A study of surface enrichment in polystyrene/poly(vinyl methyl ether) blends using attenuated total reflectance infra-red spectroscopy: 1

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Surface enrichment of one-phase and phase-separated blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) by the latter component, which has the lower surface free energy, has been examined using attenuated total reflectance infra-red spectroscopy. The apparent surface concentration of PVME, determined by assuming compositional homogeneity within the depth probed, as a function of blend composition, agrees well with data derived by other methods. Although no effect due to variations in the PS molecular weight was evident, star-shaped PS appears to behave differently from linear PS.

(Keywords: surface enrichment; polystyrene; poly(vinyl methyl ether); blends; attenuated total reflectance spectroscopy)

INTRODUCTION

Small-molecule mixtures have long been recognized to exhibit surface compositions which differ from that of the bulk[1,2]. The classic expression of this surface phenomenon using the Gibbs adsorption isotherm invokes differences in the surface energies of the components as the driving force[3]. Polymer systems similarly respond to differences in surface energies. Block copolymers exhibit enrichment by the block of lower surface tension[4,5] and random copolymers display a tendency for the segments of lower surface tension to migrate to the air–polymer interface[6,7]. The surfaces of semicrystalline homopolymers may be controlled by choosing substrates which promote different degrees of surface crystallinity in a drive to minimize the interfacial energy[7].

In an idealized two-phase binary homopolymer mixture one would expect the surface to be dominated by the component of lower surface tension since bulk thermodynamics favour complete demixing. Indeed, real systems have been shown to approximate to this expectation[8,9]. One-phase homopolymer blends may be regarded as potentially two-phase since the interaction of a component at the surface with its neighbours differs from that in the bulk. A lowered equilibrium surface energy, which results from placement at the surface of the lower surface energy component, is bought at the cost of maintaining a composition gradient between the surface and bulk compositions. Surface segregation in polymer blends thus reflects a balance of surface forces and bulk mixing thermodynamics, and recent theoretical descriptions have been proposed which consider this balance in terms of a mean-field formalism[10-12].

Surface enrichment may be probed by a number of techniques, each with its own inherent depth resolution. X-ray photoelectron spectroscopy (X.p.s.)[8,9,13,14] gives information on the top 0–6 nm. Neutron reflectivity[15,16] and forward recoil elastic scattering[15,17] have been employed for mixtures of hydrogenous and deuterated polymers to determine composition profiles over the first few tens of, and hundreds of, nanometres, respectively. The more classical contact angle and surface tension measurements[7,13,18] presumably probe the top few molecular layers, although the latter is applicable to polymer melts only.

In this paper we examine the surfaces of blends using attenuated total reflectance Fourier transform infra-red spectroscopy (ATR *FT*i.r.). The surface sensitivity of this technique is of the order of 0.5–3 μm and as such is significantly different from those mentioned above. The blend chosen for study is the traditional work-horse polystyrene/poly(vinyl methyl ether) (PS/PVME), which exhibits either one- or two-phase behaviour depending on the casting solvent. PS/PVME is thus, in general terms, a marginally miscible binary homopolymer mixture. The surface tensions (γ_i) of the two homopolymers are $\sim$29 and $\sim$35 dyn cm^{-1} for PVME and PS, respectively[13,19], and the expectation from the above, that binary blends should be surface-rich in PVME, has been confirmed by both X.p.s. and surface tension measurements[13,14]. To our knowledge the work presented here describes the first use of ATR *FT*i.r. to determine surface enrichment in polymer blends.

EXPERIMENTAL

The linear polystyrene (PS) and star polystyrene (s-PS) samples were primary narrow distribution standards from Polysciences and were used as received. The 12-arm s-PS

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was quoted by the supplier to have a molecular weight of 7×10^3 g mol^{-1} per arm. PVME was purchased from Aldrich and was precipitated three times from toluene into petroleum spirit. G.p.c. gave $M_n = 45 \times 10^3$ g mol^{-1} and $M_w/M_n = 2.2$, in terms of polystyrene equivalents.

Films were prepared on aluminium foil stretched over levelled glass plates from 5% wt/vol toluene or chloroform solutions of PS/PVME mixtures, using a bar spreader with an extrusion height of 200 μm. Nominal film thicknesses were therefore 10 μm. Films were vacuum dried at 333 K for 24 h and then cut to the appropriate size (on the aluminium backing) for i.r. studies.

The polymer–air interfaces of PS/PVME blends of varying composition were examined in reflectance using a Specac model 302 ATR attachment, at a fixed angle of incidence (θ) of 51.2°, mounted in a Perkin Elmer 1720X FTi.r. spectrometer. The ATR element was a Spectra-Tech KRS-5 45° face angle 50 mm rhomboid. The data from 32 scans were averaged. The extinction coefficients [$\varepsilon_i(\mu$m$^{-1})$] of the PS aromatic ring out-of-plane bending mode at 699 cm^{-1} and the PVME C–O–C stretching mode at 1084 cm^{-1} were determined as the slopes of plots of absorbance against film thickness from the transmission spectra of a series of toluene-cast homopolymer films. *Figure 1* shows the experimental data.

The glass transition temperatures (T_gs) of the one-phase blends were measured using a Perkin Elmer DSC-2 differential scanning calorimeter. Cloud-point temperatures (*CPT*s) were determined as the first visible signs of turbidity on heating blends, cast onto cover slips, using a Linkam PR600 variable temperature microscope hot-stage. The T_g and *CPT* values are summarized in *Table 1*.

DATA ANALYSIS

In reflectance spectroscopy, the ratio of the intensity of the reflected light (I) to that of the incident light (I_0) defines the reflectivity (R). At the ATR element (1)–sample (2) interface R is less than unity if the non-propagating (evanescent) electric field in the sample can couple with an absorbing species. The strength of the
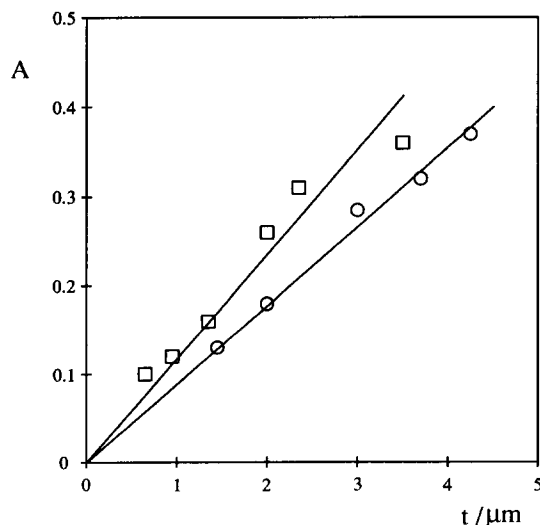
Table 1 Glass transition and cloud point temperatures for toluene-cast PS/PVME blends

PVME (vol%)	T_g(°C) a	CPT(°C) a	CPT(°C) b
10	80	125	136
25	42	120	128
50	−14	141	135
75	−24	159	152
90	−28	180	170

^{a} PS = 575 000 g mol^{-1}
^{b} PS = 100 000 g mol^{-1}

coupling is governed by the same coefficient of extinction (α) as pertains in transmission spectroscopy via[20]:

$$a = (n_{21}E_0^2/\cos\theta) \int_0^\infty \alpha e^{-2z/dp} dz \qquad (1)$$

where $a = (1 - R)$ is the amount of light, incident at an angle θ and of initial amplitude E_0 at the surface, absorbed in one reflection. The exponential term expresses the decay of the evanescent field with distance z into the sample. The characteristic decay length dp is often, and incorrectly, referred to as the depth of penetration, but is actually the distance over which the electric field strength falls to 1/e of its initial value. n_{21} is the ratio of the refractive indices of the element and sample. For uniform absorption, Harrick[21] has defined an effective sample thickness (d_e) as:

$$d_e = n_{21}E_0^2 dp/2\cos\theta \qquad (2)$$

so that on integration equation (1) becomes simply:

$$a = \alpha d_e \qquad (3)$$

For N reflections, the instrumentally measured absorbance $A = \log(I_0/I)$ is related to the reflectance by:

$$A = -\log R^N = -N\log(1 - a) \qquad (4)$$

and by setting $\ln(1 - a) \approx -a$ for small values of a, it follows that $a \approx A/N$. α is normally expressed as the product εC, where ε is a concentration extinction coefficient and C is concentration. With ε_i in μm^{-1}, the measured apparent surface volume fraction of PVME (ϕ_S) within the sampling depth of the ATR technique is independent of N and is given by:

$$\phi_S = C_{PVME}/(C_{PVME} + C_{PS}) \approx A_{PVME}/(A_{PVME} + \lambda A_{PS}) \qquad (5)$$

where $\lambda = dp_{PVMR}\varepsilon_{PVME}/dp_{PS}\varepsilon_{PS}$. The respective depths of penetration are calculated according to Harrick[21] at 1084 cm^{-1} for PVME and at 699 cm^{-1} for PS. With $n_1 = 2.38$ and $n_2 = 1.5$ (the average of the refractive indices of PS and PVME[19]), $dp_{PVME} = 1.33 \mu$m and $dp_{PS} = 2.04 \mu$m.

RESULTS AND DISCUSSION

The 'apparent' surface volume fraction of PVME (ϕ_S) plotted against the bulk (i.e. made-up) volume fraction of PVME (ϕ_B) for toluene-cast one-phase PS/PVME blends is shown in *Figure 2*. The reproducibility of each point is estimated from multiple measurements to be $\sim \pm 0.02$ in ϕ_S. The ATR FTi.r. measurements reveal a significant surface enrichment of PVME. Blends which are rich in PVME show a lesser relative surface enhancement than those rich in PS, in accordance with
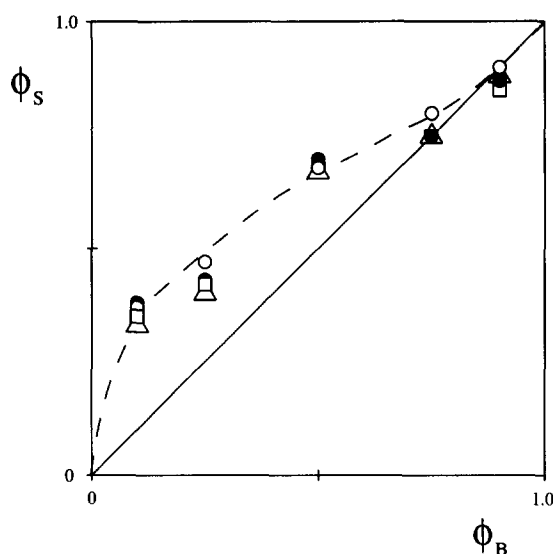
Figure 2 Plot of apparent surface volume fraction of PVME (ϕ_S) *versus* bulk volume fraction of PVME (ϕ_B) for PS/PVME toluene-cast blends. PS $= 10^3 M_n \, \mathrm{g \, mol^{-1}} = 1.5$ ($\square$), 100 ($\triangle$) and 575 ($\bigcirc$). Filled symbols for annealed samples

Table 2 Ratio of surface volume fraction of PVME (ϕ_S) to bulk volume fraction of PVME (ϕ_B) for PS/PVME blends

ϕ_B	ϕ_S/ϕ_B			
	a	b	c	d
0.10	3.7	3.7	3.3	2.3
0.25	1.9	1.5	1.7	1.6
0.50	1.5	1.2	1.1	1.3
0.75	1.1	1.1	1.0	1.0
0.90	1.0	1.0	1.0	1.0

[a] Toluene-cast miscible blends
[b] Two-phase chloroform-cast blends
[c] Thermally induced two-phase blends by heating above *CPT*
For a–c, PS $= 575 \times 10^3 \, \mathrm{g \, mol^{-1}}$
[d] Miscible blends with 12 arm s-PS ($84 \times 10^3 \, \mathrm{g \, mol^{-1}}$)

the idea that the system will attempt to minimize the surface free energy. Annealing of the films at 373 K caused no further significant changes in the measured surface compositions, suggesting that an equilibrium situation has been readily established.

Heating toluene-cast films above their *CPT*s for 24 h to induce phase separation, followed by rapid cooling to room temperature, produced a slight reduction in the surface PVME concentration. As-cast phase-separated blends prepared from chloroform similarly showed a slight reduction in PVME surface enrichment compared with the miscible system. This result is actually contrary to that reported by Pan and Prest[14] for the PS/PVME system who, using X.p.s., detected an increase in surface PVME in biphasic blends. However X.p.s. and ATR differ substantially in surface sensitivity and return data integrated over very different depths. The data for the two-phase systems are compared with the miscible blends in *Table 2*.

Figure 2 displays identical behaviour to that observed by X.p.s. and surface tension studies[13,14] illustrating that the ATR technique can be satisfactorily used to quantify surface enrichment. Second-order effects, possibly very close to the surface (those mentioned above may be an

example), might well be invisible to ATR due to its relatively deep overall sampling depth. For example, we were unable to detect any significant change in surface enrichment using PS samples of different molecular weights (*Figure 2*). According to Bhatia *et al.*[13] the surface fraction of PVME should follow a power dependence on molecular weight identical to that for γ_{PS}, suggesting that selective surface absorption on the basis of molecular weight does not occur and that only differences in surface tension are important.

A final variable shown in *Table 2* is that of styrenic architecture. s-PS/PVME blends do show enrichment levels detectably less than PS/PVME blends, but it seems unlikely that this derives simply from a lower molecular weight per arm in view of the above remarks. Furthermore, the phase behaviour of s-PS/PVME and PS/PVME blends appears to be similar[22] leaving any balance between bulk and surface unaffected by branching. A possible motive for a reduction in enrichment may be entropic in the sense that shorter chains are preferred at neutral surfaces thereby minimizing conformational entropy losses[23]. A star-shaped polymer is a conformationally restricted analogue of an equivalent linear chain, in a sense entropically conditioned to a surface environment. Even in the absence of any entropic preference, the s-PS structure restricts PVME mobility and normal interpenetration close to the branch point, and this alone may increase the detected styrene content within the ATR sampling window.

It can be concluded that the ATR *FT*i.r. technique is extremely useful for the measurement of surface enrichment in suitable polymer blends, and has considerable practical advantages in terms of ease of application and sample preparation. Expression (5) is derived assuming a uniform distribution of absorbing species and strictly ignores the possibility of concentration profiles within the ATR sampling depth hence the reason for quoting 'apparent' surface volume fractions rather than absolute values. It is an approximation to an integrated surface excess for non-uniform distributions. We will address the analysis of surface concentration profiles by ATR *FT*i.r. in a future publication.

Finally, although indisputably 'driven' by surface tension differences, equilibrium surface compositions result from a minimization of the *overall* system free energy, thus bulk thermodynamics are allied in a significant sense to surface enrichment phenomena. In a subsequent paper we will examine the effect of introducing changes to the PS–PVME interaction on the blend surface composition.

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