

Surface Modification of Polyimide Films by Graft Copolymerization

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SYNOPSIS

Surface modifications of polyimide (PI) films by Ar-plasma, O₂-plasma, and O₃ pretreatment and by near-UV light-induced graft copolymerization with water-soluble monomers, such as acrylamide (AAm), acrylic acid (AAc), and sodium salt of 4-styrenesulfonic acid (NaSS), have been carried out. The angle-resolved x-ray photoelectron spectroscopy (XPS) results show that surface pretreatment results in the formation of peroxide species on the polymer film surfaces and leads to a substantial enhancement of the density of surface graft. The XPS results further suggest that in the case where substantial grafting has taken place, the grafted polymer either forms a surface layer uniformly intermixed with the substrate chains, or a graft-rich surface layer in the case of sterically hindered migration of the graft. The resulting surface structures are further supported by dynamic water contact angle measurements. These surface structures are probably associated with the thermoset character of PI, as they differ from the stratified microstructures observed on most thermoplastic films after surface modification by graft copolymerization with hydrophilic monomers.

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INTRODUCTION

Surface modification of polymers is a convenient and effective process in 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 specialty polymers, having tailored surface structure and composition that are suitable for specific applications such as protein/enzyme immobilization in biomedical applications.³⁻⁵ Recently, there has been considerable activities in studying novel polyimides and their surface modification to enhance metal adhesion for electronic applications.⁶

In this report, we present the results of our investigation on the surface microstructures of some surface modified polyimide (PI) films. Surface modification was achieved via graft copolymerization with hydrophilic polymers such as acrylamide (AAm), acrylic acid (AAc), and sodium salt of 4-styrenesulfonic acid (NaSS). The grafting process on pristine, Ar-plasma-, O₂-plasma-, or O₃-pretreated PI films was carried out in the presence of near-UV light irradiation. Near-UV light-induced graft copolymerization of AAm onto pristine and pretreated high-density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) films has been reported.⁷⁻¹⁰ Recently, we have also successfully performed surface graft copolymerization on Ar-plasma-pretreated poly(tetrafluoroethylene)¹¹ and polyaniline¹² films, as well as on O₃-pretreated poly(3-alkylthiophene)¹³ films. 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 co-

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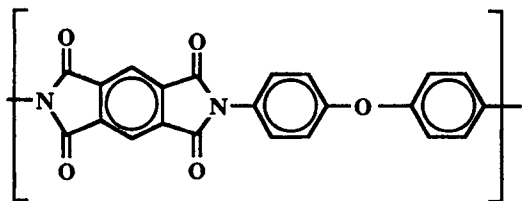


Figure 1 Molecular structure of polyimide.

polymer surfaces and interfaces, as well as the effect of surface pretreatment on the extent of grafting, were investigated.

EXPERIMENTAL

The poly[(*N,N'*-oxydiphenylene) pyromellitimide] or PMDA-ODA films (Kapton HTM, Du Pont Chemical Co.), having a thickness of about 50 μm , was used. The film was purified by Soxhlet extraction with methanol for 6 h and then stored in a desiccator. The water-soluble monomers used for graft copolymerization include AAm, AAc, and NaSS, and were used as received from Aldrich Chemical Co. The Ar and O₂ plasma treatments of the polymer films were carried out on a modified Balzers evaporator system with a rotating sample stage. The DC plasma system was operated at a potential of 325 V and an electrode separation of about 7.8 cm. The gas pressure was maintained at about 0.07 Torr during the treatment. The treatment time was chosen to be 10 min and 5 min for Ar and O₂ plasma treatment, respectively. O₃ pretreatment for 10 min was carried out using a ultraviolet ozone cleaning system (UVOCS Ins. Montgomeryville, PA, 1893, Model T10X10). The treatment times were so chosen as they had been found earlier to be sufficient in activating the polymer surface without introducing excessive crosslinking and degradation of the polymer surface. The Ar-plasma-pretreated films were exposed to atmosphere for about 1–2 h before the grafting experiment. In the case of O₂-plasma- and O₃-pretreated films, the grafting experiment was carried out almost immediately. In graft copolymerization with AAm, the film strip of about 1.5 \times 3.5 cm in size was placed in a Pyrex tube (transparent to near-UV light of wavelength \geq 290 nm) containing an aqueous solution of 20 mL of 10 wt % AAm. The reaction mixture was thoroughly degassed and sealed off under nitrogen atmosphere. The reaction mixture was then exposed to near-UV light at 25–30°C from a 150 W Xenon Arc lamp. The ex-

posure time for the grafting experiment was kept at about 30 min. Similar procedures were used for the graft copolymerization with AAc and NaSS. After each of the grafting experiment 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 residue homopolymer. The grafted films were then allowed to dry in air for 8 h.

Both the pristine and surface-treated polymer surfaces before and after graft copolymerization were characterized by angle-resolved XPS and contact angle measurements. For the XPS measurements, the poly-

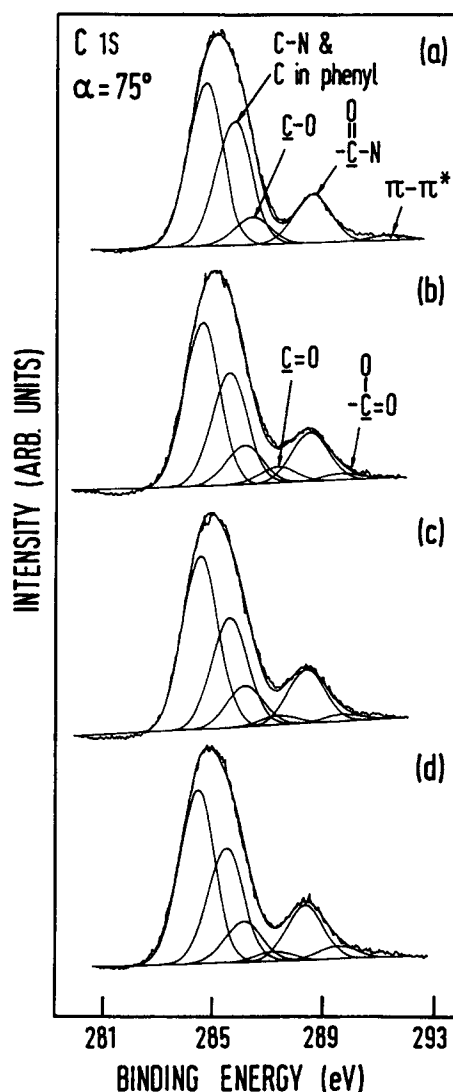


Figure 2 XPS C1s core-level spectra of (a) pristine PI, (b) Ar-plasma-treated PI, (c) O₂-plasma-treated PI, and (d) O₃-treated PI measured at $\alpha = 75^\circ$.

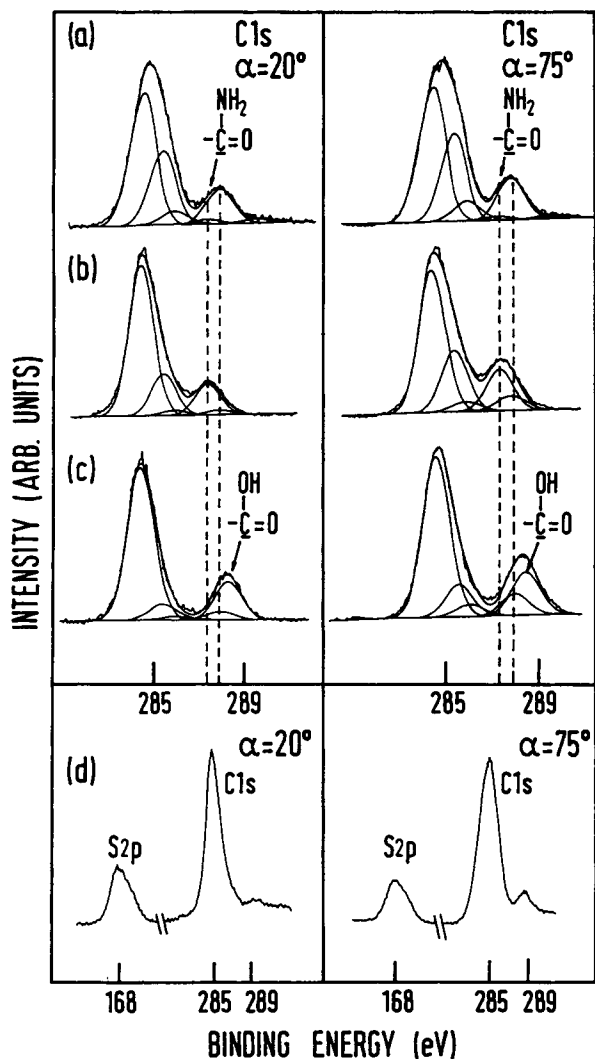


Figure 4 Angle-resolved XPS C1s core-level spectra of (a) pristine PI grafted with AAm, (b) Ar-plasma-pretreated PI grafted with AAm, (c) O₃-pretreated PI grafted with AAc, and (d) O₂-plasma-pretreated PI grafted with NaSS, showing also S2p core-level spectra.

RESULTS AND DISCUSSION

The molecular structure of polyimide PMDA-ODA, is shown in Figure 1. The XPS results of the pristine PI film show an O/C and N/C ratio of 0.19 and 0.09, respectively. These values are comparable with the theoretical ratios of 0.23 and 0.09 for PI. The C1s XPS core-level spectrum of pristine PI measured at $\alpha = 75^\circ$ is shown in Figure 2(a). Four major peaks, including the $\pi-\pi^*$ satellite at a binding energy (BE) of about 291.2 eV, are clearly discernible. Peak synthesis of the C1s core-level spectrum gives component peaks with BEs at 284.6, 285.7, 286.2,

and 288.4 eV. These peaks are attributable to the aromatic carbon, the phenyl carbon of the pyromellitic-dianhydride (PMDA) unit and carbon bonded to nitrogen, carbon singly bonded to oxygen in the *o*-oxydianiline (ODA) unit, and lastly, the carbonyl group of the PMDA chain, respectively.¹⁴

Surface pretreatment of PI by Ar-plasma, O₂-plasma, and O₃ all results in the enhancement of the C—O species at about 286.2 eV, and the formation of additional carbon species at BEs of about 287.4 and 289.6 eV. These peaks correspond, respectively, to carbonyl species, different from the carbonyl of the PMDA chain, and to ester bonded to nitrogen species.¹⁵ The O/C ratios increased to about 0.26 and 0.24, respectively, for Ar-plasma- and O₃-treated PI, as determined from the corrected O1s and C1s core-level spectral area ratios. The increase in O/C ratio in the case of O₂ plasma-treated PI film is, however, less evident. The XPS C1s core-level spectra of Ar-plasma-, O₂-plasma- and O₃-pretreated PI films, measured at $\alpha = 75^\circ$, are shown in Figures 2(b) to (d). The possible mechanisms of Ar-plasma, O₂-plasma, and O₃ reaction with saturated hydrocarbons have been extensively reported.^{11,16,17} Although an increase in the amount of C—O species and in O/C ratio would be consistent with the formation of peroxide or hydroxy-peroxide species, it has also been suggested that during plasma treatment of PI films, the imide groups cleave and result in the formation of secondary amine and carboxyl groups as the main hydrophilic components.¹⁸ For near-UV light-induced graft copolymerization of polymer surface pretreated with Ar-plasma and O₂-plasma, a peroxide-initiated mechanism has also been suggested.^{11,19} The presence of the secondary amine species is, indeed, observed in the broadening of the N1s core-level spectrum towards lower BE, resulting in an additional peak component at about 399.7 eV. Pristine PI has a single N1s peak component at about 400.5 eV. Figure 3 shows the XPS N1s core-level spectra of pristine and Ar-plasma-treated PI film measured at $\alpha = 20^\circ$.

Graft Copolymerization of Pristine and Surface-Pretreated PI Films with AAm, AAc, and NaSS Polymer

The AAm polymer has a characteristic C1s peak component at about 287.8 eV, attributable to the NH₂—C=O functional group.²⁰ The density of the AAm polymer graft copolymerized onto the PI film, defined as the molar ratio of the AAm unit to the substrate monomer unit, can be calculated from the

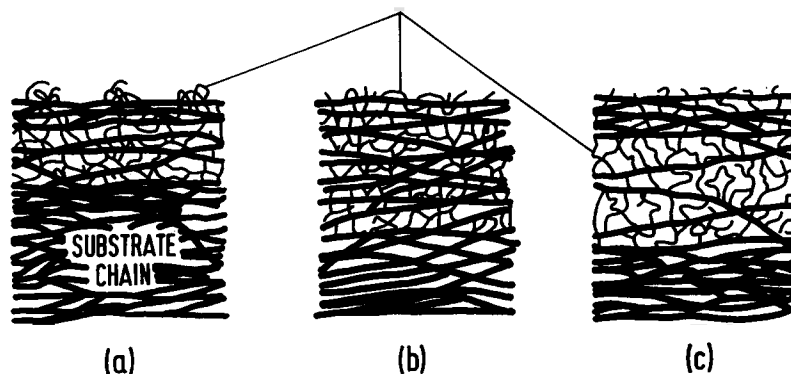


Figure 5 Schematic representation of plausible graft structures: (a) partial penetration model, (b) intermixing model, and (c) complete penetration model (grafting of thermoplastics).

$$\frac{M_{\text{AAm}}}{M_{\text{PI}}} = \frac{\text{C1s area of NH}_2 - \text{C} = \text{O}}{[\text{total C1s area} - (\text{C1s area of NH}_2 - \text{C} = \text{O}) \times 3] \times \frac{1}{23}}$$

The factors 3 and 1/23 take into account of the fact that there are three carbon atoms in 1 mol of AAm and 23 carbon atoms in one repeating unit of PI, respectively. Similarly, the density of the surface graft of AAc and NaSS polymers can be calculated by modifying eq. (1), taking into consideration the stoichiometry and the functional groups present in the AAc and NaSS polymers. The density of surface graft of AAm, AAc, and NaSS, measured at $\alpha = 20^\circ$ and 75° , as well as the advancing and receding water contact angles of the pristine and the various surface-pretreated PI films are summarized in Table I. The pristine PI films are susceptible to some extent to the near-UV light-induced graft copolymerization with AAm, AAc, and NaSS monomers, as indicated by graft densities of about 0.29, 0.80, and 0.58, respectively, when measured at $\alpha = 75^\circ$.

The advancing/receding water contact angles change from about $71^\circ/37^\circ$ for the pristine PI film to about $67^\circ/14^\circ$, $48^\circ/8^\circ$ and $51^\circ/20^\circ$, respectively, for the Ar-plasma-, O_2 -plasma-, and O_3 -pretreated films, respectively. The decrease and the hysteresis in water contact angles after pretreatment are consistent with the formation and reorientation, respectively, of surface polar groups.²³ The greatest increase in surface hydrophilicity of the films is achieved, however, after the introduction of surface

grafts, as shown in Table I. It can be seen that surface pretreatment by all of the three methods enhances the extent of surface grafting. The XPS C1s core-level spectra taken at two take-off angles ($\alpha = 20^\circ$ and 75°) for pristine and Ar-plasma-pretreated PI films after graft copolymerization with AAm are shown in Figures 4(a) and (b). The corresponding XPS C1s core-level spectra of O_3 -pretreated PI films grafted with AAc polymer are shown in Figure 4(c). Figure 4(d) shows the C1s and S2p XPS core-level spectra, measured at $\alpha = 20^\circ$ and 75° , of an O_2 -plasma-pretreated PI film after graft copolymerized with NaSS.

The data in Table I show that the densities of surface grafted AAm and AAc polymers are comparable at the XPS take-off angles of 20° and 75° . The variations generally are less than 10% in most cases. This would imply that the surface morphology of the grafted PI probably consists of a uniform mixture of the graft polymer and the substrate polymer. This graft-substrate intermixing morphology is in contrast with the stratified surface microstructures proposed in our earlier work,²¹ for the similarly surface graft copolymerized thermoplastic polymers, such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), and poly(ethylene terephthalate) (PET). The formation of the subsurface layer was attributed to the migration and counter migration of the substrate and the grafted chains during drying and storage of the polymer films, as a result of a lowering in glass transition temperature (T_g) of the

substrate chains in the surface region after pretreatments and graft copolymerization. The reorientation and migration of polar groups beneath the hydrophobic polymer surfaces have been known to be thermodynamically favorable process.²³ The lack of polymer and graft migration in the case of PI is probably attributable to the fact that PI is a partial thermoset material having a T_g as high as 385°C.²² The less efficient penetration of the NaSS graft at the substrate polymer surface is evident in the XPS data shown in Table I. A higher density of NaSS polymer graft is detected at the more glancing take-off angle of $\alpha = 20^\circ$. The lack of penetration of the NaSS graft must have resulted, in addition to PI being a partial thermoset, from the sterically hindered migration of the graft with bulky substituents. Schematic models illustrating the intermixing surface layer and the partial penetration morphology of the PI film surfaces after graft copolymerization are shown in Figures 5 (a) and (b), respectively. For comparison purpose, the stratified surface microstructure associated with thermoplastic films after graft copolymerization with hydrophilic monomers is shown in Figure 5 (c).

The applicability of the proposed model for the surface-modified and graft-copolymerized PI films are further examined using the dynamic water contact angle data. The water contact angles of the Ar-plasma-, O₂-plasma- and O₃-pretreated substrates show large differences between the advancing and receding contact angles. This hysteresis effect suggests the presence of polar groups reorientation. Similar phenomenon has been observed for polypropylene surface after O₂-plasma treatment²³ as well as LDPE, HDPE, PP, PS, and PET after Ar-plasma treatment.²⁰ Graft copolymerization of the pristine and surface pretreated PI films with hydrophilic polymers results in a significant decrease in both the advancing and receding contact angles, as shown in Table I. The hysteresis effect, however, is not apparent for surfaces extensively graft copolymerized with AAm, AAc, and NaSS. The lack of an obvious hysteresis effect would readily suggest the presence of hydrophilic species at the outer surface of the polymer film. Thus, the dynamic water contact angle data are consistent with the proposed surface microstructures of Figure 5 (a) and 5 (b).

CONCLUSION

Angle-resolved XPS and dynamic water contact angle measurements have been used to study the

surface structure and morphology of various surface-pretreated PI films after graft copolymerized with hydrophilic AAm, AAc, and NaSS polymers. For the PI films graft copolymerized with AAm and AAc, the polymer graft is shown to be retained on a surface layer arising from the uniform intermixing of the graft and the substrate chains. For aliphatic graft with bulky substituent, such as the NaSS polymer, the grafted polymer only partially penetrates into the substrate polymer, forming a surface layer richer in the grafted polymer. The relatively small water contact angle and a lack of hysteresis effect arising from the difference in the advancing and receding contact angles for the heavily grafted surfaces gives further evidence to the retention of the hydrophilic species in the surface layer, in contrast with the stratified surface microstructure generally observed for the thermoplastic films after surface graft copolymerization with a hydrophilic monomer.

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