Improvement in surface-related properties of poly(ethylene terephthalate)/cotton fabrics by glow-discharge treatment

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Poly(ethylene terephthalate)/cotton fabrics have been treated in low-temperature plasmas to increase the hydrophilicity and, therefore, to impart soil resistance and to improve dyeability. The fabrics have been treated in glow-discharge apparatus using acrylic acid and water plasmas. Two alternative modifications were applied. The plasma conditions, such as exposure time and discharge power, were varied to control the extent of plasma surface modification in the first approach, while the acrylic acid content and the incubation time were changed in the second approach. It is observed that the glow-discharge treatment significantly improves the wettability of the fabrics. More hydrophilic surfaces are created due to the treatment and, therefore, the dyeability of the fabrics is much better. No significant colour change, neither with repeated washing cycles nor with long period of storage, is observed.

Keywords: Dyeability, Glow-discharge treatment, PET/cotton fabric, Soil resistance, Wettability

1 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 properties. Attention has also been paid to improve wettability, water repellency, soiling, soil release, printing, dyeing and other finishing processes of textile fibres and fabrics by using plasma technology. In most of these studies, two major types of discharge, namely high-frequency discharge (low-pressure plasma) and low-frequency discharge (corona discharge), have been considered. Recently, low-temperature plasma under atmospheric pressure was applied by Wakida et al. The plasma treatment for surface modification of textiles was performed usually by two main procedures, namely depositing and non-depositing plasmas. In case of depositing plasmas, the plasma was usually applied by using saturated and unsaturated gases such as fluorocarbons, hexamethylenedisiloxane (HMDS) and C2H4 or vapours (monomers) such as acetone, methanol, allylamine and acrylic acid. Several reactive etching (Ar, He, O2, N2 and F2) and non-polymerizable gases (H2O and NH3) were used in non-depositing plasmas.

In the present study, the surface properties of PET/cotton fabrics have been modified by glow-discharge treatment using acrylic acid and water plasmas. The changes in surface hydrophilicity (wettability), soil resistance and dyeability of the fabrics after glow-discharge treatment, which were applied at different discharge powers and exposure times, have also been evaluated. The details of the surface modification and characterization have already been discussed elsewhere.

2 Materials and Methods

2.1 Materials

PET/cotton woven fabric (commercially available) was used for the study. Acrylic acid, obtained from Merck (Germany), was purified by passing through active alumina and then used. All the other reagents used were of the commercial grade.

2.2 Methods

2.2.1 Modification of Fabrics

To incorporate acrylic acid on the surface of the PET/cotton fabrics, two different modifications were
employed. The fabrics were treated in a radio frequency glow-discharge apparatus (Fig. 1), directly in acrylic acid and water plasmas. The discharge power and exposure period were varied to control the structure and thickness of the plasma-deposited acrylic acid-liked and water-liked polymeric films on the PET/cotton fabrics.

The glow-discharge reactor was 52 cm long and had 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 thin glass frame at a stationary and horizontal position in the centre of the reactor supported a fabric sample. 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 was maintained at 0.5 torr for the entire glow-discharge period. The power of the plasma was set between 5 W and 20 W. After creating the selected conditions, the plasma was ignited and the fabrics were exposed to plasma for required exposure time ranging from 1 min to 60 min. After the glow was turned off, the 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.

2.2.2 Wettability

To observe wettability (hydrophilicity) of the untreated and modified PET/cotton fabrics, a water-drop test was carried out according to AATCC standard. The fabrics were washed (one or five times) in a washing machine (LHD-EF Launder-Ometer, 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 kept at a distance of 1 cm from the fabric. The time for the disappearance of the water mirror on the surface (i.e. the time for the water drop to lose its reflective power) was measured as the wetting time. The test was carried out for both unwashed and washed fabrics.

2.2.3 Dyeing

The dyeability of the PET/cotton fabrics treated at different conditions was studied using 1% (w/v) aqueous solution of a basic dye (Astrazon GTL, C.I. Basic Red 18, Bayer, Germany). $Na_2SO_4$ (6%, w/v) was added in the dye bath and the dyeing was carried out at pH 9, adjusted with 1 M NaOH. After dyeing, the fabrics were rinsed sequentially with cold-hot-cold water and then dried at room temperature.

The colour intensity of the dyed fabric was measured by using a Dataplot TexFlash Instrument (Model 3881, Dataplot AG, Switzerland) over the range of 390-700 nm. In a typical test, the 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 colour strength ($K/S$) value was then observed according to the following Kubelka-Munk equation where $K$ and $S$ stand for the absorption and scattering coefficients respectively:

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

2.2.4 Soiling Behaviour

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 environment. Many types of artificial preparation have been proposed, and many of them contain carbon black due to its powerful effect on light reflectance. In this study, the soiling behaviour of the fabrics was observed according to the following procedure. A solution was prepared by thoroughly mixing 10 g of carbon black powder (passed through a 150-mesh sieve) and 90 g of liquid paraffin (MERK, Germany). 10 g of this suspension was diluted by adding 90 g of CCl$_4$. A piece of the unmodified and treated PET/cotton fabric (3 x 3 cm) was placed in this diluted suspension for about 1 min and then squeezed to remove most of the suspension until a wet weight equal to the two times of the dry weight of the fabric.
was achieved. The fabric was left in air for 24 h and then washed in a washing machine (AEG fully automatic, Turkey) using detergent solution containing 4 g of Ariel Colourmatik (Turkey) per litre without bleaching agent at 40°C for 90 min. To observe the effect of number of washing cycles, the fabric was washed one and five times. To study the soiling data, the relative colour intensity (ΔE) of the fabric was obtained by measuring the reflectance of the washed and unwashed fabrics with a Datacolor TexFlash Instrument (Datacolor AG, model 3881, Switzerland).

3 Results and Discussion

3.1 Wettability

The surface wettability is directly related to the surface energy; more energetically stable surface results in less wettable surface. Fabrics with low wettability (less hydrophilic or more hydrophobic), such as polyester and polypropylene, exhibit poor dyeability and low soil resistance. Low-temperature plasma treatment is one of the well-recognized and effective means of improving the surface wettability of many polymeric surfaces. The improved wettability is attributed to the increase in the amount of polar groups, surface oxidation and increase in surface roughness.

In this study, two different techniques, namely in situ plasma polymerization of acrylic acid and water, were applied to improve the wettability of PET/cotton fabrics. The wetting time of untreated and treated fabrics was measured by a water-drop technique as described before. Fig. 2 shows the wetting time of the PET/cotton fabrics modified by different in situ plasma polymerization. The original unwashed PET/cotton fabric has a wetting time of 366 s, indicating that it is quite hydrophobic. However, the wetting time decreases very significantly to a value of 23 s after 5-time washing (still hydrophobic). This may be attributed to the increase in the water permeability in woven PET/cotton matrix due to loosening.

In situ polymerization of acrylic acid on the PET/cotton surface causes a pronounced effect at all glow-discharge conditions studied. The optimal discharge power is found to be 10 W which gives the shortest wetting time (the highest hydrophilicity) of about 1.75 s. Even 1 min of plasma polymerization is enough to decrease the wetting time down to about 1 s. Further increase in the exposure time causes slight increase in the hydrophilicity (shorter wetting time) which may be due to the change in the surface chemistry and/or surface roughness.

Another important result which may be drawn from Fig. 2 is the effect of washing on the plasma-treated PET/cotton samples. In both the processes, there is only slight increase in the hydrophobicity which may be due to the loss in loosely attached hydrophilic groups from the surface and/or the change in surface morphology (surface roughness) by washing. It is observed that this increase is much smaller for the PET/cotton fabrics treated for longer duration. This may be due to more crosslinking occurred in longer period, thus leading to more strongly bonded surface groups and/or rough surface after long time plasma treatment. Fig. 2 also shows effect of stability of plasma treatment of unwashed PET/cotton fabrics after six months. Low-temperature plasma modification of poly(ethylene terephthalate) fabrics for improving wettability was also studied by other researchers using different plasmas, e.g. Ar, He, O2, N2, NH3, CO2 and air, at reduced atmospheric pressure. All of these studies have confirmed that there is an increase in the surface wettability of poly(ethylene terephthalate) fabrics due to the formation of several hydrophilic (polar) groups (e.g. NH3, -CN, -C=O, -COOH, -C-OH and -CHO) on the fabric surface during plasma or through post-plasma reactions. Our studies in which acrylic acid was plasma polymerized reveals that the poly(acrylic acid)-like deposit generated on the poly(ethylene terephthalate)/cotton fabric surface contains a variety of oxygen atom based functional groups which lead to highly hydrophilic poly(ethylene terephthalate)/cotton fabrics.

3.2 Dyeability

The dyeability of hydrophobic fabrics, including PET/cotton fabrics, is very poor. It is known that the introduction of hydrophilic sites on the hydrophobic
fabrics can improve the dyeability of these fibres. Plasma modification resulting in unsaturated bonds and/or free radicals on the surface of the fabrics has a significant influence on the overall surface charge and consequently on dyeability. Grzegorz et al. reported that the dyeability of polyester fibres is improved by air plasma treatment. However, Wakida et al. indicated that the crystallinity of the O₂ plasma-treated polyester increases and the saturation dye uptake value decreases with the increase in gas pressure and plasma treatment time. Okuno et al. concluded that when poly(ethylene terephthalate) and nylon 66 are exposed to an air plasma, the plasma preferentially interacts with the amorphous macromolecular domains, and the etching of these domains in plasma significantly reduces the dyeability. In a recent study of Sarmadi and Kwon, it was observed that the dyeability of CF₄ plasma-treated polyester samples markedly improves while water uptake of the samples (wettability) decreases with the plasma treatment. 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.

Fig. 3 shows the change in surface dyeability of the modified PET/cotton fabrics (by in situ polymerization of acrylic acid and water) with the plasma exposure time.

The relative colour strength (K/S value) of the fabrics first increases profoundly with the exposure time, reaches a maximum generally at about 15 min and then slightly decreases 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. Most probably, the chemical groups created on the plasma-modified PET/cotton surface with an exposure time of 15 min are the most suitable groups to react with the specific dye used and at the dyeing conditions applied in this study. Sarmadi and Kwon reported K/S values between 0.3-1.5 for the poly(ethylene terephthalate) fabrics treated in CF₄ plasma at different discharge powers (10-100 W) and plasma exposure time. They found similar effects of plasma conditions on the in situ plasma polymerization. It is observed that there is no significant colour change neither with repeated washing cycles nor with long period of storage indicating the stability of dye attachment to the fabrics. It is concluded that the PET/cotton fabrics treated with acrylic acid and water plasma exhibit much higher surface wettabilities than the untreated PET/cotton fabrics.

3.3 Soiling Behaviour

The hydrophobic synthetic fibres attract soil to a greater extent than the natural fibres because of the development of electrostatic charges on the surface. It has been reported that the soiling increases rapidly when the moisture content of the fibres decreases below 4%. The soiling tendency can be reduced by applying antistatic treatments. Recently, it was reported that soil repellency can also be improved by low-temperature plasma treatment. To present soiling data, the relative colour intensities (ΔE) of the fabrics have been observed. Fig. 4 shows the ΔE values for the PET/cotton fabrics modified by in situ polymerization of acrylic acid and water.
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