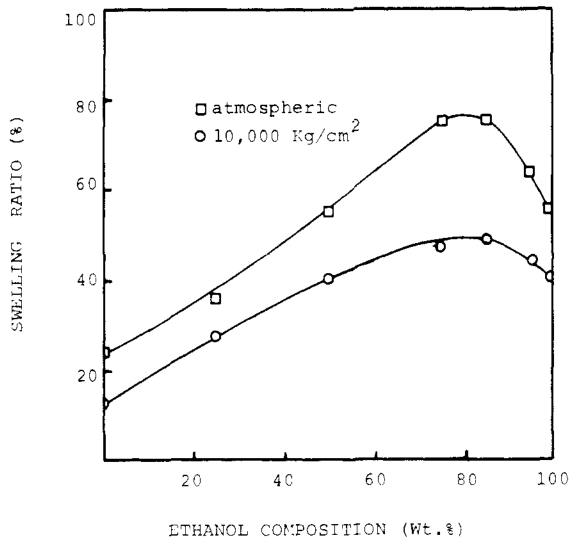

Figure 11. Equilibrium swelling ratio vs. solvent composition for the SIN's of U50S50 synthesized at atmospheric pressure (□) and 10 000 kg/cm^2 (○) (solvent: water/ethanol).

taining hydrophilic and hydrophobic microdomains in water or ethanol is influenced strongly by the degree of intermixing as well as the phase structure.

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Registry No. (HDI)·(PTMEG)·(PEG)·(TMP) (copolymer), 99809-28-6; (DVB)·(styrene) (copolymer), 9003-70-7.

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Studies of Surface Composition and Morphology in Polymers. 2. Bisphenol A Polycarbonate and Poly(dimethylsiloxane) Blends

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ABSTRACT: Results from X-ray photoelectron spectroscopy and ion scattering spectroscopy analyses are presented for blends of bisphenol A polycarbonate (BPAC) and poly(dimethylsiloxane) (DMS). Analysis of these results shows surface enrichment of the lower surface energy DMS component. A model is presented describing the morphology of the top 50 Å of the sample surface. A structural comparison to earlier work on copolymers of BPAC/DMS is also presented. Results show that all blends of less than 11% bulk DMS reach a surface concentration of approximately 85% DMS over the topmost 50 Å. All results show that no gradient exists over this depth, unlike the results for block copolymers. In addition, comparisons to previous work on other two-component block/blend systems show that surface energy differences alone cannot predict the degree of segregation in such polymers. Scanning electron micrographs allow confirmation of composition/morphology relationships.

Introduction

In a previous paper,[1] the near-surface region of block copolymers consisting of bisphenol A polycarbonate (BPAC) and poly(dimethylsiloxane) (DMS) were examined, via X-ray photoelectron spectroscopy (XPS or ESCA) and low-energy ion scattering spectroscopy (ISS), in order to quantify the degree of surface segregation of the DMS segments present in these materials. The results showed a dramatic increase of the DMS segment at the air/polymer interface that was in agreement with previous work[2,3] on other concentrations of DMS/BPAC block copolymers. In our work segregation was quantified in order to give the weight percent of BPAC and DMS present in the surface region, which can be compared to that of the bulk. The ability to predict the amount of each component of the block copolymer present at the surface for a given bulk concentration should greatly aid in the development of engineering materials that require specific surface properties.

This work also demonstrated the usefulness of ISS as a complement to ESCA for the study of polymers. By combining these techniques it was possible to study the surface of the polymers at different depths in a "nondestructive" way and also gain quantitative information without the use of sensitivity factors or electron mean free paths. Results obtained with ESCA sampled approximately 50 and 25 Å into the sample, while the results obtained with ISS where representative of only the top 3–5 Å of the sample.

In the present paper, results obtained by ESCA and ISS will be used to quantify the near-surface region of blends of BPAC/DMS. As with the block copolymer samples, this information should prove useful in understanding the surface properties of these materials. By characterizing the surface region of both the block copolymers and the blends of BPAC/DMS, it will be possible to compare the effect of the greater mobility present in the blend samples in terms of the amount of surface segregation seen. In their studies of poly(ethylene oxide) (PEO)/polystyrene (PS), using angle-resolved ESCA, Thomas and O'Malley[4,5] found that the surface region of both the block copolymers and the blends were similar; however, the blends showed less surface preference of the lower surface energy PS. In this case the greater mobility present in the blend samples was not an important factor in the amount of surface segregation taking place in the PEO/PS system. In the present paper it will be shown that the lower surface energy[6] DMS segregates to a much greater extent in the blends of BPAC/DMS than it does in the block copolymers. This segregation will be quantified, and the surface morphology of the blends will be compared to those proposed for the block copolymers.[1]

Experimental Section

Sample Preparation. Poly(dimethylsiloxane) (MW = 3 000 000), methyl terminated gum, was obtained from Polyscience Inc., Warrington, PA 18976. Bisphenol A polycarbonate (MW = 24 000) homopolymer was provided by Dr. Roger Kambour of the General Electric Co., Schenectady, NY. Blends were prepared by solvent casting mixtures of the homopolymers from 1% chloroform solutions onto a glass petri dish. The BPAC homopolymer films were cleaned by ultrasonic solvent extraction in hexane to remove residual siloxane type impurities (≲1%) to below the level of ESCA detectability.[1] Surface segregation of contaminants of this type have been reported previously by Clark et al.[7] All other samples were run after solvent casting on a glass petri dish with no further treatment. If siloxane impurities were present in the blends at the level of the pure BPAC, the contribution to total surface DMS would be negligible, since the level was so low in BPAC.

Instrumentation. ESCA spectra were recorded on a Physical Electronics Model 5100 ESCA with Mg $K\alpha_{1,2}$ exciting radiation. Standard operating conditions for the X-ray source were as follows: 300 W, 15.0 kV, and 20 mA. The base pressure was maintained at 1×10^{-9} torr and a pass energy of 18 eV, leading to a resolution on the Ag $3d_{5/2}$ line of 0.86 eV at 110 000 counts/s. No radiation damage was observed during 3 times the data collection time. Charge correction in the binding energy scale was accomplished by setting the CH_x peak of the carbon 1s envelope to 285.0 eV.

ISS spectra were recorded on a Physical Electronics Model 560 ESCA/SAM with ISS modification. A 2-keV beam of $^3He^+$ ions was utilized with a scattering angle of 144°. Current densities were 3–5 nA/cm^2. A tungsten filament electron emitter was used for charge neutralization, set at 2-mA emission current and 0-eV acceleration.

All data manipulations were accomplished with the standard Physical Electronics data system on the respective instruments.

SEM micrographs were taken with an Amray Model 1000 SEM. The base pressure in the instrument was 1×10^{-6} Torr. The samples were not coated, but silver paint was used to make electrical contact with the stage. A 1.0-kV electron beam was used, and the secondary electrons were detected with the sample stage at a 55° tilt and a magnification of 1400×.

Results and Discussion

As discussed in the previous paper,[1] quantification of the ESCA data was accomplished by resolving the carbon 1s envelope into contributions from the individual polymers. This was done by integrating the area under the high binding energy peak (as it is related only to the BPAC) and using this information to split the main carbon 1s peak into contributions from BPAC and DMS. Results were converted to percent DMS by weight in order to facilitate comparison to the bulk concentrations.

Table I

sample	bulk DMS, %	surface DMS, %		
		20° (±15%)	45° (±5%)	70° (±15%)
I	1.4	89	87	*a*
II	2.6	72	87	88
III	8.4	96	87	90
IV	10.8	87	86	100
V	26.2	*a*	100	*a*

[a] Data not taken at these angles.

Table II
ISS Results for Blends of BPAC/DMS

% bulk DMS	% surface DMS (±15%)
1.56	86.7
2.50	81.5
3.52	72.7
6.55	80.1

A first attempt was made to study blends with a DMS concentration similar to those present in the block copolymers. However, at bulk DMS concentrations greater than 20% we observed visible phase separation due to incompatibility of the components. ESCA analysis of these samples showed no high-energy peak due to BPAC in the carbon 1s region; therefore, the surface can be represented as an overlayer of DMS with a thickness greater than the ESCA sampling depth.

We then investigated samples with a much lower bulk DMS concentration. For samples with a bulk DMS concentration of 1.4–10.8%, it was possible to cast compatible films that were used for the ensuing study. Compatibility is defined in this case as those samples that form a continuous transparent film. It is not implied that the individual polymer chains are interacting in the bulk, yielding a single phase, as shown for some compatible polymer blends reported by Coleman and Painter.[8] Table I lists the angle-resolved ESCA results for these samples. From these results we calculated that each composition studied had a surface DMS concentration of approximately 87 ± 5%.

The angle-resolved ESCA experiment utilized take-off angles of 70, 45, and 20°. From a simple escape-depth model, this gives a sampling depth of approximately 50, 35, and 17 Å.[9] This enabled us to determine if the differences in surface composition showed a gradient over the ESCA sampling depth. While the results of the 70 and 20° take-off angles did not provide the precision found at 45° (which we attribute to instrumental geometry) no statistical differences are seen at the different angles. This indicates that the samples were uniform over the ESCA sampling depth (~17–50 Å).

The results obtained with ISS for the blends of BPAC/DMS are shown in Table II and Figure 1. The weight percent values were found by plotting the Si/O ratios vs. the bulk percent of DMS. By assuming a linear interpolation between Si/O ratios for pure BPAC (0% DMS) and pure DMS (0% BPAC), one can calculate the amount of DMS required to give the observed Si/O ratio. Again, as in the ESCA data, the ISS measurements show that the composition of the near-surface region (top 3–5 Å)[10] of all the samples (1.4–10.8% bulk % DMS) is

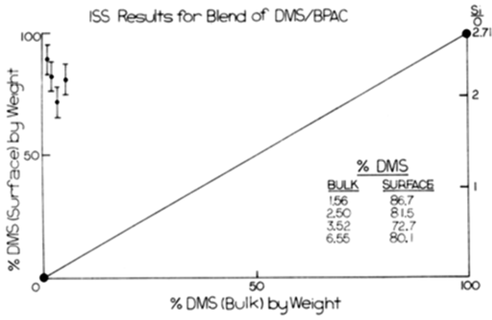

Figure 1. Plot of ISS data for blend samples. Si/O peak height ratios are presented vs. bulk DMS content.

equivalent within experimental error, and consists of about 85 ± 10% DMS.

The data from both methods can be compared to the results obtained for the block copolymers of BPAC/DMS. It is apparent that the blends of BPAC/DMS behave in a similar fashion to the block copolymers of BPAC/DMS in that the lower surface energy DMS component shows a preference for the surface. In the blends, however, the degree of the DMS surface enrichment is much greater than that seen in the block copolymers. At bulk DMS concentrations greater than 20% the blends consist of an overlayer of DMS that is greater than the ESCA sampling depth, while in the block copolymers ESCA detected the polycarbonate component even for bulk DMS concentrations of 65%. At bulk DMS concentrations between 1.4 and 10.8% the near-surface region of the blends is dominated by DMS with about 15% BPAC interspersed.

The interesting difference between the blends of BPAC/DMS and the block copolymers of BPAC/DMS as seen by the ISS data is the fact that the blends do not show the distinct increase in DMS concentration when compared to the ESCA data as was seen for the block copolymers. It is well-known[11] that "shadowing" can affect the results obtained by ISS. This "shadowing" effect, where a surface atom blocks a lower atom from the ion beam, allows ISS to give structural information as demonstrated by Strehlow and Smith[12] and our ongoing work.[13] While polymer samples would not be expected to show "shadowing" due to a highly ordered structure as seen on single crystals,[12] if the surface has a regular raised profile the protruding material could effectively "shadow" the material residing in the valleys. In order to determine if this type of surface structure could explain the differences seen in the ISS between the blends of BPAC/DMS and the block copolymers, scanning electron microscopy (SEM) was employed in order to study the surface roughness of the samples. Figure 2 shows representative SEM micrographs for a blend and a copolymer sample each cast under similar conditions. The copolymer sample has a much rougher surface than does the blend sample. When viewed on a scale of several microns the surface of the block copolymers appears to be comprised of peaks and valleys, while the surface of the blends is smooth.

Therefore, when the results from ESCA and ISS are interpreted in light of the surface topography found by SEM, the following observations can be made. The blends and block copolymers of BPAC both show a surface preference for the lower surface energy DMS component, with the amount of segregation much greater for the blends. However, the block copolymers have a morphology consisting of microdomains of each component oriented perpendicularly to the surface, with the DMS segments as the likely regions protruding above the surface. The surface morphology of the blends can be interpreted in two possible ways. The first model (two-phase heterogeneous) consists of a DMS continuum with BPAC microdomains dispersed within it, as seen for DMS/BPAC block copolymers with low BPAC concentrations.[14] The second interpretation (one-phase homogenous compatible) is that the surface region of the blends is comprised of a single phase of BPAC/DMS due to chemical or conformational interactions that lead to a compatible film in the sense described by Coleman and Painter.[8] The present results do not enable us to distinguish between these two possibilities; however, subsequent experiments using attenuated total reflection FT-IR will be employed to further investigate this point. Figure 3 illustrates the proposed surface

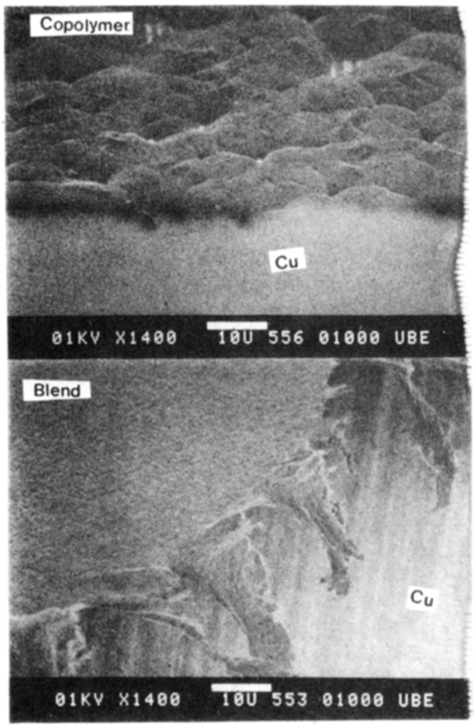

Figure 2. SEM micrograph of (a) block copolymers of BPAC/DMS, and (b) blend of BPAC/DMS.

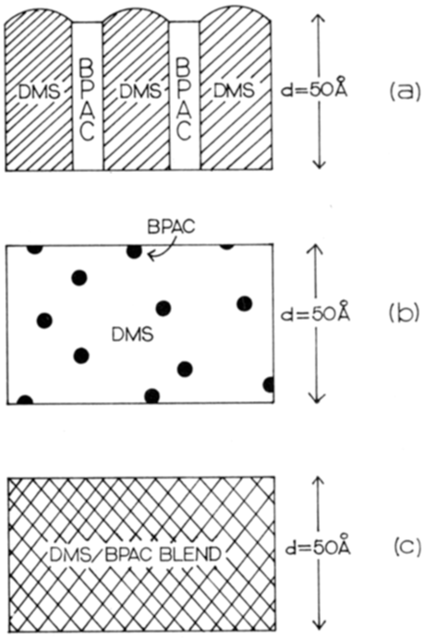

Figure 3. Models for the surface morphology of BPAC/DMS samples: (a) copolymers; (b) two-phase heterogeneous blend model, regions of BPAC interspersed in DMS continuum; (c) single-phase compatible blend model, mixture of BPAC and DMS over ESCA sampling depth.

structure for both the blends and the block copolymers of BPAC/DMS. By combining the data from several techniques (ESCA, ISS, and SEM), we see that while the surface concentration of the blends and block copolymers differs greatly from that of the bulk, the morphology of this region is consistent with those found in bulk samples with a concentration equivalent to the surface concentration.[14]

It is interesting to compare the findings of this work on the BPAC/DMS system with the work published by Thomas and O'Malley[4,5] on blends and block copolymers consisting of poly(ethylene oxide) (PEO) and polystyrene (PS). By the use of angle-resolved ESCA they showed the surface region of the block copolymers to contain an excess of the lower surface energy PS component, which is consistent with the results obtained for BPAC/DMS block copolymers.[1] However, for blends of PEO/PS the amount of surface segregation present was less than that found in the block copolymers. This is the opposite of that found for the BPAC/DMS system, even though the differences in the surface energy for each system were approximately the same (PEO/PS = 44/36 dyn/cm, BPAC/DMS = 34/24 dyn/cm).[6]

This analysis demonstrates that while surface energy values are useful for predicting which species should show a surface preference, they alone are not useful for predicting the degree of surface enrichment expected. The amount of surface segregation appears to be dependent on the degree of "compatability" (by any definition) present in the system and the final morphology of the sample.

Conclusions

In this work we employed a multitechnique approach to gain a detailed understanding of the surface region for blends of BPAC/DMS. This approach leads to a quantitative understanding of the degree of surface enrichment present for the lower surface energy DMS component. The ESCA quantification was accomplished without the need to use sensitivity factors or electron mean free paths, which can complicate the accuracy of results. In addition to quantitative descriptions of the surface concentration of each component, the multitechnique approach allowed for the elucidation of the surface morphology of these samples. All samples containing 1.4–10.8% bulk DMS showed equivalent surface composition and morphology.

When the results obtained for blends of BPAC/DMS are combined with previous work on block copolymers of BPAC/DMS, a detailed understanding of the surface region is obtained for these materials. In the block copolymers the surface region shows a increased concentration of the DMS component and has a morphology similar to that of the bulk. However, for the blends of BPAC/DMS the surface segregation of the DMS component is much greater than that seen for the block copolymers. Also, the morphology of this surface region is different than that of the bulk.

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Registry No. Bisphenol A polycarbonate (SRU), 24936-68-3; (bisphenol A)·(carbonic acid) (copolymer), 25037-45-0.

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Polymer Swelling. 3. Correlation of Aromatic Carbon-13 NMR Line Width with Cross-Link Density in Poly(styrene-*co*-divinylbenzene)

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ABSTRACT: The aromatic carbon-13 NMR line widths ($\nu_{1/2}$) of ten styrene–divinylbenzene copolymers, swelled to equilibrium in $CDCl_3$, were measured at +21 °C. The line width (in Hz) increases exponentially with cross-link density $\tilde{\chi}$ and is given by $\nu_{1/2} = 6 \times 10^4 \tilde{\chi}^{1.6}$.

Introduction

We have reported[1-3] that the volume of liquid, S, absorbed per gram of cross-linked polymer at equilibrium swelling increases with the average number of atoms λ in the backbone of the polystyrene segments between cross-link junctions in accordance with the equation

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) = C(\tilde{\chi}^{-1/3} - \tilde{\chi}_0^{-1/3}) \qquad (1)$$

where C is a constant characteristic of the swelling liquid, λ is the average number of carbon atoms in the polymer

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