Protonation of Polyaniline by Surface-Functionalized Polymer Substrates

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SYNOPSIS

The protonation of solution-coated emeraldine (EM) base by sulfonic and carboxylic acid groups on surface-functionalized low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), poly(ethylene terephthalate) (PET), and polytetrafluoroethylene (PTFE) films were characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and conductivity measurements. Surface functionalizations were achieved by sulfonation (for LDPE, HDPE, PP, and PET), by hydrolysis (for PET), and by near-UV-light-induced surface graft copolymerization with the Na salt of styrene sulfonic acid and acrylic acid (for all substrates). The efficiency of surface functionalization by graft copolymerization is substantially enhanced for substrates pretreated with O_3 or Ar plasma. Protonation levels of 50% can be readily achieved for EM coated on sulfonic acid, but not carboxylic acid, functionalized surfaces. The extent of protonation, however, is also dependent on the microstructures of the modified substrate surfaces. In all cases, charge transfer interactions between the EM layer and the functionalized substrates readily result in good adhesion of the electroactive polymer on the polymer substrates to give rise to conductive surface structures. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Surface modification of polymers is a convenient and effective means of incorporating specific physicochemical properties, such as hydrophilicity, biocompatibility, adhesion, and lubricative properties.[1-3] A large number of techniques have been developed for chemical modification of polymer surfaces. They include plasma treatment,[4,5] corona discharge,[6] ozone treatment,[7] electron beam bombardment,[8] ultraviolet (UV) irradiation,[9] X-ray irradiation,[10] acid etching,[11,12] and surface graft copolymerization.[13-17] A variety of polar and functional groups are generated on the polymer surfaces as a result of these modifications. Graft copolymerization appears to be one of the most versatile methods in the molecular design of polymer surfaces to achieve specific functionalities and applications, such as en-

zyme–protein immobilization and coupling via covalent bonding with the grafted functional groups.[18,19] Earlier work[20] has also demonstrated that the surface of electroactive polymer films, such as polyaniline (PAN) films, can be rendered self-protonated and conductive via graft copolymerization with acrylic acid (AAc) and styrenesulfonic acid (SSAc). Accordingly, it should be interesting to explore the charge transfer interactions between the electroactive polymer and the surface-functionalized polymer substrates. The latter includes pristine, O_3, or Ar plasma pretreated conventional polymer films, such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), poly(ethylene terephthalate) (PET), and poly(tetrafluoroethylene) (PTFE) after surface modification via graft copolymerization with AAc and SSAc. Other substrate surface functionalization techniques, such as sulfonation (for LDPE, HDPE, PP, and PET) and hydrolysis (for PET) have also been explored. An earlier study[21] reported on the characterization of polypyrrole coated on the surfaces of sulfonated polyethylene films.

EXPERIMENTAL

Materials

The PET, LDPE, PP, and PTFE films with thicknesses of about 100, 125, 130, and 100 μm, respectively, were obtained from Goodfellow Inc. (U.K.). The HDPE films with a thickness of about 20 μm were of commercial grade. All the films were cut into strips of about 1.5 × 3.5 cm in size and were purified by Soxhlet extraction with methanol for about 6 h. The aniline, AAc, and Na salt of styrenesulfonic acid (NaSS) monomers were used as received from Aldrich Chemical Co.

Film Pretreatments and Graft Copolymerization

The procedures, conditions, and equipment used for Ar plasma[14] and ozone[22] pretreatments were similar to those described earlier. Ozone pretreatments of PET, LDPE, PP, and HDPE were carried out in a Fisher model 500 ozone generator with a pure oxygen input flow rate of 100 L h^{-1} and an O_3 production rate of about 3 g h^{-1}. An O_3 pretreatment time of 20 min was found to be sufficient in activating the polymer surfaces. Due to the relative inertness of the PTFE film to O_3 pretreatment, Ar plasma pretreatment was employed instead. The plasma pretreatment of PTFE films was carried out in a parallel plane electrode reactor with an Ar pressure of about 0.15 Torr at ignition. The electrical power maintaining the plasma was supplied by a RF generator operating at 28 W and 13.56 MHz. The pretreatment time was fixed at 10 s. This pretreatment time has been found to be sufficient in activating the PTFE surface without causing excessive surface crosslinking and degradation.[14]

The near-UV-light-induced graft copolymerization of AAc or NaSS monomers on the pristine and pretreated substrates was carried out in a Pyrex tube containing 20 mL of 10 wt % aqueous monomer solution, according to the procedures reported earlier.[14] The monomer solution was thoroughly degassed and sealed off under a N_2 atmosphere. It was then subjected to near-UV irradiation (150-W xenon source) for about 30 min.

Sulfonation and Hydrolysis

Surface functionalization via sulfonation was also carried out for the PET, LDPE, PP, and HDPE films. In each case, the polymer films were exposed to 30% fuming sulfuric acid for periods ranging from 15 min to 15 h in a 500-cm^3 evacuated chamber at a SO_3 partial pressure of about 3.5 mmHg. The sulfonated films were first washed with methanol and then throughly rinsed with deionized water. The weights of films before and after sulfonation were recorded. In the case of PET films, surface modification via hydrolysis reaction was also performed. The films were exposed initially to NaOH concentrations of 0.1, 0.5, 1.0, and 2.0M for periods of 1–19 h, either at room temperature or at 65°C. The base-treated samples were then hydrolysed in 1M $HClO_4$ for about 24 h before being thoroughly rinsed with deionized water.

Coating of the Electroactive Polymer

The surface-functionalized polymer substrates were immersed in a 0.1 wt % N-methylpyrrolidinone (NMP) solution of the neutral emeraldine (EM) base. The EM base in powder form was prepared according to the method reported in the literature.[23] The coated film was pumped to dryness, followed by soaking in deionized water for 48 h to remove the residual NMP.

Surface Characterization

The functionalized surfaces before and after coating of polyaniline were characterized by angle-resolved X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and conductivity measurements. XPS measurements were made on a VG ESCALAB MkII spectrometer with a MgKα X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). To compensate for surface charging effects, all binding energies (BEs) were referenced to the C_{1s} neutral carbon peak at 284.6 eV. In peak synthesis, the linewidth (fullwidth at half maximum) of 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 is accurate to within ±10%. The core-level spectra were obtained at photoelectron take-off angles (α, measured with respect to the film surface) of 20° and 75°. FTIR measurements were performed on a Shimadzu model DR 8101 spectrophotometer under both the transmission and attenuated total reflection (ATR) modes. The electrical conductivities of the modified film surfaces were measured using the standard four-probe and two-probe techniques. Static water contact angles for the hydrolysed PET surfaces were

measured by the sessile drop method, using a 3-μL water droplet in a telescopic goniometer [Ramé-hart, model 100-00-(230)].

RESULTS AND DISCUSSION

Surface Functionalization by Sulfonation

Figure 1 shows the weight change behavior of LDPE, HDPE, PP, and PET substrates as a function of sulfonation time under the present experimental conditions. Both LDPE and HDPE films show a continuous weight gain with sulfonation time. However, after 15 h of sulfonation, both films become brittle and porous. For PP and PET films, prolonged sulfonation results in degradation and a continuous loss of the film materials, although a small weight gain has been observed during the first hour of sulfonation in PP films. The extent of sulfonation in the surface region for each film, expressed as the [—SO_3^-]/[substrate monomer] mole ratio, can be evaluated from the S_{2p} and stoichiometry-corrected C_{1s} core-level spectral area ratio. The S_{2p} core-level spectra for the sulfonated samples show a characteristic $S_{2p_{3/2}}$ BE at about 167.8 eV, attributable to the covalently bonded sulfonic acid (—SO_3^-) group.[24] Figure 2 summarizes the extents of surface sulfonation, as a function of sulfonation time, for
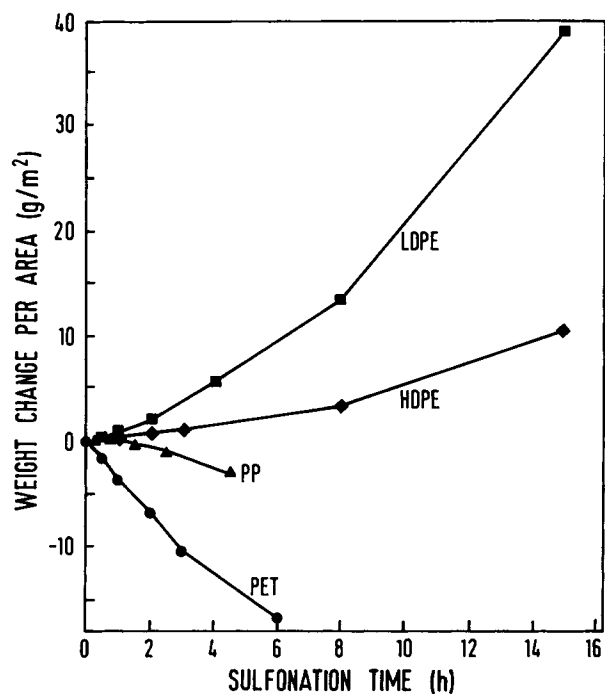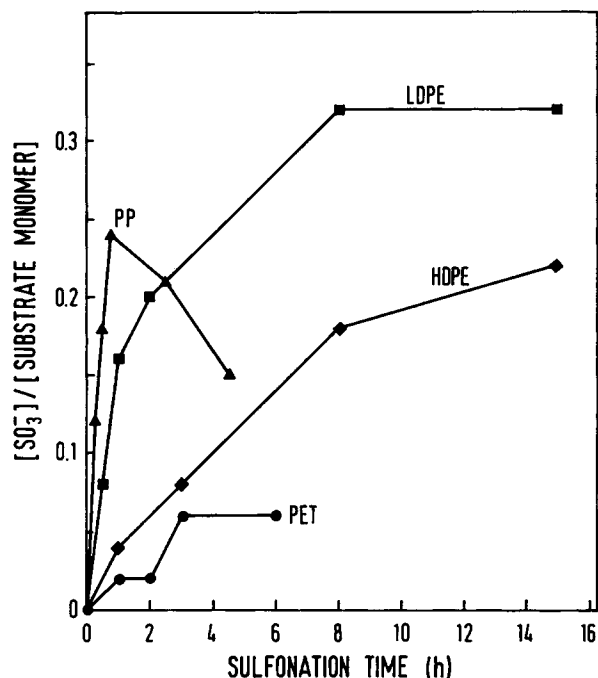
Figure 2   Sulfonic acid to substrate monomer ratios as a function of sulfonation time.

the four types of polymer substrates studied. The extents of sulfonation for some selected samples used for subsequent coating of electroactive polymers are given in Table I. Prolonged sulfonation (> 1 h) can also result in the oxidation of the polymer chain. This conclusion is based on the fact that the ATR-IR spectra of LDPE, HDPE, and PP films, which do not contain any carbonyl group initially, reveal the presence of a weak carbonyl absorption band in the region of 1650–1850 cm^{-1}, in addition to the stretching modes[25] of sulfonic acid groups at about 1040 and 1200 cm^{-1}, after prolonged exposure to fuming H_2SO_4. Figures 3(a)–3(c) compare the lineshapes of the respective C_{1s} core-level spectra for the pristine, 1-h sulfonated, and 8-h sulfonated LDPE films. Thus, increasing the extent of sulfonation readily results in the enhancement of the intensity of the C_{1s} high BE tail, attributable to the carbon species with various degrees of oxidation, such as the $\underline{C}$ — O, $\underline{C}$ = O and O — $\underline{C}$ = O species at BEs of about 286.2, 287.8, and 288.7 eV, respectively.[26]

The XPS data in Table I also reveal that the extent of sulfonation for each substrate does not appear to exhibit any dependence on the photoelectron take-off angle, α. This result readily suggests that sulfonation occurs uniformly, at least within the probing depth of the XPS technique.

Figure 1   Weight change per unit area as a function of sulfonation time for the various polymer substrates.

Table I   XPS Results for EM Base Coated on Various Sulfonated Substrates

Substrate	Sulfonation Time (h)	α^a	$\dfrac{[-SO_3^-]}{[\text{Monomer}]^b}$	$\dfrac{[-SO_3^-]}{[N]}$	$\dfrac{[-COO^-]}{[N]}$	$\dfrac{[N^+]}{[N]}$	$\dfrac{[-NH-]}{[N]}$	$\dfrac{[=N-]}{[N]}$	Surface Resistance $(\Omega/\square)$
LDPE	0.5	20	—	—	—	—	—	—	
		75	0.08	0.22	0.0	0.25	0.65	0.10	10^6
LDPE	1.0	20	0.16	0.65	0.16	0.48	0.52	0.0	
		75	0.16	0.72	0.11	0.49	0.51	0.0	10^4
LDPE	8.0	20	0.32	0.86	0.31	0.51	0.49	0.0	
		75	0.32	0.89	0.25	0.48	0.52	0.0	10^3
HDPE	1.0	20	0.04	0.13	0.0	0.23	0.61	0.16	
		75	0.04	0.12	0.0	0.27	0.60	0.13	10^7
HDPE	8.0	20	0.18	0.79	0.22	0.51	0.49	0.0	
		75	0.16	0.80	0.16	0.50	0.50	0.0	10^4
PP	0.25	20	—	—	—	—	—	—	
		75	0.12	0.16	0.0	0.31	0.59	0.10	10^6
PP	0.5	20	0.18	0.53	0.0	0.45	0.55	0.0	
		75	0.15	0.49	0.0	0.42	0.58	0.0	10^4
PET	1.0	20	—	—	—	—	—	—	
		75	0.02	0.08	1.20^c	0.21	0.53	0.26	10^7
PET	3.0	20	0.06	0.10	1.80^c	0.25	0.62	0.13	
		75	0.05	0.11	1.50^c	0.28	0.56	0.16	10^7

^{a} α = XPS photoelectron take-off angles (with respect to film surface) in degrees.

^{b} $[-SO_3^-]$ to [substrate monomer] mole ratios measured before coating of the EM base.

^{c} Including contributions from neutral $O-\underline{C}=O$ groups of PET substrates.

Surface Functionalization by Hydrolysis

It is well-known that the ester groups of PET are readily susceptible to hydrolysis in the presence of a base.[27] The formation of the carboxylic acid groups also gives rise to a more hydrophilic PET surface. For example, the static water contact angle is reduced from about 75° for the pristine PET film to about 50° after the film has been exposed to $1M$ NaOH for 19 h. The concentrations of the carboxyl groups generated on PET surfaces become rapidly saturated at about 10^{-8} mol/cm^2, as determined by the dye interaction method,[27] after 1 h of exposure to $1M$ NaOH. Increasing the base concentration to $2M$ or hydrolysis temperature to 65°C does not appear to result in a significant increase in the surface carboxyl concentration.

Surface Functionalization by Graft Copolymerization

The possible reaction mechanisms between ozone and saturated hydrocarbons have been extensively studied.[28] Besides the peroxide groups, other functional and polar groups, such as the carbonyl and carboxyl groups, may also form upon prolonged O_3 exposure. The formation of peroxide groups on O_3

and Ar plasma-pretreated polymer surfaces has been evaluated quantitatively.[7,13] In the present work, the O_3-pretreated LDPE, HDPE, PP, and PET films, as well as the plasma-pretreated PTFE films, are functionalized by near-UV-light-induced graft copolymerization with NaSS and AAc monomers.

The presence of surface-grafted NaSS polymer is indicated by the appearance of the S_{2p} core-level signal at a BE of about 168 eV. The density of the surface graft can be determined from the sensitivity factors corrected S_{2p} and C_{1s} peak area ratio. For instance, in the cases of surface-grafted LDPE and HDPE films:

$$\frac{\text{NaSS}}{\text{Substrate}} = \frac{\text{area of } S_{2p} \text{ peak}}{[\text{Total } C_{1s} \text{ area} - (\text{area of } S_{2p} \times 8)] \times \frac{1}{2}}$$

The stoichiometric factors of 8 and $\frac{1}{2}$ are introduced to account for the fact that there are, respectively, 8 carbons in each NaSS units and 2 carbons per each repeating unit of the substrate polymer. In the cases of PET and PP substrates, the factor of $\frac{1}{2}$ is replaced by $\frac{1}{10}$ and $\frac{1}{3}$, respectively. The amount of the NaSS polymer grafted to the PTFE surface can be
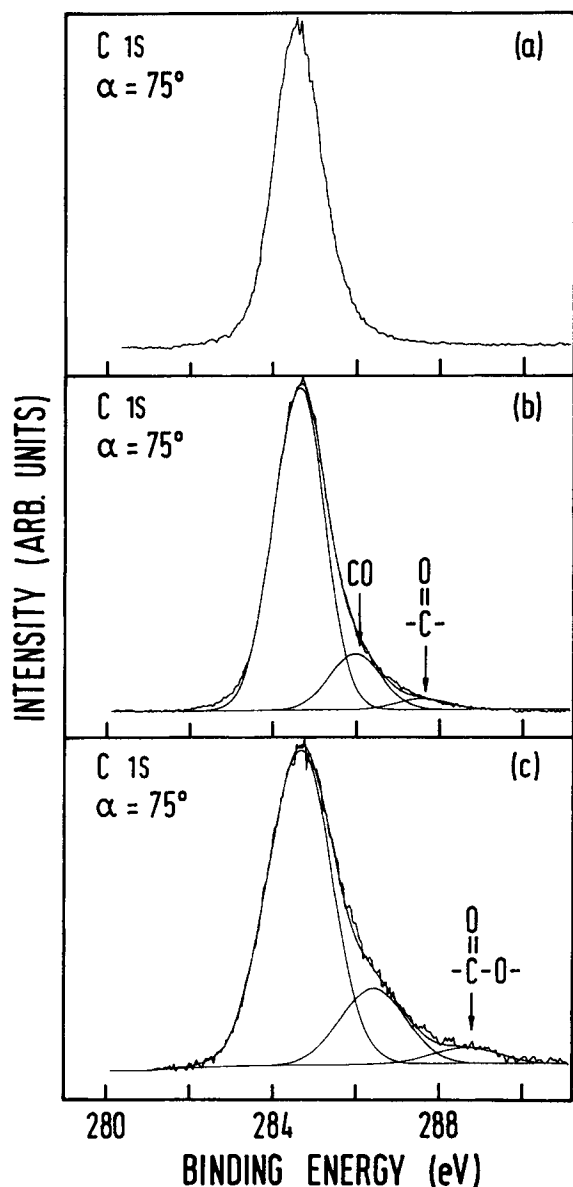
Figure 3 C_{1s} core-level spectra for (a) a pristine LDPE film, (b) a 1-h sulfonated LDPE film, and (c) a 8-h sulfonated LDPE film.

readily determined from the sensitivity factors corrected S_{2p} and F_{1s} core-level spectral area ratio.

The AAc polymer has a distinct C_{1s} peak component at a BE of about 288.7 eV, attributable to the COOH functional groups. The amount of the AAc polymer grafted on PTFE can be determined directly from the [COOH]/[F] mole ratio. For the polyolefin films, the amount of the AAc polymer grafted is determined by comparing the COOH component area in the C_{1s} core-level spectrum and the main neutral C_{1s} peak at 284.6 eV, taking into

account the fact that each AAc monomer unit also contributes two carbon atoms to the latter peak component. For a PET film grafted with AAc polymer, the difference in the C_{1s} core-level spectral areas of the $O-\underline{C}=O$ component (BE $\sim$ 288.7 eV) and the $\underline{C}-O$ component (BE $\sim$ 286.2 eV) yields the area of the $O-\underline{C}=O$ component arising from the grafted AAc polymer as pristine PET has equal amounts of the two components.

Table II summarizes the graft densities, as revealed by the XPS analyses and expressed as the molar ratios (based on monomer units) of the surface graft to the substrate polymers, at two photoelectron take-off angles of 20° and 75°. Both the pristine and pretreated substrates are presented for comparison purpose. In each case, the density of surface grafting is enhanced by ozone (in the cases of LDPE, HDPE, PP, and PET films) or Ar plasma (in the case of PTFE film) pretreatment. This observation is consistent with a peroxide-initiated polymerization mechanism suggested earlier. The XPS data in Table II further suggest that a lower density of grafting is generally detected at the more surface sensitive take-off angle of 20°, especially in the cases where substantial graftings have occurred. Thus, the angular-dependent XPS results clearly indicate that the hydrophilic graft is somewhat submerged beneath a very thin surface layer, which is richer in the substrate polymer. This surface microstructure must have resulted from the migration and countermigration of the substrate and the graft chains during copolymerization and subsequent drying and storage. This process is made possible probably by the fact that modification of the substrate polymer chains in the surface region by ozone or plasma pretreatment, UV irradiation during grafting, and finally graft copolymerization must have substantially lowered their glass transition temperature.[14] The reorientation of polar groups into the hydrophobic bulk phase has been known to be a thermodynamically favorable process.[29] This stratified microstructure may also account for the reduced protonation efficiency of the sulfonic acid groups of the grafted polymer (see below).

Interaction between EM Base and Surface-Functionalized Polymer Substracts

XPS has also been shown to be an ideal tool for the study of the intrinsic structure and charge transfer interaction in N-containing electroactive polymers.[30] In the case of PAN, the quinonoid imine ($=N-$), benzenoid amine ($-NH-$), and positively charged nitrogens, corresponding to any particular intrinsic

Table II   XPS Results for EM Base Coated on Substrates with Surface-Grafted NaSS Polymer

Substrate	Pretreatment before Grafting	α^a	Density of Grafting[b]	[—SO$_3^-$] [N]	[N$^+$] [N]	[—NH—] [N]	[=N—] [N]	Surface Resistance (Ω/□)
LDPE	None	20	0.21	0.24	0.27	0.59	0.14	
		75	0.33	0.31	0.32	0.57	0.11	10^7
LDPE	Ozone	20	1.21	0.73	0.45	0.55	0.0	
		75	6.50	0.60	0.46	0.54	0.0	10^5
HDPE	None	20	0.56	0.44	0.29	0.61	0.10	
		75	0.86	0.41	0.28	0.61	0.11	10^7
HDPE	Ozone	20	1.08	0.53	0.28	0.60	0.12	
		75	2.01	0.48	0.28	0.60	0.11	10^6
PP	None	20	0.56	0.26	0.27	0.62	0.11	
		75	0.57	0.23	0.27	0.59	0.14	10^7
PP	Ozone	20	2.38	0.71	0.42	0.58	0.0	
		75	8.57	0.61	0.40	0.57	0.03	10^5
PET	None	20	1.97	0.60	0.36	0.54	0.10	
		75	1.16	0.43	0.34	0.55	0.11	10^6
PET	Ozone	20	2.90	0.43	0.34	0.57	0.09	
		75	2.04	0.41	0.34	0.57	0.09	10^6
PTFE	None	20	—	—	—	—	—	
		75	—	—	—	—	—	—
PTFE	Ar plasma	20	4.08	0.50	0.35	0.57	0.08	
		75	6.08	0.52	0.37	0.55	0.08	10^6

[a] α = XPS photoelectron take-off angles in degrees.

[b] Expressed as [—SO$_3^-$] to [substrate monomer] mole ratios within the probing depth of the XPS technique and measured before the coating of EM layer.

redox state and protonation level, can be quantitatively differentiated in the properly curve-fitted N$_{1s}$ core-level spectrum. They correspond to peak components with BEs at about 398.2, 399.4, and > 400 eV, respectively. It has been well established that protonation of the 50% intrinsically oxidized EM base (containing approximately equal amounts of imine and amine nitrogens) occurs preferentially at the imine nitrogens.[23] The amine nitrogens are susceptible to protonation only under certain conditions.[31]

The N$_{1s}$ core-level spectra in Figure 4 illustrate the effect of sulfonation times (and thus the extents of sulfonation) of two HDPE substrates on the protonation levels of the coated EM base. The N$_{1s}$ core-level spectrum for EM base coated on 1 h sulfonated HDPE film is characteristic of that of the partially protonated EM base with about equal amounts of the imine and N$^+$ components [Fig. 4(a)]. Complete protonation was observed for the HDPE substrate exposed to 8 h of fuming H$_2$SO$_4$, as indicated by the complete disappearance of the imine nitrogens and the appearance of about 50% of positively charged nitrogens [Fig. 4(b)]. The EM base does not coat on pristine HDPE and PP films and adheres only

poorly on pristine LDPE and PET surfaces when cast from dilute NMP solutions. Good adhesion, however, was observed on all the modified substrates. The ATR-FTIR spectra for the pristine LDPE and 1 h sulfonated LDPE films after coating of EM base are shown in Figures 5(a) and 5(b), respectively. The latter spectrum reveals an enhanced and broadened absorption band at about 1150 cm^{-1}, which is associated with high electrical conductivity and a high degree of electron delocalization in the highly protonated and conductive polyaniline.[32] The N$_{1s}$ core-level spectrum of this sample also shows a protonation level of about 50%.

Table I summarizes the chemical states of the EM base, as revealed by XPS, when coated on the various sulfonated substrates. Thus, under the present experimental condition, 1 h of sulfonation of LDPE produces sufficient —SO$_3^-$ groups for the complete protonation of the imine nitrogens in the coated EM base. A substantially reduced sulfonation time of 15 min is sufficient for a PP film to yield a protonation level of almost 50% in the coated EM. On the other hand, prolonged sulfonation (8 h) is required for the functionalization of the HDPE surface to achieve 50% protonation in EM. The gen-
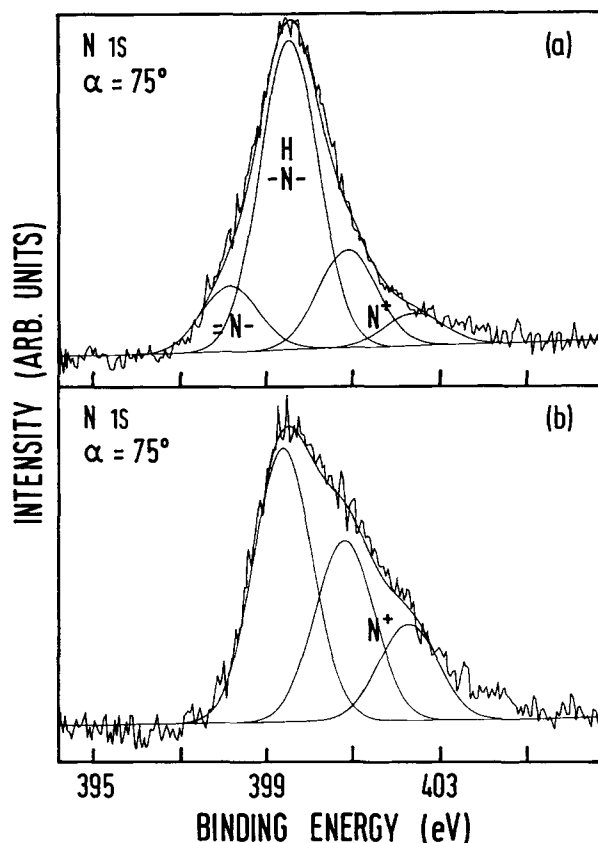
Figure 4 N_{1s} core-level spectra for EM base coated on (a) a 1-h sulfonated HDPE film and (b) a 8-h sulfonated HDPE film.

erally low protonation levels observed for the sulfonated PET surface are attributable to the continuous loss of the highly sulfonated substrate materials from the film surface during exposure to fuming H_2SO_4. The lack of any angular dependence of the protonation levels on all substrate surfaces readily indicates that protonation occurs uniformly throughout the coated EM layers. The thickness of the EM coating with reference to the contacting substrate chains is probably in the order of 7–10 nm or that of the sampling depth of the XPS technique.* This estimation is consistent with the fact that core-level signals from the underlying substrate chains are still discernible in all cases. Finally, the electrical resistances of the substrate surfaces with a fully ($\sim$ 50%) protonated EM layer are reduced to the order of 10^3–10^4 $\Omega/\square$.

We next investigate the charge transfer interaction between EM base and the surface-functional-

* Assuming the sampling depth to be 3λ, the approximate thickness of the coated layer is estimated from the product 3λ sin α, where λ and α are taken to be 2.5 nm and 75°, respectively.

ized substrates from graft copolymerization with NaSS and AAc. Figures 6(a) and 6(b) show the N_{1s} core-level spectra of the EM base coated on NaSS graft copolymerized pristine and ozone-pretreated PP films, respectively. The enhanced density of surface grafting in ozone-pretreated substrate readily gives rise to a protonation level close to 50% in the EM layer. Similar protonation behavior is observed in the case of pristine and ozone-pretreated LDPE films after graft copolymerization with NaSS. However, in the cases of HDPE and PET substrates, the increase in the efficiency of surface grafting of the NaSS polymer is less significant. As a result, the protonation level of the coated EM layer remains substantially below 50%, even for the ozone-pretreated films. The chemical states of the coated EM base on the various NaSS graft-copolymerized substrates are summarized in Table II. Due to the inertness of the PTFE substrate, the near-UV-light-induced graft copolymerization with NaSS occurs *to a significant extent only on the Ar plasma-pretreated PTFE surfaces.*[14] The protonation level of the EM coated on this NaSS polymer-grafted PTFE surface is only in the order of 30%. Again, the lack of any significant angular dependence of the $[N^+]/[N]$ ratios for all the substrates readily suggests that the EM layers are uniformly protonated.
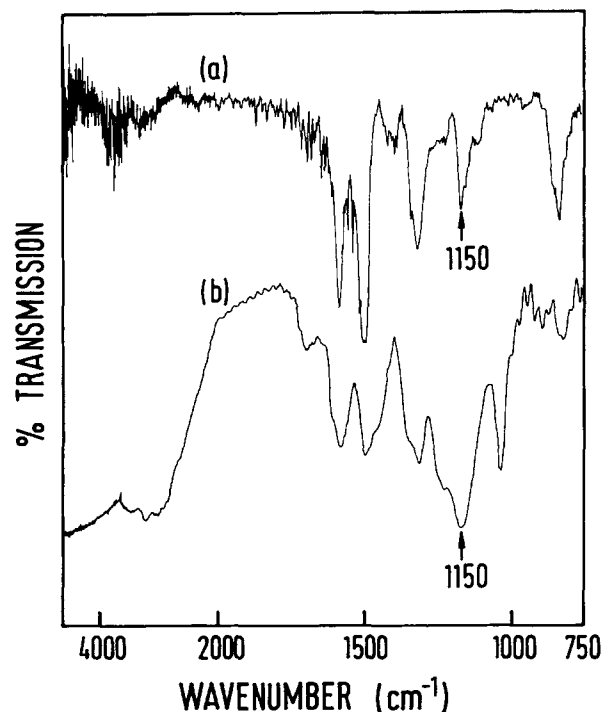

Figure 5 ATR-FTIR spectra for EM base coated on (a) a pristine LDPE film and (b) a 1-h sulfonated LDPE film.

For all the NaSS graft-copolymerized substrate surfaces, the absence of any appreciable Na_{1s} core-level signals readily indicates that the functional groups of the surface graft exist predominantly as sulfonic acid groups. However, comparison of the $[-SO_3^-]$/[monomer], $[-SO_3^-]$/[N], and $[N^+]$/[N] ratios in Tables I and II suggests that the $-SO_3^-$ groups of the grafted NaSS polymer is less effective than the $-SO_3^-$ groups of the sulfonated surface in protonating the coated EM base. This phenomenon is probably attributable to factors, such as stereo-specificity and steric effects, associated with the grafted NaSS polymer. Furthermore, the tendency for the surface-grafted polymer to migrate or submerge below a substrate-rich top layer, as indicate by the angular-dependent XPS data, may further reduce the protonation efficiency of the sulfonic acid groups of the grafted polymer.

The protonation efficiency of the surface-grafted polymer is further reduced when the sulfonic acid functional groups are replaced by a weak organic acid, such as carboxylic acid groups. The XPS results
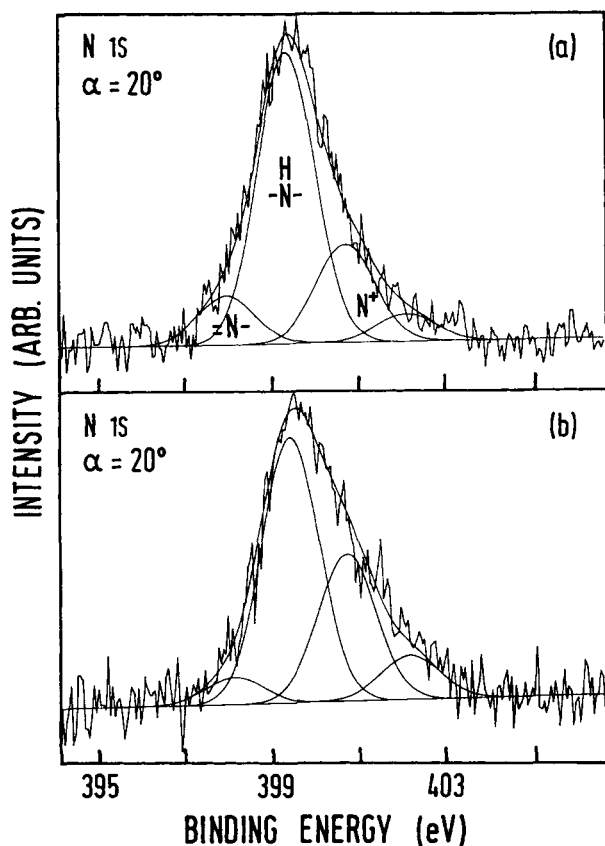

Figure 7 N_{1s} core-level spectra for EM base coated on a hydrolysed PET surface ($[COOH] \sim 10^{-8}$ mol/cm^2).

in Table III show that coating of EM base on an AAc polymer-grafted substrate will also result in an inherently protonated surface structure. However, the protonation levels are usually much below 50%, even in the presence of a large excess of the COOH functional groups or a [COOH]/[N] ratio much greater than 1. As a consequence, the electrical conductivities of these surface compositions are usually 3 to 4 orders of magnitude below those of the surface structures with sulfonic acid as the functional groups. Our recent studies on the direct protonation of EM base films by poly(acrylic acid) indicate that protonation levels substantially below 50% are always obtained even in the presence of a large excess of the acid.

The relatively poor protonation efficiency of the carboxylic acid group is further demonstrated by the N_{1s} core-level spectrum (Fig. 7) of the EM base coated on an extensively hydrolysed PET surface ($[COOH] \sim 10^{-8}$ mol/cm^2 and $[COOH]/[N] \sim 3.1$).* The relatively low $[N^+]$/[N] ratio and the persistence of a large proportion of the imine nitrogens readily indicate that the EM base is only partially protonated.

Finally, it is appropriate to emphasize that the adhesion of the electroactive polymer on the functionalized polymer substrates has been substantially improved by the electrostatic interaction at the interface. The interaction is made possible through direct protonation of the coated polyaniline by the

Figure 6 N_{1s} core-level spectra for EM base coated on NaSS graft-copolymerized (a) pristine PP film and (b) O_3-pretreated PP film.
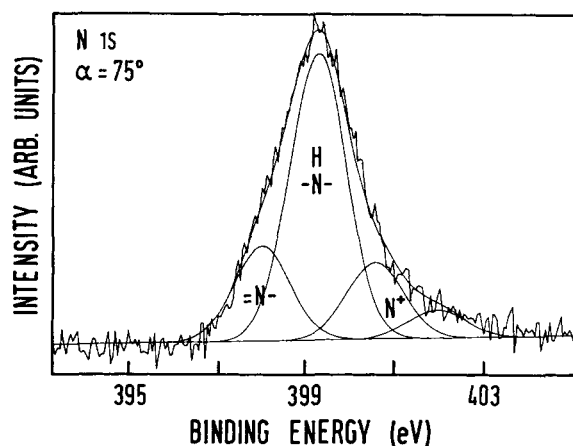
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* Estimation based on an EM layer with thickness in the order of that of the probing depth of the XPS technique, say about 75 Å. This assumption is valid as the underlying $\underline{C}OOH$ and $O=\underline{C}-O$ groups of the hydrolysed PET substrate are still visible in the C_{1s} core-level spectrum.

Table III XPS Results for EM Base Coated on Substrates with Surface-Grafted AAc Polymer

Substrate	Pretreatment before Grafting	α[a]	Density of Grafting[b]	[—COO⁻] [N]	[N⁺] [N]	[—NH—] [N]	[=N—] [N]	Surface Resistance ($\Omega/\square$)
LDPE	None	20	0.11	6.60[c]	0.24	0.62	0.14	
		75	0.15	4.36	0.26	0.60	0.14	$> 10^7$
LDPE	Ozone	20	0.18	1.17	0.26	0.60	0.14	
		75	0.39	1.03	0.19	0.63	0.18	10^7
HDPE	None	20	0.25	2.00[c]	0.20	0.60	0.20	
		75	0.20	2.20	0.34	0.53	0.13	$> 10^7$
HDPE	Ozone	20	0.65	0.73	0.21	0.61	0.18	
		75	0.52	0.66	0.24	0.60	0.16	10^7
PP	None	20	0.12	2.06[c]	0.23	0.62	0.15	
		75	0.12	1.72	0.24	0.61	0.05	$> 10^7$
PP	Ozone	20	0.48	1.83	0.30	0.63	0.07	
		75	0.63	1.64	0.30	0.62	0.08	10^7
PET	None	20	0.93	0.46	0.19	0.60	0.21	
		75	0.32	0.51	0.22	0.58	0.20	$> 10^7$
PET	Ozone	20	2.12	1.67	0.25	0.64	0.11	
		75	2.17	1.83	0.21	0.64	0.15	10^7
PTFE	None	20	—	—	—	—	—	
		75	—	—	—	—	—	—
PTFE	Ar plasma	20	1.64	2.31	0.33	0.57	0.09	
		75	4.64	2.20	0.29	0.56	0.15	10^7

[a] α = XPS photoelectron take-off angles in degrees.
[b] Expressed as [COOH] to [substrate monomer] mole ratios within the probing depth of the XPS technique and measured before the coating of EM layer.
[c] The unusually high ratios arise from poor coating of the EM base (low [N] concentration).

covalently-bonded protonic acid groups on the substrate surface. The EM base does not adhere on the pristine HDPE, PP, and PTFE surfaces and adheres only poorly on other pristine substrate surfaces, when cast from dilute NMP solutions. The coating can be readily removed via the "peel test" method whereby a piece of Scotch tape is applied to the surface and subsequently removed.[33] On the other hand, however, the electroactive polymer layer was not removed from the functionalized polymer surfaces in the simple peel test. This conclusion is based on the persistence of high surface conductivity and the high [N⁺]/[N] ratio in the N_{1s} core-level spectrum of the EM layer after the test. A recent study has also reported on the improved adhesion of electroactive polymers on the fluoropolymer surface modified by chemical treatment, hydrogen plasma, UV-laser, or electron beam.[34]

CONCLUSION

The coating of a thin film of polyaniline in its neutral EM state on polyolefin, polyester, and fluoropolymer

substrates is facilitated by charge transfer interaction between the electroactive polymer and the surface-functionalized substrates. Functionalization of the surfaces of substrate polymers with sulfonic acid groups, either through sulfonation or near-UV-light-induced graft copolymerization with NaSS, can result in a highly protonated and conductive EM coating. Lower protonation levels, and hence conductivity, were observed on the substrate surfaces functionalized with carboxylic acid groups, either through hydrolysis or graft copolymerization with AAc. The extent of protonation is also governed by the microstructures of the modified substrate surfaces.

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