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Structural studies of polyethylene, poly(ethylene terephthalate) and polystyrene films modified by near u.v. light induced surface graft copolymerization

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Near u.v. light induced graft copolymerizations of water-soluble monomers such as acrylamide, acrylic acid, the sodium salt of 4-styrenesulfonic acid and *N,N*-dimethylaminoethyl methacrylate onto pristine and Ar plasma pretreated film surfaces of high-density polyethylene, poly(ethylene terephthalate) and polystyrene were carried out. Using angle-resolved X-ray photoelectron spectroscopy (XPS), the chemical composition and structure of each copolymer surface and interface were investigated. The XPS results show that in each case Ar plasma treatment leads to a substantial enhancement of the density of the surface graft, and, in the case where substantial grafting takes place, the grafted polymer penetrates or becomes partially submerged beneath a thin surface layer which is much richer in the substrate polymer. The resulting surface structures were further confirmed and distinguished by data obtained using dynamic water contact angle measurements.

(Keywords: polyethylene; poly(ethylene terephthalate); polystyrene)

INTRODUCTION

Surface modification of polymers is a convenient and effective process for producing polymers with improved physicochemical properties such as wettability, adhesion, lubrication and biocompatibility[1,2]. Among the many techniques used, surface modification by graft copolymerization appears to be one of the most versatile in the preparation of speciality polymers having tailored surface structures and compositions which are suitable for specific applications[3,4].

In this report, we present the results of our investigation of the surface microstructures of some modified hydrophobic polymers, namely high-density polyethylene (HDPE), poly(ethylene terephthalate) (PET) and polystyrene (PS). Surface modifications were achieved via graft copolymerizations with hydrophilic monomers such as acrylamide (AAm), acrylic acid (AAc), the sodium salt of 4-styrenesulfonic acid (NaSS) and *N,N*-dimethylaminoethyl methacrylate (DMAEMA). The grafting process on both the pristine and radio frequency (r.f.) Ar plasma pretreated polymers was carried out in the presence of near u.v. light irradiation. Near u.v. light induced graft copolymerization of AAm on pristine and pretreated HDPE and PET has already been reported[5-8]. Recently, we have also successfully performed surface graft copolymerizations on Ar plasma pretreated polyaniline films[9] and on O_3-pretreated poly(3-alkylthiophene) films[10]. The present work can therefore be viewed as a further study into the graft copolymerization of some commodity polymers with the various water-soluble monomers mentioned above. Using angle-resolved X-ray photoelectron spectroscopy (XPS) and dynamic water contact angle measurements as the main analytical tools, the physical and chemical structures of the copolymer surfaces and interfaces, as well as the effect of plasma pretreatment on the extent of grafting, were investigated. It is well known that the hydrophilicity of the polymer substrate surface will improve upon graft copolymerization and that 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 or enzyme immobilization[3,4,11].

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EXPERIMENTAL

The PET and PS films were of commercial grade with a thickness of about 50 μm. An HDPE film of 50–60 μm thickness was obtained from Showa Denko, Japan. All films were purified by Soxhlet extraction with methanol for 20 h and then stored in a desiccator. The water-soluble monomers used for grafting were AAm, AAc, NaSS and DMAEMA. They were used as received from Aldrich.

The equipment and conditions used for Ar plasma treatment of the polymer films were similar to those described earlier[9]. The frequency applied was 5 kHz at a plasma power of 28 W (280 V and 100 mA) and an electrode separation of about 6.5 cm. The Ar pressure was maintained at about 0.03 torr (1 torr = 133.3 Pa) during the treatment. The treatment time was chosen to be 10 s as this had been found earlier to be sufficient in activating the polymer surface without introducing excessive polymer crosslinking and degradation. The Ar plasma pretreated film strips about 1.5 × 3.5 cm in size were exposed to the atmosphere for 1–2 h before the grafting experiments. In the graft copolymerization with AAm, the film strip was placed in a Pyrex tube (transparent to near u.v. light of wavelength $\geqslant$290 nm) containing an aqueous solution made up of 20 ml of 10 wt% AAm and 5 ml of 0.053 mM riboflavin. The dissolved oxygen, which could have inhibited the radical polymerization, was consumed by photoreaction with the riboflavin[12]. The reaction mixture was sealed in a test-tube with a silicone rubber stopper and then exposed to near u.v. light (wavelength $\geqslant$290 nm) at 25–30°C in a rotary photochemical reactor equipped with a 400 W high-pressure Hg lamp (Riko Rotary model RH400-10W). The exposure time for all AAm-grafting experiments was kept at about 15 min. Similar procedures were used for graft copolymerization with NaSS, except a 0.5 M aqueous NaSS monomer solution was used instead. In graft copolymerization with AAc or DMAEMA, each film strip was immersed in 20 ml of 10 wt% aqueous monomer solution in a Pyrex tube. The reaction mixture was thoroughly degassed and sealed off under a nitrogen atmosphere. It was then subjected to near u.v. irradiation for about 30 min. After each of the grafting experiments described above, the 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 vigorously stirred water bath for at least 48 h to remove the residual homopolymer. The grafted films were then allowed to dry in air for 8 h.

Both the pristine and Ar plasma pretreated polymer film surfaces before and after graft copolymerization were characterized by XPS and contact angle measurements. For XPS measurements, the polymer films were mounted on standard sample studs by means of double-sided adhesive tape. Core level spectra 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 MgKα radiation (1253.6 eV photons) at a constant retard ratio of 40. To minimize radiation damage to the polymer films, the X-ray source was operated at a reduced power of 120 W (12 kV and 10 mA). Throughout the measurements, the pressure in the analysis chamber was maintained at 10^{-8} mbar (1 bar = 10^5 Pa) or lower. To compensate for the surface-charging effect, all binding energies were referenced to the C1s neutral carbon peak at 284.6 eV. Surface chemical compositions were determined from peak area ratios, corrected with appropriate experimentally determined sensitivity factors, and were liable to a ±10% error.

Dynamic water contact angles were measured at 21°C and 45% relative humidity using a telescopic goniometer (Ramèhart model 100-00-(230)). The telescope (magnification of 23×) was equipped with a protractor of 1° graduation. The advancing and receding contact angles were measured using both the drop and the angle of tilt methods. The angles reported were liable to a ±3° error.

RESULTS AND DISCUSSION

Surface modifications of poly(ethylene terephthalate) (PET) films

For the Ar plasma treatment time employed (10 s), the XPS C1s core level spectrum of the plasma-treated PET film shows only minor changes in the functional group components of the polymer, although an increase in the O/C ratio, as determined from the corrected O1s and C1s core level spectral area ratio, is discernible. New, high binding energy (BE) components have been reported for PET films treated with nitrogen microwave plasma systems[13]. For the pristine film, the characteristic C1s core level peak components consisting of the aromatic carbon (284.6 eV), carbon singly bonded to oxygen (286.2 eV) and carboxylate carbon (288.6 eV) in the approximate area ratio of 3/1/1 are in close agreement with the theoretical predictions[14–16]. *Figure 1* shows the respective XPS C1s core level spectra taken at two take-off angles ($\alpha = 20°$ and 75°) for pristine and plasma-pretreated PET prior to and after graft copolymerization with AAm. *Table 1* summarizes the graft densities, expressed as the molar ratios of the surface grafts to the substrate monomer units, at two α values for the pristine and plasma-pretreated PET films after graft copolymerization with AAm, AAc, NaSS and DMAEMA. It can be seen that plasma pretreatment has, as expected, enhanced considerably the extent of grafting. This phenomenon is consistent with the peroxide-initiated polymerization mechanism generally suggested for the near u.v. induced graft copolymerization of polymer surfaces pretreated with a glow discharge[5].

Polymeric AAm has a characteristic C1s peak component at about 287.8 eV attributable to the $NH_2–C{=}O$ functional group[17]. The molar ratio of AAm polymer grafted onto PET film can be calculated from the XPS C1s core level spectrum of the grafted surface using the expression[8]

$$|M_{\mathrm{AAm}}/M_{\mathrm{PET}}| = (\text{C1s area of } NH_2\text{–}C{=}O)/\{[\text{total C1s area} - 3(\text{C1s area of } NH_2\text{–}C{=}O)]/10\} \quad (1)$$

The stoichiometric factors of 3 and 10 have been introduced to account for the fact that there are three carbons in each AAm unit and 10 carbons in each PET monomer. AAm readily graft copolymerizes onto pristine PET film, as shown by the substantial molar ratio of the surface graft of about 2.36 when measured at $\alpha = 75°$. This graft density corresponds[8] to about 1.9 μg cm^{-2}, as determined using the ninhydrin method. Alternatively, the graft molar ratios for AAm polymer on PET can be calculated from the C1s and N1s area ratios. The results,

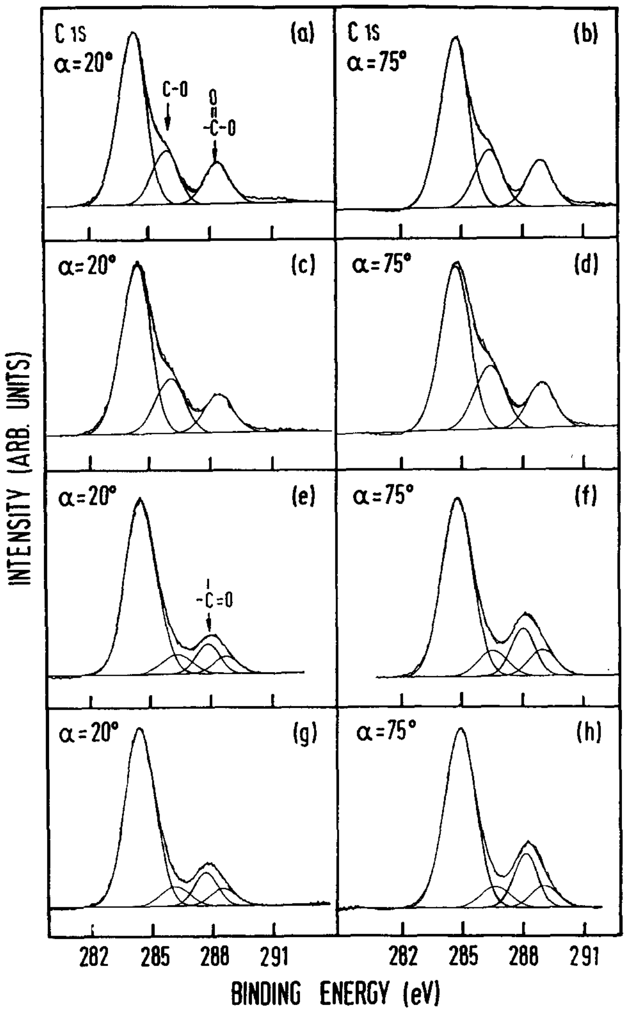

Figure 1 Angle-resolved XPS C1s core level spectra: (a, b) pristine PET; (c, d) Ar plasma pretreated PET; (e, f) pristine PET grafted with AAm polymer; (g, h) Ar plasma pretreated PET grafted with AAm polymer

Table 1 Graft densities (measured at $\alpha = 20°$ and $\alpha = 75°$) and water contact angles of PET[a] films after graft copolymerization with AAm, AAc, NaSS and DMAEMA

Sample	XPS take-off angles α (°)	Graft molar ratios	Advancing/receding contact angles (°)
PET (pristine) + AAm	20	1.39	70/24
	75	2.36	
PET (plasma-pretreated) + AAm	20	1.63	50/20
	75	3.02	
PET (pristine) + AAc	20	0.45	43/19
	75	1.46	
PET (plasma-pretreated) + AAc	20	1.66	35/15
	75	4.11	
PET (pristine) + DMAEMA	20	0.04	71/33
	75	0.02	
PET (plasma-pretreated) + DMAEMA	20	0.09	48/13
	75	0.06	
PET (pristine) + NaSS	20	1.21	10/6
	75	1.02	
PET (plasma-pretreated) + NaSS	20	1.32	17/13
	75	3.67	

[a] The water contact angles of pristine PET and plasma-pretreated PET are 77°/62° and 70°/34° (advancing/receding), respectively

however, are similar to those obtained using equation (1). For the plasma-pretreated PET films, the molar ratio of the graft increases to about 3.02. The advancing and receding water contact angles change from about 77° and 62° for pristine PET film to about 70° and 34° for the plasma-pretreated film, consistent with the formation and some reorientation of polar surface groups. The greatest increase in surface hydrophilicity of the films is achieved, however, after the introduction of the surface grafts, as shown in *Table 1*.

Polymeric AAc has functional groups similar to those of PET. For PET grafted with AAc polymer, the difference in the XPS C1s core level spectral areas of the O–C═O component and the C–O component yields the area of the O–C═O component attributable to grafted AAc polymer. Thus, to calculate the molar ratio of AAc polymer grafted onto the PET surface, the following expression can be used

$$|M_{\mathrm{AAc}}/M_{\mathrm{PET}}| = (\text{C1s area of O–C═O} - \text{C1s area of C–O}) / (\{\text{total C1s area} - [\text{C1s area of O–C═O} - 3(\text{C1s area of C–O})]\}/10) \qquad (2)$$

AAc also graft copolymerizes onto untreated PET film to give a molar ratio of about 1.46, as measured at $\alpha = 75°$. Again, plasma pretreatment increases the graft density and results in a more hydrophilic surface.

The successful grafting of NaSS polymer onto PET can easily be detected by the appearance of the S2p core level spectrum at a BE of about 168.0 eV, attributable to the covalently bonded $\mathrm{SO_3^-}$ species[9] (*Figure 2*). Hence, the molar ratio of NaSS polymer grafted onto the PET surface can be calculated from the sensitivity factor corrected S2p and C1s core level spectral areas using

$$|M_{\mathrm{NaSS}}/M_{\mathrm{PET}}| = (\text{total S2p area}) / \{[\text{total C1s area} - 8(\text{total S2p area})]/10\} \qquad (3)$$

Similarly, in the case of graft copolymerization with DMAEMA, the presence of the acrylate group at about 288.6 eV in the C1s core level spectrum and the amino

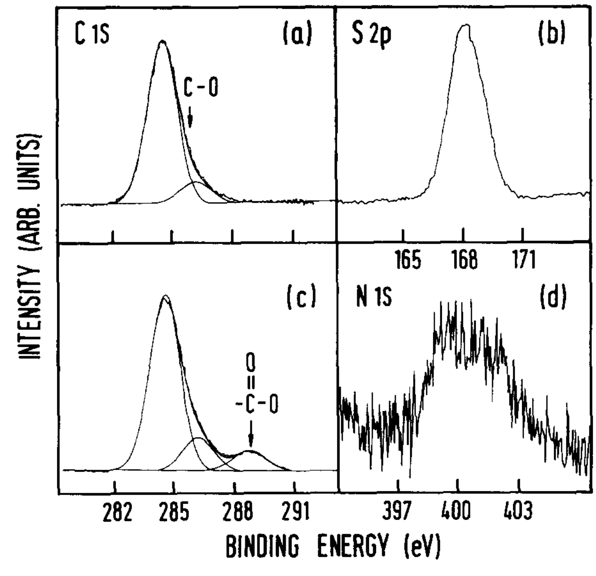

Figure 2 XPS core level spectra (measured at $\alpha = 75°$) of Ar plasma pretreated PET films: (a, b) grafted with NaSS polymer; (c, d) grafted with DMAEMA polymer

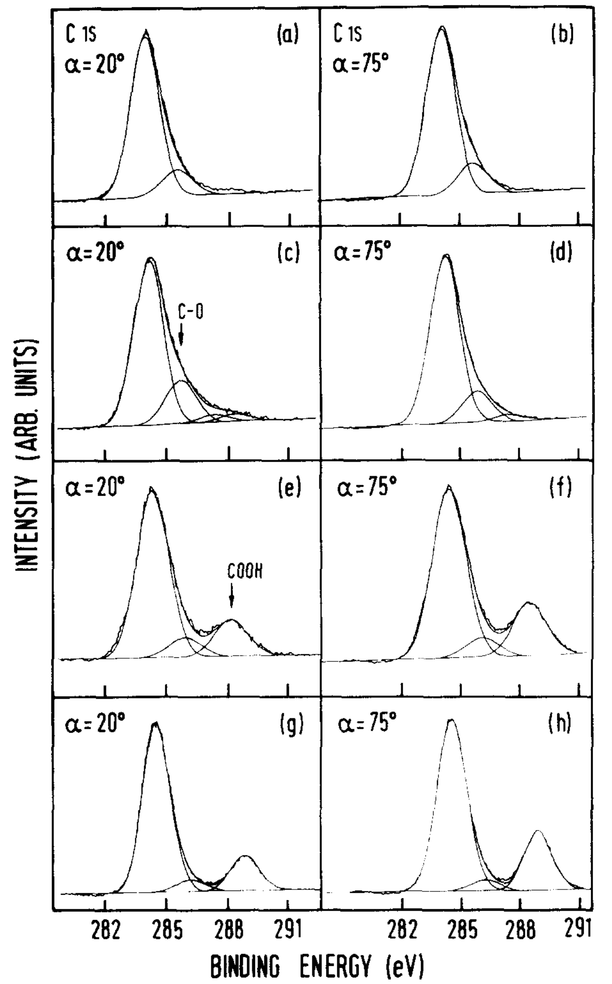

Figure 3 Angle-resolved XPS C1s core level spectra: (a, b) pristine PS; (c, d) Ar plasma pretreated PS; (e, f) pristine PS grafted with AAc polymer; (g, h) Ar plasma pretreated PS grafted with AAc polymer

group with an N1s core level BE at about 399.4 eV, as shown respectively in *Figures 2c* and *2d*, indicates the successful grafting of the acrylate polymer. The molar ratio of the grafted DMAEMA polymer can be derived from the sensitivity factor corrected N1s and C1s core level spectral areas using

$$|M_{\mathrm{DMAEMA}}/M_{\mathrm{PET}}| = (\text{total N1s area})/\{[\text{total C1s area} - 8(\text{total N1s area})]/10\} \quad (4)$$

Substantially lower graft efficiency was observed in the grafting of DMAEMA polymer onto PET using the present near u.v. light induced graft copolymerization technique. Graft molar ratios of only about 0.02 and 0.06, as measured at $\alpha = 75°$, were observed for the pristine and plasma-pretreated PET films, respectively, after graft copolymerization.

Surface modifications of polystyrene (PS) films

Pristine PS film has advancing and receding water contact angles of 85° and 71°, which are higher than those of the PET film. However, the Ar plasma pretreated PS surface (water contact angles of 64° and 33°) is more hydrophilic than the similarly treated PET surface. Pristine PS only shows a trace amount of surface-adsorbed oxygen. However, the C–O component in the C1s core level spectrum is substantially enhanced, especially near the top surface of the film, upon plasma treatment and subsequent atmospheric exposure. *Figure 3* shows the XPS C1s core level spectra of pristine and plasma-pretreated PS films prior to and after grafting with AAc polymer. The successful grafting of AAm, NaSS and DMAEMA polymers onto plasma-pretreated PS films is revealed by the XPS core level spectra of the resulting copolymer surfaces in *Figure 4*. The presence of AAm and DMAEMA polymer grafts is indicated by the appearance of the N1s peak at about 399.4 eV and the high binding energy C1s component at about 287.8 eV, while the NaSS polymer graft exhibits an S2p peak component at about 168.0 eV.

The molar ratios of the grafted water-soluble polymers can be conveniently determined by modifying equations (1)–(4) to take into consideration the decrease in the total number of carbons and the lack of any O–C=O species in the substrate polymer. *Table 2* summarizes the graft densities at two XPS take-off angles for both pristine and plasma-pretreated PS films after graft copolymerization with the various monomers. The corresponding water contact angles for the grafted surfaces are also presented. Although pristine PS film graft copolymerizes readily with AAc, it exhibits poor susceptibility towards near u.v. induced graft copolymerization with AAm and NaSS. No AAm polymer grafting was detected on the pristine PS film, while a graft density of only 0.08 was observed for NaSS polymer at $\alpha = 75°$ under the present experimental conditions. A significant increase in the graft densities of

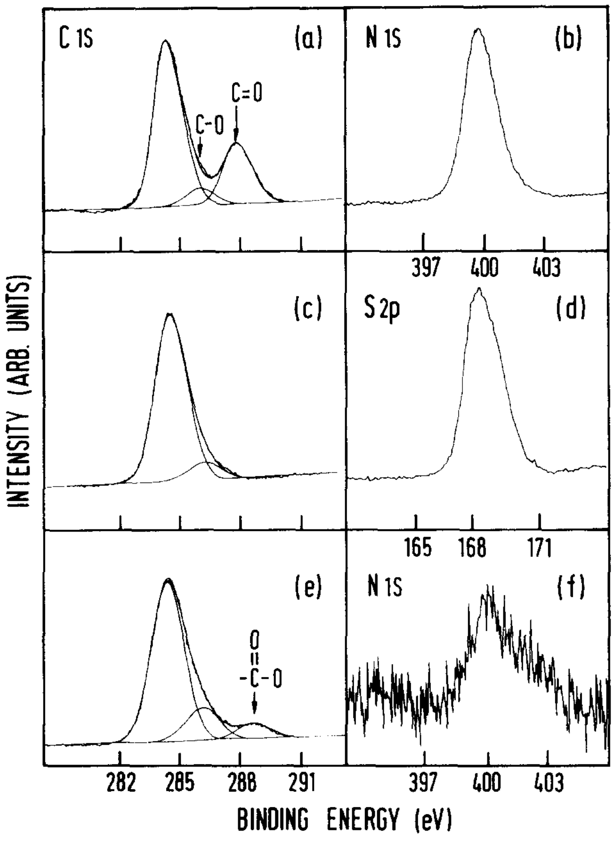

Figure 4 XPS core level spectra (measured at $\alpha = 75°$) of Ar plasma pretreated PS films: (a, b) grafted with AAm polymer; (c, d) grafted with NaSS polymer; (e, f) grafted with DMAEMA polymer

Table 2 Graft densities (measured at $\alpha = 20°$ and $\alpha = 75°$) and water contact angles of PS[a] films after graft copolymerization with AAm, AAc, NaSS and DMAEMA

Sample	XPS take-off angles α (°)	Graft molar ratios	Advancing/receding contact angles (°)
PS (pristine) + AAm	20	0.01	75/71
	75	0.01	
PS (plasma-pretreated) + AAm	20	3.37	76/13
	75	8.48	
PS (pristine) + AAc	20	2.66	64/25
	75	5.12	
PS (plasma-pretreated) + AAc	20	2.56	60/15
	75	7.11	
PS (pristine) + DMAEMA	20	0.11	55/16
	75	0.09	
PS (plasma-pretreated) + DMAEMA	20	0.07	60/15
	75	0.06	
PS (pristine) + NaSS	20	0.08	26/15
	75	0.05	
PS (plasma-pretreated) + NaSS	20	1.32	16/10
	75	2.94	

[a] The water contact angles of pristine PS and plasma-pretreated PS are 85°/71° and 64°/33° (advancing/receding), respectively

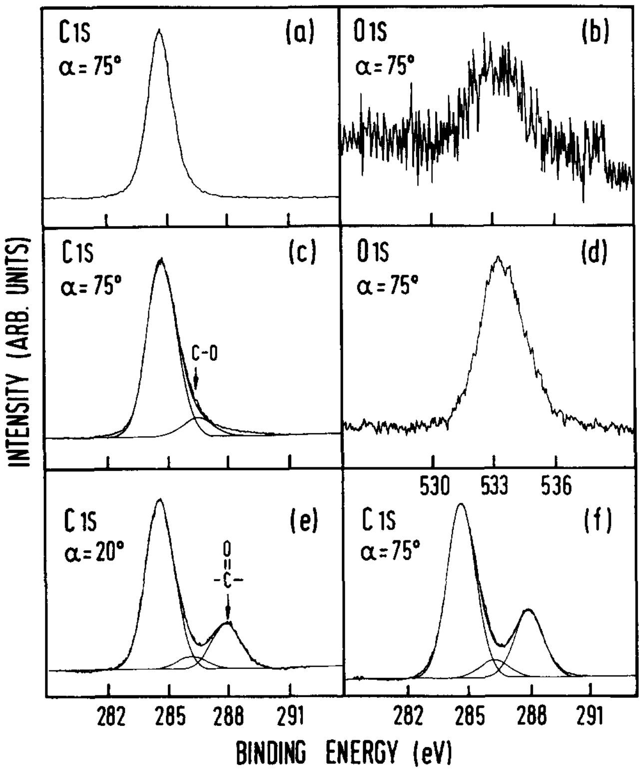

Figure 5 Angle-resolved XPS C1s and O1s core level spectra: (a, b) pristine HDPE; (c, d) Ar plasma pretreated HDPE; (e, f) Ar plasma pretreated HDPE grafted with AAm polymer

the AAm and NaSS polymers was observed, however, for PS films pretreated with Ar plasma. As expected, the resultant surfaces are extremely hydrophilic.

Surface modifications of high-density polyethylene (HDPE) films

Pristine HDPE film is highly hydrophobic, with advancing and receding water contact angles of about 98° and 85°. Trace amounts of adsorbed oxygen can be observed on the pristine HDPE surface, as suggested by the presence of a weak O1s core level signal. The concentration of the oxygen species was substantially enhanced after the Ar plasma treatment and subsequent air exposure. *Figures 5a–d* compare the C1s and O1s core level signals of the HDPE film before and after 10 s of plasma treatment. Similar to the PET and PS films, plasma treatment results in an enhancement of the C–O component. Plasma treatment also results in a decrease in the advancing and receding contact angles of the HDPE film to about 80° and 55°.

As in the cases of graft-copolymerized PET and PS surfaces, the densities of grafting are determined by modifying equations (1)–(4) to take into consideration the fact that each ethylene monomer contains only two carbon atoms. *Table 3* summarizes the graft densities of the four hydrophilic polymers on HDPE films and their respective water contact angles. Low graft efficiencies were observed in the grafting of the four polymers onto pristine HDPE films. Again, plasma pretreatment substantially enhances the extent of grafting, as indicated by large increases in graft densities and decreases in water-contact angles in all cases. *Figures 5e* and *f* show the C1s core level spectra, obtained at α values of 20° and 75°, respectively, for an Ar plasma pretreated HDPE after grafting of AAm polymer.

The surfaces and interface structures of the graft copolymers

The data in *Tables 1–3* show a distinct trend that a higher density of grafting is detected at an XPS take-off angle of 75° than at 20° in most cases. This result clearly indicates that the grafted layer is somewhat submerged beneath a very thin surface layer which is much richer in the substrate polymer. Using 2.5 nm as an effective mean free path for C1s photoelectrons produced by MgKα X-rays in an organic matrix[18], this thin surface layer is estimated to be of the order of 2–3 nm thick. In

Table 3 Graft densities (measured at $\alpha = 20°$ and $\alpha = 75°$) and water contact angles of HDPE[a] films after graft copolymerization with AAm, AAc, NaSS and DMAEMA

Sample	XPS take-off angles α (°)	Graft molar ratios	Advancing/receding contact angles (°)
HDPE (pristine) + AAm	20	0.20	70/41
	75	0.16	
HDPE (plasma-pretreated) + AAm	20	0.99	55/20
	75	1.95	
HDPE (pristine) + AAc	20	0.05	90/65
	75	0.06	
HDPE (plasma-pretreated) + AAc	20	0.20	61/25
	75	0.22	
HDPE (pristine) + DMAEMA	20	0.02	81/34
	75	0.02	
HDPE (plasma-pretreated) + DMAEMA	20	0.03	63/23
	75	0.02	
HDPE (pristine) + NaSS	20	0.16	18/15
	75	0.30	
HDPE (plasma-pretreated) + NaSS	20	0.41	12/11
	75	0.58	

[a] The water contact angles of pristine HDPE and plasma-pretreated HDPE are 98°/85° and 80°/55° (advancing/receding), respectively

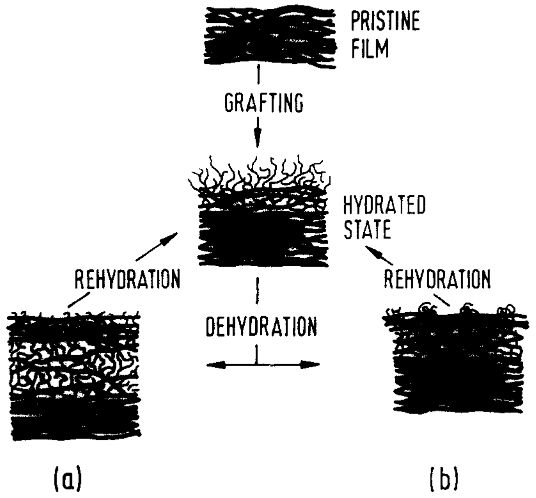

Figure 6 Schematic representations of plausible graft structures: (a) complete penetration model: (b) partial penetration model

the case of graft copolymerization with AAm, AAc and NaSS, plasma-pretreated PET, PS and HDPE films all show substantially higher graft densities, typically two to three times higher at $\alpha = 75°$ than at $\alpha = 20°$. The presence of the graft in the subsurface layer could be attributed to the migration and countermigration of the substrate and the polymer graft during drying and storage. This is possible because modifications of the substrate polymer chains in the surface region by Ar plasma treatment, u.v. irradiation during grafting and finally graft copolymerization must have substantially lowered the glass transition temperature (T_g) of the substrate polymer in this region. The effects of polar group orientation, polymer chain mobility and substrate permeability on the stability of the grafted layer have been discussed by Ratner *et al.*[19] for poly(dimethylsiloxane), poly(ester urethane) and polystyrene grafted with 2-hydroxyethyl methacrylate, AAm and ethyl methacrylate polymers. The reorientation of polar groups into the hydrophobic bulk phase has also been shown to reduce the overall free energy of the system[20]. On the basis of the angle-resolved XPS results, the graft structures and morphologies at the present film surfaces can be described by either of the two schematic models shown in *Figure 6*. Both the complete penetration of the grafted layer below the substrate polymer (*Figure 6a*) and the partial penetration with clustering together of some of the grafts on the surface after the sample has been dehydrated (*Figure 6b*) can account for the decreasing graft signal towards the outermost surface. As all the film surfaces become very hydrophilic after grafting and are readily rehydrated after drying, the outermost surface layer of the model in *Figure 6a* must consist of a mixture of grafts and the substrate polymer to account for the surface sensitivity (typically of 1 nm or less)[21] of the contacting water molecules.

The applicability of the two models to the present plasma-modified and graft-copolymerized surfaces can be further discriminated using the contact angle data. First of all, the hysteresis effect shown by the large difference between advancing and receding contact angles for the three substrates after Ar plasma treatment readily suggests reorientation of the polar groups. A similar phenomenon has been observed for a polypropylene surface after O_2 plasma treatment[22]. Graft copolymerization of pristine and plasma-pretreated films with hydrophilic polymers results in a significant decrease in both the advancing and receding contact angles (see *Tables 1–3*). A significant hysteresis effect, however, is observed only for surfaces graft copolymerized with AAm, AAc and DMAEMA. 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 model in *Figure 6a* seems to be appropriate. For all surfaces graft copolymerized with NaSS, the relatively small surface contact angles and the lack of an obvious hysteresis effect would tend to suggest the presence of hydrophilic species at the outer surface, as represented by the model in *Figure 6b*. The less efficient penetration of the NaSS graft at the surface must have resulted from the migration of the graft being sterically hindered by bulky substituents. It should be noted, however, that although the angle-dependent molar ratio of graft to substrate is also somewhat reduced for the NaSS polymer grafted films, the XPS data still indicate the presence of a substrate-rich top surface.

Finally, the penetration of the AAm graft below the film surface to form a submerged layer is consistent with the featureless morphology of the air-dried surface when observed by scanning electron microscopy (SEM). On the other hand, a textured surface and dendrite formations of the polymer graft on the substrate surface were observed in the SEM images of freeze-dried samples of comparable graft density[23].

CONCLUSIONS

Angle-resolved XPS data and contact angle hysteresis effects have been used to study the graft structures and morphologies of pristine and Ar plasma pretreated films of PET, PS and HDPE after near u.v. induced graft copolymerization with hydrophilic AAm, AAc, NaSS and DMAEMA monomers. For film surfaces graft copolymerized with AAm, AAc and DMAEMA, the polymer grafts were shown to penetrate into the substrate polymers to form a subsurface layer. For an aliphatic graft with a bulky substituent, such as the NaSS polymer, the relatively small contact angles and lack of hysteresis effect in the difference between advancing and receding contact angles call for a partial penetration model for the graft.

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