Plasma Enhanced Chemical Vapor Deposition of Tetraethylorthosilicate and Hexamethyldisiloxane on Polyester Fabrics Under Pulsed and Continuous Wave Discharge

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ABSTRACT: The article reports plasma enhanced chemical vapor deposition (PECVD) of $SiO_xC_yH_z$ polymers on polyester fabric using tetraethylorthosilicate (TEOS) and hexamethyldisiloxane (HMDSO) precursors. Modulated discharge was used to study the effect of duty cycle on the hydrophobic properties of plasma treated-polyester fabrics. T_{on} and T_{off} periods in modulated discharge were adjusted in such a way to get duty cycle values of 0.25, 0.50, 0.83, and 1.00, respectively. The hydrophobicity of the treated samples was evaluated by static contact angle measurement. Incorporation of Si—O, Si—CH$_3$ groups on the surface of polyester fabric was evidenced in Fourier transform infrared (FTIR) spectroscopic analysis. In addition, organic–inorganic character of HMDSO plasma polymer derived under modulated discharge and continuous wave discharge was investigated by FTIR spectroscopy. For equal treatment durations (T_{total}), the plasma polymer deposited under pulsed discharge at lower duty cycle showed relatively higher organic content indicating comparatively greater structural retention of the original monomer in modulated discharge. However, structural analysis showed that treatment duration is more critical factor than duty cycle in determining organic character of $SiO_xC_yH_z$ plasma polymers. Ash content results indicated that plasma polymerization proceeds even during T_{off} period. Evaluation of mechanical properties of polyester fabrics showed decrease in tear strength in both TEOS and HMDSO plasma-treated samples. The durability of plasma polymers to washing showed promising prospects of use of PECVD for functional finishing of polyester fabrics. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: pulsed plasma; duty cycle; polyester fabric; TEOS; HMDSO; structural retention; infrared spectroscopy

INTRODUCTION

The "plasma polymerization" refers to the formation of polymers from initial monomers in non-thermal discharge.[1] Surface modification with cold plasma offers advantages such as use of any volatile chemical compound as a monomer, coating in one-step, and requirement of only small quantities of starting materials.[2] The films produced by plasma polymerization are usually insoluble, pinhole free, highly cross-linked and adhere well to substrates. In addition, plasma polymerization appears to be relatively simple one-step process.[3,4] Thin films with tailored surface composition and structure can be produced by plasma enhanced chemical vapor deposition (PECVD) technique.[5]

Plasma polymers exhibit a structure with high degree of cross-linking and close-knit network.[6] The film properties and the deposition process are difficult to control in continuous wave (CW) discharge due to the diversity of functional groups produced by the multitude of possible chemical reactions.[7] On the other hand, pulsed plasma systems allow better control over the physical and chemical properties of the thin film deposition.[8] Therefore, to meet the specific requirements of surface functionalities, polymerization by pulsed discharge technique is a better option. Greater retention of the chemical structure of a monomer is achieved in pulsed plasma polymerization.[9–11] Pulse parameters in pulsed discharge allow the incorporation of desired chemical groups and structurally defined units at the surface.[12] Lower substrate temperatures can be maintained by varying duty cycles in pulsed plasma.[13,14] Hence, pulsed plasma is considered as a simple and typical method to control the chemistry of plasma polymers.

There are numerous studies in the field of plasma polymerization of hexamethyldisiloxane (HMDSO)[15,16] and tetraethylorthosilicate (TEOS).[17,18] However, the effect of duty cycle on structural retention of

TABLE I
Experimental Parameters Used During Plasma Treatment

S. No.	Monomer	T_{on} (ms)	T_{off} (ms)	Duty cycle	$T_{total} = T_{on\ Cumulative} + T_{off\ Cumulative}$ (s)	$T_{on\ Cumulative}$ (s)	Power (Watt)	Helium flow (L/min)
1	TEOS	5	15	0.25	60	15		
2	TEOS	5	5	0.50	60	30	4000	5
3	TEOS	5	1	0.83	60	50		
4	TEOS	CW*	0	1.00	60	60		
5	HMDSO	5	15	0.25	60	15		
6	HMDSO	5	5	0.50	60	30	4000	5
7	HMDSO	5	1	0.83	60	50		
8	HMDSO	CW*	0	1.00	60	60		

* Continuous wave discharge.

HMDSO and TEOS during pulsed plasma polymerization so far has not been reported. Moreover, the influence of pulse parameters on mechanical properties needs to be investigated. Therefore, the present paper reports the structural properties of $SiO_xC_yH_z$ plasma polymers obtained in pulsed and CW discharge generated from HMDSO and TEOS precursors.

EXPERIMENTAL

Materials

PECVD of TEOS and HMDSO was carried out on 100% polyester fabric. The warp and weft yarn count in the fabric was 44 Ne each. The weight of the fabric was 77 g/m^2. Prior to plasma treatment, fabric samples were washed with 2 g/L standard soap and 0.5 g/L sodium carbonate at 70°C for 2 h in washing machine followed by drying. TEOS and HMDSO (Aldrich 98%) were used as precursors for PECVD. Helium (99.9%) was used as a carrier gas for plasma generation.

Plasma treatment

Pulsed plasma polymerization of HMDSO and TEOS was carried out at atmospheric pressure on the plasma system, PLATEX 600 (make Grinp S.R.L., Italy). The detailed features of the plasma system are described elsewhere.[19,20] In pulse plasma systems, duty cycle (δ) is defined by the relative duration of the pulse-ON time [eq. (1)].[13]

$$\delta = \frac{T_{on}}{T_{off} + T_{on}} \quad (1)$$

Discharge power could be supplied in CW mode or in pulsed mode. Variable duty cycle values may be obtained by varying T_{on} and T_{off} periods. In this study, plasma on time (T_{on}) was kept constant at 5 milliseconds (ms) and off time (T_{off}) was kept at 15,

5, 1, and 0 ms, respectively. The duty cycles values thus obtained were δ = 0.25, 0.50, 0.83, and 1.00, respectively. For example, δ = 0.25 refers to T_{on} = 5 ms and T_{off} = 15 ms. It implies that in a single cycle of 20 ms, plasma is on for 5 ms and off for 15 ms. Therefore, at this duty cycle, when total treatment duration (T_{total}) is 60 s, the cumulative on time ($T_{on\ Cumulative}$) is 15 s. Increase in duty cycle refers to increase in cumulative T_{on} time for a given treatment duration. The different plasma parameters used during the experiment are listed in Table I. The flow rate of the monomer was maintained at 1 mL/min.

Characterization techniques

The contact angle on polyester fabrics after plasma treatment were measured using "Easy Drop" standard drop shape analysis system (make-KRUSS GmbH, Germany), equipped with high-speed camera IEEE1394b interface. Three test liquids, viz. water, ethylene glycol (20%), and formamide were used to measure the static contact angle.

Scanning electron microscopy was used to study the surface topography of the polyester fabric using JEOL SEM model JSM 5400. Surface chemical composition of the polyester samples was studied by attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR). The FTIR spectra were recorded on Perkin–Elmer spectrometer model system 2000. The residual ash content of HMDSO plasma-treated sample was determined by IS 199 : 1989 method. Predetermined weight of the fabric sample was transferred to crucible and it was then subjected to complete ashing at about 750°C for 1 h in a furnace. Finally, weight of the residue was determined and % residual ash content was calculated based on the initial weight of the sample and weight of the residue. The tear strength of polyester samples after plasma treatment was measured using Elmendorf tear strength tester by ASTM D1424-09 method. To assess durability to washing, plasma-
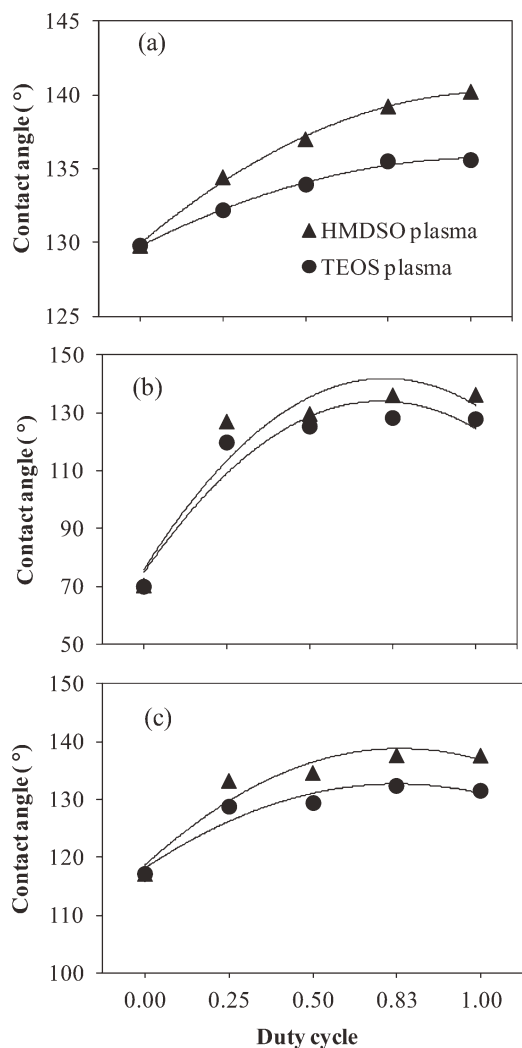
Figure 1 Contact angle measured on plasma-treated polyester fabrics using (a) water, (b) formamide, and (c) ethylene glycol.

treated polyester fabrics were subjected to repeated number of washing cycles as per AATCC 61(2A)-2006 method.

RESULTS AND DISCUSSION

Contact angle

Contact angle determination is widely used for studying the wetting/non-wetting phenomena on a solid material.[21] Figure 1 depicts the effect of duty cycle on contact angle of polyester fabrics. The contact angle was measured with three different test liquids, namely water, formamide and ethylene glycol (20%). Water contact angle (WCA) on untreated polyester fabric was 129°. WCA of polyester fabric gradually increased at higher duty cycles in case of both TEOS and HMDSO plasma treatments. For $\delta = 1.0$, WCA of HMDSO and TEOS plasma-treated samples were 141.7° and 135.6°, respectively. Since

polyester fabric is inherently hydrophobic, the increase in WCA is not very large after PECVD treatment. However, contact angles (measured with formamide and ethylene glycol) on HMDSO and TEOS plasma-treated samples exhibited abrupt increase when compared to contact angle values on the untreated polyester fabric. For example, formamide contact angle on the untreated fabric was 70.1°. For $\delta = 1$, it then increased to 136.2° and 127.9° after treatment with HMDSO and TEOS plasma, respectively [Fig. 1(b)]. There appears saturation of hydrophobicity imparted by plasma treatment beyond duty cycle value 0.8. In addition, it may be noted that irrespective of duty cycle or test liquid used, the contact angles on HMDSO plasma-treated samples are higher than those observed in case of TEOS plasma-treated samples.

Structural studies of plasma polymers

FTIR spectra of monomers

Figure 2 depicts IR transmission spectra of HMDSO and TEOS liquid monomers. The IR spectrum of HMDSO liquid exhibits absorption bands due to Si—O/Si—O—Si stretching near 1051 cm^{-1} and Si(CH$_3$)$_3$ rocking at 1252 cm^{-1}.[22] The peaks due to Si—CH$_3$ stretching are observed near 839 cm^{-1} and 754 cm^{-1}. In addition, bands pertaining to asymmetric and symmetric stretching of methyl groups occur near 2958 cm^{-1} and 2900 cm^{-1}, respectively. The peak at 687 cm^{-1} may be attributed to asymmetric stretching of Si—C.[23]

As could be seen from Figure 2, asymmetric stretching of Si—O—C vibrations occurs near 1000–1100 cm^{-1} in IR spectrum of TEOS. Due to typical structure of TEOS [Si—(—O—C$_2$H$_5$)$_4$], the peak at 1078 cm^{-1} may be attributed to Si—O groups. The absorbance band at 1167 cm^{-1} may be due to
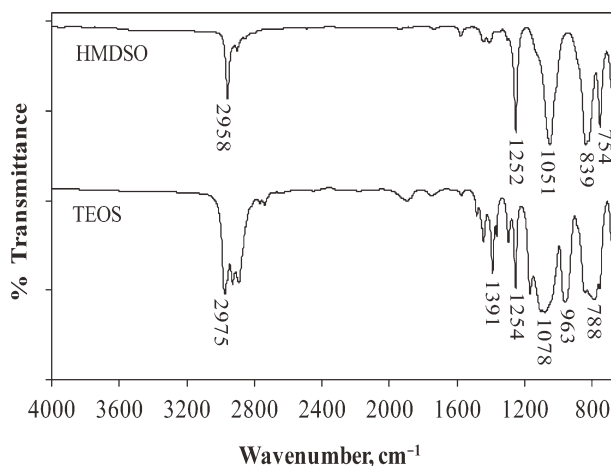

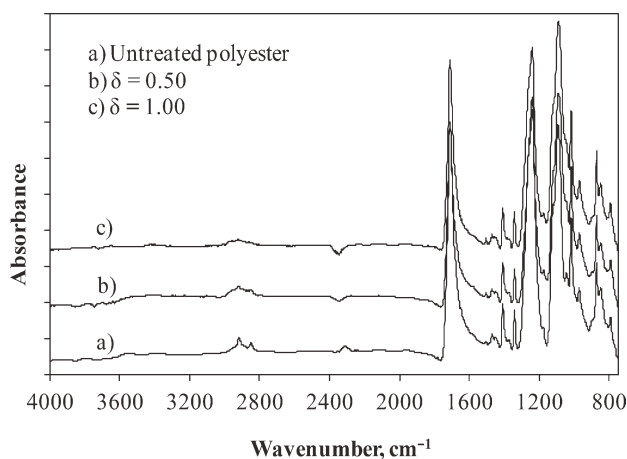**Figure 2** FTIR spectra of HMDSO and TEOS liquid monomers.

Figure 3 FTIR spectra of polyester fabric treated with TEOS plasma at different duty cycles (Discharge power 4000 W, T_{total} 60 s, helium flow 5 L/min, TEOS flow 1 mL/min).

Si—O—CH$_2$— groups[24] and peak at 2975 cm^{-1} may be assigned to CH$_3$ asymmetric stretching vibration. Symmetric deformation band of methyl group is denoted by the peak at 1391 cm^{-1}.

FTIR spectroscopic analysis of polyester fabric

FTIR spectra of the polyester fabrics before and after TEOS plasma treatment are depicted in Figure 3. The inherent peak at 1715 cm^{-1} in the IR spectrum of polyester fabric may be assigned to C=O stretching of aromatic ester and strong band at 1235 cm^{-1} is due to asymmetric stretching of aromatic ester.[25,26] Ring C—H out of plane bending and ring ester C—C out of plane bending vibrations are denoted by the peak 871 cm^{-1}. The peak near 721 cm^{-1} is attributed to C=O out-of-plane bending and ring CH out-of-plane bending.[27]

FTIR spectra of TEOS plasma-treated polyester fabric (Fig. 3) do not show any marked difference when compared to IR spectrum of the untreated fabric. On the other hand, FTIR spectra of HMDSO plasma-treated polyester fabrics (Figure 4) exhibit small change near the wave number 839 cm^{-1} and 790 cm^{-1} that may be assigned to Si—C rocking vibrations. The very small or no change exhibited by FTIR spectroscopic analysis may be attributed to short plasma treatment durations or it may be due to overlapping of absorption peaks of plasma polymers with inherent absorption peaks of polyester fabric. The deposition of the plasma polymer on the fabric surface ($T_{total} = 60$ s) is perhaps too little to detect all the characteristic peaks by FTIR spectroscopy.

The normalized FTIR spectra of HMDSO plasma-treated polyester fabric ($T_{total} = 60$ s) amplified over the peaks at 2958, 839, and 790 cm^{-1}, is depicted in

Figure 5. It is clear from the Figure 5(x) that the peak at 2958 cm^{-1}, which is absent in IR spectra of untreated polyester fabric, appears only after HMDSO plasma treatment. The same peak was observed in IR spectrum of HMDSO monomer (Fig. 2). Therefore, the peak at 2958 cm^{-1} can be assigned to asymmetric stretching of methyl groups. In addition, there appears intensification of the peaks at 839 and 790 cm^{-1} after HMDSO plasma treatment [Fig. 5(y)]. Therefore, quantitative data were derived by integrating absorption intensities of the characteristic peaks at 2958, 839, and 790 cm^{-1} (Table II). It could be seen from the Table II that there is a gradual increase in integrated absorption intensities of the characteristic peaks when duty cycle is increased. It suggests higher concentration of —CH$_3$ and Si— groups on the surface of polyester fabric treated at higher duty cycles. It implies increase in deposition of HMDSO plasma polymer when duty cycle is increased. It may be attributed to increased plasma *on* time (i.e., $T_{on\ Cumulative}$) at higher duty cycles, which provides better chances for fragmentation of a monomer and subsequent deposition on the fabric surface.

Effect of cumulative T_{on} time on structural properties

Further experiments were performed to get insights of the mechanism of plasma polymerization and to investigate role of duty cycle and plasma *on* time on the structural properties of SiO$_x$C$_y$H$_z$ plasma polymer. The treatment duration (T_{total}) was adjusted in such a way that, cumulative plasma *on* time ($T_{on\ Cumulative}$) was equal for different duty cycles. For example, to obtain $T_{on\ Cumulative}$ of 60 s, polyester samples were treated at $\delta = 1$ for 60 s, at $\delta = 0.5$ for 120 s, and at $\delta = 0.25$ for 240 s. The
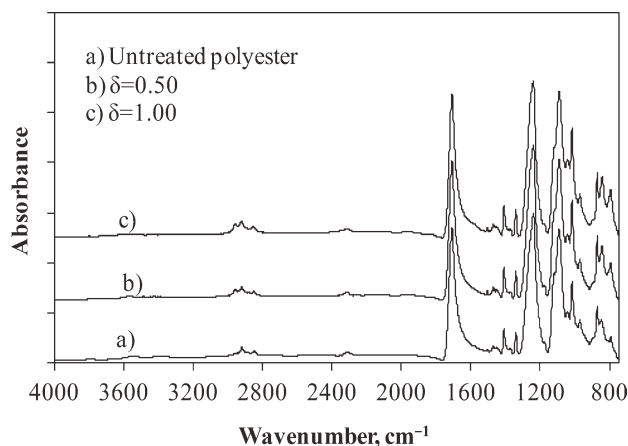

Figure 4 FTIR spectra of polyester fabric treated with HMDSO plasma at different duty cycles (Discharge power 4000 W, T_{total} 60 s, helium flow 5 L/min, HMDSO flow rate 1 mL/min).
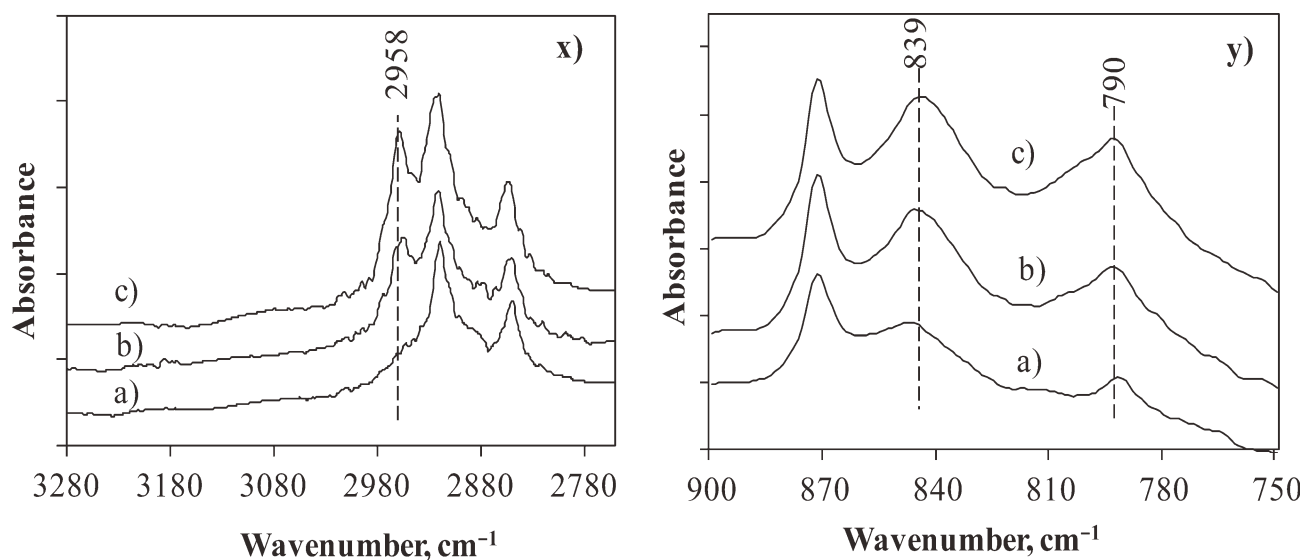
Figure 5 Amplified IR spectrum of HMDSO plasma-treated polyester fabric for absorption peak at (x) 2958 cm^{-1} and (y) 839 & 790 cm^{-1}. (a) Untreated polyester fabric, (b) duty cycle 0.5, and (c) duty cycle 1.0.

experimental details used for investigating the influence of duty cycle and $T_{\text{on Cumulative}}$ are given in Table III.

The FTIR spectra of samples CW1, PW1a, PW1b are shown in Figure 6. Four characteristic bands at wave number 1250, 1015, 839, and 790 cm^{-1} were observed in the IR spectra. The stronger absorption band in the range 1000–1150 cm^{-1} may be assigned to Si—O—Si symmetric stretching mode.[28] The band at 1250 cm^{-1} is due to CH$_3$ symmetric bending in Si—CH$_3$.

FTIR spectra show that, for equal cumulative T_{on} times of 60 s, sample PW1b ($\delta = 0.25$, $T_{\text{total}} = 240$ s) showed higher absorption intensities of the characteristic peaks than sample PW1a ($\delta = 0.5$, $T_{\text{total}} = 120$ s) and CW1 ($\delta = 1$, $T_{\text{total}} = 60$ s). Although cumulative T_{on} time is equal (i.e., 60 s) for samples CW1, PW1a, and PW1b; FTIR spectroscopy point toward higher surface concentration of Si—O and Si—CH$_3$ on the surface of sample PW1b. The propensity of absorption intensity is found in the order PW1b > PW1a > CW1.

TABLE II
Integrated Absorption Intensities of Characteristic Peaks in IR Spectrum of HMDSO Plasma Treated Fabric

Duty cycle	Integrated absorbance intensity (A cm^{-1})		
	2958 cm^{-1}	790 cm^{-1}	839 cm^{-1}
$\delta = 0.0$ (untreated)	0.04	1.08	1.55
$\delta = 0.25$	0.21	1.58	2.24
$\delta = 0.50$	0.24	1.63	2.40
$\delta = 0.83$	0.42	2.15	3.71
$\delta = 1.0$ (CW)	0.58	2.24	4.13

The Si—(CH$_3$)$_3$ bond represents the organic nature of the plasma polymer, whereas Si—O bond represents the inorganic nature. The ratio of organic and inorganic parts of the plasma polymer film reveals the fundamental differences in the structure of plasma polymer.[29] The organic–inorganic nature of HMDSO polymer films can be studied with FTIR spectroscopy. The relative ratio $\gamma_{(SiCH_3)}$ is calculated by taking ratio of integrated absorption intensity of the peak at 1250 cm^{-1} (Si—CH$_3$) to integrated absorption intensity of the peak at 1015 cm^{-1} (Si—O—Si). The eq. (2) gives organic content of the SiO$_x$C$_y$H$_z$ plasma polymer.[30] Therefore, $\gamma_{(SiCH_3)}$ may provide information about the structural properties of HMDSO plasma polymer obtained under continuous and modulated discharge.

$$\gamma_{(SiCH_3)} = \frac{\int SiCH_3 \ (1250 \ cm^{-1})}{\int SiOSi \ (1015 \ cm^{-1})} \qquad (2)$$

Three different aspects were considered while studying the influence of duty cycle and cumulative T_{on} time on structural properties of plasma polymers obtained under pulsed and CW discharge. In first case, comparison was made between different duty cycles when treatment duration (T_{total}) is equal. The organic content of HMDSO plasma polymer, γ_{SiCH_3}, for different duty cycles (for $T_{\text{total}} = 60$ s and 120 s) is shown in Figure 7. It clearly shows that for equal treatment duration (T_{total}), the organic content of the polymer decreases with increase in duty cycle. In other words, with increase in cumulative T_{on} time, the organic content of the plasma polymer goes down (Fig. 7). This behavior was observed for both treatment durations, i.e., $T_{\text{total}} = 60$ s and 120 s. At

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TABLE III
Discharge Parameters Used for Comparison of Pulsed and CW Discharge

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Sample	Duty cycle	T_{on} (ms)	T_{off} (ms)	Treatment duration ($T_{total} = T_{on\ Cumulative} + T_{off\ Cumulative}$) (s)	$T_{on\ Cumulative}$ (s)	Power (W)
CW1	1	5	0	60	60	4000
PW1a	0.5	5	5	120	60	4000
PW1b	0.25	5	15	240	60	4000
CW2	1	5	0	120	120	4000
PW2a	0.5	5	5	240	120	4000

lower duty cycles, the lesser fragmentation of a monomer owing to shorter cumulative T_{on} times may be responsible for higher retention of methyl groups in the structure of plasma polymer. The Figure 7 suggests that, for equal treatment duration (T_{total}), the methyl groups are preserved to a greater extent in plasma polymerization carried out at lower duty cycles.

In second case, comparison was made between different treatment durations (i.e., T_{total}) at fixed duty cycle. For example, at $\delta = 0.25$, γ_{SiCH_3} values of 0.79, 0.61, and 0.45 were obtained in samples treated for $T_{total} = 60$, 120, and 240 s, respectively. At any fixed duty cycle, increase in T_{total} caused decrease of organic character of HMDSO plasma polymer.

In third case, treatment durations were adjusted in such a way that cumulative T_{on} time is equal. As given in Table III, samples CW1, PW1a, and PW1b represents treatment duration (T_{total}) of 60, 120, and 240 s, respectively. However, cumulative T_{on} time for these samples was kept invariant at 60 s. The organic–inorganic ratio, γ_{SiCH_3}, was calculated for $\delta = 0.25$, 0.5, and 1.0. Figure

8 shows notable difference in structure (organic character) of plasma polymers derived under different duty cycles even though cumulative T_{on} time is constant. Sample CW1 ($\delta = 1$, $T_{on\ Cumulative} = 60$ s, $T_{total} = 60$ s) exhibits higher organic character than sample PW1a ($\delta = 0.5$, $T_{on\ Cumulative} = 60$ s, $T_{total} = 120$ s). Similarly, sample PW1a exhibited more organic nature than sample PW1b ($\delta = 0.25$, $T_{on\ Cumulative} = 60$s, $T_{total} = 240$s). For equal $T_{on\ Cumulative}$, increase in organic content with increases in duty cycle was observed. In other words, decrease in T_{total} times, caused increase in organic character of the polymer film (Fig. 8).

The decrease in organic content with increase in T_{total} time may be illustrated based on the mechanism of plasma polymerization proposed by Wrobel et al. (Reaction 3, 4, 5).[31] Primary cation obtained from Reaction 3 reacts with a monomer molecule and subsequently results in formation of high molecular weight products by abstraction of Si—CH$_3$ groups. Plasma polymerization proceeds with detachment of CH$_3$ groups from the monomer. At, longer T_{total} or $T_{on\ Cumulative}$ times, more number of CH$_3$ groups may get detached during the process of plasma polymerization. This mechanism is perhaps responsible for lower organic content in SiO$_x$C$_y$H$_z$ polymer obtained under longer T_{total} or $T_{on\ Cumulative}$ times.
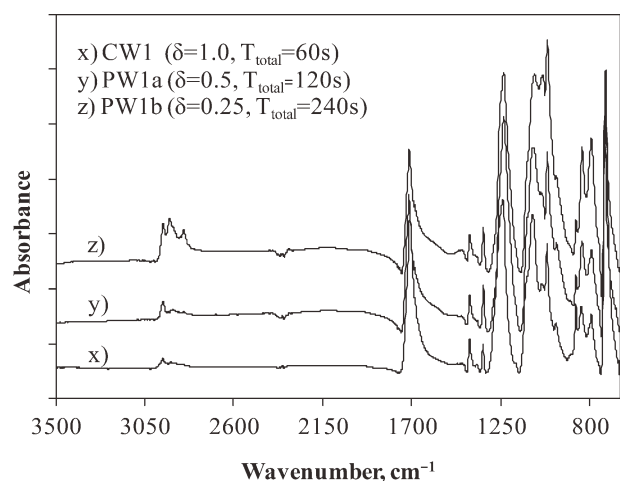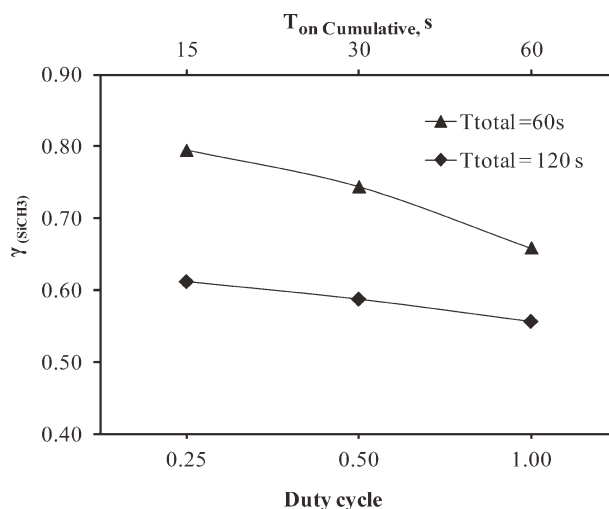
Figure 6 FTIR spectra of polyester samples treated under HMDSO plasma for equal cumulative T_{on} times at different duty cycles. Sample CW1: $\delta = 1.0$, T_{on} Cumulative 60 s, T_{total} 60 s; Sample PW1a: $\delta = 0.5$, T_{on} Cumulative 60 s, T_{total} 120 s; Sample PW1b: $\delta = 0.25$, T_{on} Cumulative 60 s, T_{total} 240 s (Power 4000W, helium flow 5 L/min, HMDSO flow 1 mL/min).

Figure 7 Organic–inorganic ratio, γ_{SiCH_3} of HMDSO plasma polymer obtained at different duty cycles.

(3)

(4)

(5)
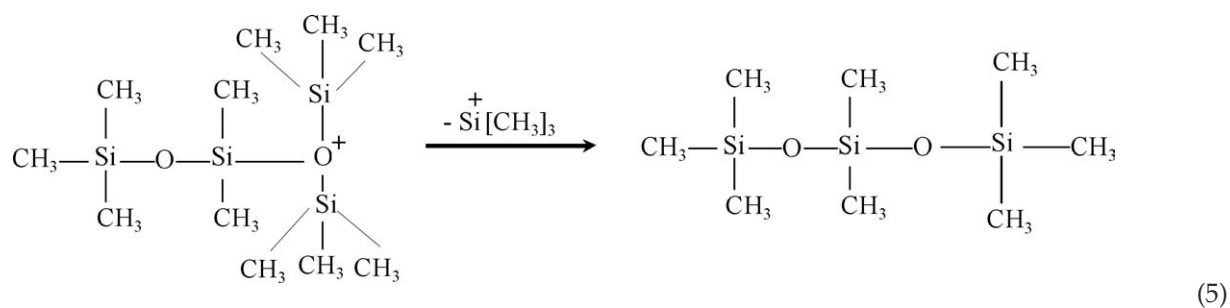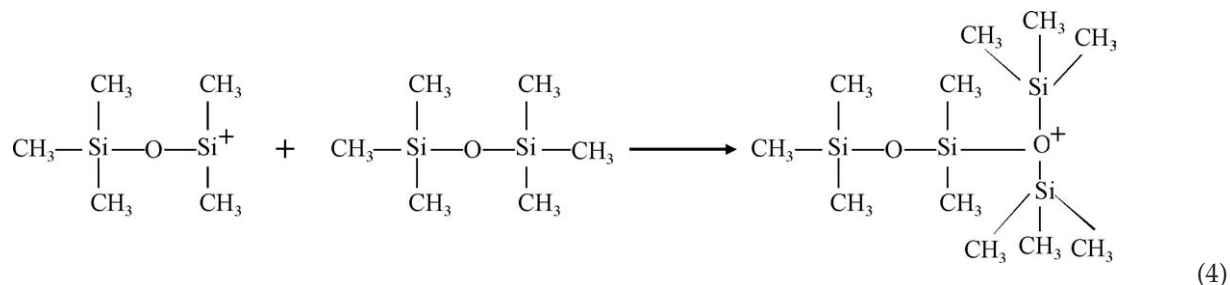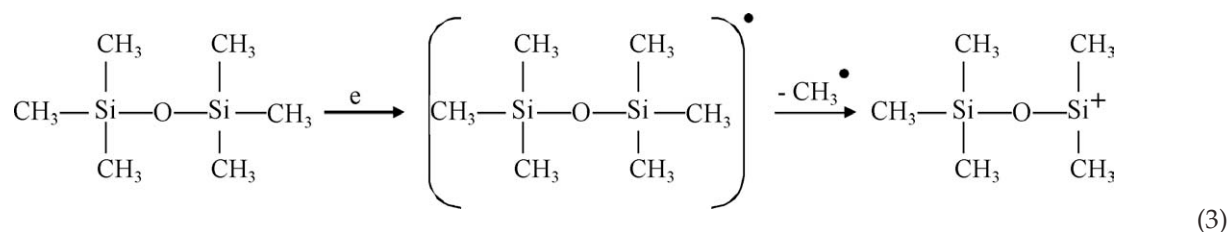
Overall structural analysis of HMDSO plasma polymer points toward comparatively greater retention of methyl groups at shorter durations of T_{total}
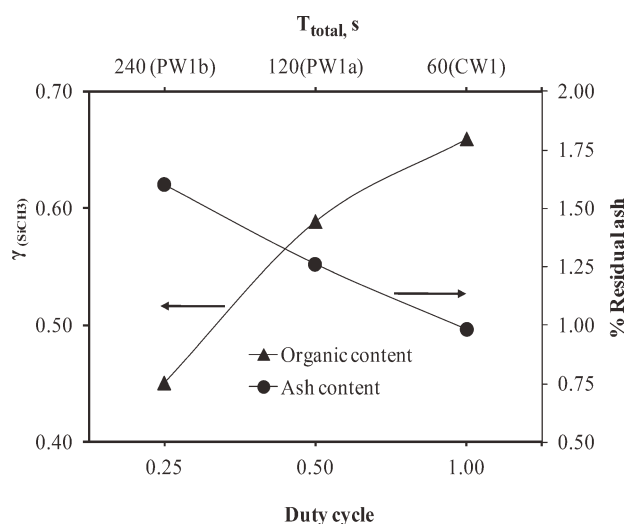

Figure 8 Organic–inorganic ratio (γ_{SiCH_3}) and % residual ash contents in the polyester samples (T_{on} cumulative is constant at 60 s; HMDSO plasma; δ = 0.25, 0.50, and 1.0; power = 4000 W).

and $T_{on\ Cumulative}$. This study shows that treatment duration (T_{total}) or $T_{on\ Cumulative}$ is probably the more prominent factor than duty cycle in determining structural properties of HMDSO plasma polymer.

Residual ash contents

FTIR spectroscopic analysis of polyester samples showed presence of Si containing groups. The Si present in the fabric tends to remain as a residue when sample is subjected to complete ashing. More deposition of Si—O and Si—CH$_3$ would cause increase in the residue. Therefore, measurement of residual ash in plasma-treated samples may give indication of extent of deposition of SiO$_x$C$_y$H$_z$ polymer. The % residual ash in the polyester samples treated under different discharge conditions is shown in Figure 9. For T_{total} = 60 s, there is a gradual increase in residual ash content with increase in duty cycle which can be attributed to higher $T_{on\ Cumulative}$ periods. Similar behavior was noticed in samples treated for T_{total} = 120 s. These results are in agreement with the FTIR spectroscopic
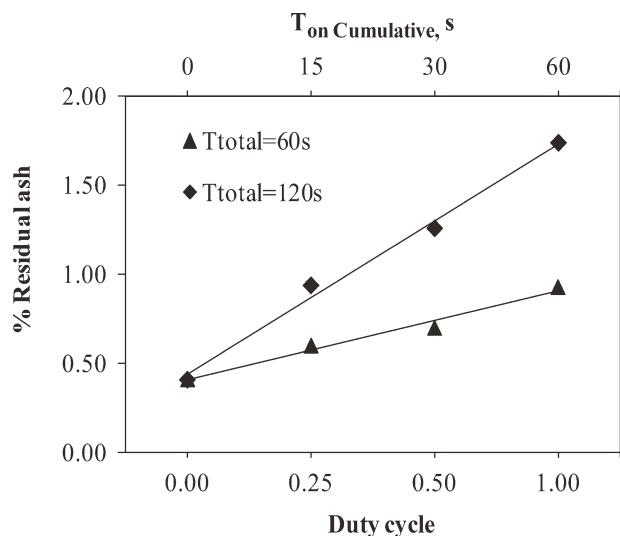
Figure 9 Residual ash contents in polyester samples treated at different duty cycles. T_{total} = 60 s and 120 s.

analysis of HMDSO plasma-treated samples [Fig. 5(x,y) and Table II]. Perhaps greater deposition takes place at higher duty cycles owing to longer $T_{on\ Cumulative}$ periods.

Figure 8 shows residual ash contents of samples CW1 (δ = 1, $T_{on\ Cumulative}$ = 60 s, T_{total} = 60 s); PW1a (δ = 0.5, $T_{on\ Cumulative}$ = 60 s, T_{total} = 120 s) and PW1b (δ = 0.25, $T_{on\ Cumulative}$ = 60 s, T_{total} = 240 s). Even though $T_{on\ Cumulative}$ period are same in all samples, the residual ash contents exhibited the trend PW1b > PW1a > CW1. The sample treated at lower duty cycle and for longer treatment duration (T_{total}), shows higher deposition of plasma polymer. If deposition occurs only during T_{on} times, the deposition for equal T_{on} times must be equal. However, difference in ash contents of CW1, PW1a, and PW1b indicate that the deposition perhaps occurs in T_{off} period also. Bousquet et al.[32] has reported that deposition proceeds even in post discharge period. Fragmentation and dissociation of monomer molecules occurs during T_{on} period of each pulse due to applied discharge power.[33] Although power is shut down during T_{off} period, fragments can still remain chemically active for certain durations. Their concentrations may undergo decay at different rates. However, as long as the length of T_{off} time is comparable with that of the fragments' life time, the continuation of the deposition may proceed even during T_{off} period or at least during major part of the T_{off} period. For given experimental conditions of T_{on} and T_{off} period, the charged species in the plasma probably does not decay completely in post discharge period resulting in some deposition even during T_{off} period.

The FTIR spectroscopy has shown that T_{total} and $T_{on\ Cumulative}$ periods have greater impact than duty

cycle on organic character of the HMDSO plasma polymer. On the other hand, residual ash contents suggest that duty cycle has greater influence on the deposition rate of plasma polymer since some deposition also occurred during T_{off} period.

Structural analysis of TEOS plasma polymer

FTIR spectra of polyester fabric treated with TEOS plasma (T_{total} = 5 min) with δ = 0.5 and δ = 1.0 are shown in Figure 10. The prominent peaks appearing at about 1070 and 790 cm^{-1} may be attributed to Si—O—Si stretching and Si—O—Si bending modes in siloxane linkage.[34] It can be noticed from Figure 10 that the inherent absorption peaks of polyester fabric has been considerably masked after TEOS plasma treatment. The masking of the inherent peaks of the fabric appears more prominent in case of CW discharge (δ = 1), which is most probably due to higher deposition in CW discharge than in pulsed discharge. These findings show that for constant T_{total} times, higher deposition occurs in CW discharge than pulsed discharge owing to relatively higher $T_{on\ Cumulative}$ times. The absorption peak at 1070 cm^{-1} is attributed to both Si—O—Si and Si—O—C. Therefore, as in case of HMDSO, characteristic peaks pertaining organic groups (i.e., CH$_3$, C$_2$H$_5$) could not be separately noticed in IR spectra of TEOS plasma-treated samples. Hence, organic–inorganic ratio could not be determined in case of TEOS plasma polymerization.

Surface morphology

Scanning electron microscopy was used to investigate the effect of pulsed plasma polymerization on the topographical properties of polyester fabrics. Surface morphology of TEOS plasma-treated
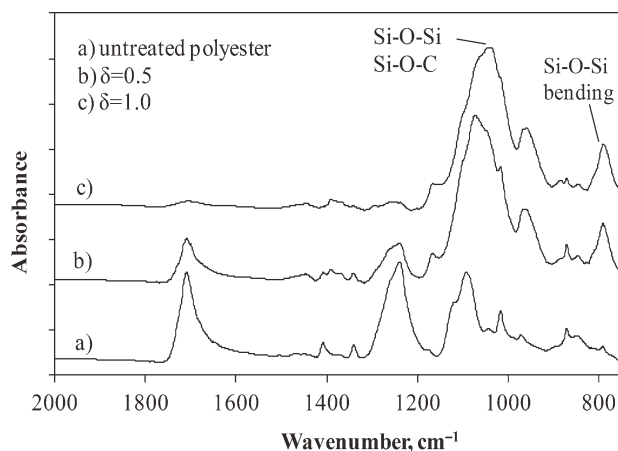

Figure 10 Normalized IR spectra of polyester fabric treated with TEOS plasma (Discharge power 4000 W, treatment duration 5 min, helium flow rate 5 L/min, and TEOS flow rate 1 mL/min).

polyester demonstrates that smooth surface of the polyester fiber has turned into a rough surface with deposits [Fig. 11(b)]. However, HMDSO plasma treatment has resulted in smooth coating of the surface on polyester fibers [Fig. 11(c)]. When compared to TEOS plasma polymer, HMDSO plasma polymer formed smooth and continuous coating on the polyester fabric surface.

Effect of plasma treatment on tear strength

Tear strength of polyester samples treated with different duty cycles is depicted in Figure 12. Tearing strength of untreated polyester fabric was 2131 gf. Figure 12 shows gradual reduction in tear strength of HMDSO plasma-treated polyester fabrics when
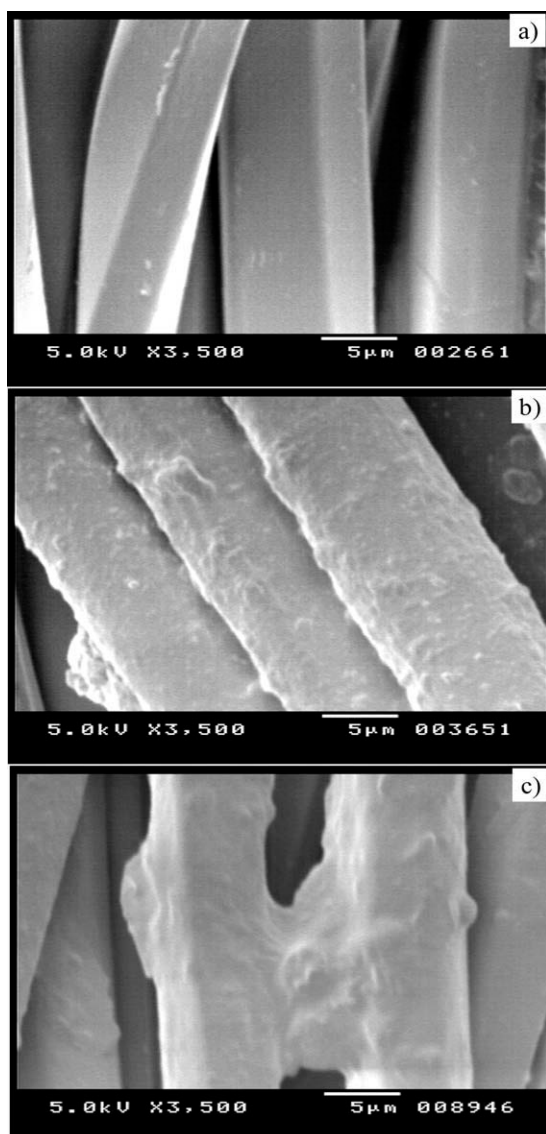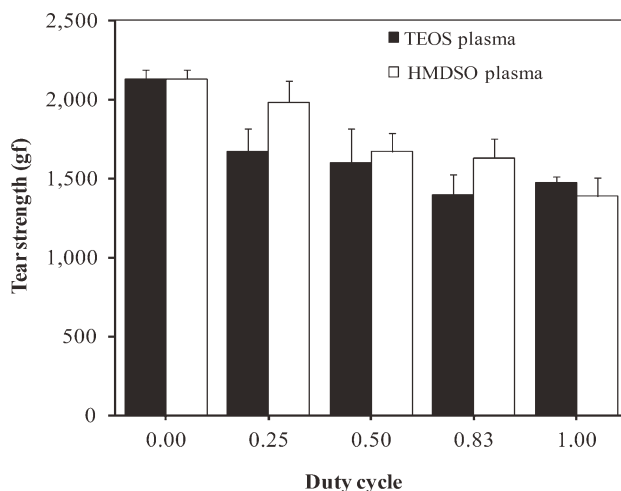
Figure 12 Tear strength of polyester fabric after PECVD (Power 4000 W, treatment duration 1 min).

duty cycle value is increased. The tear strength values of 1984, 1670, 1632, and 1388 gf were observed in samples treated with $\delta = 0.25$, 0.50, 0.80, and 1.00, respectively. There was about 6.9, 21.6, 23.4, and 34.8% reduction in the tear strength at these δ values. Polyester fabrics treated with TEOS plasma also showed similar kind of loss in tear strength at higher duty cycles. The loss in tear strength may be attributed to deposition of plasma polymer at the surface of fabric samples. When higher duty cycles are used, comparatively higher deposition and heavy crosslinking between plasma polymers might be taking place due to more fragmentation of a monomer. These crosslinked plasma polymers might be responsible for decrease in tear strength. The reduction in tear strength of HMDSO plasma-treated fabric has also been reported by Rosace et al.[35]

Durability to washing

HMDSO plasma-treated polyester fabric (treatment time: 1 min; $\delta = 0.83$) was subjected to 25 washing cycles. After every five washing cycles, contact angle on the sample was measured with three test liquids, namely water, formamide, and ethylene glycol (20%). Contact angle of the fabric after successive washing is depicted in Figure 13. HMDSO plasma-treated polyester fabric before washing exhibited $\theta = 138.5°$, 137.2°, and 136.0° with water, ethylene glycol (20%) and formamide, respectively. After five washing cycles, contact angle slightly decreased to 136.5, 136, and 134.6°, respectively. Increase in number of washing cycles has resulted in further decrease of contact angle for given test liquids. After 25 washing cycles, WCA of HMDSO plasma-treated polyester fabric, has reached the level of the untreated fabric ($\approx 130°$). However, in case of

Figure 11 SEM photographs of polyester fabric (a) Before treatment; (b) TEOS plasma treated, $\delta = 1$; (c) HMDSO plasma treated, $\delta = 1$.
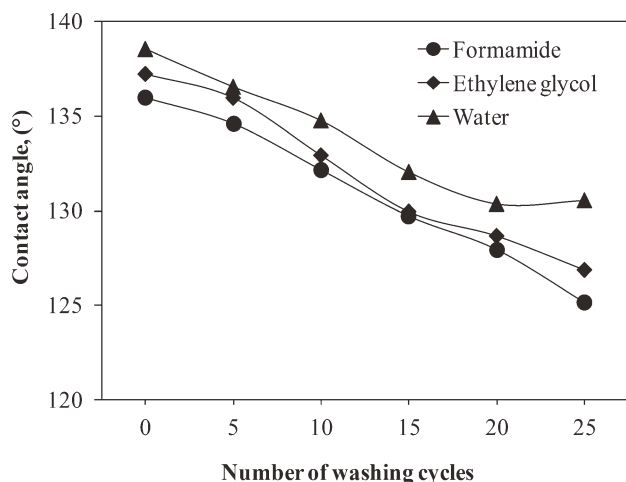
Figure 13 Effect of number of washing cycles on the contact angle of HMDSO plasma-treated polyester fabric (Discharge power 4000 W, treatment duration 1 min, and duty cycle 0.83).

formamide and ethylene glycol test liquids, CA values even after 25 washing cycles were 125.2° and 126.9°.

The gradual drop in contact angle values indicates deterioration of hydrophobic properties with successive washing cycles. It may be attributed to removal of plasma polymer from the surface of fabrics during washing. In case of TEOS plasma-treated samples, WCA values drastically reduced to level of the untreated fabric in just five washing cycles. Contact angle data of the polyester fabric shows that, HMDSO is a better precursor than TEOS for obtaining hydrophobic polyester fabrics with good durability. Moreover, it is interesting to note that treatment duration of 60 s is enough for developing hydrophobic polyester fabrics with good durability to washing by PECVD route.

CONCLUSION

$SiO_xC_yH_z$ polymers were deposited on the surface of polyester fabrics by PECVD technique using TEOS and HMDSO precursors under pulsed dielectric barrier discharge. The contact angle values on polyester fabric were found to be increased with increase in duty cycle for both HMDSO and TEOS plasma. It was observed that duty cycle of 0.83 imparts about equivalent hydrophobic properties that can be achieved with CW plasma. In addition, HMDSO plasma yielded more hydrophobic surfaces with good durability to washing when compared with TEOS plasma. Presence of Si—O—Si, Si—O—R, and Si—CH_3 groups were evidenced in IR spectrum of fabrics treated with HMDSO and TEOS plasma.

For constant treatment durations (T_{total}), the extent of structural retention of a monomer was comparatively higher in pulsed plasma than in CW plasma. However, decrease in organic content of HMDSO plasma polymer was noticed when cumulative T_{on} and T_{total} times were increased. Studies of organic–inorganic character of HMDSO plasma polymer indicated that T_{on} and T_{total} times has prominent role in deciding the structural properties of HMDSO plasma polymer. On the other hand, duty cycle in modulated discharge showed considerable influence as deposition also proceeds in post discharge period. Decrease in tear strength was observed in samples treated with TEOS and HMDSO plasma. Durability of select samples demonstrated gradual decrease in the contact angle with increase in the number of washing cycles. PECVD technique with modulated discharge showed promising prospects for hydrophobization of polyester fabrics.

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