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Surface enrichment of the solution-cast poly(methyl methacrylate)/poly(vinyl acetate) blends

Won-Ki Lee, Won-Jei Cho and Chang-Sik Ha*
Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

and Atsushi Takahara and Tisato Kajiyama
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan
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The surface enrichment of blend films of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) cast from various solvents has been investigated by contact angle, X-ray photoelectron spectroscopic and attenuated total reflection Fourier transform infra-red spectroscopic measurements. The composition of each component was fixed at 50 wt%. The surfaces of miscible PMMA/PVAc blend films are found to be enriched in PVAc regardless of casting solvents. It was found that the surface enrichment of PVAc in the PMMA/PVAc blend is reduced when the as-cast blend film shows phase separation or when the phase-mixed blend is heated above the lower critical solution temperature and exhibits thermally induced phase separation.

(Keywords: surface enrichment; poly(methyl methacrylate); poly(vinyl acetate))

INTRODUCTION

The surface structure of solid films composed of multiphase polymers has been attracting much interest from both theoretical and practical viewpoints, since there are differences between the composition of the surface and the bulk of the multiphase polymers[1-4]. Surface enrichment by the component of lower surface energy has been demonstrated in random copolymers of hexamethylene sebacate with dimethylsiloxane and ethylene oxide with propylene oxide or block copolymers of styrene and methyl methacrylate[5,6].

The surface structure has been characterized by a number of techniques, each with its own inherent depth resolution, such as X-ray photoelectron spectroscopy (X.p.s.)[4,6,7], attenuated total reflection Fourier transform infra-red (a.t.r. *FT*i.r.) spectroscopy[8], as well as the classical contact angle and surface tension measurements[7,9].

The X.p.s. technique has a depth resolution in the range of the top few tens of angstroms of a surface as a consequence of extremely short (<5 nm) mean free paths of photoelectrons. On the other hand, the angular-dependent X.p.s. studies enable measurement of the average composition profile as a function of depth. The surface sensitivity of the a.t.r. *FT*i.r. technique is of the order of 0.5–3 μm. The classical contact angle measurements presumably probe the top few molecular layers.

Recently the surface structure of miscible polymer blend systems has been reported by several authors[7,8,10,11]. One of the most extensively investigated systems is the polystyrene (PS)/poly(vinyl methyl ether) (PVME) blend. The surfaces of the miscible PS/PVME films have been found to be enriched in PVME by X.p.s. or a.t.r. *FT*i.r. techniques. The result is not surprising since classical thermodynamics can predict that a surface concentration gradient exists in multicomponent systems where the surface is enriched with the component with lower surface free energy. In the case of the PS/PVME system, the surface tensions of the two homopolymers are 29 and 35 dyn cm^{-1} for PVME and PS, respectively[8].

Meanwhile, the measured miscibility of a blend, when prepared by solvent casting, is strongly dependent upon the choice of solvent; the polymer blend exhibits a clear film when cast from one solvent, but yields an opaque film when cast from another solvent. The solvent selected im/miscibility may be explained by the so-called $\Delta\chi$ effect for instance[12-16] but is not the subject of this paper. The miscibility of the solution-cast poly(methyl methacrylate) (PMMA)/poly(vinyl acetate) (PVAc) blend has been intensively investigated but studies using different solvents to obtain the blend films have reached different conclusions with respect to the miscibility[17,18].

In our previous work, the effect of solvent on the miscibility of PMMA with PVAc has been carefully re-examined using d.s.c., cloud-point measurement, *FT*i.r. spectroscopy and scanning electron microscopy (SEM)[19]. It was found that the 1/1 PMMA/PVAc blends are miscible when cast from benzene, chlorobenzene and cyclohexanone but a two-phase blend is generated when using ethyl acetate as the casting solvent. The choice of

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*To whom correspondence should be addressed the film-casting solvent had a profound influence on sample morphology and in turn these morphological changes were expected to be accompanied by changes in surface composition.

Thus, the purpose of this work is to investigate the surface structure of the PMMA and PVAc mixture of 50/50 w/w composition when the films are cast from the above solvents. The surfaces of the PMMA/PVAc blend were examined using X.p.s. and a.t.r. *FT*i.r. measurements on thin films as well as contact angle measurements.

EXPERIMENTAL

Materials and blend preparations

PMMA having a weight-average molecular weight $(M_w) = 99\,300$ and polydispersity $(M_w/M_n) = 1.53$ was obtained from Lucky Co. Ltd, while PVAc with $M_w = 78\,800$ and $M_w/M_n = 1.46$ was purchased from Junsei Co. All solvents and non-solvents used were of reagent grade.

Blend films containing PMMA and PVAc mixtures were prepared by casting from 12 wt% solutions of one of four different solvents (benzene, chlorobenzene, cyclohexanone and ethyl acetate). The films were dried slowly in a glass plate at room temperature and then kept in a vacuum oven to constant weight at 60°C. The composition of PMMA and PVAc was fixed at 50 wt% unless otherwise specified.

The thermally induced phase-separated PMMA/PVAc blends were prepared by heating the miscible blend cast from benzene, chlorobenzene or cyclohexanone in a vacuum oven from room temperature to 160°C [above the lower critical solution temperature (*LCST*)] at a rate of $\sim 1^{\circ}\mathrm{C\,min^{-1}}$, holding at this temperature for 10 min, and then slowly cooling to room temperature.

Contact angle measurements

The static contact angle of water and methylene iodide onto the surface of samples was measured using a Kyowa contact angle meter, where there was no evidence of interaction with methylene iodide by any of the sample films. The measurements were carried out in the presence of the saturated vapours of the probe liquids but the equilibrium pressure of the adsorbed vapour of the liquids on the polymer films was assumed to be negligible[20], since the contact angles measured here were moderately large values (65–85° for water and 28–45° for methylene iodide, respectively). The precision in the contact angle measurements was 0.1°. Ten measurements were averaged with the confidence limit of 95%. The surface free energy of sample films was calculated by Owens's method[21].

X.p.s. measurements

The X.p.s. spectra were obtained with an ESCA 750 X-ray photoelectron spectrometer (Shimadzu) by using MgKα radiation. Typical operating conditions were: X-ray source, 8 kV, 30 mA, and pressure in the analytical chamber -10^{-5} Pa. The analytical depth at an emission angle of 90° was ~10 nm.

Transmission and a.t.r. FT*i.r. spectroscopy*

The transmission *FT*i.r. and a.t.r. *FT*i.r. spectra were taken with a Nicolet 1720X FTi.r. spectrometer. The data of 32 scans were averaged. For a.t.r. *FT*i.r. spectra, a SpectraTec model 302A ATR attachment was mounted, at a fixed angle of incidence (θ) of 51.2°. The a.t.r. element was a SpectraTec-5 45° face angle 50 nm rhomboid.

RESULTS AND DISCUSSION

Contact angle and surface free energy

The magnitudes of surface free energies of the blends of PMMA and PVAc and the corresponding homopolymers were determined from their contact angle measurements. The magnitudes of the solid state surface free energy of PVAc and PMMA at room temperature (20°C) were given as 36.8 ± 0.05 and $42.6 \pm 0.05\ \mathrm{dyn\,cm^{-1}}$, respectively. The surface free energy data of the 1/1 PMMA/PVAc blends cast from three different solvents were calculated from the contact angle measurements with 95% confidence limits and are listed in *Table 1* together with their significance levels. The *t*-distribution was applied to the contact angle data.

In the PMMA/PVAc system, it can be expected from the differences in the solid state surface free energies of PVAc and PMMA that the PVAc component would dominate at the surface when PMMA and PVAc are mixed. The most miscible system (here benzene-cast film) has the lowest surface energy. Usually at the air–polymer interface the surface energy is an important component of the total free energy of the system which consists of three terms: the entropy of mixing, the interaction energy between polymer segments, and the surface free energy[10]. The preferential presence of the lower surface free energy component at the interface is the result of the minimization of the total free energy of the system. The surface fraction of PVAc in *Table 1* was estimated from equation (1), assuming that the surface free energy of the blend was proportional to the fractional surface coverage of each constituent[7]:

$$f_{\mathrm{PVAc}} = (\gamma_{\mathrm{blend}} - \gamma_{\mathrm{PMMA}})/(\gamma_{\mathrm{PVAc}} - \gamma_{\mathrm{PMMA}}) \qquad (1)$$

It should be noted that the ethyl acetate-cast blend film exhibiting phase separation shows slightly lower f_{PVAc} compared to benzene- or cyclohexanone-cast blend films. The lowest surface enrichment in PVAc was observed for the phase-separated as-cast blend system. The values of f_{PVAc} in *Table 1* clearly show that there is more PVAc enrichment the higher the degree of mixing in the bulk.

Table 1 also shows the effect of annealing the 1/1 PMMA/PVAc blends films cast from benzene or cyclohexanone at the temperature above the *LCST* where phase separations are thermally induced. The surface free energies of the blends were higher than those of as-cast phase-mixed blends cast from the same solvents, meaning that the surface enrichment of PVAc is reduced. It is not clear at present why lower surface free energy component enrichment at the surface is greater when the system is

Table 1 Surface free energy and surface composition evaluated on the basis of equation (1) at 293 K for 1/1 PMMA/PVAc blends cast from three different solvents

Solvents	Surface free energy $(\mathrm{mJ\,m^{-2}})$	f_{PVAc}
Benzene (as-cast)	37.2 ± 0.05	0.93 ± 0.01
Benzene (annealed)	37.9 ± 0.10	0.81 ± 0.03
Cyclohexanone (as-cast)	37.4 ± 0.05	0.90 ± 0.02
Cyclohexanone (annealed)	38.0 ± 0.10	0.79 ± 0.02
Ethyl acetate (as-cast)	38.4 ± 0.10	0.72 ± 0.02

phase mixed rather than when the system is phase separated. More details, however, will be discussed later.

X.p.s.

The X.p.s. core level spectra for PMMA and PVAc are shown in *Figure 1*. The spectra for both PMMA and PVAc show two peaks for the C_{1s} level and a single peak for the O_{1s} core level. The C_{1s} spectra for both homopolymers contain unresolved contributions from the ether carbon (at 286.6 eV) and neutral carbon (at 285 eV). The O_{1s} core level is located at 533.6 eV.

Figure 2 shows typical X.p.s. spectra for the 1/1 PMMA/PVAc blends cast from benzene and ethyl acetate, exhibiting superposition of the two homopolymer spectra. It is seen that the ratio I_{C-O}/I_{C-H} in the C_{1s} core level and the O_{1s} spectrum peak of the miscible PMMA/PVAc blend cast from benzene are both much higher than those of the phase-separated PMMA/PVAc blend cast from ethyl acetate as well as those of PMMA homopolymer.

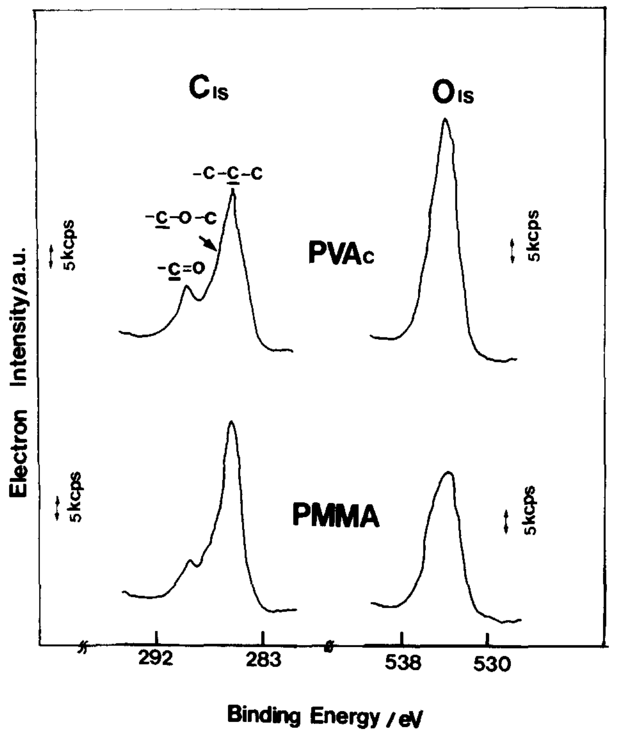

Figure 1 X.p.s. spectra of PMMA and PVAc homopolymers. The photoelectron emission angle is 90°

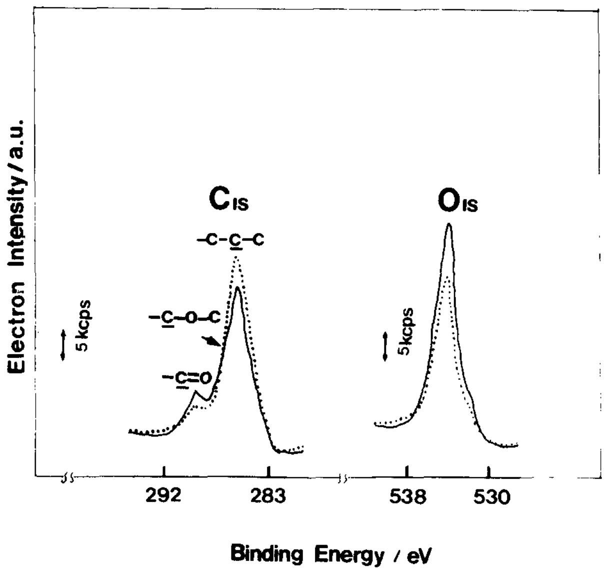

Figure 2 C_{1s} and O_{1s} spectra of 1/1 PMMA/PVAc blends cast from benzene (——) and ethyl acetate (......) solution. The photoelectron emission angle is 90°

Table 2 Typical O_{1s}/C_{1s} ratios of 1/1 PMMA/PVAc blends

Solvents	O_{1s}/C_{1s} ratio
Benzene (as-cast)	0.52
Benzene (annealed)	0.50
Chlorobenzene (as-cast)	0.50
Chlorobenzene (annealed)	0.47
Cyclohexanone (as-cast)	0.49
Cyclohexanone (annealed)	0.47
Ethyl acetate (as-cast)	0.48

Qualitative analysis of the X.p.s. data for the PMMA/PVAc blend was performed using the ratio of the total integrated area of the carbon signal (a doublet) to the single oxygen signal. If each homopolymer is completely phase mixing and shows no surface enrichment of any component, the PMMA/PVAc blend having a 1/1 composition should have an almost intermediate O_{1s}/C_{1s} ratio between the extreme values of each homopolymer. A higher O_{1s}/C_{1s} ratio indicates a greater surface enrichment of PVAc. Thus, the surface enrichment of the component of lower surface energy, PVAc here, is consistent with that deduced from the surface energy measurements and other reported results for the PS and PVME blend system.

Table 2 shows typical O_{1s}/C_{1s} ratio data. Corrections for the photoionization cross-section and the mean free path of photoelectrons in the sample films have been carried out for these data. The ratio was larger in the order benzene ≅ chlorobenzene > cyclohexanone > ethyl acetate, when the blends were cast from the four different solvents. Thus, the results in *Table 2* imply that the surface of the blend is enriched in PVAc in the phase-mixed miscible blend but is reduced in the phase-separated immiscible blend system. This result is contrary to that reported by Pan and Prest for the PS/PVME system using X.p.s.[10]. They reported that the lower the degree of mixing in the bulk, the more PVME was observed in the surface. However, the present result is in accordance with that reported by Cowie *et al.* for the same PS/PVME system using a.t.r. *FT*i.r.[8]. The free surfaces of the miscible PS/PVME blends were significantly enriched in PVME but the enrichment of the PVME component of the surface was reduced when the PS/PVME blends were phase-separated. The a.t.r. *FT*i.r. results for the present PMMA/PVAc system will be described later. Our X.p.s. results are totally in accordance with the surface energy considerations from the contact angle measurements. *Table 2* also shows the O_{1s}/C_{1s} ratios of the miscible PMMA/PVAc blends after they were heated at 160°C for 10 min. The data in *Table 2* demonstrate that the surface of the thermally induced phase-separated blend is less enriched in PVAc than that of the as-cast phase-separated blend. This result is again in accordance with the a.t.r. *FT*i.r. results of Cowie *et al.*[8] but in contrast to the results of Pan and Prest[10].

A.t.r. FT*i.r. studies*

It has been revealed that the a.t.r. *FT*i.r. technique is 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[8]. The surface sensitivity of this technique is of the order of 0.5–3 μm and, as such, is expected to be significantly different from the X.p.s. results mentioned above.

Figure 3 shows typical a.t.r. *FT*i.r. spectra of homopolymers around the 1150–1250 cm^{-1} region. Careful inspection of the spectra indicates that a strong peak is observed around 1150 cm^{-1} for PMMA and around 1250 cm^{-1} for PVAc. Thus, the peaks around 1150–1250 cm^{-1} can be used to define the surface enrichment of PVAc. The peak around 1150 cm^{-1} is assigned to the ν_a(C–O–C) of PMMA and the 1250 cm^{-1} peak is due to the C–O stretching of PVAc[22,23]. *Figure 4* shows typical transmission *FT*i.r. and a.t.r. *FT*i.r. spectra of blends cast from several different solvents. One can see from the a.t.r. *FT*i.r. spectra that the relative intensity of the peak at 1250 cm^{-1} is larger than that at 1150 cm^{-1} for the blend cast from chlorobenzene or cyclohexanone while the relative intensity of the peak at 1150 cm^{-1} is larger than that at 1250 cm^{-1} for the blend cast from ethyl acetate. *Table 3* summarizes the relative absorbance intensity ratio of peaks at 1250 cm^{-1} (I_{1250}) and 1140 cm^{-1} (I_{1140}) for the 1/1 PMMA/PVAc blends cast from three different solvents.

In *Table 3*, only relative intensities are given, since the exact interpretation of a.t.r. *FT*i.r. data is difficult because the penetration depth strongly depends on wavelength. The blends cast from chlorobenzene and cyclohexanone exhibit larger relative surface enrichment in PVAc, whereas the blend cast from ethyl acetate shows a smaller relative surface enrichment in PVAc. In other words, the as-cast phase-separated blend shows a slight reduction in PVAc surface enrichment compared to the miscible systems. The effective path length may be different due to differences in optical element/sample contact and is affected by wavenumber *versus* penetration depth effects. Thus, the a.t.r. spectra of mixtures should be compared with the transmission spectra of a 50/50 blend of reasonable thickness. In this regard, *Figure 4* also shows the *FT*i.r. transmission spectra of a 50/50 PMMA/PVAc blend of ~10 μm thickness.

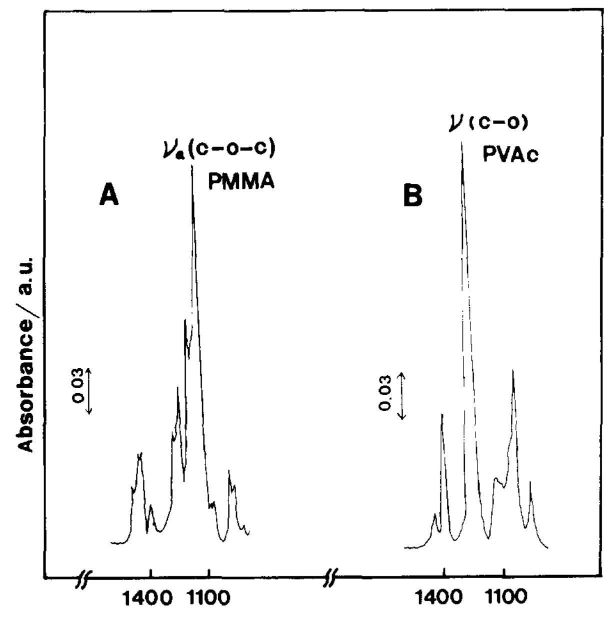

Figure 3 A.t.r. *FT*i.r. spectra of PMMA (A) and PVAc (B) homopolymers

Table 3 Relative intensity ratio of the peaks at 1250 cm^{-1} (I_{1250}) and 1140 cm^{-1} (I_{1140}) for the PMMA/PVAc blends cast from three different solvents

	I_{1250}	I_{1140}	I_{1250}/I_{1140}
PMMA	6.4	13.65	0.469
PVAc	14.28	3.2	4.463
Chlorobenzene	12.96	8.05	1.610
Cyclohexanone	12.88	8.39	1.535
Ethyl acetate	11.7	14.96	0.782

Comparisons of the transmission spectra and a.t.r. spectra indicate that for the transmission spectra there are no significant differences in the relative absorbance intensity ratio of peaks at 1250 cm^{-1} (I_{1250}) and 1140 cm^{-1} (I_{1140}) for the same PMMA/PVAc blends cast from three different solvents, when compared to those of the corresponding a.t.r. spectra. Note, however, that the frequencies of the peaks around 1150 cm^{-1}, assigned to the ν_a(C–O–C) of PMMA, were observed at slightly different positions for the PMMA/PVAc blends cast from three different solvents. The frequency was observed at 1147 and 1147.1 cm^{-1} for PMMA homopolymer and the blend cast from ethyl acetate, respectively, but the frequency was observed at 1151.6 and 1149.7 cm^{-1} for the blends cast from chlorobenzene and cyclohexanone, respectively. The frequency shifts in the transmission spectra imply a specific polar interaction between PMMA and PVAc. The *FT*i.r. transmission spectra, therefore, show that the miscibility was better in the order chlorobenzene > cyclohexanone > ethyl acetate when the blends were cast from the three different solvents. No information on surface enrichment was obtained from the *FT*i.r. transmission spectra, whereas the transmission spectra shed light on the bulk miscibility of the blends.

The a.t.r. *FT*i.r. results showing the surface enrichment of PVAc in miscible blend systems are in agreement with the X.p.s. and contact angle measurement data. Annealing of cast films above the *LCST* to thermally induce phase separation produced a slight reduction in the surface PVAc concentration. These results imply that the lower the degree of mixing in the bulk, the less PVAc is observed at the surface.

DISCUSSION

By applying the techniques of contact angle measurements, X.p.s. and a.t.r. *FT*i.r. spectroscopy to the study of solvent-cast PMMA/PVAc blend films, we were able to obtain detailed information on the topography at the air–polymer interface from the outermost surface (top few molecular layers) to the surface of the order of 0.5–3 μm deep. The combination of X.p.s. and a.t.r. *FT*i.r. for determination of surface structure constitutes a powerful means for investigating the surface properties of polymer blends. A substantial surface enrichment of

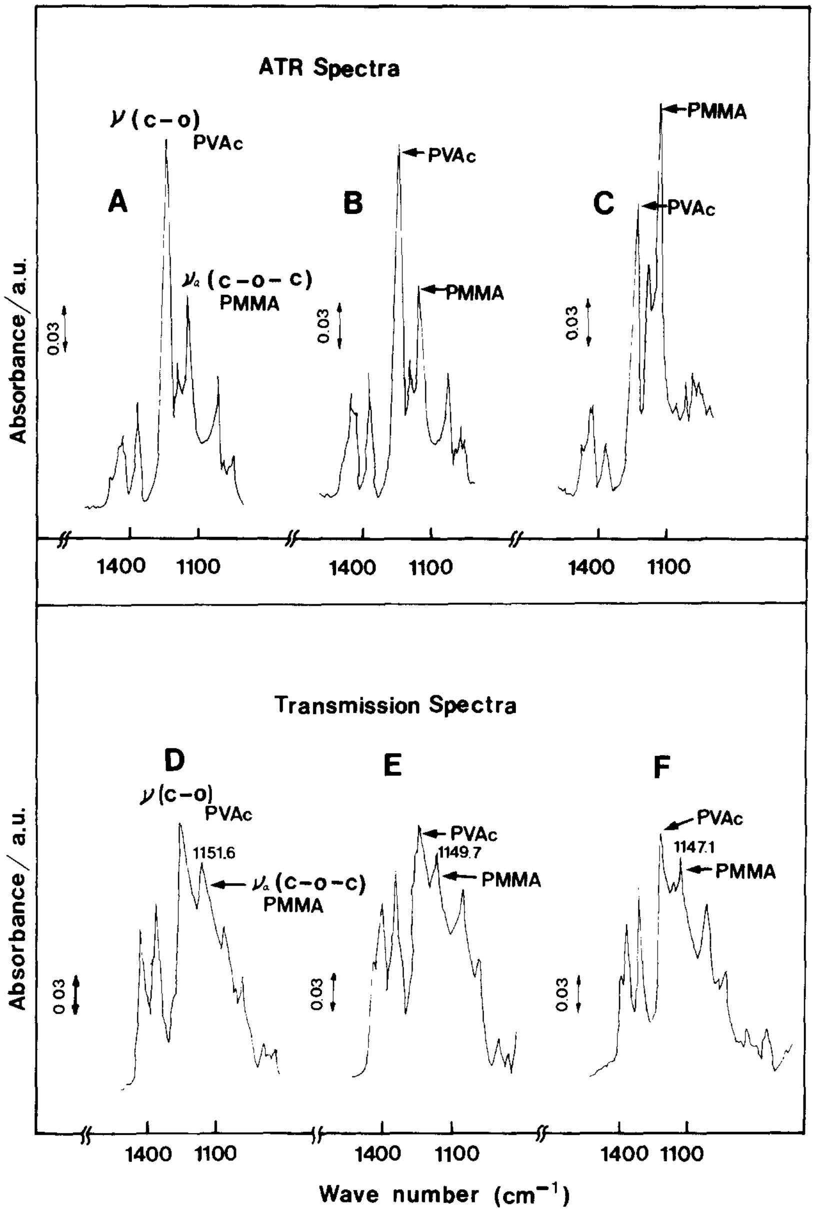

Figure 4 Transmission *FT*i.r. and a.t.r. *FT*i.r. spectra of 1/1 PMMA/PVAc blends cast from different solvents: (A, D) chlorobenzene; (B, E) cyclohexanone; (C, F) ethyl acetate

PVAc was observed for the miscible blends when they were cast from benzene, chlorobenzene or cyclohexanone. The experimental results showed that the surface enrichment of PVAc was reduced when the as-cast blend showed phase separation or when the blend exhibited thermally induced phase separation by heating above the *LCST*. The trends in surface enrichment are the same for the PMMA/PVAc blends regardless of the techniques used, even though the surface sensitivity and data integrated over very different depths are substantially different.

The results are in contrast with those for the PS/PVME system reported by Pan and Prest[10], since they reported that the lower the degree of mixing in the bulk, the more the component of lower surface energy (PVME) was observed at the surface. They reported that this was only possible when the PVME-rich phase could move into the surface during the process of bulk phase separation. The results in this work imply that the PVAc phase cannot easily move into the surface during the process of bulk phase separation in our PMMA/PVAc system when compared to the PS/PVME system.

Recently, Jones and Kramer[24] analysed the surface composition and surface excess of the lower surface energy component of a miscible polymer blend at equilibrium. They suggested that the total surface excess is more strongly dependent on the value of the Flory–Huggins interaction parameter between the segments of the two polymers than on the differences in surface energies between the components of the blend.

The thermodynamic drive for surface enrichment is now operating on a heterogeneous system which contains two phases. Presumably each phase domain will experience preferential surface enrichment. Thus, it is not surprising that different systems (PS/PVME) could exhibit opposite effects to our PMMA/PVAc systems.

CONCLUSIONS

The surface enrichment of PMMA/PVAc blends with 50/50 wt% composition was investigated using contact angle measurement, X.p.s. and a.t.r. *FT*i.r. spectroscopy. A substantial surface enrichment of PVAc was observed for the miscible blends when they were cast from benzene, chlorobenzene or cyclohexanone. The surface enrichment of PVAc was reduced when the blend was cast from ethyl acetate and showed phase separation. A similar reduction in the surface enrichment of PVAc was also observed when the blend exhibited thermally induced phase separation by heating above the *LCST* of the PMMA/PVAc blend.

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