

Effect of the Stereoregularity of Poly(methyl methacrylate) on Interaction and Boundary Phase Structure between Poly(methyl methacrylate)/Poly(hydroxypropyl ether of bisphenol A) Blend and Polyamide Substrate

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ABSTRACT: The interaction and boundary phase structure between poly(methyl methacrylate) (PMMA)/poly(hydroxypropyl ether of bisphenol A) (PHPE) blend (PMMA/PHPE blend) and polyamide substrate were studied by using the PMMA/PHPE blend composite reinforced with short Kevlar® fiber and the PMMA/PHPE film formed on nylon-6 plate in relation to the stereoregularity of PMMA. The interaction between the matrix and reinforcement is estimated to be weaker for the composite made with isotactic (i-) PMMA/PHPE blend compared with composites made with syndiotactic (s-) PMMA/PHPE and atactic (a-) PMMA/PHPE blends from the mechanical dispersion data. The boundary phase in contact with the substrate is comprised of a mixture of PMMA and PHPE for the i-PMMA/PHPE and s-PMMA/PHPE blends from the X-ray photoelectron spectra. The boundary phase of a-PMMA/PHPE blend is composed of almost PMMA alone as reported previously. These differences of the interaction and boundary phase structure can mainly be attributed to differences of such a molecular characteristic of PMMA as overall molecular conformation or degree of constraint on the rotation of molecular chains and the difference of the compatibility of PMMA with PHPE, depending on the stereoregularity of PMMA.

KEY WORDS Poly(methyl methacrylate) / Poly(hydroxypropyl ether of bisphenol A) Blend / Stereoregularity / Polyamide Substrate / Substrate-Polymer Interaction / Boundary Phase Structure / Mechanical Dispersion / X-Ray Photoelectron Spectroscopy / Molecular Conformation / Compatibility /

It is generally known that the structures of blend polymers are not always the same with that of the bulk at the surface region in contact with the air and at the boundary phase in contact with a substrate. For composite material, adhesive bonded and paint coated substances, above all, the boundary phase have a vital effect on their performance, and interest has been directed to the explanation of the relation between the structure and properties of the boundary phase by many workers. Our previous work¹ on the study of the boundary phase structure between blend polymers and

polyamide substrate was also a trial to obtain insight into the problem. The boundary phase structure can be considered to be formed depending on the balance of the miscibility of blend polymers and interactions between the substrate and polymers.

The purpose of this work is to correlate the interaction between polyamide substrate and poly(methyl methacrylate) (PMMA)/poly(hydroxypropyl ether of bisphenol A) (PHPE) blend (PMMA/PHPE blend) with the boundary phase structure formed in contact with the substrate in relation to difference of tac-

ticity of PMMA. The mechanical dispersion is measured for the PMMA/PHPE blend reinforced with short fiber of Kevlar® 49 (Kevlar) and the nonreinforced polymers to estimate the interaction between the polyamide and PMMA/PHPE blend and the compatibility of blend polymers. The X-ray photoelectron spectrum (XPS spectrum) is measured for the PMMA/PHPE blend film formed on nylon-6 substrate (Nylon), which is usable as a model compound for Kevlar,¹ to probe the boundary phase structure. A preliminary report was made in our previous short note² on the XPS spectrum of atactic PMMA/PHPE blend film formed on Nylon. It was reported in previous papers^{1,3-5} that the boundary phase structure between polyamide substrate and stereoregular PMMA or PHPE, probed by the XPS spectrum, is well correlated with the interaction between the polymer and substrate, investigated by mechanical dispersion.

EXPERIMENTAL

Material

The PMMA samples used in this work were obtained from Polymer Laboratories Inc. and used as received. The characterizing data of these polymers from supplier are shown in Table I. PHPE used in this work was obtained from General Science Co. and used as received. The molecular weight is reported to be 32000 from the supplier. Kevlar was obtained from du Pont de Nemours Co., Inc. and used as a cut fiber of 5 mm long. Nylon (Novamide 1010) was obtained from Mitsubishi Chemical

Industries.

Specimen for Measurement of Mechanical Dispersion

The PMMA/PHPE mixture at a 1/1 ratio by weight was dissolved in tetrahydrofuran to obtain a 5% solution and Kevlar fiber was added to this solution and dispersed uniformly by stirring. The mixing ratio of PMMA/PHPE was selected as the interaction with the substrate was maximized in the vicinity of this blend ratio.⁶ This matrix-reinforcement mixture was cast onto a glass plate. After removal of the solvent, the composite specimen was obtained by compressing at 250, 260, and 275°C for the composites made with isotactic (i-) PMMA/PHPE, atactic (a-) PMMA/PHPE and syndiotactic (s-) PMMA/PHPE, respectively, under a pressure of 3.9×10^7 Pa. Thus, the specimen prepared in this work was a discontinuous fiber-reinforced composite made with random in-plane fiber orientation. The volume fraction of the reinforcement in the composite was estimated at 0.08 by considering the density (1.45 g cm^{-3}) of Kevlar. The specimens of nonreinforced blend polymers were also prepared by compressing the cast material at 200, 240, and 250°C for i-PMMA/PHPE, a-PMMA/PHPE, and s-PMMA/PHPE, respectively. The film of nonreinforced polymers thus obtained was slightly turbid, but the clarity of i-PMMA/PHPE and s-PMMA/PHPE films was superior to that of a-PMMA/PHPE.

Specimen for Measurement of XPS Spectrum

The PMMA/PHPE mixture at a 1/1 ratio by weight was dissolved in tetrahydrofuran to obtain a 2% solution. The plate of Nylon with a thickness of *ca.* 1 mm, obtained by compressing the material under a pressure of 3.9×10^7 Pa at 200°C between two flat metal plates, was dip-coated with the solution at a thickness of *ca.* 0.5 mm by repeated coatings, and the solvent was removed in a vacuum oven at elevated temperature. The film formed on Nylon

Table I. Characterization data for PMMA samples

Sample	$\bar{M}_w \times 10^{-3}$	\bar{M}_w/\bar{M}_n	Tacticity, %triads		
			<i>mm</i>	<i>mr</i>	<i>rr</i>
Isotactic	302	10.2	90	6	4
Atactic	140	1.1	7	40	53
Syndiotactic	262	2.6	6	18	76

was carefully separated from the substrate after 1 week so as not to damage the film surface. Leaving the coated specimen for 1 week in the air made it easy to separate the film from the substrate.

Measurement

The mechanical dispersion was measured on a Rheovibron DDV-II (Toyo Baldwin Instrument Co.) at 11 Hz.

The XPS spectra were obtained with a VG HB 50A scanning electron microscope equipped with an XPS option. The X-rays source was an aluminum anode source producing AlK_{α} X-rays at 1486.6 eV and operating at 12 kV and 20 mA. An instrumental vacuum of at least 1×10^{-6} Pa was used for all analyses. The sample film was mounted on double-stick tape. The data were analyzed on the high-resolution spectra of the C_{1s} region after background subtraction. The overlapping peaks of the C_{1s} spectra were resolved into their individual components by assuming a Gaussian-type symmetric function^{7,8} with respect to the photoelectron intensity versus binding energy relation. The resolution was tried three times for several spectra. The value of relative peak area of each individual component obtained for the second and third trials did not differ more than $\pm 10\%$ from that obtained for the first trial. Where binding energy assignments for component Gaussian curves were made, the peak for the hydrocarbon component was used as the reference and was assigned a value of 285.0 eV to compensate for charging effects.

Angular-dependent XPS measurements

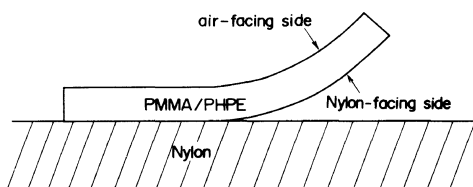


Figure 1. Schematic of the sample preparation for measurement of XPS spectrum.

were carried out by tilting the surface of sample so that the effective sampling depth would decrease with decreasing take-off angle of photoelectron (θ), which is the angle between the surface of the sample and electron analyser axis.

The XPS spectrum was measured for the separated film from Nylon substrate on both surfaces, that which had faced the air (air-facing side) and that which had faced the Nylon plate (Nylon-facing side), as shown schematically in Figure 1. The Nylon-facing side of the film can be considered to have a structure similar to the boundary phase of the composite.

RESULTS

Mechanical Dispersion

The storage modulus E' and loss modulus E'' versus temperature curves of the composites made with i-PMMA/PHPE, s-PMMA/

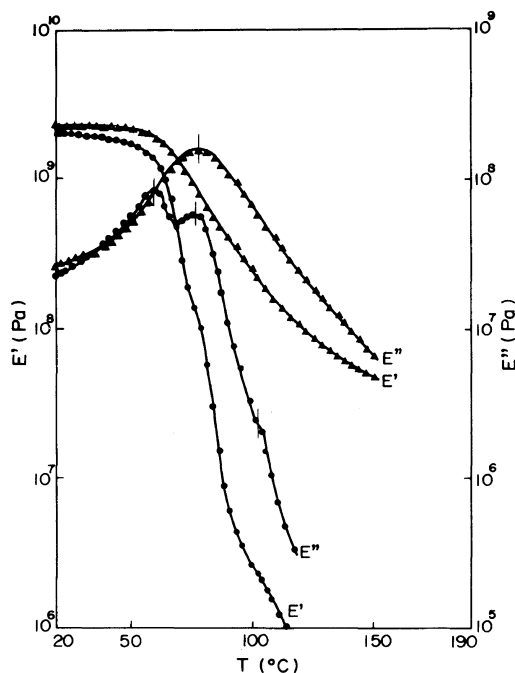


Figure 2. E' , E'' vs. temperature curves for i-PMMA/PHPE blend polymers (\bullet) and i-PMMA/PHPE blend polymers reinforced with Kevlar (\blacktriangle).

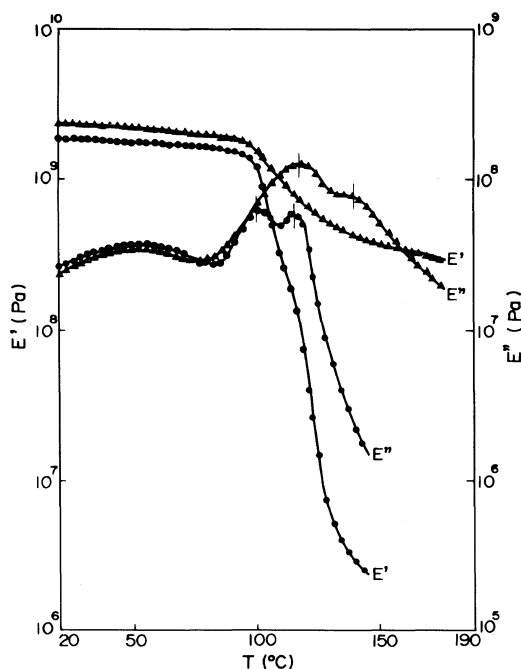


Figure 3. E' , E'' vs. temperature curves for s-PMMA/PHPE blend polymers (●) and s-PMMA/PHPE blend polymers reinforced with Kevlar (▲).

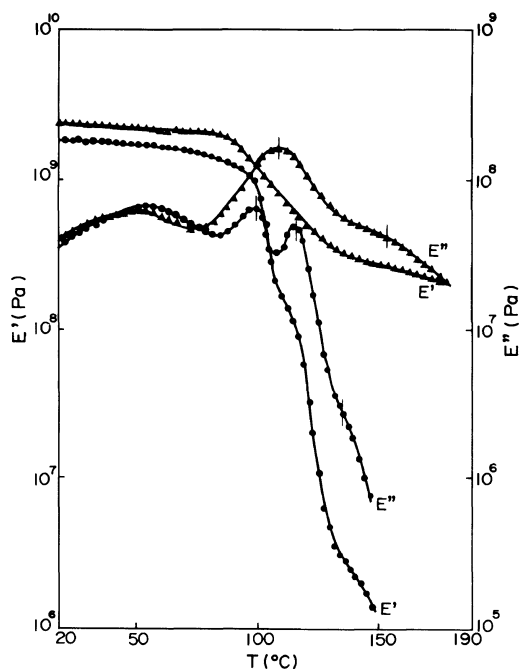


Figure 4. E' , E'' vs. temperature curves for a-PMMA/PHPE blend polymers (●) and a-PMMA/PHPE blend polymers reinforced with Kevlar (▲).

PHPE, and a-PMMA/PHPE as matrix are shown in Figures 2 to 4 together with those of the nonreinforced blend polymers. (For the composite made with a-PMMA/PHPE and the nonreinforced polymers, the mechanical dispersion is reported in the previous paper,⁶ but the samples used in that work were prepared by using the material and processing conditions differing from those of this work.) In the first place, Figures 2 to 4 show the phase separation of the nonreinforced blend polymers. That is, three dispersions can be observed in the figures (dispersion temperature is indicated by vertical short line on E'' curves) for the cases of i-PMMA/PHPE and s-PMMA/PHPE. The lower temperature dispersions of i-PMMA/PHPE and s-PMMA/PHPE appear almost at the same temperature as the primary dispersion of i-PMMA and PHPE,^{3,5} respectively. The second dispersions, which appear at the intermediate temperature between the primary

dispersion temperatures of the blend components, can be considered to arise from mutual solubilization of PMMA and PHPE. The highest temperature dispersions of i-PMMA/PHPE and s-PMMA/PHPE, which can only be observed as shoulders, nearly correspond to the primary dispersions of PHPE and s-PMMA,^{3,5} respectively. For the case of a-PMMA/PHPE, two dispersions can be observed. The lower and higher temperature dispersions almost coincide with the primary dispersions of PHPE and a-PMMA,^{3,5} respectively.

For the cases of the composite, one broad dispersion (primary dispersion) appears over the dispersions of the nonreinforced blend polymers, showing apparent increase of the compatibility of the blend components by reinforcement. Though only a dispersion appears for the case of i-PMMA/PHPE-Kevlar, additional dispersion appears at the higher

Interaction and Boundary Phase Structure

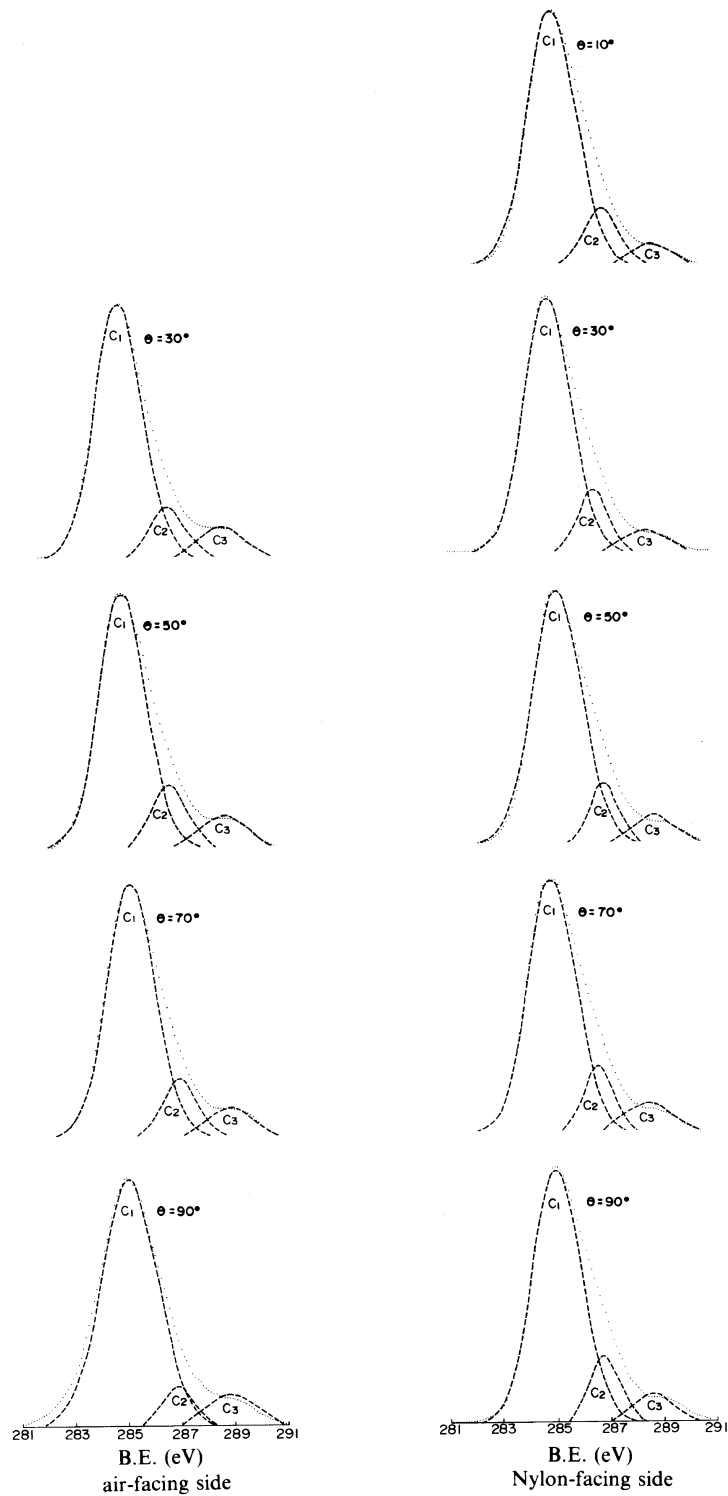


Figure 5. XPS spectra for i-PMMA/PHPE films.

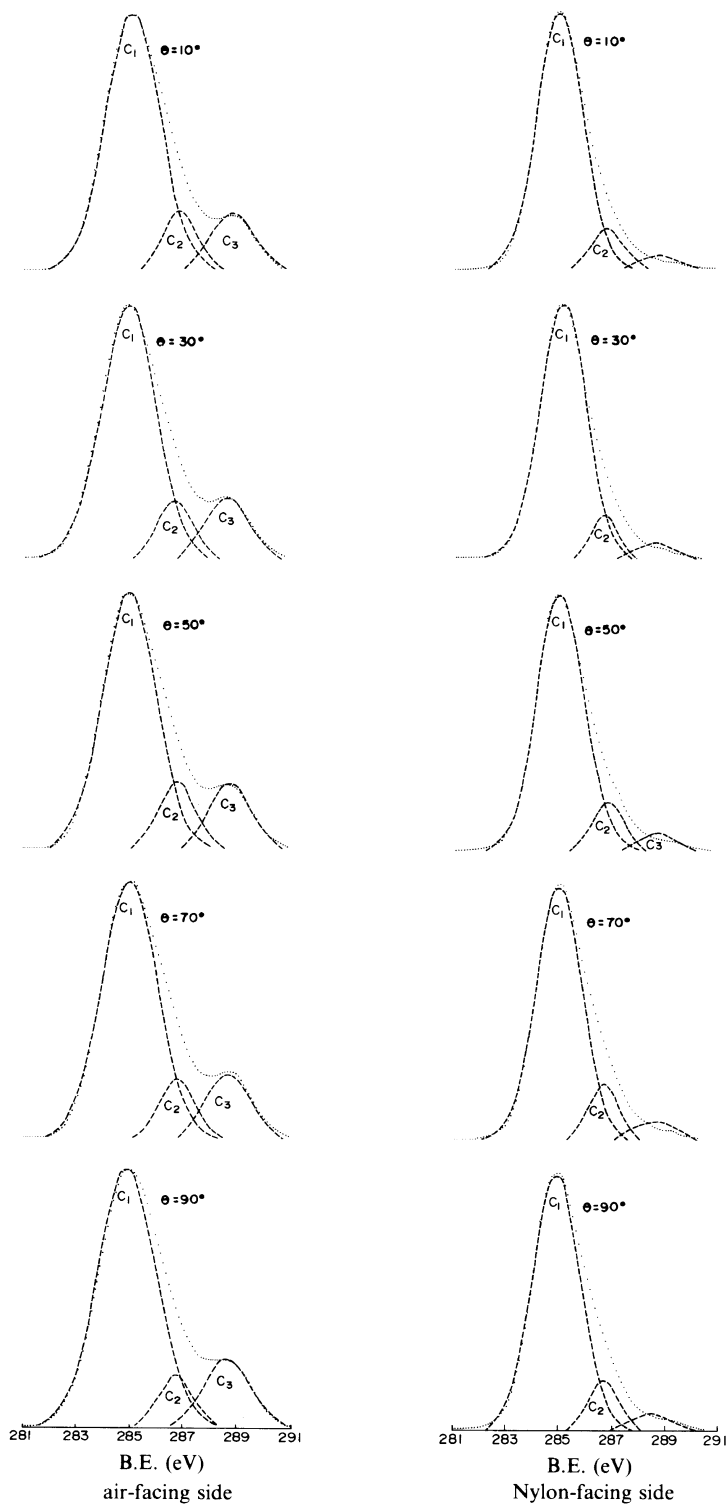


Figure 6. XPS spectra for s-PMMA/PHPE films.

temperature side of dispersions for the cases of s-PMMA/PHPE-Kevlar and a-PMMA/PHPE-Kevlar. The additional dispersions of s-PMMA/PHPE-Kevlar and a-PMMA/PHPE-Kevlar appear almost at the same temperature as those of s-PMMA reinforced with Kevlar and a-PMMA reinforced with Kevlar,⁵ respectively. The appearance of the former, however, is somewhat ambiguous compared with that of the latter. These additional dispersions can be attributed to the boundary phase formed in the vicinity of the reinforcement by the strong interaction with matrix, and show subtle change in magnitude and shape depending on the degree of interaction as reported previously.⁹⁻¹² Furthermore, the decrease in E' with increase of temperature is substantially larger for i-PMMA/PHPE-Kevlar compared with the cases of other composites, though the degree of decrease in E'

is slightly larger for s-PMMA/PHPE-Kevlar than for a-PMMA/PHPE-Kevlar. From these experimental results it can be said that the interactions of the blend polymers with Kevlar are weaker in the order of i-PMMA/PHPE-Kevlar, s-PMMA/PHPE-Kevlar, and a-PMMA/PHPE-Kevlar.

XPS Spectrum

In Figures 5 and 6, the observed C_{1s} spectra (dotted curve) and resolved components (broken curve) are shown for both the air-facing and Nylon-facing sides at various take-off angles for i-PMMA/PHPE and s-PMMA/PHPE. The spectra of a-PMMA/PHPE are shown in our previous short note.²⁾ The resolved components C_1 , C_2 , and C_3 in Figures 5 and 6 can be assigned to C-CH_x , C-O , and O-C=O , respectively. As the component C_3 comes from PMMA alone, C_3 can be used as a

Table I. Relative peak areas (%)

Sample	θ ($^\circ$)	C_1		C_2		C_3	
		Obs. ^a	Obs.	Re-est. ^b	Obs	Re-est.	
i-PMMA/PHPE air-facing side	90	80.5	12.3	21.4	7.2	12.5	
	70	80.9	12.2	21.7	6.9	12.2	
	50	79.1	13.6	22.1	7.3	11.8	
	30	80.7	11.4	20.0	7.9	13.9	
i-PMMA/PHPE Nylon-facing side	90	80.0	13.2	22.4	6.8	11.5	
	70	79.2	12.7	20.7	8.1	13.2	
	50	80.9	11.5	20.5	7.5	13.4	
	30	80.4	13.0	22.5	6.6	11.4	
	10	83.5	12.0	24.7	4.5	9.2	
s-PMMA/PHPE air-facing side	90	76.7	8.1	14.0	15.2	26.0	
	70	75.2	10.2	16.5	14.6	23.5	
	50	74.2	12.4	19.2	13.4	20.8	
	30	74.9	11.1	17.7	14.0	22.3	
	10	76.2	10.7	18.0	13.1	22.0	
s-PMMA/PHPE Nylon-facing side	90	85.4	10.5	24.5	4.0	9.4	
	70	83.2	11.2	22.6	5.6	11.3	
	50	86.1	10.1	24.6	3.8	9.3	
	30	87.2	8.0	21.2	4.8	12.7	
	10	88.0	9.1	25.7	2.9	8.2	

^a Observed value.

^b Re-estimated value.

measure of the behavior of PMMA in the blend.² The relative peak areas of C_1 , C_2 , and C_3 components are tabulated in Table II and plotted against the take-off angle ($\sin \theta$) in Figure 7 for i-PMMA/PHPE. The numbers of $\underline{C}H_x$, $\underline{C}-O$, and $O-\underline{C}=O$ in a chemical repeating unit of PMMA are 3, 1, and 1, respectively, and those in the case of PHPE are 13, 5, and 0, respectively. Therefore, the atomic % of $\underline{C}H_x$, $\underline{C}-O$, and $O-\underline{C}=O$ anticipated from the chemical structure and composition for the PMMA/PHPE blend can be calculated at 66.1, 23.9, and 10%, respectively. The observed relative peak area of C_1 is larger than the value anticipated from the chemical structure and composition. This is probably due to the increase in relative peak area of the C_1 component on account of the hydrocarbon contamination layer deposited on the sample during measurement.¹³ {Our XPS instrument detects the component corresponding to C_1 at *ca.* 15% or more even for poly(ethylene oxide),¹ which does not contain $\underline{C}H_x$ in the chemical structure.} By assuming simply the relative peak area of C_1 , which is free from the hydrocarbon contamination (C_1^{ant}), to be 66.1% in the range of $\sin \theta$ measured at both the air-facing and Nylon-facing sides (that is, the

effect of hydrocarbon contamination was assumed to appear only on C_1 component), the relative peak areas of C_2 and C_3 were re-estimated (C_2^{re-est} and C_3^{re-est}) from the observed values (C^{obs}) according to the relations:

$$C_2^{re-est}(\%) = \frac{(100 - C_1^{ant}) \cdot C_2^{obs}}{C_2^{obs} + C_3^{obs}},$$

$$C_3^{re-est}(\%) = \frac{(100 - C_1^{ant}) \cdot C_3^{obs}}{C_2^{obs} + C_3^{obs}}$$

The re-estimated values of C_2 and C_3 as tabulated in Table II and plotted in Figure 7 come close to those anticipated from the chemical structure and composition compared with the observed values at both the air-facing and Nylon-facing sides.

The results for s-PMMA/PHPE are also tabulated in Table II and plotted in Figure 8. The observed C_3 becomes somewhat larger than the observed C_2 at the air-facing side. This means enrichment of the PMMA component at the air-facing side. Therefore, the relative peak areas of C_2 and C_3 were re-estimated from the observed values by assuming the relative peak area of C_1 to be 60%, which is the value anticipated from the chemical structure of PMMA free from the hy-

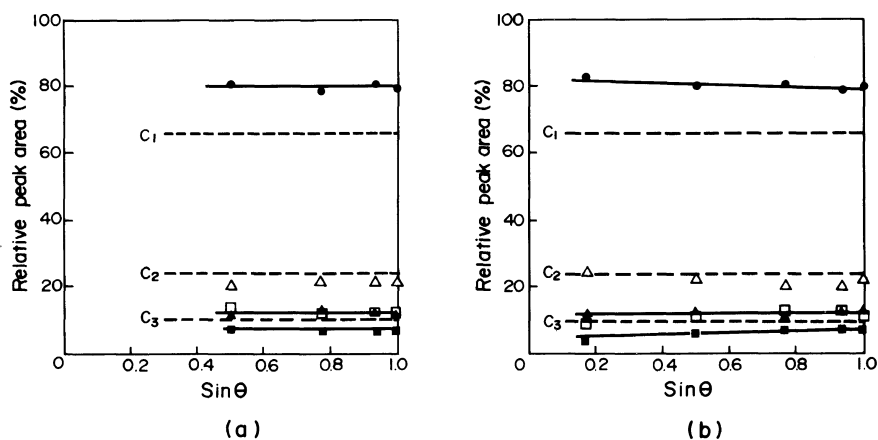


Figure 7. Relative peak area vs. electron take-off angle relations for observed values (C_1 , ●; C_2 , ▲; C_3 , ■), re-estimated values (C_2 , △; C_3 , □) and anticipated values from chemical structure and composition for PMMA/PHPE blend at 1/1 ratio by weight (----). (a) and (b) are the results of air-facing side and Nylon-facing side of i-PMMA/PHPE samples, respectively.

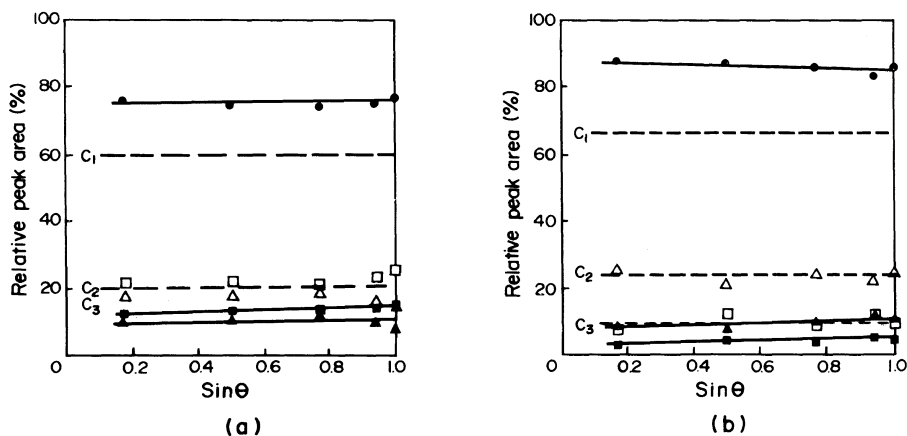


Figure 8. Relative peak areas vs. electron take-off angle relations for observed values (C_1 , ●; C_2 , ▲; C_3 , ■), re-estimated values (C_2 , △; C_3 , □), anticipated values from chemical structure for PMMA (—) and anticipated values from chemical structure and composition for PMMA/PHPE blend at 1/1 ratio by weight (---). (a) and (b) are the results of air-facing side and Nylon-facing side of s-PMMA/PHPE samples, respectively.

drocarbon contamination, according to the above relations. The re-estimated values of C_2 and C_3 as shown in Table II and Figure 8 come close to the relative peak areas of C_2 and C_3 anticipated from the chemical structure of PMMA homopolymer. This means that the air-facing side is composed of almost PMMA alone. At the Nylon-facing side, the relative peak areas of C_2 and C_3 were re-estimated from the observed values by assuming the relative peak area of C_1 to be 66.1% as in the case of i-PMMA/PHPE. The re-estimated values of C_2 and C_3 come close to those anticipated from the chemical structure and composition as for the case of i-PMMA/PHPE.

DISCUSSION

The boundary phase of a-PMMA/PHPE sample consists almost of a-PMMA alone as reported previously²⁾, and the a-PMMA/PHPE blend polymers can be said to be comprised of nearly pure PHPE and a-PMMA phases as shown in Figure 4. Nylon and PHPE are known to self-associate through strong hydrogen bonding.¹⁴⁻¹⁶ Therefore, the non-self-associated a-PMMA in a-PMMA/PHPE

blend tends to concentrate on the substrate exclusively, and may give rise to the prominent boundary phase dispersion at the same temperature as that of a-PMMA reinforced with Kevlar as observed.

As mentioned above, both PMMA and PHPE components can be found from XPS spectra at the Nylon-facing side for i-PMMA/PHPE and s-PMMA/PHPE samples in contrast to the case of the a-PMMA/PHPE sample. The mechanical dispersion, however, shows that though the boundary phase dispersion arising from the interaction of s-PMMA with the substrate can be found for s-PMMA/PHPE-Kevlar, such dispersion cannot be found for i-PMMA/PHPE-Kevlar. From these facts it can be said that though the interactions between the substrate and the blend polymers differ with each other, the boundary phase structure of i-PMMA/PHPE probed by XPS is similar to that of s-PMMA/PHPE.

As mentioned above, the phase comprised of mutually solubilizing PMMA and PHPE components is found in i-PMMA/PHPE and s-PMMA/PHPE blends at considerable fraction. The presence of this phase and the superiority as mentioned in experimental sec-

tion suggest the higher degree of compatibility and uniformity of the blends as a whole compared with the case of a-PMMA/PHPE blend. If so, i-PMMA/PHPE and s-PMMA/PHPE blends may be deposited on the Nylon-surface at nearly the same composition as the bulk composition, contrary to the case of a-PMMA/PHPE blend. Nonself-associated PMMA in contact with Nylon-surface may cause specific interactions with the substrate. The interactions of s-PMMA itself with the substrate is stronger than that of i-PMMA itself on account of differences in the chain conformation or constraint on the rotation of the molecular chain,⁵ and the interaction of s-PMMA/PHPE with the substrate also becomes stronger compared with the case of i-PMMA/PHPE. That is, the interaction of the substrate with PMMA in the PMMA/PHPE blend mainly depends on the molecular characteristic of PMMA itself. {PHPE itself can also cause interactions with the polyamide substrate, and consequently boundary phase dispersion around 135°C.⁶ For the composite made with PMMA/PHPE blend polymers, the boundary phase dispersion assigned to PHPE, however, could not be observed.} A somewhat ambiguous boundary phase dispersion of s-PMMA/PHPE-Kevlar compared with that of a-PMMA/PHPE-Kevlar can mainly be attributed to the smaller concentration of s-PMMA on Nylon-surface.

The compositions at the air-facing side of i-PMMA/PHPE and a-PMMA/PHPE samples are nearly the same with the bulk composition. But the surface region of s-PMMA/PHPE is almost composed of s-PMMA alone. The surface region is generally enriched with the lower surface energy component for two component systems.^{17,18} The surface energy of i-PMMA is smaller than that of s-PMMA according to contact angle data¹⁹ (the surface energy of PHPE is larger than that of PMMA according to correlation of the solubility parameter with the critical surface tension^{20,21}) and thus the segregation of s-PMMA at the air-facing

side cannot be explained by the general trend only. The apparent solubility coefficient of s-PMMA for oxygen and nitrogen gases are substantially larger than those of i-PMMA and a-PMMA.²² Though this may be a factor for the segregation of s-PMMA, comprehensive discussion is necessary for a consistent explanation of this behavior.

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