

Modification of Polyester and Polyamide Fabrics by Different in Situ Plasma Polymerization Methods

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In order to increase the hydrophilicities, and therefore to impart soil resistance and to improve dyeability, poly(ethylene terephthalate) (PET) and polyamide (PAm) fabrics were treated in low-temperature plasmas. Five different modification types were applied. Fabrics were directly treated in acrylic acid, water, air, O₂ and argon plasma. The plasma conditions (i.e., exposure time and discharge power) were changed to control the extent of plasma surface modification. Wettability, soil resistance and dyeability of PET fabrics were significantly improved by this method. More hydrophilic surfaces were created by all the methods.

Key Words: PET and PAm fabrics, Plasma Polymerization, Modification, Wettability, Dyeability, Soil resistance

Introduction

Over the past decade there has been rapid exploration and commercialization of low-temperature plasma technology to improve the surface properties of polymeric materials without changing the bulk properties¹⁻⁵. Increased attention has also been paid to improving several properties (i.e., wettability, water repellence, soiling, soil release, printing, dyeing and other finishing processes) of textile fibers and fabrics by plasma technology⁶⁻¹⁶. In most of these studies two major types of discharges have been considered, i.e., high frequency discharge (low pressure plasma) and low frequency discharge (corona discharge). Low-temperature plasma under atmospheric pressure was also applied by Wakida et al.¹⁷. Plasma treatments for surface modification of textiles were performed by usually two main procedures, i.e., depositing plasmas and nondepositing plasmas. Depositing plasmas were usually applied by using saturated and unsaturated gases (e.g., fluorocarbons, HMDS, C₂H₄) or vapors (monomers) (e.g., acetone, methanol, allyamine, acrylic acid). Several reactive etching (i.e., Ar, He, O₂, N₂, F₂) or nonpolymerizable gases (H₂O, NH₃) were used in nondepositing plasmas.

In the present study we incorporated functional groups on the surfaces of poly(ethylene terephthalate) (PET) and polyamide (PAm) fabrics using five alternative plasma treatment procedures to modify their wettabilities for improving their dyeabilities and soil resistances.

In situ polymerization of acrylic acid, water, air, argon and O₂ was achieved in a glow-discharge reactor. The plasma conditions (i.e., exposure time and discharge power) were changed to control the extent of plasma surface modification. Details of surface modifications and characterization have been given elsewhere in detail^{18–24}. This article compares modifications in the properties of the PET and PAm fabrics achieved with these five alternative plasma treatment techniques.

Materials and Methods

Materials

Commercial poly(ethylene terephthalate) (PET) and polyamide (PAm) woven fabric were used in all experiments. Acrylic acid was obtained from Merck (Germany), it was purified by passing through active alumina and used as received. Argon gas (high purity) and O₂ gas (high purity) were supplied by Bos Comp., Turkey. In the experiments bidistilled water was used. All other reagents were of a commercial grade of purity.

Modification of Fabrics

In order to incorporate acrylic acid onto the surfaces of the PET fabrics, five different modifications were employed. The fabrics were treated in the glow-discharge apparatus described below, directly in an acrylic acid, water, air, argon and O₂ plasma. Discharge power and exposure period were changed in order to control the structure and thickness of the plasma-deposited carboxyl and hydroxyl containing polymeric film on the PET and PAm fabrics and etching argon, air and O₂ gas. Fabrics were treated in a radio frequency glow-discharge apparatus, which is schematically shown in Figure 1. The glow-discharge reactor is 52 cm long and has an internal diameter of 6 cm. A radio frequency (13.56 MHz) generator was coupled with a matching network to the reactor through two external copper capacitor plates (4x14 cm).

In a typical glow-discharge treatment, a fabric sample was supported by a thin glass frame at a stationary and horizontal position in the center of the reactor. Air in the system was first displaced with argon by flushing argon through the reactor with the outlet open. The outlet was then closed, and the reactor was pumped down to a pressure of 0.5 torr, while a continuous flow of argon (or acrylic acid) of 30 ml/min was allowed. The pressure remained at 0.5 torr for the entire glow discharge period. The power of the plasma was changed as 5, 10, 15, and 20 wats.. After creating the selected conditions, the plasma was ignited and the fabrics were exposed to plasma for the required exposure time ranging from 1 to 90 min. After the glow was turned off, pressure in the reactor was slowly raised to atmospheric pressure by backfilling with argon and opened to atmosphere. For each glow-discharge condition, three fabric samples were used.

Wettability

In order to obtain the wettability (or hydrophilicity) of the untreated and modified PET and PAm fabrics, a water-drop test was applied according to AATCC standard²⁵. The fabrics were washed (one or five times) in a washing machine (LHD-EF Laundermeter, Atlas, Germany) without using soap or detergent at 40°C

for 30 min, and then dried in air. In the absorbency test, the wetting time was determined by placing a drop of distilled water on the stretched fabric sample (3x3 cm) from a burette held 1 cm from the fabric.

The time for the disappearance of the water-mirror on the surface (in other words the time for the water drop to lose its reflective power) was measured as the wetting time. This procedure was applied to both unwashed and washed fabrics.

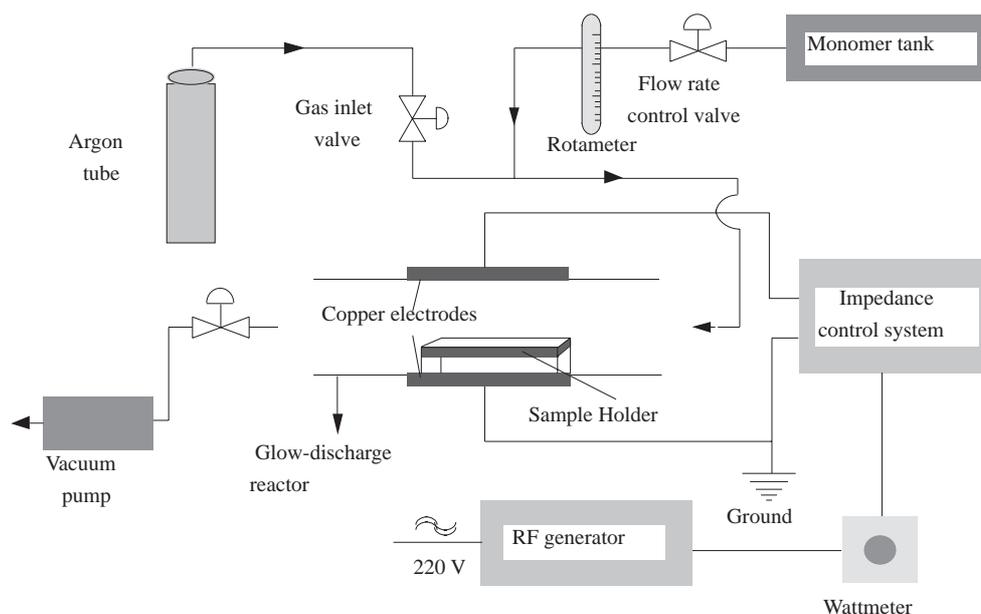


Figure 1. Schematic representation of Glow-Discharge System.

Dyeing

Dyeability of the PET and PAm fabrics treated under different conditions were investigated by using a 1% (w/v) aqueous solution of a basic dye (i.e., Astrazonrot GTL, C.I. Basic Red 18, Bayer, Germany). Na_2SO_4 was included in the dyeing medium (6%, w/v). Dyeing was performed at pH 9, which was adjusted with 1 M NaOH. After dyeing, the fabrics were rinsed with cold-hot-cold water and then dried at room temperature. Colour intensities of the dyed fabrics were measured by using a Datacolor Texflash Instrument (Model 3881, Datacolor AG, Switzerland) over the range of 390-700 nm. In a typical test, reflectance values were measured, and by dividing the smallest value (which corresponds the maximum absorption value) by 100, the reflection factor (R) was obtained. The relative color strength (K/S values) was then established according to the following Kubelka-Munk equation, where K and S stand for the absorption and scattering coefficients, respectively²⁶:

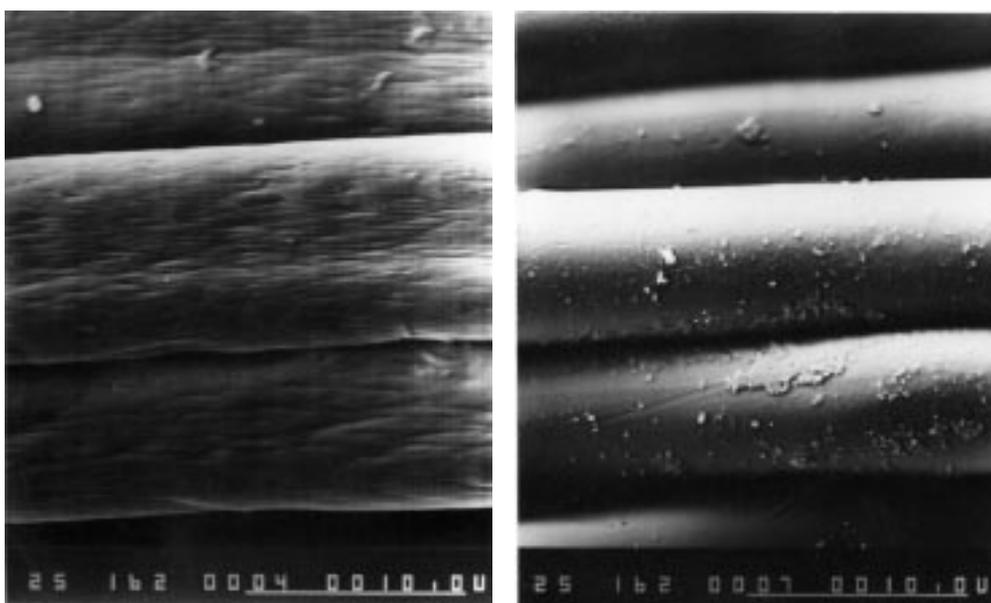
$$K/S = \{(1 - R)^2/2R\}$$

Soiling Behavior

Several attempts have been made to simulate soil in a fabric artificially. However, this task was reported to be difficult because of the nature of soil and the environment²⁷. Many types of artificial preparations have been proposed, and many of them contain carbon black due to its powerful effect on light reflectance. In this study, the soiling behavior of the fabrics was investigated according to the following procedure²⁸. A stock solution was prepared by thoroughly mixing 10 g of carbon black powder (passed through a 150-mesh sieve) and 90 g of liquid paraffin (Merck, Germany). Then 10 g of this suspension was diluted by adding 90 g of CCl₄. Pieces of the unmodified or treated PET and PAm fabric samples (3x3 cm) were placed in this diluted suspension for about 1 min, and then squeezed to remove most of the suspension until a wet weight equal to two times the dry weight of the fabrics was reached, and left in air for 24 h. After that, they were washed in a washing machine (AEG full automatic, Turkey) in a detergent solution containing 4 g of Ariel Colormatik (Turkey) per liter but no bleaching agent, at 40°C for 90 min. To obtain the effect of the number of washing cycle, the fabrics were washed also one and five-times. In order to present the soiling data, relative color intensities ("ΔE") of the fabrics were obtained by measuring the reflectances of the washed and unwashed fabrics with a Datacolor Texflash Instrument (Datacolor AG, model 3881, Switzerland).

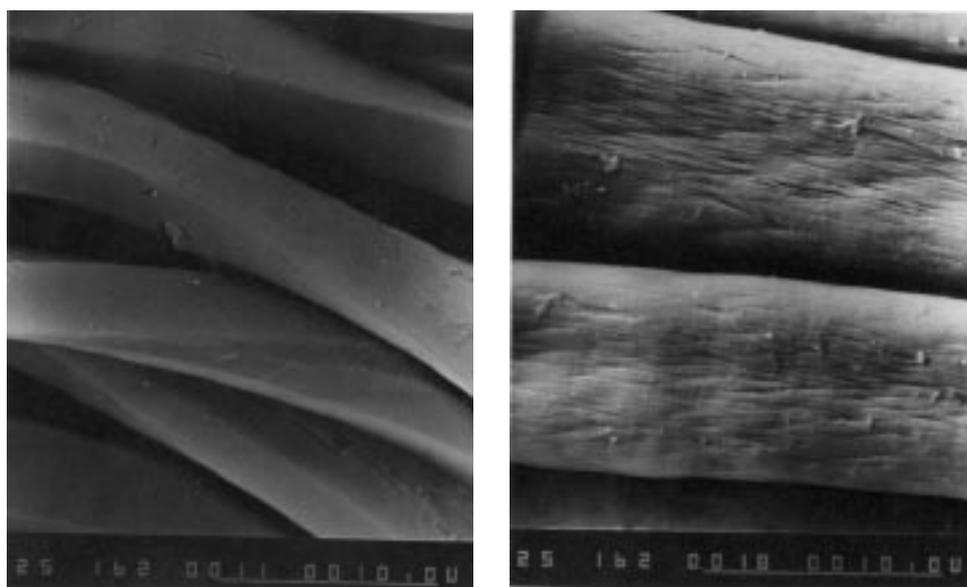
Results and Discussion

In this study we applied low-temperature plasma modification to improve the surface properties of PET and PAm fabrics. Figure 2 shows representative SEM micrographs of the untreated and acrylic acid-plasma treated PET and PAm surfaces. As seen here, surface morphology changes significantly after plasma treatment due to deposition of a thick film on the surfaces of the fabric fibers.



(A) PET fibers before treatment;

(B) PET fibers after treatment;



(C) PAm fibers before treatment;

(D) PAm fibers after treatment.

Figure 2. SEM micrographs of PET and PAm fibers (x1600 magnification).

Surface wettability is directly related to surface energy; an energetically more stable surface results in a less wettable surface. Fabrics with low wettabilities (less hydrophilic, or in other words more hydrophobic), such as polyesters and polypropylene, exhibit poor dyeabilities and low soil resistances. Low-temperature plasma treatment is known as one of the well-recognized and effective means of improving the surface wettabilities of many polymeric surfaces^{1–16}. The improved wettability has been attributed to increasing amounts of polar groups^{29–30}, surface oxidation^{11,31}, and increased surface roughness^{10,32}.

Wetting times of untreated and treated fabrics were measured by a water-drop technique as described above. Figures 3 and 4 show the wetting times (SN values) of the PET and PAm fabrics modified by different in situ plasma polymerizations, respectively. The original (untreated) unwashed PET and PAm fabrics have wetting times of 615.6 and 300 sec, respectively, which means they are quite hydrophobic. However, the wetting time of PET and PAm fabrics decreased very significantly to 205 and 20.5 after five washes (still hydrophobic), and also 9.8 and 19.12 after six months, respectively. This may be attributed to the increase of the water permeability in the woven PET and PAm matrices due to loosening.

In situ plasma polymerization on the PET and PAm surfaces caused a pronounced effect with all glow-discharge treatment types used in this study (Figures 3 and 4). The optimal discharge power for AAC-plasma seems to be 10 wats, which gave the shortest wetting time (the highest hydrophilicity), about 0.7 s. Even one minute of plasma polymerization was enough to reduce the wetting time to about 0.8 s. Note that here also, almost the same results were obtained with all exposure times and glow-discharge power used for all glow-discharge treatment type. Further increase in the exposure time caused a slight increase in the hydrophilicity. Shorter wetting times of the PET and PAm may be due to changes the surface chemistry and/or surface roughness^{10,11,29–32}.

Another important result which may be drawn from Figures 3 and 4 is the effects of washing on the plasma-treated PET and PAm samples. In almost all cases there were only slight increases in the hydrophobicity possibly due to the loss of some weakly attached hydrophilic groups from the surface and/or

the change in surface morphology (surface roughness) by washing. These increases were much smaller for the PET and PAm fabrics treated for longer times, possibly due to more cross-links formed in longer periods, thus leading to more strongly bonded surface groups, and/or already rougher surfaces after long plasma treatment. Also, another important result from Figures 3 and 4 is the effects of stability of plasma treatment on unwashed PET and PAm fabrics after six months before use.

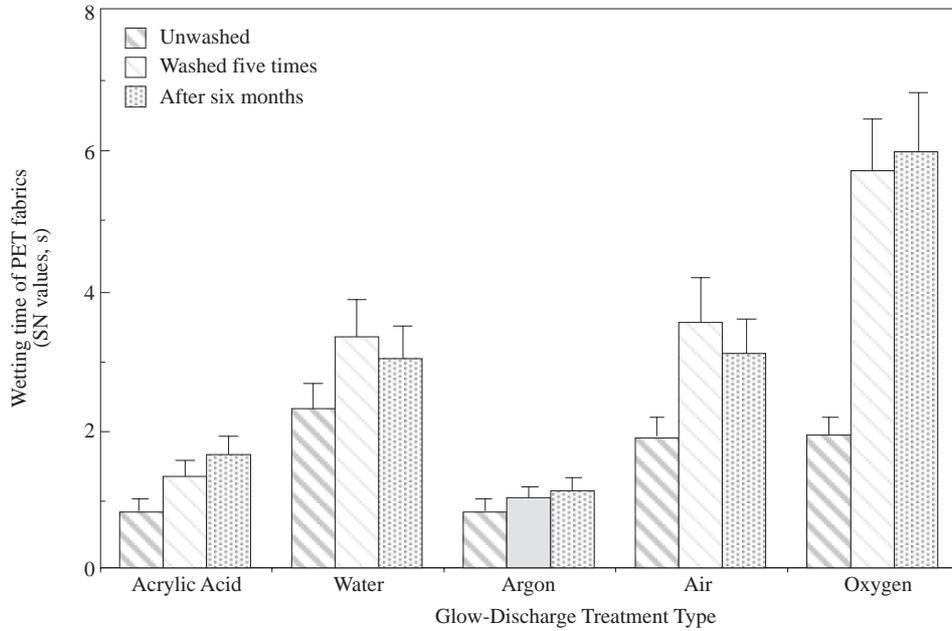


Figure 3. Wetting times of PET fabrics modified by different in situ plasma polymerizations

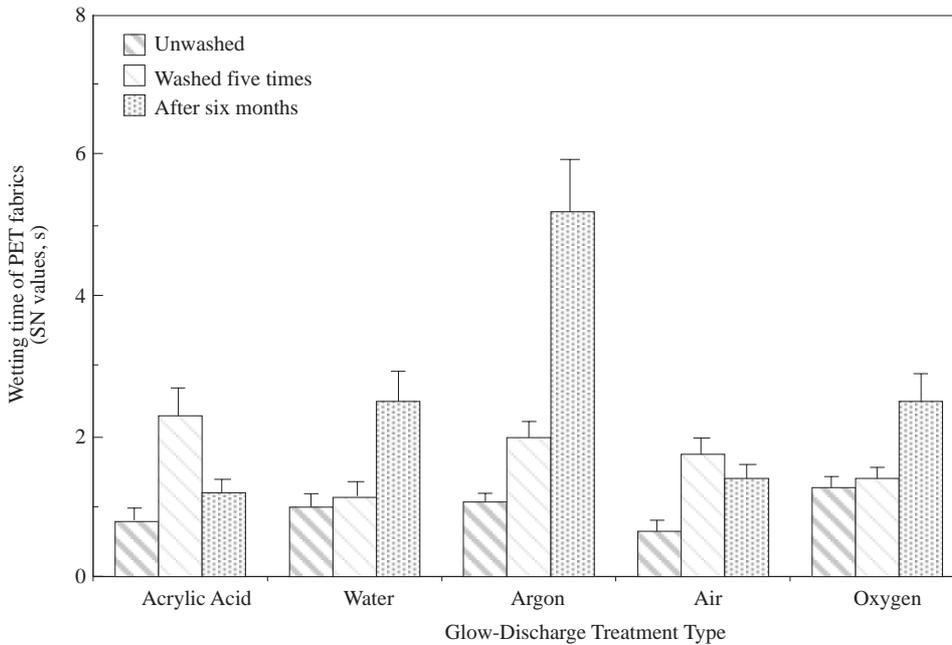


Figure 4. Wetting times of PAM fabrics modified by different in situ plasma polymerizations

Low-temperature plasma modification of PET fabrics for improving of wettabilities was also studied by others, by applying different plasma (e.g, Ar, He, O₂, N₂, NH₂, CO₂, air) at reduced and atmospheric pressure⁹⁻¹⁷. All of these studies have confirmed that there is an increase in the surface wettability of PET fabrics, due to formation of several hydrophilic (polar) groups (e.g., -NH, -CN, -N:N, -C=O, -COOH, -C-OH, -CHO) on the fabric surfaces during plasma or through post-plasma reactions. Our studies, in which acrylic acid was plasma polymerized, revealed that the poly(acrylic acid)-like deposit generated on the PET and PAm fabric surfaces contains a variety of oxygen atom based functional groups¹⁸, which led to highly hydrophilic PET and PAm fabrics.

Dyeabilities of PET Fabrics

The dyeability of hydrophobic fabrics, such as the PET and PAm fabrics we evaluated in this study, is very poor. It is known that introducing hydrophilic sites on the hydrophobic fabrics can improve the dyeability of these fibers. Plasma modifications resulting in unsaturated bonds and/or free radicals on the surface of the fabrics have a significant influence on the overall surface charges and consequently on dyeability. Grzegorz et al. reported that the dyeability of polyester fibers is improved by air plasma treatment³⁴. However, Wakida et al. indicated that the crystallinity of the O₂ plasma-treated polyester increased and the saturation dye uptake value decreased with an increase in gas pressure and plasma treatment time³⁵. Okuna et al. concluded that when PET and nylon 66 in the fiber structure are exposed to an air plasma, the plasma preferentially interacts with the amorphous macromolecular domains, and the etching of these domains in plasma causes a significantly reduced dyeability¹⁵. In the recent study of Sarmadi and Kwon, it was shown that the dyeability of CF₄ plasma-treated polyester samples markedly improved while water uptake of the samples (wettability) decreased with the plasma treatment¹⁶. They explained these apparently contradictory results (lower water uptake and higher dyeability) by the dehydrogenation and consequent unsaturated bond formation trapped stable free radicals formation polar groups generation through post-plasma reaction and generation of increased surface roughness through preferential amorphous structure ablation processes.

In this study we investigated the dyeabilities of five different modification types of plasma polymerization on PET and PAm fabrics with a basic dye (i.e., Astrazonrot) solution containing Na₂SO₄, as described in the Experimental. Table 1 shows the change in surface dyeability of the modified PET and PAm fabrics by different in situ polymerizations.

The relative color strength (K/S value) of the fabrics was first increased profoundly with the plasma polymerization modification time, reached a maximum generally at about 15 min, and was then stable in about 60 min. As pointed out in the related literature, the surface chemistry of a plasma-treated material changes depending on the plasma conditions even if one uses the same gas or monomer plasma, due to different degrees of deposition/etching occurring^{1-5,16}.

Most probably, the chemical groups created on the plasma-modified PET surfaces with an exposure time of 15 min were the most suitable groups to react with the specific dye used under the dyeing conditions applied in this study. Sarmadi and Kwon reported K/S values between 0.3 and 1.5 for the PET fabrics treated in CF₄ plasma at different discharge powers (10-100 wats) and at different plasma exposure times and found similar effects of plasma conditions¹⁶.

Table 1. Surface Dyeability of PET and PAm fabrics modified by different in situ plasma polymerizations.

Fabric type	Surface Dyeability* (K/S values)
Untreated PET	0.345
PET treated with Acrylic acid	0.920
PET treated with Water	0.750
PET treated with Argon	0.720
PET treated with Air	0.760
PET treated with Oxygen	0.530
Untreated Pam	8.17
PAm treated with Acrylic acid	9.16
PAm treated with Water	8.60
PAm treated with Argon	6.70
PAm treated with Air	6.46
PAm treated with Oxygen	6.26

* Plasma polymerization conditions: Glow-discharge Power: 10 watts, Exposure time: 15 min, pressure: 0.5 torr. Dyeing conditions were: pH 9, Astrozonrot GTL with 6% Na₂SO₄.

Note that there were no significant color changes either with repeated washing cycles or with a long period of storage, which indicates the stability of dye attachment to the fabrics. We can sum up the dyeability results considering the wettabilities of the respective surfaces given in the previous section as follows. The PET and PAm fabrics treated with acrylic acid, water, argon, air and O₂ plasma exhibit much higher surface wettabilities than the untreated PET and PAm fabrics.

Soiling Behaviour of PET Fabrics

The hydrophobic synthetic fibers attract soil to a greater extent than natural fibers because of the development of electrostatic charges on the surface³⁶. It was also reported that soiling increased rapidly when the moisture content of the fibers dropped below 4%³⁷. The soiling tendency can be reduced by applying antistatic treatments³⁸. Recently it was reported that soil repellency can also be improved by low temperature plasma¹⁴. In this study we investigated soiling behaviour of PET and PAm fabrics modified by five different plasma polymerization methods as described in the Experimental. In order to present the soiling data, relative colour intensities (DE) of the fabrics were obtained. Figures 5 and 6 give the DE values for the PET and PAm fabrics modified by different in situ plasma polymerizations, respectively. important results from these figures are the effects of stability on the in situ plasma polymerization of unwashed PET and PAm fabrics after six months. The original unwashed PET and PAm fabrics have color intensities (ΔE) of 5 and 4.7, respectively, which means it is quite hydrophobic. However, the wetting time of PET and PAm fabrics shortened very significantly to 4.4 and 4.2 after five washes, and also 4 and 3.3 after six months, respectively.

Conclusion

In this study we applied five different techniques, namely in situ plasma polymerization of acrylic acid, argon, water, air and oxygen, in order to improve the wettabilities of PET and PAm fabrics. All the in situ polymerization types caused a pronounced increased in the surface wettabilities of the fabrics. The relative

color strength (K/S value) of the fabrics was increased profoundly with the plasma treatment in all cases, in parallel to the increase in the surface wettabilities. Significant increases in the soil resistance (ΔE value) of the fabrics were observed. In conclusion, all in situ plasma polymerization types improve wettabilities, and therefore dyeability and soil resistance of the fabrics.

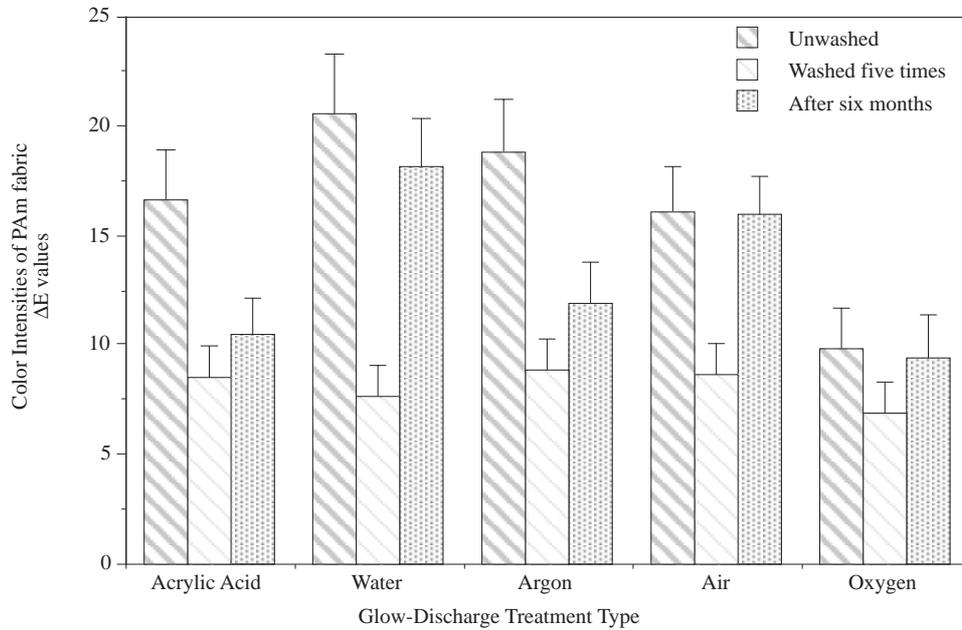


Figure 5. Relative color intensities (ΔE) of PET fabrics modified by different in situ plasma polymerizations.

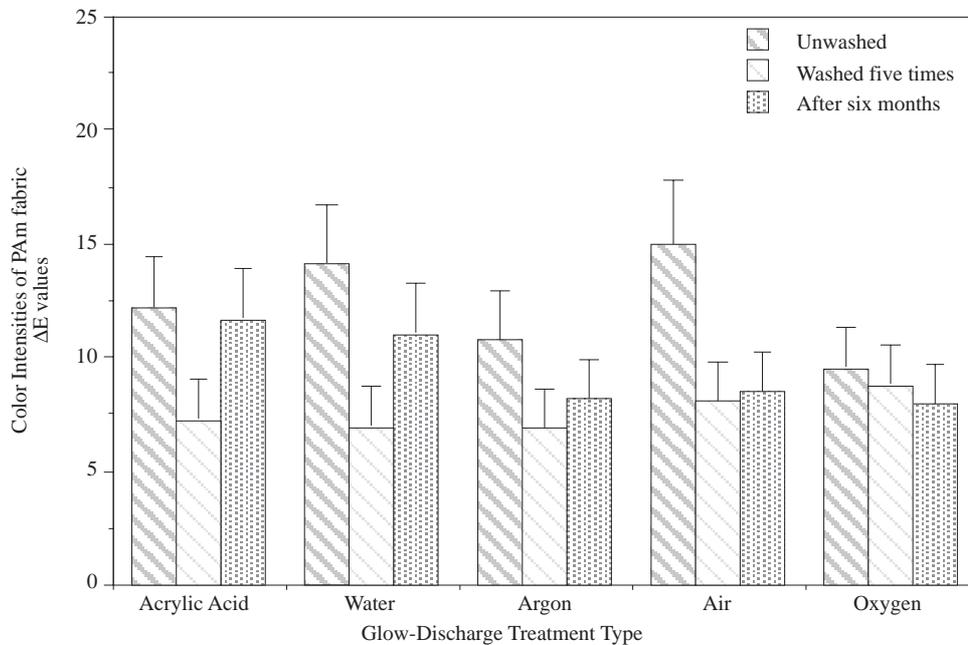


Figure 6. Relative color intensities (ΔE) of PAm fabrics modified by different in situ plasma polymerizations.

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