

# Study of Plasma Polymerization of Dichloromethane on Cotton and Polyester Fabrics

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**ABSTRACT:** Dichloromethane (DCM) was polymerized on cotton and polyester fabrics in nonequilibrium low-temperature plasma for different durations and the effects obtained were discussed. The modified cotton and polyester fabrics were dyed with Reactive Red HE 8BI and C.I. Disperse Red 364 dyes, respectively. The relative color strength of polymerized dyed fabrics was measured and compared with that of untreated dyed fabrics. The color parameters of polymerized fabrics were evaluated by the CIE system of color measurement, with standard illuminant D65 and 10° standard observer, by a Dataflash 100 color measurement

spectrophotometer equipped with Colortools QC 1.3 color quality control software. The chemical structures of untreated and polymerized fabrics were studied by attenuated total reflectance-infrared spectroscopy. The presence of free radicals, attributed to the polymerization, was measured by electron spin resonance spectroscopy. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2014–2021, 2004

**Key words:** color strength; dichloromethane; plasma polymerization; fibers; polyesters

## INTRODUCTION

Interaction between plasma and textile materials has been explored by researchers for improving surface properties of textile materials without altering their bulk properties.<sup>1–3</sup> Research groups have modified the surface morphology of textile materials using a plasma process to enhance certain properties.<sup>4,5</sup> It has been established that plasma treatment plays a key role in the enhancement of properties of textile fibers and fabrics, such as wettability, water repellency, desizing, and dyeing, for example.<sup>6–13</sup> Attempts have also been made to measure the free radicals generated by plasma treatment with the help of electron spin resonance (ESR) spectroscopy<sup>14,15</sup> and their applications in the finishing of textile materials.<sup>1</sup>

In the present investigation, an attempt was made to study the effect of polymerization of dichloromethane (DCM) on surface properties and dyeing behavior of cotton and polyester fabrics in nonequilibrium low-temperature plasma.

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## EXPERIMENTAL

### Materials

Cotton fabric, 100% bleached and mercerized (specification 65 g/m<sup>2</sup>, 40/40, 120/80, and 89 cm finished width) and 100% polyester fabric (120 ends/in. × 92 picks/in.; 96 g/m<sup>2</sup>) were provided by M/s Hindustan Spinning and Weaving Mills Ltd. (Mumbai, India) and M/s Spectrum Dyes and Chemicals Ltd. (Surat, Gujarat, India), respectively.

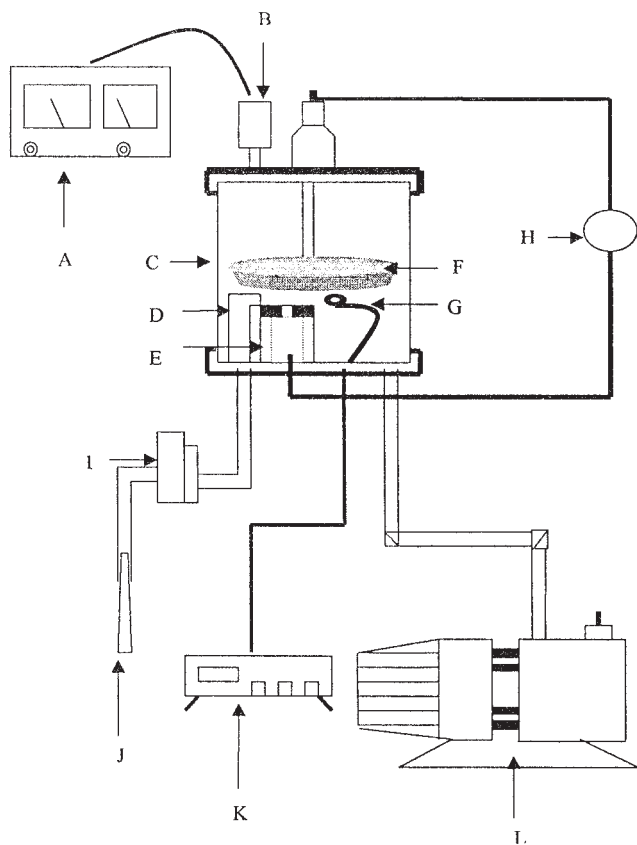
Reactive Red HE 8BI and C.I. Disperse Red 364 dyes were procured from M/s Clariant Ltd. (Mumbai, India) and M/s Spectrum Dyes and Chemicals Ltd., respectively.

### Polymerization of DCM

A fabric sample (1 g) was placed on top of the electrode of a bell jar-type plasma reactor (Fig. 1). The plasma reactor was purged two times with DCM vapor and the working pressure was adjusted to 0.1 mbar by keeping the flow rate at 20 SCCM (standard cm<sup>3</sup>/min). Inductively coupled plasma was produced using RF generator of frequency 13.56 MHz, which was capable of supplying a power output of 100 W. Plasma polymerization of DCM vapor was carried out on fabrics over different durations of time ranging from 10 s to 5 min.

### Measurement of weight change

The fabric was weighed before polymerization of DCM using a Mettler (Model AE 240; Mettler, Zurich,



A- Vacuum monitor, B- Pirani gauge, C- Bell jar, D- Monomer inlet, E- Live electrode, F- Ground electrode, G- Piezoelectric crystal, H- RF source, I- Flow control unit, J- Monomer tube, K- Thickness monitor, L- Vacuum pump.

**Figure 1** Schematic diagram of plasma processing chamber (Bell jar type).

Switzerland) single-pan high precision balance ( $\pm 10 \mu\text{g}$  accuracy). For each sample, five readings were taken and an average value was determined. Percentage deviation of weight was calculated and found to be 0.012%. After polymerization, the fabric was weighed immediately and the percentage change of weight was calculated as follows:

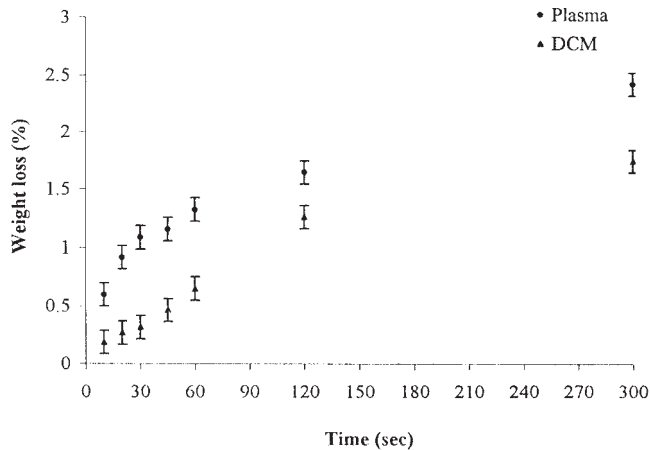
$$\text{Weight change (\%)} = \frac{W - W_0}{W_0} \times 100$$

where  $W_0$  is initial weight and  $W$  is weight of the substrate after treatment.

Positive change implies a gain in the weight and negative change indicates weight loss of the substrate. For each treatment, two samples were processed and an average of the data was taken for interpretation.

**Measurement of color parameters and yellowness index**

Color parameters of untreated and polymerized samples were calculated by CIE (International Commis-



**Figure 2** Weight loss of plasma-induced polymerized cotton fabric.

sion on Illumination) standard formulas<sup>16</sup> and yellowness index (YI), as described in ASTM D1925-70<sup>17</sup>:

$$YI = \frac{100(1.28X_{CIE} - 1.06Z_{CIE})}{Y_{CIE}}$$

where  $X_{CIE}$ ,  $Y_{CIE}$ , and  $Z_{CIE}$  are the CIE tristimulus values of the measured samples.

**Moisture content**

Levels of moisture content of the samples (both untreated and polymerized) were determined by the standard method after conditioning the fabric at 65% relative humidity and 27°C room temperature (RT) for 72 h.<sup>18</sup>

**Mechanical properties**

For testing tensile strength retained and elongation at break values, a fabricated yarn (length 5 cm) was mounted on an Instron 1026 tensile tester (Canton, OH) at a crosshead speed of 50 mm/min. The results

**TABLE I**  
**Color Parameters of Plasma Polymerized Cotton Fabric**

Sample	Treatment time (s)	Color parameters					YI <sup>a</sup>
		L*	a*	b*	C*	h <sup>0</sup>	
Untreated	—	94.05	0.11	2.18	2.18	87.02	4.29
Polymerized	10	93.70	-0.08	3.14	3.15	91.54	5.99
	20	94.08	-0.20	3.33	3.34	93.51	6.23
	30	94.00	-0.22	3.79	3.80	93.36	7.08
	45	94.02	-0.26	3.86	3.87	93.91	7.18
	60	93.96	-0.26	3.95	3.96	93.70	7.36
	120	94.17	-0.34	4.12	4.14	94.78	7.59
	300	93.94	-0.37	4.59	4.60	94.62	8.45

<sup>a</sup> YI, yellowness index.

**TABLE II**  
Moisture Content (%) of Plasma Polymerized Cotton Fabric

Sample	Treatment time (s)	Moisture content (%)
Untreated	—	5.2
Polymerized	10	5.3
	20	5.35
	30	5.15
	45	4.9
	60	4.65
	120	4.3
	300	4.15

are based on the average of five measurements for each sample.

#### Attenuated total reflectance–infrared spectroscopy (ATR-IR)

ATR-IR experiments were carried out on a Perkin-Elmer FTIR spectrophotometer (Model Paragon-500; Perkin Elmer Cetus Instruments, Norwalk, CT).

#### Electron spin resonance (ESR)

ESR experiments were carried out on a Varian E-112 E-line century series ESR spectrometer (Varian Associates, Palo Alto, CA), using 100-kHz field modulation.

#### Dyeing

Dyeing was carried out on Pyrotec MB2 IR two bath dyeing machine supplied by Roaches Int. (London, UK).

Polymerized and untreated cotton fabric was immersed in a dyebath with a liquor ratio of 50 : 1 at RT. The temperature was increased to 50°C (at 1°C/min). Glaubar salt (50 g/L) was added in three lots at intervals of 10 min. The temperature was then increased to 85°C (at 1.5°C/min) and soda ash solution (8 g/L) was added in two lots at intervals of 10 min. Dyeing was

carried out at this temperature for about 75 min. The dyebath was cooled to 50°C (at 2°C/min) and then the liquor was drained off. Neutral soaping and washing of the dyed fabric was carried out.

Polymerized and untreated polyester samples were immersed in a dyebath (pH 4.5, adjusted with acetic acid) of liquor ratio 50 : 1 at RT. The temperature was increased to 105°C (at 3°C/min) and allowed to run for 10 min and then further increased to 115°C (at 1°C/min) and continued for 15 min. The temperature was increased to 130°C (at 1°C/min) and dyeing continued for 30 min. The dyebath was cooled to 60°C (at 2°C/min) and then the liquor was discharged. Neutral soaping and washing were applied to the dyed fabric.

#### Color strength measurement

Reflectance values of dyed samples were measured in visible range of 400–700 nm at a bandwidth of 10 nm.<sup>19</sup> Relative color strength ( $K/S$ ) value was calculated using the Kubelka–Munk equation<sup>20</sup>:

$$\frac{K}{S} = \left[ \frac{(1 - R)^2}{2R} \right] - \left[ \frac{(1 - R_0)^2}{2R_0} \right]$$

where  $R$  is the decimal fraction of reflectance of the colored sample,  $R_0$  is the decimal fraction of reflectance of the uncolored sample,  $K$  is the absorption coefficient, and  $S$  is the scattering coefficient.

## RESULTS AND DISCUSSION

#### Cotton fabric

Figure 2 illustrates the result of weight change attributed to the plasma polymerization of DCM on cotton fabric. It can be seen that the weight loss resulting from polymerization of DCM in the plasma chamber is less compared to that resulting from the direct exposure of fabric into air plasma, which confirms that polymerization has occurred. Although a continuous weight loss in the polymerized fabric may be observed with increasing treatment time, this may be attribut-

**TABLE III**  
Mechanical Properties of Plasma Polymerized Cotton Fabric

Sample	Treatment time (s)	Load at break (g)	Elongation at break (%)	Tensile strength retained (%)
Untreated	—	410.0	11.50	100.00
Polymerized	10	409.0	10.40	99.76
	20	407.0	10.25	99.27
	30	406.0	10.00	99.02
	45	403.0	9.80	98.29
	60	401.0	9.40	97.80
	120	395.5	8.90	96.46
	300	384.0	7.85	93.66

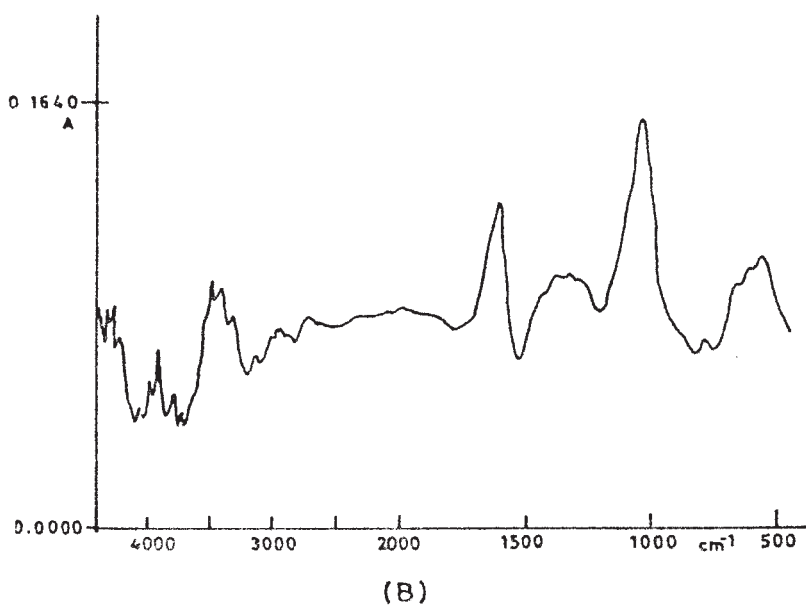
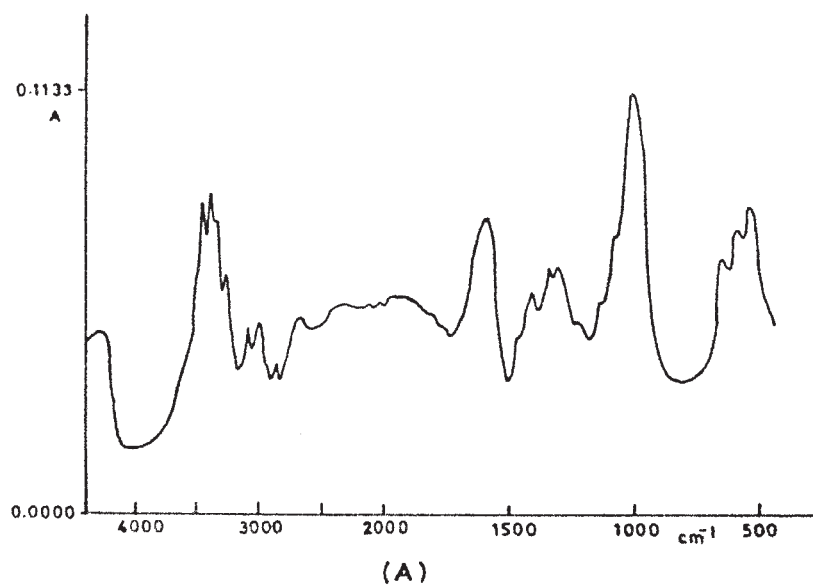


Figure 3 IR spectra of cotton fabric: (A) polymerized; (B) untreated.

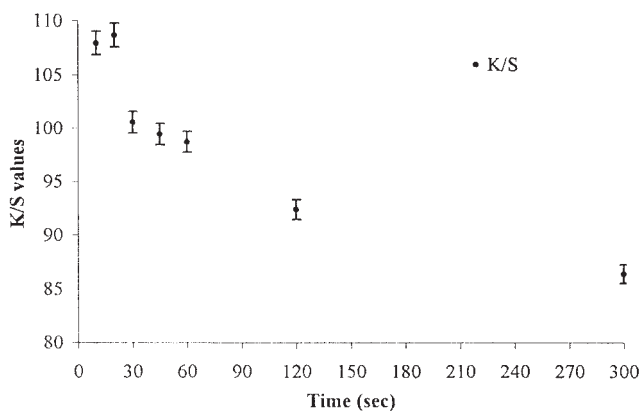


Figure 4 Variation of dye strength of plasma-induced polymerized cotton fabric dyed with Red HE 8BI reactive dyes with time.

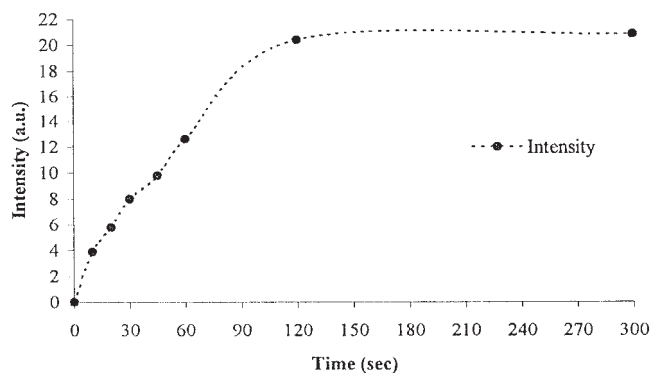
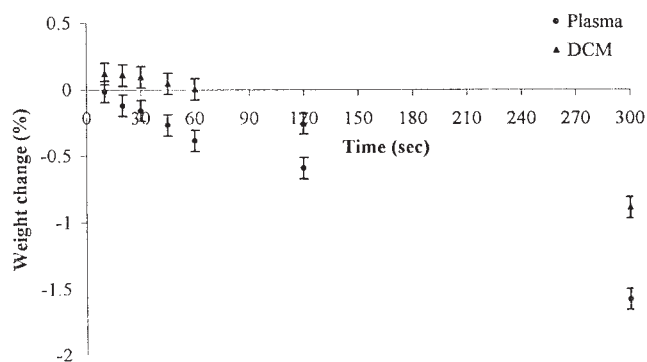


Figure 5 Variation of ESR intensity of plasma-induced polymerized cotton fabric with time.



**Figure 6** Weight change of plasma-induced polymerized polyester fabric.

able to simultaneous action of plasma etching and polymerization onto the surface of cotton fabric. From Table I, it can be observed that the  $b^*$  value increases with increasing treatment time, which indicates the increase of yellowness in the polymerized cotton sample with increasing polymerization time of DCM. This may be ascribed to generation and deposition of free radicals of both plasma and vapor of DCM onto the cotton surface and this deposition ultimately increases with further duration of polymerization time, causing yellowness of the surface.

Table II shows that a longer duration of polymerization gives rise to an etching action (from 30 s onward), whereas shorter duration promotes significant improvement in moisture content. Also, the tensile strength of the polymerized cotton fabric is not altered, which may be observed from Table III.

Because plasma modifies the surface of a material only at the micron level, analysis of ATR-IR spectra, rather than transmission spectra, is found to be an appropriate technique. Figure 3 demonstrates the ATR-IR spectra of untreated and cotton fabric polymerized for 2 min. Some new peaks may be seen in the polymerized cotton fabric [Fig. 3(B)] compared to the spectrum of the control fabric [Fig. 3(A)]. The absorption at  $2936.8\text{ cm}^{-1}$  in the polymerized sample is at-

tributed to  $\text{CH}_3$  stretching vibrations; the peak at  $1269.8\text{ cm}^{-1}$  is attributed to  $\text{C}-\text{CH}_3$  deformation vibration; the shoulder at  $1098.6\text{ cm}^{-1}$  is attributed to  $\text{C}-\text{O}$  linkage; and the peaks at  $1029.3\text{ cm}^{-1}$  are attributed to stretching vibration of  $\text{CO}$  group, whereas the peaks at  $875$  and  $787.3\text{ cm}^{-1}$  are attributed to stretching vibrations of  $\text{C}-\text{C}$  and  $\text{C}-\text{Cl}$  groups, respectively. Therefore,  $\text{CH}_3$ ,  $\text{C}-\text{CH}_3$ ,  $\text{C}-\text{O}$ ,  $\text{C}-\text{C}$ , and  $\text{C}-\text{Cl}$  groups are formed on the cotton fabric upon polymerization.

To investigate the effectiveness of the modified cotton fabrics, both untreated and polymerized cotton fabrics were dyed with Red HE 8BI reactive dyes at 2% concentration. Figure 4 shows the variation of  $K/S$  values of the dyed cotton fabrics (both untreated and plasma polymerized with DCM). As seen from Figure 4, the  $K/S$  value increases up to 20 s of treatment time, after which an adverse effect was caused with increase in treatment time.

This enhancement of dyeability is mainly attributed to the polymerization of DCM, which improves the surface reactivity of modified fabric by creating more radical sites. To encounter these radical sites, it was considered necessary to measure the presence of free radicals deposited onto the modified fabric by ESR. From Figure 5, it can be seen that the number of free radicals generated onto the cotton surface increases with increasing treatment time. After 2-min treatment time, however, there is only a marginal increment in the intensity of free radicals.

### Polyester fabric

Figure 6 shows that the weight loss attributed to polymerization is less compared to that resulting from direct exposure of fabric into air plasma, which further confirms the occurrence of polymerization, as already evidenced in the case of cotton fabric. Weight gain is obtained with treatment times of shorter duration, which may be attributable to the deposition of free radicals of DCM during purging in the plasma cham-

**TABLE IV**  
Color Parameters of Plasma Polymerized Polyester Fabric

Sample	Treatment time (s)	Color parameters					YI
		$L^*$	$a^*$	$b^*$	$C^*$	$h^0$	
Untreated	—	94.14	0.18	1.13	1.14	80.92	2.32
Polymerized	10	93.34	-0.01	3.23	3.23	90.20	6.22
	20	93.38	-0.15	4.03	4.03	92.07	7.62
	30	93.20	-0.18	4.39	4.40	92.33	8.30
	45	92.95	-0.22	4.79	4.80	92.67	9.03
	60	93.02	-0.13	4.82	4.83	91.50	9.19
	120	92.89	-0.21	4.93	4.93	92.38	9.30
	300	92.80	-0.30	5.74	5.75	93.02	10.75

**TABLE V**  
Moisture Content (%) of Plasma Polymerized Polyester Fabric

Sample	Treatment time (s)	Moisture content (%)
Untreated	—	0.3
Polymerized	10	1.3
	20	1.5
	30	1.8
	45	1.9
	60	2.1
	120	1.8
	300	1.5

ber, given that etching and polymerization processes act simultaneously on the surface of fabric, resulting in a continuous weight loss with further polymerization time. There is a marginal increase in the weight change in 10-s duration, after which it decreases with increasing treatment time. Up to 1 min of treatment time this trend of weight gain is maintained, although it is comparatively less at a shorter duration time of 10 s. This could be ascribed to the formation of free radicals on polyester fabric in the initial stage of plasma polymerization; that is, at 10 s thereafter the simultaneous actions of plasma polymerization and plasma etching result in weight loss in the fabrics.

From Table IV, it can be observed that the  $b^*$  value increases with increasing treatment time, which indicates an increase in yellowness of the polyester fabrics with increasing polymerization time. This may be attributed to the generation and deposition of free radicals of both air plasma and DCM vapor on the polyester surface with treatment times of longer duration. This increase in  $b^*$  value results in the increase of YI with respect to that of untreated control polyester fabric.

The moisture absorption capacity of plasma polymerized polyester fabric is improved compared to that of untreated polyester fabric, as can be seen from Table V. This may be in consequence of the formation of polar groups on the surface of modified polyester fabrics during polymerization, which results in en-

hancement of hydrophilicity of the polyester fabric. Also development of voids and cracks on the surface of the polyester fiber facilitate the penetration of moisture. From Table VI, it can be seen that there is a marginal change in tensile strength retained and elongation at break values for a shorter period of treatment time of 1 min, compared to values of the fabric that was subject to a treatment time of >1 min. These values decrease with increasing polymerization time.

Figure 7 demonstrates the ATR-IR spectra of untreated and polyester fabric polymerized for 2 min. It can be seen that there is no remarkable change in the spectrum of untreated [Fig. 7(A)] and polymerized polyester [Fig. 7(B)] fabrics, except for changes in the relative intensities and positions of the stretching vibrations of the functional groups, which determine various properties of the polyester fabric, and Table VII elucidates this effect.

Figure 8 shows the variation of  $K/S$  values of dyed polyester fabrics (both untreated and polymerized) with treatment time.  $K/S$  values increase up to 45 s of treatment time and thereafter sharply decrease with increasing treatment time. This may be attributable to the decrease in intensity of free radicals generated onto the surface of the polyester fabrics after 1 min, which was seen previously in % weight change. From Figure 9, it can be observed that the number of free radicals generated on the polyester surface increases sharply up to 1 min of treatment time, after which there is a slow decrease in the intensity of free radicals with increasing treatment time. This may be attributable to crosslinking, which may occur during treatment times of longer duration.

## CONCLUSION

To modify the property of cotton and polyester fabrics, plasma polymerization of DCM was found to be extremely effective. In the case of cotton fabric, properties such as moisture content and dyeability increase during polymerization for 10–20 s, but beyond that, an adverse effect was seen: the moisture content

**TABLE VI**  
Mechanical Properties of Plasma Polymerized Polyester Fabric

Sample	Treatment time (s)	Load at break (g)	Elongation at break (%)	Tensile strength retained (%)
Untreated	—	358	34.50	100.00
Polymerized	10	356	33.25	99.44
	20	353	32.95	98.60
	30	351	32.60	98.04
	45	348	32.30	97.21
	60	346	32.10	96.65
	120	341	31.30	95.25
	300	332	30.40	92.74

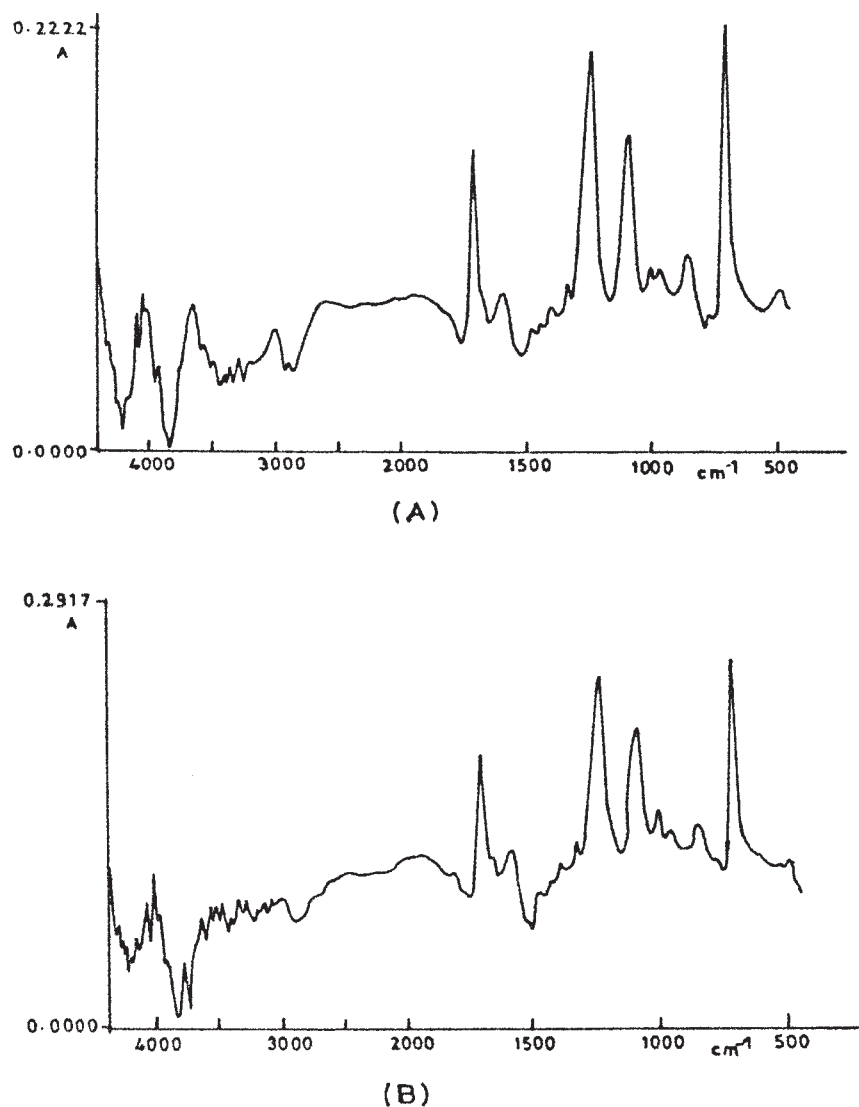


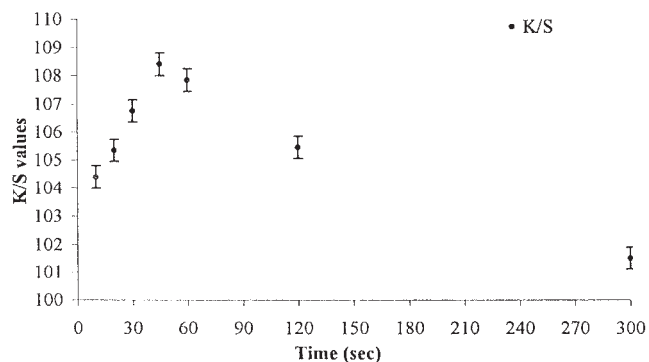
Figure 7 IR spectra of polyester fabric: (A) polymerized; (B) untreated.

decreases along with color strength. This decrease in moisture content shows a hydrophobic behavior of cotton fabric with a consequent effect on the dyeability

of modified fabric. The other properties remained unchanged. Thus, the optimum period of polymerization with DCM in the presence of air plasma for cotton

TABLE VII  
Relative Intensities of Untreated and Polymerized Polyester Fabric

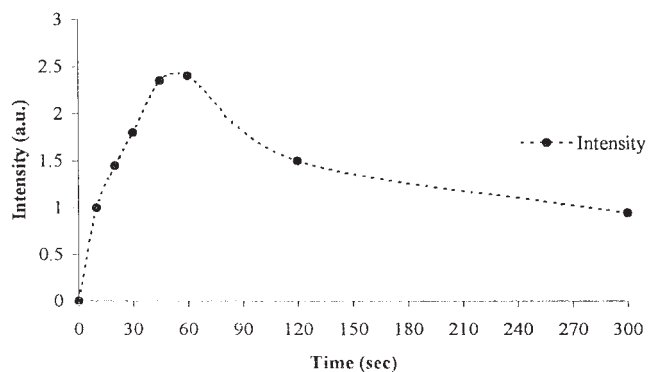
Functional group	Relative intensity	
	Untreated	Polymerized
OH stretching vibration	0.2945 (at 3634.3 $\text{cm}^{-1}$ )	0.3465 (at 3632.9 $\text{cm}^{-1}$ )
CH <sub>3</sub> stretching vibration	0.2867 (at 3018 $\text{cm}^{-1}$ )	0.3539 (at 3017.6 $\text{cm}^{-1}$ )
C=O stretching vibration	0.7012 (at 1713.7 $\text{cm}^{-1}$ )	0.7169 (at 1712 $\text{cm}^{-1}$ )
C=C stretching vibration	0.3762 (at 1592.5 $\text{cm}^{-1}$ )	0.4672 (at 1588.9 $\text{cm}^{-1}$ )
C—CH <sub>3</sub> deformation vibration	0.9437 (at 1248.1 $\text{cm}^{-1}$ )	0.9380 (at 1245.8 $\text{cm}^{-1}$ )
C—O stretching vibration	0.7385 (at 1101.0 $\text{cm}^{-1}$ )	0.7966 (at 1097.2 $\text{cm}^{-1}$ )
	0.4347 (at 1016.8 $\text{cm}^{-1}$ )	0.5842 (at 1017.9 $\text{cm}^{-1}$ )
C—C stretching vibration	0.4617 (at 869.6 $\text{cm}^{-1}$ )	0.5446 (at 871.5 $\text{cm}^{-1}$ )
CH <sub>3</sub> deformation vibration	1.0000 (at 722.6 $\text{cm}^{-1}$ )	1.0000 (at 723.3 $\text{cm}^{-1}$ )



**Figure 8** Variation of  $K/S$  values of plasma-induced polymerized polyester fabric dyed with CI Red 364 disperse dyes with time.

fabric may be 10–20 s in which better performance of the fabric can be achieved.

In the case of polyester fabric, properties such as moisture content and dyeability were enhanced on polymerization without affecting other properties. In view of the increase in dyeability, an optimum period for plasma polymerization may occur over a period of 30–45 s, beyond which an adverse effect was observed.



**Figure 9** Variation of ESR intensity of plasma-induced polymerized polyester fabric with time.

The present experiment was carried out on a laboratory scale and thus a study on bulk-scale adaptation could not be made.

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