Plasma Surface Treatment on Nylon Fabrics by Fluorocarbon Compounds

YU IRIYAMA, TAKESHI YASUDA,* D. L. CHO,† and H. YASUDA,‡ *Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65401*

Synopsis

Nylon fabrics were treated by low temperature fluorocarbon plasmas. All of the fluorocarbon plasmas applied altered the surface of nylon fabrics to be hydrophobic and water-repellent. The durability of hydrophobicity and water repellency was examined by measurements of the water contact angle, the water droplet rolling-off angle, and the breakthrough water pressure after plasma-treated fabrics were washed. It was found that the structure of starting fluorocarbon and the plasma energy input were important factors in the durability. After washing, surface dynamics were investigated on different drying conditions. It was found that chemical composition and water repellency were dependent on drying conditions because of rotation of hydrophobic segments on the surface of fabrics.

INTRODUCTION

Glow discharge (low temperature plasma) treatment is one of the methods used to modify surfaces in a dry process. Advantages of this technique, compared to a conventional wet process, are: (1) because of the very thin treatment layer, only the surface is modified without changing any bulk properties; and (2) the process is simpler—fewer steps and less time are required. Plasma treatment is distinguished from plasma polymerization by the nature of the gases used. For example, most organic compounds, even methane, can polymerize in a plasma state to form thin layer, a process referred to as plasma polymerization. In this case, the top of the substrate is covered by a plasma polymer. On the other hand, inert gases, such as He, Ne, and Ar, never form polymers in a plasma state. However, these plasmas can cause some chemical and physical reactions at the surface of substrates because of highly energetic species and UV irradiation. There are also some compounds which do not form polymers by themselves but react with and are incorporated into substrate polymers, e.g., H_2, N_2, O_2, NH_3, and CF_4. The latter two cases are referred to as plasma treatment, in which the substrate surface itself is modified by use of non-polymer-forming gases.

In past years, the plasma treatment technique has been applied to improve some properties of fibers and fabric surfaces. One of the chief applications on

*Present address: Department of Textile Science, Mukogawa Women's University, Ikebiraki, Nishinomiya 663, Japan.

†Present address: Institute for Surface Science, Box 5607, S-114 86 Stockholm, Sweden.

‡Present address: Department of Chemical Engineering, University of Missouri-Columbia, Columbia, MO 65211.

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fabric was to improve dyeability. The simplest way to improve dyeability was to remove paste or dust from the fiber's surface in order to make it clean and more hydrophilic. Yasuda et al. found weight loss of many kinds of fabrics by simply using air plasma.[1-3] Wrobel et al.,[4] Rakowski et al.,[5] and Wakida et al.[6] reported improved wettability of PET treated by non-polymer-forming plasma. Ward et al. also obtained improved hydrophilicity on cotton fabric.[7,8] These etchings and hydrophilizations were reported to improve dyeability. There are some other applications on fabrics which have been achieved by plasma treatment; e.g., prevention of shrinking of wool[9,10] and color deepening of dyed polyester or nylon fabric.[11]

A plasma treatment of short duration can make a fabric surface hydrophilic or hydrophobic, depending on the gas used. In hydrophobization of fabrics, usually fluorocarbon compounds are used. After a fluorocarbon plasma treatment, the surface becomes hydrophobic and water-repellent, like the surface of Teflon film. However, there is a significant difference between the fabric and film, although both surfaces have identical hydrophobicity. In a hydrophobic fabric, liquid water cannot penetrate through the fabric unless pressure is applied. However, water vapor can easily go through the fabric because there are many macroscopic holes (interstices). In a hydrophobic film, neither liquid water nor water vapor can go through the film in a crude practical sense. This difference is significant when the product is applied to a certain area. Take a raincoat as a simple example. If the purpose is only to protect the inside of the coat from rain (water), a plastic film, such as PE, nylon, or Teflon, can perform the task adequately. However, the inside of the coat will be extremely uncomfortable because of the high humidity created. If a hydrophobic fabric is used, water vapor is expelled as the surface is repelling water; thus there is less humidity (it is more comfortable) inside the coat. Gore-Tex (expanded porous tetrafluoroethylene) may be the most ideal product having both characteristics, i.e., water repellency and water vapor permeability. However, Gore-Tex film itself cannot be applied as a final product without a supporting fabric. The final product using Gore-Tex film is called Gore-Tex fabric, in which Gore-Tex film is laminated with two layers of fabric (one layer for each side).

Compared with Gore-Tex fabric, plasma-treated fabrics appear to have many advantages. Some advantages include: The initial materials (fabrics) are cheaper; the process is simpler and vapor permeation of the fabrics may be much higher. One disadvantage is the extent of durability. Because of the fact that a very thin plasma-treated layer is found on a soft material of nylon, durability may not be too good. The ultimate goal of the research was to make a durable and water repellent plasma treated fabric with high water vapor permeability. In this paper, as the first step, hydrophobicity of a nylon fabric surface will be discussed on the molecular level after fluorocarbon plasma treatment and a washing test.

EXPERIMENTAL

Materials

White nylon 6 fabric woven of 210 denier fabric was used as a substrate. The maximum size of samples was 10 × 10 cm. Gases used in this experiment

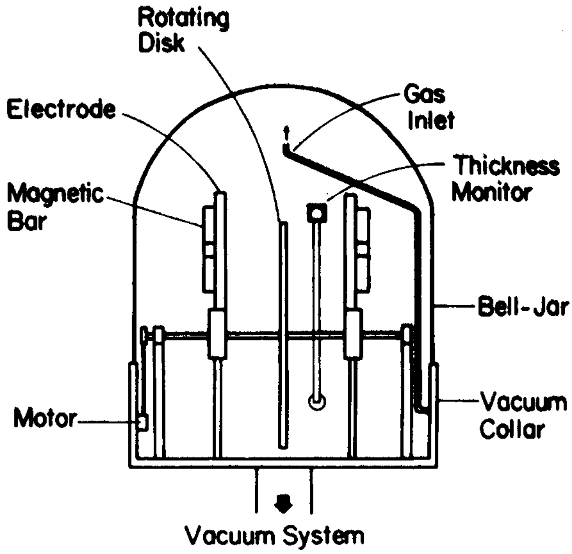

Fig. 1. Schematic illustration of plasma polymerization/treatment apparatus.

were: (1) saturated fluorocarbons, C_nF_{2n+2} (n = 1–4 and 6); (2) unsaturated fluorocarbons, C_2F_4 and C_3F_6; and (3) $CF_4 + H_2$ mixture. CF_4 and C_2F_6 were purchased from Matheson Gas Products, Inc., and the other fluorocarbons from PCR Specialty Chemicals, Inc.

Plasma Treatment and Polymerization

A bell-jar type reactor (Shimadzu Plasma Polymerization Apparatus, LCVD-1200-400A) was used for plasma treatment and polymerization (Fig. 1). Glow discharge was created at the frequency of 10 kHz with magnetic enhancement. Nylon fabric samples were mounted on an aluminum rotating disk [14 in. (35.6 cm) diameter], which was placed between aluminum electrodes [7 in. (17.8 cm) × 7 in.]. The disk had four holes which enabled both sides of four samples (10 × 10 cm max) to be exposed to plasma. For uniform treatment, the disk was rotated at a speed of about 50 rpm during the process.

The flow rate of gaseous monomers (all but C_6F_{14}) was controlled with a Tylan mass flow controller. Flow rate of the liquid monomer (C_6F_{14}) was controlled with a needle valve. During plasma polymerization, pressure of the system was measured with a MKS Baratron pressure meter. Deposition rate was estimated with a XTM Inficon thickness monitor.

Durability Test

After plasma polymerization or treatment, fabric samples were washed in a washing machine (Maytag Co., Model N2LS). Before washing, samples were sewed on a sheet (167 × 243 cm). Three mL liquid detergent Woolite® (Boyle-Midway Inc.) was added to 40 L water. The sheet was washed at room temperature. After being washed, the samples were rinsed in a large amount of distilled water and dried. Washing time was 30 min and drying was at room temperature for 12 h, unless otherwise specified. When samples were dried at higher temperature, an air circulating oven was used.

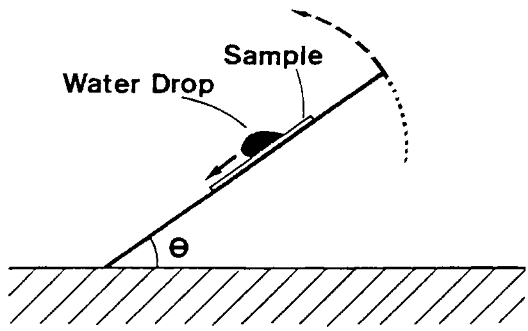

Fig. 2. Principle of the measurement of water droplet rolling-off angle (WDRA).

Contact Angle Measurement

For contact angle measurement, a 0.06 mL distilled water drop was placed on fabric samples. Then pictures of the water drop were taken through a microscope at low magnification within 5 s. Contact angles were measured with a protractor after the pictures were enlarged. It should be noticed that the untreated original nylon fabric is so hydrophilic that contact angle cannot be measured because as soon as a water drop is placed on the fabrics, the fabric absorbs it.

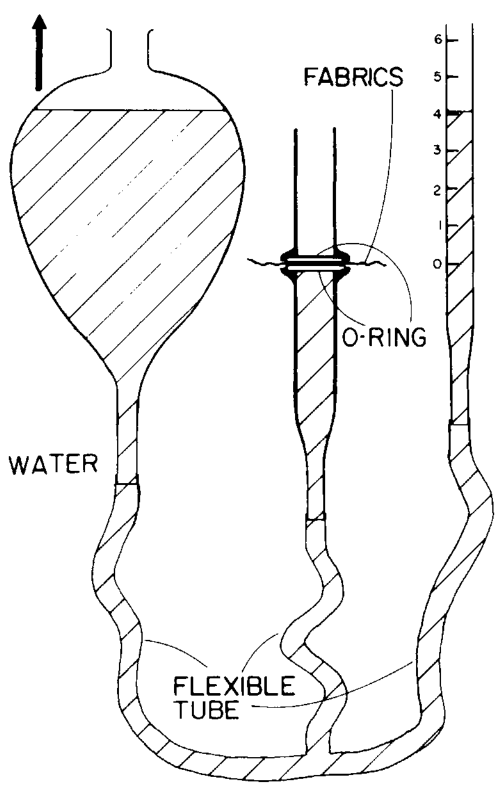

Fig. 3. Schematic illustration of breakthrough water pressure measurement apparatus.

Measurement of Water Droplet Rolling-Off Angle (WDRA)

The principle of the measurement of WDRA is shown in Figure 2. Samples were fixed on a smooth-flat-surfaced supporting material such as a slide glass. First, at the horizontal level, 0.3 mL distilled water was placed on a sample. WDRAs were measured when the water drop started rolling down as the slide glass was gradually inclined. The measurement was performed within 30 s of the water drop being placed. Lower WDRA indicates higher water repellency.

Breakthrough Water Pressure Measurement

Breakthrough water pressure was measured with an apparatus illustrated in Figure 3. A sample was clamped tightly between two O-rings. The water container was raised gradually. At a certain height of water level, water starts penetrating through a sample. Water pressure is calculated from the water level, which can be read on a small glass tube with a scale beside the water container.

Surface Composition

The chemical nature of the surface of plasma-treated fabric was examined by electron spectroscopy for chemical analysis (ESCA) (Physical Electronics Industries, Inc.).

RESULTS AND DISCUSSION

Hydrophobicity of Plasma-Treated Fabric Surfaces—Contact Angle Measurement

Water contact angle measurements are most useful in evaluating the hydrophobicity (or hydrophilicity) of material surfaces. The water contact angle can be measured on the surface of a fabric if the water drop is not absorbed. As an example, Figure 4 shows the contact angles of water on the surface of a nylon fabric after treatment with several saturated fluorocarbon plasmas (solid line) and after 30 min of washing as a durability test (broken line). Before the plasma treatment, the contact angle of the original fabric could not be measured because the fabric absorbed water immediately. After the treat-

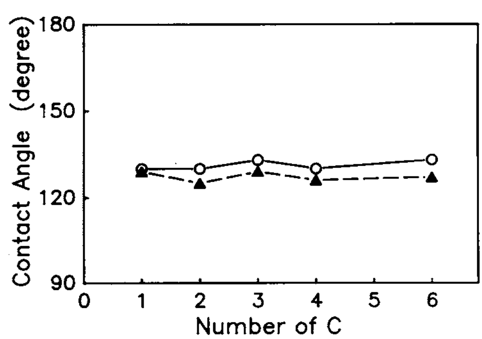

Fig. 4. Contact angles on nylon fabric treated by saturated fluorocarbon plasmas (—○—) and after 30 min washing test (—▲—) vs. the number of fluorocarbons used as monomers.

ment by the fluorocarbon plasmas, the surface became very hydrophobic and water drops remained on the surface. As shown in Figure 4, the values of contact angle are very high regardless of the molecular size of the fluorocarbon used, as high as over 130°, which represents a high degree of hydrophobicity. After the washing test, these contact angles became a little smaller, but the changes were negligible. There was also no dependence on the number of carbons in the C_nF_{2n+2}. When judged from the results of the contact angle measurements, the hydrophobicity does not appear to be changed by the washing test.

However, there seems to be a significant difference between water repellency or hydrophobicity of the surface and contact angle of water. Contact angles of water on the surface which are treated with fluorocarbon plasma always show very high values regardless of nature of fluorocarbons used, and after treatment such as washing, as will be shown in the following sections. One important aspect which might be responsible for this situation is that the contact angle merely reflects the balance of force at the water–air–surface, and can represent the hydrophobicity or hydrophilicity of a surface only if the surface is totally unperturbable by the presence of water droplet. Surfaces of polymers are generally far from this ideal case, and the contact angle of water on fluorocarbon plasma-treated polymer surfaces becomes very insensitive measure of the hydrophobicity of the surface.

The contact angles observed with fabrics are further complicated by the fact that surfaces of fabrics are not smooth. The observed contact angle is highly dependent on the morphology of the surface and also on air trapped between interstices. For example, if the hydrophobicity of fabric is equal to a smooth surface, which has over 90° of contact angle, an observed contact angle on the fabric will be much higher. If the surface roughness is identical in two fabrics with different hydrophobicity, contact angles will be similar regardless of the real hydrophobicity of the fabrics. The contact angle cannot detect a small difference in hydrophobicity. If the surface is hydrophilic, on the other hand, i.e., assuming the theoretical contact angle is less than 90°, the fabric is susceptible to absorption of water because of the capillary effect.[12] The contact angle cannot detect the difference in hydrophobicity, either. Therefore, it is dangerous to draw conclusions from the results of contact angle measurement alone. More sensitive evaluation methods are required to judge the properties of fabric surfaces.

Water Repellency of Plasma-Treated Fabrics Surfaces—Measurement of the Water Droplet Rolling Off Angle

The measurement of the water droplet rolling-off angle (WDRA) is a unique method with which to evaluate the water repellency of a surface.[13,14] The principle of the measurement of WDRA is described in the experimental section and diagrammed in Figure 2. A lower WDRA means that the surface is more water-repellent. This method was taken into consideration because it was suspected that contact angle measurement was not adequate to evaluate fabric surfaces. Also, this measurement is more practical than contact angle measurement because the fabrics will be used not only at the horizontal level in applications.

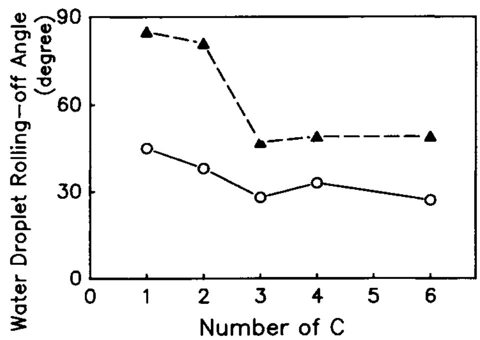

Fig. 5. Water droplet rolling-off angle (WDRA) on nylon fabric treated by saturated fluorocarbon plasmas (—○—) and after 30 min washing test (—▲—) vs. the number of carbons in fluorocarbons used as monomers.

Figure 5, for example, shows the WDRA values on a nylon fabric treated by saturated fluorocarbon plasmas before (solid line) and after the washing test (broken line). Before the plasma treatment, the WDRA could not be measured because the fabrics absorbed the water. After a plasma treatment with a saturated fluorocarbon, the surface became very water-repellent and the WDRA was low, similar to the results of the contact angle measurements. After a 30-min washing, however, values of the WDRA increased significantly, especially when the fluorocarbon was low in carbon, i.e., CF_4 and C_2F_6. From these results, it is clear that the measurement of the WDRA is sensitive enough to detect differences in water repellencies before and after washing, whereas the contact angle measurement technique is not.

Values of the WDRA do not seem to be an important factor, practically, as long as water drops do not penetrate fabrics. As far as vapor permeability is concerned, however, if water drops do not roll down easily, the permeability will be lowered because of the reduced effective surface area. Further, if the water drops remain for a long time, the surface composition or morphology might be altered, which would result eventually in water penetration.

As an evaluation method for the fabric surfaces, in this paper, the measurement of the WDRA is mainly used, together with measurements of the breakthrough water pressure, which will be described later.

Effect of the Monomer Structure on Durability

Plasma Surface Treatment vs. Plasma Polymerization

In the plasma state, the reaction mechanisms of saturated and unsaturated fluorocarbons are different. As mentioned in the Introduction section, the difference between plasma polymerization and plasma treatment comes from the difference in the nature of the gases used. In general, fluorocarbons can be divided into two categories: It is usually said that saturated fluorocarbons are polymer-forming and unsaturated fluorocarbons are non-polymer-forming. Although this classification cannot be applied strictly,[15-17] we assume, for convenience, that a saturated fluorocarbon plasma is used for surface treatment and an unsaturated fluorocarbon plasma is used for polymerization.

TABLE I
Contact Angle and Water Droplet Rolling-Off Angle (WDRA) on the Surface of Nylon Fabrics after Plasma Polymerization by Unsaturated Fluorocarbon, and Then after 30 min Washing

	Contact angle (deg)		WDRA (deg)	
Monomer	Before washing	After washing	Before washing	After washing
C_2F_4	130	125	43	*
C_3F_6	131	125	32	*
$CF_4 + H_2$	135	132	43	*

[a] Higher than 90 deg.

In the plasma surface treatment of nylon fabrics with saturated fluorocarbons, as shown in Figures 4 and 5, the surface becomes very hydrophobic, probably because of the implantation of some hydrophobic segments and possible some polymerization associated with the substrate. The implantation forms chemical bonds between the substrate and the hydrophobic segments, which are expected to have good durability. Although the water repellency is decreased after the washing test (broken line in Fig. 5), the WDRA is still in a measurable range.

The same experiments were carried out with nylon fabrics coated by plasma polymerized unsaturated fluorocarbons. The results are summarized in Table I. The table shows the contact angle and the WDRA on fabrics that were coated by unsaturated fluorocarbon plasmas before and after the 30-min washing test. A CF_4–H_2 mixture is included in this table because a saturated fluorocarbon could be polymerized when H_2 was present.[18,19] After the plasma polymerization, similar to the saturated fluorocarbon plasma, the contact angle was high and the WDRA was low. After the washing test, the contact angles of the surfaces were still high, possibly due to the rough surface. However, the surface was not water repellent enough to measure the WDRA. In most of the cases, water drop remained on the fabric surface, as shown in Figure 6. A drop did not roll down even for inclinations of 90° or more.

When an unsaturated fluorocarbon plasma is used, polymerization takes place easily on the fabric, and the surface becomes hydrophobic because of the hydrophobic polymer film. However, there is probably not much interaction between the plasma polymer and the surface. This may be the reason that the fabrics treated in an unsaturated fluorocarbon plasma do not show good durability when compared with fabrics treated in a saturated fluorocarbon plasma.

Effect of Monomer Size on Plasma Surface Treatment

Even with treatment in a saturated fluorocarbon plasma, not all surfaces can acquire good durabilities. From the results in Figure 5, the durability was better when the number of carbons in C_nF_{2n+2} was three or more. Because of the longer chains, much more complicated reactions took place; e.g., many different sizes of segmentation, dimerization, oligomerization, crosslinking formations, etc. in addition to ablation. Longer chains and/or tighter network formation may constitute other important factors in determining the durabil-

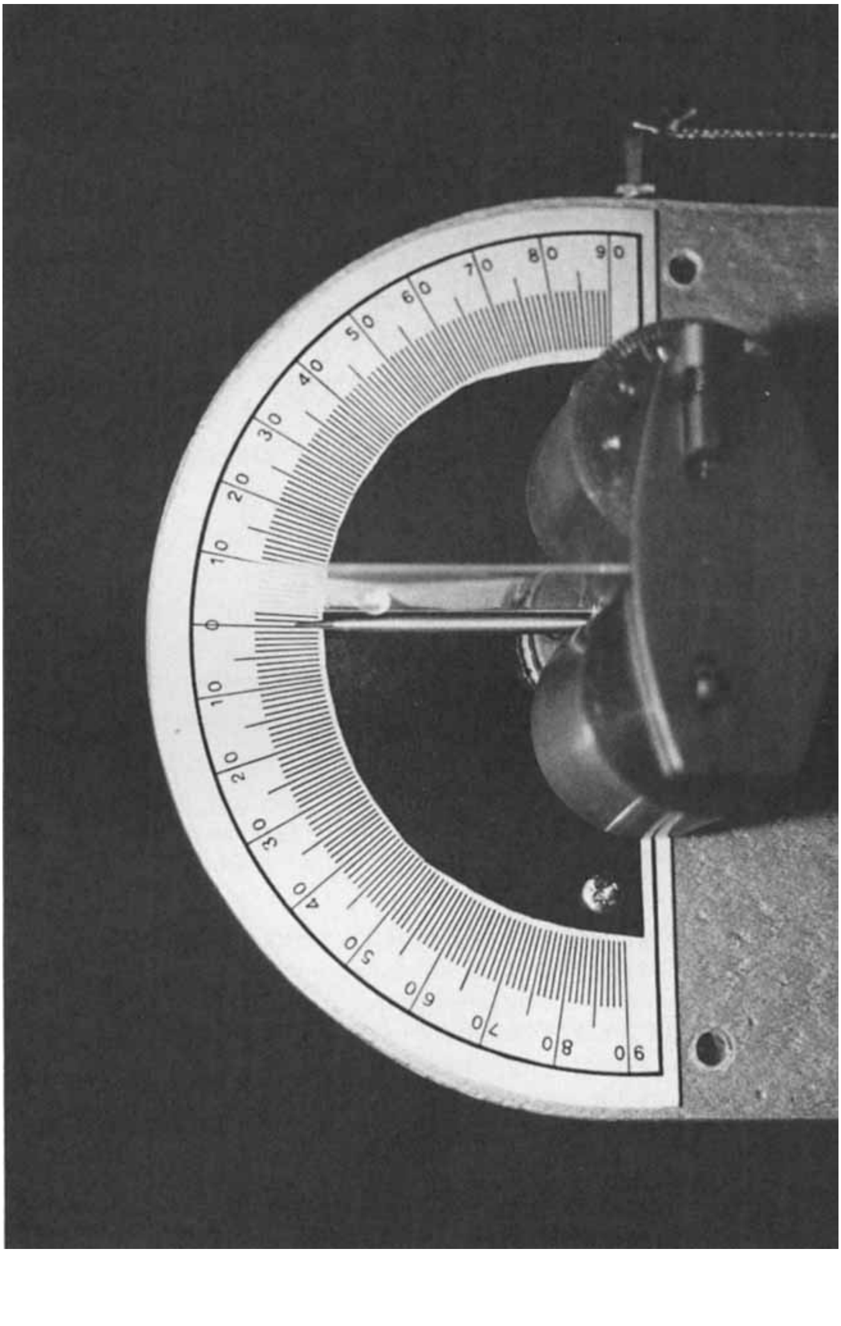

Fig. 6. A picture of measurement of water droplet rolling-off angle (WDRA). The samples were washed after a fluorocarbon plasma treatment.

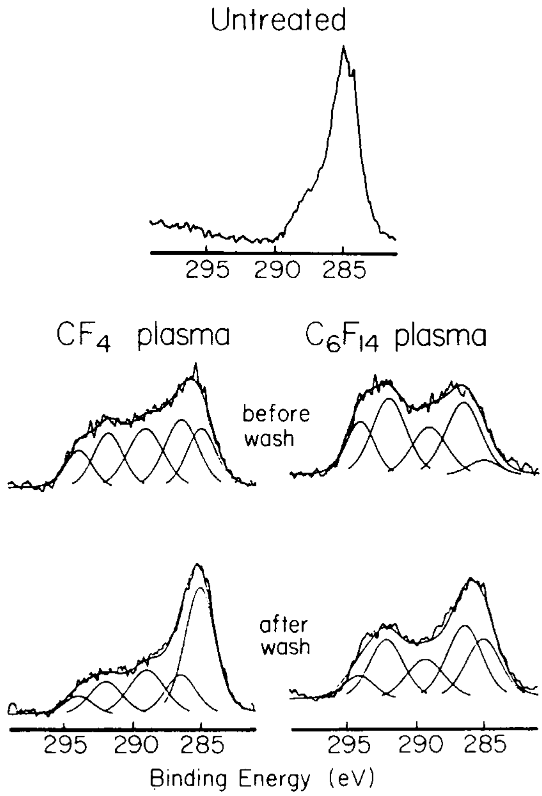

Fig. 7. C_{1s} ESCA spectra of the surface of CF_4 and C_6F_{14} plasma-treated nylon fabric before and after 30 min washing test. CF_4 plasma: 1.0 cm^3 (STP)/min, 50 W, 100 s, $(W/FM)t = 76$ GJ s/kg; C_6F_{14} plasma: 0.5 cm^3 (STP)/min, 100 W, 60 s, $(W/FM)t = 48$ GJ s/kg.

ity as well as chemical bond formation at the surface. In order to effect specific reactions on the surface which will enhance the durability, the plasma operating parameters must be controlled properly.

Figure 7 shows the C_{1s} ESCA spectra of nylon fabrics treated with CF_4 and C_6F_{14} plasmas before and after the washing test. Although the plasma conditions are quite different, the total energy supplied per mass, unit of $(W/FM)t$, is at the same level, and those samples exhibited the best durability in each corresponding plasma. CF_4 is well known as an efficient fluorination gas for plasmas. However, in order for the fabric to acquire a better durability after a CF_4 plasma treatment, the implantation of short segments alone is not adequate. A higher energy input, which sacrifices simple fluorination but increases active species and active sites on the surface, which could extend the chain or enhance crosslinking, is required. After the plasma treatment, in Figure 7, a C_6F_{14}-treated nylon surface has more fluorine (F/C = 1.49) than one treated with CF_4 (F/C = 1.12). There are fewer CF_3 groups after the CF_4 plasma treatment. Nevertheless, the difference of fluorine content on the surface at this stage (before washing) does not make much difference as far as the measurement of the WDRA or the contact angle is concerned (Fig. 5). After the washing test, the amount of fluorine decreases in both cases but the C_6F_{14}-treated fabric still had a higher F/C ratio relative to those treated with

CF_4 (1.20–0.90). There are differences in the measurement of the WDRA after washing (Fig. 5), i.e., the WDRA of the CF_4-treated nylon surface increased roughly 45° while that of the C_6F_{14}-treated one increased only 20°.

Dependence of Durability on Power Input

Experiments on the plasma power dependence of durability were carried out with the monomers C_4F_{10} and C_6F_{14}. As a characterization of plasma power, a composite parameter, $(W/FM)t$, is used. This parameter represents the total plasma energy per mass, whose SI unit is J s/kg, where W is the discharge power of plasma, F is the flow rate of gas, M is the molecular weight of gas, and t is the plasma duration. In a plasma polymerization, usually the parameter W/FM, which represents energy input per unit mass of monomer, is used because most properties of plasma polymers are highly dependent on values of W/FM.[20–23] In saturated fluorocarbon plasma, many kinds of reactions take place, which are not necessarily polymerizations. In such cases, not all energy is consumed by polymerization or material deposition. The surface is modified by the results of the combination of many reactions. Therefore, it is difficult to characterize the surface by the parameter

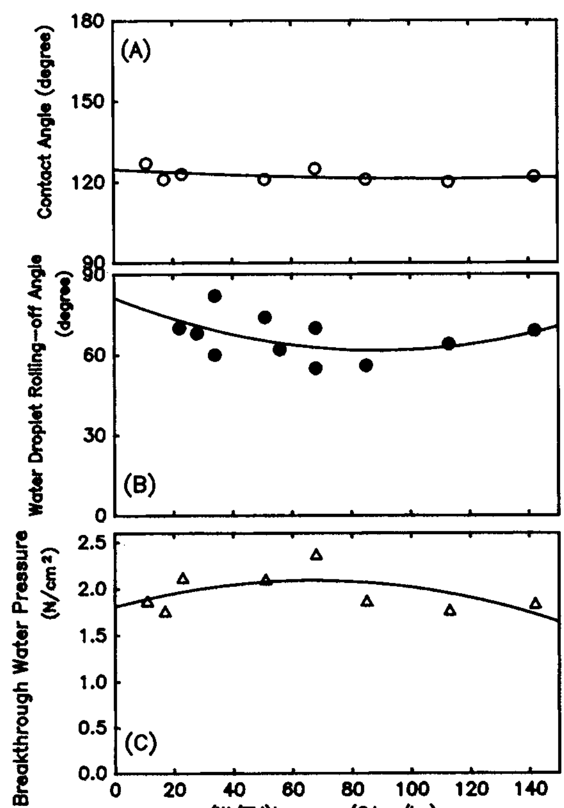

Fig. 8. Contact angle (A), water droplet rolling-off angle (WDRA) (B), and breakthrough water pressure (C) on C_4F_{10} plasma-treated nylon fabric after 30 min washing test vs. composite parameter of total plasma energy $(W/FM)t$.

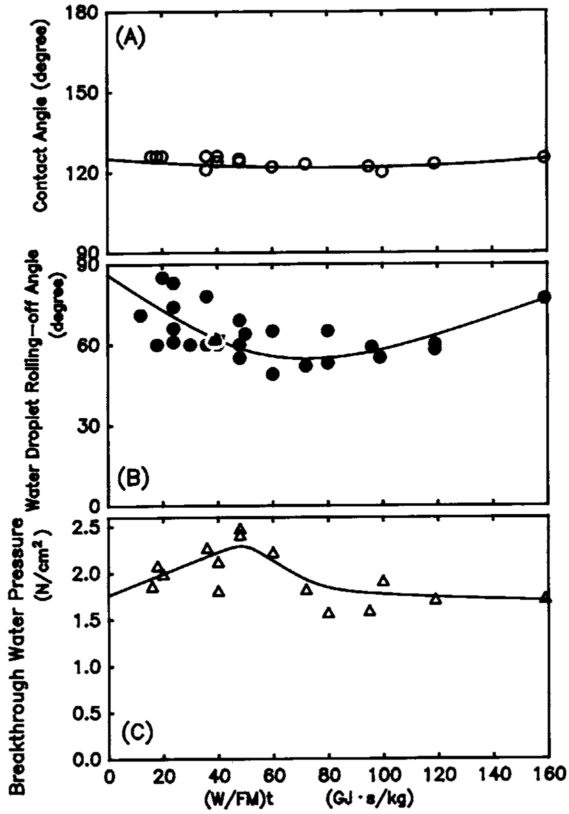

Fig. 9. Contact angle (A), water droplet rolling-off angle (WDRA) (B), and breakthrough water pressure (C) on C_6F_{14} plasma-treated nylon fabric after 30 min washing test vs. composite parameter of total plasma energy $(W/FM)t$.

W/FM. The important factor for durability is how much of these reactions take place on the surface. $(W/FM)t$ may be a better parameter because it represents the total energy input for all reactions happening in the plasma.[24]

In Figures 8 and 9, the contact angle (A), the WDRA (B), and the breakthrough water pressure (C) on C_4F_{10} and C_6F_{14} plasma-treated nylon fabric after the 30 min washing test are plotted against the parameter $(W/FM)t$, respectively. The measurement of the breakthrough water pressure is introduced in order to characterize the property of the fabric from another point of view and possibly support the results of the WDRA. The setup and procedure are described in the Experimental section and diagrammed in Figure 3. This measurement is very practical, and represents how well a fabric prevents penetration of water. The values of water pressure depend on not only the hydrophobicity and water repellency but also the size of the holes (interstices). A higher breakthrough water pressure indicates that it is more difficult for water to penetrate the fabric. As with contact angle and WDRA measurements, the water pressure could not be measured on the original fabric, i.e., the breakthrough water pressure is zero.

Before the washing test, the contact angles and water pressures were high, and the WDRAs were low regardless of the $(W/FM)t$ value. For the contact angle measurements [Figs. 8(A) and 9(A)], the values are about 125° before and after washing, and there is no dependence on $(W/FM)t$. For the WDRA measurements, the angles are 30–40° before washing. However, they become higher after the washing and are slightly dependent on the plasma power [Figs. 8(B) and 9(B)]. There are minimum points of the WDRA at about 70–80 GJ s/kg for C_4F_{10} [Fig. 8(B)] and 60–70 GJ s/kg for C_6F_{14} [Fig. 9(B)], where the best durability is obtained. This result indicates there is a suitable range of plasma energy input for obtaining greater durability. When the energy input is low, there are not enough reactions to result in good modification of the surface. When the energy input is very high, probably, etching/ablation or too much unnecessary reaction, along with heating, take place. For the measurement of breakthrough water pressure, the values are about 2.5 N/cm^2 before washing. After the washing, the water pressure decreased [Figs. 8(C) and 9(C)] and a slight dependence on $(W/FM)t$ can be seen. The maximum value of the water pressure, which represents the best durability, for C_4F_{10} is at $(W/FM)t$ of about 70 GJ s/kg [Fig. 8(C)], and at about 50 GJ s/kg for C_6F_{14} [Fig. 9(C)]. These values of $(W/FM)t$ are very close to those observed at the minimum WDRAs in Figures 8(B) and 9(B). It can be also said that measurements of the WDRA and the breakthrough water pressure are compatible.

Surface Dynamics Aspect

It is clear that the water repellency decreases after the washing test. However, mechanical abrasion on the surface may not be the only reason for the low water repellency after washing. The drying conditions could be another factor affecting the hydrophobicity of the surface. Figure 10 shows the breakthrough water pressure of a C_4F_{10} plasma-treated nylon fabric after the washing test vs. the washing time. The open circles denote the values of the water pressure of the sample dried at room temperature for 12 h. The water pressure decreases as the washing time increases. This trend can be explained simply as resulting from abrasion. However, when the washed samples were dried at 100°C for 1 h, the water pressures (filled triangle) were not as low as those dried at room temperature for 12 h. This result can be explained by rotational and diffusional migration of the hydrophobic molecular moieties.[25-27] When a sample is being washed in water, the hydrophobic groups tend to turn inside because the bulk property of nylon is more hydrophobic compared to the surface surrounded by water. After washing, when the sample is dried at room temperature, almost no rotation of the segments take place because the fabric dries gradually and the conditions of both the inside and the surface are similar. There is little driving force for the hydrophobic segments to turn outside. Consequently, the hydrophobic groups stay inside, which makes the surface less hydrophobic. However, when the fabric is dried at higher temperatures, the surface dries quickly compared with the interior of the nylon fabric, which is still wet. There is then a driving force between the surface and the interior which rotates the hydrophobic segments. Of course, the segments go to the outside, which results in a more hydrophobic surface. Indeed, the water pressure after drying at 100°C is higher than one dried at room temperature.

In order to confirm that rotation of the segments took place, the surfaces were analyzed by ESCA. The C_{1s} ESCA spectra are shown in Figure 11. After

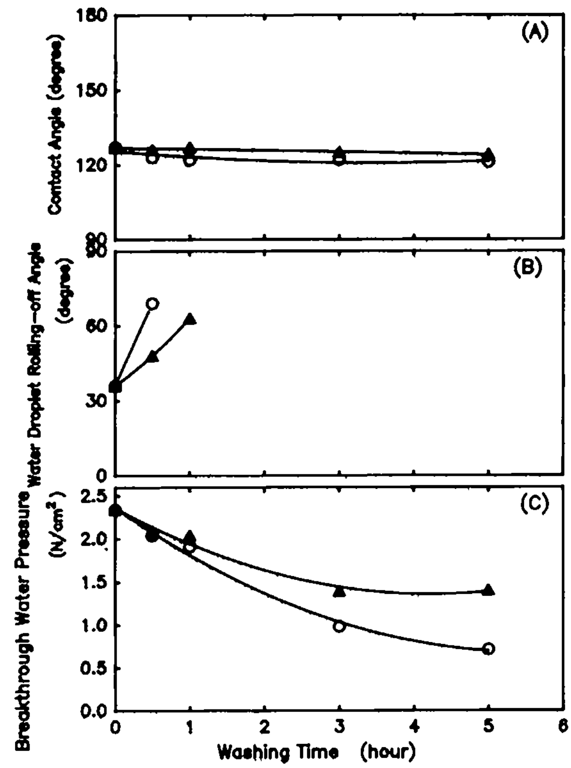

Fig. 10. Contact angle (A), water droplet rolling-off angle (B), and breakthrough water pressure (C) on C_4F_{10} plasma treated nylon fabric at different drying conditions after washing test vs. washing time. Drying condition: (—○—) room temperature 12 h; (—▲—) 100°C 1 h. C_4F_{10} plasma: 1.0 cm^3 (STP)/min, 150 W, 100 s, $(W/FM)t$ = 85 GJ s/kg.

the C_4F_{10} plasma treatment, a fluorine-related wide peak was found at the range around 290–295 eV. The atomic ratio of the F/C peak was 1.51. After the washing test, the wide peak still remained but it decreased a little. Further, there was a difference between the two samples dried under different conditions. The one dried at 100°C for 1 h had a bigger peak at a higher binding energy (290–295 eV) than the one dried at room temperature for 12 h. The F/C ratios were 1.13 and 0.93, respectively. Obviously, as expected, the surface composition varies depending upon the drying conditions. These results also correspond with the water pressure measurement, i.e., higher fluorine content on the surface results in a higher water pressure. Also, the results support the idea that rotation of the segments occurred.

The changes of surface characteristics due to rotational and diffusional migration of the moieties introduced by plasma polymerization do not occur if a plasma polymer is deposited on the surface of rigid materials, such as glass.[28] However, if the same plasma polymer is deposited on a polymeric substrate, some extent of surface change attributable to the migration of surface moieties are generally observed, indicating that the influence of substrate polymer extends into a considerable thickness of plasma polymer layer. In our study of surface treatment by saturated fluorocarbon plasma (not plasma polymerization), there can be found still many relatively short

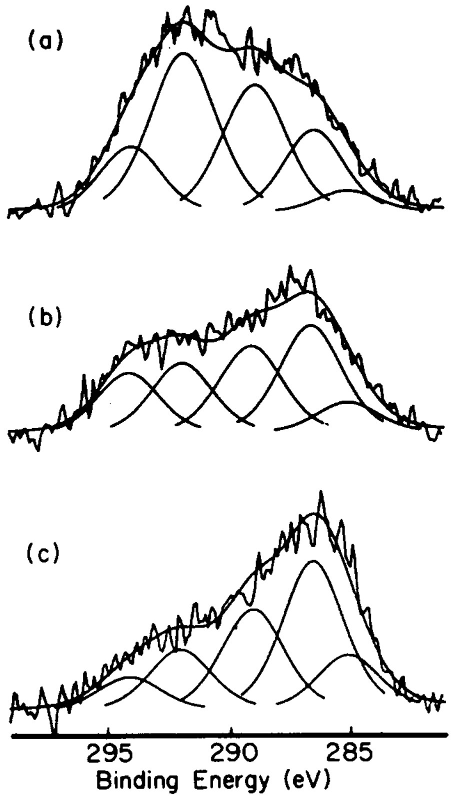

Fig. 11. C_{1s} ESCA spectra of C_4F_{10} plasma-treated nylon fabric: (a) before washing; (b) dried at 100°C for 1 h after washing; (c) dried at room temperature for 12 h after washing. C_4F_{10} plasma: 1.0 cm^3 (STP)/min, 150 W, 100 s, $(W/FM)t$ = 85 GJ s/kg.

segments, which are much easier to rotate on the surface of polymer such as fabrics. This rotation of segments may be one of the reasons that plasma-treated fabrics by small molecules, such as CF_4 and C_2F_6, did not show a good durability. In order to avoid the rotation and keep hydrophobic segments on the surface, it is necessary to form a tighter network or longer segments.

From the results above, it appears that in order to have a good durability, in the first step, good adhesion between the surface and hydrophobic segments (or deposited materials) is required. In the second step, the segments should be either crosslinked or have grown long enough so that the hydrophobic segments will not disappear from the surface. The combined plasma energy inputs and monomer selections may be able to meet these two criteria. This is left for future investigation.

CONCLUSIONS

The surface of nylon fabrics became hydrophobic and water-repellent after fluorocarbon plasma treatment and polymerization. The durability of hydrophobicity was examined after a 30 min washing test. Hydrophobicity and water repellency of the surfaces were determined by contact angle, water droplet rolling-off angle (WDRA), and breakthrough water pressure measurements. Among these tests, contact angle measurement was found to be inadequate for estimating water repellency of fabrics. Surfaces treated with saturated fluorocarbons had better durability than those treated by unsaturated fluorocarbons, although unsaturated fluorocarbons formed polymer easily. In saturated fluorocarbon plasma, monomers with longer chains had better durability. There was a range of plasma power input, in which strong interaction for good durability was found. The water repellency after the washing test was influenced by the drying condition because of rotation of molecular segments. Drying at higher temperatures seems to bring the hydrophobic segments back to the surface. However, at lower temperatures, the segments stayed inside, which made the surface less hydrophobic. In order to keep the surface hydrophobic, fixation of longer hydrophobic segments, which prevents the rotation of segments, seems to be advantageous.

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