has mainly acid-basic sites: carboxylic and amine groups. Hence, it is global charge depend to the pH of bah solution.

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In this study, air atmospheric plasma has been investigated to improve the hydrophilicity of polyethylene terephtalate PET woven fabric. In order to assure the durability of the surface modification behavior, the PET fabrics were grafted with Sericin. The physical and chemical properties of fabrics treated and grafted were explored with several analyses such as the measurements of water contact angle (°), capillarity (%) and the surface global charges using zeta potential measurement. X ray analysis was used to investigate the chemical composition of samples. The fabric surface morphology was studied by a scanning electron microscopy (SEM).

II. Experimental

A. Materials

The polyester fabric used was purchased from *Bekir's Modern weaving company*, Tunisia. The properties of fabric are given in Table 2. Sericin powder, with a molecular weight of 20, was purchased from *Shantou TJ Fine Chemical Co., LTD* , China. Acetic Acid, Glutaraldehyde (*Sigma*) and Toluidine Blue (*Sigma).*

Fabric type	Area density (g/m²)	Wraps/cm	Wefts/cm	Structure
Polyester	100	30	24	Plain

Table 2. Properties of woven fabric used

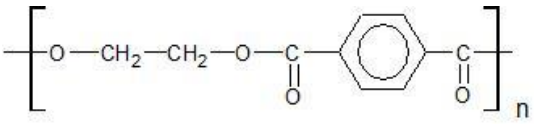

Fig. 1. Chemical structure of polyester.

B. Activation of textile surface using DBD Plasma

Fabric samples were previously scoured to remove spinning oil and contaminants on the fabrics surface, then rinsed with deionized water and finally dried for 24h at ambient temperature.

Polyester samples were treated with an air atmospheric plasma machine called ''Coating Star'' manufactured by Ahlbrandt System (Germany). It consisted of two electrodes made of ceramic, the difference potential between them creates a glow discharge called Dielectric Barrier Discharge [21]. The distance between counter electrode and electrodes was adjusted to 1.5cm. The following machine parameters were kept constant: electrical power of 750 W, frequency of 30 kHz and speed of 2 m/min. The both sides of fabric were exposed to the plasma discharge.

C. Immobilization of plasma functional groups

Plasma treated and untreated polyester samples were padded in a water solution with 1% (w/w) glutaraldehyde GTA and 4 g/L Sericin at ambient temperature for 60 min. The pH was maintained at 3.5 by using acetic acid. The samples were then squeezed and dried at 40°C for 30 min. The grafted fabrics were washed separately several times at 30°C for 10 min until removing the unfixed Sericin.

D. Characterization of polyester fabrics

The hydrophilicity of fabric was determined by means of water contact angle (°) and capillarity (%) measurements. The test was carried out with tensiometer "3S Balance" from GBX instruments according to the Wilhelmy principle method. As it is shown in Fig.2, the rectangular-shaped fabric sample was brought in contact with liquid in the container which could move vertically up and down.

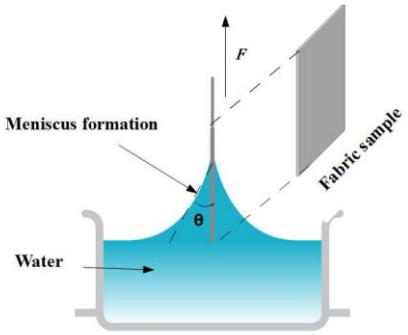

Fig. 2. Principle of contact angle measurement using Wilhelmy method

The water contact angle of textile samples can be determined using equation (1):

$$W_m \times g = \gamma_L \times \cos\theta \times p \qquad (1)$$

Where p is sample perimeter in contact with the liquid (mm), W_m is calculated meniscus weight (g), g is equal to 9.81 $g.s^{-2}$, γ_L indicates surface tension of the liquid (mN m^{-1}) and θ is contact angle (°).

The meniscus weight W_m is determined using the following equation:

$$W_m = W_t - W_c \qquad (2)$$

Where *Wt* indicates the total weight at the end (g) and W_c is the capillarity weight at the end (g).

The capillarity is the ratio between the capillarity weight (W_c) and the initial weight (W_i) of the dried sample:

$$C\% = \frac{W_c}{W_i} \times 100 \qquad (3)$$

The surface zeta potential was measured by Zetacad equipment. The measurement was carried out with a KCl electrolyte solution (0.001mol /L) at the pH 7 and at the pH region of 3-10. Samples were kept in the electrolyte solution for 24 h to reach equilibrium before making measurements.

The chemical composition of polyester fabric samples were analyzed by X-ray Photoelectron Spectroscopy (XPS). XPS spectra were performed in a VG ESCALAB 220XL spectrometer by means of non-monochromatic Mg Kα x-radiation source. The analyser pass energy was 160 eV for survey scans and 40 eV for high resolution scans. The measurements were carried out in a vacuum atmosphere (around 10^{-7} Pa).

The fabric surface morphology was investigated by a scanning electron microscopy (SEM).

III. Results and Discussion

The Dielectric Barrier Discharge plasma unit used allows to treat continuously the woven fabrics. It is one of the most effective atmospheric plasma sources for industrial applications in view of its adaptability to various systems [22].

A. *Contact angle and Capillarity measurements*

The results in Fig. 3 and Fig. 4 show a significant enhancement in the hydrophilicity of polyester fabric surface using air atmospheric plasma. Here, the measurements of water contact angle and capillarity of fabrics was made firstly after one day of plasma treatment, then after one month and six months. As it is shown in Fig. 3, after one day, the water contact angle decreases with plasma treatment from 81° to 39°. The same result was achieved after Sericin crosslinking. In fact, the interaction of air plasma species (ions, electrons radicals,…) with polymers causes the creation of C=O, OH and COOH groups [6]-[8]. Besides, the increase of the fabric's capillarity (Fig. 4.) from 3% to 50% proves that plasma irradiations can achieve the inner layers of the treated surface. The higher capillarity value 85% was reached after grafting Sericin on the plasma treated fabric. It is very important to make a durable surface enhancement. Therefore, we have analyzed the samples hydrophilicity after one month and after six months. The results in Fig.3 show that the hydrophilicity improved was more permanent for the samples plasma-treated then Sericin-grafted. After 6 months, the plasma treated fabric surface get back to its original behavior while the treated –grafted Polyethylene Terephtalate maintains its achieved state independently of time. In this case, the increase in wettability of surface is caused by the polar groups added by Sericin's polymers. Therefore, it allows the benefit of the functional groups created by plasma treatment to gaft Sericin polymers.

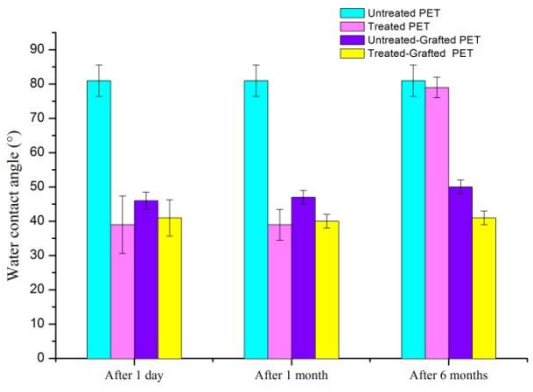

Fig.3. The durability of hydrophilic modification in terms of water contact angle (°) of the woven polyester fabric treated differently.

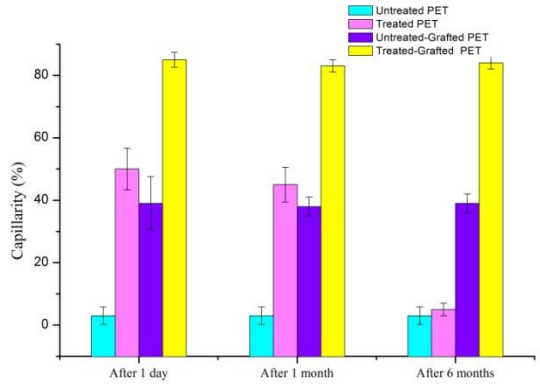

Fig.4. The durability of hydrophilic modification in terms of % capillarity of the woven polyester fabric treated differently.

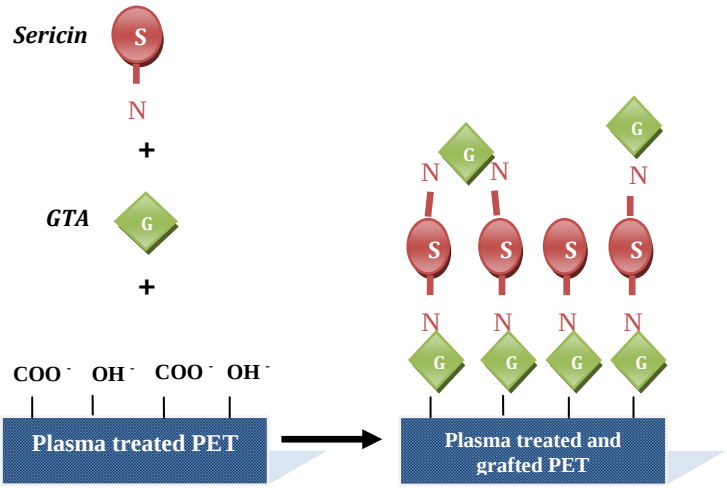

Fig. 5. Representation of Sericin crosslinked onto a plasma treated surface reaction.

However, Glutaraldehyde GTA, the crosslinking agent used in our study, tends to induce intra-molecular crosslinking by enhancing the probability that sericin functional groups react with the PET surface ones. The reaction of sericin crosslinking is presented in Fig. 5. GTA highly reacts with proteins [23] by forming bonds with amine groups [24]. On the other side, GTA reacts with the PET surface groups generating a chemically stable crosslinks. Therefore, the functional groups introduced in plasma treated surface fabrics allow the improvement of the hydrophilicity by crosslinking much more Sericin polymers than the untreated fabrics.

B. *Zeta potential measurements*

The zeta potential was investigated to determine the functional groups of the surface fabrics. The negative charges of the PET fabric are due to the carboxylic groups present at

the chain ends which are expected to add hydrophilic character to the treated samples. As it is shown in Fig. 6, the decrease of zeta potential values of fabric treated with plasma is due to the increase of COO- groups created on the surface of PET which are more significant with plasma treated surface fabric. Indeed, as pH increases the surface of PET becomes more negatively charged due to the ionization of carboxylic acid groups into carboxylate ions COO^- groups. But, for the fabrics grafted with Sericin and independently of plasma treatment, the surface charges were positive indicating the presence of NH_3^+ groups which are related to the existence of Sericin on PET surface.

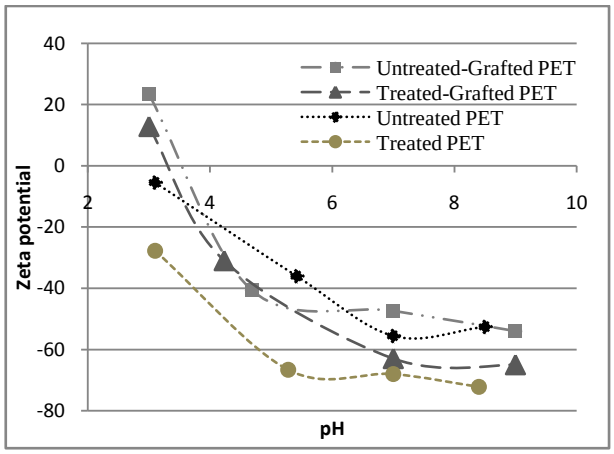

Fig.6. Zeta potential measurements of the polyethylene terephtalate surface.

C. XPS analysis

Surface modification and crosslinking were examined by X-ray Photoelectron Spectroscopy (XPS). Peaks of carbon, oxygen and nitrogen binding energy are located at 285 eV, 532 eV and 400 eV respectively. The results presented in Table 3 show that the C1s peak of the plasma treated surface is lower than of the untreated one and similar to treated-grafted with Sericin. Besides, the O1s peak decreases after Sericin grafting. However, the appearance of N1s atomics is assigned to Sericin polymers incorporated onto PET grafted surface and contributing to the improvement of hydrophilcity.

Surface chemical compositions [%]	Untreated PET	Treated PET	Treated grafted PET
C 1s	75	72	76
O 1s	23	22	17
N 1s	0	0	4,406
O/C	31,23	30,74	22,87
N/C	0,00	0,00	5,76

Table 3. Atomic compositions on the plasma-treated surface and Sericin-grafted.

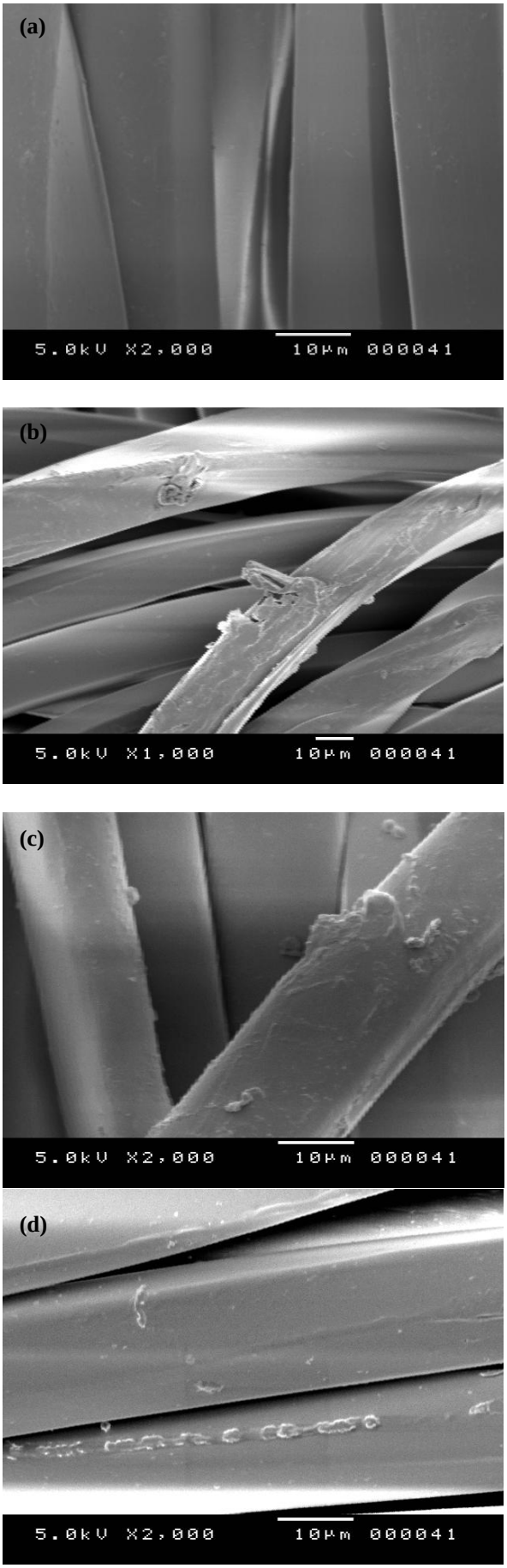

Fig. 7. SEM micrographs of PET (a) untreated (b) treated (c) untreated and grafted (d) treated and grafted.

A. *Surface morphologies of PET surface*

The SEM micrographs illustrated with Fig. 7. present the surface morphologies of the polyester surface fabrics. Fig. 7 (a) shows a slight degradation of the polyester surface after plasma treatment. In fact, polyester as thermoplastic fibers can be exposed to a thermal degradation at a high power. Thus, this morphological distinction is attributed to the fragmentation of polymer chains caused by plasma irradiations. The bisters on the surface grafted, illustrated by Fig. 7 (c) and (d), are mainly attributed to the polymerization of Sericin with the PET surface.

IV. Conclusion

Surface modification of polyester woven fabric by plasma treatment has been of increasing interest. Nevertheless, the functional groups, and mainly created under air as a plasma gas, are not stable over time and the surface can restore its original state. The grafting of Sericin proteins onto the plasma treated surface decreases the water contact angle from 81° for the untreated PET to 39° for the plasma treated-grafted one. Besides, the capillarity increases from 3% to 85%. The most important is that the Sericin grafting allows a durable enhancement of hydrophilicity of the polyethylene terephtalate fabric surface. This is mainly attributed to the introduction of polar groups after air atmospheric plasma treatment which are significantly reacting with Sericin polymers. Therefore, the existence of Sericin onto PET surface was proved by zeta potential measurements, XPS analysis and SEM micrographs. Consequently, the plasma treatment opens ideal perspectives in the textile industry to achieve an ecological dry processing and costs saved in order to enhance the hydrophilicity of polyester fabrics. Likewise, we can benefit from biological products such as Sericin to ensure the durability of this treatment as continuity of the ecological process.

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