Surface Studies of Polymer Blends. 2. An ESCA and IR Study of Poly(methyl methacrylate)/Poly(vinyl chloride) Homopolymer Blends

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ABSTRACT: Angle-dependent ESCA and ATR-FTIR results are presented for homopolymer blends of poly(methyl methacrylate) and poly(vinyl chloride). Blends over the entire composition range were cast from tetrahydrofuran (THF) and methyl ethyl ketone (MEK). Surface enrichment of PMMA was present at all compositions of blends cast from THF, while blends cast from MEK exhibited surface compositions that were within error limits equivalent to the bulk compositions of the blends.

Introduction

Polymer blends have become a very important subject for scientific investigation in recent years because of their growing commercial use.[1] Blends are an inexpensive route to the modification of polymer properties. Examples of the properties of interest that may be altered upon blending are impact resistance, fatigue behavior, heat distortion, and improved processability.[2]

In some blend systems, the effective property modification is dependent upon the miscibility or "compatibility" (i.e., the ability to form a homogeneous mixture) of the two homopolymers. Compatibility of polymers in a blend has been defined in a number of ways. The simplest definition of polymer compatibility in a blend is optical clarity upon preparation.[3] Another definition of blend compatibility[4] involves the glass transition temperatures of the homopolymers and the blend. Compatible blends must exhibit a single glass transition temperature (T_g) between the T_g's of the homopolymers, while incompatible blends will have two T_g's that correspond to those of the homopolymers. A third definition of compatibility involves the use of infrared spectroscopy. Coleman and Painter[5] have proposed that if two polymers are compatible, then the infrared spectra obtained for the blend should include band shifts and broadening when compared to the scaled addition of the infrared spectra of the homopolymers. These changes could be due to functional group interactions (hydrogen bonding or dipolar interactions) between the monomer units in the constituent polymers, helping in part to overcome entropic effects in the polymer blends. Coleman and Painter have now refined an approach to determine microscopic heat of mixing components in terms of a general Flory–Huggins χ parameter. Specifically, hydrogen-bonding components of the heat of mixing have been determined through the use of infrared spectroscopy.[6] Paul et al.[7,8] has utilized a modified Guggenheim quasi-chemical group contribution method to predict heat of mixing contributions for liquids, polymer repeat units, and polymers.

However, successful compatibility, as evaluated by each of the definitions, does not necessarily mean that mixing is taking place on a molecular scale. A blend that is optically clear may not meet the T_g definition of compatible, because clarity may be due to equivalent refractive indices of the homopolymers[4] or if one component is in low concentration. Further, films that meet the optical clarity criterion can have inhomogeneities on the order of 1000 Å.[4] A blend that exhibits a single T_g can have inhomogeneities on the order of 100–150 Å.[9] The infrared definition of compatibility involves shift and broadening of peaks; in some cases this can be due to mismatches in the refractive indices of the homopolymer. In addition interactions between monomers may not give rise to detectable shifts in the midinfrared spectral region.

Over the past 10 years electron spectroscopy for chemical analysis (ESCA or XPS) has been widely used to study the surface of polymers and polymer blends.[10,11] Generally in multicomponent polymer blends or copolymers the homopolymer constituent or block having the lower surface energy will migrate to the surface of the material.[14] Most previous ESCA studies[13-16] have reported this effect for poly(styrene)/poly(ethylene oxide),[13,16] poly(dimethylsiloxane) (DMS) and Bisphenol A polycarbonate (BPAC),[15] and poly(styrene)/poly(vinyl methyl ether).[16]

Busscher et al.[17] have utilized ESCA and contact angle measurements to study melt cast blends of PMMA/PVC. Their work claimed an enrichment of PVC at the surface of the melt-cast blends produced. Some ascepts of the work shed some doubt upon their conclusions. For example, the PVC used in their study contained oxygen, which was attributed to added stabilizers. Thus, in their calculations of the blend surface composition from ESCA, it was necessary for them to correct for the oxygen present in the PVC and for the effects of dechlorination due to X-ray damage. Further, contact angle measurements were used to calculate surface free energies for the homopolymers and blends. Yet, their samples were washed in 1% sodium dodecylsulfate followed by a wash in 4% hydrofluoric acid. The values of surface free energy that were obtained for PMMA were much larger than those obtained by other investigators.

In the present work we have chosen to study solution-cast films of poly(methyl methacrylate) (PMMA) and poly(vinyl chlorie) (PVC). Disagreement exists as to the bulk compatibility as measured by thermal analysis of PMMA/PVC blends. Krause[4] lists the compatibility of PMMA/PVC blends as ambiguous. Two results from the literature are typical; Razinskaya et al.[18] were unable to produce compatible blends of PMMA/PVC from tetrahydrofuran (THF) and, Walsch and McKeown[19] have reportedly produced compatible blends using methyl ethyl ketone (MEK) as a mutual solvent. The T_g in these cases was measured by dynamic mechanical testing. In addition, using the same materials, Walsch and McKeown were unable to produce transparent blends from THF. Others

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Table I
Composition of PMMA/PVC Blends Studied in Weight %

THF	MEK	THF	MEK
100/0	100/0	30/70	40/60
99/1	90/10	10/90	30/70
90/10	80/20	1/99	20/80
70/30	70/30		10/90
50/50	60/40	0/100	0/100
40/60	50/50		

including Jager et al.[20] and Tremblay and Prud'homme[21] have also produced compatible blends from MEK.

The goal of this paper was to provide a quantitative analysis of the *surface region* of well-characterized, clean, additive-free PMMA/PVC blends over the entire composition range using ESCA and infrared spectroscopy. This system is of interest because of the surface energetics. Solid surface tensions have been determined by contact angle measurements. Values of 41.2 dyn/cm for PMMA[22] and 42 dyn/cm for PVC[23] were determined, which are equivalent within error limits of ±1 dyn/cm. These values are similar to those reported by Dalal[24] for PMMA (40.5 dyn/cm) and PVC (41.4 dyn/cm). Since solid surface tensions can be related to the surface free energy of polymeric systems and the lower surface energy component would normally enrich the surface of a polymer blend, no excess or a very slight surface excess of PMMA would be expected in these systems. In addition the effect of casting solvent on the surface composition will be examined over the entire composition range (Table I) for the blends cast from THF and MEK. Further studies of this system will focus on the effect of molecular weight of the homopolymer constituents.[25]

Experimental Section

Sample Preparation. Atactic PMMA (MW = 93 300) was obtained from Poly Sciences; PVC (MW = 190 000) was purchased from Aldrich Chemical. Both the PMMA and the PVC have polydispersity indices of 2. Reagent-grade THF and MEK were purchased from Fisher Scientific. THF was distilled to remove traces of water. PVC was purified by dissolving the polymer in THF, filtering, and recrystallizing by adding ethanol. This procedure removed oxygen-containing contamination, as detected at the surface of the PVC, below the level of ESCA detectability (Figure 1). Blends were prepared by solvent-casting mixtures of the homopolymers from 1% by weight solutions of THF and MEK. Samples for ESCA analysis were cast onto silver coupons. Samples were cast onto copper foil for ATR analysis and onto KCl windows for transmission FTIR analysis. The films produced were optically transparent. In all cases the air-facing surface was analyzed.

The casting of films from THF had to take place on days of low humidity. If casting took place on humid days the resulting films were cloudy. This problem was not exhibited by films cast from MEK. Before analysis the films were vacuum desiccated for a period of 24 h. The homopolymers and blends were ultrasonically extracted for 30 s in *n*-hexane to remove residual siloxane type impurities to below the level of ESCA detectability. Ultrasonication of the polymer films did not result in the degradation of the polymer films as analyzed by changes in ESCA, infrared, or weight loss.

Instrumentation. ESCA spectra were recorded on a Physical Electronics Models 5100 and 5400 with a Mg $K\alpha_{1,2}$ X-ray source (1253.6 eV). The standard operating conditions of the X-ray source were 300 W, 15 kV, and 20 mA. The base pressure of the instrument was 2×10^{-9} Torr and an operating pressure of 2×10^{-8} Torr typically. A pass energy of 35 eV was utilized. The PHI 5100 was equipped with a hemispherical analyzer and a single-channel detector. The 5400 model was outfitted with a hemispherical analyzer and a multichannel detector. Both instruments were calibrated such that the Ag $3d_{5/2}$ peak of sputter-cleaned Ag had a binding energy of 367.9 eV ± 0.1 eV. The fwhm of the Ag $3d_{5/2}$ was found to be 0.8 eV at a count rate of 80 000 cps.

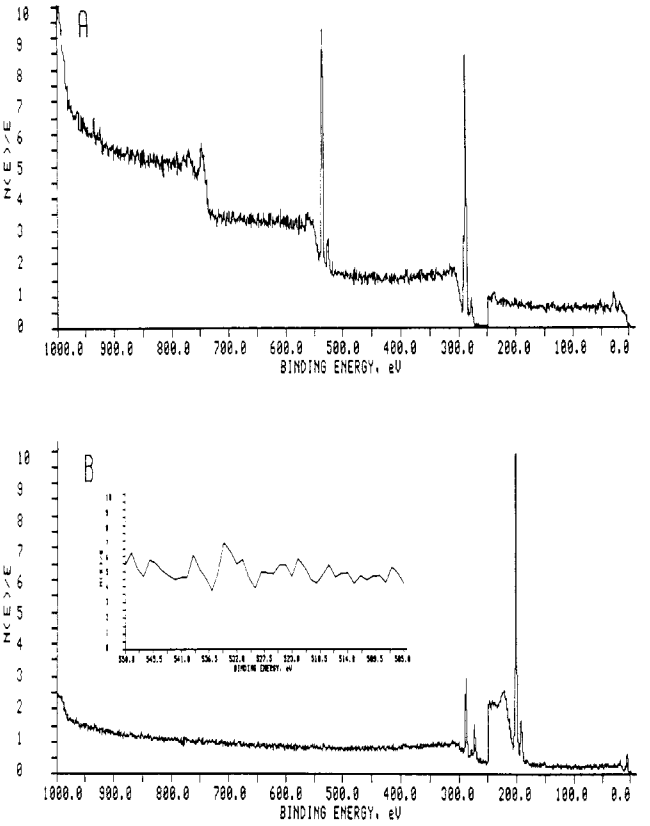

Figure 1. ESCA survey spectra for (A) PMMA and (B) PVC.

Angle-dependent measurements were acquired at 15, 45, and 90°. This allows sampling depths of approximately 22, 61, and 86 Å.[26] All data analysis (curve fitting, linear background subtraction, and peak integration) was accomplished using a Perkin-Elmer 7500 computer running PHI ESCA version 2.0 software.

PVC is known to dechlorinate when exposed to X-ray radiation.[27,28] PVC was found to show the effects of dechlorination (i.e., loss of chlorine and changes in the C 1s line shape) after approximately 18 min of X-ray exposure in both instruments. The critical exposure time was determined by examination of the C/Cl peak area ratio and atomic concentrations of a series of 20 PVC samples. These samples were analyzed for 4 min each. Atomic concentrations of carbon and chlorine were determined for this set of samples and were found to fall within 3% of the theoretical values for PVC. The C/Cl peak area ratios were determined for the series, and a standard deviation was calculated. PVC samples were then exposed to X-ray radiation for longer periods of time. When the C/Cl peak area ratio fell outside of 1 standard deviation unit the sample was determined to be dechlorinating. This was found to take place after approximately 18 min. Angle-dependent measurements were acquired in 14 min to be well within a period of time where the effects of X-ray damage were determined to be minimal.

ATR-FTIR analysis was performed on a Nicolet 7199A spectrometer outfitted with a variable-angle Harrick XBC-50N ATR attachment. A liquid-nitrogen-cooled HgCdTe detector was utilized in all cases. The blends were analyzed against 10 × 5 × 1 mm micro sampling plates. The internal reflection elements chosen were 45° KRS-5 and 60° Ge. The spectra obtained from samples pressed against KRS-5 and 60° Ge were a sum of 1000 and 10 000 scans, respectively. Reproducible sample contact was achieved with the use of a torque wrench. A setting of 6.5 ft·lb provided sufficient contact to provide reproducible results. The infrared experiments were reproduced three to five times for each blend composition. All spectra were recorded at a resolution of 4 cm^{-1}.

Results and Discussion

Bulk analysis of the blends was carried out by transmission FTIR. Band shifts and broadening were not observed for any of the blends cast from either THF or MEK.

Table II
Surface Wt % PMMA from THF-Cast PMMA/PVC Blends

bulk wt % PMMA	surf wt % C/O	surf wt % O—C=O	surf wt % C-Cl
99	98 ± 2	97 ± 2	98 ± 1
90	95 ± 3	92 ± 2	92 ± 4
70	87 ± 3	90 ± 4	93 ± 2
50	84 ± 4	88 ± 3	80 ± 3
40	58 ± 5	58 ± 4	56 ± 4
30	46 ± 4	50 ± 3	49 ± 3
10	39 ± 6	45 ± 4	36 ± 3
1	8 ± 4	7 ± 2	9 ± 3

Table III
Surface Wt % PMMA from MEK-Cast Blends of PMMA/PVC

bulk wt % PMMA	surf wt % C/O	surf wt % O—C=O	surf wt % C-Cl
90	96 ± 3	95 ± 3	97 ± 3
80	88 ± 5	86 ± 4	87 ± 5
70	80 ± 5	78 ± 5	81 ± 3
60	64 ± 4	66 ± 3	65 ± 4
50	57 ± 3	58 ± 5	55 ± 4
40	47 ± 3	46 ± 3	48 ± 4
30	37 ± 3	35 ± 3	38 ± 3
20	26 ± 3	27 ± 4	25 ± 4
10	17 ± 2	18 ± 5	19 ± 4

PVC cannot be observed in the transmission experiments at concentrations of PVC less than 50% by weight. This is due to the low absorptivity of PVC. A more detailed discussion of the infrared results will follow.

Quantitive ESCA analysis (Tables II and III) of the PMMA/PVC blends was accomplished in two ways, first, by utilizing an empirical "sensitivity factor" derived from the carbon to oxygen ratio of pure PMMA and, second, by curve fitting of the C 1s envelope. The C/O ratio used in this analysis is derived from raw peak areas of the C 1s and O 1s regions. The equation that was used to determine the surface percentage of PMMA is

$$\frac{2(1-\omega)/62.5}{5\omega/100.15} + 1 = \frac{(C/O)_{blend}}{(C/O)_{PMMA}} \quad (1)$$

where ω is the surface weight percent of PMMA. A ratio technique was also derived from a C/Cl ratio for the PMMA/PVC blends. The surface weight percent PMMA determined from the C/Cl ratio was within experimental error of the results obtained from the C/O ratio.

Surface weight percentages were also determined by curve fitting the C 1s spectrum.[15] The following approach was used for this study. In determining the initial parameters for the fit, the full-width at half-maximums and peak positions were held constant. Standard peak positions were used. Goodness of fits (χ^2) were typically below 1. The parameters used to fit the PMMA/PVC blends were determined from the curve fits of the homopolymers. PMMA was fit with three peaks that correspond to the O—C=O (289.0 eV), C-O (286.7 eV), and C-H (285 eV). A 1:1:3 ratio (within error limits of 2%) was obtained for areas of the O—C=O, C-O, and C-H of pure PMMA. The C/O ratio of PMMA was found to be independent of takeoff angle; this and the fact that a 1:1:3 fit was obtained for each of the takeoff angles indicate a PMMA surface that is free of oxygen-containing contaminates. The C 1s envelope of PVC was fit with two peaks, which correspond to the C-Cl at 286.3 eV and the C-H at 285 eV. A 1:1 ratio of the C-Cl to the C-H of PVC was obtained. Since the O=C—O of PMMA was the easiest peak to fit, it was first used to determine the composition of the blend. The area of the O=C—O represents ≈20% of the total area that is due to PMMA. The surface percent of PMMA could then be easily calculated. The area of the C-Cl was also used to determine the surface composition of PMMA. This was the most difficult peak to fit due to the overlap of the peaks in that region of the C 1s envelope. The surface percentage of PMMA calculated by both methods in the curve fitting agree within the error limits. The equation that was used to calculate the surface percentage of PMMA from the curve fits is

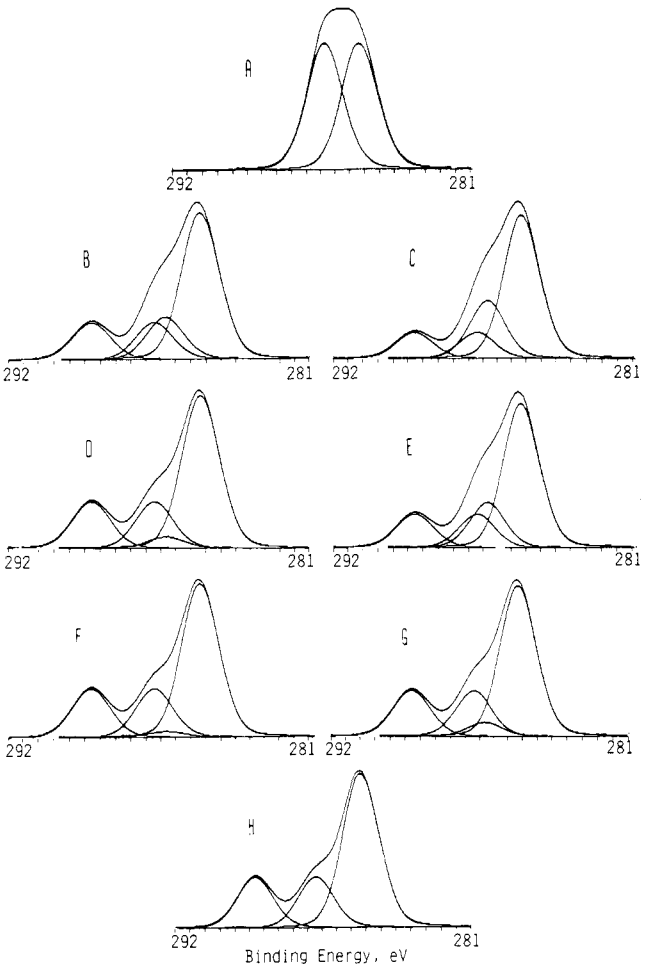

Figure 2. Curve-fitting analysis of the C 1s region: (A) PVC, (B) 30/70 THF cast, (C) 30/70 MEK cast, (D) 50/50 THF cast, (E) 50/50 MEK cast, (F) 70/30 THF cast, (G) 70/30 MEK cast, and (H) PMMA.

$$\frac{I_{PMMA}}{I_{PVC}} = \frac{5\omega/100.15}{2(1-\omega)/62.5} \quad (2)$$

where ω is the surface weight percent of PMMA.

Examples of typical curve fits for PMMA, 70/30, 50/50, 30/70, and PVC cast from THF and MEK are shown in Figure 2. One can easily see that there is consistently more PMMA detectable at the surface of the blends cast from THF by observing the intensity of the C-Cl peak at 286.3 eV. A graphical representation of the surface composition of the blends cast from THF and MEK derived from both the C/O ratio and curve fitting are shown in Figure 3. The diagonal line in each graph indicates a surface composition that is equivalent to the bulk composition of the blend. Comparison of the experimental values to this line allows the evaluation of the surface excess. These ESCA results for both THF and MEK show a surface excess of PMMA. The THF data exhibits an "s" shape or step while the MEK data appears to be a straight line. In every case the THF-cast blends have a much greater surface excess of PMMA than the blends produced from MEK. In addition, while the MEK cast blends show

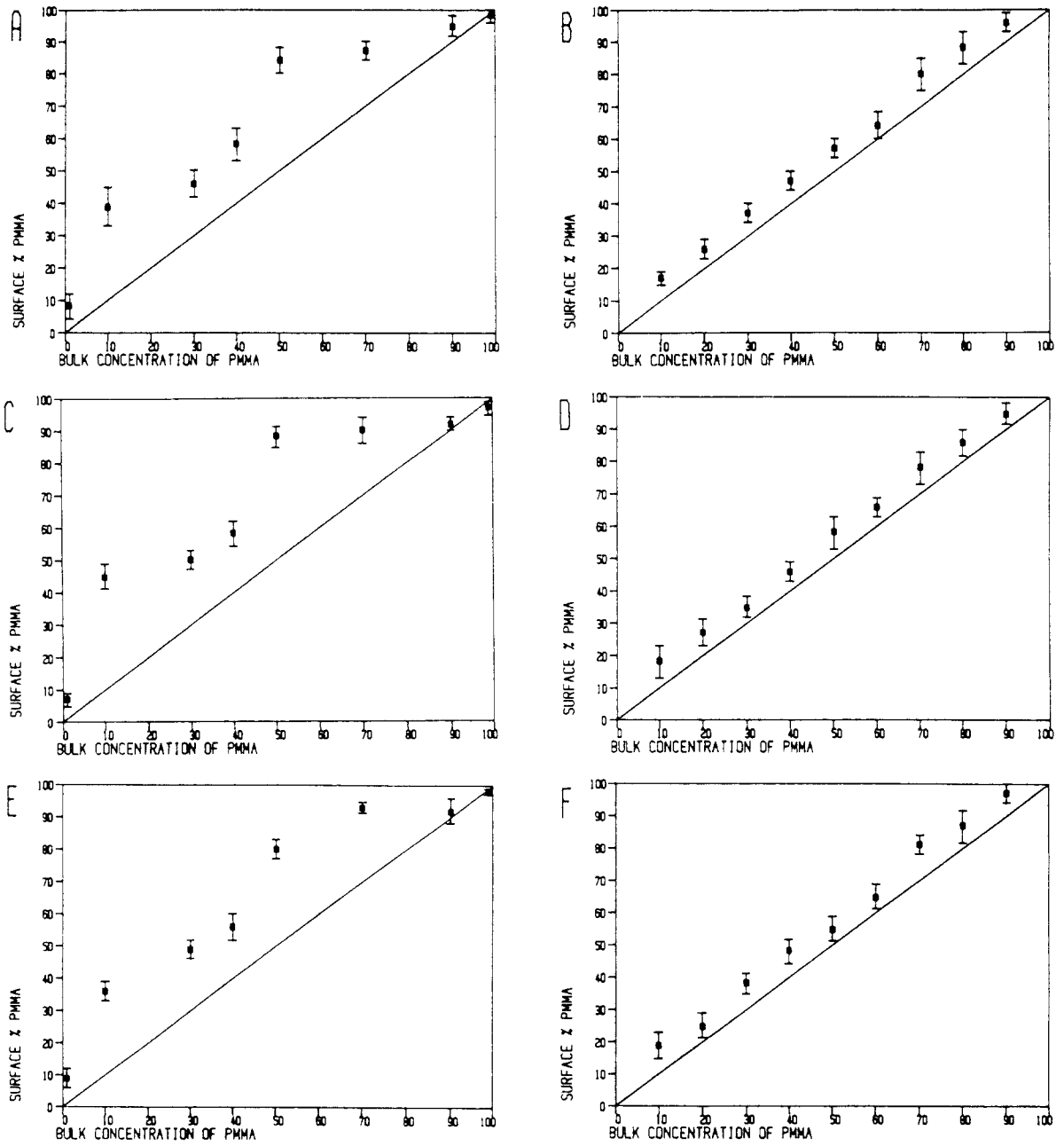

Figure 3. Surface vs bulk composition of PMMA/PVC blends: (A) surface % PMMA THF-cast blends using the C/O, (B) surface % PMMA MEK-cast blends using the C/O, (C) surface % PMMA THF-cast blends using the O—C=O, (D) surface % PMMA MEK-cast blends using the O—C=O, (E) surface % PMMA THF-cast blends using the C–Cl, (F) surface % PMMA MEK-cast blends using the C–Cl.

a systematic excess of PMMA at the surface, these values are within error limits of bulk composition. The surface compositions determined by both the C/O ratio and the curve fitting are equivalent within error limits to each other.

Angle-dependent ESCA measurements that were performed at 15, 45, and 90° showed that there were no significant differences in composition over the ESCA sampling depths for either the THF- or MEK-cast blends. This result would tend to indicate a local equilibrium over the top 100 Å of the PMMA/PVC blends. The blend surface composition differs depending on the solvent chosen, but every blend produced has a constant composition over the top 100 Å.

Since no band shifts were detected in the transmission infrared experiments, ATR infrared analysis that was performed could only determine the surface composition of the PMMA/PVC blends albeit at a much deeper depth. This can allow the evaluation of a surface excess profile and where distinct microdomains are formed can provide an estimate of the domain size. In ATR, the depth of penetration for a nonabsorbing medium, defined as the distance required for the electric field amplitude to fall to e^{-1} of its value at the surface, has been given by Harrick[29]

$$d_p = \frac{\lambda/n_1}{2\pi(\sin\theta - (n_1/n_2)^2)^{1/2}} \quad (3)$$

where n_1 is the refractive index of the sample and n_2 is the refractive index of the ATR element. Mirabella[30] has shown that sampling depth for polymeric materials is about three times d_p. If one were analyzing polymers which have refractive indices of approximately 1.5, sampling depths of bands appearing at 3000, 1730, and 630 cm^{-1} would be 2.22, 3.86, and 10.6 μm for a sample analyzed

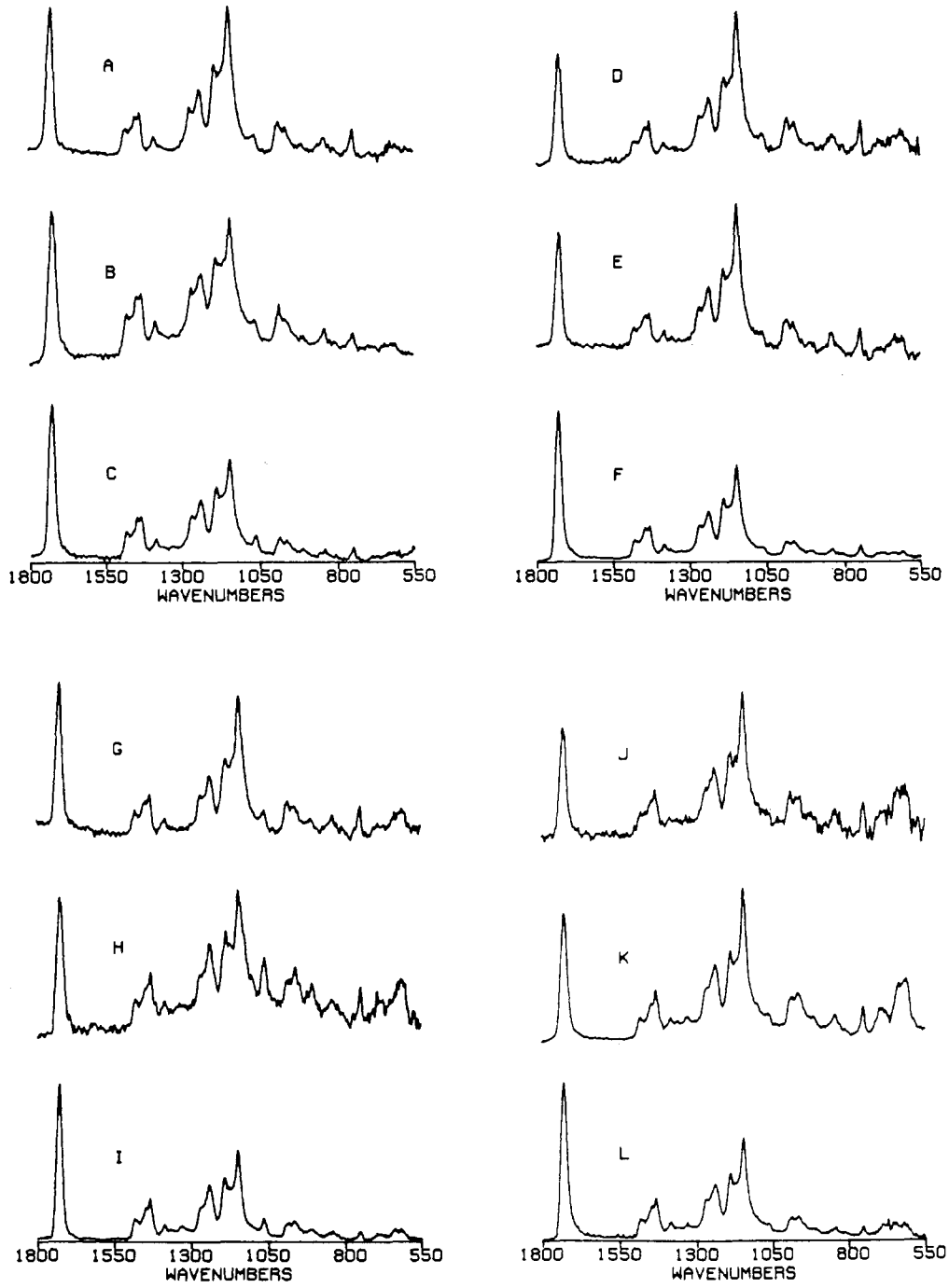

Figure 4. ATR and transmission FTIR spectra for (A) 70/30 THF-cast 60° Ge ATR, (B) 70/30 THF-cast 45° KRS5 ATR, (C) 70/30 THF-cast transmission, (D) 70/30 MEK-cast 60° Ge ATR, (E) 70/30 MEK-cast 45° KRS5, (F) 70/30 MEK-cast transmission, (G) 50/50 THF-cast 60° Ge ATR, (H) 50/50 THF-cast 45° KRS5 ATR, (I) 50/50 THF-cast transmission, (J) 50/50 MEK-cast 60° Ge ATR, (K) 50/50 MEK-cast 45° KRS5 ATR, and (L) 50/50 MEK-cast transmission.

on a 45° KRS-5 element and 0.51, 0.88, and 2.43 μm for a sample analyzed on a 60° Ge element. The films analyzed were approximately 0.25-mm thick. a 45° KRS-5 experiment at 630 cm^{-1} is sampling approximately 4% of the material present.

Band shifts and broadening that are indicative of compatibility were not observed in the ATR analysis of the THF or MEK cast blends of PMMA/PVC. PVC could not be detected in the ATR or transmission experiments for blend compositions lower than 50% PVC. This is due to the lower absorptivity of PVC as compared to PMMA. A quantitative peak ratio analysis could not be accomplished easily with the PMMA/PVC blends due to the overlap of the bands that takes place. For this to be done successfully for ATR analysis the bands selected must be separated but relatively close (within 50 cm^{-1}) due to the wavelength dependence of the sampling depth in ATR. The only bands that are fully separated are the carbonyl stretch of PMMA and the C–Cl stretch of PVC, but they are separated by approximately 1100 cm^{-1}. Subtraction techniques were attempted but did not prove to be fruitful, again due to the low absorptivity of PVC. However, relative quantitative comparisons of band intensities can be made between ATR spectra taken on 45° KRS-5 and 60° Ge ATR elements and between solvents.

Figure 4 displays transmission, 45° KRS-5 ATR, and 60° Ge ATR for 70/30 and 50/50 blends of PMMA/PVC cast from THF and MEK. PVC cannot be observed in the ATR or the transmission experiments of the 70/30 blends cast from THF. The ATR spectra of the 70/30 blends cast

from MEK exhibit a C–Cl stretch from PVC at about 630 cm^{-1}. There is more PVC detectable in the surface region as measured by ATR in the 70/30 MEK-cast blend than there is present in the same surface region in the 70/30 THF-cast blend. When the ATR spectra of 50/50 blends cast from THF and MEK are compared, it also appears that there is more PVC present in the surface region of the MEK-cast blend. This result is consistent with the ESCA results, which show more PMMA at the surface of the THF-cast blends. Further, when the relative intensities in the 45 and 60° ATR spectra of the MEK-cast blends are compared, they appear to be identical. If the 60° Ge spectra is compared to the 45° KRS5 spectra for the 50/50 THF blend, there appears to be less PVC in the shallower surface region that is measured in the 60° ATR experiment. Thus the 50/50 blend cast from THF does not appear to be homogenous over the sampling depth of the ATR experiment.

Lower surface energy components in blend systems normally enrich the surface of the blend. PMMA and PVC have solid surface tensions of 41.2[22] and 42.0[23] dyn/cm, respectively. PMMA is thus expected to slightly enrich the surface of the PMMA/PVC blends. However, as the results show the degree of enrichment clearly differs depending on the casting solvent. We observed a complex, systematic surface enrichment of PMMA in the THF-cast blends and a very slight enrichment in the MEK-cast blends.

ESCA analysis of the THF-cast blends of PMMA/PVC demonstrates that there is a concentration gradient in the THF-cast blends because the surface composition of the blends differs greatly from the bulk concentration; however, the concentration is constant over the sampling depths of the angle-dependent ESCA measurements. The ATR analysis of the THF blends also exhibits the presence of a concentration gradient over the sampling depth of the ATR experiment, which has a sampling depth that is approximately 500 times deeper than that of ESCA. The concentration gradients and degree of surface enrichment are different for the various compositions of the blends cast from THF.

PMMA/PVC blends cast from MEK must involve a greater degree of mixing in the surface region, possibly at a molecular level. The surface composition as determined by ESCA analysis is within error limits equivalent to bulk composition although all the data points fall above the line indicating bulk composition in Figure 3. The ATR analysis of the MEK-cast blends shows that the blends are homogeneous over the sampling depth of the ATR experiment. The greater degree of mixing present in the blends cast from MEK corresponds well with all of the T_g analysis that has been performed by others done previously.[18-21]

Solubility parameters have been used to explain the effects of the solvent on polymeric systems.[31] THF and MEK have solubility parameters of 9.52 (w_d = 7.77, w_p = 4.40, w_h = 2.50)[32] and 9.27 (w_d = 8.22, w_p = 2.80, w_h = 3.90),[32] respectively. Both solvents are mildly hydrogen bonding. PMMA and PVC have solubility parameters of 9.5[33] and 9.6,[33] respectively. The small differences in solubility parameters do not offer a simple explanation of the differences in composition that are being observed in the surface region of the PMMA/PVC blends.

However, it is clear that the blends resulting from THF casting yield microdomain structure, surface segregation, and surface heterogeneity. This seems to correlate with the lack of agreement in the literature with respect to the compatibility of THF-cast PMMA/PVC blends. Futher, our results from MEK show that homogeneous mixtures, with little detectable surface segregation, can be produced, where surface energetics would predict little surface driving forces for segregation. Ongoing work will address effects of the molecular weight of the homopolymers.

Conclusions

The means for quantitative analysis of surface composition for well-characterized additive-free PMMA/PVC blends have been accomplished over a range of compositions. Casting solvent (THF of MEK) systematically effects the surface composition as well as the bulk compatibility, showing that microphase segregation will be exaggerated at the air interface. ATR infrared studies show heterogeneity in the THF-cast samples and homogeneity for the MEK-cast samples.

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Registry No. PMMA, 9011-14-7; PVC, 9002-86-2.

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Surface Studies of Polymer Blends. 3. An ESCA, IR, and DSC Study of Poly(ϵ-caprolactone)/Poly(vinyl chloride) Homopolymer Blends

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ABSTRACT: Angle-dependent electron spectroscopy for chemical analysis (ESCA or XPS), Fourier transform infrared spectroscopy with attentuated total reflectance (ATR-FTIR), and differential scanning calorimetry (DSC) results are presented for miscible and immiscible solvent-cast blends of poly(ϵ-caprolactone) (PCL; MW = 33 000) and poly(vinyl chloride) (PVC; MW = 190 000). The DSC results showed that blends with less than 50 wt % PCL were miscible, with a single glass transition temperature. In addition, for blends with greater than or equal to 50 wt % PCL a melting temperature was detected and attributed to crystalline PCL. Since the blends in this composition range contained both crystalline and blended PCL, they were considered immiscible or incompatible. Analysis of the polymer/air interface by ESCA showed that the surface composition of the blends is equivalent to the bulk composition for blends with less than 50 wt % PCL. For blends with bulk composition between 50 and 90 wt % PCL, the surface composition analysis yielded a surface excess of PCL while the 90 wt % PCL blend exhibited an enrichment of blended PVC. The ATR-FTIR and transmission infrared results indicated that the PCL/PVC blends with less than 50 wt % PCL are homogeneous. ATR-FTIR results indicated that the relative amount of amorphous or blended PCL to semicrystalline PCL increases with greater sampling depths for blends containing 50–60 wt % PCL. From the infrared studies, shifts in the carbonyl stretch and C–O bending bands indicate that the PCL becomes semicrystalline in blends with greater than or equal to 50 wt % PCL. The results taken together support a model of surface composition of homopolymer blends which directly relates to bulk miscibility.

Introduction

The blending or simple mixing of polymers is an easy and inexpensive method of modifying various properties of a polymer, such as flexibility, heat distortion, and fatigue behavior.[1] It is believed that property modification is directly related to the compatibility or miscibility of the polymers forming the blend.[2] The general goal of research in our laboratory is to develop the means to quantitatively evaluate the surface composition of multicomponent polymers. The previous paper[3] reports results of surface analytical studies on the homopolymer blends of poly(methyl methacrylate) and poly(vinyl chloride), a system where the two components have nearly equivalent surface energies. The goal of the present paper is to explore the effect of "crystallinity" of a component on surface composition in a homopolymer blend system.

In general, it is found that the majority of polymer blends are incompatible, exhibiting segregation or multiphase behavior.[4] One exception to this is the blend system of poly(ϵ-caprolactone) (PCL) and poly(vinyl chloride) (PVC).[4–8] These blends have been studied extensively, and an excellent review of the various studies has been presented by Coleman and Zarian.[4] From these studies, this blend system has been found to be miscible, in the amorphous or molten state, throughout the entire composition range 10–90 wt % PCL. These studies[4–9] have shown that some PCL becomes crystalline upon solidification in blends with 50 wt % or more PCL present. Russell and Stein[9] have studied the effects of polymer purity on the amount of crystalline PCL in PCL/PVC blends, using small-angle X-ray scattering, and concluded that the presence of contaminants and/or various molecular weight homopolymers in a PCL/PVC blend has a significant effect on domain size and miscibility.

In the present work, ESCA, infrared spectroscopy (ATR-FTIR and transmission), and DSC results were used to determine the surface composition for comparison to the bulk composition and miscibility of a series of PCL/PVC blends. Previous ESCA studies of multicomponent polymer systems have been reviewed in the previous paper.[3] ESCA experiments yield quantitative information over a sampling depth of 80 Å, while ATR-FTIR samples much deeper into the surface, 1–10.9 μm. While these techniques measure the surface composition, bonding, and structure and provide a limited compositional profile, transmission FTIR and DSC experiments measure the bulk characteristics of the PCL/PVC blends.

To complement ESCA data, infrared spectroscopy with attenuated total reflectance (ATR-FTIR) can be used. The multiple internal reflectance technique yields information about a surface region with a greater sampling depth (1–10.9 μm)[10,11] than does the ESCA technique. In addition to the deeper sampling depth, the ATR-FTIR ex-

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