

XPS Surface Studies of Injection-Molded Poly(phenylene ether)/Nylon 6,6 and Poly(phenylene ether)/HIPS Blends

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SYNOPSIS

The surface compositions of a series of poly(phenylene ether)/nylon 6,6 blends (PPE/PA), and PPE/HIPS blends, prepared by melt compounding and injection molding, have been quantitatively measured using XPS. For PPE/PA blends, the surface is dominated by the PA component for blends containing more than 25 wt % PA in the bulk. The enrichment of the PA component, which is actually the component of highest surface free energy, is rationalized in terms of the bulk morphology that consists of PPE domains in a PA continuous phase. Blends prepared by reactive extrusion processes, which form compatibilizing PPE/PA copolymers, show a decrease in surface PA enrichment with increasing copolymer content in the final blend. PPE/HIPS blends have a surface composition equal to the formulated value over the entire composition range, for both molded and solvent cast blends. The addition of 5% PVME to a 60/40 PPE/HIPS blend results in a molded surface containing 35–40 wt % PVME. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that the surface compositions of multicomponent polymers can differ substantially from the bulk formulation. In many reported systems, the component with the lowest surface free energy is enriched at the surface (polymer–air interface), although other factors such as block lengths or molecular weight, morphology, and sample preparation are also important. X-ray photoelectron spectroscopy (XPS) has been used to study these effects for block copolymers,^{1–13} miscible blends,¹⁴ and immiscible polymer blends.¹⁵ Many of these studies have been conducted on solvent-cast polymer films where the sample preparation and annealing sequences provide a surface that is at or near equilibrium. Although most applications of polymer alloys involve molding operations, relatively few studies on polymer blend surfaces formed by melt compounding and molding have been reported. It is expected that surfaces formed by molding would

be additionally affected by miscibilities and unique morphologies that exist in the melt, and by the process of solidification when the melt contacts the mold surface. In this work we have measured the surface compositions of injection-molded poly(phenylene ether)/nylon 6,6 (PPE/PA) and PPE/high-impact polystyrene (PPE/HIPS) blends using X-ray photoelectron spectroscopy (XPS), as a function of bulk formulation. The first blend, PPE/PA, is an immiscible system, and the surface composition is shown to be affected by bulk morphology and processing conditions, including copolymer formation during reactive extrusion. In contrast, the PPE/HIPS system forms a totally miscible blend and the surface composition reflects the bulk formulation.

EXPERIMENTAL

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was obtained from GE Plastics and had an intrinsic viscosity of 0.4 dL/g measured in chloroform at 25°C. Nylon 6,6 (hereafter polyamide, PA) was obtained from Monsanto. Blends were compounded on a

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Welding-Engineer's 20-mm nonintermeshing, twin-screw extruder. In some cases a styrene-ethylene, butylene-styrene (SEBS) impact modifier was additionally present in the blends at 10 wt %. Specimens with different degrees of PPE/PA copolymer formation, prepared by reactive extrusion with functionalized PPE, were obtained from T. Shea and J. Campbell, et al., prepared and characterized as described in Ref. 16.

All specimens were obtained from injection-molded tensile bars or plaques. The molded specimens had an average surface roughness of approximately $1\ \mu\text{m}$ [see Fig. 6(b)]. Additionally, solvent-cast films of homopolymers and PPE/HIPS blends were prepared by spin coating at 1000 rpm onto clean glass cover slips. The solvents used were hexafluoroisopropanol for PA and toluene for PPE, HIPS, and PPE/HIPS mixtures. The film samples were air dried at room temperature prior to analysis.

X-ray photoelectron spectroscopy measurements were obtained using a Surface Science Instruments X-probe system. Spectra were obtained using a fo-

cused, monochromatic Al $k\alpha$ source with a 600- or 300- μm spot size. The fixed spectrometer pass energy of 150 eV was used for survey scans, and high-resolution scans of the C 1s, O 1s, and N 1s regions were acquired using pass energies of 50 or 25 eV. The photoelectron take-off angle was 35° with respect to the sample plane, which provides an integrated sampling depth (3λ) of approximately 40 Å (assuming an electron escape depth of 25 Å for the C 1s photoelectron). An electron flood gun was used to control surface charging, and the spectra were mathematically shifted (after acquisition) to align the C—H component of the C 1s line at 284.6 eV. The high-resolution spectra were curve fit using mixed Gaussian/Lorentzian (85/15) peak shapes. Atomic concentrations were computed using empirical sensitivity factors derived from the pure homopolymer spectra (PPE and PA). The relative sensitivity factors for C, N, and O were 1.0, 1.6, and 2.4, respectively, agreeing well with those supplied with the instrument software (Surface Science Instruments).

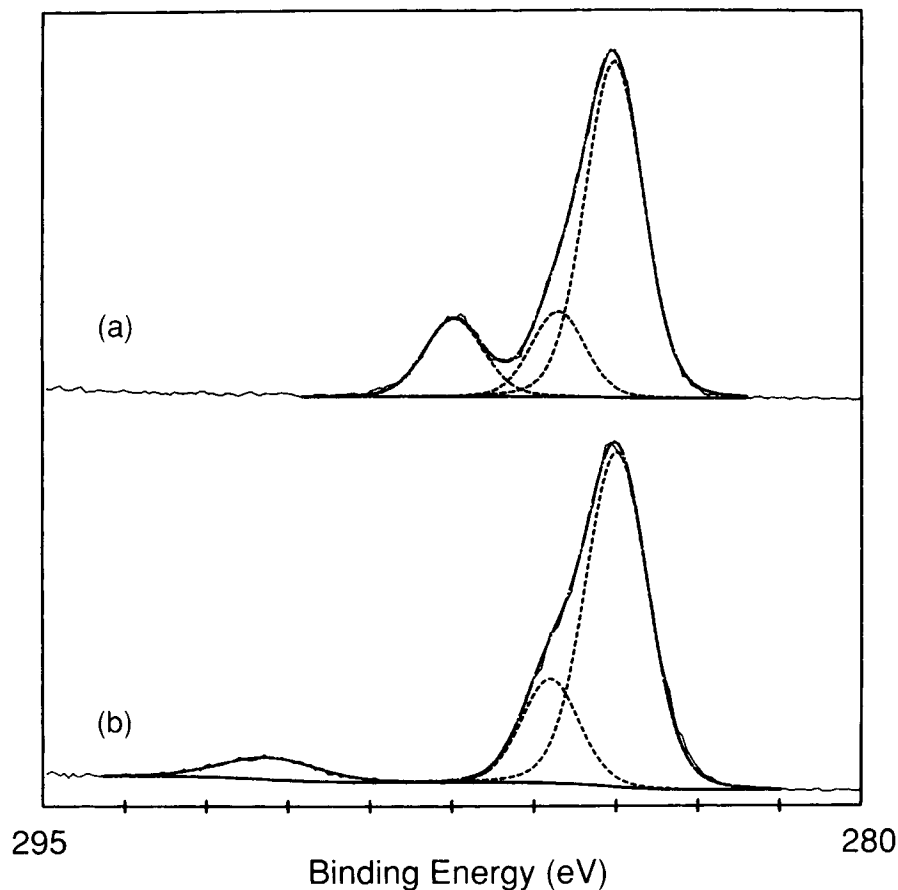


Figure 1 Carbon 1s spectra from (a) PA (nylon 6,6) and (b) PPE. The peak positions and relative intensities are summarized in Table I.

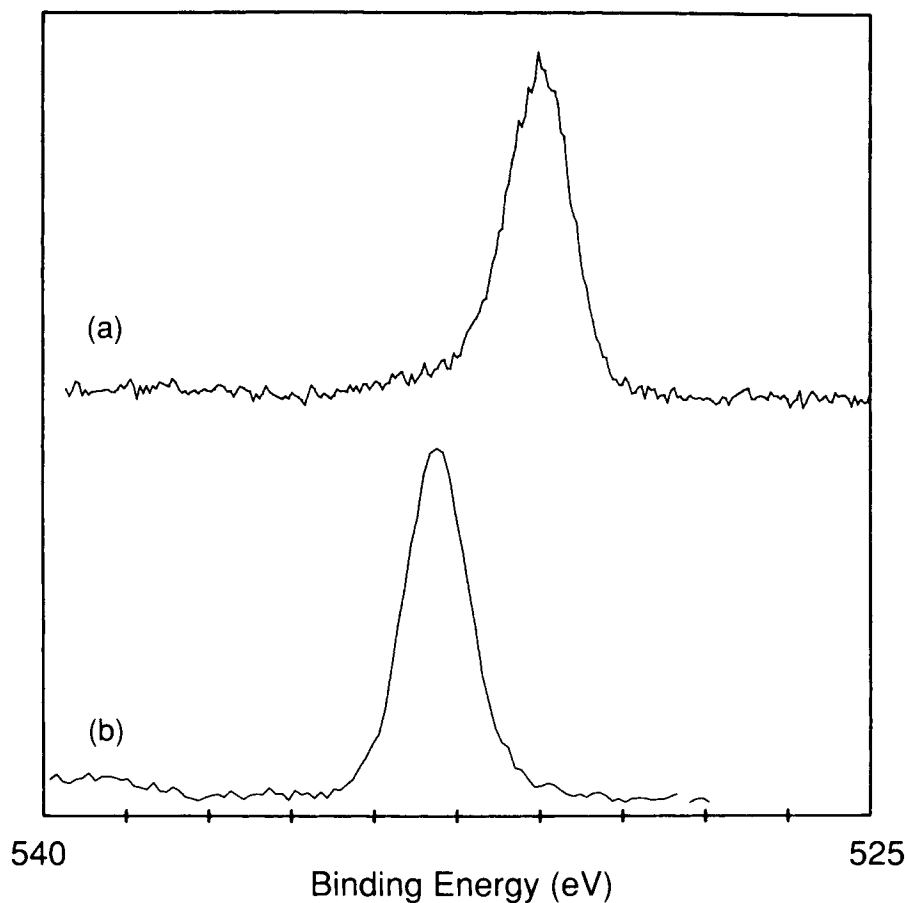


Figure 2 Oxygen 1s spectra from (a) PA and (b) PPE.

RESULTS AND DISCUSSION

PPE/PA Blends

Figures 1 and 2 show the C 1s and O 1s photoemission spectra obtained from solvent-cast films of the

Table I Binding Energies and Relative Intensities of Homopolymer XPS Spectra

	Component	Binding Energy	Area %
PPE C1s	C—H	284.6	69
	C—O	285.8	23
	π - π^*	291	8
Nylon 6,6 C1s	C—H	284.6	68
	C—N	285.6	16
	C=O	287.5	16
HIPS C1s	C—H	284.6	93
	π - π^*	291	7
PPE O1s	O—C	533.0	
Nylon 6,6 O1s	O=C	531.0	

pure homopolymers. For PA [Fig. 1(a)], the C 1s line shows three components due to C—H, C—N, and C=O carbon types. The experimental area fractions for each of the peak components found by curve fitting are summarized in Table I. The O 1s line [Fig. 2(a)] at 531.0 eV exhibited a slight asymmetry at the high binding energy side of the peak. The N 1s line (not shown) consists of a single component at 399.4 eV. The C 1s spectrum for PPE [Fig. 1(b)] consists of three contributions due to C—H, C—O, and an π - π^* shakeup peak due to the phenyl rings. A single O 1s peak [Fig. 2(b)] at 533.0 eV is observed.

Blend compositions ranging from 10–70 wt % PA were examined by XPS. The weight fraction of PA (ω) in the PPE/PA blend surface is computed from the XPS data by three methods. Based on the exclusive presence of nitrogen in the PA component, ω is computed from the elemental composition as

$$\omega = \frac{\text{atom \% N}}{11.7 + 0.062 \text{ atom \% N}} \quad (1a)$$

The PPE/PA ratio computed from the atom % N assumes no extraneous surface contamination or other effects such as surface oxidation. The weight fraction of PA in the PPE/PA blend can also be computed from the high resolution C 1s or O 1s spectra. Representative spectra from blends showing contributions from PA and PPE are shown in Figures 3 and 4. The surface PA content is determined from the area percent of the C=O component $I_{C=O}$ since it is due only to the PA constituent (see the Appendix):

$$\omega = \frac{0.0667(I_{C=O})}{0.88 + 0.0136I_{C=O}} \quad (1b)$$

The O 1s spectra [Fig. 1(b)] from the homopolymers each consist of a single component due to O=C in PA (531.0 eV) and O=C in PPE (533.0 eV). The weight fraction of PA can be obtained from the area percent of the O=C and O—C components as

$$\omega = \frac{I_{O=C}}{I_{O=C} + 1.06 I_{O-C}} \quad (1c)$$

The values of ω determined for a series of injection-molded plaques of PA/PPE blends using expressions (1a)–(1c) are summarized in Figure 5. There is reasonable agreement (± 5 wt %) between each of the data reduction methods for each blend. The plaque surface and bulk compositions are nearly equivalent for formulations at or below 25 wt % PA. An abrupt transition to a surface highly enriched in PA—90–95 wt %—is observed for formulations containing 30 wt % or more of the PA component. The enrichment of PA is contrary to the thermodynamic expectation of lower surface energy component enriching the surface. The surface free energies of nylon 6,6 is ca. 46 dyn/cm¹⁹ and that of PPE is 38 dyn/cm.²⁰ We suggest that in this blend, the surface composition is controlled the bulk blend morphology. Previous microscopy studies^{16–18} have

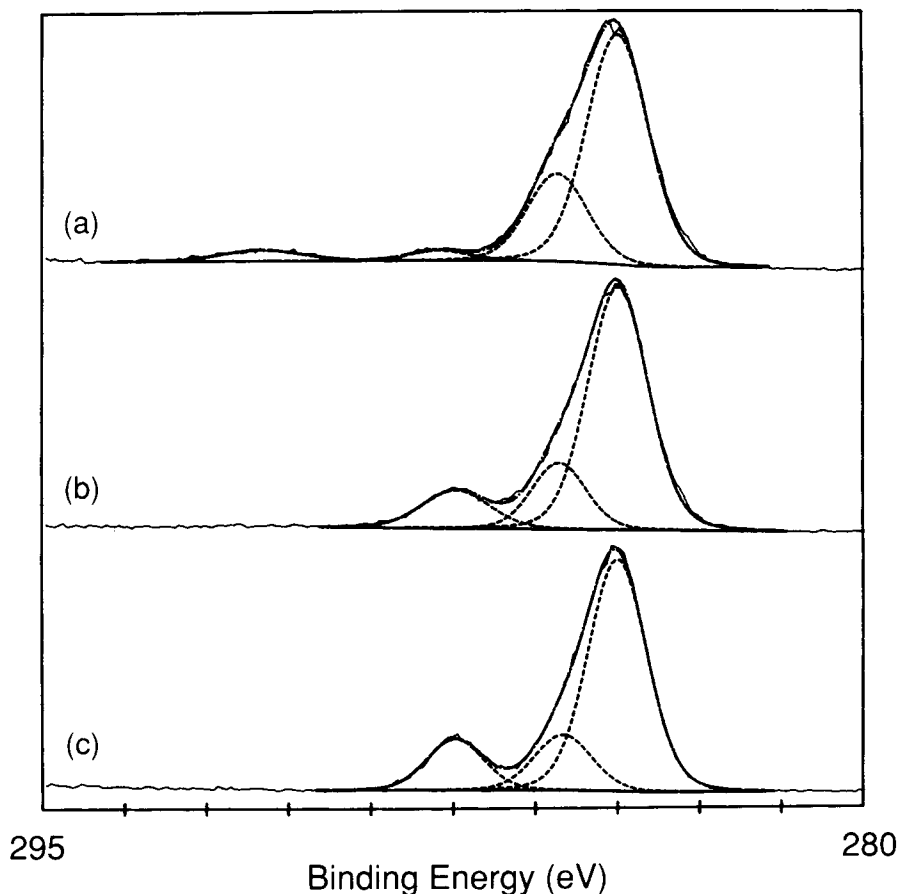


Figure 3 Carbon 1s spectra from PPE/PA blends. (a) 50/50, (b) 30/70, and (c) 20/80.

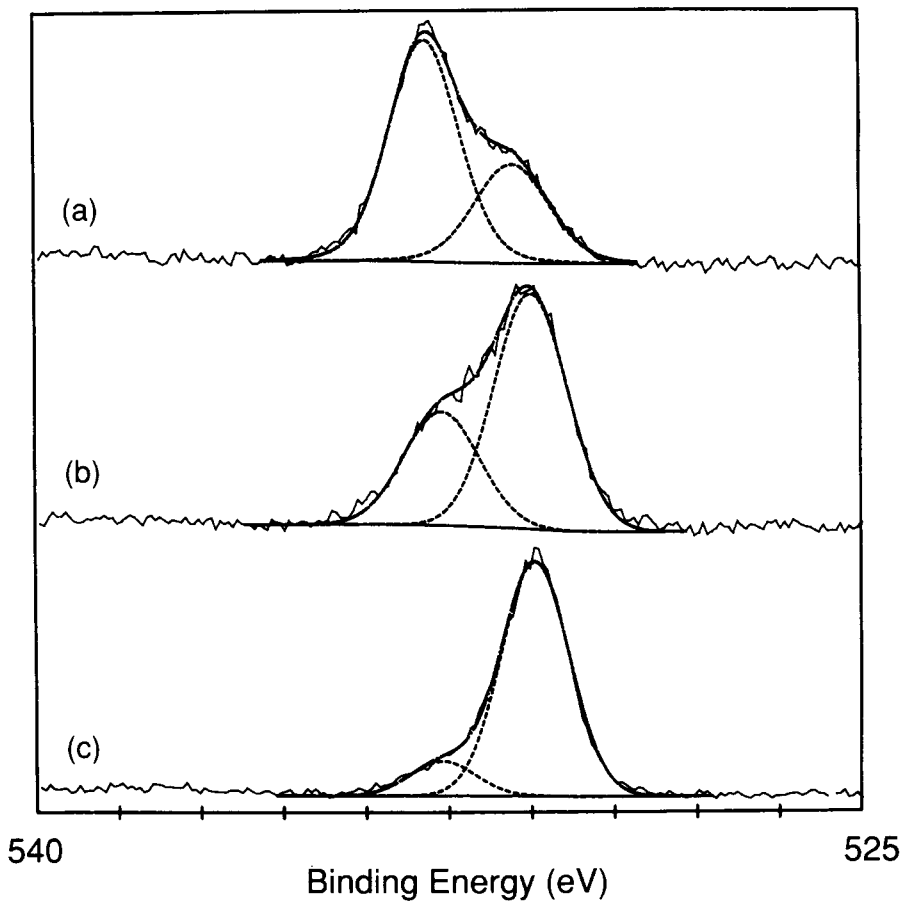


Figure 4 Oxygen 1s spectra corresponding to Fig. 3.

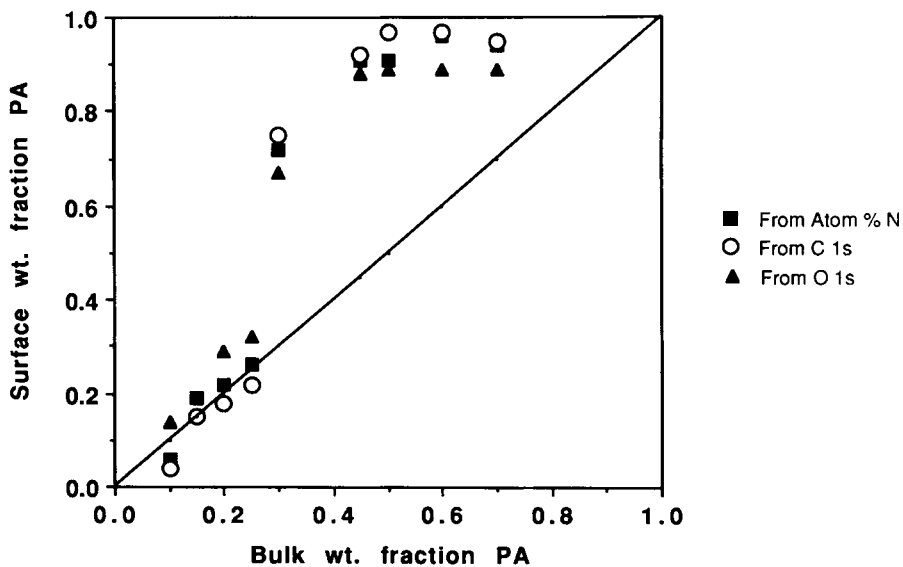
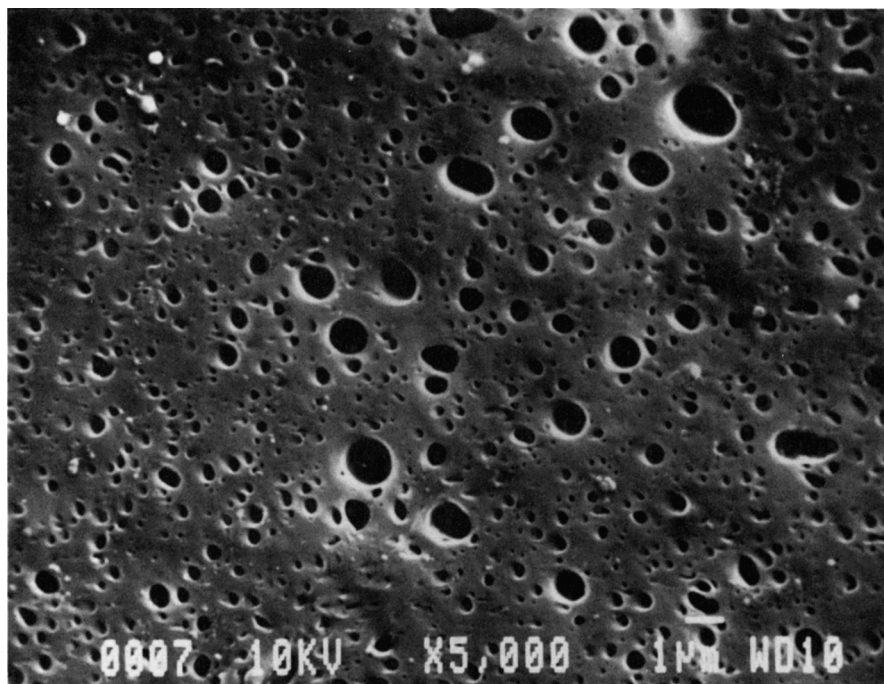
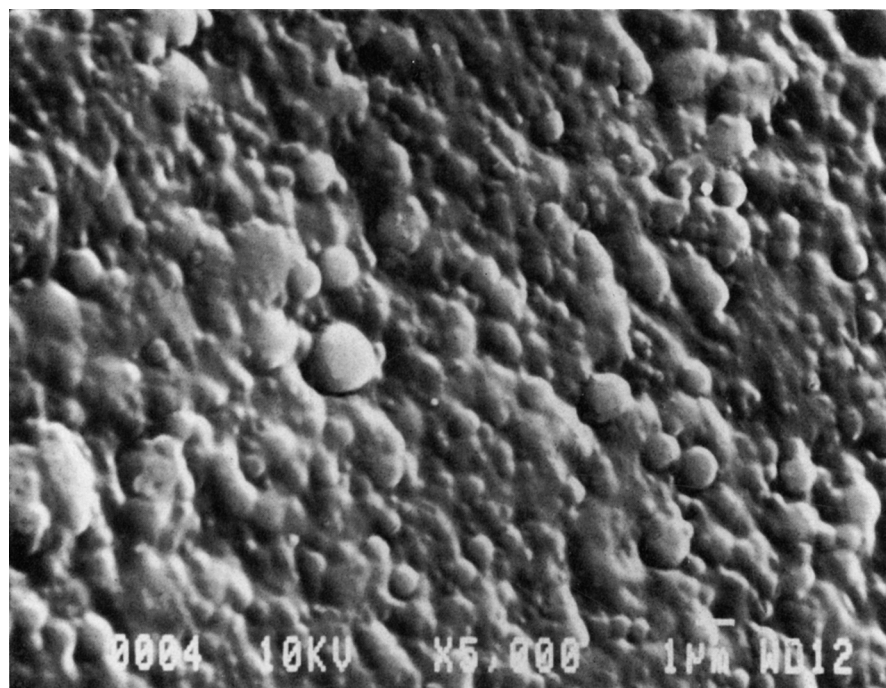


Figure 5 Surface wt % PA versus bulk formulation, showing surface PA enrichment for blends above 25 wt % PA.



(a)



(b)

Figure 6 Photomicrographs obtained from molded plaque of PPE/PA/rubber (49/41/10) blend. (a) Cross section of bulk, approximately 5 μm below molded surface, etched with chloroform to partially remove PPE domains for contrast. (b) Surface of the same plaque.

shown that for blends containing less than about 25% PA, the morphology consists of PA strands in a PPE matrix. For blends above 30 wt % PA, a phase inversion occurs and the bulk morphology consists of PPE domains in a PA continuous phase. Figure 6(a) shows a photomicrograph of a cross section from which the PPE domains have been etched using chloroform. The tendency of PA to form the continuous phase even when it is the minority component is due to its lower viscosity in the melt. The surface topography, indicated by the photomicrograph in Figure 6(b), shows features of the same size and shape as the PPE domains seen in the bulk. However, the XPS results show considerably less PPE at the surface than suggested by Figure 6(b). Our explanation is that the dispersions of PPE are surrounded by the PA continuous phase at the molded surface, resulting in a PA-rich surface composition. The surface layer of PA is too thin to be revealed by the present microscopy measurements but is indicated by the XPS surface compositional results. For blends below 25 wt % PA, a co-continuous phase morphology begins to develop in the bulk, which is manifest at the surface by the presence of both PPE and PA. These results indicate that in injection-molded specimens of PPE/PA immiscible blends, the component that tends to be the continuous phase dominates the surface of the material.

Compatibilized Blends

PPE/PA blends have been prepared using functionalized PPE derivatives, which results in the for-

mation of PPE/PA copolymers during processing (reactive extrusion). The increase in interfacial adhesion between the continuous and dispersed phases, and reduction of the size of the dispersed phase, leads to improvements in impact and tensile properties.^{16,17} Most commercial formulations also include the addition of a rubber phase to achieve the required toughness. We have applied XPS to characterize the surfaces of a series of PPE/PA/rubber blends (49/41/10 by wt %) each containing a different degree of copolymer in the reactively extruded material, controlled by varying the ratio of PPE and functionalized PPE derivatives in the initial formulations.¹⁶ The blends studied were prepared by two different compatibilization technologies that provide either graft or block copolymers.

The rubber particles are totally encapsulated within the PPE phase and do not contribute to the XPS signal from the surface, as observed previously for other rubber-toughened blends.¹⁵ The absence of rubber at the surface was verified by static SIMS, which showed only fragments due to PA and PPE. Hence, the XPS spectra are treated as described above for the unmodified PA/PPE blends. Figure 7 shows the surface PA content as a function of the fraction of the total PPE that is bound in PA/PPE copolymer. Blends with no copolymer show PA-rich surfaces analogous to uncompatibilized blends analyzed in the previous section. As the amount of copolymer formation increases, there is a decrease in the amount of PA enrichment at the surface. Blends with graft copolymer exhibit a larger decrease

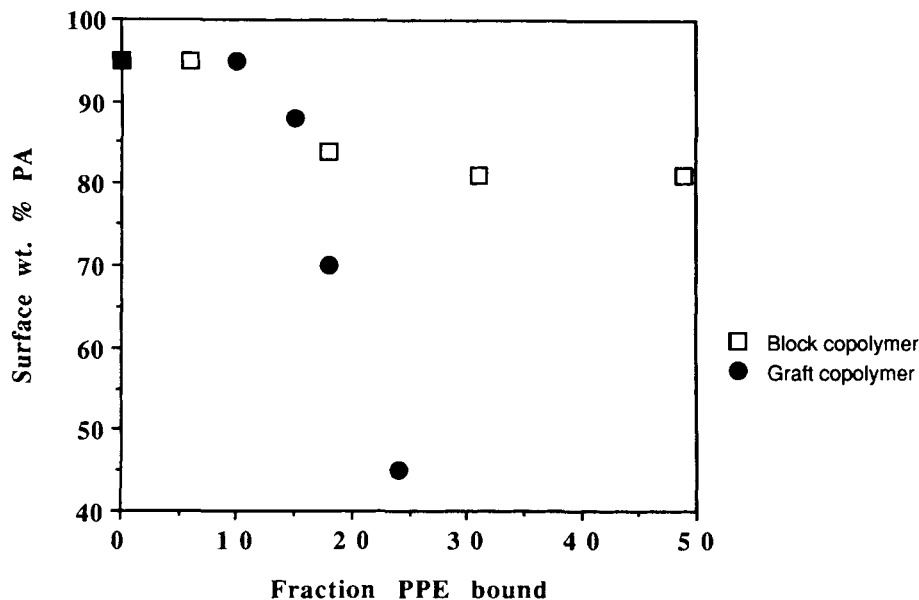


Figure 7 Surface PA content as a function of PPE/PA copolymer formation.

in surface PA enrichment than those with block copolymers. (Part of this difference may be related to the compositions of the copolymers that are formed. The graft copolymers have an average PA/PPE ratio of ca. 1.2, whereas for the block copolymers the PA/PPE ratio is 0.6.) Two explanations have been considered for explaining these surface analysis results. First, a change in the surface morphology to co-continuous PPE and PA domains may be occurring. Previous microscopy studies of the bulk morphology show a decrease in the size of the dispersed PPE domains as the copolymer content is increased,¹⁶ although a co-continuous morphology was not observed. However, it is possible that the transition to a co-continuous phase morphology occurs at the surface prior to the bulk transition seen in the microscopy measurements. A second explanation for the increased surface PPE content is the presence of copolymer molecules at the surface. Even if PA forms the continuous phase, the PA/PPE copolymer may have some solubility in the PA and

therefore be present at the surface. It is not possible using XPS to distinguish if the observed PPE is free or bound as PA/PPE copolymer.

PPE/HIPS Blends

The surface compositions of injection-molded PPE/HIPS specimens were determined by XPS for a complete range of formulations. The relative PPE or HIPS content can be quantified from the atomic composition, based on the exclusive presence of oxygen in the PPE:

$$\omega_{\text{PPE}} = \frac{0.0927\% \text{O}}{1 + 0.0023\% \text{O}} \quad (2a)$$

Another measure of the relative amounts of PPE and HIPS can be obtained from the high-resolution C 1s spectra. Figure 8 shows the C 1s spectra from HIPS, PPE, and a 60/40 blend. The spectrum from

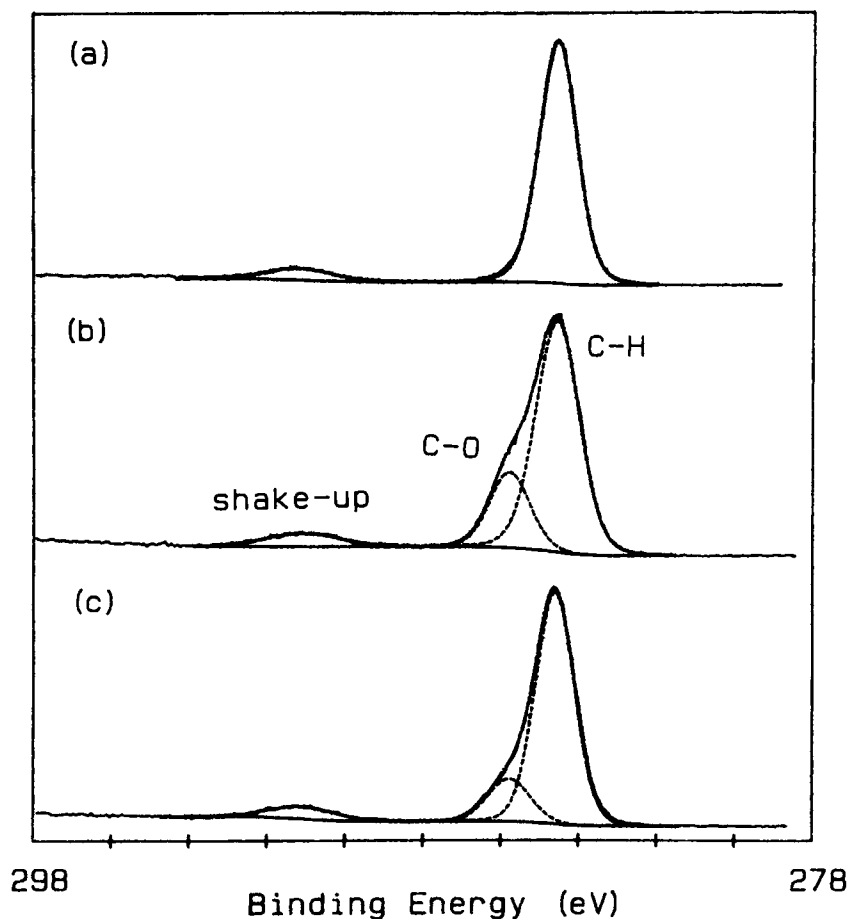


Figure 8 C 1s spectra for (a) HIPS, (b) PPE, and (c) 40/60 PPE/HIPS blend.

HIPS shows a single component at 284.6 eV due to the C—H (aromatic + backbone), with a prominent shakeup peak centered at 291 eV due to the aromatic ring. The spectrum is indistinguishable from that of linear PS. The spectrum of PPE, as described above, contains a shoulder at 286 eV due to the C—O linkages. Using the experimentally determined C 1s intensities from the homopolymer spectra (including the shakeup contributions), the weight fraction of PPE can be determined from the relative areas of the C—H and C—O components as

$$\omega_{\text{PPE}} = \frac{4.28I_{\text{C-O}}/I_{\text{C-H}}}{1 + 1.50I_{\text{C-O}}/I_{\text{C-H}}} \quad (2b)$$

Figure 9 summarizes the surface PPE content determined for a range of formulations using expressions (2a) and (2b). These results show that the surface composition is very close to the formulated value, with no preferential surface enrichment occurring. Although no oxygen is present in pure HIPS, a small amount is detected as the result of surface oxidation during processing, or possibly the presence of an additive. If the surface composition is determined only from the oxygen content, the amount of PPE may be overestimated unless this slight surface oxidation is accounted for. This effect is small, however, as shown by the agreement with surface compositions computed from the C 1s data. To further remove any ambiguity associated with extraneous surface oxygen, solvent-cast films of

chemically pure PPE and PS were prepared, as well as several blends. The pure PS showed no oxygen, as expected. The compositions of the films are included in Figure 9 along with the molded plaque results. In both types of specimens, the surface composition is identical to the bulk formulation. In miscible polymer blends the driving force for preferential surface adsorption comes mainly from the surface energy differences. PS and PPE have surface tension of 40 dyn/cm¹⁹ and 38–40 dyn/cm,²⁰ respectively, thus the driving force for surface segregation is small.

Effect of PVME Addition

Previous studies^{14,21} of solvent-cast films of miscible blends of PS with poly(vinyl-methyl-ether) (PVME) showed an excess of PVME at the surface, due to its lower surface energy. It was of interest in the present study to determine whether PVME would be enriched at the surface if added to injection-molded PPE/HIPS blends. Figure 10 shows the C 1s XPS spectra of a molded specimen of 40/60/05 PPE/HIPS/PVME. The C—O peak in the PVME-modified blend is significantly larger as compared to a 40/60 PPE/HIPS blend. Assuming that the PPE/HIPS ratio is the same as the bulk value, quantitative analysis of the spectrum shows that the surface of the blend consists of 35–40 wt % PVME, indicating surface enrichment of PVME. Preliminary results indicate an increase in water-

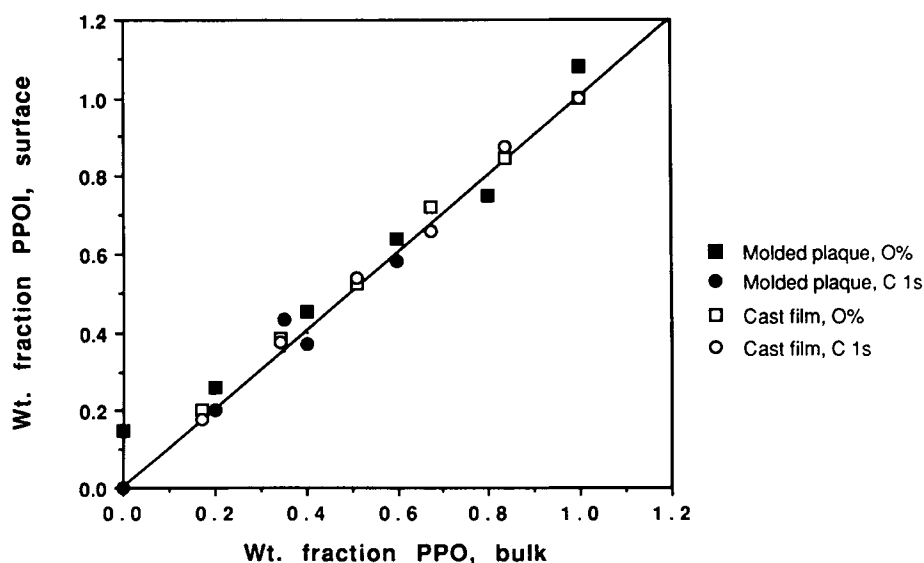


Figure 9 Surface wt % PPE as a function of bulk formulation.

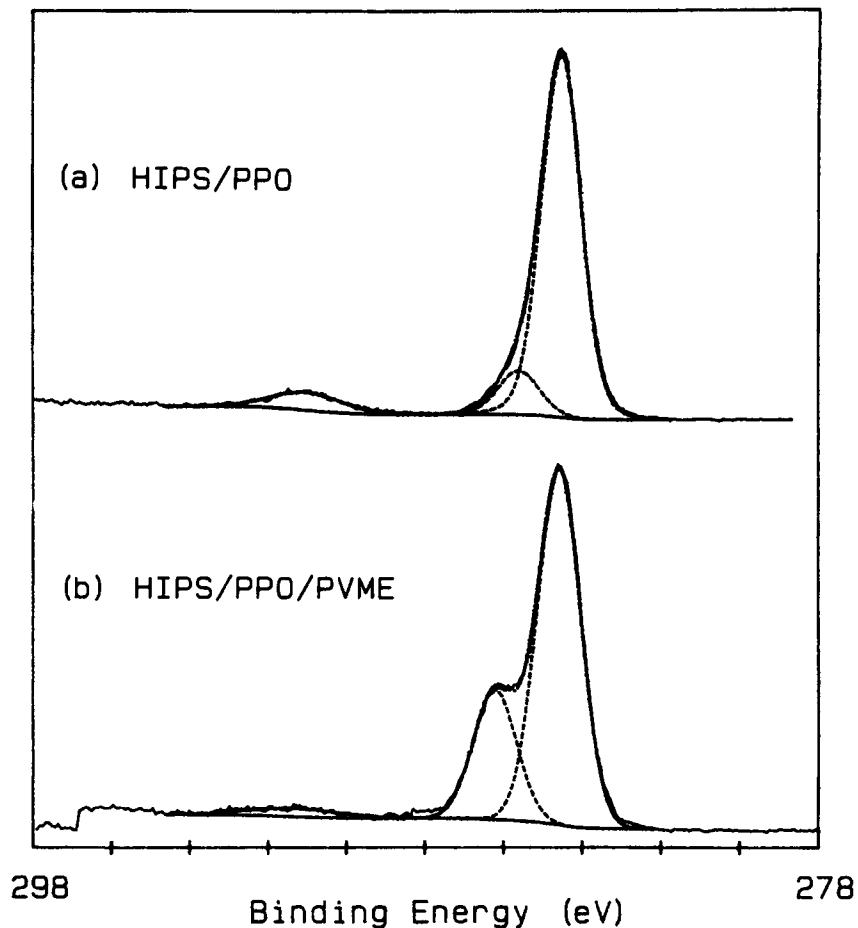


Figure 10 C 1s spectra for (a) 40/60 PPE/HIPS and (b) 40/60/05 PPE/HIPS/PVME.

borne paint adhesion for the PVME-modified blend compared to the straight PPE/HIPS (0.5–0.6 versus 0.3–0.4 lb/in.), possibly due to the greater affinity of PVME for water. Thus, the surface properties of injection-molded PPE/HIPS blends can be modified by the addition of minor amounts of a polymeric additive when it segregates to the surface.

CONCLUSIONS

1. The surface compositions of PPE/nylon 6,6 blends prepared by melt compounding are similar to the formulated stoichiometry for blends containing less than 25 wt % nylon, but are highly enriched in nylon (90–95% nylon) for formulations containing more than 30 wt % nylon in the bulk. This corresponds to the onset of a nylon continuous phase in the bulk microstructure.
2. PPE/nylon 6,6 blends prepared by reactive extrusion show a decrease in the amount of nylon enrichment as the content of copolymer increases. Graft PPE/PA copolymer shows a larger effect on the surface composition than block PPE/PA, likely due to a lower PA/PPE ratio.
3. Injection-molded PPE/HIPS blends have surface compositions equal to the bulk formulation over the entire composition range. A similar result is obtained for PPE/PS solvent-cast films.
4. Modification of 40/60 PPE/HIPS blends with 5% PVME produces injection-molded surfaces enriched in the PVME constituent.

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APPENDIX

ω is the wt % PA

MW PA repeat unit = 226

MW PPE repeat unit = 120

The C 1s spectrum is resolved into three components. The number of carbon atoms per repeat unit that contribute to each component is

C=O (287.5 eV) due only to PA

(2C=O per repeat unit)

$$I_1 = 2\omega/226$$

C—N + C—O (285.8 eV) due to

both PA and PPE

$$I_2 = 2\omega/226 + 2(1 - \omega)/120$$

C—H (284.6 eV) due to both PA and PPE

$$I_3 = 8\omega/226 + 6(1 - \omega)/120$$

The area % of the C=O peak is given by $I_1 \times 100 / (I_1 + I_2 + I_3)$. Solving for ω gives the expression shown in Eq. (1c) in the text.

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