Surface Structure of Blend Films of Styrene/Acrylonitrile Copolymer and Poly(methyl methacrylate)(PMMA) or Hydrolyzed PMMA

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The compatibility and the surface structure of blends of poly(styrene-co-acrylonitrile) (SAN) with either poly (methyl methacrylate) (PMMA) or hydrolyzed PMMA (H-PMMA) were studied in terms of film thickness, interaction, and surface free energy difference on the basis of X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform IR spectroscopy and atomic force microscopy. The. XPS measurement showed that the surface enrichment of (PMMA/SAN) blends with different AN contents of SAN and with different carboxyl acid contents of PMMA was dependent on the molecular interaction, the surface free energy difference between components and the sample preparation history. It was found that the compatibility of H-PMMA and SAN was reduced with increasing carboxyl acid content of PMMA.

Introduction

The surface-layer properties have recently received great attention in practical applications, such as biomaterials, adhesives, paintings, and so on, since the surface structure and the surface molecular motion of materials are fairly different from those in the bulk. The component of a lower surface free energy in multiphase blend systems is usually enriched in the surface region in order to minimize the air/material interfacial free energy.[1-3] The glass transition temperature (T_g) at the surface, in comparison with that of bulk, is also significantly depressed due to the localization of chain end groups at the surface.[4-8] In order to design the highly functionalized surface, it is necessary to understand molecular behaviors at the surface and to control surface properties. The authors[8,9] investigated the surface structure of [poly (methyl methacrylate)/poly(vinyl acetate)] (PMMA/PVAc) blend whose compatibility is strongly dependent on the casting solvent on the basis of X-ray photoelectron spectroscopy (XPS), attenuated total reflection fourier transform infrared (ATR-FT IR) spectroscopy and contact angle measurements. It was revealed that the surface structure of polymer blends is affected by several factors, such as interaction, sampling conditions, film thickness, difference in surface free energy of each component.

On the other hand, the compatibility can occur in AB-type random copolymer/C homopolymer blends if the intermolecular mutual repulsion between the dissimilar segments A and B in the copolymer is large enough, even through the homopolymers of A or B and the homopolymer C are immiscible each other and each segment (A or B) dislikes each other. In this case, the compatibility of the blends over a certain range of copolymer composition does not originate from any specific interactions but arises from the strong repulsion between the dissimilar segments A and B in the copolymer. Hereafter, we call it "compatibility due to repulsive effect". Details of the repulsive effect in random copolymer/homopolymer blends have been well described by Paul *et al.*[10]

PMMA and the random copolymer (SAN) of styrene (S) and acrylonitrile (AN) form a compatible blend over the entire composition range within certain limits of AN content (9-33 wt %) by repulsive effect.[10] The propose of this work is to investigate the compatibility and the surface structure of blends of SAN and PMMA or hydrolyzed PMMA (H-PMMA) on the basis of XPS, ATR-FT IR spectroscopic and atomic force microscopic (AFM) measurements.

Experimental

Materials. PMMA (M_w=120,000) was purchased from Aldrich Co. and purified with toluene/methanol solvent/nonsolvent system. SAN with 14, 20 and 30 wt % AN were obtained from Asahi Chem. Co.. SAN X indicates that the AN contents in the SAN is X wt % AN. PMMA was partially hydrolyzed by dissolving PMMA in 96% sulfuric acid, followed by stirring at room temperature. The solution was precipitated in an ice/water mixture, filtered, dissolved in water with KOH and heated to 373 K for 1 hr to remove anhydride functionalities. Details for the synthesis were reported elsewhere.[11] Each H-PMMA contains 4, 14, and 24 mol % of carboxyl groups, respectively and is designated by the degree of hydrolysis. For instance, H4-PMMA denotes that the carboxyl group in hydrolyzed PMMA is 4 mol %. The purification of SAN was accomplished by reprecipitation in methanol from methyl ethyl ketone (MEK) solution.

Film preparations. Blend films including H-PMMA were prepared by casting from N,N-dimethyl acetamide (DMAc) solution. Other blend films were prepared by both spin-coating method and casting method using MEK, to investigate the effects of thickness and interface environment (air/polymer and polymer/substrate) on the surface structure, respectively. The thickness of ultrathin film was evaluated as follows; after a crater was formed in the polymer film by ion beam etching, its step height, which could be defined as the film thickness, was measured by AFM observation.

Contact angle measurement. The contact angles of water and methylene iodide on the surface of samples were measured by Kyowa contact angle meter. The measure-

ments were carried out in the presence of the saturated vapor of the probe liquids but the equilibrium pressure of the adsorbed vapor of the liquids on the polymer films was assumed to be negligible. The surface free energy of sample films was calculated by Owens' method.[12] The surface free energies (γ_{SV}) of PMMA, SAN 14, SAN 20, and SAN 30 equal to 42, 43, 44, and 44.5 (mN·m^{-1}), respectively.

X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained with ESCA 750 X-ray photoelectron spectrometer (Shimadzu) by using MgK radiation. Typical operating conditions were 8 kV, 30 mA x-ray source and under pressure in the analytical chamber-10^{-5} Pa. The analytical depth at the emission angle of 90 deg. is *ca.* 10.5 nm.[10]

Attenuated total reflection Fourier transform infrared (ATR-FT IR) spectroscopy. The ATR-FT IR spectra were taken with Nicolet 1720X FT IR spectrometer, in which a Spectratec model 302A ATR attachment is mounted, at a fixed angle of incidence (θ) of 51.2°. The ATR element was a spectra-Tech-5 45 face angle 50 mm rhomboid. The data of 100 scans were averaged.

Atomic force microscopy (AFM). Surface morphology was investigated on the basis of AFM observation. The AFM images were obtained by SFA 300 with SPI 3700 controller (Seiko Instrument Industry Co. Ltd.) at room temperature. The AFM cantilever used was microfabricated from Si$_3$N$_4$ and its spring constant was 0.022 N·m^{-1}. AFM imaging was carried out in a repulsive force.

Results and Discussion

In order to investigate the effect of AN content on the surface composition of the miscible (PMMA/SAN) blend films, XPS measurements were performed. The surface composition was evaluated on the basis of the ratio of XPS peak intensity for the carbon (C$_{1s}$) and the nitrogen (N$_{1s}$) corrected with the experimentally determined sensitivity. In the case of (PMMA/SAN 30), the equation that was used to determine the surface percentage of PMMA (*w*) is

$$\frac{I_{N1S}}{I_{C1S}} = \frac{\dfrac{1-w}{M_{SAN}}}{\dfrac{6.5(1-w)}{M_{SAN}} + \dfrac{5w}{M_{MMA}}}$$

where I_i is the integrated intensity of a core-electron photoemission spectrum. M$_{MMA}$ and M$_{SAN}$ are the molecular weights of methyl methacrylate repeat unit and the average molecular weight of styrene and acrylonitrile units on the basis of acrylonitrile content, respectively. Figure 1 shows the surface chemical composition of the (PMMA/SAN) blends with different AN contents of SAN on the basis of XPS measurement. As expected, PMMA with lower surface free energy than SAN was enriched at the surface for all the blends. The difference of surface free energy between PMMA and SAN is increased with AN content of SAN and the degree of PMMA surface enrichment is increased in the order (PMMA/SAN 30) > (PMMA/SAN 20) > (PMMA/SAN 14) blends. Jones and Kramer[13] theoretically reported that the total surface excess is more strongly dependent on the values of the Flory-Huggins interaction parameter between the segments of the two polymers than on the differences in surface free energies between the components of
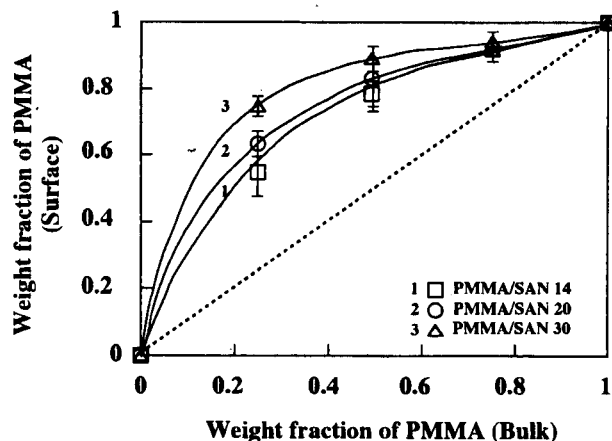
Figure 1. Surface weight fraction versus bulk weight fraction of PMMA of (PMMA/SAN) blend films with different AN contents of SAN.

a miscible blend at equilibrium. However, the interaction force between components in (PMMA/SAN) blends with different AN contents is increased in the order SAN 20 > SAN 14 > SAN 30.

Figure 2 shows the transmission IR spectra of PMMA and SAN 30 homopolymers. In the spectrum of PMMA, stretching peaks of C=O and C-O-C absorptions were observed at around 1720 cm^{-1} and 1273 cm^{-1}, respectively. On the other hand, the peaks of aromatic C=C absorption in the spectrum of SAN 30 were observed at 1500-1400 cm^{-1}. The ratio of C-O-C absorption at 1273 cm^{-1} (I_{1273}) for PMMA and C=C absorption at 1453 cm^{-1} (I_{1453}) for SAN 30, were taken to evaluate the surface enrichment of the (PMMA/SAN 30) blend films. The composition distribution of (PMMA/SAN 30) blend at the surface was analyzed by ATR-FT IR at the incidence angle 45°. Comparison of transmission IR spectra and ATR-FT IR spectra shows that the magnitudes of (I_{1273}/I_{1453}) by transmission IR are smaller than those by ATR-FT IR over all the compositions, as shown in Table 1. The result implies that PMMA is enriched at surface. Also, the surface chemical composition at both the air/polymer and the polymer/substrate interfaces showed similar behavior, that is, PMMA was enriched at
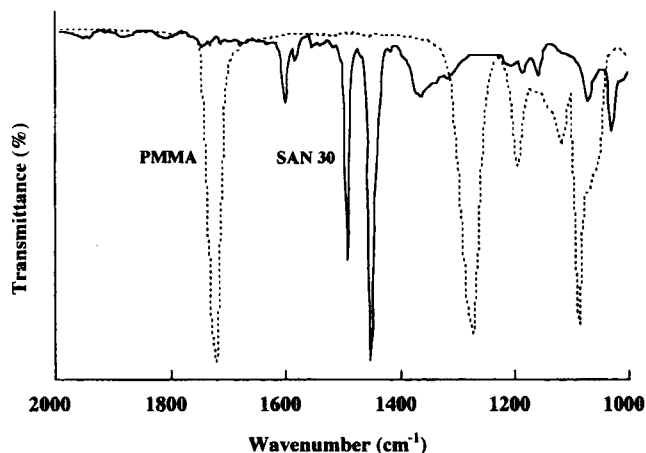
**Figure 2.** Transmission IR spectra of PMMA and SAN 30 homopolymers.

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Table 1. The intensity ratio of the peaks at 1273 cm^{-1} (I_{1273}) and 1453 cm^{-1} (I_{1453}) for the (PMMA/SAN 30) blend films at the air/polymer and the polymer/glass interfaces

| Composition (PMMA/SAN 30) (w/w)	Intensity ratio (I_{1273}/I_{1453})		
	Transmission IR	ATR-FT IR	
		air/polymer	polymer/glass
33/67	1.20	1.59	1.61
50/50	2.10	4.06	3.04
annealing[a]		7.90	5.12
67/33	2.54	9.54	7.60

[a] annealed at 433 K for (PMMA/SAN 30 50/50) blend film.

both interfaces and the concentration of PMMA was increased after annealing above its cloud point. This result can be explained by the minimization of the air/polymer and the polymer/glass interfacial free energies.

The repulsive effect and the surface structure on the miscibility were also investigated in other way by examining the phase behavior of SAN copolymer with MMA-based copolymers with methacrylic acid (H-PMMA). The surface free energies of H-PMMA were increased with the carboxyl content in PMMA, as shown in Figure 3. Figure 4 shows the surface morphology of (H-PMMA/SAN 30) blend films on the basis of AFM observation. The domain size in the blend becomes larger as the carboxyl group in PMMA is increased. The result implies that the carboxyl group in the (H-PMMA/
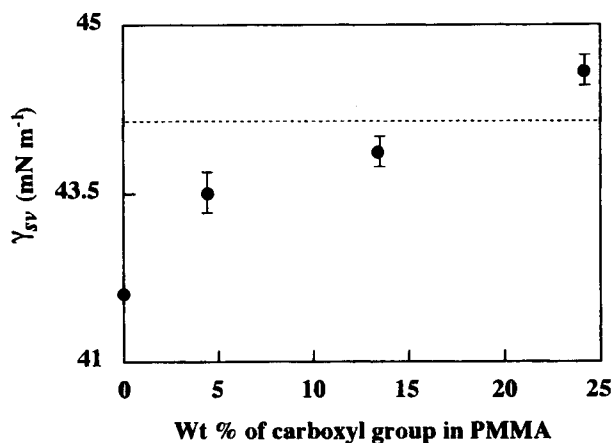
Figure 3. γ_{sv} *versus* mole fraction of carboxyl acid group in PMMA. The broken line indicates the surface tension of SAN 30.

10 μm
(H4-PMMA/SAN 30)

10 μm
(H14-PMMA/SAN 30)

30 μm
(H24-PMMA/SAN 30)
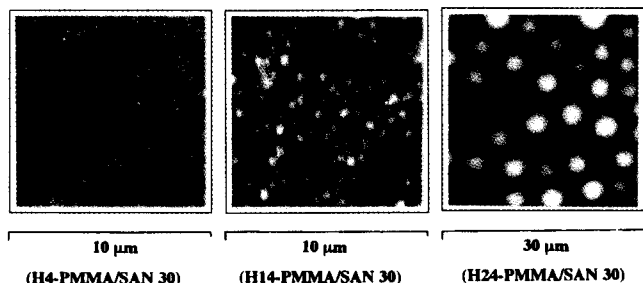
Figure 4. AFM topographic images of (H-PMMA/SAN 30 50/50 w/w) blend films with different carboxyl acid contents of H-PMMA.
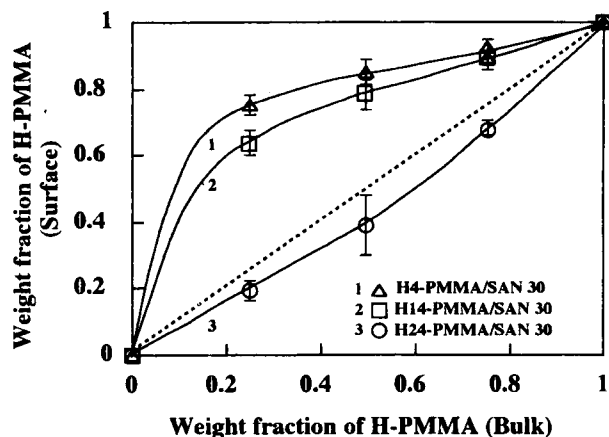
Figure 5. Surface weight fraction versus bulk weight fraction of H-PMMA of (H-PMMA/SAN) blend films with different carboxyl acid contents of H-PMMA.

SAN 30) blend dilutes the strong repulsive force between S and AN. Figure 5 illustrates XPS results to show the weight fraction of H-PMMA at surface of the blend films of SAN 30 with H4-, H14- and H24-PMMA as a function of the weight fraction of H-PMMA in bulk. Surface compositions of blends with H4-PMMA and H14-PMMA were enriched in H-PMMA, but surface enrichment of SAN 30 was observed in (H24-PMMA/SAN 30) blend system. It is seen that the surface free energy of H-PMMA is less than that of SAN 30, except H24-PMMA. This result supports that the surface-enriched component in the (H-PMMA/SAN) blends is mainly controlled by the difference between surface free energies of components. Although the magnitude of difference of surface free energy between PMMA and SAN 30 was larger than that between H4-PMMA and SAN 30, the surface compositions of both blends was similar. From the fact that the introduction of carboxyl acid in (PMMA/SAN 30) reduced the miscibility caused from the dilution of the repulsive effect, the result means that the degree of surface enrichment is dependent on both the difference of surface free energy and the intermolecular interaction between components. However, the surface structure of a polymer blend is strongly affected by the sample preparation history such as what kind
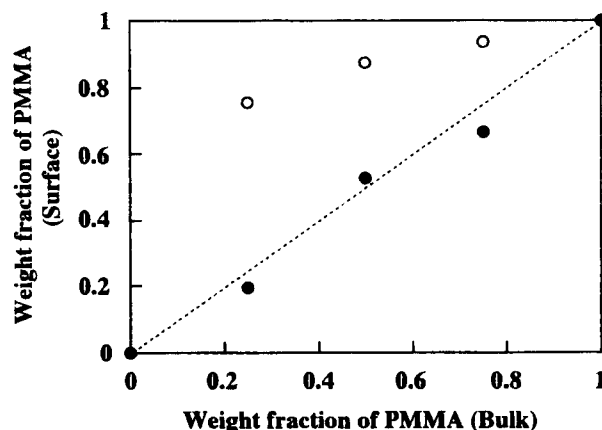
Figure 6. Film thickness dependence of the surface composition for (PMMA/SAN 30) blend films. (●: ultrathin film ○: thick film) The broken line indicates the bulk weight fraction in blend.

of casting solvent was used and how they are dried. Therefore, the surface structure of a polymer blend is not a simple function of the surface free energy difference or the molecular interaction.

Figure 6 shows XPS results of (PMMA/SAN 30) ultrathin films with *ca.* 13 nm thick and thick films with 2 μm thick. Polymeric films with thickness less than about 2 Rg of the higher weight component, here PMMA (2 Rg= 14.6 nm), was defined as the ultrathin blend films.[8] Since polymeric chains at the interface, in general, are thermodynamically unstable, the molecular aggregation structure in the ultrathin film of binary polymer blend must be greatly different from that in the thick film. The surface structure of ultrathin film did not show any surface enrichment of PMMA, the lower surface free energy component in the blend. This result was agreed with that of (PMMA/PVAc) ultrathin films, that is, the mobility of chains in a blend film with this thickness is restricted due to its very narrow space.[8]

Conclusion

The surface structure of (PMMA/SAN) blends with various AN contents of SAN and in the carboxyl acid contents of PMMA was investigated on the basis of XPS, ATR-FT IR and AFM measurements. It was revealed that the degree of surface enrichment in phase mixed- and phase-separated systems is not a simple function of the surface free energy difference, entropy of mixing, or molecular interaction. The component enriched at the surface of a blend is strongly dependent on the difference of surface free energy between components in the blend whereas the degree of surface en-

richment is dependent on several factors such as surface free energy difference, intermolecular interaction and sample preparation history. The carboxyl group in H-PMMA reduces the compatibility of (PMMA/SAN 30) blend due to the dilution of the repulsive force between S and AN unit.

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Rates of Conformational Change of 3,3-Dimethylpiperidine and Solvent Effects on Its Conformation When Coordinated to the Paramagnetic Undecatungstocobalto(II)silicate Anion Studied by ¹H NMR Spectroscopy

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¹H NMR spectra of 3,3-dimethylpiperidine (**1**) at − 70 to 30 °C exhibit gradual change from slow to rapid exchange between two alternate chair forms. The exchange rate constant was determined as a function of temperature by simulating the line shape of the signal from the two methyl groups using the modified Bloch equations. The resulting free energy of activation is $\Delta G^* = 44.4 \pm 1.9$ kJ mol⁻¹ at 298 K. The ¹H NMR spectrum of a D_2O or dimethylsulfoxide-d_6 (DMSO-d_6) solution containing **1** and $[SiW_{11}Co^{II}O_{39}]^{6-}$ exhibits separate signals for the free ligand and the complex, indicating that the ligand exchange is slow on the NMR time scale. In D_2O the piperidine ring is frozen as a chair form even at room temperature with the cobalt ion bonded to the axial position of the nitrogen atom. When DMSO-d_6 is added to the D_2O solution, the NMR spectral change suggests that a rapid exchange occurs between the chair form and another conformer. It is proposed that the conformation of **1** coordinated to $[SiW_{11}Co^{II}O_{39}]^{6-}$ in DMSO-d_6 is close to a twist form.

Introduction

Numerous NMR studies have been carried out on pi-

peridine and its derivatives to elucidate their conformations. A recent book on piperidine devoted three chapters to conformational analysis and ¹H and ¹³C NMR spectroscopies of