

# Dielectric Barrier Discharge Plasma Induced Surface Modification of Polyester/Cotton Blended Fabrics to Impart Water Repellency Using HMDSO

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**ABSTRACT:** Continuous treatment of polyester/cotton blended fabric samples was carried with hexamethyldisiloxane (HMDSO) plasma on the pilot scale atmospheric pressure plasma reactor. The mixture of helium and argon was used as carrier gas for generating dielectric barrier discharge plasma. The effect of discharge power and treatment time on the water repellent properties of samples were evaluated with contact angle (CA) and spray test measurements. Spray test and CA results showed improved resistance to wetting with water. The effect of discharge conditions on the surface morphology and surface chemistry of plasma treated samples were investigated by scan-

ning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopic analysis, respectively. The presence of Si-O-Si and Si-CH<sub>3</sub> groups in the structure of plasma polymer deposited at the surface of P/C samples was revealed by FTIR spectroscopy. Further, structural differences in HMDSO plasma polymer deposited under different discharge conditions were reported with reference to organic/inorganic nature of plasma polymer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1092–1100, 2011

**Key words:** HMDSO; plasma polymer; water repellency; polyester/cotton fabric; infrared spectroscopy

## INTRODUCTION

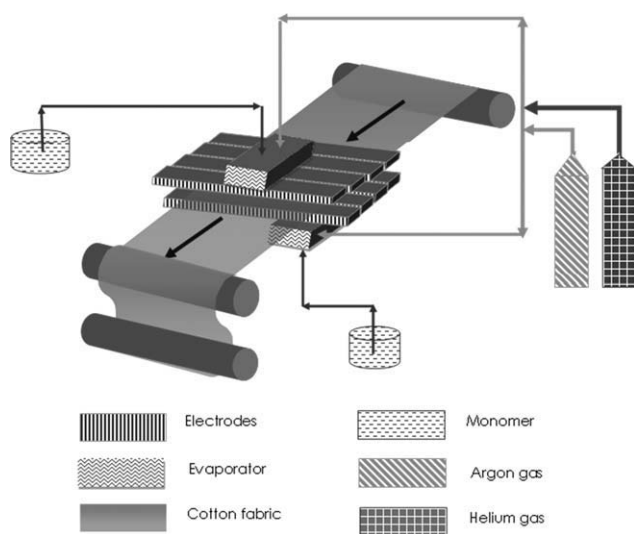
Plasma induced polymers differ significantly from those produced by classical synthesis techniques in their chemical structure and degree of cross-linking.<sup>1</sup> Unlike conventional polymerization, plasma polymerization process tends to form irregular three dimensional structures, where chemical structure of the plasma polymer may be quite different from a conventional polymer which has been derived from the same monomer.<sup>2</sup> Moreover, conventional polymerization needs a double bond or a functional group to polymerize. On the other hand, plasma can induce polymerization by breaking single bonds.<sup>3</sup> Plasma polymerization is a very complex phenomenon where different processes like activation, formation of free radicals, recombination of radicals etc. simultaneously take place. However, it is possible to control the properties of plasma polymer films with use of well-defined reactor geometry enabling homogeneous plasma conditions.<sup>4</sup>

Plasma technology being a dry and clean process provides a cost effective and environmentally friendly alternative to many industrial processes as the plasma processing produces no unwanted waste

products.<sup>5</sup> In addition, plasma surface modification technique allows controlling the chemistry and morphology of the fiber surface without affecting the bulk properties.<sup>6</sup> The chemical, morphological, and performance properties of plasma polymers' surface are principally controlled by chemical nature of a monomer used. In addition, process parameters such as power, monomer flow rate, electrode distance, treatment time, electrode geometry influence the mechanism, and rate of plasma polymerization for a given monomer.<sup>7,8</sup>

Various researchers have extensively explored the plasma polymerization of organosilicon monomers for different technological and industrial applications like coating for scratch resistance, chemical barrier, optical barrier, and corrosion resistance.<sup>9–13</sup> Hexamethyldisiloxane (HMDSO) is often preferred over other organosilicones for plasma polymerization because of its highly organic nature as well as its high vapor pressure.<sup>14</sup> The kinetics and mechanism of HMDSO plasma polymerization and properties of HMDSO plasma polymer is a subject of interest as seen from the substantial amount of research being carried out. Plasma polymerization of HMDSO on various natural as well as synthetic textile substrates such as cotton, polyester, wool, polypropylene etc. has been studied by various researchers.<sup>15–19</sup> Even our previous research work on cotton<sup>20</sup> has yielded excellent water repellent properties with the plasma polymerization technique. However, besides

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**Figure 1** Schematic diagram of atmospheric pressure plasma treatment unit PLATEX 600 (make-GRINP, S. R.L., Italy).

discharge conditions, the substrate used also plays a critical role in the plasma surface modification technique.

This article discusses about the experimental data on continuous online plasma polymerization of HMDSO on polyester/cotton blended fabric for imparting super hydrophobic properties. The alterations in surface morphology and surface chemistry of the fabric samples due to deposition of plasma polymer are discussed in relation with their performance properties.

## EXPERIMENTAL

### Materials

Hexamethyldisiloxane (HMDSO-98%, Alfa Aesar) was used as a monomer precursor for plasma polymerization. The experiments were carried out on commercially available polyester/cotton (P/C) blended ready for dyeing (RFD) fabric. The warp and weft counts of the fabric were 41 Ne and 38 Ne, respectively. Thread density in warp and weft direction was 102 and 74. The weight of the P/C fabric was 105 g per square meter and the blend composition of polyester and cotton part was 67% and 33%, respectively.

### Plasma reactor and operating conditions

Plasma polymerization of HMDSO was carried out on atmospheric pressure plasma reactor, PLATEX-600 (make GRINP S.R.L., Italy). The schematic of the plasma reactor is shown Figure 1. The system operates in continuous mode where online treatment of fabric is possible. The length of plasma zone (total

length of electrodes in the direction of fabric movement) is 12 cm and width is 55 cm. The minimal possible gap of 0.5 mm was kept in-between the electrodes since previous research<sup>21,22</sup> showed better efficiency of plasma treatment at narrower interelectrode gap.

Carrier gases like helium and argon are often added to the polymerizing gas plasma mixture to increase homogeneity and stability of plasma.<sup>23</sup> Helium has certain properties like high-energy metastable state, thermal conductivity, and chemical inertness which reduce instabilities in the plasma.<sup>24</sup> Though argon is widely used for deposition of plasma polymers, in this study, helium was mixed with argon for generating uniform and homogeneous nonthermal plasma. Liquid monomer (HMDSO) at a fixed flow rate of 0.65 mL/min was fed continuously to each evaporator. At the evaporator, monomer (HMDSO) was vaporized to a gaseous form at a temperature of about 150°C and then the monomer in vapor phase was mixed with carrier gas. This mixture of inert gas and vaporized monomer was then fed to the electrode system where electrical power was applied to the electrodes to generate plasma.

Four sets of experiments were carried out to capture the data on various parameters. The discharge power for plasma generation was kept at 2000 W, 3000 W, 4000 W, and 5000 W in experimental set I, II, III, and IV, respectively. In each experimental series, the plasma exposure duration was kept at 15 s, 30 s, 60 s, and 120 s. The plasma is generated from the mixtures of HMDSO (0.65 mL/min), Helium (flow rate: 2 L/min), and argon (3 L/min). The discharge conditions used for plasma polymerization and corresponding sample codes are given in Table I.

### Characterization techniques

The contact angle (CA) measurements were carried out using sessile drop method on "Easy Drop" standard drop analysis system of KRUSS GmbH, Germany, equipped with high speed camera IEEE1394b interface. The drop of distilled water of 5  $\mu$ L volume was placed on the plasma treated fabric sample with automatic dosing system followed by measurement of CA with sessile drop fitting method (Young Laplace fitting). An average of 30 reading was recorded for each sample. In addition, water repellency of polyester/cotton fabric treated under different discharge conditions was evaluated as per American Association of Textile Chemist and Colorist (AATCC) test method 22-2005.

The morphological changes in P/C samples after plasma treatment were investigated by scanning electron microscopy (SEM) photographs recorded on

**TABLE I**  
**Process Parameters Used during HMDSO Plasma Polymerization on Polyester/Cotton Blended Fabric**

Sr. No.	Set	Sample code	Treatment time (s)	Power (Watt)	Monomer flow rate (ml/min)	Argon flow (LPM)	Helium flow (LPM)
1	p <sub>0</sub> t <sub>0</sub> (Control)	–	–	–	–	–	–
2	I	p <sub>1</sub> t <sub>1</sub>	15	2000	0.65	3	2
3		p <sub>1</sub> t <sub>2</sub>	30				
4		p <sub>1</sub> t <sub>3</sub>	60				
5		p <sub>1</sub> t <sub>4</sub>	120				
6	II	p <sub>2</sub> t <sub>1</sub>	15	3000	0.65	3	2
7		p <sub>2</sub> t <sub>2</sub>	30				
8		p <sub>2</sub> t <sub>3</sub>	60				
9		p <sub>2</sub> t <sub>4</sub>	120				
10	III	p <sub>3</sub> t <sub>1</sub>	15	4000	0.65	3	2
11		p <sub>3</sub> t <sub>2</sub>	30				
12		p <sub>3</sub> t <sub>3</sub>	60				
13		p <sub>3</sub> t <sub>4</sub>	120				
14	IV	p <sub>4</sub> t <sub>1</sub>	15	5000	0.65	3	2
15		p <sub>4</sub> t <sub>2</sub>	30				
16		p <sub>4</sub> t <sub>3</sub>	60				
17		p <sub>4</sub> t <sub>4</sub>	120				

JEOL SEM model JSM 5400. The surface chemistry of polyester/cotton blended fabric was studied by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. The FTIR spectra were recorded at a resolution of 4 cm<sup>-1</sup> using a Perkin-Elmer spectrometer model system 2000 using zinc selenide (ZnSe) horizontal ATR accessory. The scanning range used was 4000–650 cm<sup>-1</sup> and an average of 50 scans was recorded.

## RESULTS AND DISCUSSION

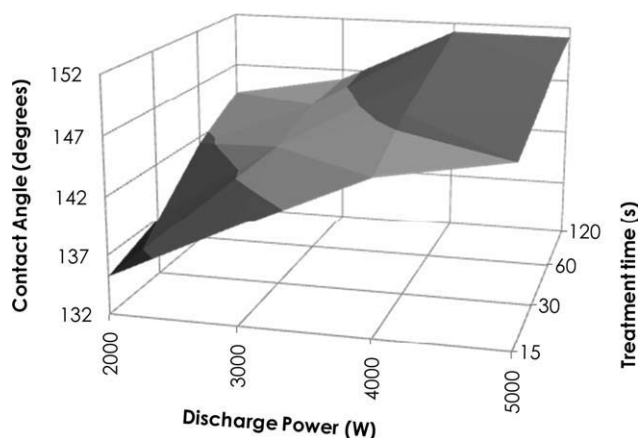
### Contact angle

Contact angle measurement is one of the established methods to determine the hydrophobicity or hydrophilicity of the textiles and polymer films. Since the untreated P/C blended sample gradually absorbed the water droplet placed on it, its CA value is considered as zero. The influence of treatment time and discharge power on the surface wetting properties of P/C samples are evaluated by CA measurements.

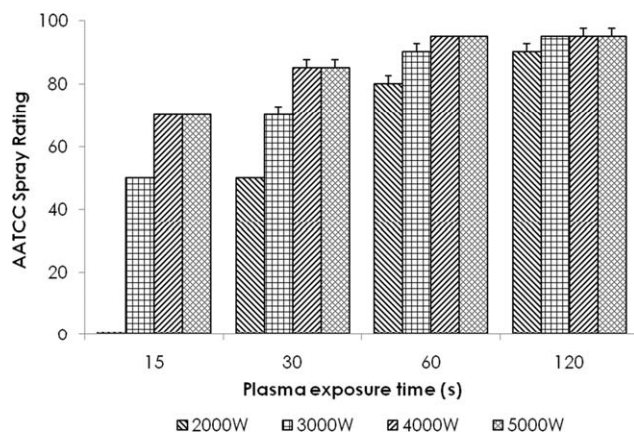
The CA values of fabric samples treated under different discharge conditions were plotted along with treatment time and discharge power. Figure 2 shows the influence of both discharge power and plasma treatment time on the CA of P/C samples. It can be seen from the Figure 2 that increase in plasma exposure time has resulted in higher CA values. The CAs of sample treated with 2000 W (Experimental set I) for 15 s, 30 s, 60 s and 120 s are 135°, 137°, 141.4°, and 144.2°, respectively. Similar trend is exhibited by the samples of experimental set II (3000 W), III (4000 W), and IV (5000 W). During plasma processes, the monomer molecules undergo selective chemical bond breaking and recombination proc-

esses to form macromolecules.<sup>25</sup> The improved water repellency in HMDSO plasma treated samples can be attributed to the introduced silicon atoms on the fiber surface.<sup>26</sup>

In addition, there is also an increase in the CA values with the increase in discharge power. For example, at a fixed exposure time of 60 s, CA values of 141.4°, 145.7°, 149.5°, and 150.1° are obtained for samples treated with discharge powers of 2000 W (p<sub>1</sub>t<sub>3</sub>), 3000 W (p<sub>2</sub>t<sub>3</sub>), 4000 W (p<sub>3</sub>t<sub>3</sub>), and 5000 W (p<sub>4</sub>t<sub>3</sub>), respectively. Figure 2 illustrates the enhanced hydrophobic character of the plasma treated fabric when exposure time and discharge power are increased. Although there is an increasing trend in the CA with increase in discharge power, yet the changes in CA values of 4000 W and 5000 W plasma treated samples are very small. It appears therefore



**Figure 2** The effect of treatment time and discharge power on contact angle values of plasma treated P/C samples.



**Figure 3** AATCC spray rating of HMDSO plasma treated fabric.

that the saturation of hydrophobic properties after discharge power of 4000 W take place.

### Water repellency by AATCC spray test

For many applications, CA measurement does not fulfill the requirement of water repellency. Since this study deals with imparting super hydrophobic properties to the textiles by the novel approach of plasma polymerization; more severe tests like AATCC spray test is used to determine the water repellent properties. In the spray test, water is sprayed on the taught textile fabric surface in controlled conditions. The results of AATCC spray test for samples treated under different discharge conditions are depicted in histogram (Fig. 3). The untreated P/C fabric sample was assigned with "0" spray rating due to complete wetting of both upper and lower surfaces. Irrespective of discharge power used, there is a noticeable increase in the spray rating with increase in plasma exposure time. For example, samples treated with discharge power of 3000 W for 15 s, 30 s, 60 s, and 120 s have exhibited spray rating values of 50, 70, 90, and 95, respectively. These observations of improved resistance to wetting with water are in accordance with the results reported by Young-Y Ji et al.<sup>26</sup> on polyester fabric.

In addition, at a fixed treatment time, there is an increase in spray rating with higher discharge powers. For example, spray ratings of samples treated for 60 s with discharge powers of 2000 W ( $p_{1t_3}$ ), 3000 W ( $p_{2t_3}$ ), 4000 W ( $p_{3t_3}$ ), and 5000 W ( $p_{4t_3}$ ) are 80, 90, 95, and 95, respectively. It can be noted from Figure 3 that, the effect of water repellency is getting leveled after discharge power of 4000 W. The chemical changes on the surface of HMDSO plasma treated fabric samples at different discharge powers are elaborately discussed in FTIR spectroscopic analysis section in this article. It is interesting to note that treatment with discharge power of 4000 W for 60 s

has shown spray rating of 95, which indicates very good water repellent properties. The treatment time of 60 s appears to be appropriate for the purpose of commercial scale textile processing. The enhanced hydrophobicity of plasma treated samples treated with higher discharge powers for longer durations may be attributed to higher amount of deposition of plasma polymer. Increase in deposition thickness of plasma polymer with increase in treatment time is reported by Morent et al.<sup>27</sup>

### Surface morphology by scanning electron microscopy

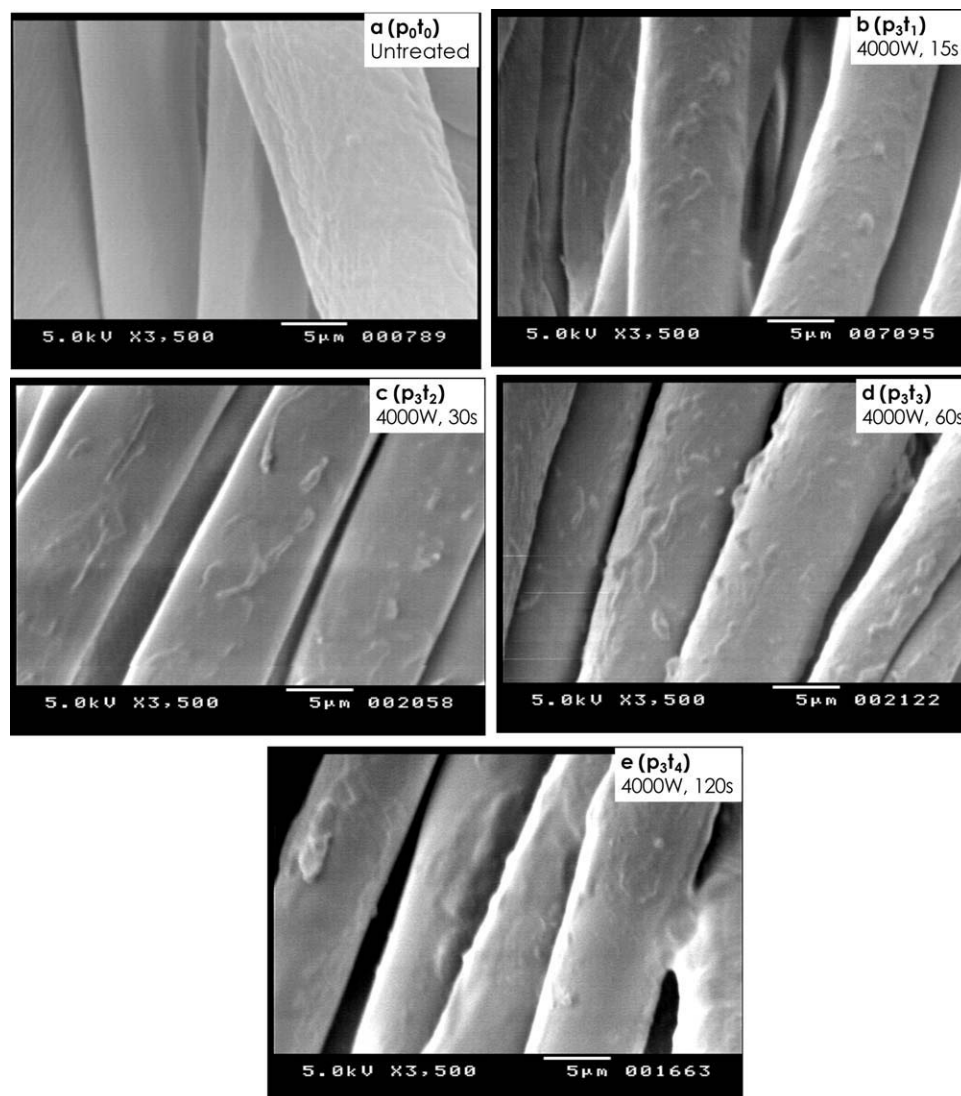
SEM was used to study the surface morphological changes in the polyester/cotton blended fabric treated with different discharge conditions. The SEM of untreated sample showed hardly any deposition or coating on the surface [Fig. 4(a)]. The SEM photographs of samples treated with 4000 W for 15 s ( $p_{3t_1}$ ), 30 s ( $p_{3t_2}$ ), 60 s ( $p_{3t_3}$ ), and 120 s ( $p_{3t_4}$ ) are shown in Figure 4(b–e), respectively. All samples treated with HMDSO exhibit deposition of plasma polymer on their surfaces. In addition, it may be pointed out that there is an increase in the deposition of plasma induced polymer with respect to treatment time. The sample treated for 120 s ( $p_{3t_4}$ ) showed higher deposition of plasma polymer on its surface. A similar kind of enhanced deposition with increase in plasma exposure time was observed in other samples treated with discharge powers of 2000 W, 3000 W, and 5000 W.

The effect of discharge power on the extent of deposition of plasma polymer is illustrated by Figure 5(f–i). These figures represent the SEM photographs of samples treated for 60 s with discharge power of 2000 W ( $p_{1t_3}$ ), 3000 W ( $p_{2t_3}$ ), 4000 W ( $p_{3t_3}$ ), and 5000 W ( $p_{4t_3}$ ), respectively. It is evident from the figures that, more deposition is observed in samples treated with 4000 W and 5000 W when compared with that in samples treated with 2000 W and 3000 W. However, no significant difference in the deposition on samples treated with discharge power of 4000 and 5000 W was noticed as can be seen from Figure 5(h,i).

From the above discussion it is clear that, longer treatment times and higher discharge powers result in more deposition of plasma polymer on the surface of the samples. The difference in wetting behavior of samples observed during spray test appears to be in accordance with SEM photographs, i.e., samples with higher deposition (i.e., samples treated for longer treatment times for higher powers) showed better spray rating value.

### FTIR spectroscopic analysis

The polyester/cotton blended fabric used for the current experiment contains polyester as a major



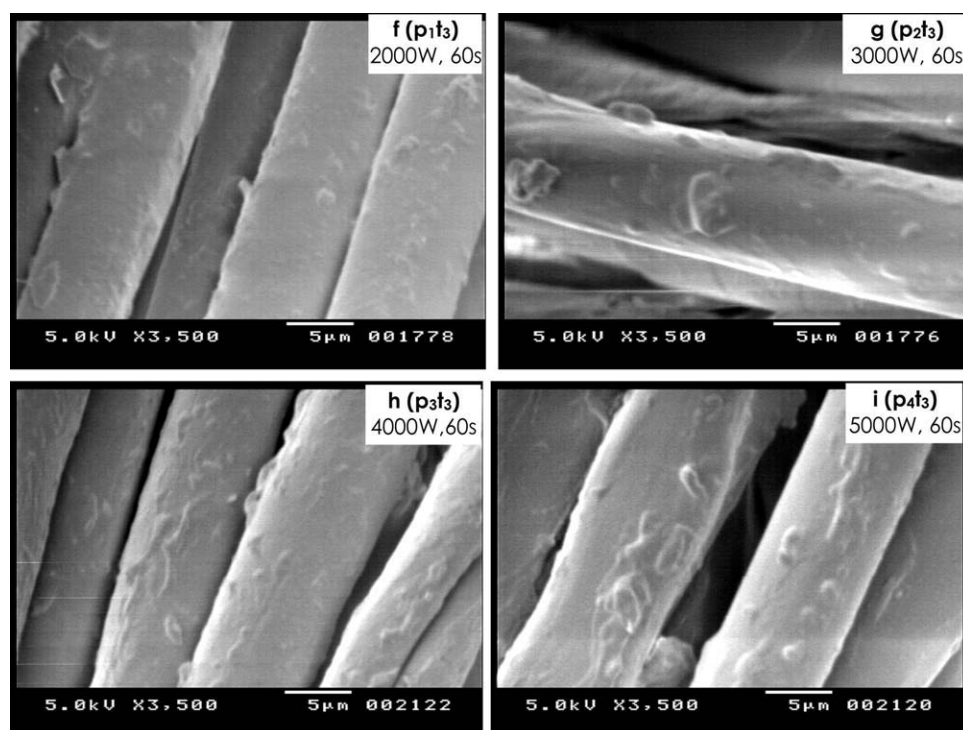
**Figure 4** SEM photographs of (a) untreated sample, and samples treated with 4000 W for (b) 15 s, (c) 30 s, (d) 60 s, and (e) 120 s.

component with a blend percentage of 67 (%). Therefore, the FTIR spectrum of untreated P/C blended fabric [Refer Fig. 6(a)], predominantly exhibits peaks at  $1709\text{ cm}^{-1}$ ,  $1233\text{ cm}^{-1}$ , and  $721\text{ cm}^{-1}$  pertaining to polyester component of the blend. The peak at  $1709\text{ cm}^{-1}$  can be assigned to stretching vibration of C=O group in ester and the peak at wavenumber  $1233\text{ cm}^{-1}$  can be assigned to asymmetric stretching of aromatic ester.<sup>28</sup> The peak at  $721\text{ cm}^{-1}$  can be attributed to aromatic C—H out of plane vibrations.

The ATR-FTIR spectra of samples treated with discharge power of 3000 W for 15 s (sample  $p_2t_1$ ), 30 s (sample  $p_2t_2$ ), 60 s (sample  $p_2t_3$ ), and 120 s (sample  $p_2t_4$ ) are shown in Figure 6. The ATR spectra of all the HMDSO plasma treated samples show distinct peaks at the wavenumber  $839\text{ cm}^{-1}$  and  $793\text{ cm}^{-1}$ . The occurrence of these peaks can be attributed to Si—C rocking vibrations in the Si—CH<sub>3</sub> groups.<sup>29</sup>

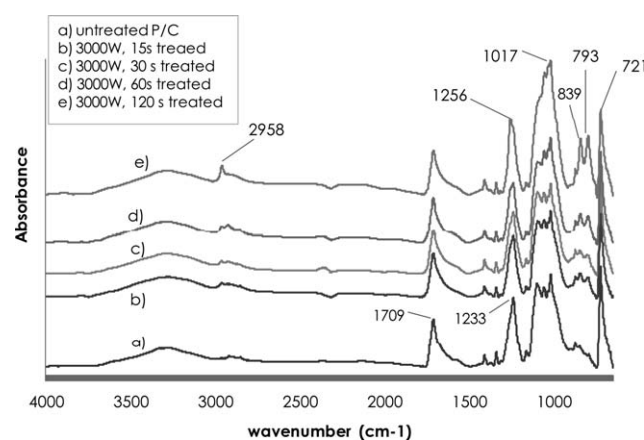
Figure 6 also shows gradual intensification of absorbance intensity of these characteristic peaks at  $839\text{ cm}^{-1}$  and  $793\text{ cm}^{-1}$  with increase in plasma exposure time. Increase in absorbance intensity indicates higher concentration of Si—CH<sub>3</sub> groups on the surface of plasma treated fabric. In addition, slight increase in the absorbance intensity of the peak at  $2958\text{ cm}^{-1}$  can be noticed with treatment time which can be attributed to CH<sub>3</sub> asymmetric stretching.<sup>30</sup>

It may be pointed out that the absorbance band at  $1017\text{ cm}^{-1}$  requires individual consideration as the same peak is present in the spectra of both untreated and plasma treated samples. The difference between the absorbance intensity of the peak at  $1017\text{ cm}^{-1}$  in untreated and plasma treated samples can be easily differentiated. There is a gradual increase in the peak intensity at  $1017\text{ cm}^{-1}$  with longer plasma exposure times. In addition it can be observed that, the



**Figure 5** SEM images of P/C samples treated for 60 s under different discharge powers; (f) 2000 W, (g) 3000 W, (h) 4000 W, and (i) 5000 W.

position of the peak  $1233\text{ cm}^{-1}$  in control sample has shifted to  $1256\text{ cm}^{-1}$  in plasma treated samples. This shift in peak at  $1256\text{ cm}^{-1}$  may be attributed to symmetric  $\text{CH}_3$  deformation. Further, to quantify the results of FTIR spectra and to investigate the influence of plasma exposure time, absorbance ratios of characteristic peaks are calculated. These results are used to discuss the influence of the discharge conditions on the chemistry and structure of plasma polymer deposited on the surface of the P/C fabric.



**Figure 6** ATR-FTIR spectra of untreated and plasma treated P/C samples with 3000 W for 15, 30, 60, and 120 s.

### Quantitative analysis of the FTIR spectra

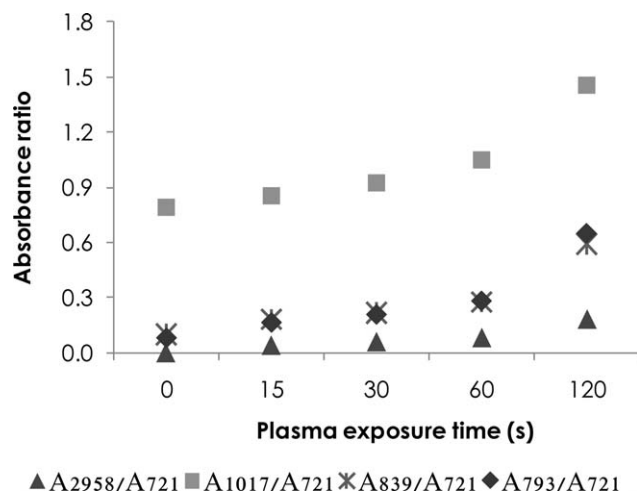
Quantitative FTIR spectroscopic analysis is done by way of analyzing the ratio of absorbance intensity at specific characteristic bands and to discuss the effect of treatment time and discharge power on chemical nature of plasma polymer. The intensity of peak at  $721\text{ cm}^{-1}$  was found to be least affected by the different plasma treatment conditions. Therefore, it was considered as a reference peak for absorbance ratio calculations. The ratio of absorbance intensity was calculated as follows

Absorbance Ratio

$$= \frac{\text{Absorbance Intensity of Characteristic peak}}{\text{Absorbance Intensity of reference peak}}$$

### Effect of treatment time on surface chemistry

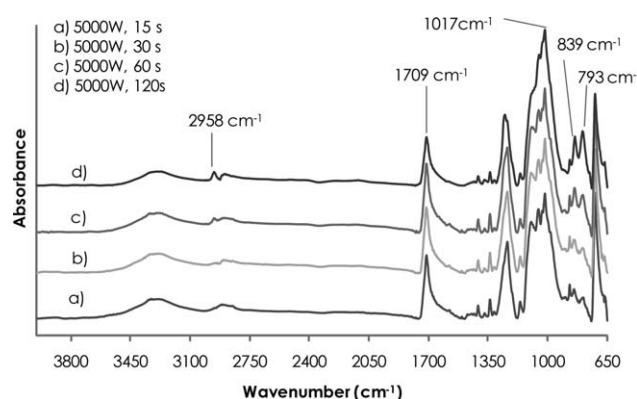
Here absorbance ratio refers to the ratio of corrected heights of the peaks. The effect of treatment time on the absorbance ratios of characteristic peaks *viz.*  $A_{2958}/A_{721}$ ,  $A_{1017}/A_{721}$ ,  $A_{839}/A_{721}$ ,  $A_{793}/A_{721}$ , are shown in Figure 7. It is evident from the Figure 7 that, with increase in duration of plasma treatment, there is a gradual increase in absorbance ratios of all the characteristic peaks. The ratios  $A_{839}/A_{721}$  obtained for plasma treatment time of 0 s (untreated), 15 s, 30 s, 60 s, and 120 s are, 0.10, 0.18,



**Figure 7** Absorbance ratios of characteristic peaks at 2958  $\text{cm}^{-1}$ , 839  $\text{cm}^{-1}$ , 793  $\text{cm}^{-1}$ , 1017  $\text{cm}^{-1}$  (Discharge power 3000 W, time of treatment 15 s, 30 s, 60 s, and 120 s).

0.22, 0.27, and 0.59, respectively. Similarly, absorbance ratios  $A_{793}/A_{721}$  and  $A_{2958}/A_{721}$  showed considerable increase with respect to treatment time.

The peak at 1017  $\text{cm}^{-1}$  also show increase in absorbance ratio at longer treatment times. For example, absorbance ratio  $A_{1017}/A_{721}$  for untreated sample is 0.79, which then gradually increased almost by two times to the value of 1.457 for plasma exposure time of 120 s. It is pertinent to note that Morent has reported strong absorption band at 1020  $\text{cm}^{-1}$  which can be assigned to Si—O—Si stretching vibrations.<sup>27</sup> In this study, the monomer HMDSO, contain Si—O—Si in its backbone. Therefore, the increase in absorbance intensity of the peak at 1017  $\text{cm}^{-1}$  may be assigned to Si—O—Si groups in the plasma polymer deposited on the surface of the polyester/cotton blended fabrics.

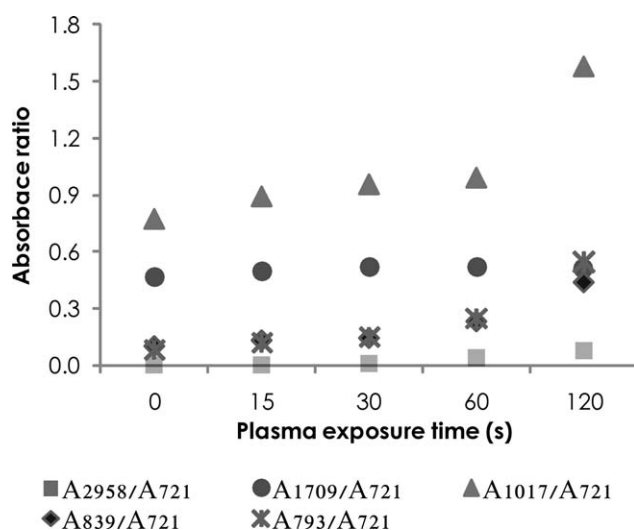


**Figure 8** ATR-FTIR spectra of plasma treated P/C samples with 5000 W for 15, 30, 60, and 120 s.

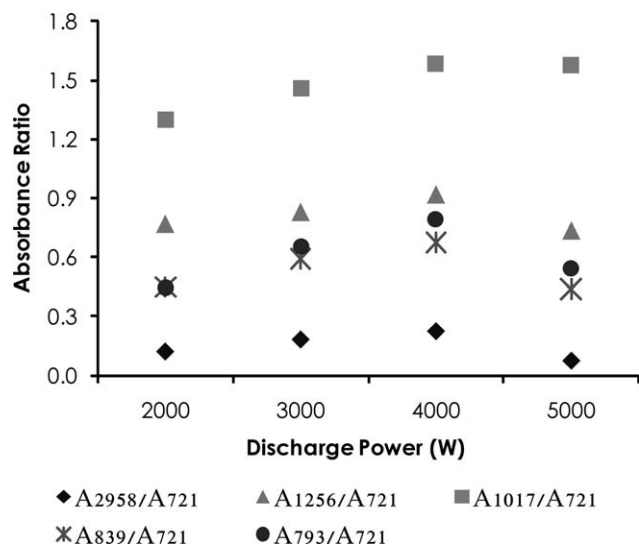
The FTIR spectra of samples treated with 5000 W for 15 s ( $p_{4t_1}$ ), 30 s ( $p_{4t_2}$ ), 60 s ( $p_{4t_3}$ ), and 120 s ( $p_{4t_4}$ ) are shown in Figure 8. Similar to the 3000 W plasma treated samples, the ATR spectra of samples treated with 5000 W, exhibit characteristic peaks at 2958  $\text{cm}^{-1}$ , 1017  $\text{cm}^{-1}$ , 839  $\text{cm}^{-1}$ , and 793  $\text{cm}^{-1}$ . Moreover, the absorbance ratios of these characteristic peaks namely  $A_{2958}/A_{721}$ ,  $A_{1017}/A_{721}$ ,  $A_{839}/A_{721}$ , and  $A_{793}/A_{721}$  showed similar trend at longer treatment times (Refer Fig. 9). However, it is interesting to note that the ratio  $A_{1709}/A_{721}$  remains practically unaltered for all the treatment times. This behavior of the peak at 1709  $\text{cm}^{-1}$  signifies the fact that HMDSO plasma treatment does not alter composition of carbonyl group in the fabric. From quantitative analysis of FTIR spectra, it can be inferred that, the increase in absorbance intensity or absorbance ratio is most probably due to higher deposition of HMDSO plasma polymer at longer treatment times.

#### Effect of discharge power on surface chemistry

The change in absorbance ratio of characteristic peaks with respect to power is shown in Figure 10. The ratios are obtained for samples treated for 120 s with 2000 W ( $p_{1t_4}$ ), 3000 W ( $p_{2t_4}$ ), 4000 W ( $p_{3t_4}$ ), and 5000 W ( $p_{4t_4}$ ). It could be seen from the Figure 10 that, initially with increase in discharge power from 2000 W to 4000 W, there is a gradual increase in the absorbance ratio of all the characteristic peaks at 2958  $\text{cm}^{-1}$ , 1256  $\text{cm}^{-1}$ , 1017  $\text{cm}^{-1}$ , 839  $\text{cm}^{-1}$ , and 793  $\text{cm}^{-1}$ . Increase in deposition rate of plasma polymer at higher discharge powers is reported by FANG et al.<sup>31</sup> They have attributed it to more fragmentation of a monomer providing better chances of polymerization.



**Figure 9** Absorbance ratios of characteristic peaks at 2958  $\text{cm}^{-1}$ , 839  $\text{cm}^{-1}$ , 793  $\text{cm}^{-1}$ , 1017  $\text{cm}^{-1}$  (Discharge power 5000 W, time of treatment 15 s, 30 s, 60 s, and 120 s).

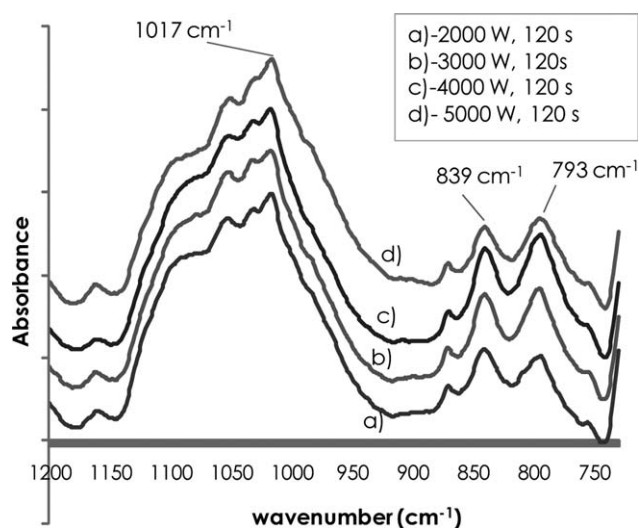


**Figure 10** Effect of discharge power on the absorbance ratios of characteristic peaks at 2958  $\text{cm}^{-1}$ , 839  $\text{cm}^{-1}$ , 793  $\text{cm}^{-1}$ , 1017  $\text{cm}^{-1}$ .

However, beyond 4000 W, further increase in discharge power (i.e., to 5000 W) showed decrease in the absorbance ratios  $A_{2958}/A_{721}$ ,  $A_{1256}/A_{721}$ ,  $A_{839}/A_{721}$ , and  $A_{793}/A_{721}$ . It may be pointed out that the peaks at 839  $\text{cm}^{-1}$  and 793  $\text{cm}^{-1}$  represent organic character of a plasma polymer film due to  $\text{CH}_3$  groups. Decrease in absorbance ratios of these peaks may be due to reduction in organic character of plasma polymer at higher discharge power of 5000 W. Whereas, it is interesting to note that, unlike other characteristic peaks, the absorbance ratio of peak at 1017  $\text{cm}^{-1}$  shows continuous increase even at 5000 W. The peak at 1017  $\text{cm}^{-1}$  may be assigned to inorganic nature of plasma polymer due to Si—O—Si groups. Therefore, further analysis was carried out to get an idea about the organic/inorganic nature of plasma polymer deposited on the surface of P/C blended fabric.

$$R = \frac{\text{Sum of corrected area under peaks (839 cm}^{-1} + 793 \text{ cm}^{-1})}{\text{Corrected area under peak 1017 cm}^{-1}}$$

It may be noted that, increase in the ratio  $R$  indicates increase in organic nature, whereas decrease in ratio  $R$  shows more inorganic nature of the plasma polymer deposited on the fabric surface. The effect of discharge power and treatment time on the ratio  $R$  is shown in Figure 12. It can be noticed that, initially there is increase in the  $R$  value with increase in discharge power from 2000 W to 4000 W. Schmachtenberg et al.<sup>33</sup> have reported increase in the organic character of plasma polymer



**Figure 11** Normalized FTIR spectra of samples treated for 120 s with discharge power of 2000 W (p1t4), 3000 W (p2t4), 4000 W (p3t4), and 5000 W (p4t4).

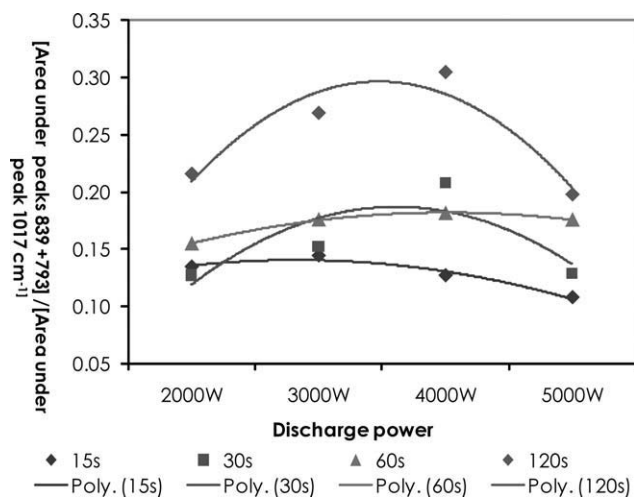
#### Organic–inorganic nature of plasma polymer

Data on absorbance ratio signify the importance of different process parameters on the deposition rate and chemical nature of plasma induced polymer. The Si—O group represents the inorganic nature of the films, while the Si—( $\text{CH}_3$ ) represents the organic nature of plasma polymer. The ratios organic and inorganic IR bands reflect the fundamental differences in the chemical structure of HMDSO plasma polymer.<sup>32</sup> To evaluate the effect of discharge power on the chemical nature of plasma polymer, samples treated for 120 s with different discharge powers are taken into consideration. The peak at 1017  $\text{cm}^{-1}$  for all the samples was normalized to the absorbance value of 1.5. The normalized FTIR spectra of samples treated for 120 s with different discharge powers is shown in Figure 11.

The ratio of organic to inorganic part of the plasma polymer is calculated as follows:

at higher discharge powers. However, further increase in discharge power led to drop in the ratio  $R$ , indicating thereby the loss in the organic character of the plasma polymer. It may be inferred from the above results that, up to 4000 W, plasma polymer shows a tendency to retain its original  $\text{CH}_3$  groups in the structure. On the other hand, further increase in power has caused decline in organic structure due to very high fragmentation of a monomer.





**Figure 12** Effect of discharge power and treatment time on the organic-inorganic nature of the HMDSO plasma polymer.

## CONCLUSIONS

The continuous deposition of plasma induced HMDSO polymer on polyester/cotton blended fabric was effectively carried out with pilot scale plasma reactor for imparting water repellent properties. The CA and spray rating results showed excellent resistance to wetting with water owing to deposition of water repellent plasma polymer on the surface of the fabric. The treatment time of only 60 s has resulted in spray rating of 95. The treatment time of 60 s is well within the commercial scale textile processing requirements.

In addition, the plasma treatment parameters *viz.*, duration of treatment and discharge power are found to have significant role in controlling the structure and properties of the plasma polymer. The deposition of plasma polymer was evidenced by SEM photographs. The surface chemical analysis using FTIR spectroscopy has shown considerable increase in absorbance ratio of characteristic peaks at  $839\text{ cm}^{-1}$ ,  $793\text{ cm}^{-1}$ , and  $1017\text{ cm}^{-1}$ , which indicates the presence of Si-containing groups in the structure of plasma polymer. In addition, it was observed that, organic nature of the plasma polymer initially increased with increase in discharge power up to 4000 W. Further increase in discharge power has resulted in decrease in organic nature of plasma polymer.

The chemical and morphological changes occurred at the surface of sample under different discharge conditions were evident as seen from different characterization techniques. However, the diagnosis of plasma using mass spectroscopy with reference to actual changes in deposited plasma polymer would provide more precise information about structural changes due to discharge conditions.

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