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Effect of dichlorodimethylsilane on plasma-treated cotton fabric*

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Abstract. Cotton fabric was treated with dichlorodimethylsilane (DCDMS) solution by two methods. In the first method, the fabrics were directly dipped into DCDMS solution for different time intervals and in the second method, the fabric was first subjected to radiofrequency (RF) plasma treatment for different durations and optimized exposure power condition and then immersed in DCDMS solution. The physical properties of cotton fabrics, treated with DCDMS in the presence/absence of air plasma have been compared with those of the control fabrics. Changes in the surface morphology structure and composition were observed through scanning electron microscopy and attenuated total reflectance-IR. The change in colour parameters of the fabric due to the treatment was assessed by Dataflash 100 colour measurement spectrophotometer with colourtools QC 1.3 colour quality software. The water repellent property of untreated and modified fabrics was studied using AATCC test method 39 (1971). The effectiveness of the water repellent property was checked by washing the treated fabrics up to ten cycles.

Keywords. Cotton; dichlorodimethylsilane; plasma; water repellency.

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1. Introduction

Adsorption and grafting processes of molecules onto a surface have been studied for a long time. A major aim in this domain is the design of a third material, often called coupling agent, to stick together two materials that were primarily

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incompatible. These applications aim to change the mechanical properties, water repellent property etc. of the subjected material.

In order to modify the properties of the fabric like water repellent property, organochlorosilanes are considered to be very effective, as they are acting as cross-linking agents for fibers having nucleophilic groups. Earlier, many researchers have used the silicone compounds for modifying the textile fabrics. One US patent describes the effect of siloxanes on cellulosic fibers for rendering the fibers water repellent [1]. Porter studied the effect of silicone softeners on resin-treated cotton [2]. Many efforts have been made by various researchers in order to modify different textile substrates with organosilanes [3–6].

Plasma modification of textiles is a promising technique with several advantages like energy and space saving, instant on–off control, reduction in process wastes and pollution free. Plasma treatment has been employed to modify the surface of textile substrates and to modify the surface morphology of the substrate without altering their bulk properties. Over the past few decades there has been rapid exploration and commercialization of low-temperature plasma technology for improving the surface properties of the material [7–11].

In the present study an effort was made to modify the water repellent properties of cotton fabric by incorporating it in DCDMS solution and also to study the effect of prior exposure of plasma to the cotton fabric onto the reaction of DCDMS solution.

2. Experimental

2.1 *Materials*

(a) Hundred per cent cotton fabric of specification 103 g/m^2 40/40, 120/80 and 116.5 cm finished width was supplied by M/s Hindustan Spinning and Weaving Mills Ltd., Mumbai, India.

(b) Dichlorodimethylsilane was procured from Merck (India) Limited.

2.2 *Plasma treatment*

Fabric sample (1 g) was placed on top of the electrode of bell jar type plasma reactor (figure 1). Radiofrequency (RF) power was applied through a 13.56 MHz RF generator (1.5 kW capacity) supplied by Universal R.F. Equipment (Mumbai, India). Fabric sample was kept perpendicular to the electrodes, which were at a distance of 3 cm apart. The working pressure was adjusted to 0.1 mbar with a rotary vacuum pump. Evacuation was carried out for the duration of 10 min and then the RF supply was switched on and the plate current was increased until glow discharge was initiated. The delivering power between the electrodes was adjusted to 30 W by adjusting the power setting knob of the RF generator. The glow discharge was maintained at the required plate current. Fabric was exposed to the low-temperature cold plasma for the required duration, after which it was switched off and the sample was allowed to be in vacuum for another 10 min; the vacuum pump was then turned off after which the tube was purged with air and the treated sample was removed for the study.

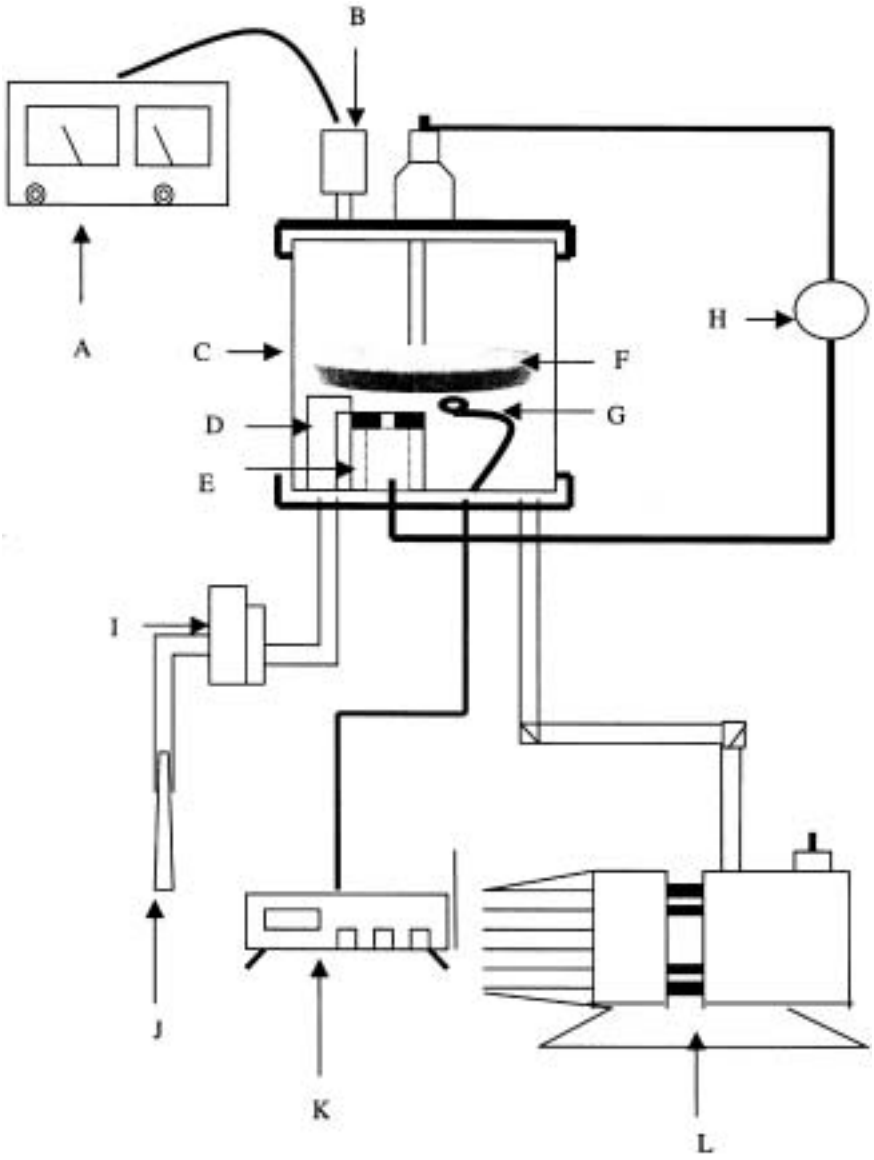


Figure 1. Schematic diagram of plasma processing chamber (bell jar type). A – Vacuum monitor, B – Pirani gauge, C – Bell jar, D – Monomer inlet, E – Live electrode, F – Ground electrode, G – Piezoelectric crystal, H – RF source, I – Flow control unit, J – Monomer tube, K – Thickness monitor, L – Vacuum pump.

2.3 *DCDMS treatment*

Cotton samples (3 cm × 6 cm) – both control and plasma treated, were immersed in DCDMS solution (25 ml) for different durations of time, varying from 10 s to

10 min. These samples were then allowed to dry at room temperature (∼25°C, 65% RH) for 24 h.

2.4 *Measurement of %weight change*

The fabric was kept in bell jar type plasma reactor under vacuum condition for 10 min and then removed to weigh before treatment using a Mettler (Model-AE 240) single pan high precision balance (±10 μg 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 treatment, the fabric was weighed immediately and the percentage weight change was calculated.

$$\%\text{Weight change} = \frac{W - W_0}{W_0} \times 100, \tag{1}$$

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

A positive change implies a gain in the weight whereas a negative change implies weight loss in the substrate. For each type of treatment, two samples were processed and an average was taken. Statistical analysis of the method for eight samples showed an error of less than 2%.

2.5 *Measurement of colour parameters*

The %reflectance values of the samples were measured on Dataflash 100 colour measurement spectrophotometer with Colortools QC 1.3 colour quality control software supplied by Datacolor International, USA. For each sample, readings were taken at three different positions and an average was obtained to minimize the error. Colour parameters of untreated and treated samples were calculated using C.I.E. standard formulae [12].

2.6 *Mechanical properties*

For testing tensile strength retained and elongation at break values, a yarn of length 5 cm was mounted on Instron 1026 Tensile-Tester at a cross-head speed of 50 mm/min. The results were the average of ten measurements for each sample.

2.7 *Surface morphology studies*

In order to assess the change in the surface morphology of cotton fabric due to the treatment, micrographs of both untreated and treated cotton samples were taken by Philips scanning electron microscope (SEM), Model XI-30.

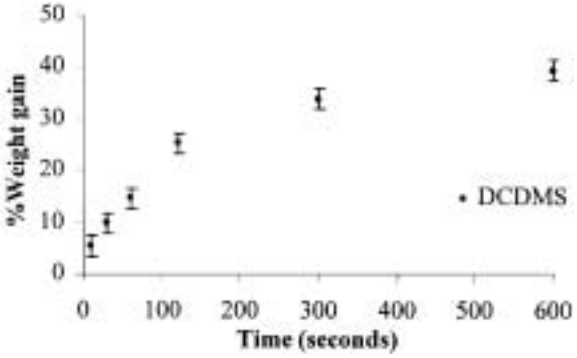


Figure 2. Percentage weight change of cotton fabric treated with DCDMS.

3. Results and discussion

Figure 2 demonstrates the effect of DCDMS treatment on the weight change of cotton fabric. From figure 2, a continuous weight gain can be seen, which may be attributed to the formation of silane layers onto the cotton surface during treatment with increasing treatment time.

In order to assess the effect of DCDMS on the visual appearance of fabric, colour parameters of the untreated and treated cotton samples were measured. From table 1, it can be clearly seen that treatment with DCDMS brings about some changes on the visual appearance of cotton fabric. Also b^* value increases marginally with increase in treatment time, which further indicates the increase in yellowness of the fabric.

It was interesting to see the influence of DCDMS treatment onto the bulk properties of the cotton fabric. In table 2, a drastic change in strength of the cotton fabric can be seen due to the treatment with DCDMS solution. This is attributed mainly due to condensation reaction, which is taking place during the treatment and also due to the liberation of HCl vapours, which reacts with cotton fabric resulting in the loss of tensile strength. This can also be seen from figure 3, in which one can clearly see the effect of action of DCDMS solution with cotton fabric.

Table 1. Colour parameters of DCDMS-treated cotton fabric.

Treatment time	Colour parameters				
	L^*	a^*	b^*	C	h
Control	93.5	−0.03	2.21	2.21	90.66
10 s	93.34	−0.55	3.95	3.99	97.87
30 s	93.05	−0.52	4.17	4.20	97.08
1 min	93.12	−0.61	4.26	4.31	98.20
2 min	92.85	−0.63	4.34	4.38	98.23
5 min	93.02	−0.68	4.42	4.47	98.74
10 min	92.62	−0.86	4.64	4.72	100.53

Table 2. Mechanical properties of DCDMS-treated cotton fabric.

Treatment time	Load at break (g)	Elongation at break (%)	Tensile strength retained (%)
Control	267.17	8.05	100.00
10 s	93.8	4.45	35.11
30 s	89.0	4.2	33.31
1 min	85.3	4.0	31.93
2 min	64.9	3.6	24.29
5 min	56.67	3.28	21.21
10 min	43.11	2.68	16.13

It is well-known that formation of silane group on any sample results in its water retardancy. Hence, it was thought necessary to check the water repellent behaviour of treated cotton fabric. In order to obtain wettabilities (or hydrophilicities) of the untreated and modified cotton fabrics, a water drop test was done according to the AATCC standard [13]. The fabric was washed in Roaches Pyrotec MB2 IR two bath dyeing machine at 60°C for 30 min without using any soap or detergent, and then dried in air at room temperature. In the absorbency test, the wetting time was determined by placing a drop of distilled water on the fabric from a microsyringe positioned 1 cm above the fabric. The time for the disappearance of the meniscus (in other words the time for the water drop to lose its reflective power) was measured as the wetting time. This procedure was applied for both unwashed and washed fabrics.

From table 3, it can be observed that the wetting time increases with increase in treatment time. Further, the fabric has good water repellent property even after washing ten times. The water repellent behaviour can also be seen from figure 4 and it was found that even when the fabric was treated for a short duration of only 10 s, the fabric shows good water repellent property and does not absorb the water droplets even after 30 min.

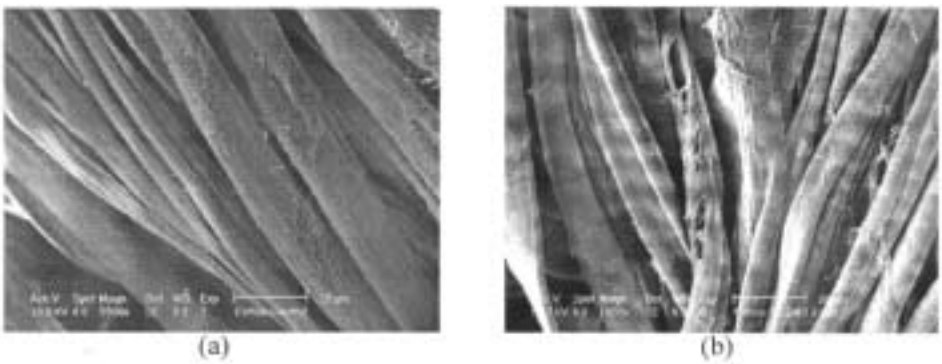


Figure 3. SEM micrograph of (**a**) untreated cotton fabric and (**b**) 2-min DCDMS treated cotton fabric.

Table 3. Wetting times of DCDMS-treated cotton fabrics.

	Wetting time (s)				
Sample	WC_0	WC_1	WC_2	WC_5	WC_{10}
Cotton	0.2	0.2	0.2	0.2	0.2
10 s	*	1832.4	1751.4	1563.0	1197.5
30 s	*	2934.9	2732.6	2341.4	2059.6
1 min	*	3552.5	3471.0	3398.6	3248.1
2 min	*	*	*	*	*
5 min	*	*	*	*	*
10 min	*	*	*	*	*

Note: WC_n implies n no. of washing cycle and * indicates wetting time $>$ 1 h, i.e., 3600 s.

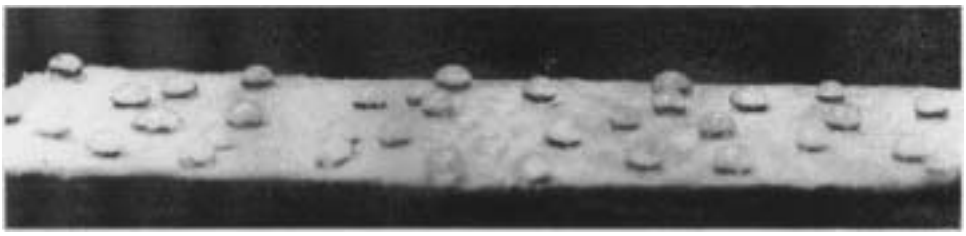


Figure 4. Photograph of 10-s DCDMS-treated cotton fabric.

In order to assess the effect of plasma treatment on the treatment of cotton fabric with DCDMS solution, cotton fabrics were exposed to radiofrequency (RF) plasma for various durations of treatment time, varying from 10 s to 5 min at optimized exposure power (i.e. 10.13 Pa) condition. The exposed fabric was immersed in DCDMS solution for a period of 2 min when all the liberated HCl vapours seemed to have evaporated.

From figure 5, it can be seen that exposure of cotton sample in plasma causes a continuous loss in its actual weight, which may be attributed to etching. A continuous weight gain due to the treatment with DCDMS solution can also be seen in case of prior exposure of cotton fabric up to a period of 1 min to plasma treatment. This may be attributed to the initial cleaning action of plasma treatment, which takes place onto the cotton substrate and in return provides a good absorbancy. When the fabric is exposed to further plasma treatment, i.e., after 1 min, due to the continuous action of etching, the deposition of silane group decreases marginally and is less when compared to that directly immersed in solution. Hence it was thought necessary to expose the cotton fabric under plasma chamber for the duration of 1 min and then immerse it in DCDMS solution for different durations of treatment time. It was observed that prior exposure of plasma treatment to the cotton fabric before DCDMS treatment gives good repellency even for shorter duration (i.e. 10 s) and do not absorb the water droplets even after 1 h of wetting time, although the fabric was washed up to 10 cycles.

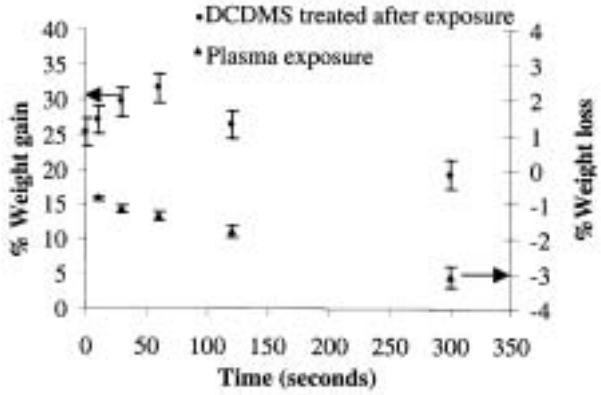


Figure 5. Percentage weight change of cotton fabric after plasma treatment.

In order to assess the generation and formation of different functional groups, attenuated total reflectance-IR (ATR-IR) study was carried out. Figure 6 shows ATR-IR spectra of untreated and different processed cotton fabrics.

From figure 6, it can be noticed that plasma exposure of cotton fabric does not make any remarkable change in the spectrum as compared to untreated cotton fabric except for changes in the relative intensities of the stretching vibrations of the functional groups, which determines various properties of the cotton fabric. But when the fabric is treated with DCDMS solution some new peaks may be seen when compared to the spectrum of control fabric. Similar observations can also be made in the case of prior exposure of plasma before treatment. The absorption at 2964.8 cm^{-1} in the sample treated with DCDMS solution is due to the CH_3 stretching vibrations. The peak at 1259.5 cm^{-1} is due to the Si–CH_3 deformation vibration. The shoulder at 1085.7 cm^{-1} is because of the Si–O linkage. The peaks at 1019.6 cm^{-1}, 864 cm^{-1} and 794 cm^{-1} are due to Si–O–C, stretching vibration of Si–C and stretching vibration of Si–Cl group respectively. So, in general CH_3, Si–CH_3, Si–O, Si–O–C, Si–C and Si–Cl groups are formed onto the cotton fabric after DCDMS treatment. These are also the groups found when the fabrics were treated with plasma followed by immersing in DCDMS solution, only difference being the change in their relative intensities; which can also be seen from table 4.

It is evidenced that the relative intensity of prior exposure of plasma-treated cotton fabric treated with DCDMS solution for CH_3, Si–O and Si–O–C functional group is less when compared to cotton fabric treated directly with DCDMS solution. But it is also noticed that there is a drastic change in the relative intensity of Si–CH_3 deformation vibration of plasma exposed cotton fabric rather than those treated with DCDMS solution. And the enhancement of silane deposition onto the cotton fabric may be attributed to the Si–CH_3 functional group, due to which the water repellent behaviour of plasma exposed cotton fabric was found to be more as compared to the untreated cotton fabric. Also the wave numbers 3200 cm^{-1} to 4000 cm^{-1} representing the stretching vibrations of –OH functional group has been totally vanished to a certain extent after the prior exposure of plasma before DCDMS treatment compared to those treated directly, which can be seen clearly

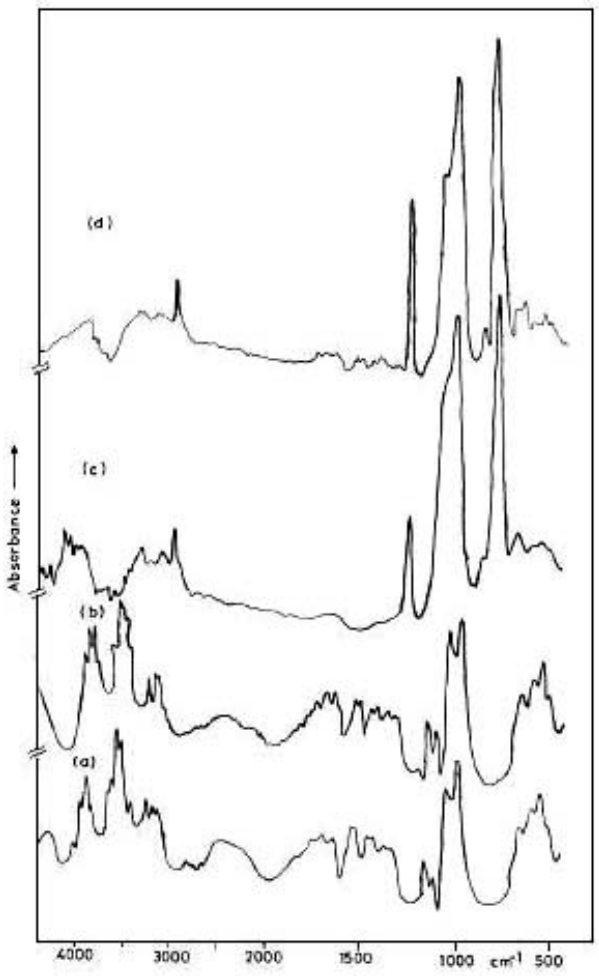


Figure 6. IR spectra of cotton fabric. (**a**) Untreated, (**b**) 2-min plasma exposed, (**c**) 2-min DCDMS treated and (**d**) 2-min DCDMS treated after exposure by plasma for 2 min.

from figure 6. Percentage weight change and wetting time study also elucidate the effect to this result.

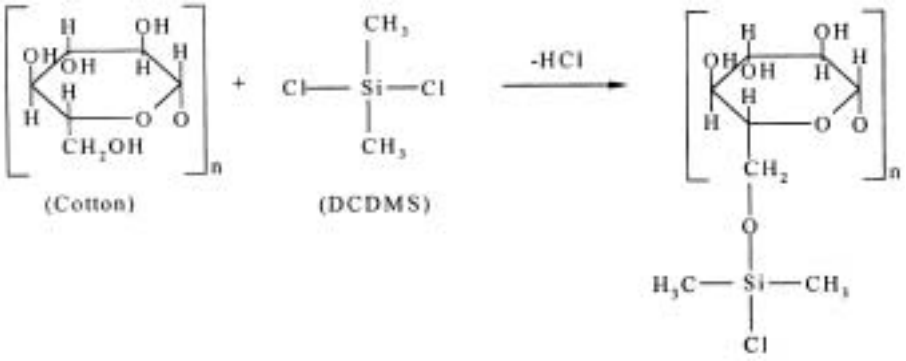
4. Conclusion

From the present investigation, it can be concluded that cotton fabric can be modified suitably by treating with DCDMS solution so as to make it water repellent. Although the fabric looses its original strength after the treatment, it attains good

Table 4. Relative intensities of DCDMS-treated cotton fabric.

Functional groups	Relative intensity	
	Cotton fabric treated with DCDMS	Plasma-treated cotton fabric followed by DCDMS
CH_3, stretching vibration	0.3173 (at 2964.8 cm^{-1})	0.2977 (at 2963.5 cm^{-1})
Si–CH_3, deformation vibration	0.3510 (at 1259.5 cm^{-1})	0.5216 (at 1259.6 cm^{-1})
Si–O linkage	0.7608 (at 1085.7 cm^{-1})	0.6012 (at 1075 cm^{-1})
Si–O–C	0.9390 (at 1019.6 cm^{-1})	0.8945 (at 1015.6 cm^{-1})
Si–C, stretching vibration	0.1327 (at 865.3 cm^{-1})	0.1442 (at 864.8 cm^{-1})
Si–Cl, stretching vibration	1.0000 (at 794.9 cm^{-1})	1.0000 (at 793.4 cm^{-1})

water repellent property even after washing with water for ten cycles. The condensation reaction of cotton with DCDMS results in the liberation of HCl.



Prior exposure of cotton fabric to plasma before treatment with DCDMS solution modifies the fabric leading to deposition of more and more silane groups making it water repellent as compared to control cotton. But care should be taken while exposing the fabric to plasma, as longer duration of exposure and subsequent treatment with DCDMS leads to lower deposition of silane groups as compared to 1-min plasma treatment, making it less water repellent.

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