

Surface Modification of Poly(tetrafluoroethylene) Film by Plasma Graft Polymerization of Sodium Vinylsulfonate

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ABSTRACT: Poly(tetrafluoroethylene) (PTFE) surface was modified by the graft polymerization of sodium vinylsulfonate, and the chemical composition of the graft-polymerized PTFE surface was analyzed by X-ray photoelectron spectroscopy. Peroxides were formed on the PTFE surface by a combination procedure of argon plasma irradiation and air exposure, and the graft polymerization of sodium vinylsulfonate was initiated by the peroxide groups at 65–80°C. The peroxide concentration is $3 \times 10^{+13}$ to $5 \times 10^{+13}$ numbers/cm². The average degree of polymerization of the graft polymers was 3.4×10^3 . The graft polymer is distributed over the PTFE surface, but part of the PTFE surface remains uncovered. The coverage with the graft polymer is 43%. The PTFE surface graft polymerized with sodium vinylsulfonate was somewhat hydrophilic, but the hydrophilicity was lower than that of the PTFE surface modified by plasma treatment. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 77–84, 1997

Key words: surface modification; plasma graft copolymerization; Poly(tetrafluoroethylene); sodium vinylsulfonate; peroxide; hydrophilic; hydrophobic

INTRODUCTION

Fluorine-containing polymers, e.g., poly(tetrafluoroethylene) (PTFE), possess good properties such as hydrophobic surface, good thermal and chemical resistance, and low electrical conductivity, which are based on the low polarizability of C—F bonds. The hydrophobicity of PTFE is a useful property in the field of water repellents and releasing agents, but it is a troublesome property when contacting with hydrophilic media such as water. When water flows in the capillary of PTFE, the surface of the capillary wall is not wetted completely and sometimes air bubbles are formed on the capillary wall. The air bubbles disturb the smooth flow of water and act in resisting the flow.

Many techniques for hydrophilic surface modi-

fication of PTFE have been reported to improve adhesion to other polymers such as epoxy resins, rubbers, and metals. These are chemical etching with sodium naphthalene complex; graft polymerization of hydrophilic monomers such as acrylic acid, acrylamide, and *N*-vinylpyrrolidone; sputtering; plasma treatment^{1–3}; and excimer laser irradiation.^{4,5} Sodium vinylsulfonate is easy to polymerize by radical initiators to yield water-soluble polymers. These polymers also possess sulfonate groups, which show strong acidity and blood anticoagulation.⁶ In this study, we have focused on the surface modification of PTFE by the graft polymerization of sodium vinylsulfonate. To initiate the graft polymerization, peroxy groups were formed on the surface of PTFE by a combination procedure of argon plasma irradiation and air exposure.

When PTFE was irradiated with argon plasma, three types of radicals—midchain radicals, $\sim\text{CF}_2\text{—}\dot{\text{C}}\text{F—CF}_2\sim$, end-chain radicals, $\sim\text{CF}_2\text{—}\dot{\text{C}}\text{F}_2$,

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and dangling-bond sites (structureless radicals)—are easily formed on the PTFE surface.⁷ The radicals were rapidly modified into corresponding peroxy radicals by contacting with air, and the formed peroxy radicals are stable at room temperature for a long time.⁷ The peroxy radicals may be preferable initiators to graft polymerize sodium vinylsulfonate, because the radicals exist mainly on the PTFE surface.

EXPERIMENTAL

Materials

The PTFE film, which was received from Nitto Denko Co. (Nitofuron NO900UL) as 300 mm wide and 100 μm thick, was cut to a dimension of 10 \times 30 mm and used as a specimen for surface modification experiments. Prior to the experiment, the film was washed with acetone in an ultrasonic washer and dried at room temperature under vacuum. Sodium vinylsulfonate, which was purchased from Tokyo Kasei Kogyo Co., as an aqueous solution of 25%, was used as a monomer for graft polymerization without further purification. Argon used for argon plasma irradiation was pure grade (99.995% purity).

Plasma Graft Polymerization

The plasma graft polymerization of sodium vinylsulfonate on the PTFE film surface was carried out in two steps: the formation of peroxides on the PTFE surface by the irradiation of argon plasma and the graft polymerization of sodium vinylsulfonate from the peroxides. The PTFE film surface was irradiated for 10–300 sec with an argon plasma to form carbon radicals on the PTFE surface and was subsequently exposed to air for 5 min to modify them to peroxides, which were able to initiate the graft polymerization. The apparatus used for the argon plasma irradiation was a homemade, glass-tubular reactor (170 mm in diameter, 300 mm long), which was described elsewhere.⁸ The reactor contained a micrometering valve for an argon gas inlet, a pressure gauge, and a vacuum system composed of a combination of a diffusion and a rotary pump. The electric power, at a radio frequency of 13.56 MHz for generating argon plasma, was supplied from an rf generator (Samco International Inc., Kyoto, Japan; model FRG-200) into the reactor through a

capacitively coupled system with electrodes wound on the outside of the reactor. The argon plasma was operated at an rf (13.56-MHz frequency) power of 25–100 W at an argon pressure of 13.3 Pa.

The PTFE film irradiated with argon plasma and exposed to air was immersed in an aqueous solution of sodium vinylsulfonate (25%), in which dissolved air had been removed by repeating the procedure of freezing and fusion before graft polymerization. The graft polymerization reactions were conducted under nitrogen atmosphere at 65–80°C for 1–72 h. After the graft polymerization, the PTFE film was washed with hot water using a Soxhlet apparatus, to remove homopolymer of sodium vinylsulfonate, and dried at 50°C under vacuum.

Peroxide Concentration Generated at PTFE Film Surface

The concentration of peroxides generated on the PTFE film surface by a combination of the argon plasma irradiation and air exposure was determined by means of the iodide method.⁹ Peroxides on the surface of the PTFE film were quantitatively reacted with sodium iodide in a mixture of isopropanol and benzene (6 : 1 volume ratio) containing a trace of ferric chloride (1 ppm) at 60°C for 10 min to yield iodine. From the absorption intensity (at 360 nm) of the iodine in the mixture solution, the concentration of peroxide on the PTFE surface was determined.

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra of the plasma-graft-polymerized PTFE films were obtained on a Shimadzu ESCA K1 using a non-monochromatic MgK_{α} photon source. The anode voltage was 12 kV, the anode current was 20 mA, and the background pressure in the analytical chamber was 1.5×10^{-6} Pa. The size of the X-ray spot was 2 mm in diameter, and the take-off angle of photoelectrons was 90° with respect to the sample surface. The XPS spectra were referenced with respect to the 292.5-eV carbon 1s core level for CF_2 groups in the PTFE film or the 285.0-eV carbon 1s level in poly(sodium vinylsulfonate) observed for hydrocarbon to eliminate the charge effect. The smoothing procedure of the spectra was not done. The C_{1s} , F_{1s} , O_{1s} , and S_{2p} spectra were decomposed by fitting a Gaussian-Lorentzian mixture

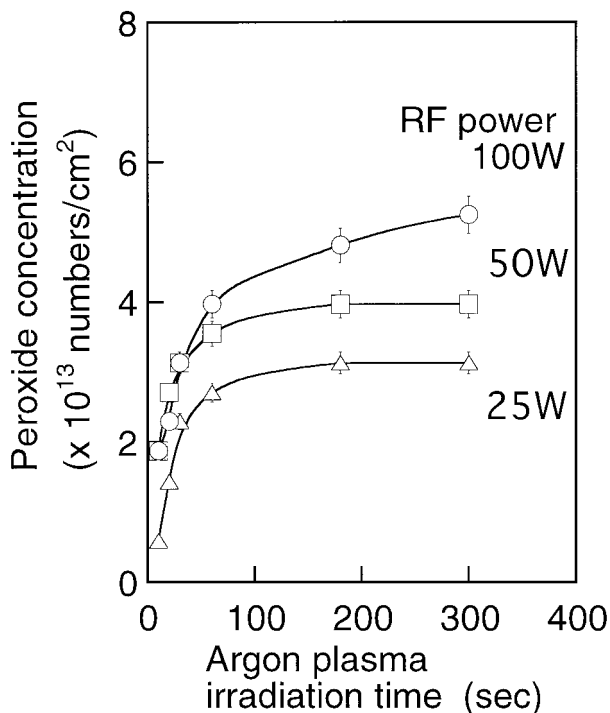


Figure 1 Peroxide concentration on PTFE surface as functions of rf power and argon irradiation time.

function (80 : 20 mixture ratio) to an experimental curve using a nonlinear, least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu.

Contact Angles of Grafted PTFE Film Surface

The contact angle of water on the graft-polymerized PTFE surface was measured in air at 20°C by the sessile method¹⁰ using a contact-angle meter with a goniometer (Erma Co., Tokyo, Japan; model G-1). The contact angle was an average of 10 measurements with a standard deviation of one degree.

RESULTS AND DISCUSSION

Graft Polymerization of Sodium Vinylsulfonate on PTFE Surface

Irradiation of argon plasma forms three types of radicals on the PTFE surface, which are midchain radicals, $\sim\text{CF}_2-\dot{\text{C}}\text{F}-\text{CF}_2\sim$, end-chain radicals, $\sim\text{CF}_2-\dot{\text{C}}\text{F}_2$, and dangling-bond sites (structureless radicals).⁷ The formed radicals, when contacted with air, are rapidly modified into corresponding peroxy radicals, which are stable at room temperature for a long time.⁷

Figure 1 shows typical results of peroxides

formed on the PTFE surface as functions of the argon plasma irradiation time and the rf power. The peroxide concentration increases with increasing the argon plasma irradiation time up to 180 sec as well as the rf power. After an argon irradiation time of 180 sec, the increase, except for that at 100 W, becomes small. The peroxide concentration at an irradiation time of 180 sec is 3.1×10^{13} , 4.0×10^{13} , and 4.8×10^{13} numbers/cm² at rf powers of 25, 50, and 100 W, respectively. The peroxide concentration on the PTFE surface is lower by about one order than that formed on the polyolefine surface (an order of 10^{14} numbers/cm²),¹¹ indicating that the C—F bond in PTFE is more difficult to break down than the C—H bond in polyolefines. Scanning electron microscopy (SEM) observations showed that a longer irradiation time than 180 sec with an argon plasma of 100 W caused heavy degradation of the PTFE surface. Therefore, we chose an argon plasma irradiation at an rf power of 100 W for 180 sec as a preferable condition to form peroxides on the PTFE surface.

Graft polymerization of sodium vinylsulfonate, which was initiated from the peroxide groups, was carried out at temperatures of 65–80°C for 25–75 h. Figure 2 shows typical results of the graft

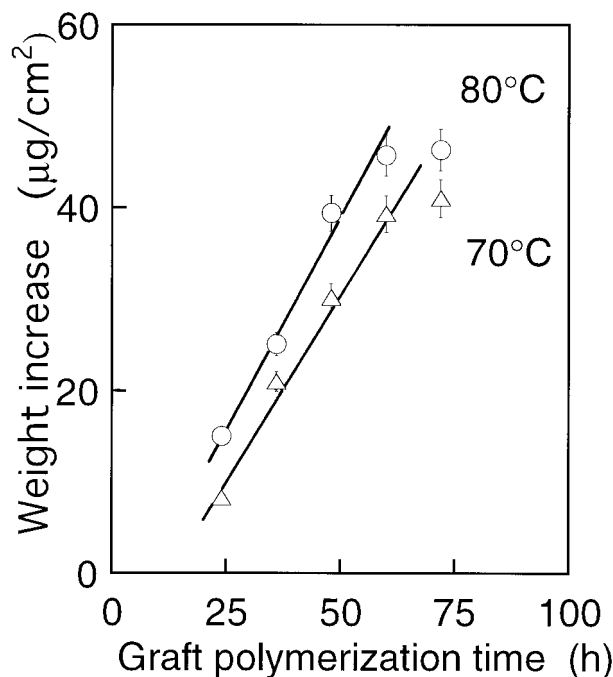


Figure 2 Weight increase by graft polymerization of sodium vinylsulfonate as a function of graft temperature and graft polymerization time.

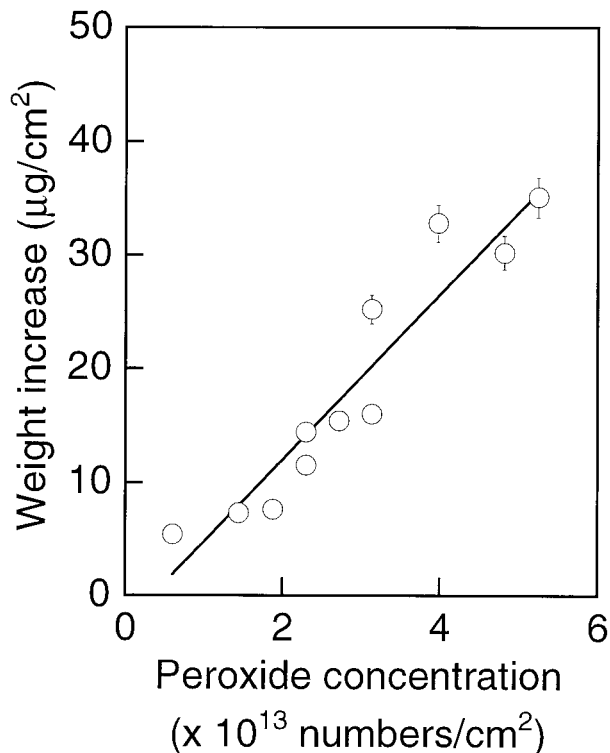


Figure 3 Relationship between weight increase by graft polymerization and peroxide concentration on PTFE surface.

polymerization as functions of the graft polymerization time and the graft polymerization temperature. The graft polymerization was evaluated from weight increase after the graft polymerization. Weight increase by the graft polymerization, as shown in Figure 2, is linear with increasing polymerization time up to 50 h, and the slope of the linear relationship gives the rate of the graft polymerization. From the Arrhenius equation, $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$, where k_1 and k_2 are the rates of graft polymerization at the graft polymerization temperatures of T_1 and T_2 , respectively, and E_a is an apparent activation energy for the graft polymerization,¹² an apparent activation energy for the graft polymerization of sodium vinylsulfonate, using graft polymerization rates at 70 and 80°C (Fig. 2), was calculated to be 13.6 kJ/mol, which is lower than that for sodium acrylate (67.5–72.1 kJ/mol).¹³

Figure 3 shows a relationship between the peroxide concentration and weight increase. Using the PTFE films having different peroxide concentrations (0.6–5.2 numbers/cm²) formed by chang-

ing the rf power and the plasma irradiation time, the graft polymerization was carried out at 70°C for 48 h. The weight increase by the graft polymerization, as shown in Figure 3, shows a linear relationship with the peroxide concentration, and the slope is 7.3×10^{-13} µg/peroxide unit. This slope means an average amount (in weight) of the propagation of vinylsulfonate. An average of the degree of polymerization (\overline{DP}) of the graft polymers can be estimated from the slope of the linear relationship. In eq. (1), 130 g/mol is the molecular weight of the repeating unit (sodium vinylsulfonate).

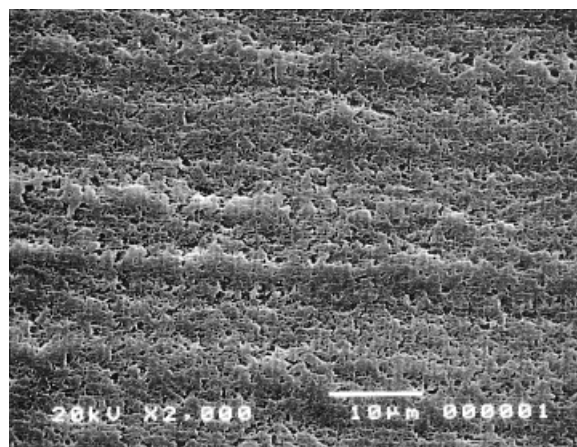
$$\begin{aligned} \overline{DP} \text{ of graft polymers} &= \frac{7.3 \times 10^{-13} \times 10^{-6}}{130} \\ &\times \text{Avogadro number} = 3.4 \times 10^3 \quad (1) \end{aligned}$$

The \overline{DP} of the graft polymers is estimated to be 3.4×10^3 .

Figure 4 shows SEM pictures for the graft-polymerized PTFE surface, the original PTFE surface, and the argon plasma-irradiated PTFE surface. The graft-polymerized PTFE specimen is the film irradiated by argon plasma at 100 W for 180 sec and graft polymerized at 70°C for 48 h. The original PTFE surface, as shown in Figure 4, is rough with dents of about 0.3 µm in diameter. The argon plasma-irradiated PTFE surface is as rough as the original PTFE; therefore, the argon plasma irradiation did not affect the surface morphology. On the other hand, the graft-polymerized PTFE surface is different from the former. The deposition of some polymer on the surface can be observed. Therefore, we conclude from the weight increases and the SEM observation that the graft polymerization of sodium vinylsulfonate occurred on the PTFE surface.

Chemical Composition of Graft-Polymerized PTFE Surface

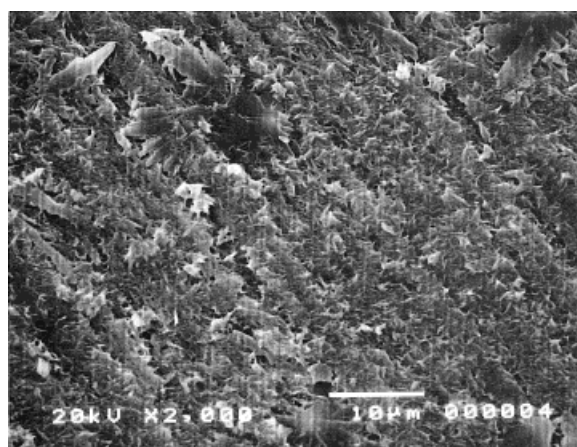
The chemical composition of the graft-polymerized PTFE surface was analyzed by XPS. The wide scanning of XPS for the graft-polymerized PTFE specimen showed the presence of sulfur and oxygen, as well as carbon and fluorine. Typical C_{1s}, F_{1s}, O_{1s}, and S_{2p} spectra for the graft-polymerized PTFE specimen are shown in Figures 5 and 6, accompanying the original and argon plasma-irradiated PTFE films and the homopolymer of vinylsulfonate. The graft-polymerized PTFE speci-



(a)



(b)



(c)

Figure 4 SEM picture of graft-polymerized PTFE surface.

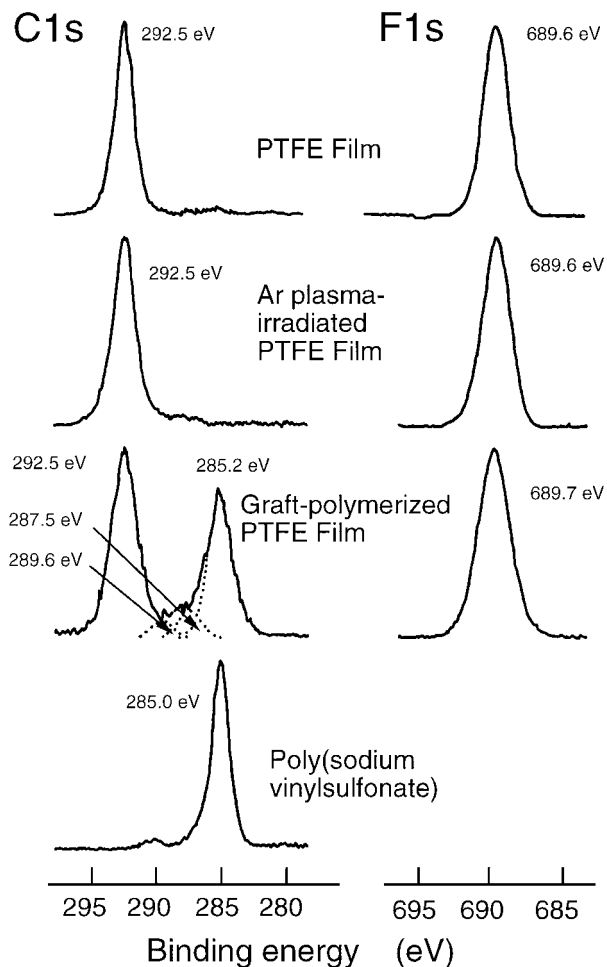


Figure 5 XPS (C_{1s} and F_{1s}) spectra of graft-polymerized PTFE surface.

men is the PTFE film graft polymerized at 70°C for 48 h. The original and argon plasma-irradiated PTFE films show similar and strong C_{1s} and F_{1s} spectra at 292.5 and 689.6 eV due to CF_2 units, respectively,¹⁴ although the C_{1s} spectrum for the argon plasma-irradiated PTFE film has an additional but weak peak near 288 eV. The homopolymer of sodium vinylsulfonate shows a simple C_{1s} spectrum at 285.0 eV due to CH_2 and CH groups, a strong O_{1s} spectrum at 531.9 eV (assigned to SO_3^- group),¹⁴ and an asymmetrical S_{2p} spectra, which is decomposed into two components. The S_{2p} components with $\frac{3}{2}$ and $\frac{1}{2}$ spins appear at 168.1 and 169.3 eV (assigned to \underline{SO}_3^- group), respectively,¹⁴ and a relative peak area is 2.1 : 1.0. On the other hand, the graft-polymerized PTFE specimen, as shown in Figure 5, shows a complex C_{1s} spectrum with two main peaks at 292.5 and 285.2 eV, of which a relative peak area is 1.3 : 1.0, and

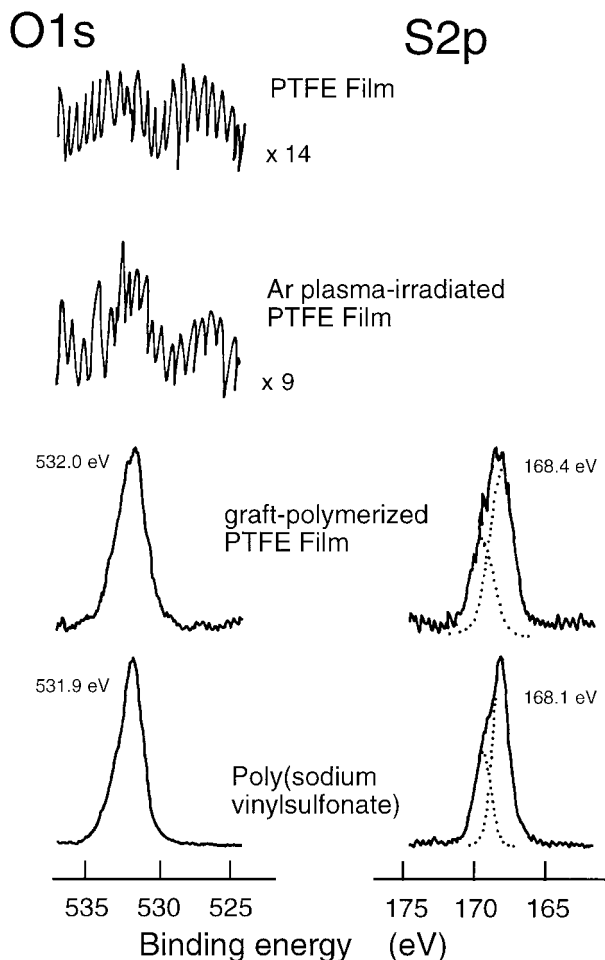


Figure 6 XPS (O_{1s} and S_{2p}) spectra of graft-polymerized PTFE surface.

a strong F_{1s} spectrum at 689.7 eV. The C_{1s} spectrum is decomposed into four components, 285.2, 287.5, 289.6, and 292.5 eV, which are assigned to $\underline{C}H$, $\underline{C}H-CF_n$, $\underline{C}F-CF_n$, and $\underline{C}F_2$ groups (the underlined carbon atom is the assigned atom), respectively.¹⁴ Furthermore, a strong O_{1s} spectrum appears at 532.0 eV (assigned to $\underline{S}O_3^-$ group¹⁴; the underlined atom is the assigned atom), and an asymmetrical S_{2p} spectrum also appears (Fig. 6). The S_{2p} spectrum is decomposed into two components: S_{2p} components with $\frac{3}{2}$ and $\frac{1}{2}$ spins appear at 168.4 and 169.8 eV (assigned to $\underline{S}O_3^-$ group), respectively,¹⁴ and the relative peak area is 2.0 : 1.0.

From results of the XPS spectra, we can conclude that polymeric chains of vinylsulfonate were graft polymerized on the PTFE surface. However, the graft polymer did not completely cover all of the PTFE surface, because the CF_2 component (at 292.5 eV) and the fluorine component (at 689.7

eV) of the PTFE still appear in the XPS spectrum after the graft polymerization.

There are two possibilities related to the incomplete coverage of the PTFE surface with the graft polymer. The first is that all of the PTFE surface is covered with the graft polymer, but the graft polymer is thinner than the sampling depth of photoelectrons. As a result, photoelectrons from the PTFE component come out through the thin layer of the graft polymer. The other possibility is that the graft polymer is thicker than the sampling depth, but the PTFE surface is not completely covered with the graft polymer and a part of the PTFE component comes out on the surface. As a result, photoelectrons from the PTFE component are observed.

The sampling depth (d) is calculated from eqs. (2) and (3),¹⁵ where λ is the mean-free path of photoelectrons, θ is the take-off angle of photoelectrons against the specimen surface (90°), E is the kinetic energy of photoelectrons (950–970 eV), and ρ is the density of the graft polymers ($1.0 \times 10^3 \text{ kg/m}^3$).

$$d = 3\lambda \sin \Theta \quad (2)$$

$$\lambda = \frac{49}{10^{-3}\rho E^2} + \frac{0.11E^{0.5}}{10^{-3}\rho} \quad (3)$$

From eqs. (2) and (3), the sampling depth is estimated to be 10.2–10.5 nm. Therefore, the graft polymer layer should be thinner than 10.2–10.5 nm if the first possibility is valid, and the graft polymer layer should be thicker than 10.2–10.5 nm if the second is possible. The weight increase by the graft polymerization was $36.5 \mu\text{g/cm}^2$, which corresponds to $36.5 \times 10 \text{ nm}$ thickness, assuming homogeneous deposition of graft polymers over all of the PTFE surface. The graft polymer layer ($36.5 \times 10 \text{ nm}$) calculated from the homogeneous deposition is larger by about 35 times than the sampling depth (10.2–10.5 nm) and is thick enough for photoelectrons from PTFE to disappear. Therefore, we conclude that incomplete coverage rather than complete coverage with a thin layer may be reasonable to explain the appearance of the CF_2 component in the XPS spectrum. Such heterogeneous deposition of graft polymers has been observed in the graft polymerization of polyimide (Kapton) films by vinylimidazole.¹⁶ The incomplete coverage can be calculated from the relative intensity of the CH_2 and CF_2 components (1.0 : 1.3) in the C_{1s} spectrum for the graft-poly-

Table I Contact Angle of Water Against Graft-Polymerized PTFE Surface

Sample	Contact Angle of Water (°)
Original PTFE	111
Graft-polymerized PTFE	84
Plasma-treated PTFE	75

merized PTFE. The coverage with the graft polymer is calculated to be 43% [$1.0/(1.0 + 1.3) = 0.43$].

A possible structure of the graft-polymerized PTFE surface, based on results of the XPS analyses and weight increase by the graft polymerization, is that the PTFE surface contains globules of the graft polymer, with an average size of about 849 nm high and occupying 43% of the PTFE surface. We can explain why such globules were formed on the PTFE surface. Graft polymer chains of vinylsulfonate would be swollen in an aqueous solution, and all surfaces of the PTFE film, if the film was in an aqueous solution, would be covered with the graft polymer chains. The graft-polymerized PTFE surface was removed from the aqueous solution after graft polymerization, and as water is removed from the swollen graft polymer, the graft polymer chains would begin to aggregate on the PTFE surface. Finally, globules of the graft polymer would be formed on the PTFE surface in order to cancel the surface energy difference between hydrophilic graft polymer and hydrophobic PTFE. Hydrogen bonding between sulfonate groups in the graft polymer and water may also help aggregation.

Surface Properties of Graft-Polymerized PTFE

The contact angle of water against the graft-polymerized PTFE surface was measured by the sessile drop method. The specimen for the measurement was the same as that used for the XPS measurement, graft polymerized at 70°C for 48 h. Results of the measurement are listed in Table I. The contact angle against the graft-polymerized PTFE film is 84°, and that against the original PTFE film is 111°. This indicates that the graft polymerization modifies the PTFE surface to be more hydrophilic, but the surface is not as hydrophilic as expected. The hydrophilicity of the graft-polymerized PTFE surface is higher than that of polyethylene (the contact angle is 99°), but lower

than that of the plasma-treated PTFE surface (the contact angle is 75°). Poly(sodium vinylsulfonate) chains have a high affinity to water because they are soluble in water. The low hydrophilicity of the graft-polymerized PTFE surface may be related to incomplete coverage with the graft polymer.

CONCLUSION

The PTFE surface was modified by the graft polymerization of sodium vinylsulfonate in two steps: the formation of peroxides on the PTFE surface by irradiation of argon plasma and the graft polymerization of sodium vinylsulfonate from the peroxide groups. The main results are summarized as follows.

1. Peroxides are formed on the PTFE surface by argon plasma irradiation. The peroxide concentration is 3×10^{13} to 5×10^{13} numbers/cm².
2. The graft polymerization of sodium vinylsulfonate is initiated from peroxide groups on the PTFE surface at 65–80°C. An average degree of polymerization of the graft polymers is 3.4×10^3 .
3. The graft polymer does not distribute over all of the PTFE surface; a part of the PTFE surface is not covered. The coverage with graft polymer is 43%.
4. The graft polymerization of sodium vinylsulfonate modifies the PTFE surface to be more hydrophilic. However, the hydrophilicity is lower than that of the PTFE surface modified by plasma treatment.

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