Atmospheric pressure glow discharge of helium-oxygen plasma treatment on polyester/cotton blended fabric

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Received 30 March 2010; revised received and accepted 27 July 2010

Polyester/cotton blended woven fabric has been treated with atmospheric pressure glow discharge plasma to improve its hydrophilic properties. Discharge has been generated at radio frequency using pure helium and helium-oxygen gas mixtures. The role of various plasma process parameters, such as discharge intensity, exposure time, gas flow rate, inter-electrode distance and type of gas, on the hydrophilic and surface properties of the fabric has also been studied. The efficiency of the plasma treatment is assessed through capillary rise measurements, whereas surface characterization is performed with FTIR and SEM. It is observed that plasma process parameters play a key role in deciding properties of the plasma-treated fabric. Use of even low amount of oxygen as a reactive gas has been proved to be very effective in producing hydrophilic properties of plasma-treated polyester/cotton blended fabric.

Keywords: Atmospheric pressure glow discharge, Helium-oxygen plasma, Polyester/cotton fabric, Plasma process parameters, Wicking height

1 Introduction

Polyester/cotton (P/C) blended fabrics are becoming increasingly popular due to the desired properties of comfort and aesthetic look, which are rather difficult to get altogether individually either in cotton or in polyester (PET) products. But often in P/C blended fabrics, hydrophilic properties are still found to be inferior especially when the PET component is in the larger proportion.

The potential of plasma technology has been explored extensively for imparting the hydrophilic and adhesive properties to the natural and synthetic textile materials. Significant changes in the morphological and chemical properties of the plasma-treated textile surfaces have been reported. Plasma treatment can induce changes in textile surface properties in terms of wettability. Low-pressure plasma techniques have been effectively used for surface modification of textiles; however, they do not meet the requirements of online continuous processing of textiles. Moreover, low-pressure plasma treatments can be performed only in a batch process, where it is required to create and sustain vacuum or low-pressure conditions. Therefore, new methods based on atmospheric plasma treatments seem to be quite attractive for the textile industry. Plasma can bring surface modification of textiles in variety of ways, like etching, cleaning, activation and polymerisation. The use of non-thermal plasma for various applications including wettability, adhesion promotion, printability and coatings has been discussed elaborately in a review paper by R Morent et al.

The atmospheric pressure glow discharge (APGD) plasma is one of the atmospheric pressure plasma varieties suitable for continuous treatment of textiles. It is non-thermal and radio frequency generated plasma, which does not require vacuum. As compared to other forms of atmospheric pressure plasma, APGD can deliver higher uniformity. Due to wide range of applications, APGD is intrinsically capable of meeting the needs of plasma assisted textile processing. The electron densities of APGD are in the range of $10^{11}$-$10^{12}$/cm$^3$, which is denser than other types of atmospheric pressure plasma, i.e. DBD and
corona. Various factors in the plasma treatment, namely energy density, gas flow, gas type and exposure time, are considered as vital from point of view of development of recipe and to understand the interactions of plasma with the substrate under different conditions.

The improvement in hydrophilicity by using atmospheric pressure plasma for textile materials has been reported earlier by several researchers. However, optimization of different parameters, especially in high-density plasma like APGD, has not been reported so far in detail. Even the use of APGD for blended textiles like P/C is yet to be studied. The study reported in this paper has been carried out on P/C blended fabric to improve its hydrophilic properties with the use of APGD plasma generated from helium and oxygen. The influence of process parameters in plasma treatment, viz. discharge power, duration of treatment, gas flow, nature of gas and electrode spacing on the hydrophilic properties of treated fabric has been studied. Wettability of P/C samples treated with helium (carrier gas) plasma and He-O$_2$ (oxygen plasma) is compared by wicking height measurements. Changes in the surface morphology and surface chemistry after plasma treatment have been studied using SEM and ATR-FTIR techniques respectively.

2 Materials and Methods

2.1 Materials

A bleached polyester/cotton (P/C) blended woven fabric of the composition 67:33 was used for the APGD plasma treatment studies. Ends/inch, picks/inch and weight of the fabric were taken as 90, 70 and 88 g/m$^2$ respectively.

2.2 Plasma Treatment

Atmospheric pressure glow discharge plasma, operating at the frequency of 13.56 MHz was used for the treatment of P/C blended woven fabric. A laboratory scale model of e Rio$^TM$ APPR-300-13 Atmospheric Pressure Plasma System of APJeT Inc. (Fig. 1) was used for the treatments. The system works in semi continuous mode where fabric sample is placed on the bottom flat electrode, which facilitates the movement of fabric through the plasma zone. No monomers were used in this research; rather changes were made to the plasma gas composition and flow rate.

Fabric samples of size 25 cm × 25 cm were passed through the plasma zone at different discharge conditions. To know the effect of an individual process parameter, the remaining parameters were kept invariant during the study, i.e. to study the effect of discharge power on the plasma-treated fabric, other parameters like duration of treatment, gas flow and electrode spacing were kept constant. Parameters used for studying the effect of different discharge conditions are given in Table 1. Effect of each parameter was studied both in presence and absence of oxygen. The flow rate of oxygen was kept at 0.15 SLPM (standard litre per minute) during the studies in presence of oxygen gas. The RF (radio frequency) discharge power was varied between 400 W and 700 W. The speed of the moving plate in the plasma zone was maintained in such a way that the duration of the plasma treatment was 14-37 s. Distance between the electrodes where fabric passes through was changed from 0.28 cm to 0.38 cm.

![Fig.1—Schematic diagram of laboratory plasma unit APPR-300-13](image-url)

| Table 1—Process parameters used for plasma treatment of P/C blended fabric |
|------------------------|------------------|
| Parameter              | Value            |
| RF discharge power, W  | 400, 500, 600, 700 |
| Exposure time under plasma, s | 14, 20, 25, 37 |
| Helium gas flow rate   | 30, 40, 50, 60   |
| (in presence of oxygen), SLPM |
| Helium gas flow rate   | 10, 20, 30, 40, 50, 60 |
| (in absence of oxygen), SLPM |
| Inter-electrode spacing, cm | 0.28, 0.30, 0.33, 0.36, 0.38 |
flow rate of helium in the absence of oxygen was kept between 10 SLPM and 60 SLPM, whereas that in the presence of oxygen was changed from 30 SLPM to 60 SLPM.

2.3 Wettability Studies by Capillary Rise Method
The rate of vertical capillary rise in plasma-treated samples was measured using the method as described in ISO 9073-6: 2000(E). Test specimens were conditioned at 65% RH and 27°C temperature for 24 h. Then specimen strips were suspended vertically in the liquid and checked for rise in capillary height for predetermined times. Measurements of the wicking heights were carried out using triplicate samples to ensure repeatability. In this work, the height of the capillary rise of liquid was measured for 30 min with the time intervals of 5 min.

2.4 ATR-FTIR Studies
The surface chemical analysis of plasma-treated P/C blended fabric was carried out by attenuated total reflectance (ATR–FTIR) spectroscopy on a Perkin-Elmer FTIR spectrometer model system 2000 using the zinc selenide horizontal ATR accessory. The scanning range used was 4000-650 cm\(^{-1}\) and an average of 50 scans was recorded.

2.5 SEM Study
The SEM photomicrographs were recorded using a JEOL SEM (Model JSM 5400) to study the changes in the surface morphology of helium and oxygen plasma-treated fabrics.

3 Results and Discussion
3.1 Effect of Plasma Discharge Intensity
Radio frequency power of plasma discharge was varied from 400 W to 700 W (Table 1). Time of plasma exposure, helium flow and inter-electrode spacing were kept invariant at 25s, 40 SLPM and 0.28 cm respectively. The height of capillary rise was recorded for different wicking durations up to 30 min, such as 5, 10, 15, 20, 25 and 30 min. The value of capillary height recorded for predetermined time for both helium and oxygen plasma is plotted against the wicking time.

Figure 2a shows the changes in wicking height of samples treated in helium plasma under different discharge powers. It is observed that at all prefixed wicking times, the value of wicking height of all plasma-treated samples is greater than that of untreated sample. The wicking height of untreated P/C sample after 30 min of wicking time is found to be 2.4 cm. After plasma treatment, the values of capillary heights obtained for 400, 500, 600 and 700 W power are found to be 3.3, 3.9, 5.0 and 4.8 cm respectively. It can be said that at any point of wicking time, as the discharge power is increased from 400 W to 600 W, there is a gradual increase in the wicking height. This indicates that an increase in discharge power results in an improvement in the efficiency of the plasma treatment\(^ {15-18}\). In helium discharge plasma, the electron and ion density tends to increase with increasing power\(^ {19}\). As the gas flow (number of gas molecules) is constant, the increase in the input energy (discharge power) leads to more acceleration of the plasma constituent species. Bombardment of these high-energy species and resultant surface interactions lead to more hydrophilic character on the plasma-treated surface. However, as the discharge power is increased beyond 600 W, the hydrophilic effect appears to be stabilized. This suggests that the optimum value of power for the given parameters and substrate is in between 600 W and 700 W. Saturation of plasma effect at higher discharge powers is supported by the study of other researchers\(^ {15, 20, 21}\).

Figure 2b shows the effect of discharge power in oxygen plasma (the term 'oxygen plasma' means a plasma gas that consists of a mixture of helium and oxygen, where oxygen is the reactive gas and helium is the carrier gas). Similar to the helium plasma treatments, the oxygen plasma treated samples also show improvement in the height of capillary with increased power. Furthermore, capillary heights obtained for oxygen plasma treated samples appear to be higher than that of helium plasma treated samples. The per cent increase in the heights of capillary rise of oxygen plasma treated samples over helium plasma treated samples at 400, 500, 600 and 700 W discharge power is found to be 84, 67, 40 and 47 respectively. Therefore, it can be said that oxygen plasma treatment results in better wettability in P/C samples than the helium plasma treatment.

3.2 Effect of Duration of Plasma Treatment
To study the effect of different exposure durations (Table 1), RF power, helium gas flow and inter-electrode spacing were kept constant at 600 W, 40 SLPM and 0.33 cm respectively. Similar kinds of increase in capillary heights were recorded with the increase in duration of plasma exposure. At the given experimental conditions, the optimum capillary height
is recorded for the exposure time of 37 s. The increase in the efficiency of treatment with exposure time is already reported by other researchers.\textsuperscript{16, 22, 23}

### 3.3 Effect of Gas Concentration

The effect of helium gas flow rate was studied both in presence and absence of oxygen gas (Table 1). The other process parameters, viz. discharge power, inter-electrode spacing and treatment time were kept as 650 W, 0.30 cm and 25 s respectively. Figure 3a shows the effect of gas concentration on the capillary height in helium plasma treated samples. It is observed that as the helium flow rate is increased from 10 SLPM to 30 SLPM, there is a gradual increase in the capillary height. It can be attributed to an increase in the density of the charged particles due to the increase in gas flow in the plasma zone. It is evident from Fig.3a that at the given experimental conditions, the optimum value of wicking height is obtained at the helium flow rate of 30 SLPM. However, beyond 30 SLPM, further increase in the gas flow rate decreases the capillary height. Flow rate greater than 30 SLPM causes a drop in efficiency of the plasma treatment.

The drop in the plasma efficiency at higher gas flow values may be attributed to the dilution of active species in plasma. Increase in the gas flow beyond optimum value will lead to more number of gas molecules/atoms per unit volume. However, the energy supply to the gas (discharge power) is constant in the experiments. Therefore, the energy experienced by individual gas molecule/atom decreases at higher gas flow rate. Moreover, at the elevated gas flow rate, the mean free path will be decreased due to increase in number of gas molecules/atoms per unit volume. Thus, the probability of recombination of charged species will also be greater at higher flow rates. Therefore, the increase in the gas flow rate (above optimum value) causes a quenching effect in the resultant plasma. However, the optimum gas flow rate may actually be different for different discharge powers. Additional investigations are needed for complete understanding of the relation between input energy and optimum gas flow rate.

During the experiments with oxygen plasma (oxygen flow rate 0.15 SLPM), the values of helium gas flow rates were kept 30, 40, 50 and 60 SLPM. It is observed that the flux of the plasma is not uniform in the cross-section, when helium flow rate is below 30 SLPM. The stable and uniform glow discharge in the normal plasma shrank in area, at flow rates below 30 SLPM. For this reason, flow rate of helium in He-O\textsubscript{2} plasma is kept above 30 SLPM during the experiments. Similar kinds of instabilities have also been reported for the plasma generated from the mixture of noble gas (argon) and oxygen.\textsuperscript{24} Like helium plasma treated samples, oxygen plasma treated samples also exhibit initial increase and then decrease in the wicking heights (Fig.3b). However, the optimum helium flow rate is found to be 50 SLPM in oxygen plasma. It is clear from the above results that gas flow rate plays a critical role in the plasma treatment of a textile substrate. It may be said that the value of optimum flow rate (keeping other parameters constant) varies from gas to gas or their mixtures.
3.4 Effect of Inter-electrode Spacing

Height of capillary rise decreases with the increase in inter-electrode spacing (Fig. 4). The wicking height of 5.7 cm is recorded after 30 min of wicking time for P/C sample treated at inter-electrode spacing of 0.28 cm. However, as the electrode gap is widened, wicking heights of 4.9, 4.7, 4.6, 3.8 cm are obtained for samples treated at inter-electrode spacing of 0.30, 0.33, 0.36 and 0.38 cm respectively. With the given experimental conditions, the highest value of wicking height is obtained at an electrode spacing of 0.28 cm, i.e. at the narrower inter-electrode spacing. Similar results are also reported for cotton treated with DC glow discharge. The significance of inter-electrode spacing can be understood with the help of Paschen’s law. The breakdown voltage of a gas is a function of system pressure and electrode distance, which is given by the following Paschen’s law:

\[ V_b = f(p,d) \]

where, \( V_b \) is the breakdown voltage; \( p \), the pressure of the system; and \( d \), the inter-electrode spacing. At fixed external applied voltage, if pressure rises towards atmospheric pressure, the electrode spacing must be decreased. In other words, if the pressure is constant, the increase in the inter-electrode gap will lead to increase in the breakdown voltage. However, in the present study, the pressure (atmospheric pressure) and the supply of electrical energy (discharge power) are constant. Therefore, the increase in the breakdown voltage (i.e. increase in the energy required to ignite plasma) may lead to low energy of the resultant plasma species. Moreover, the electrical field decreases with the increase in the distance from the cathode. The decrease in the value of electric field may cause less amount of energy transfer to the gas molecules, resulting in poor efficiency of plasma treatment at greater inter-electrode spacings.

3.5 Effect of Gas Composition

To study the effect of plasma on the substrate, it is essential to understand the interaction between the plasma and the substrate. Even if only a single gas is used for plasma generation, the interactions of plasma with the substrate are very complicated due to involvement of multiple species like electrons, photons, ions and neutrals. The use of mixture of gases further complicates the situation. The chemical as well as morphological changes in the textile surfaces are closely dependent on the type of gas used for plasma treatment.

The effects of helium plasma and He-O2 plasma on wetting properties of the P/C fabric are investigated separately. It is interesting to note that a small amount of oxygen (0.15 SLPM, which is about 0.35% of the total volume of helium used for plasma generation) has a noticeable effect on the wicking behaviour of plasma treated P/C fabric. The per cent increase in the capillary height (measured for 5 min wicking time) of oxygen plasma treated samples over helium plasma treated samples at various inter-electrode spacing is found to be 48, 117, 144 and 150 for inter-electrode spacings of 0.11, 0.12, 0.13 and 0.14 cm respectively. It is observed that oxygen plasma treated samples exhibit better wicking properties as compared to helium plasma treated samples. The per cent increase...
in capillary height of oxygen plasma treated samples over helium plasma treated samples at different exposure time is found to be 120, 45, 33 and 10 for the treatment time 14, 20, 25 and 37 s respectively. These results indicate that ‘He-O₂’ plasma is efficient than ‘He’ plasma for imparting the hydrophilic properties on P/C blended fabric.

3.6 Surface Chemical and Morphological Characterization

FTIR spectra of three P/C samples, namely untreated sample, helium plasma treated sample (power 700 W) and oxygen plasma treated sample (power 700 W) are shown in Fig.5. Polyester/cotton blended fabric used for the experiments contains polyester (67%) as a major component. Therefore, the peaks appearing in the ATR spectra at 1709, 1233, and 721 cm⁻¹ can be attributed to polyester component of the blend. The peak at 1709 cm⁻¹ can be assigned to stretching vibration of C=O group in ester. The peaks at 1233 cm⁻¹ and 721 cm⁻¹ can be assigned to asymmetric -C=O stretching vibration and aromatic C-H out of plane vibrations respectively.

It is found that the FTIR spectra of untreated and plasma treated samples do not indicate any significant difference in the surface chemical composition. Therefore, the ratio of absorbance intensity of characteristic peaks at 1709 cm⁻¹ and 1233 cm⁻¹ with respect to absorbance intensity at 721 cm⁻¹ was calculated. The absorbance ratios $A_{1709}/A_{721}$ and $A_{1233}/A_{721}$ are given in Table 2. As compared to control sample, there is a decrease in the values of absorbance ratio for helium plasma treated sample and slight increase in absorbance ratio ($A_{1709}/A_{721}$) for oxygen plasma treated sample. Table 2 indicates that the surface chemistry of P/C samples is altered.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_{1709}/A_{721}$</th>
<th>$A_{1233}/A_{721}$</th>
</tr>
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<tbody>
<tr>
<td>Untreated P/C</td>
<td>0.52</td>
<td>0.77</td>
</tr>
<tr>
<td>Helium plasma treated</td>
<td>0.45</td>
<td>0.75</td>
</tr>
<tr>
<td>Oxygen plasma treated</td>
<td>0.55</td>
<td>0.77</td>
</tr>
</tbody>
</table>
slightly after oxygen plasma treatment. Increase in the oxygen content of PET after oxygen plasma treatment is also reported by several researchers. Absence of any distinctive differences in the FTIR spectra of control and plasma-treated samples can be attributed to the fact that the interaction of plasma takes place at very thin surface layer (50-500 Å), whereas sampling depth of ATR-FTIR techniques is many times larger to detect structural alteration after plasma treatment. Analysis of surface chemistry of plasma-treated P/C samples with more sensitive techniques like X-ray photoelectron spectroscopy (XPS) would provide quantitative and more accurate information.

SEM image of helium plasma treated sample does not show any marked difference in surface morphology of the fibres. However, slight etching is observed on the fibre surface of oxygen plasma treated sample. Similar kind of small alterations in surface morphology of helium-oxygen plasma treated PET samples has been reported by Hwang et al. It is important to note that in spite of small changes in the surface morphology, considerable improvement in the hydrophilic properties is witnessed after APGD plasma treatment. In other words, mild plasma treatment does give rise to hydrophilic characteristics of the textile surface without causing significant damage to the surface.

The polyester fibre is a major component (67%) in the P/C blended fabric (67:33) used for the study. It is the polyester component in the P/C blended textiles, which renders hydrophobicity to the material. More hydrophobic property is displayed by the material especially when the per cent of polyester component in the blend is high. However, after plasma treatment the improved wettability of P/C samples is observed. It may be attributed to the enhanced hydrophilicity of the polyester component in the blend. However, detailed study of plasma treatment of P/C blended fabrics with different blend compositions may provide better information about the role of each bend component in improved wettability.

4 Conclusion
Hydrophilic properties of the polyester/cotton blended textiles have been found to be improved after the treatment with APGD plasma. Good wetting properties are obtained for the samples treated at higher discharge power and for longer treatment duration. However, the flow rate of helium essentially influences the efficiency of plasma treatment, as excess helium flow (beyond optimum concentration) results in poor efficiency of the plasma. Moreover, higher efficiency of plasma treatment is observed with a narrow electrode gap.

The use of even small amount of oxygen (as a reactive gas) has shown noticeable effect on the wicking properties of plasma treated fabric. SEM analysis of helium plasma treated sample does not exhibit any marked difference with control sample. However, oxygen plasma treated samples show small changes in surface morphology due to etching mechanism. Slight increase in absorbance ratio $A_{700}/A_{721}$ is observed in oxygen plasma treated sample, indicating the slight increase in the oxygen content of surface after plasma treatment.

Acknowledgement
Authors are thankful to the Ministry of Textiles (Government of India) for funding the project (Sanction Number 10/5/2006-CT-I). Thanks are also due to the Textile Engineering, Chemistry and Science Department of North Carolina State University for giving permission to use the facilities at their plasma laboratory. Authors are very grateful to Dr A N Desai, Director, BTRA, Dr G S Nadiger and Prof N V Bhat, for their precious help in realizing this project work.

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