Hydrophobic Cotton Fabric Coated by a Thin Nanoparticulate Plasma Film

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ABSTRACT: The audio frequency (AC) plasma of some kind of fluorocarbon chemical was applied to deposit a nanoparticulate hydrophobic film onto a cotton fabric surface. The measurement of the video contact angle showed that the superhydrophobicity of the cotton fabric was obtained with a treatment of only 30 s. The softness, water retention, moisture regain, color retention, abrasion, friction, and permeability were thoroughly investigated by a standard method that compared the fabric with a commercial Scotchgard-protector-sprayed cotton fabric. The results showed that the textile performances of the plasma-coated fabric were superior to those of Scotchgard-sprayed samples, except for the moisture regain, which was almost the same. A post-treatment at a high temperature was conducive to increasing the hydrophobicity and the recovery of the water repellency of the plasma-coated fabric after it was washed. Atomic force microscopy images and time-of-flight secondary-ion mass spectra of plasma thin films on silicon wafers indicated that some physical and chemical changes took place during the post-treatment process. J Appl Polym Sci 88: 1473–1481, 2003

Key words: films; plasma polymerization

INTRODUCTION

The manufacturing of water-resistant and dirt-resistant fabrics has long been an interesting subject attracting a great deal of research. Various treatment methods have been used. Examples include spraying with Scotchgard protector, which contains fluorochloro polymers and CF_4, and siloxane plasma treatment;[1,2] vapor phase treatment with amines;[3] and ultraviolet treatment with alkali inorganic salts.[4] Plasma treating or coating has extensively been studied and proved to be a promising method for conferring to a fabric or fiber hydrophilicity to improve dyeing, printing, wetting, shrinkproofing, and adhesion properties.[3–7] Recently, attention has been focused on the plasma treatment using perfluorocarbon chemicals because it has many advantages over other methods. First, it is an environmentally friendly dry process and does not need additional manipulations of a fabric, such as a wetting and drying process. Second, it provides a very thin coating that does not significantly affect the original characteristics of the fabric, such as its breathability, feel, and softness, but does confer to the surface a very low surface energy,[8,9] which makes the fabric water-repellent or dirt-repellent. Third, the plasma coating is more durable than traditional sprayed finishes because the coating is chemically bonded to the treated fabric.

In this work, an AC plasma of some kind of fluorocarbon chemical (FC) was applied to deposit a thin hydrophobic film onto a cotton fabric surface and to improve its water repellency. For the determination of potential uses for the coating in fabric finishes, the softness, water retention, moisture regain, color retention, abrasion, friction, and permeability of the fabric were thoroughly investigated by standard methods that compared the fabric with a commercial Scotchgard-protector-sprayed cotton fabric.

EXPERIMENTAL

The plasma polymerization coating was completed in a commercial AC plasma reactor with some kind of FC. The coating process was the same as before.[9] The measurement of the water contact angle was carried out in a computer-video-processed goniometer (VCA-2000, AST Products, Inc., Billerica, MA) A sessile drop of water was dispensed, and its image was captured by a video camera and displayed on a computer monitor. The contact angle of the droplet to the coated cotton fabric was determined with proprietary soft-

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ware. This value could be applied to express the hydrophobic character of the fabric. The larger the water contact angles were, the greater the hydrophobicity was. The feel of the fabric was estimated with a TRI softness tester and a Kawabata friction tester. The color changes of the fabric after it was coated were tested with a color appearance tester. The abrasion test was performed in a Nu-Matindale abrasion and pilling tester under standard temperature and humidity conditions. After 30,000 abrasion cycles, the samples were removed from the holder, and the weight of each sample was recorded. The weight percentage was calculated as the abrasion resistance according to the following equation. The lower the weight was, the better the abrasion resistance was:

$$\text{Weight loss (\%)} = (\text{Initial sample weight} - \text{Abraded sample weight})/\text{Initial sample weight} \times 100\% \quad (1)$$

The moisture regain test was completed in an infrared moisture determination balance. The samples were conditioned at 70°F and 65% relative humidity overnight, and then the moisture regain (%) was determined with the balance with this equation:

$$\text{Moisture regain (\%)} = (\text{Initial sample weight} - \text{Absolute dry weight})/\text{Initial weight} \times 100\% \quad (2)$$

The water vapor permeability index was tested with a cup method and was determined as follows:

$$\text{Water vapor permeability index} = \frac{\text{Water vapor permeability of the test sample}}{\text{Water vapor permeability of the reference sample}} \quad (3)$$

where

$$\text{Water vapor permeability} = \text{Loss in mass/time between weighing} \times \text{Internal area of the dish} \quad (4)$$

In the test, each sample was sealed over the open mouth of a dish containing water and placed under a standard atmosphere. After a period of time for establishing equilibrium, successive weightings of the dish were made, the rate of water vapor transfer through the sample (water vapor permeability) was determined, and the water vapor permeability index was calculated.

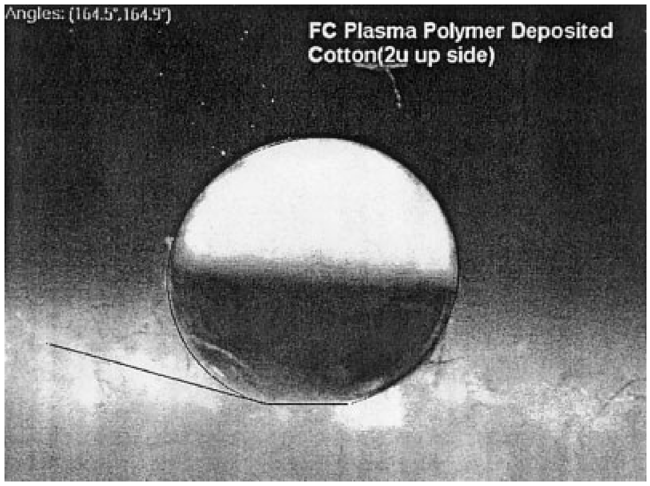


Figure 1 Image of a water drop on a plasma-coated cotton surface.

Atomic force microscopy (AFM) images of the non-post-treated and post-treated plasma films were obtained on a Burleigh Instructional atomic force microscope (Burleigh Instruments, Inc., Fishers, NY) so that we could investigate the topographic changes in the coated film before and after post-treatment. Time-of-flight secondary-ion mass spectrometry (TOF-SIMS) of the plasma thin films on silicon wafers was used to investigate the chemical changes taking place during the post-treatment process, and it was performed with an IONTOF model IV instrument manufactured by Cameca GmbH (Muenster, Germany).

RESULTS AND DISCUSSIONS

Measurement of the water contact angle

The water contact angle was about 164° for an FC plasma-polymer-coated cotton (an average for five samples) and about 137° for the Scotchgard-protector-coated cotton. The image of a plasma-polymer-coated cotton sample with a water drop is shown in Figure 1. This measurement indicated that the water resistance in the statistic condition for the FC plasma-polymer-coated cotton was superior to that for the protector-coated sample. This superhydrophobicity was attributable to both the deposited film composition and the roughness of the cotton fabric surface. The water contact angle of the film on a glass slide deposited under the same working conditions was 110°. According to the Wenzel equation,

$$\cos\theta_r = r\cos\theta_s \quad (5)$$

where θ_r is the contact angle on the rough surface and θ_s is the contact angle on the smooth surface. r is the roughness correction factor. It equals the ratio of the

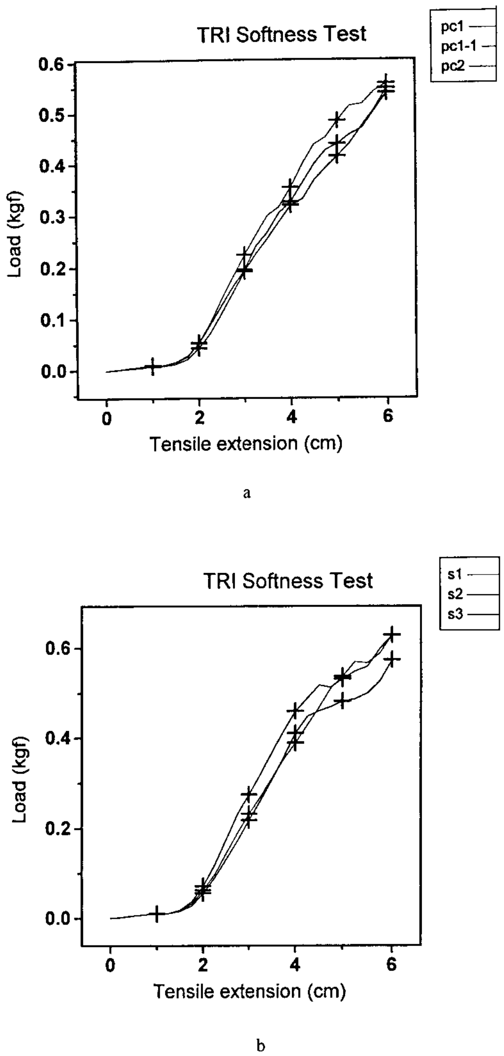


Figure 2 Force–displacement curves of plasma-film-coated fabrics: (a) pc1, pc1-1, and pc2 represent plasma-film-coated cotton samples under the same working conditions and (b) s1, s2, and s3 represent Scotchgard-protector-sprayed cotton samples under the same spraying conditions.

surface actual area to the apparent project area. When θ_s is less than $\pi/2$, cos θ_s is greater than 0, and θ_r decreases as r increases. When θ_s is greater than $\pi/2$, cos θ_s is less than 0, and θ_r increases as r increases. Therefore, the roughness of the fabric surface contributed to the superhydrophobicity of the coated cotton fabric.[10]

Softness comparison

The softness of the fabric was compared with an Instron instrument equipped with a softness tester and special software. A fabric was extracted through a nozzle so that a force–displacement curve of the fabric was generated, and the fabric softness value was calculated by the softness software. Figure 2 shows the force–displacement curves of a plasma-film-coated cotton fabric [Fig. 2(a)] and those of a Scotchgard-sprayed cotton fabric [Fig. 2(b)]. The three curves express separately the force–displacement relations of three samples obtained under the same working conditions. The softness value was calculated from an average of the three curves. Table I provides a softness comparison of a control sample, plasma-film-coated samples with and without heating post-treatment, and Scotchgard-sprayed samples with and without heating post-treatment during different washing cycles. The softer the fabric was, the greater the softness value was. This table shows that the softness of a cotton sample increased after plasma film coating but decreased a great deal after Scotchgard protector spraying. This implies that the plasma film was very thin and that it only affected the surface properties of the samples, but the sprayed coating affected the bulk properties. Therefore, the softness of the Scotchgard-sprayed sample was greatly reduced. For clothing, a plasma film coating would be superior to Scotchgard spraying with respect to its feel.

Table I also indicates that the softness became worse after standard washing cycles for the control and plasma-film-coated fabrics. The softness became better after standard washing cycles for the sprayed fabric, but it was still not as good as that of the control and plasma-film-coated fabrics after nine washing cycles.

It should be noted that the heating post-treatment was beneficial for the maintenance of the softness of

TABLE I
Softness Comparison

Sample	Unwashed		Three-cycle wash		Nine-cycle wash	
	Softness	Standard deviation	Softness	Standard deviation	Softness	Standard deviation
Control	3.57	0.06	2.53	0.26	2.90	0.21
Plasma	3.70	0.03			2.45	0.21
PlasmaPT	3.69	0.08	2.89	0.05	3.06	0.19
Scotchgard	1.74	0.12	2.55	0.12	—	—
ScotchgardPT	1.67	0.18	2.20	0.01	2.30	0.14

Plasma = plasma-film-coated cotton samples; plasmaPT = plasma-film-coated cotton samples with heating post-treatment; Scotchgard = Scotchgard-sprayed cotton samples; ScotchgardPT = Scotchgard-sprayed cotton samples with heating post-treatment.

TABLE II
Color Measurement of the Cotton Samples

Sample	L	a	b	WI CIE*	ΔE
Control	93.38	−0.19	2.37	75.85	
Plasma-coated	94.45	−0.35	3.34	73.60	1.45
Sprayed	94.99	−0.39	4.83	65.67	2.95

* Whiteness index determined according to CIE L * a * b color space.

the plasma-film-coated cotton. This might have been due to the adherence changes in the coated film after the heating post-treatment.

Other textile properties

The color change (ΔE) and whiteness (WI CIE) of the cotton fabric were measured, and the results are given in Table II. ΔE is defined as a unit of measurement expressing the color changes of a fabric. It is mathematically expressed as follows:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \quad (6)$$

where ΔL is the white change, Δa is the red or green change, and Δb is the yellow or blue change. The lower the number is, the less the color changes. Table II shows that WI CIE of the plasma-film-coated fabric was close to that of the control sample. ΔE was smaller than ΔE for the sprayed fabrics. Therefore, the color changes of the plasma-film-coated fabric were not as great as those of the Scotchgard-sprayed fabrics.

Table III provides a comparison of the average weight loss, friction coefficient, water retention percentage, moisture regain, and permeability index of plasma-coated and Scotchgard-sprayed cotton samples. The average weight loss from the rubbing of a fabric sample against a standard was used to evaluate the abrasion resistance; the abrasion resistance of the plasma-film-coated fabric was the highest. The permeability index and water retention of the plasma-film-coated fabric were higher than those of the sprayed ones. The friction coefficient of the plasma-film-coated cotton sample was lower than that of the Scotchgard-sprayed fabrics. The moisture regain of the plasma-film-coated fabric was a little lower than that of the sprayed fabric. This might have been caused by the properties of the spraying chemicals.

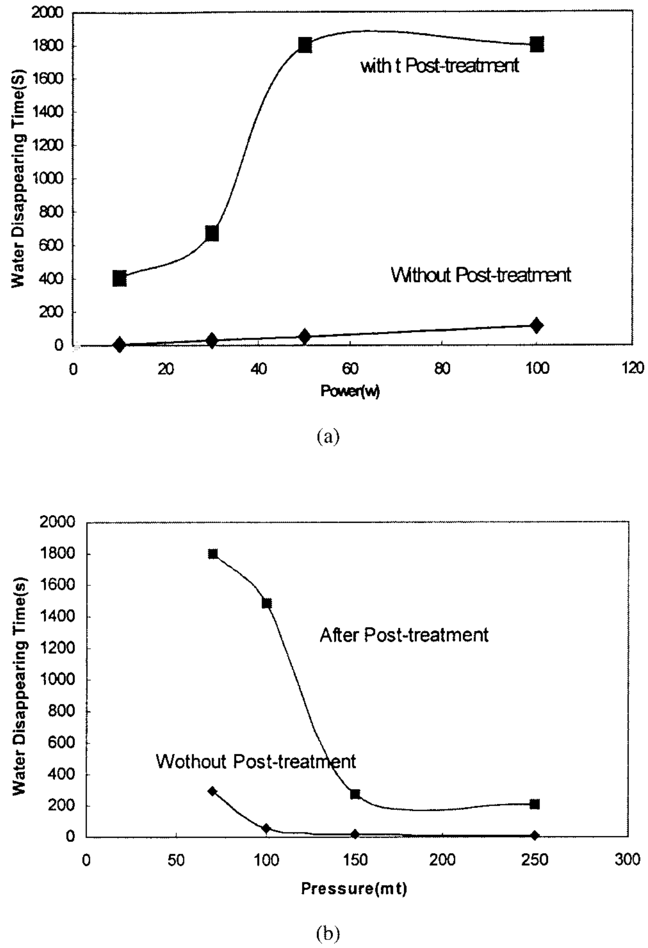
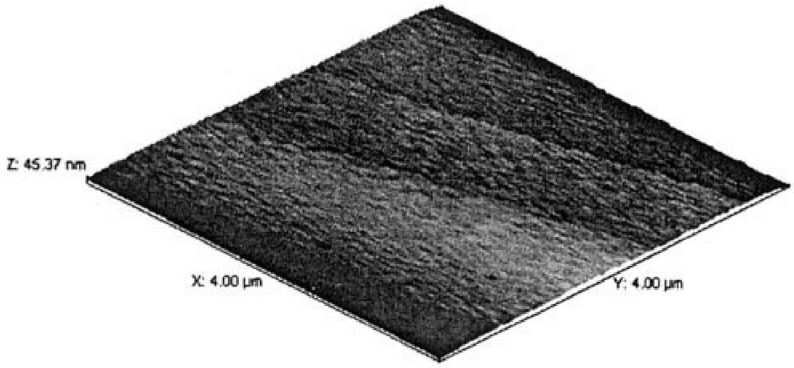


Figure 3 Water drop absorbing time changes with power (a) and pressure (b) before and after the heating post-treatment.

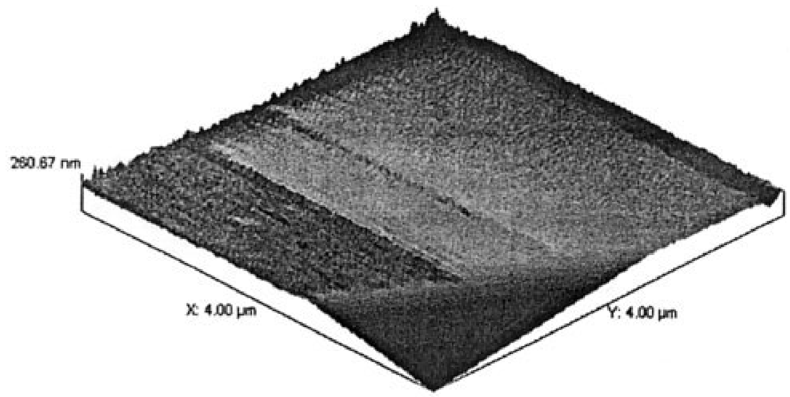
In conclusion, the color change, the softness and feel, the abrasion resistance, the water retention, and the permeability of the plasma-film-coated cotton were superior to those of the Scotchgard-sprayed samples. Therefore, FC plasma film coating could be a useful method for water- or oil-resistance treatment of clothing fabrics.

TABLE III
Other Textile Properties

	Control	Plasma-coated	Scotchgard-sprayed
Average of weight loss	17.08	14.80	16.65
Friction coefficient	0.3	0.37	0.52
Water retention (%)	0.72	0.66	0.48
Moisture regain	7.93	7.35	7.58
Permeability index	—	0.985	0.970



(a)



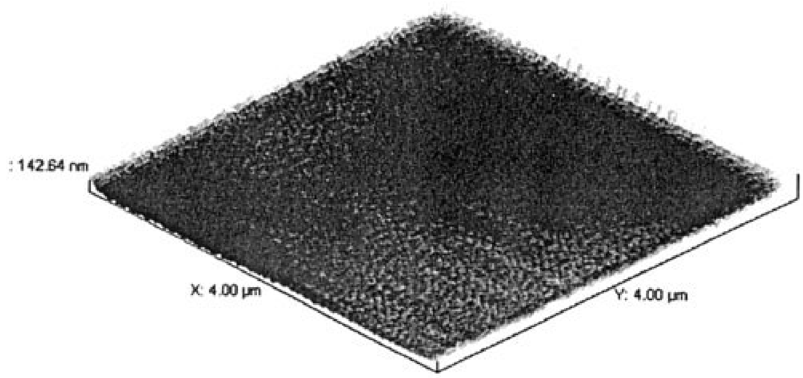
(b)

Figure 4 AFM images of the silicon substrate and the plasma film surface: (a) the silicon wafer without etching, (b) the silicon wafer with etching, (c) the plasma particulate film without post-treatment, and (d) the plasma particulate film with post-treatment.

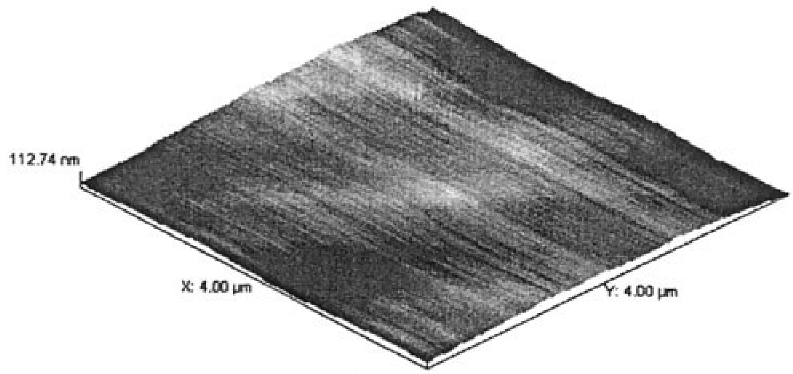
Effects of the heating post-treatment on the hydrophobicity of the plasma-film-coated cotton

As shown in Figure 1, when the water contact angle on the plasma-film-coated fabric was large enough, the water drop on the fabric surface was not absorbed by the cotton fabric. We lowered the coating time to some extent (other working conditions remained the same), and the water drop on the cotton fabric was absorbed by the fabric. Therefore, an absorbing time was found to exist. The coverage of the film on the cotton surface, the depth of the film, the chemical properties, and the physical roughness of the film had an influence on the absorbing time. The absorbing time could be served as another index for evaluating the hydrophobicity of the fabric.

Figure 3(a,b) provides the absorbing time of the plasma-coated cotton with the discharge power and pressure, respectively. The curves with the post-treatment in Figure 3 were obtained after samples were heated for some time and stored at standard temperature and humidity for 8 h. As the discharge power increased and the discharge pressure decreased, the absorbing time rose. After the heating post-treatment, the curves of the absorbing time moved up in the two cases, and the absorbing time increased because of the heating post-treatment. The same phenomenon was



(c)



(d)

Figure 4 (*Continued from the previous page*)

observed for the cotton fabric after washing cycles. These phenomenon indicate that some changes took place after the heating post-treatment. Therefore, a heating post-treatment is good for the recovery of the hydrophobicity of a fabric after it is washed.

To investigate the influence of the heating post-treatment on the absorbing time, we deposited a film on a smooth silicon wafer, heated it, and performed AFM and TOF-SIMS analyses.

AFM results

AFM images of the plasma films deposited on silicon wafers are shown in Figure 4, and the cross sections of the film are shown in Figure 5. From Figures 4 and 5, it can be seen that a nanoparticulate film was obtained on the smooth surface of the silicon wafer. The up-and-down depth was about 25 nm. Before the post-

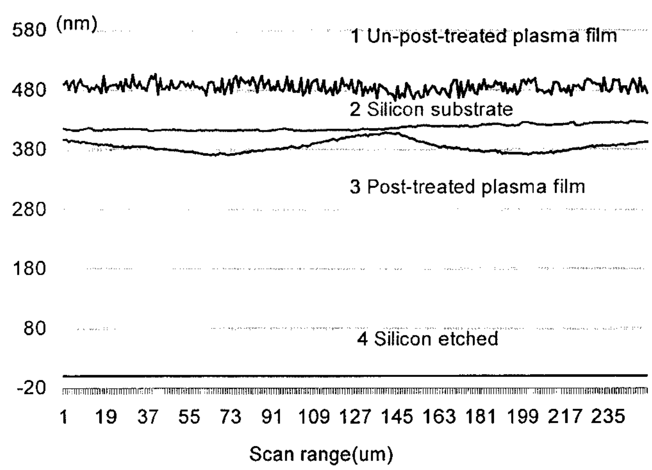
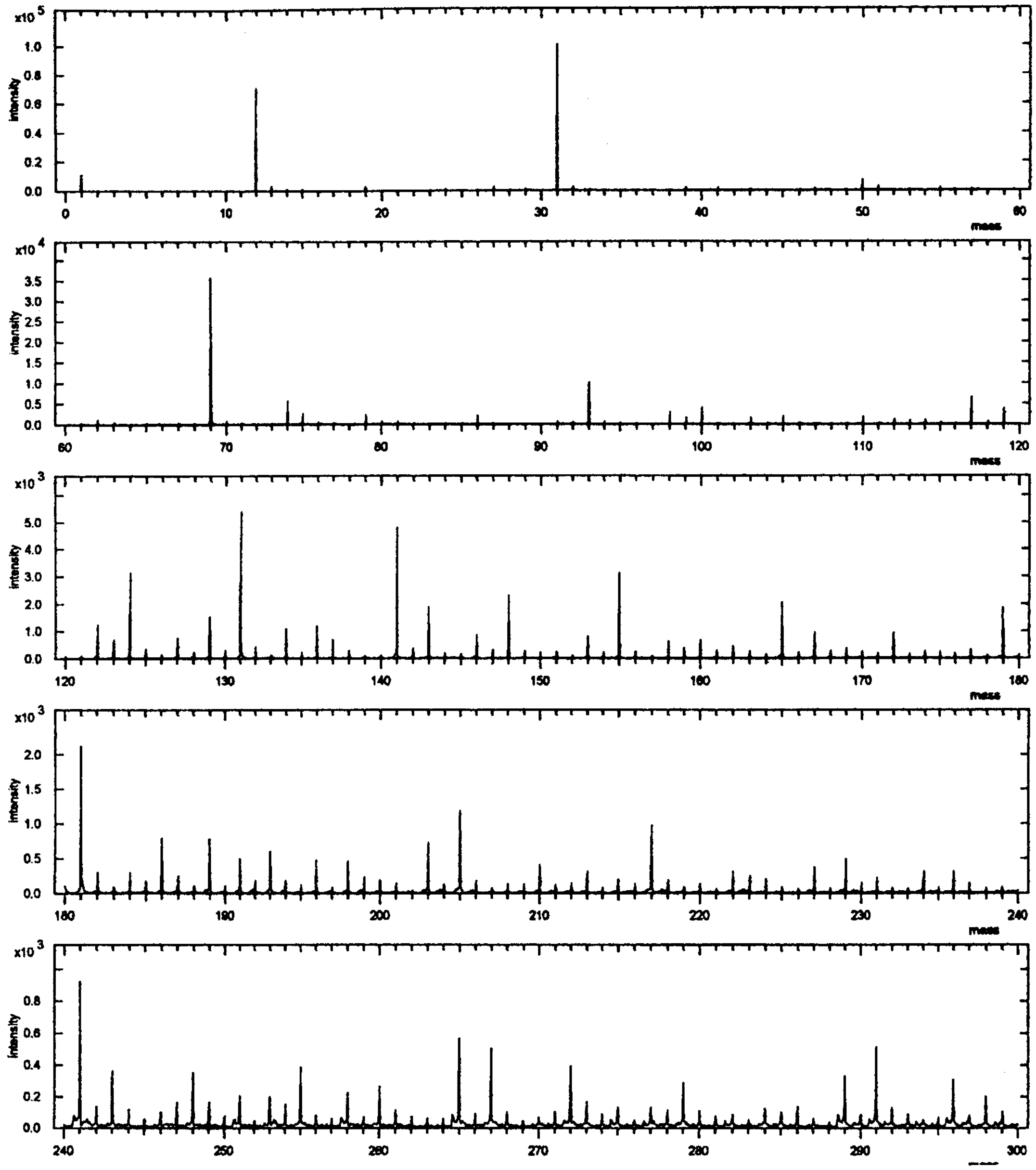


Figure 5 Cross sections of the substrate and plasma film surface.



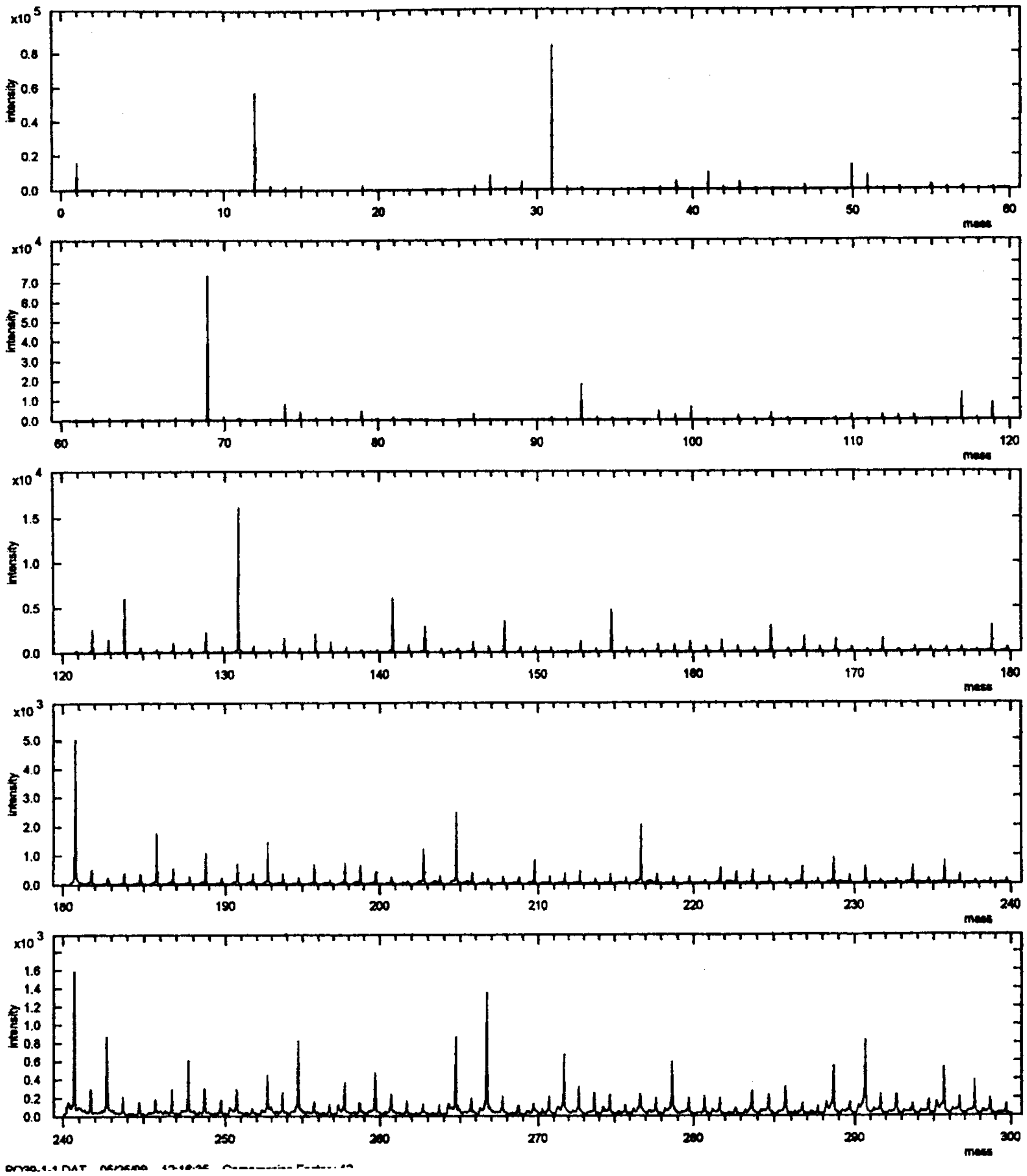
(a)

Figure 6 TOF-SIMS spectra of the films: (a) before post-treatment, (b) after post-treatment at a low temperature, and (c) after post-treatment at a high temperature.

treatment, the surface of the film was basically dense and featureless, with a uniform nodule distribution. After the post-treatment, the morphology of the films was different. The surface became broader in its features, and the uniform nanoparticulate nodules disappeared. It seems that the nanoparticulate film contracted during the heating treatment, and the film adhering to the substrate was tightened.

TOF-SIMS spectra

Figure 6 shows positive-ion TOF-SIMS spectra for the films before and after post-treatment at a low temperature and at a high temperature (deposited under the same working conditions). These spectra look like similar, typically having H^+ (1 amu), C^+ (12 amu), CF^+ (31 amu), CF_3^+ (69 amu), $CF_3CF_2^+$ (119 amu), and other unsaturated structure such as $CF_2{=}C{=}CF^+$ (93 amu), $CF_2{=}CF_2^+$ (100 amu), $CF_2{=}C{=}CF_2^+$ (131 amu), $C_4F_5^+$ (143 amu), $C_4F_6H_3^+$ (165 amu), $C_4F_7^+$ (181 amu), $C_9F_7^+$ (241 amu), and $C_{11}F_7^+$ (265 amu). Although the monomer is a fluorocarbon compound and does not contain hydrogen, the spectra clearly show the existence of hydrogen in the films before and after the heat treatment. Figure 6 shows that the relative intensity of the hydrogen peak H^+ (1 amu) increased with the post-treatment temperature, and it was estimated that some hydrogen was combined into the



(b)

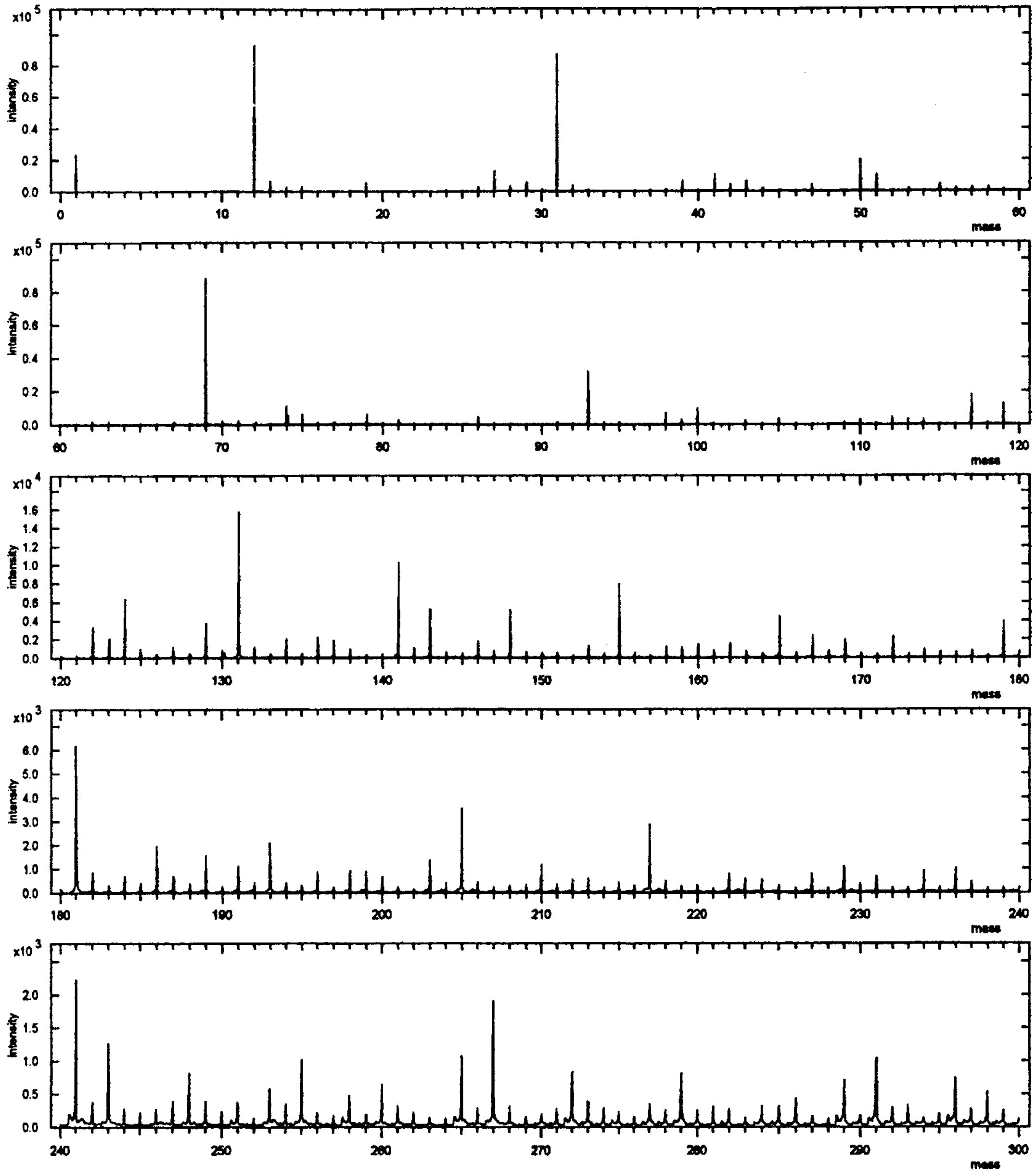
Figure 6 (*Continued from the previous page*)

film during the deposition and post-treatment. Comparing the three spectra, we found that the carbon-ion and unsaturated-structure-ion peak intensity increased with the treatment temperature. The unsaturated structure developed even more with the temperature. This chemical change of the film could have contributed to the surface hydrophobicity changes after the heating post-treatment.

CONCLUSIONS

A nanoparticulate film was obtained by the plasma polymerization of some kind of fluorocarbon compound. Superhydrophobicity was imparted to the cotton fabric surface by the film being coated onto the cotton surface in a very short deposition time. The roughness of the fabric contributed to the superhydrophobicity.

The softness, feel, color, permeability, abrasion resistance, water retention, and friction coefficient of the plasma-film-coated cotton were measured and found to be superior to those of the Scotchgard-sprayed cotton fabric. The softness and abrasion resistance were even better than those of the control samples. Therefore, it has been verified that plasma nanoparticulate film coating is a useful treatment of water- or oil-resistant cotton fabrics.



(c)

Figure 6 (*Continued from the previous page*)

After the heating post-treatment, the hydrophobicity (absorbing time) increased a lot. AFM and TOF-SIMS measurement showed that some physical and chemical changes took place in the film surface, and they were the cause of this increase.

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