Surface Modification and Functionalization of Polytetrafluoroethylene Films

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ABSTRACT: Argon plasma-pretreated polytetrafluoroethylene (PTFE) films were subjected to further surface modification by near-UV light-induced graft copolymerization with acrylic acid (AAc), sodium salt of styrenesulfonic acid (NaSS), and *N*,*N*-dimethylacrylamide (DMAA). The surface compositions and microstructures of the modified films were characterized by angle-resolved X-ray photoelectron spectroscopy (XPS). A stratified surface microstructure with a significantly higher substrate-to-graft chain ratio in the top surface layer than in the subsurface layer was always obtained for PTFE surface with a substantial amount of the hydrophilic graft. The stratified surface microstructure was consistent with the observed hysteresis in advancing and receding water contact angles. The graft yield increased with Ar plasma pretreatment time and monomer concentration. Covalent immobilization of trypsin on the AAc polymer-grafted PTFE films was facilitated by water-soluble carbodiimide (WSC). The effective enzyme activities increased initially with increasing surface concentration of the grafted AAc polymer but became saturated at a moderate AAc polymer concentration. The immobilized enzyme could still retain close to 30% of its original activity. Solution-coating of the polymeric acid-modified PTFE films with the emeraldine (EM) base of polyaniline readily resulted in an interfacial charge transfer interaction and a semiconductive PTFE surface.

Introduction

Surface modification of polymers via molecular design is one of the most versatile means of incorporating new functionalities into the existing polymers.[1,2] These new functionalities have included improved surface hydrophilicity,[3] hydrophobicity,[4] biocompatibility,[5] conductivity,[6,7] lubricative properties,[8] and adhesive properties,[9] just to name a few. Surface modifications of polytetrafluoroethylene (PTFE) and fluoropolymers have been of particular interest, as these polymer substrates are one of the most important families of engineering polymers well known for their physical and chemical inertness.[10] The latter properties, however, also dictate the use of more drastic chemical and physical means[11−14] for achieving the required surface modifications. A large amount of work has been devoted to the surface modification of fluoropolymers by plasma treatment.[15−22] One of the major drawbacks of plasma treatment is that the physicochemical characteristics of the modified polymer surfaces, including surface compositions, are time-dependent. Chain and polar group reorientation in the surface region[23] can result in gradual deterioration of the surface reactivity. Furthermore, anomalous changes in oxygen and fluorine contents, and therefore also surface compositions, may result from the presence of surface hydrocarbon contamination during plasma treatment.[21] One method of eliminating the time- and surface-dependent effects of plasma treatment is to subject the plasma-pretreated PTFE film to further modification, for example, via surface graft copolymerization. The latter process can result in permanently modified polymer surfaces. Most important of all, specific functional groups can be designed and incorporated into the polymer surface to allow subsequent surface functionalization, such as enzyme and protein immobilization via covalent bonding.

In the present work, surface modification of Ar plasma pretreated PTFE film was carried out via near-UV light-induced graft copolymerization with water-soluble monomers of acrylic acid (AAc), sodium salt of styrenesulfonic acid (NaSS), and *N*,*N*-dimethylacrylamide (DMAA). The effects of plasma pretreatment time and the concentration of the monomer solution used during copolymerization on the copolymer composition and surface microstructure were deduced from angle-resolved X-ray photoelectron spectroscopy (XPS). The structure of the graft-copolymerized surface was also characterized by the dynamic contact angle technique. The AAc polymer-modified PTFE surfaces were further functionalized via covalent immobilization of a model enzyme, trypsin. Preliminary attempts were made to correlate the biological activity of the immobilized enzyme to the structure of the graft-copolymerized surface. The acrylic and styrenesulfonic acid polymer-modified surfaces were also functionalized via solution-coating of an electroactive polymer base, such as the emeraldine (EM) phase of polyaniline. The interfacial charge transfer interactions between the grafted chains and the coated electroactive polymer chains not only give rise to a semiconductive PTFE surface but also result in strong adhesion of the electroactive polymer on the PTFE surface.

Experimental Section

Materials. Polytetrafluoroethylene film having a thickness of about 0.01 cm and a density of 2.18 g/cm^3 was used in this study and was obtained from Goodfellow Inc., Cambridge, U.K. The surfaces of the films were cleaned by Soxhlet extraction in methanol for 6 h before use. The water-soluble monomers used for graft copolymerization include acrylic acid (AAc),

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sodium salt of styrene sulfonic acid (NaSS), and *N*,*N*-dimethylacrylamide (DMAA). They were obtained from Wako Pure Chemical Industries Ltd., Tokyo, Japan. The water-soluble 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (WSC) was purchased from Dojindo Laboratories, Kyoto, Japan, and was used as received. Trypsin from bovine pancreas (type III) was purchased from Sigma Chemical Co. *N*-α-Tosyl-L-arginine methyl ester hydrochloride (TAME), used for the assay of enzyme activities, was purchased from Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan. The Dulbecco's phosphate buffer solution or PBS (containing 8000 mg of sodium chloride, 200 mg of potassium chloride, 1150 mg of anhydrous disodium phosphate, and 200 mg of anhydrous monopotassium phosphate in 1 L), used for the enzyme immobilization work, was obtained from Nissui Pharmaceutical Co., Kyoto, Japan. The solvents and other reagents were of analytical grade and were used without further purification. The electroactive polyaniline in its neutral emeraldine (EM) base form was prepared by oxidative chemical polymerization of aniline by ammonium persulfate in 1 M sulfuric acid, followed by deprotonation in 0.5 M NaOH.[24]

Graft Copolymerization and Surface Characterization. The PTFE films were cut into strips of about 1.5 cm × 3.5 cm. They were pretreated with Ar plasma before graft copolymerization. A bell jar-type glow discharge cell, Model LCVD 12, manufactured by Shimadzu Corp. (Kyoto, Japan), was used for the plasma treatment. The frequency applied was 5 kHz at a plasma power of 28 W (280 V, 100 mA). The films were fixed on a stainless steel sample holder rotating between two flat plate electrodes. The electrode separation was about 8.0 cm. The pressure in the bell jar was maintained at about 0.04 Torr of Ar when the polymer films were subjected to glow discharge for 5−40 s. The Ar plasma-pretreated films were then exposed to the atmosphere before the graft copolymerization experiment. In the case of graft copolymerization with AAc, each PTFE film was immersed in 20 mL of the aqueous monomer solution in a Pyrex tube. The concentrations of the AAc solutions were varied from 1 to 10 wt %. Each reaction mixture was thoroughly degassed and sealed under a nitrogen atmosphere. It was then subjected to near-UV irradiation (wavelength > 290 nm) for about 30 min in a rotary photochemical reactor equipped with a 1000 W high-pressure Hg lamp (Riko Rotary Model RH400-10W). The reactor was equipped with a constant temperature water bath. All near-UV light-induced graft copolymerizations were carried out at a constant temperature of 28 °C. After each grafting experiment, the PTFE film was removed from the viscous homopolymer solution and washed with a jet of doubly distilled water. It was then immersed in a 60 °C water bath with continuous stirring for 24 h, followed by rinsing in copious amounts of distilled water to remove the residual homopolymer. Similar procedures were used for the graft copolymerization with NaSS and DMAA, except the degassing process was replaced by the use of 5 mL of 0.05 mM riboflavin. In this case, the dissolved oxygen, which could inhibit the radical-initiated polymerization, was consumed by photochemical reaction with riboflavin.[25] Both the degassing and the riboflavin addition processes produce NaSS or DMAA graft-copolymerized PTFE films of similar quality, as revealed by the X-ray photoelectron spectroscopic (XPS) results.

The polymer films after graft copolymerization were characterized by angle-resolved XPS and dynamic water contact angle measurements. XPS measurements were made on a VG ESCALAB MKII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The polymer films were mounted on the standard sample studs by means of double-sided adhesive tapes. For most samples, the core-level signals were obtained at photoelectron take-off angles (α, with respect to sample surface) of 20° and 75°, although signals were also collected at intermediate α's for some samples. The X-ray source was run at a reduced power of 120 W (12 kV, 10 mA). This power did not cause any appreciable damage to the sample during the time required (∼10−12 min) to acquire the full set of the angle-dependent XPS data, as the core-level line shapes of the sample did not change significantly in a repeated scan. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during each measurement. All binding energies (BEs) were referenced to the C1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (full width at half-maximum, fwhm) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to ±5%. The elemental sensitivity factors were calibrated using stable binary compounds of well-established stoichiometries. Dynamic water contact angles were measured at 25 °C and 50% relative humidity using a telescopic goniometer (Ramehart Model 100-00(230)). The telescope with a magnification power of 23× was equipped with a protractor of 1° graduation. The advancing and receding contact angles were measured using the angle-of-tilt method. The angles reported were reliable to ±3°.

The surface concentrations of the grafted AAc, NaSS, and DMAA polymers were expressed simply as the [COOH]/[F], [S]/[F], and [N]/[F] ratios, respectively, and were determined from the XPS-derived surface stoichiometries. These ratios can be readily converted to the number of repeating units of the grafted polymer per repeating unit of the PTFE chain. Toluidine blue (TB) uptake was also used to determine the total concentration, in weight per unit area, of the surface-grafted AAc polymer. An aqueous solution of 5×10^{-4} M TB, adjusted to pH 10 with NaOH, was added to the grafted samples of a fixed surface area. The formation of ionic complexes between the COOH groups of the grafted chains and the cationic dye was allowed to proceed for 2 h at room temperature, followed by rinsing the sample substrates with NaOH solution (pH 10) to remove the noncomplexed TB molecules. Desorption of the dye was performed in 50 wt % acetic acid solution. The amount of the grafted AAc polymer was calculated from the optical density of the desorbed dye at 633 nm, with the assumption that 1 mol of TB had complexed with 1 mol of the carboxyl group of the AAc polymer.[26]

Trypsin Immobilization and Assay. For covalent immobilization of trypsin onto the AAc polymer-grafted PTFE films, the COOH groups were preactivated with WSC (5 mg/mL) at 4 °C in 0.1 M PBS containing 0.6 wt % acetic acid (pH adjusted to 4.5 with NaOH) for 1 h. The grafted PTFE substrate was then transferred to the 0.1 M PBS (+) (pH 7.4 with 0.02 M $CaCl_2$ added) containing trypsin at a concentration of 1 mg/mL. The immobilization was allowed to proceed at 4 °C for 24 h. After that, the reversibly bound trypsin was desorbed in copious amounts of PBS (+) for 1 h at 25 °C. The PTFE films with immobilized trypsin were stored at −10 °C after lyophilization. Physical adsorption of trypsin was conducted in a similar manner, except that the preactivation of films with WSC was omitted. The amount of immobilized enzyme on each PTFE film surface was determined by the ninhydrin method.[27]

The activities of the free and immobilized trypsin were assayed using 1.04 mM TAME solution in 0.04 M Tris-HCl (+) buffer (pH 8.1 with 0.02 M $CaCl_2$ added).[28] The initial rate of absorbance increase at 247 nm was used to evaluate the activities of the free and covalently bonded enzyme. In all cases, the activities of the enzyme were assayed after 5 min in TAME solution.

Coating of the Electroactive Polymer. The AAc and NaSS polymer-grafted PTFE substrates were immersed in a 0.1 wt % *N*-methylpyrrolidinone (NMP) solution of the neutral emeraldine (EM) base. The coated films were dried under reduced pressure, followed by soaking in deionized water for 48 h to remove the residual NMP. The amounts of coated EM base and the extents of interfacial charge transfer interactions were determined by the XPS technique.

Results and Discussion

Surface Graft Copolymerization. Figure 1 shows the effect of the Ar plasma treatment on the surface composition, in particular the [O]/[F] and [F]/[C] ratios, of the PTFE film. The ratios were determined from the

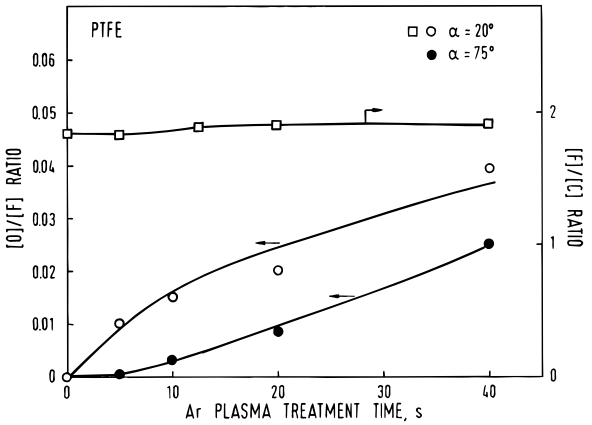

Figure 1. Effect of the Ar plasma treatment on the surface composition of the PTFE film.

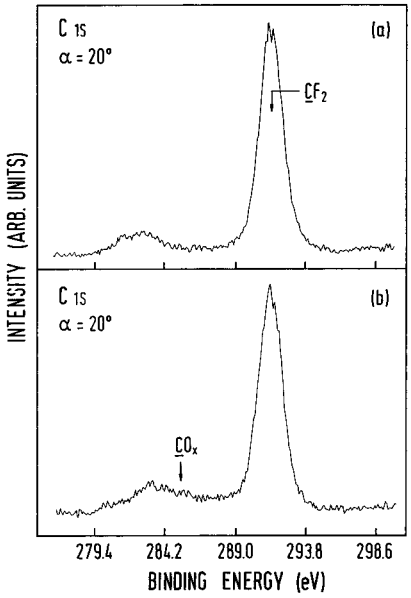

Figure 2. C1s core-level spectra obtained at $\alpha = 20°$ for (a) a pristine and (b) a 40 s Ar plasma-pretreated PTFE film.

sensitivity factor-corrected O1s, F1s, and C1s core-level spectral area ratios. For the pristine PTFE film, the absence of an O1s core-level signal and the presence of a [F]/[C] ratio close to the theoretical value of 2.0 suggest that the PTFE surface is relatively free from contamination. The [F]/[C] ratio and the C1s line shape did not change significantly with plasma treatment time for the glow discharge conditions used in the present work. Figure 2 shows the respective C1s core-level spectra of a PTFE film before (a) and after (b) 40 s of Ar plasma treatment. Each C1s spectrum consists of a main component with a BE of 291.4 eV, attributable to the CF_2 species, and a broad minor component at about 8 eV below the main peak. The minor component can be attributed mainly to the contribution of the X-ray satellite peaks arising from Mg $K\alpha_{3,4}$ radiation. In the case of plasma-treated sample, the contribution of oxidized carbon species to this minor component is also discernible. On the other hand, a steady increase in the [O]/[F] ratio was observed upon increasing the plasma treatment time. The [O]/[F] ratio reaches a value of about 0.04 at a plasma treatment time of 40 s. The fact that a higher [O]/[F] ratio is always observed at the more surface-glancing XPS angle of 20° is consistent with a surface oxidation process. Direct and quantitative comparison of the Ar plasma-induced

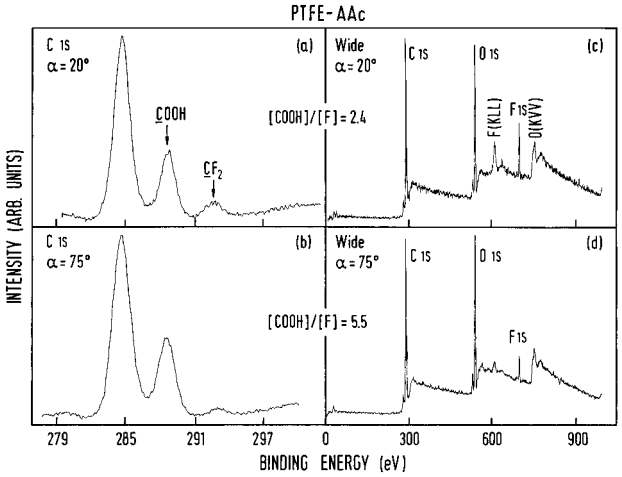

Figure 3. Angular-dependent C1s core-level and wide-scan spectra of a 5 s Ar plasma-pretreated PTFE film after graft coplymerization in 10% AAc solution.

changes in surface compositions ([F]/[C] and [O]/[F] ratios) with those reported in the literature might be difficult, as different glow discharge conditions, such as plasma power, oscillator frequency, sample−electrode configuration, Ar pressure, etc., were used in each case. For instance, in the work of Youxian et al.,[19] a plasma power of 12.5 W, an oscillator frequency of 700 kHz, and an Ar pressure of 0.6 Torr were used, while Golub et al.[21] used a plasma power of 160 W, an oscillator frequency of 13.56 MHz, and an Ar pressure of 0.385 Torr.

Figure 3 shows the C1s core-level spectra obtained respectively at photoelectron take-off angles (α's) of 20° (a) and 75° (b) for a 5 s Ar plasma-pretreated PTFE film after having been subjected to near-UV light-induced graft copolymerization in 10% AAc solution. The corresponding wide-scan spectra of the film are shown in Figure 3, parts c and d. The presence of surface-grafted AAc polymer can be deduced from the C1s component at the BE of 288.7 eV, attributable to the *C*OOH species.[29] The concentration of surface-grafted AAc polymer is expressed as the [COOH]/[F] ratio. Comparison of the C1s-to-F1s component intensity ratios in the wide-scan spectra or the *C*OOH-to-CF_2 component intensity ratios in the C1s core-level spectra at the two photoelectron take-off angles readily reveals the presence of a higher proportion of the substrate PTFE chains in the more surface-glancing angle of 20°. The angular-dependent XPS results suggest that the hydrophilic AAc polymer graft must have become submerged beneath a thin surface layer, which is richer in the substrate chains, to form a stratified surface microstructure.

The stratified surface microstructure must have resulted from a substantial rearrangement of the chains in the surface region, involving the migration and countermigration of the substrate and the grafted chains. This microstructure was always observed for PTFE films with a substantial amount of surface-grafted hydrophilic polymers. (See also Figure 7 below.) In the case of graft copolymerization with AAc, a significantly higher [COOH]/[F] ratio was always observed at $\alpha = 75°$ than at $\alpha = 20°$ for copolymerization carried out in 10% AAc solution on 5−40 s Ar plasma-pretreated PTFE films. The stratified surface microstructure was either not observed or less well-developed for copolymerization carried out in less concentrated AAc solutions, which give rise to a lower graft yield. Figure 4 shows the respective C1s core-level spectra

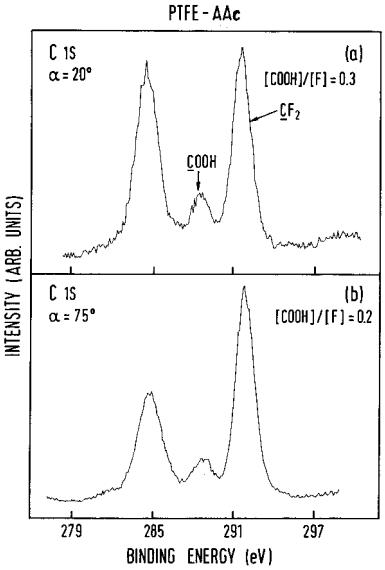

Figure 4. C1s core-level spectra, obtained at (a) $\alpha = 20°$ and (b) $\alpha = 75°$, for a 10 s Ar plasma-pretreated PTFE film after graft copolymerization in 2.5% AAc solution.

obtained at α's of 20° (a) and 75° (b) for a 5 s Ar plasma-pretreated PTFE film after having been subjected to near-UV light-induced graft copolymerization in 2.5% AAc solution. In this case, the simultaneous presence of a large amount of the PTFE chains at the surface allows a higher concentration of the grafted AAc chains to be present at the top surface than in the subsurface layer. Thus, the presence of "surface restructuring" at high coverage of the hydrophilic graft suggests that the modified PTFE essentially strives to re-establish its original surface. The reorientation of polar groups into the hydrophobic bulk phase has been widely observed[23,30,31] and has also been known to reduce the overall free energy of the surface.[32] Using 2.5 nm as an effective mean free path (λ) for C1s photoelectrons produced by the Mg Kα X-ray in an organic matrix,[13] the angle-resolved data show that the thickness of the thin top surface layer corresponding to $\alpha = 20°$ is in the order of 2−3 nm ($3\lambda \sin \alpha$).

Similar surface microstructures were observed for PTFE films at high and low extents of surface modification by graft copolymerization with NaSS and DMAA. The concentration of surface-grafted styrenesulfonic acid polymer (as no Na signal is detected) is expressed as the [S]/[F] ratio and is determined directly from the sensitivity factors-corrected S2p and F1s core-level spectral area ratio. The stratified surface microstructure is observed unambiguously, as indicated by a significantly lower [S]/[F] ratio at $\alpha = 20°$ than at $\alpha = 75°$, for instance, in the 40 s Ar plasma-pretreated PTFE film, in which a substantial amount of surface graft copolymerization has occurred. In the case of PTFE films graft-copolymerized with DMAA, the amount of surface-grafted DMAA polymer is expressed as the [N]/[F] ratio, which is determined directly from the corrected N1s and F1s core-level spectral area ratio. The similarities in the surface microstructure are again revealed by a slightly higher [N]/[F] ratio at the outermost surface for the lightly grafted sample and a substantially lower [N]/[F] ratio at the outermost surface for the heavily grafted sample.

The effects of Ar plasma pretreatment time on the amounts of surface-grafted AAc, styrenesulfonic acid, and DMAA polymers on PTFE films are summarized

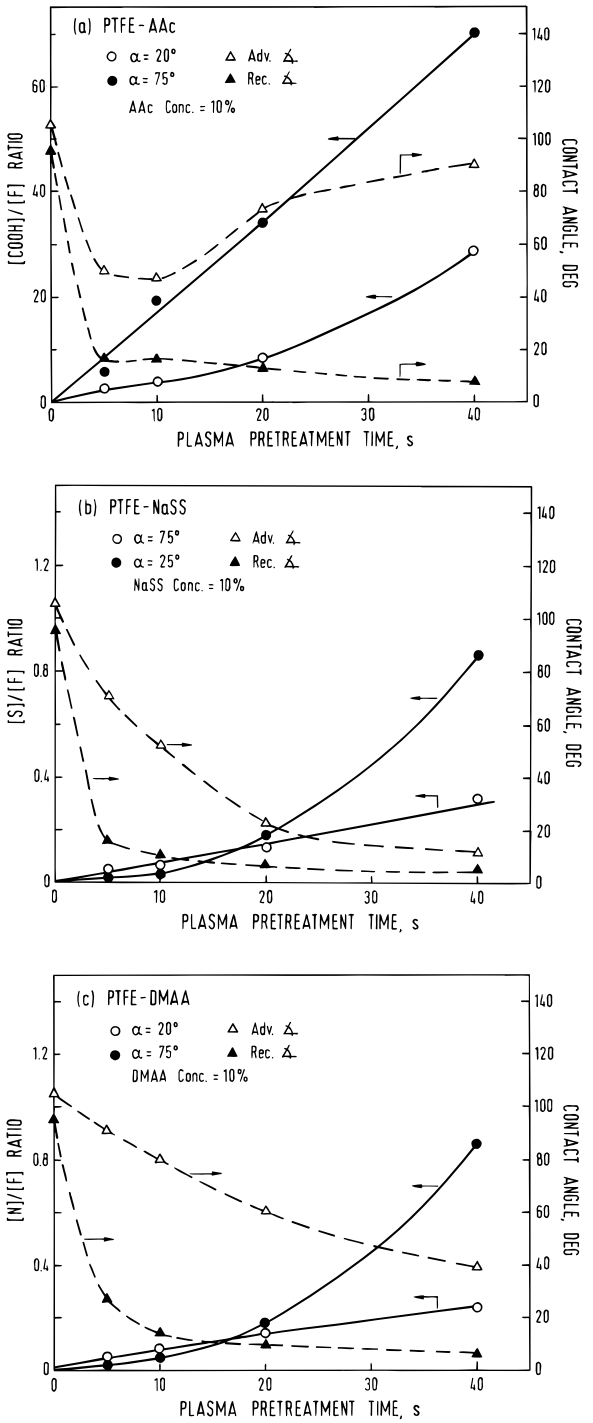

Figure 5. Effect of Ar plasma pretreatment time on the amount of surface-grafted (a) AAc, (b) styrenesulfonic acid, and (c) DMAA polymer on PTFE films.

in Figure 5a−c, respectively. The dependence of the surface microstructure on the extent of surface graft copolymerization is also clearly revealed by the XPS angular-dependent surface compositions. In all cases, the concentration of surface-grafted polymer increases with increasing plasma pretreatment time for the plasma pretreatment time used in the present study. This phenomenon, together with the increase in [O]/[F] ratio on plasma treatment, is consistent with a peroxide- or hydroxyl peroxide-initiated surface polymerization mechanism generally proposed for the near-UV light-induced graft copolymerization.[3] In general, graft copolymerization with the hydrophilic monomers readily gives rise to hydrophilic PTFE surfaces, as indicated by

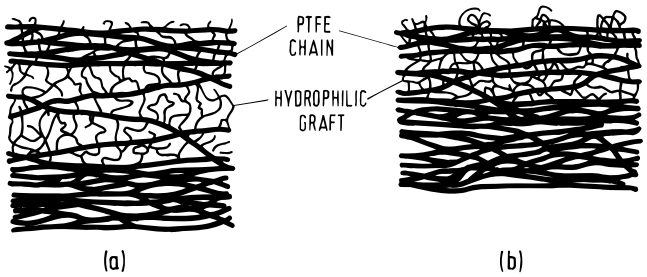

Figure 6. Schematic representation of the stratified surface microstructure: (a) complete penetration model and (b) partial penetration model with surface cluster formation.

the significant decreases in both the advancing and receding contact angles in Figure 5. Since the advancing edge of the water droplet always "sees" a polymer/air interface with submerged hydrophilic groups, whereas the receding edge "sees" a rehydrated interface with most of the hydrophilic groups reoriented, the presence of a hysteresis effect is suggestive of a restructured surface. The presence of contact angle hysteresis, even at low extent of surface grafting, indicates that surface contact angle is an even more surface-sensitive technique than XPS (1 nm or less[33] in the former versus an effective mean free path of 2.5 nm for C1s photoelectrons in an organic matrix[34] for the latter). However, it should be noted that earlier studies[30] had shown that the difference in composition between a hydrated and a dehydrated polymer surface could be resolved by the XPS technique using an *in situ* freeze-dried method. The substantially enhanced hysteresis effect in the case of PTFE films heavily graft-copolymerized with AAc is consistent with the presence of a stratified surface microstructure which is well-developed and involves a more complete penetration of the grafted chains beneath a thin surface layer that is much richer in the substrate chains, as shown schematically in Figure 6a. For PTFE surfaces more heavily grafted with styrenesulfonic acid and DMAA polymer, the hysteresis in advancing and receding contact angles becomes less obvious, although the angular-dependent XPS results still dictate the presence of a substrate-rich top surface layer. A partial penetration model with surface cluster formation, as depicted schematically in Figure 6b, can account for the decreasing contact angle hysteresis while still maintaining a substrate-rich surface structure. The partial penetration of the substrate chains must have resulted, at least in part, from the steric effect associated with the bulky substituent in styrenesulfonic acid and DMAA polymer.

The concentrations of surface-grafted AAc polymer, expressed as the [COOH]/[F] ratios from XPS analyses at $\alpha = 75°$, as a function of the AAc monomer concentrations used during graft copolymerization for PTFE films with 20 and 40 s of Ar plasma pretreatment are shown in Figure 7a. The corresponding amounts of the grafted AAc polymer in $\mu g/cm^2$, as determined from the amounts of complexed TB dye, are shown in Figure 7b for comparison. Thus, a good correlation is observed for the amounts of surface-grafted AAc polymer derived from the two analytical techniques. The amounts of grafted AAc polymer in $\mu g/cm^2$ on the present PTFE surfaces are also comparable in magnitude to those reported on other polymer substrates, such as Ar plasma-pretreated poly(ethylene terephthalate).[35] Figure 7c,d shows respectively the concentrations of surface-grafted styrenesulfonic acid polymer (expressed as the [S]/[F] ratios at $\alpha = 75°$) and the concentrations of

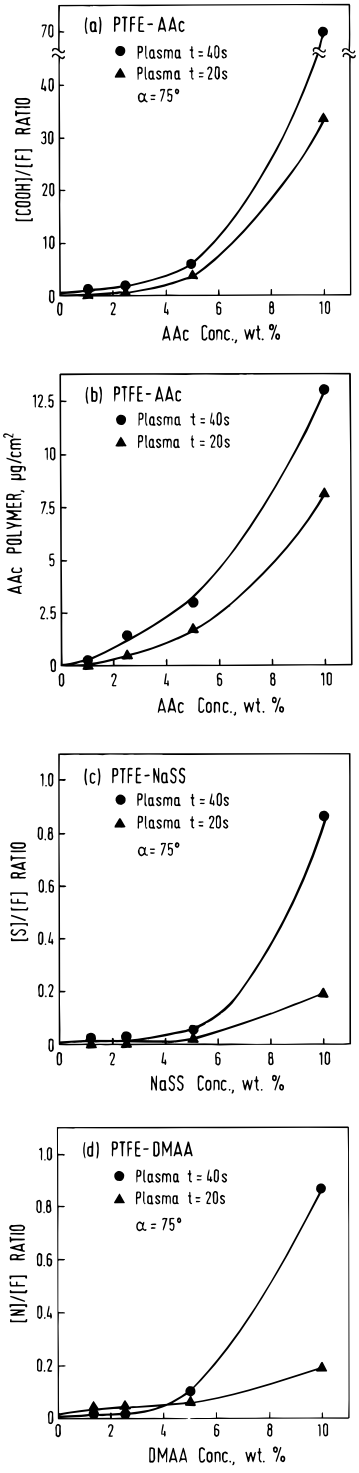

Figure 7. Surface concentrations of the grafted (a and b) AAc, (c) styrenesulfonic acid, and (d) DMAA polymers as a function of the respective monomer concentrations used during graft copolymerization.

surface-grafted DMAA polymer (expressed as the [N]/[F] ratios at $\alpha = 75°$) as a function of the respective monomer concentrations for PTFE films with 20 and 40 s of Ar plasma pretreatment. In general, the graft yields of the AAc, styrenesulfonic acid, and DMAA polymers increase with increasing monomer concentrations in the reaction media, with the sharpest increase observed for monomer concentrations above 5%.

Enzyme Immobilization and Assay. In the present study, attempts were made to correlate the activities of the covalently immobilized enzyme and the structure

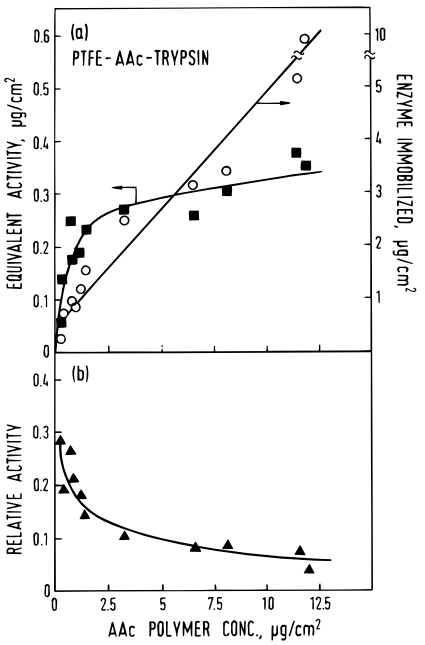

Figure 8. Surface concentrations and equivalent activities (a) and relative activities (b) of covalently immobilized trypsin as a function of the surface concentrations of grafted AAc polymer.

of the graft-copolymerized surface. Figure 8a shows the surface concentrations of covalently immobilized trypsin as a function of the surface concentrations of grafted AAc polymer. For the extent of graft copolymerization carried in the present work, the amounts of covalently immobilized trypsin increase almost linearly with increasing AAc polymer concentrations for grafted surfaces preactivated with water-soluble carbodiimide (WSC). The covalent immobilization was accomplished through amide linkage formation between the amino groups of trypsin and WSC-activated carboxyl groups of the grafted AAc polymer.[36] In the absence of a WSC intermediate, only a negligible amount of adsorpted or covalently bonded trypsin was detected on the AAc polymer-grafted surface, as suggested by the ninhydrin test. From the slope of the linear curve in Figure 8a, it is estimated that one immobilized enzyme molecule is associated with about 310 repeating units of AAc polymer chain. The activities of the covalently immobilized enzyme as a function of the surface AAc polymer concentrations are also plotted in Figure 8a. The surface enzyme activity, defined as the amount of free enzyme with an equivalent activity, is proportional to the concentration of the grafted AAc polymer only up to an AAc polymer concentration of about 2 μg/cm^2 and becomes saturated at higher AAc polymer concentrations. The saturation phenomenon at high surface AAc polymer concentration must have resulted from the hindered diffusion of the TAME molecules in the dense AAc polymer layer. The trypsin molecules at the top surface must have completely digested the TAME molecules before they can reach other active sites deep in the subsurface region. As a result, a considerable amount of the enzyme molecules remain dormant. A similar saturation phenomenon has also been observed for trypsin covalently immobilized on the AAc polymer-modified poly(ethylene terephthalate).[36]

The decrease or loss in enzyme activities as a result of covalent bond formation during immobilization and as a result of increasing interaction with the carboxyl groups at high AAc polymer concentration is illustrated

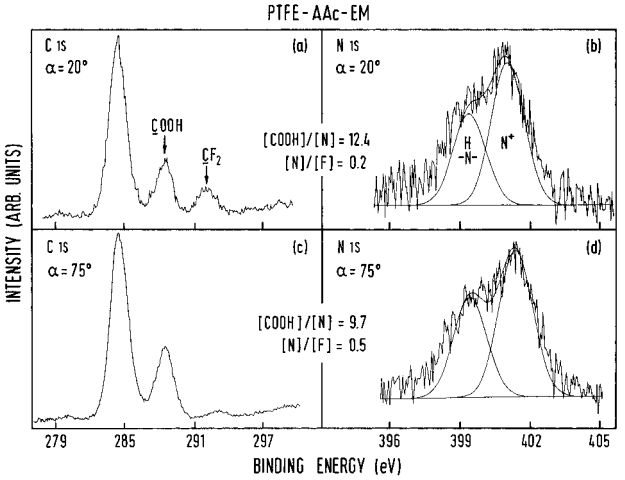

Figure 9. C1s and N1s core-level spectra, obtained at (a and b) $\alpha = 20°$ and (c and d) $\alpha = 75°$, for a 5 s Ar plasma-pretreated and 10% AAc graft-copolymerized PTFE film after coating of EM base.

by the changes in relative enzyme activities as a function the surface AAc polymer concentrations (Figure 8b). The relative activity at a particular AAc polymer concentration is simply defined as the ratio of the observed surface enzyme activity over the actual amount of the enzyme immobilized. In general, covalent immobilization can result in a substantial loss in enzyme activity. The phenomenon is probably associated with the loss of active sites due to covalent bond formation or the reorientation of the active sites after covalent bonding. Nevertheless, under optimum conditions, about 20−30% of the enzyme activities still remain. The relative activity of the enzyme also decreases with increasing amount of surface-grafted AAc polymer. This further loss in enzyme activity upon increasing the surface concentration of the AAc polymer, as discussed earlier, suggests that the dense AAc polymer layer must have substantially hindered the diffusion of TAME molecules to the active sites of trypsin which are buried deep inside the AAc polymer layer. Thus, in the presence of increasing diffusion limitations, the proportion of the enzyme that remains dormant increases with increasing AAc polymer concentration.

Interfacial Charge Transfer Interaction. The PTFE films with surface-grafted AAc and styrenesulfonic acid polymers can also be functionalized to render the film surface conductive and antistatic. Solution-coating of the neutral emeraldine (EM) base on the polymeric acid-modified PTFE surface readily results in the interfacial charge transfer interaction (protonation) between the coated EM base and the grafted polymer. XPS again provides a unique tool for the analysis of this charge transfer interaction. Figure 9 shows the respective C1s (a) and N1s (b) core-level spectra, obtained at $\alpha = 20°$, of a 5 s Ar plasma-pretreated and 10% AAc graft-copolymerized PTFE film after solution-coating of a thin layer of EM base. The corresponding C1s and N1s core-level spectra, obtained at $\alpha = 75°$, are shown in Figure 9c,d. Earlier XPS studies[37,38] have shown that the quinonoid imine (=N−), benzenoid amine (−NH−), and positively charged nitrogen atoms associated with a particular intrinsic redox state and protonation level of polyaniline can be quantified in the N1s curve-fitted spectrum. They correspond respectively to peak components with BEs at 398.2, 399.4, and >400 eV. Thus, the N1s core-level spectrum of the 50% intrinsically oxidized EM base can be curve-

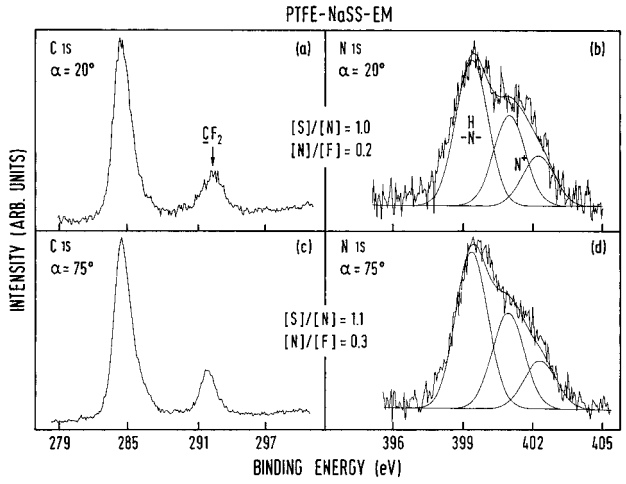

Figure 10. C1s and N1s core-level spectra, obtained at (a and b) $\alpha = 20°$ and (c and d) $\alpha = 75°$, for a 20 s Ar plasma-pretreated and 10% styrenesulfonic acid graft-copolymerized PTFE film after coating of EM base.

fitted with two major components of about equal areas. In the presence of a [COOH]/[N] ratio substantially above 0.5, as in the present case, not only all the imine nitrogen atoms but also some of the amine nitrogen atoms are protonated, as indicated by a $[N^+]/[N]$ ratio greater than 0.5.

The stratified surface microstructure resulting from the rearrangement of the grafted and substrate chains in the surface region persists even after coating of the aniline polymer. A higher CF_2/COOH intensity ratio is again observed at $\alpha = 20°$ than that at $\alpha = 75°$ in the C1s core-level spectra of the EM-coated films. Furthermore, a higher [N]/[F] signal intensity ratio is also observed in the subsurface layer at an α of 75°. Thus, the strong affinity of the imine nitrogen atoms of the EM base for the protonic acid groups of the grafted chains and the accompanying protonation must have caused the coated electroactive polymer chains to become submerged, together with the AAc polymer, beneath a thin surface layer. Interfacial charge transfer interactions between the coated EM base and the grafted AAc polymer reduce the surface resistivity of the PTFE film to only in the order of 10^7 Ω/□. This conductivity value, however, is substantially below that of about 10 S/cm observed in the fully protonated EM base[24] and must have resulted from the continuing presence of the stratified surface microstructure, even after the coating of EM base, as well as the fact that only a thin layer of the EM base was coated.

In the case of EM coated on PTFE films with surface-grafted styrenesulfonic acid polymer, the [N]/[F] ratios obtained at the two take-off angles do not differ substantially, although a slightly higher ratio is still discernible in the subsurface layer. This observation is consistent with the presence of a stratified surface microstructure, which is less well-developed in the case of styrenesulfonic acid graft-copolymerized PTFE surface (see Figure 6b). Figure 10 shows the respective C1s and N1s core-level spectra obtained at two take-off angles for a 20 s Ar plasma-pretreated and a 10% styrenesulfonic acid graft-copolymerized PTFE film after coating of a thin layer of EM base. Based on the fixed fwhm approach in peak synthesis used in the present work, the high BE tail in each N1s spectrum, attributable to the protonated (positively charged) nitrogens, has been resolved into two peaks separated at about 1.5 and 3 eV from the amine peak, respectively. Nevertheless, the high BE tail is more appropriately ascribed to positively charged nitrogens with a continuous distribution of BEs. Again, the strong charge transfer interactions between the coated EM base and the grafted sulfonic acid groups are readily revealed by the presence of $[N^+]/[N]$ ratios in the order of 50% or more. The surface conductivity values for the styrenesulfonic acid-grafted and EM-coated films are comparable in magnitude to those observed on the AAc polymer-grafted and EM-coated films. Finally, we wish to emphasize that the interfacial charge transfer interactions between the coated EM chains and the grafted polymeric acids not only give rise to a semiconductive PTFE surface but also result in strong adhesion of the electroactive polymer on the PTFE surface. The electroactive polymer layer was not removed from the modified PTFE surface in a simple peel test, in which a piece of Scotch tape was applied to the surface and subsequently removed.[39,40] This conclusion is based on the persistence of surface conductivity and the high $[N^+]/[N]$ ratio in the N1s spectrum after the test.

Conclusion

Surface modification of Ar plasma-pretreated PTFE films was carried out via near-UV light-induced graft copolymerization with AAc, NaSS, and DMAA. The structure and chemical composition of each copolymer interface were analyzed by angle-resolved XPS. For PTFE substrate with a substantial amount of grafting, the hydrophilic graft penetrated or became partially submerged beneath a thin surface layer of dense substrate chains to form a stratified microstructure. This surface microstructure was further confirmed by the dynamic contact angle results. The AAc polymer-modified PTFE films were further functionalized via covalent immobilization of trypsin. The enzyme activities became saturated upon increasing the concentration of surface-grafted AAc polymer. On the other hand, coating of the AAc or styrenesulfonic acid polymer-grafted PTFE films with a thin layer of polyaniline readily gave rise to a semiconductive PTFE surface, as a result of interfacial charge transfer interaction (protonation).

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