Surface Modification of Plasma-Pretreated Poly(tetrafluoroethylene) Films by Graft Copolymerization

K. L. Tan,* L. L. Woon, and H. K. Wong

Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

E. T. Kang and K. G. Neoh

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511

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ABSTRACT: Surface modification of poly(tetrafluoroethylene) (PTFE) films by radio-frequency argon plasma treatment as well as by graft copolymerization of the plasma-pretreated films with acrylamide (AAm) has been carried out. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical composition and structure of the modified film surfaces. XPS results show that mild plasma treatment is sufficient to cause substantial surface defluorination and oxidation. The oxygen functionalities incorporated greatly facilitate subsequent graft copolymerization in the presence of near-UV radiation. Strong plasma treatment, on the contrary, results in considerable cross-linking of polymers on the surface and thus has an adverse effect on the graft copolymerization. In the course of the present preliminary investigation, it was also found that other water-soluble polymers such as polymers of acrylic acid (AAc), the sodium salt of 4-styrenesulfonic acid (NaSS), *N,N*-dimethylacrylamide (DMAA), and (*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) are equally susceptible to grafting onto the mildly plasma-pretreated PTFE surface. In all the cases investigated, the results of XPS angle-resolved measurements suggest that the grafted polymer penetrates and becomes submerged or partially submerged beneath a thin surface layer. Contact angle measurements reveal that the hydrophilicity of the PTFE film is considerably enhanced by the surface plasma treatment and that it can be much further improved with graft copolymerization.

Introduction

Poly(tetrafluoroethylene) (PTFE) is a highly insulating polymer well known for its physical and chemical inertness.[1] It has found many applications where these properties are essential and desirable. However, its surface is extremely hydrophobic, which makes it unsuitable for use in areas involving adhesive bonding and coating. To improve its wettability and to render its surface chemically active, some form of surface treatment and functionalization of the polymer is necessary.[2]

In this report, we present the results of our preliminary investigation of surface modification of PTFE films by radio-frequency (rf) Ar plasma treatment and by near-UV radiation induced graft copolymerization of the plasma-pretreated films with hydrophilic functional polymers such as acrylamide (AAm), acrylic acid (AAc), the sodium salt of 4-styrenesulfonic acid (NaSS), *N,N*-dimethylacrylamide (DMAA), and (*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) polymers. Plasma modifications of the surface of PTFE have been widely reported in the literature.[3-6] Furthermore, surface modifications through graft copolymerization for a number of pretreated conventional polymers such as polyethylene, poly(ethylene terephthalate), poly(vinyl chloride), nylons, polypropylene, etc. have also been investigated.[7-10] Recently, we have successfully carried out the grafting of the above-mentioned water-soluble polymers onto Ar plasma-pretreated polyaniline films.[11] Accordingly, it should be of interest to extend the technique used to PTFE films. Hopefully, the hydrophilicity of the grafted film surface can thus be improved and at the same time appropriate surface functional groups can be provided to allow further modification and functionalization of the surface for possible biomedical applications such as protein/enzyme immobilization.[12-14] In this study, the modified PTFE surfaces are characterized using X-ray photoelectron spectroscopy (XPS) as a primary tool.

Experimental Section

PTFE films (thickness = 0.01 cm, density = 2.18 g cm^{-3}) used in this study were obtained from Goodfellow. They were subjected to continued washing first in 2-isopropanol for 4 h and then in methyl alcohol for more than 8 h before use. The water-soluble monomers used for grafting include AAm, AAc, NaSS, DMAA, and DMAEMA. They were used as received from Aldrich Chemical Co. Their chemical structures as well as that of PTFE are shown in Figure 1.

Plasma treatment of the PTFE films was carried out in a parallel plane electrode reactor as shown schematically in Figure 2. The volume of the stainless steel vacuum chamber was about 5×10^3 cm^3. The electrodes were in the form of circular Cu plates each of diameter 8 cm. They could be separated at a distance from 5 to 10 cm. In the present work, the separation was kept at a fixed distance of 5.5 cm. The films were first cut into strips of 1.4×5 cm^{-2} and individually subjected to plasma treatment. During treatment, the strip was kept in position on the exposed surface of the rf-powered electrode by a Cu plate holder which had an opening of surface area slightly smaller than that of the strip. Prior to the start up of the plasma, the pressure in the reactor was reduced to 10^{-6} Torr. For the experiments, pure Ar gas was introduced into the reactor via a leak valve at a flow rate of 50 mL min^{-1}, and the throttle valve to the diffusion pump was adjusted so that at ignition the plasma pressure was about 0.15 Torr. The electrical power maintaining the plasma was supplied by a rf power generator operating at 28 W and at 13.56 MHz.

The PTFE film strips after plasma treatment (treatment time ranging from 10 to 60 s) were exposed to the atmosphere for about 1–2 h before the grafting experiments. In graft copolymerization with AAm, the film strip was placed in a Pyrex tube (transparent to soft UV radiation of wavelengths > 300 nm) containing an aqueous solution of 20 mL of 10 wt % AAm and 5 mL of 0.053 mM riboflavin. The reaction mixture in the test tube was sealed with a silicone rubber stopper and then exposed to near-UV light (wavelength > 290 nm) from a 1000-W tungsten halide lamp placed at a distance from the test tube to give a UV intensity of about 5.5 mW cm^{-2} on the film surface. The exposure time for all AAm grafting experiments was kept at about 15 min. Similar procedures were used for grafting with NaSS except 0.5

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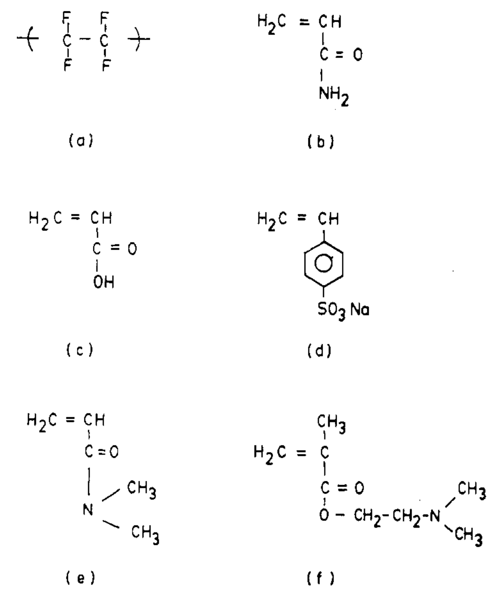

Figure 1. Chemical structures of (a) PTFE, (b) AAm, (c) AAc, (d) NaSS, (e) DMAA, and (f) DMAEMA.

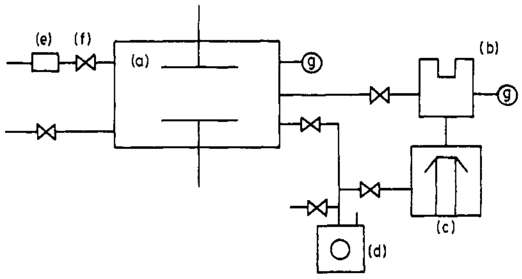

Figure 2. Schematic of the plasma reactor: (a) vacuum chamber, (b) liquid N_2 trap, (c) oil diffusion pump, (d) mechanical pump, (e) flow meter, (f) gas inlet valve, and (g) ionization gauges.

M aqueous NaSS was used. In grafting with AAc, DMAA, or DMAEMA, each film strip was immersed in 20 mL of a 10 wt % aqueous monomer solution in a Pyrex tube. The reaction mixture was thoroughly degassed, sealed off under a nitrogen atmosphere, and then subjected to UV irradiation for about 30 min. After each of the grafting experiments described above, the PTFE film strip was removed from the viscous homopolymer solution and washed with a jet of distilled water. Thereafter it was subjected to repeated rinsing and soaking in a gently stirred water bath for more than 48 h to remove the residue homopolymer.

The plasma-treated and grafted films were characterized by XPS and contact angle measurements. For XPS measurements, the films were mounted on standard sample stubs by means of double-sided adhesive tape, and core-level spectra, taken at take-off angles (α) of 20 and 75° (measured with respect to the sample surface) were obtained on a VG ESCALAB MkII spectrometer using Mg Kα radiation at a constant retard ratio of 40. To minimize radiation damage to the polymer films, the X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). Throughout the measurements, the pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower. To compensate for surface charging effect, all binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV. Surface chemical compositions were determined from peak-area ratios corrected with the appropriate experimentally determined sensitivity factors and are reliable to a ±5% error. Static water contact angles were measured at 21 °C and 45% relative humidity by the sessile drop method, using a 3-μL water droplet in a telescopic goniometer (Ramè-Hart, Model 100-00-(230)). The telescope with a magnification power of 23× was equipped with a protractor of 1° graduation. For each film, at least three measurements on different surface locations were averaged. All contact angle measurements were performed within 3 days after the surface treatment of the PTFE films. The extent of grafting was not obtained gravimetrically as in each case the amount of grafted polymer was on the order of μg per cm^2 and therefore could not be determined with consistent accuracy by this method.

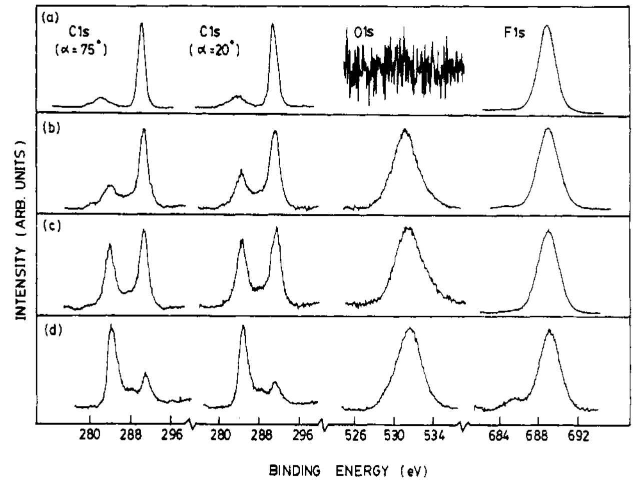

Figure 3. C 1s (α = 75 and 20°), O 1s (α = 75°), and F 1s (α = 75°) core-level spectra of (a) a pristine PTFE film, (b) a 10-s, (c) a 40-s, and (d) a 60-s plasma-treated PTFE film. (The spectral intensities, in arbitrary units, are relative values measured for each sample. The surface composition for each sample is derived from the sensitivity factor corrected spectral area ratios and is shown in Table I.)

Results and Discussion

Pristine and Plasma-Treated PTFE Film Surfaces. The XPS wide-scan spectrum of the pristine PTFE surface used in this study shows only peaks due to carbon and fluorine. However, in the XPS wide-scan spectra of plasma-treated film surfaces, additional peaks due to oxygen are discernible. The C 1s, O 1s, and F 1s core-level spectra of the untreated surface and of surfaces plasma-treated for 10, 40, and 60 s taken at α = 75° are shown in Figure 3. From Figure 3a it is observed that for the untreated surface the C 1s core-level spectrum consists of a main component peak at binding energy (BE) about 291.4 eV attributable to the $-CF_2-$ species and a broad minor component peak at about 8 eV lower in BE. The intensity of this minor component is about 15% of the total intensity of the C 1s core-level peak. It is attributable to the combined contribution of the X-ray satellite peaks arising from Mg K$\alpha_{3,4}$ radiation (about 9% of the main X-ray component) and the adventitious hydrocarbon *C*H species present on the film surface.[15] The latter, lying at BE 284.6 eV, provides a convenient reference for the BE scale. The $-CH-$ species contributes about 6% to the C 1s spectrum of the pristine PTFE. As indicated by the relative intensities of the low-BE component in the two C 1s spectra of Figure 3a, the *C*H component increases slightly relative to the $-CF_2-$ component when the sampling angle is reduced. The oxygen content on the untreated surface is negligibly small as shown by a very weak O 1s core-level peak at BE about 532.1 eV. The F 1s core-level peak, lying at BE about 689 eV, is symmetrical with a fwhm of 2.3 eV; this indicates that the fluorine existing on the untreated film surface is mainly of the $-CF_2-$ species.[3] This is supported by the fact that the F/C ratio (using a calculation based on the C 1s peak area at BE 291.4 eV) is 1.91—a value fairly close to the expected value of 2 for PTFE.

Plasma treatment followed by atmospheric exposure readily decreases the intensities of the F 1s peak and the C 1s component peak at BE 291.4 eV while concomitantly enhancing the low-BE C 1s component and the oxygen content of the PTFE film. Panels b–d of Figure 3 show these changes as the plasma treatment time is increased from 10 to 60 s. The enhancement of the C 1s low-BE component produces a combination of unresolved peaks between ca. 284 and ca. 292 eV. This is attributable to the increase in hydrocarbon, oxidized carbon, and fluorocarbon species on the treated surface; the likely main ones are *C*H, *C*–C (284.6 eV), *C*–OH, *C*–CF (286–287 eV), *C*=O, *C*–F (287–288 eV), O–*C*=O, and *C*F–CF_2 (289–290 eV).[16-18] The uptake of oxygen as shown by the O 1s signal is substantial and it increases with the plasma treatment time. The incorporation of oxygen onto the PTFE surface due to rf Ar plasma treatment is a complex process. Its exact mechanism is not known; however, from the XPS results obtained, some inference on its occurrence can be drawn:[2,5] It is probable that in the first step the C–F bonds are disrupted by the active plasma species or the UV radiation in the plasma, resulting in the loss of fluorine and the creation of backbone radicals such as $-\dot{C}F-$ on the surface. These radicals are very reactive and they would likely, in the next step, react to form a cross-linked structure (if the radicals are located on adjacent chains) or C=C bonds (if the radicals are neighbors on the same chain). Evidence in support of cross-linking[19] and double-bond formation[20] on plasma-treated PTFE surfaces has been reported. The surviving radicals which have not reacted in the plasma reactor would be attacked immediately by oxygen and oxygen-containing species as soon as the film is brought into contact with the atmosphere. The main O 1s peak at BE about 532.1 eV shows that the oxygen functionalities formed are predominantly peroxide species.[11] The amount of this species has been found to build up immediately to a maximum upon exposure to the atmosphere. It will remain so at this value for a period up to about 2 h and will decrease thereafter only gradually.

Increasing plasma treatment time results in increasing defluorination on the film surface. This is evident from Figure 3b–d, where it is shown that the intensity of the CF_2 component compared with that of the *C*–C component in the C 1s core-level spectrum reduces with increasing treatment time. In fact, for treatment time longer than ca. 50 s, the level of defluorination has been found to be such that the intensity of the former component peak will become smaller than that of the latter component. The high amount of low-BE carbon species produced by long treatment time indicates that substantial damage of polymer on the film surface has occurred as the result of massive defluorination. At high treatment time, the presence of oxygen and fluorine moieties of BE about 531 eV (C–O species) and about 684.8 eV (probably due to fluorine associated with a graphite-like carbon cluster), respectively, on the film surface has also become noticeable; see Figure 3d. The surface nature of the plasma treatment is revealed by XPS angle-resolved measurements. For comparison, C 1s core-level spectra taken at $\alpha = 20°$ are presented in Figure 3. The lower proportion of CF_2 to *C*–C species as obtained at the more surface-sensitive mode indicates that defluorination takes place predominantly at the outermost layer of the film surface.[18] This phenomenon as well as the increasing defluorination and oxidation of the surface with treatment time is clearly indicated by the chemical compositions of the various surfaces as given in Table I. Plasma treatment has also considerably improved the hydrophilicity of the film surface. Figure 4 shows the variation of water contact angle as a function of plasma treatment time. It is observed that the contact angle from 116° for a pristine PTFE surface reduces rapidly to about 65° for a surface plasma-treated only 10 s. This is the lowest contact angle observed. As the treatment time increases, this value remains somewhat constant and then increases slightly to about 80° for treatment time longer than 50 s.

Table I. Surface Compositions of Ar Plasma-Treated PTFE Films

sample	plasma treatment time (s)	C:F:O[a] $\alpha = 75°$	C:F:O[b] $\alpha = 20°$
1 (pristine)	0	1:1.58:0.01	1:1.61:0.01
2	10	1:1.03:0.19	1:0.91:0.18
3	40	1:0.74:0.24	1:0.70:0.22
4	60	1:0.28:0.37	1:0.35:0.31

[a] Corrected C 1s (entire peak from BE ca. 284 eV to ca. 292 eV), F 1s, and O 1s core-level spectral area ratios determined at XPS take-off angle (α) = 75°. [b] Same area ratios determined at XPS take-off angle (α) = 20°.

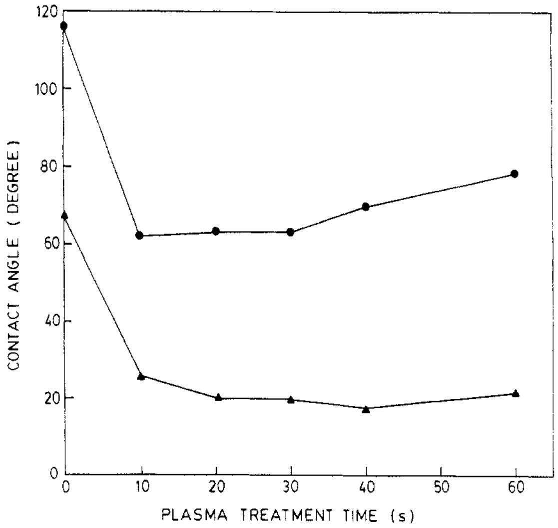

Figure 4. Water contact angles as a function of plasma treatment time for a PTFE surface (●) and for a PTFE surface grafted with AAm polymer (▲).

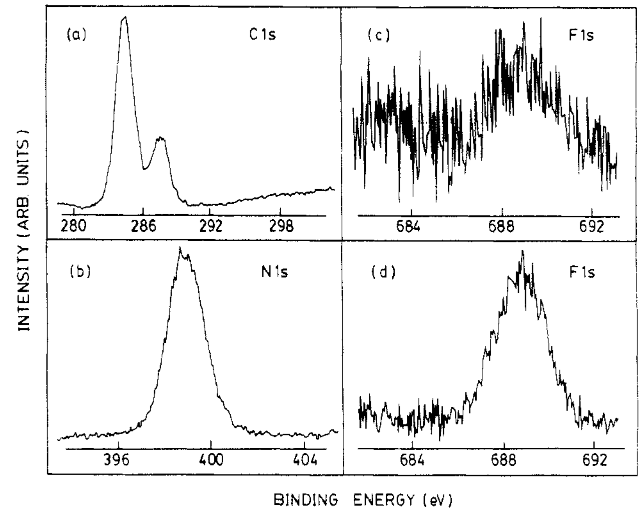

Figure 5. (a) C 1s (α = 75°), (b) N 1s (α = 75°), (c) F 1s (α = 75°), and (d) F 1s (α = 20°) core-level spectra for a 10-s plasma-pretreated PTFE film grafted with AAm polymer.

Surface Grafting of Plasma-Pretreated PTFE Films. Attempts have been made to carry out graft copolymerization of pristine PTFE films with the various graft polymers. These result only in very weak grafting. In view of the chemically inert nature of the PTFE polymer, this outcome is not unexpected. With mildly plasma-pretreated films (treatment time < 40 s), a significant extent of grafting is obtained. Figure 5 shows the C 1s, N 1s, and F 1s core-level spectra for a 10-s plasma-pretreated film grafted with AAm. The extent of the

Table II. Surface Compositions of Plasma-Pretreated PTFE Films Copolymerized with the Various Graft Polymers

sample	plasma pretreatment time (s)	graft polymer	graft density[a]	
			$\alpha = 75°$	$\alpha = 20°$
1a	10	AAm	[N]/[F] = 15.49	[N]/[F] = 3.73
1b	40	AAm	[N]/[F] = 19.31	[N]/[F] = 4.62
1c	60	AAm	[N]/[F] = 0.08	[N]/[F] = 0.03
2	10	AAc	[COOH]/[F] = 1.16	[COOH]/[F] = 0.41
3	10	NaSS	[S]/[F] = 1.52	[S]/[F] = 1.02
4	10	DMAEMA	[N]/[F] = 1.43	[N]/[F] = 0.33
5	10	DMAA	[N]/[F] = 5.02	[N]/[F] = 0.87

[a] The graft densities are determined from the various core-level spectra of the grafted surfaces at XPS take-off angles (α) = 75 and 20°. (For details, see text.)

grafting is revealed by the greatly reduced intensity of the F 1s signal and the emergence of a strong N 1s peak at about 399.4 eV attributable to the nitrogens ($-NH_2C{=}O$ structure) of the grafted AAm polymers.[11] From the C 1s core-level spectrum, it is also observed that the grafting suppresses the high-BE component of the C 1s peak at 291.4 eV attributable to the CF_2 species and contributes significantly to the peak components at 284.6 eV and about 287.5 eV attributable respectively to the hydrocarbons and carbonyl groups of the grafted AAm polymers. The grafting process taking place under near-UV irradiation is likely initiated by radicals resulting from the decomposition of the peroxide species through the cleavage of the C–O bonds. A peroxide-initiated mechanism for graft copolymerization under near-UV irradiation has been suggested for plasma-pretreated surfaces.[7] During the grafting process any oxygen present in the reaction mixture that would inhibit radical polymerization is consumed by photoreaction with riboflavin.[21] The density of the graft can be determined from the mole ratio [N]/[F]. It is found that it increases with plasma treatment time up to ca. 50 s, and thereafter because of the damage due to extensive cross-linking of polymers on the film surface, the graft density begins to decrease drastically. This trend is shown in Table II by the graft densities for three PTFE films plasma-pretreated for 10, 40, 60 s. The nature of the surface modification of the film can again be observed from angle-resolved XPS results. Comparing the F 1s core-level spectra shown in panels c and d of Figure 5 taken respectively at $\alpha = 75$ and 20°, it is noted that the F 1s signal is much increased when measured at the more surface-sensitive mode. This result together with the grafted densities at the two take-off angles given in Table II indicates that the AAm polymer has penetrated the PTFE polymer and become somewhat submerged under a thin surface layer consisting of more fluorinated polymer than the subsurface. Using 2.5 nm as an effective mean free path (λ) for C 1s photoelectrons produced by Mg Kα X-rays in an organic matrix,[18] the angle-resolved data show that the thickness of this thin surface layer is on the order of 2–3 nm.[22] As shown in Figure 4, the hydrophilicity of the PTFE is further improved by the grafted AAm polymer. It is noted that the water contact angle reduces from 116° to about 68° with only a very small amount of AAm polymer grafted onto the surface (corresponding to zero plasma pretreatment time) and it decreases further and reaches a mininium value of about 18° at a pretreatment time of 40 s.

In the present study, work has also been carried out to graft the plasma-pretreated PTFE films with AAc, NaSS, DMAEMA, and DMAA polymers. The pretreated films are found to be as susceptible to grafting with these polymers as with AAm polymer albeit not to the same extent. The densities of the grafted polymers are determined from the mole ratios [COOH]/[F] in the case of AAc graft, [S]/[F] in the case of NaSS graft, and [N]/[F] in the cases of DMAA and DMAEMA grafts. The concentrations of COOH (due to the carboxylic group of AAc), S (due to the sulfonic acid group SO_3^- of the NaSS), and N (due to the $N(CH_3)_2$ group of DMAA and DMAEMA) are determined respectively from corrected areas of the C 1s component peak at about 289 eV, the S 2p core-level peak at about 168 eV, and the N 1s peak at about 339.4 eV. For comparison, the densities of grafting with these functional polymers for 10-s plasma-pretreated PTFE films are given in Table II. This plasma treatment time is short enough to ensure the surface damage of the PTFE film is kept to a minimum (see Table I). Similar to the case with AAm polymer, the angle-dependent density data indicate that these other grafted polymers also submerge or partially submerge beneath a thin surface layer consisting of more fluorinated polymer than the subsurface. This structure is consistent with the fact that all of the graft copolymerized PTFE surfaces are hydrophilic in nature, as indicated by the more surface-specific[23] contact angle data. As an illustration, we present Figure 6, which shows the XPS wide-scan spectra for a 10-s plasma-pretreated PTFE grafted with NaSS taken at two take-off angles. It is observed that the relative intensity of F 1s to S 2p is much greater in curve a taken at $\alpha = 20°$ than in curve b taken at $\alpha = 75°$. Such a phenomenon of graft polymer migrating below the outermost layer of the substrate was similarly encountered in our earlier work on surface modification of poly(3-alkylthiophene) films by graft copolymerization.[24] The effect of polar group orientation, polymer chain mobility, and substrate permeability on the stability of graft layer has been discussed by Ratner et al.[25] for a number of polymers. The reorientation of polar groups into the hydrophobic bulk phase has also been known to reduce the overall free energy of the system.[26] Obviously, Ar plasma treatment and the accompanied surface defluorination and degradation have substantially increased the surface permeability and chain mobility of the PTFE film. As a result, the migration of the polar graft below the surface is greatly facilitated. Alternatively, plasma pretreatment, surface oxidation, defluorination, near-UV irradiation during grafting, and finally graft copolymerization may have substantially lowered the glass transition temperature (T_g) of the PTFE chains in the surface region, thus making the migration of the graft and countermigration of the substrate polymer chains possible.

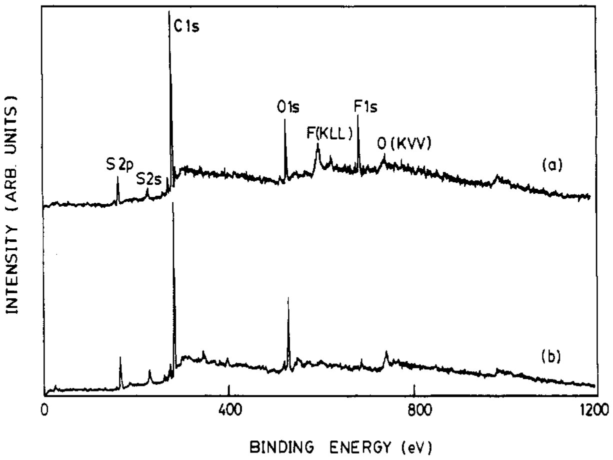

Figure 6. XPS wide-scan spectra taken at (a) $\alpha = 20°$ and (b) $\alpha = 75°$ for a 10-s plasma-pretreated PTFE grafted with NaSS.

Conclusion

PTFE films, pretreated by rf Ar plasma, have been found to be susceptible to UV-induced graft copolymerization with AAm, AAc, NaSS, DMAEMA, and DMAA. For a PTFE film which is not damaged due to excessive plasma exposure, the density of a surface-grafted polymer is greatly enhanced and is found to increase with plasma pretreatment time. In all the cases, angle-resolved XPS data suggest that the grafted polymer penetrates and becomes submerged or partially submerged beneath a thin surface layer of thickness about 2–3 nm. Contact angle measurements show that the hydrophilicity of the PTFE film is considerably enhanced by the surface plasma treatment and that it can be much further improved by graft copolymerization.

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References and Notes

(1) Koo, G. *Fluoropolymers*; Wall, L. A., Ed.; Wiley-Interscience: New York, 1972.

(2) See, for example: Yasuda, H. K., Ed. Plasma Polymerization and Plasma Interactions with Polymeric Materials. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1990**, *46*.

(3) Yasuda, H.; Marsh, H. C.; Brandt, S.; Reilley, C. N. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 991.

(4) Clark, D. T.; Hutton, D. R. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2643.

(5) Briggs, D. Applications of XPS in Polymer Technology. In *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M., Eds.; John Wiley & Sons: New York, 1983.

(6) Youxian, D.; Griesser, H. J.; Mau, A. W. H.; Schmidt, R.; Liesegang, J. *Polymer* **1991**, *32*, 1126.

(7) Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* **1986**, *19*, 1804.

(8) Uyama, Y.; Ikada, Y. *J. Appl. Polym. Sci.* **1988**, *36*, 1089.

(9) Uchida, E.; Uyama, Y.; Iwata, H.; Ikada, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2837.

(10) Uyama, Y.; Tadokoro, H.; Ikada, Y. *Biomaterials* **1991**, *12*, 71.

(11) Kang, E. T.; Neoh, K. G.; Tan, K. L.; Uyama, Y.; Morikawa, N.; Ikada, Y. *Macromolecules* **1992**, *25*, 1959.

(12) Fisher, J. P.; Becker, U.; Halasz, S. P.; Muck, K. F.; Puschner, H.; Rosinger, S.; Schmidt, A.; Suhr, H. H. *J. Polym. Sci., Polym. Symp.* **1979**, *66*, 443.

(13) Ikada, Y. In *Advances in Polymer Science*; Springer-Verlag: Berlin and Heidelberg, 1984; Vol. 57, p 104.

(14) Falb, R. D. Immobilized Enzymes: An Overview. In *Enzyme Engineering*; Wingard, L., Ed.; Wiley-Interscience: New York, 1972; p 177.

(15) Crowe, R.; Badyal, J. P. S. *J. Chem. Soc., Chem. Commun.* **1991**, 958.

(16) Kaplan, S.; Dilk, A. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1984**, *38*, 105.

(17) Occhiello, E.; Morra, M.; Garbassi, F. *Angew. Makromol. Chem.* **1989**, *173*, 183.

(18) Clark, D. T.; Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 957.

(19) Clark, D. T.; Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2321.

(20) Le Moë, A.; Duraud, J. P.; Le Gressus, C.; Okuzumi, H. *Scanning Electron Microsc.* **1986**, 1319.

(21) Holmstrom, B.; Oster, G. J. *J. Am. Chem. Soc.* **1961**, *83*, 1867.

(22) Note: Assuming the sampling depth to be 3λ, the approximate thickness of the thin surface layer is estimated from the product $3\lambda \sin \alpha$, where λ and α are taken to be 2.5 nm and 20°, respectively.

(23) Anand, M.; Cohen, R. E.; Baddour, R. F. Surface Characterization of Plasma-Fluorinated Polymers. In Dwight, D. W.; Fabish, T. J.; Thomas, H. R., Eds. *Photon, Electron, and Ion Probes of Polymer Structure and Properties. ACS Symp. Ser.* **1981**, *162*, 353.

(24) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Macromolecules* **1992**, *25*, 6842.

(25) Ratner, B.; Weathersby, P. K.; Hoffman, A. S.; Kelley, M. A.; Schorpen, L. H. *J. Appl. Polym. Sci.* **1978**, *22*, 643.

(26) Ikada, Y.; Matsunaga, T.; Suzuki, M. *Nippon Kagaku Gakkaishi* **1985**, 6, 1079.