

Surface Analysis of Cotton Fabrics Fluorinated in Radio-Frequency Plasma

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ABSTRACT: Cotton fabrics were treated by radio-frequency plasma with tetrafluoromethane (CF₄) and hexafluoropropene (C₃F₆) gases under different exposure times, pressures, and power levels. The hydrophobicity and water repellency were analyzed with measurements of the cosine of the contact angle ($\cos \theta$) and wet-out time. The hydrophobicity was enhanced with treatments of both gases. X-ray photoelectron spectroscopy (XPS) revealed increases in the surface fluorine content of 1–2% for CF₄ plasma and of 2.3–7.8% for C₃F₆ plasma. The relative chemical composition of the C_{1s} spectra after CF₄ and C₃F₆ plasma treatments

showed increases in the relative amounts of —C—O—C— and fluorocarbon groups (—CF, —CF₂, and —CF₃), whereas peak areas for —COH and —COOH decreased. The hydrophobicity was enhanced by the increase in the fluorine content and fluorocarbon groups. C₃F₆ plasma treatment resulted in higher hydrophobicity than CF₄ plasma treatment according to not only $\cos \theta$ and wet-out measurements but also XPS analysis. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2038–2047, 2003

Key words: cold plasma; ESCA/XPS; plasma polymerization

INTRODUCTION

The textile industry has long been concerned about water consumption and environmentally hazardous chemicals in effluents. Low-temperature plasma treatments have been investigated for the enhancement and/or replacement of conventional wet-chemical processing for textile materials. High-energy electrons and low-energy molecular species are generated through electrical discharges in low-temperature plasma without excessive heating of the substrate. The collisions of high-energy electrons with gas molecules can initiate the generation of ions, free radicals, and chemically active species, leading to chemical reactions (polymerization, grafting, crosslinking, and implantation) with polymer molecules on the substrate surface. New chemically active species in the plasma state do not affect bulk properties of the substrate, but they alter surface properties significantly.

Previous studies^{1–10} have shown that the chemical composition of cotton fiber surfaces is substantially changed after plasma treatment with various gases.

Changes in the surface chemical composition are highly correlated to changes in the surface properties. Ar, O₂, air, and NH₃ gas plasma treatments have been shown to result in an enhancement of wettability,^{1,11} whereas exposure to fluorinated gas plasma results in a decrease of water absorption or wettability.^{9,10} Fluorocarbon gas plasmas can change surface properties via either surface treatment or polymerization and deposition of a thin film.^{9,12–21} Hexafluoropropene (C₃F₆) gas plasma has been shown to result in the highest amount of polymer deposition among fluorocarbon gases.^{12–14}

The plasma treatment of cotton fabrics has been shown to affect the results of conventional finish processing. Low-temperature plasmas of air, O₂, and Ar gases were not effective in enhancing dyeability with reactive and direct dyes, but they increased the water absorption, crease resistance, drying rate, and soil releasing.¹¹ A combination of plasma and enzymatic treatments improved the dyeability of cotton fabrics.^{22,23} After plasma-initiated grafting with acrylamide and acrylonitrile, cotton and poly(ethylene terephthalate) fabrics had lower surface resistivities.²⁴

Free radicals generated by low-temperature plasma initiate polymerization and grafting on fiber surfaces.^{4,6–8} Benerito et al.² showed that the free radicals produced by plasma treatment initiated the polymerization of flame-retardant compounds and improved

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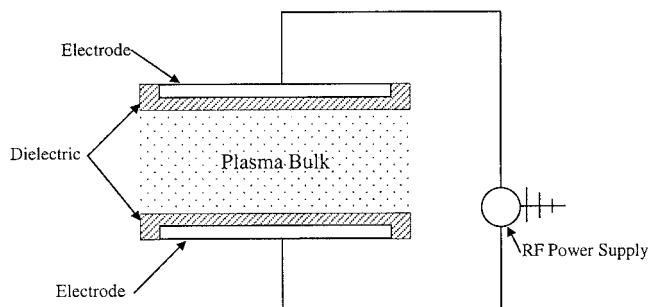


Figure 1 Diagram of a capacitively coupled plasma system (low-temperature and vacuum plasma system).

the flame retardancy of cotton fabrics. Cotton fibers have a higher rate of free-radical generation than other natural and manmade fibers, and tetrafluoromethane (CF_4) gas plasma produced the highest number of free radicals of various fluorocarbon gases.^{4,7}

In this study, CF_4 and C_3F_6 gas plasma treatments were conducted in an attempt to improve the hydrophobicity of cotton fabrics. X-ray photoelectron spectroscopy (XPS) was carried out to investigate the changes in the surface chemical composition as a result of changes in plasma parameters (power, pressure, and exposure time). The results of the XPS testing were compared with wettability measurements.

EXPERIMENTAL

Materials

Cotton fabric samples, supplied by Mt. Vernon Mills (Trion, GA) (style ICH, no. 01343), were used as specimens in the low-temperature plasma experiments. The specimens were indigo-dyed 100% cotton 3×1 twill fabric. Desizing was accomplished through a treatment with α -amylase enzymes at 48.9°C (120°F). All samples treated by the low-temperature plasma had dimensions of $15.24 \text{ cm} \times 15.24 \text{ cm}$ ($6 \text{ in.} \times 6 \text{ in.}$).

Plasma system and experiment procedure

Low-temperature (vacuum) plasma treatments were initially carried out on desized cotton fabrics in a radio-frequency (13.56 MHz) plasma chamber in a capacitively coupled mode. This low-temperature plasma system was assembled by the Center for Advanced Manufacturing and Processing of Materials at North Carolina State University. Figure 1 shows the basic elements in a capacitively coupled plasma chamber. The substrates (fabrics) were placed on the lower electrode during the treatments. Fabrics were treated by low-temperature (vacuum) plasmas with either CF_4 or C_3F_6 gases. The pressure, RF input power, and exposure time were varied according to an experimental test matrix (Table I). The RF power was varied

TABLE I
Wettability of Cotton Fabrics Treated by CF_4 and C_3F_6 Plasma Gases

Gas	Pressure (mTorr)	Power (W)	Exposure time (s)	θ		Cos θ		Wet-Out Time, s	
				Average	SD	Average	SD	Average	SD
Untreated				—	—	—	—	—	—
CF_4	50	100	30	120.8	9.8	-0.51	0.15	300 ^a	0
	50	100	60	114.9	10.7	-0.42	0.17	68.8	31.8
	50	300	30	124.2	7.6	-0.56	0.11	223.8	88.7
	50	300	60	131.0	6.3	-0.65	0.08	114.2	110.3
	75	100	30	132.1	4.3	-0.67	0.05	238.3	105.6
	75	100	60	122.4	3.9	-0.54	0.06	116.6	101.1
	75	300	30	128.1	7.4	-0.61	0.10	202	118
	75	300	60	132.8	6.7	-0.68	0.08	143.3	120.5
C_3F_6	50	50	30	145.6	2.5	-0.82	0.03	300 ^a	0
	50	50	60	152.8	2.8	-0.89	0.02	300 ^a	0
	50	160	30	150.3	5.8	-0.87	0.05	300 ^a	0
	50	160	60	153.9	1.9	-0.90	0.01	300 ^a	0
	100	50	30	145.0	2.6	-0.82	0.03	300 ^a	0
	100	50	60	138.4	2.6	-0.75	0.03	300 ^a	0
	100	160	30	137.6	2.3	-0.74	0.03	185.7	102.3
	100	160	60	145.5	4.0	-0.82	0.04	300 ^a	0
	150	50	30	139.6	5.4	-0.76	0.06	300 ^a	0
	150	50	60	139.8	3.0	-0.76	0.03	300 ^a	0
	150	160	30	143.6	2.9	-0.80	0.03	300 ^a	0
	150	160	60	145.0	3.1	-0.82	0.03	300 ^a	0

(θ = contact angle; flow rate = 50 sccm; SD = standard deviation).

^a Wet-out times were over 300 s at all testing positions on the cotton fabric surface.

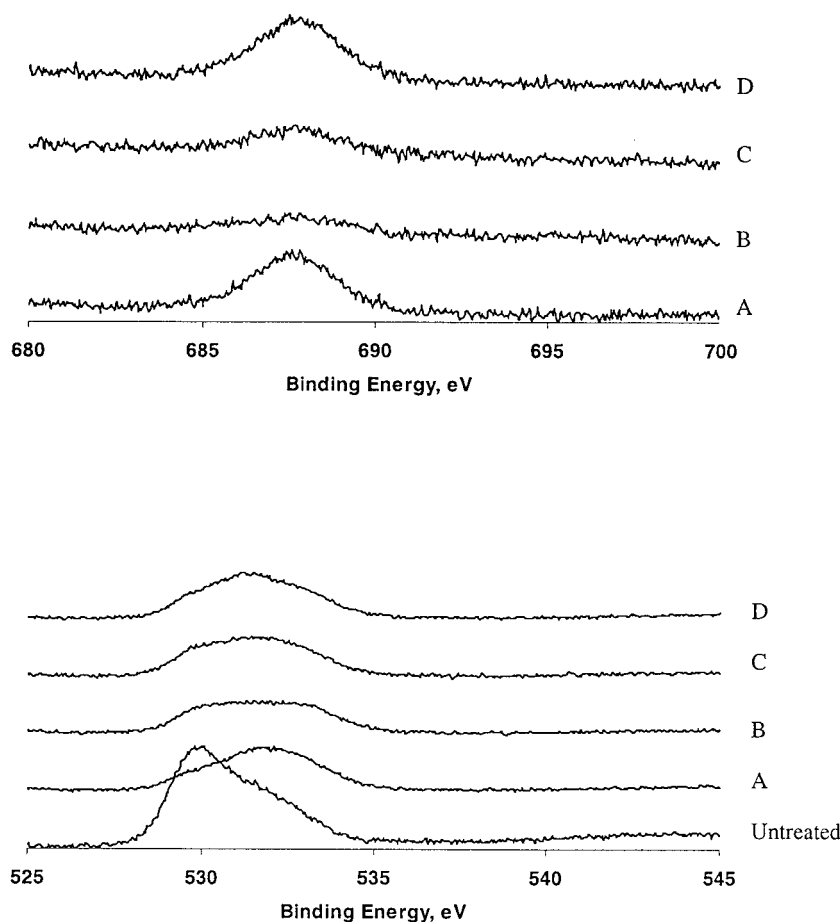


Figure 2 Deconvolution of F_{1s} (top) and O_{1s} (bottom) for cotton fabrics treated with CF_4 plasma: (A) 50 mTorr, 100 W, and 30 s; (B) 50 mTorr, 100 W, and 60 s; (C) 50 mTorr, 300 W, and 30 s; and (D) 75 mTorr, 100 W, and 30 s.

between 50 and 300 W at two exposure times (30 and 60 s), and the chamber pressure was 50, 75, or 150 mTorr. The gas flowed into the chamber at a constant rate of 50 sccm.

Measurements

The surface wettability was characterized by the measurement of the contact angles with a goniometer (model A-100, Ramé-Hart, Inc., Mountain Lake, NJ) with a telescope by the sessile drop technique. A 1- μ L distilled water droplet was placed on the fabric surface. The fluid droplet was observed through the telescope, and the contact angle of the droplet on the surface of the fabric was measured with the goniometer. The contact angles were measured in five different places. The surface wettability is proportional to the cosine of the contact angle ($\cos \theta$). As the contact angle approaches 90° , the cosine decreases to zero. Contact angles of 0 – 90° (positive $\cos \theta$) indicate spontaneous wetting of the surface, whereas those between 90 and 180° (negative $\cos \theta$)

indicate nonwetting. Liquid wetting is maximum when the contact angle is 0° , for which $\cos \theta$ is equal to 1, and it decreases as the contact angle approaches 180° , when $\cos \theta$ is equal to -1 . Therefore, higher contact angles indicate higher hydrophobicities. Wet-out time measurements were determined by AATCC test method 79-1995 (Absorbency of Bleached Textiles). A 1- μ L distilled water droplet was allowed to fall from a 5-cm height onto the cotton fabric surface, and the time required for the water droplet to be absorbed by the fabric was measured as the wet-out time. The averages of wet-out times at nine different places on the sample surface were recorded.

Chemical composition analysis for the cotton fabric surface was performed with a PerkinElmer PHI 5400 XPS photospectrometer (Wellesley, MA). The X-ray source was Mg, and the takeoff angle was 45° . The holding pressure of the XPS chamber was between 10^{-9} and 10^{-10} Torr. The computer acquisition was equipped with an RBD Enterprises model 147 controlling system (Bend, OR). This allowed for system control and data

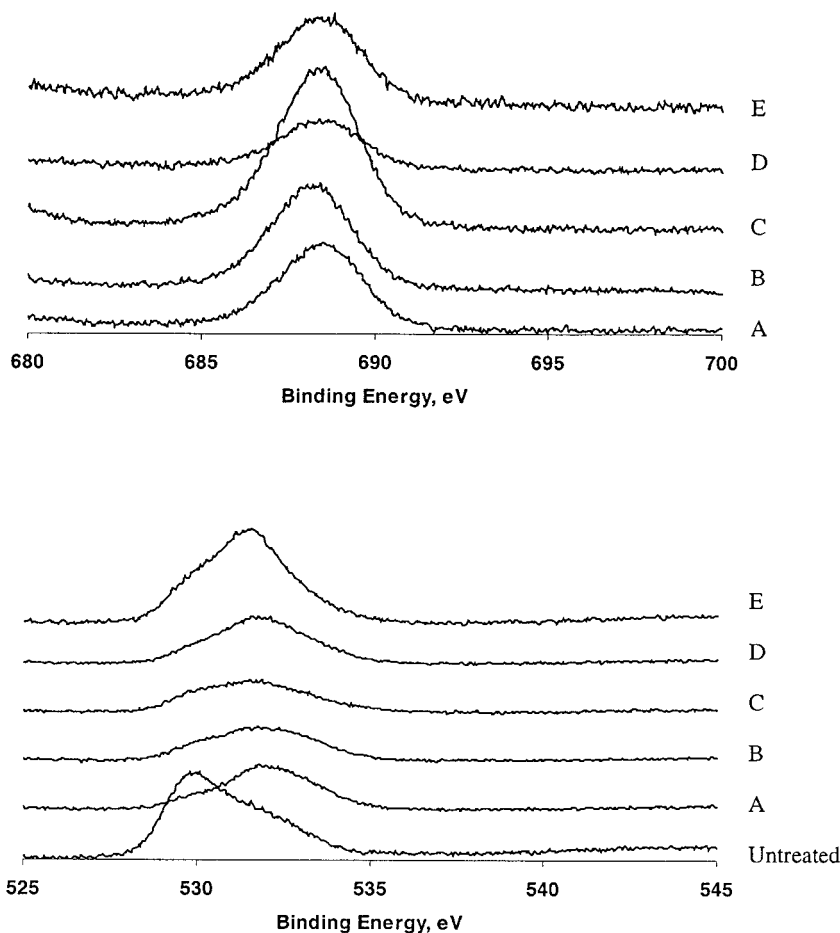


Figure 3 Deconvolution of F_{1s} (top) and O_{1s} (bottom) for cotton fabrics treated with C_3F_6 plasma: (A) 50 mTorr, 50 W, and 30 s; (B) 50 mTorr, 50 W, and 60 s; (C) 50 mTorr, 160 W, and 30 s; (D) 100 mTorr, 50 W, and 30 s; and (E) 150 mTorr, 50 W, and 30 s.

acquisition to be performed in an easy-to-use Windows®-based environment.

Statistical analysis

The effects of treatments on the wet-out time and contact angle were examined with regression analysis. The pressure, power, and treatment time were the independent variables or predictors for the models. A p value of less than 0.05 was considered significant.

RESULTS

Wettability

The effects of CF_4 and C_3F_6 gas plasma treatments on wettability were determined by measurements of the contact angle and wet-out time for water. For each sample, five measurements of the contact angle and nine measurements of the wet-out time were conducted on the front side (facing the plasma). However,

there was no measurement of the contact angle and wet-out time for the control sample because it wet out instantaneously. After the plasma treatment, the contact angle and wet-out time increased considerably; that is, the hydrophobicity of the substrate was improved.

Table I shows the wettability measurements (the contact angles and their cosines and the wet-out times) for cotton fabrics treated with either CF_4 or C_3F_6 gas plasma. The fabrics treated with CF_4 gas plasma showed substantial increases in contact angles (114–132 °) and in the magnitudes of their cosines, and this indicated extensive incorporation of hydrophobic groups onto the surface. The time to wet-out also increased (68–300 s). The $\cos \theta$ values increased (an increase in the contact angle) as pressure and power increased, but they were unaffected by the treatment time. Neither the pressure nor power had a significant effect on the wet-out times of the fabrics. The treatment time had a negative effect on the wet-out times.

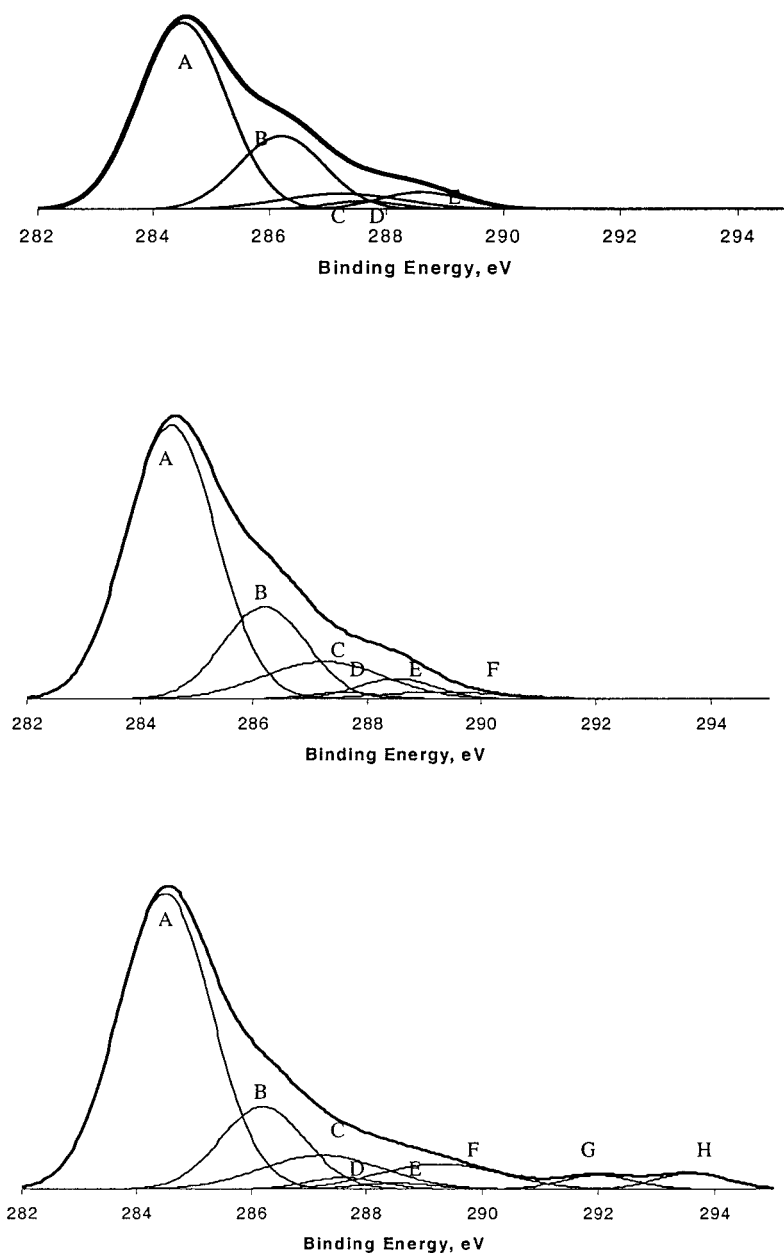


Figure 4 Line-shape analysis of high-resolution C_{1s} spectra for cotton fabrics that were (top) untreated, (middle) treated with CF_4 plasma (75 mTorr, 100 W, 30 s), and (bottom) treated with C_3F_6 plasma (50 mTorr, 160 W, 30 s): (A) $-C-C$ (284.5), (B) $-C-OH$ (286.2), (C) $-C-O-C$ (287.2), (D) $-C=O$ (287.6), (E) $-COOH$ (288.5), (F) $-CF$ (289.3), (G) $-CF_2$ (292.0), and (H) $-CF_3$ (293.6).

The increases in the contact angles and wet-out times achieved by C_3F_6 plasma treatments were substantially greater than those after treatments in CF_4 gas plasma; this indicated high substrate hydrophobicities. The contact angles increased with increases in the treatment time and power, but they decreased with an increase in pressure. The $\cos \theta$ values were dependent only on pressure and were significantly higher at 50 mTorr than at higher pressures. Wet-out times were over 300 s for all substrates treated by C_3F_6 gas plasma.

Spectral analyses of F_{1s} , O_{1s} , and C_{1s} regions

High-resolution scans of the F_{1s} and O_{1s} regions after CF_4 gas plasma treatments are shown in Figure 2. The F_{1s} peak intensities were lower for high power and long exposure conditions. The O_{1s} peak intensities were substantially lower than those for untreated fabrics, but they were uniform across treatment conditions.

Figure 3 shows the high-resolution scans of F_{1s} and O_{1s} regions for cotton fabrics treated by C_3F_6 plasma.

TABLE II
Relative Chemical Composition and Atomic Ratio Determined by XPS for Cotton Fabrics Treated by CF₄ Plasma

Pressure (mTorr)	Power (W)	Exposure time (s)	Chemical composition (%)			Ratio of atoms		
			C _{1s}	O _{1s}	F _{1s}	O/C	F/C	F/O
Untreated			66.9	33.1	0.0	0.49	0.00	0.00
50	100	30	85.3	13.1	1.6	0.15	0.02	0.12
50	100	60	85.4	13.7	0.9	0.16	0.01	0.07
50	300	30	86.0	13.3	0.7	0.15	0.01	0.05
75	100	30	82.1	15.9	2.1	0.19	0.03	0.13

The intensities of the F_{1s} and O_{1s} regions correspond to the fluorine and oxygen contents shown in Table III. An increase in the treatment pressure reduced the F_{1s} intensity, and a longer exposure time and a higher power level led to sharper and higher peaks in the F_{1s} regions. The O_{1s} intensities dropped off, apparently because of the C₃F₆ plasma treatment, but they increased again as the pressure increased.

Typical high-resolution scans of the C_{1s} region for untreated fabrics and fabrics treated with CF₄ and C₃F₆ plasma are shown in Figure 4. Line-shape analysis by the peak deconvolution shows that the C_{1s} spectrum for untreated cotton fabric contains five distinct peaks at 284.5 (—C—C), 286.2 (—COH), 287.2 (—C—O—C), 287.6 (—C=O), and 288.5 eV (—COOH). These peaks may be attributed to the bonds present in the cellulose and any residual surface contaminants (including dyestuff or size on fabrics). After CF₄ and C₃F₆ plasma treatments, the intensity of C_{1s} increased, and C_{1s} spectra showed the peaks of fluorocarbon groups at 289.3 (—CF), 292.0 (—CF₂), and 293.6 eV (—CF₃). The CF₄ plasma treatment not only deposited less fluorine than C₃F₆ but also produced fewer fluorocarbon groups than the C₃F₆ plasma treatment.

Chemical compositions of the cotton fabrics treated with CF₄ and C₃F₆ gas plasmas

Table II shows the relative chemical composition and atomic ratio for cotton fabrics treated by CF₄ gas

plasma. In comparison with untreated fabric (0%), there was a small increase in the surface fluorine content to approximately 1–2%. The same fabrics showed a 40–48% reduction in the surface oxygen content, a decrease in the ratio of oxygen to carbon (O/C), and increases in the ratios of fluorine to carbon (F/C) and fluorine to oxygen (F/O).

Table III shows the relative surface chemical compositions and atomic ratios for cotton fabrics before and after exposure to C₃F₆ gas plasma. This treatment resulted in an increase in the surface atomic fluorine (2.3–7.8%), with a 36–53% reduction in the surface oxygen. F/C and F/O ratios were much higher after C₃F₆ than after CF₄ plasma treatments.

Deconvolution of C_{1s} spectra for cotton fabrics treated by CF₄ and C₃F₆ plasma

Table IV shows the deconvolution of the C_{1s} spectra for cotton fabrics treated by CF₄ plasma. Under most conditions, there were peak area increases for —C—C, —C—O—C, and fluorocarbon groups (—CF, —CF₂, and —CF₃), whereas peak areas of —COH and —COOH decreased. At 300 W of power, —C—O—C decreased and —C=O increased.

The deconvolution of C_{1s} spectra for fabrics exposed to C₃F₆ plasma treatment shows the relative chemical carbon bonds (Table V). There were increments of —C—O—C and fluorocarbon groups after C₃F₆ plasma treatment, whereas the peak areas of —COH and —COOH decreased.

TABLE III
Relative Chemical Composition and Atomic Ratio Determined by XPS for Cotton Fabrics Treated by C₃F₆ Plasma

Pressure (mTorr)	Power (W)	Exposure time (s)	Chemical composition (%)			Ratio of atoms		
			C _{1s}	O _{1s}	F _{1s}	O/C	F/C	F/O
Untreated			66.9	33.1	0.0	0.49	0.00	0.00
50	50	30	80.1	15.1	4.8	0.19	0.06	0.32
50	50	60	80.3	14.1	5.5	0.18	0.07	0.39
50	160	30	80.2	12.0	7.8	0.15	0.10	0.65
100	50	30	81.4	15.9	2.7	0.20	0.03	0.17
150	50	30	80.1	17.6	2.3	0.22	0.03	0.13

TABLE IV
Deconvolution of C_{1s} Spectra for Cotton Fabrics Treated by CF_4 Plasma

Pressure (mTorr)	Power (W)	Exposure time (s)	Relative chemical bond area C_{1s} (%)							
			—C—C	—C—OH	—C—O—C	—C=O	—O—C=O	—CF	—CF ₂	—CF ₃
Untreated			61.4	23.5	7.3	2.3	5.5	0.0	0.0	0.0
50	100	30	67.0	16.8	10.8	1.1	2.2	1.8	0.1	0.1
50	100	60	66.5	18.7	8.8	0.2	3.6	1.9	0.0	0.3
50	300	30	71.5	17.6	1.9	4.0	3.3	1.6	0.0	0.0
75	100	30	61.9	19.3	11.3	1.2	4.0	2.2	0.0	0.0

For both plasma treatments, the percentage of —C—O—C bonds on the surface increased, whereas the percentage of —COH bonds decreased. According to Ward et al.,⁶ cellulose radicals generated by plasma treatment are a result of one of the following mechanisms illustrated in Figure 5:

1. Bond breakage between C_1 and ring oxygen.
2. Bond breakage between C_1 and glycosidic bond oxygen.
3. Dehydrogenation or dehydroxylation between C_2 and C_3 after ring opening.

In addition, —COH groups on cellulose are susceptible to replacement with fluorocarbon species (via dehydrogenation or dehydroxylation at C_6).

Determination of the hydrophobicity

Tables VI and VII show the ratios of hydrophobic surface groups (fluorocarbon) to hydrophilic surface groups (carbon groups containing oxygen) after plasma treatment. For CF_4 plasma treatment, the ratio does not appear to be related to wettability changes between the plasma conditions. Conversely, for C_3F_6 plasma treatment, the intensities of hydrophobic groups and hydrophobic/hydrophilic ratio are related to wettability. Additionally, it appears that not only the ratio of hydrophobic groups to hydrophilic groups but also the number of fluorines attached to surface carbons influence wettability.

Changes in the surface energy were much greater for the samples treated in C_3F_6 gas plasma than for

those treated in CF_4 gas plasma. This result agrees with previously published results.¹⁴ Inagaki et al.¹⁹ speculated that the surface fluorocarbon chemical composition rather than the overall surface atomic fluorine content determined hydrophobicity. The characteristic plasma particles were responsible for the different deposition rates, depending on the fluorocarbon monomer. CF_4 plasma could generate only $CH_2F \cdot$, $CHF_2 \cdot$, and $CF_3 \cdot$ radicals, whereas C_3F_6 plasma could generate a wider variety of radicals. The — CF_3 group/ F_{1s} ratio increased more with the C_3F_6 plasma treatment than with the CF_4 plasma treatment, as shown in Table VIII. Wettability measurements indicated that the — CF_3 group was more effective in increasing surface hydrophobicity than either the —CF or — CF_2 groups in C_3F_6 plasma treatment. This result correlates well with Inagaki et al.'s results. For CF_4 plasma treatment, however, the presence of some — CF_3 groups did not affect the hydrophobicity of cotton fabrics.

CONCLUSIONS

In this work, the effects of CF_4 and C_3F_6 gas plasmas on the surface properties of cotton fabrics were studied. To evaluate the wettability, we conducted measurements of the contact angle and wet-out time. XPS analysis was used to investigate the surface chemical composition.

Cotton fabrics treated with fluorocarbon gas plasmas had significantly higher contact angles and wet-out times than untreated samples. Fabrics treated in C_3F_6 gas plasma had higher contact angles (and cor-

TABLE V
Deconvolution of C_{1s} Spectra for Cotton Fabrics Treated by C_3F_6 Plasma

Pressure (mTorr)	Power (W)	Exposure time (s)	Relative chemical bond area C_{1s} (%)							
			—C—C	—C—OH	—C—O—C	—C=O	—O—C=O	—CF	—CF ₂	—CF ₃
Untreated			61.4	23.5	7.3	2.3	5.5	0.0	0.0	0.0
50	50	30	66.1	16.1	9.5	2.5	1.6	3.5	0.0	0.7
50	50	60	60.8	18.4	10.4	1.9	2.8	4.3	0.3	1.1
50	160	30	60.8	15.4	9.1	1.9	1.1	6.9	2.3	2.6
100	50	30	59.9	19.3	12.4	1.7	2.8	3.2	0.0	0.7
150	50	30	70.4	19.7	1.2	3.3	3.8	1.6	0.0	0.0

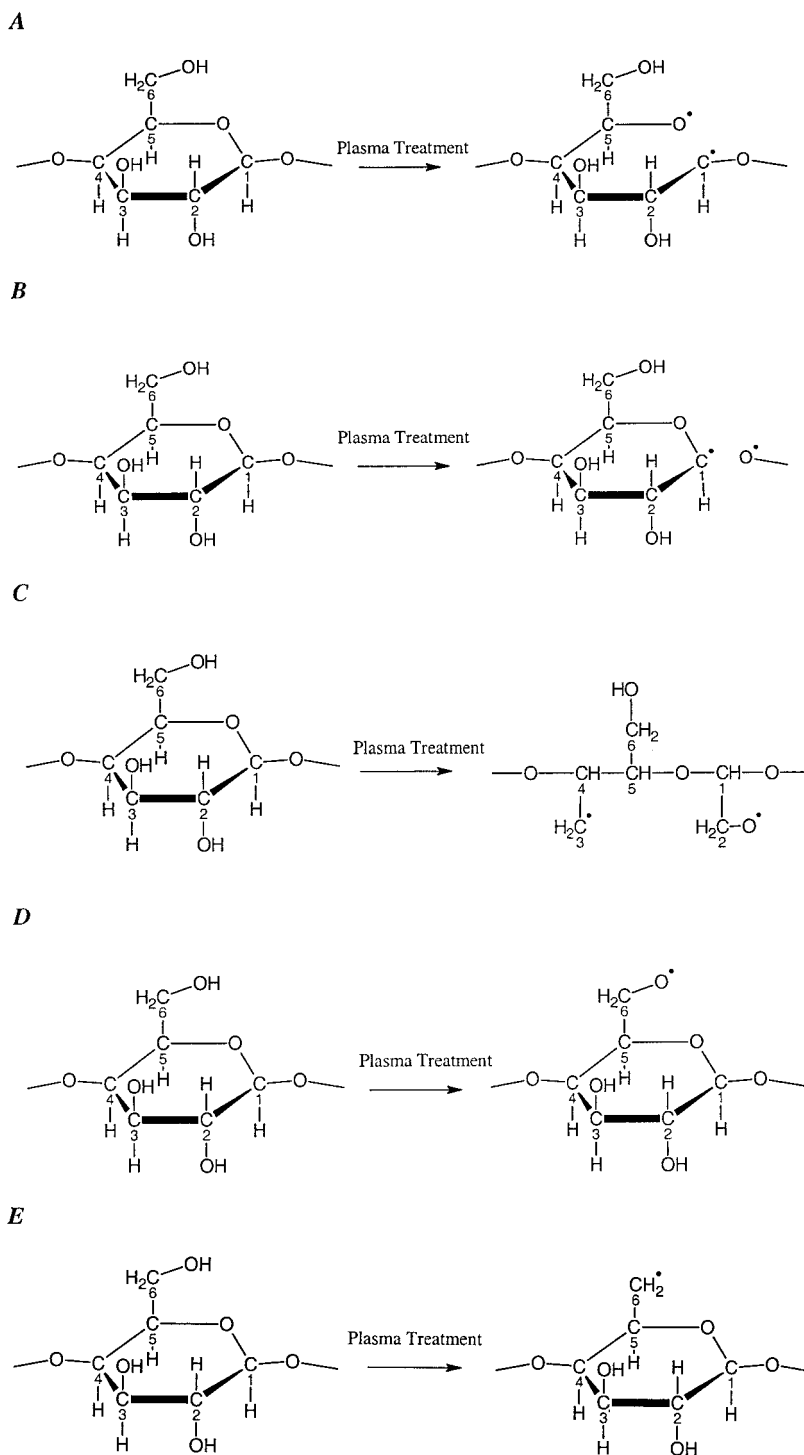


Figure 5 Radical formation by (A) bond breakage between C₁ and ring oxygen, (B) bond breakage between C₁ and glycosidic bond oxygen, (C) dehydrogenation and dehydroxylation between C₂ and C₃ after the ring opening of anhydroglucose, (D) dehydrogenation at C₆, and (E) dehydroxylation at C₆.⁶

responding cosines) and longer wet-out times than those treated in CF₄ plasma. XPS analysis revealed the extensive incorporation of fluorocarbon groups on the surface after CF₄ and C₃F₆ gas plasma treatments. Fluorine contents, F/C, and F/O for fabrics treated in

CF₄ plasma were lower than those for fabrics treated in C₃F₆ gas plasma.

The C_{1s} spectrum by peak deconvolution showed the change in the carbon bonding following plasma treatment. Both CF₄ and C₃F₆ gas plasma treatments

TABLE VI
Comparison of Hydrophobic Groups to Hydrophilic Groups for Cotton Fabrics Treated by CF₄ Plasma

Pressure (mTorr)	Power (W)	Exposure time (s)	Relative chemical bond area of C _{1s} (%)		
			Hydrophilic groups	Hydrophobic groups	Ratio
Untreated			38.6	0.0	—
50	100	30	30.9	2.0	0.06
50	100	60	31.3	2.2	0.07
50	300	30	26.9	1.6	0.06
75	100	30	35.8	2.2	0.07

increased —C—O—C and fluorocarbon groups and decreased —COH groups after plasma treatments. The breakage of glycosidic bonds and carbon bonds connecting two oxygens produced radicals that could react with fluorocarbon species on plasma bulk. Also, fluorocarbon species could react with —COH groups on cellulose molecules, and this resulted in additional —C—O—C generation.

A comparison of wettability measurements to chemical compositions by XPS showed that the intensity change of hydrophobic or hydrophilic groups was not related to a change in surface wettability. However, the fluorine contents, F/C, and F/O were highly correlated to the hydrophobicity of cotton fabrics. Line-shape analysis by peak deconvolution revealed the fluorocarbon groups (—CF, —CF₂, and —CF₃) generated by CF₄ and C₃F₆ gas plasmas. C₃F₆ gas

plasma treatment induced the surface binding of more —CF₃ groups, highly related to hydrophobicity, than CF₄ plasma treatment.

The increase in the hydrophobicity was much greater for the samples treated in C₃F₆ gas plasma than for those treated in CF₄ gas plasma. A previous study¹⁴ proposed that C₃F₆ gas plasma can generate polymers on the substrate through both plasma polymerization and plasma-induced polymerization mechanisms, whereas CF₄ gas plasma is limited to only plasma polymerization. CF₄ plasmas produce more atomic fluorine than C₃F₆ plasmas. Atomic fluorine is a highly effective etchant and ablates the deposited fluorinated polymer layer; this results in a reduction in surface fluorine and a decrease in hydrophobicity over time and with an increasing level of power. A consistent relationship between the treat-

TABLE VII
Comparison of Hydrophobic Groups to Hydrophilic Groups for Cotton Fabrics Treated by C₃F₆ Plasma

Pressure (mTorr)	Power (W)	Exposure time (s)	Relative chemical bond area of C _{1s} (%)		
			Hydrophilic groups	Hydrophobic groups	Ratio
Untreated			38.6	0.0	—
50	50	30	29.7	4.2	0.14
50	50	60	33.5	5.7	0.17
50	160	30	27.5	11.8	0.43
100	50	30	36.2	3.9	0.11
150	50	30	28.0	1.6	0.06

TABLE VIII
Comparison of —CF_x and F_{1s} Contents Generated by CF₄ and C₃F₆ Plasma Gases

Gas	Pressure (mTorr)	Power (W)	Exposure time (s)	Relative area (%)				Ratio		
				—CF	—CF ₂	—CF ₃	F _{1s}	—CF/F _{1s}	—CF ₂ /F _{1s}	—CF ₃ /F _{1s}
Untreated				0.0	0.0	0.0	0.0	—	—	—
CF ₄	50	100	30	1.8	0.1	0.1	1.6	1.13	0.06	0.06
	50	100	60	1.9	0.0	0.3	0.9	2.11	0.00	0.33
	50	300	30	1.6	0.0	0.0	0.7	2.31	0.00	0.00
	75	100	30	2.2	0.0	0.0	2.1	1.05	0.00	0.00
C ₃ F ₆	50	50	30	3.5	0.0	0.7	4.8	0.73	0.00	0.15
	50	50	60	4.3	0.3	1.1	5.5	0.78	0.05	0.20
	50	160	30	6.9	2.3	2.6	7.8	0.88	0.29	0.33
	100	50	30	3.2	0.0	0.7	2.7	1.19	0.00	0.26
	150	50	30	1.6	0.0	0.0	2.3	0.70	0.00	0.00

ment parameters and wettability was not obtained for CF_4 and C_3F_6 gas plasma treatments. For the cotton fabrics, it appears that although treatment in CF_4 gas plasma resulted in surface fluorination, the effect decreased with the treatment time and power level, most likely because of an increase in the surface etching reactions. In contrast, for the fabrics treated in C_3F_6 , increments in the treatment time and power resulted in a corresponding increase in hydrophobicity.

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