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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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Table I
Bulk Compositions of the PCL/PVC Blends

wt % PCL/PVC	n_{PCL}/n_{PVC}	wt % PCL/PVC	n_{PCL}/n_{PVC}
100/0		40/60	0.37
90/10	5.19	25/75	0.18
75/25	1.63	10/90	0.06
60/40	0.82	0/100	0.00
50/50	0.54		

periment can yield information on composition, crystallinity, and polymer/polymer (inter- and intrachain) interactions. This information is derived from band intensities and from band shifts and broadening. An example of inter- and intrachain interactions is hydrogen bonding. In the past year, a series of papers[12-16] has been published on the determination of the degree of hydrogen bonding in a variety of polymer blends through the use of infrared spectroscopy. From these studies, the microscopic heat of mixing components of hydrogen bonding, in terms of a general Flory–Huggins χ parameter, and the degree of hydrogen bonding in polymer blend systems have been determined. In our laboratory, ATR-FTIR has been used in the past to complement ESCA analysis of crystalline homopolymers and block copolymers of poly(tetramethyl-*p*-silphenylenesiloxane) and poly(dimethylsiloxane)[17,18] in order to gain information on segregation and the crystallinity of the block copolymer system.

Differential scanning calorimetry (DSC) is often the method used to determine miscibility of polymer systems. One proposed criterion to determine compatibility is the observance of a single glass transition temperature (T_g) intermediate to the characteristic T_g's of the individual homopolymers.[19]

This work was undertaken in order to evaluate the effect of crystallinity on the compatibility and surface composition of a polymer blend, by surface analytical techniques. The PCL/PVC blend system was chosen because it has been reported to be miscible throughout the entire composition range and we wanted to study the effect of crystalline PCL on the surface composition of the blend system. In this study a high molecular weight PVC was used as compared to the molecular weight of the PVC used in earlier studies.[8,9] The effect of PVC molecular weight on the miscibility and surface composition of PCL/PVC blends is currently under investigation.[20]

Experimental Section

Sample Preparation. Poly(ϵ-caprolactone) (secondary standard, MW = 33 000) was purchased from Scientific Polymer Products, Inc. (Ontario, NY) and poly(vinyl chloride) (MW = 190 000) was purchased from Aldrich Chemical. The PCL was used as received. The PVC was purified by the method used in the previous paper.[3] The purity was checked by casting films and analyzing the homopolymers for impurities. Thick films (200–300 μm) of the blends, compositions listed in Table I, were prepared by solvent-casting mixtures of the homopolymers from 2% (w/v) tetrahydrofuran (Fisher) solutions into clean Petri dishes containing clean silver coupons. The films were allowed to air dry for a minimum of 1 week before being analyzed. The silver coupons and the Petri dishes were cleaned by ultrasonic solvent extraction, in hexane, in order to remove any organic (e.g., hydrocarbon) or siloxane impurities. This extraction was performed to ensure that any contaminants from these sources would not segregate to the surface of the blends. The solutions were directly cast onto KCl windows for the transmission infrared studies. The blends were further cleaned by ultrasonic solvent extraction in *n*-hexane to remove any residual impurities to below the level of ESCA detectability ($\approx$1 atomic %). ESCA and DSC results were collected in triplicate from three separate cast films. A Ge and KRS-5 ATR-FTIR spectrum was recorded for each blend of the separate castings, to ensure reproducibility.

Instrumentation. The angular-dependent ESCA experiments were performed on a Perkin-Elmer Physical Electronics Model 5100 ESCA using a hemispherical analyzer. Mg $K\alpha_{1,2}$ X-rays ($h\nu$ = 1253.6 eV), from a dual anode source, were used as the excitation source. The source was operated at 300 W, 15 kV, and 20 mA. Base pressure of the instrument was maintained at $\leq 2.0 \times 10^{-9}$ Torr. An operating pressure of $\leq 3.0 \times 10^{-8}$ Torr, and a pass energy of 35.7 eV was used for all high-resolution experiments. These operating conditions yielded a Ag $3d_{5/2}$ peak at δ 367.9 with a full-width half-maximum of 1.06 eV and 700 000 counts/s. A continuous variable-angle sample stage (5–90°) was used. No degradation of the homopolymers, e.g., dehydrochlorination of PVC, was detected in twice the total analysis time used for the angle-dependent ESCA measurements. All binding energies were referenced to the carbon 1s CH_x component set to 285.0 eV. All data manipulation (peak area integration, curve fitting, linear background subtraction) was accomplished using a Perkin-Elmer 7500 computer running PHI ESCA version 2.0 software.

As in the previous paper,[3] two methods of quantitation are used to calculate the surface composition of a polymer material from the ESCA results. The first method simply relates peak areas of the elements of interest to a surface percentage through the use of calibration references obtained from the homopolymers. The second method of calculating the surface composition involves curve-fitting the high-resolution carbon 1s spectra. With this approach, the correction of raw peak areas with calibration standards or sensitivity factors which account for photoionization cross-sections and different inelastic mean-free paths of electrons from the various elements is eliminated because only the photoelectrons from a single orbital are being considered.[21] By curve-fitting the carbon spectra, the relative contribution from the individual polymers to the carbon 1s peak shape can be determined.

The infrared experiments were performed on a Nicolet 7199A spectrometer with a liquid-nitrogen-cooled mercury–cadmium–tellurium detector. This instrument has been fitted with a Harrick (XBC-50N) beam condenser for the ATR-FTIR experiments. Harrick 45° Ge and 45° KRS-5 (10 × 5 × 1 mm) internal reflection elements were used for all ATR-FTIR experiments. The ATR-FTIR spectra were collected at 4-cm^{-1} resolution, while the transmission spectra were collected at 2-cm^{-1} resolution. Good signal to noise levels were obtained with 20 000 scans for the ATR-FTIR and 1000 scans for the transmission experiments.

The DSC measurements were made using a Du Pont 990/1090 DSC. All samples were quench cooled to −110 °C and then heated to 120 °C at a rate of 40 °C/min with a continuous nitrogen flow rate of 20 cm^3/min. The samples were held at an isotherm for 5 min, quench cooled with liquid nitrogen, and reheated to 120 °C at a rate of 40 °C/min. The T_g was taken as the onset of the change of slope in heat capacity plots. This was determined by extrapolating both slopes to the point of intersection. The DSC results reported were taken from the first scans. The second scans contained a recrystallization exotherm of PCL at $\approx$20 °C; therefore, the first scans were felt to be representative of the films analyzed by the other techniques.

Results

Visual inspection of all the blends prepared were consistent in that optically clear films were formed for the blends containing less than 50 wt % PCL. Above this concentration the films become more opaque. From these observations alone, the PCL/PVC blends would be considered miscible (from optical clarity) in the concentration range below 50 wt % PCL.

DSC Results. Figure 1 summarizes the DSC results as a function of the PCL/PVC blend composition. On the basis of these results, one can conclude that the PCL/PVC blend system is miscible in the 0–90 wt % PCL composition range. This conclusion is based on the observance of a single T_g for each composition between the characteristic T_g's of the homopolymers. However, because of the presence of a distinct T_m above 40 wt % PCL, we conclude that two PCL phases, one crystalline and the other blended, are present at compositions greater than

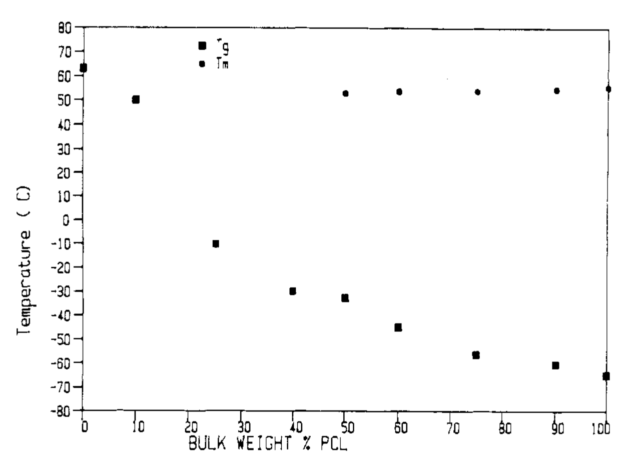

Figure 1. Plot of T_g and T_m versus PCL concentration for PCL/PVC blends.

Table II
Calculated Composition of Amorphous PCL/PVC Blends[a]

wt % PCL	% crystalline PCL	calcd amorphous PCL/PVC
100	76.3	100/0
90	43.2	83/17
75	41.9	57/43
60	28.1	44/56
50	23.9	34/66
40	0.0	
25	0.0	
10	0.0	
0	0.0	

[a] Calculations are based on % crystalline PCL as found from DSC results.

40 wt % PCL. The detection of a single T_g and a T_m indicates two phases of PCL exist, and, therefore, these blends are not completely miscible at a molecular level (i.e., some microphase heterogeneity is detected). The T_m values are relatively constant with only a slight decrease detected at the lower concentrations of PCL. This slight decrease may be due to the changes in lamellar thickness as discussed by Khambatta.[7] When the approach of Aubin and Prud'homme[8] was used, the percent crystalline PCL in the homopolymer and in the blends was calculated from the DSC results, shown in Table II. The amounts of crystalline PCL found in this study are slightly decreased compared to previous studies.[8,9] This decrease in crystalline PCL may be the result of using a higher molecular weight PVC (MW = 190 000) in this study, while the previous studies reported results for PCL/PVC blends with MW = 80 000[8] and MW = 78 000[9] PVC, respectively. Also included in this table are the calculated amorphous PCL/PVC concentrations for the blends. These calculated amorphous PCL/PVC compositions were made with the assumption that the PVC is interacting or blending with only the amorphous PCL. This assumption is supported by the observance of a single T_g for the blends containing crystalline PCL. These calculated amorphous PCL to PVC compositions will be used to interpret the IR and ESCA results.

Transmission FTIR Results. The transmission infrared spectra obtained for the homopolymers were equivalent to the spectra reported by Coleman and Zarian.[4] The PCL homopolymer spectrum contains characteristic peaks at 1722 and 1192 cm^{-1} corresponding to the C=O and C–C, C–O stretching, respectively. As demonstrated by Coleman and Zarian,[4] these peak positions are characteristic of semicrystalline PCL. The relative sensitivity of infrared analysis, specifically C=O and C–O stretching, to amorphous PCL must be much lower than the sensitivity to crystalline PCL. By DSC analysis, the semicrystalline PCL homopolymer contains 23.7 wt % amorphous PCL, Table II; however, the infrared spectrum contains a relatively sharp carbonyl band at 1722 cm^{-1} for the crystalline PCL and a slight shoulder at 1734 cm^{-1} as evidence of an amorphous PCL. The PVC homopolymer spectrum shows characteristic intense bands at 1258 and 610 cm^{-1} due to C–C and C–Cl stretching, respectively.

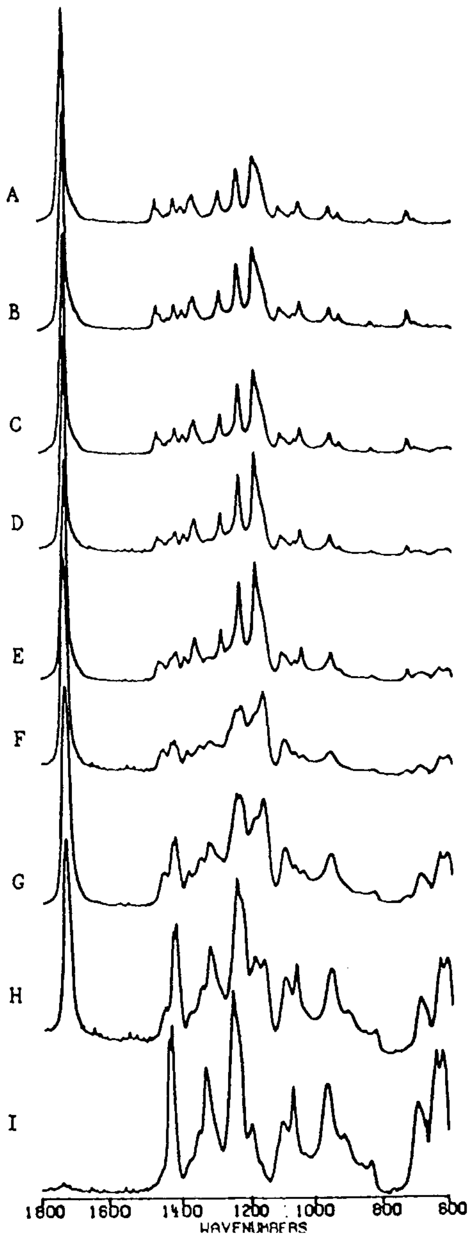

Figure 2. Transmission FTIR spectra for the entire composition range of PCL/PVC blends: (A) PCL homopolymer, (B) 90/10, (C) 75/25, (D) 60/40, (E) 50/50, (F) 40/60, (G) 25/75, (H) 10/90, (I) PVC homopolymer.

Transmission spectra of solution-cast films of the blends can be found in Figure 2. From this figure, one can see that the spectra for the blends with ≥50 wt % PCL are very similar to the semicrystalline PCL homopolymer, with detectable C–Cl stretching at ≈610 cm^{-1} up to the 75/25 PCL/PVC blend. The C=O and C–C, C–O peak positions for these blends are located at 1722 and 1190 cm^{-1}, which are equivalent to the positions obtained for semicrystalline PCL.[4] Additional evidence that supports the thesis that the sensitivity of infrared analysis is greater for crystalline

Table III
Calculated Sampling Depths of the ATR-FTIR Crystals

wavenumber, cm^{-1}	sampling depth, μm 45° Ge	sampling depth, μm 45° KRS-5	wavenumber, cm^{-1}	sampling depth, μm 45° Ge	sampling depth, μm 45° KRS-5
1730	1.15	3.86	1160	1.71	5.76
1200	1.66	5.56	610	3.26	10.95

PCL than for amorphous PCL can be detected in the transmission spectrum of the 50 wt % PCL blend. The DSC results, Table II, indicate this blend contains only 23.9% crystalline PCL, but the band positions in the infrared spectrum appear to be equivalent to the semicrystalline homopolymer infrared spectrum, which contains 76.3% crystalline PCL by DSC.

The blends with <50 wt % PCL appear to be completely amorphous with no detectable semicrystalline PCL. The carbonyl band of amorphous PCL is broader than the C=O band of crystalline PCL and is shifted to 1734 cm^{-1}. In addition, the C–C, C–O stretching band is also shifted to 1160 cm^{-1} for these blends. These changes in peak position are consistent with the results found by Coleman and Zarian[4] for amorphous PCL.

ATR-FTIR Results. Compositional profiles can be obtained at a greater sampling depth by using ATR-FTIR spectroscopy than ESCA. Harrick[10] and Mirabella[11] have shown that the sampling depth of an ATR-FTIR experiment is a function of the refractive indices of the sample and the internal reflective element or crystal, the wavelength of interest, and the incident angle of the infrared beam. The sampling depths calculated for 45° Ge and 45° KRS-5 crystals for the frequencies (cm^{-1}) of interest in this study may be found in Table III. When a 45° KRS-5 crystal is used for the ATR-FTIR experiment, the effective sampling depth is 3 times that of a 45° Ge crystal. Therefore, by comparing the ATR-FTIR spectra of a PCL/PVC blend acquired with these different crystals, one may gain information on domain size and compositional profiles.

The 45° Ge and 45° KRS-5 ATR-FTIR spectra obtained for the homopolymers were qualitatively similar to the transmission spectra. The only difference was a detectable increase in relative intensity of the C–Cl band. This increase is most likely a result of an increase in sampling depth, approximately 2.8 times deeper at 610 cm^{-1} than at 1730 cm^{-1}, of the ATR-FTIR experiment due to wavelength differences.[10,11] This variation in sampling depth is important when attempting quantitation with ATR-FTIR results. Therefore the discussion of the ATR-FTIR results of the PCL/PVC blends will be limited to a qualitative comparison of the two ATR-FTIR sampling depths.

The ATR-FTIR spectra obtained for the blends with <50 wt % PCL are essentially equivalent to the transmission spectra. An illustration of this is shown in Figure 3, in which the Ge ATR-FTIR, KRS-5 ATR-FTIR, and transmission spectra of a 40 wt % PCL blend are presented. From this figure, one can see that the peak positions and intensities of the ATR-FTIR spectra are similar to those of the transmission results accounting for the increased intensity of the C–Cl band due to sampling depth. The ATR-FTIR and transmission spectra for the blends with <50 wt % PCL suggest these blends are homogeneous over the sampling depths of the ATR-FTIR experiment.

The ATR-FTIR spectra obtained for the blends with ≥50 wt % PCL are also very similar to the transmission spectra obtained in this composition range. The transition from amorphous to semicrystalline PCL between 40 and 50 wt % PCL, indicated by the C=O and C–O band shift, can also be detected in the ATR-FTIR spectra. The Ge ATR-FTIR, KRS-5 ATR-FTIR, and transmission spectra

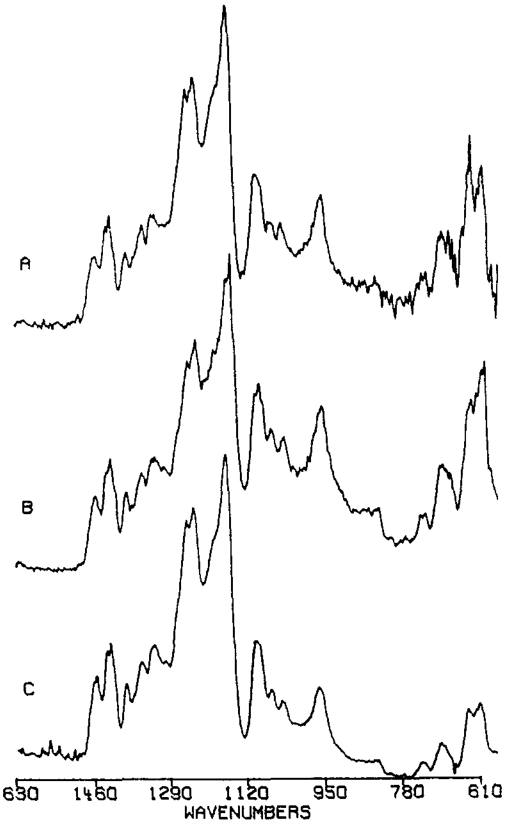

Figure 3. ATR-FTIR and transmission FTIR spectra for 40 wt % PCL blend: (A) 45° Ge ATR-FTIR, (B) 45° KRS-5, (C) transmission.

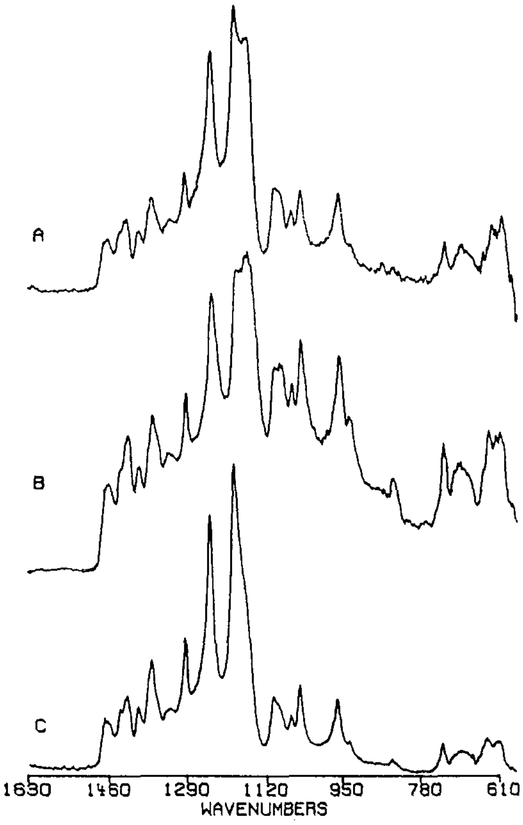

Figure 4. ATR-FTIR and transmission FTIR spectra for 50 wt % PCL blend: (A) 45° Ge ATR-FTIR, (B) 45° KRS-5, (C) transmission.

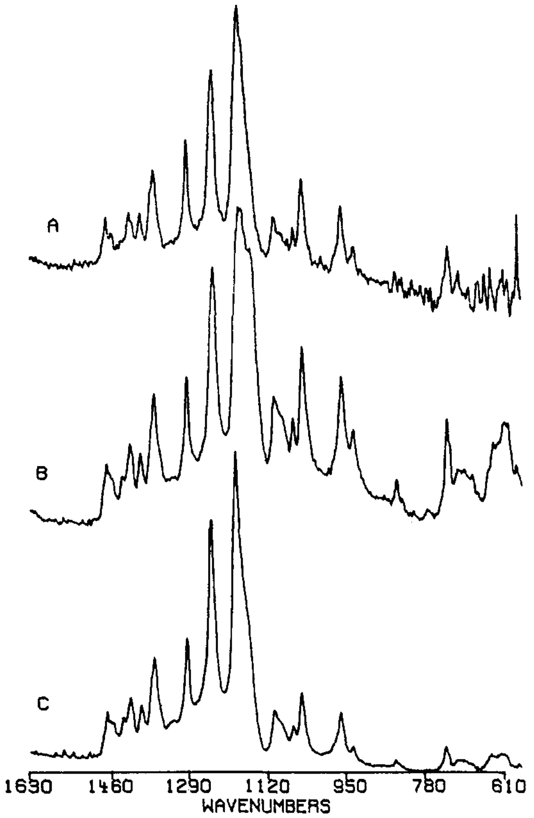

Figure 5. ATR-FTIR and transmission FTIR spectra for 60 wt % PCL blend: (A) 45° Ge ATR-FTIR, (B) 45° KRS-5, (C) transmission.

of the 50 % PCL blend may be found in Figure 4. For this blend the relative intensity of the amorphous peak at 1160 cm^{-1} was found to be increasing as one sampled deeper into the film with Ge ATR-FTIR and KRS-5 ATR-FTIR. This would suggest that the semicrystalline PCL is located within the first 1.7 μm of the film and that the relative amounts of semicrystalline to blended PCL decrease with greater sampling depth. However, the change might be very small because of the lack of sensitivity to the amorphous PCL.

The Ge ATR-FTIR, KRS-5 ATR-FTIR, and transmission spectra of the 60 wt % PCL blend may be found in Figure 5. In this figure, the 45° Ge spectra is equivalent to the transmission spectra except for the absence of the C–Cl band in the Ge ATR-FTIR spectrum. The relative intensity of the amorphous PCL band at 1160 cm^{-1} is increased, and there is a detectable C–Cl band at 610 cm^{-1} in the KRS-5 ATR-FTIR spectrum. These observations would indicate that the semicrystalline PCL domains may again be found in the top 1.7 μm of the film and that the concentration of the amorphous or blended PCL may be higher in the bulk of the film.

The only major difference between the ATR-FTIR results and the ESCA results is the 90/10 blend. As discussed below the ESCA results show a surface enrichment of blended PVC, yet both the Ge and KRS-5 ATR-FTIR spectra fail to show this enrichment. This may be explained by the fact that the PCL contribution to the spectrum is much greater than the PVC, thereby masking the weaker C–Cl band at 610 cm^{-1} from being detected.

ESCA Results. Initial ESCA analysis of the homopolymers serve to (i) ensure sample purity, (ii) determine the C/O and C/Cl peak area ratios of the pure materials, for calibration of atomic ratio quantitation, (iii) determine the binding energies of the various functional groups present in the carbon 1s spectra, and (iv) ensure that the functional group distribution, found by curve-fitting the carbon 1s high-resolution spectra, agrees with the theoretical distribution. The ESCA spectra of the homopolymers show that only peaks due to the elements expected are present, ensuring sample purity, to the level of ESCA detectability (≈1 atomic %). These peaks include the carbon 1s (285 eV) and oxygen 1s (532 eV) for PCL, while the PVC spectra contains carbon 1s (285 eV), chlorine 2p (200 eV), and chlorine 2s (270 eV). Angle-dependent results of the homopolymers show that the homopolymers are homogeneous over the topmost 80 Å.

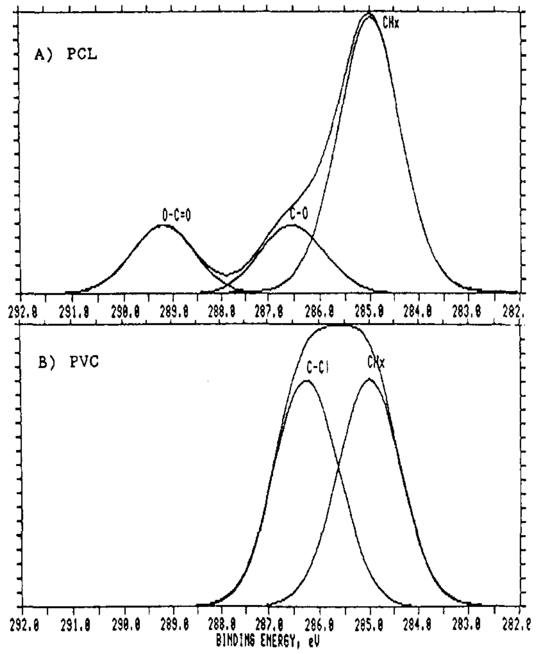

Figure 6. Curve-fitted high-resolution carbon 1s spectra of (A) poly(ϵ-caprolactone) and (B) poly(vinyl chloride).

The high-resolution carbon 1s spectra of the homopolymers that were curve-resolved into the various components are shown in Figure 6. From these results, the binding energies of the carbons associated with the various functional groups were assigned to 285.0 eV (CH_x), 286.3 ± 0.1 eV (C–Cl), 286.5 ± 0.1 eV (C–O), and 289.2 ± 0.2 eV (C—C=O), comparable to literature values. These results also show the functional group distributions of the homopolymers are equivalent to the expected values of 1:1:4 (O—C=O:C–O:CH_x) for PCL and 1:1 (C–Cl:CH_x) for PVC. The overall experimental error found for determining the relative functional group distribution from curve fitting was ±7%, relative standard deviation.

PCL/PVC blends, from three separate casts, were analyzed using takeoff angles of 15, 45, and 90°. The sampling depths estimated from an empirical approach[22] for these angles, for the carbon 1s photoelectron, are 21, 57, and 80 Å, respectively. A plot of the surface composition, calculated from the C/O peak area ratios, versus the bulk composition can be found in Figure 7. It should be noted that the surface compositions were also calculated using the C/Cl peak area ratios, and the results are equivalent to the C/O calculations, within experimental error of ±10%.

The surface composition versus bulk composition was also calculated using the C–Cl (from PVC) and the O—C=O (from PCL) relative peak areas obtained from the curve-fitted carbon 1s envelope. A plot of the surface composition measured from curve fitting versus the bulk composition may be found in Figure 8. For simplicity, the results of the three takeoff angles were averaged, and only the average is plotted, because within error limits of

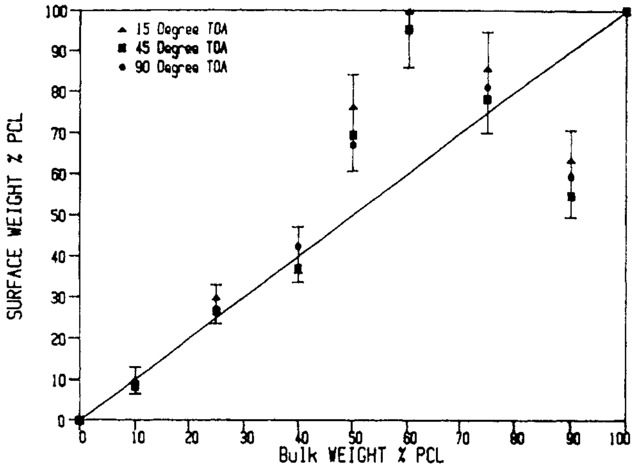

Figure 7. Plot of angle-dependent ESCA results of surface composition vs bulk composition. The surface compositions were calculated from the C/O peak area ratios.

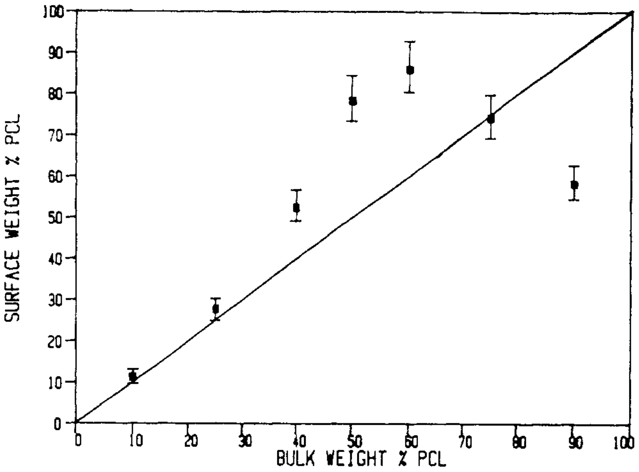

Figure 8. Plot of surface composition vs bulk composition of PCL/PVC blends. Calculated from the curve-fitted carbon 1s spectra.

±12% relative standard deviation, concentrations at all three angles were equivalent. A comparison of the curve-fit results with those obtained from the C/O and C/Cl peak area ratios reveals that both methods of quantitation give the same result, within error limits of ±10%. This comparison further strengthens confidence in the accuracy of curve fitting as a means of quantitation in an ESCA experiment.[21]

If the surface composition of each of the blends was equivalent to the bulk composition, then the experimental results would fall on the solid line in Figures 7 and 8. For blends with <50 wt % PCL, this is the case. Angle-dependent ESCA analysis indicated that the blends, in this composition range, are homogeneous over the sampling depths of the ESCA experiment, 21–80 Å. In addition, no surface enrichment of the PCL at the polymer/air interface is detected, even with the most surface-sensitive sampling depth. This result indicates the thermodynamics of mixing in this blend system can overcome the surface energy differences of the homopolymers, producing a polymer/air interface that is homogeneously mixed. These results agree with the optical clarity, DSC, and IR results showing the blends, in this composition range, miscible in the bulk.

The second region of interest, in Figures 7 and 8, is the bulk composition range of 50 ≤ wt % PCL < 90. In this concentration range, there is a surface excess of the PCL detected at the polymer/air interface. Also, angle-dependent ESCA results consistently show an increase of 5–10 wt % PCL concentration in the top 21 Å relative to the PCL concentration calculated over the first 57–80 Å. Earlier studies[4,8,9] have shown that the PCL becomes semicrystalline in blend concentratioins of ≥50 wt % PCL.

In the system under study, evaluation of the solid surface tension of semicrystalline PCL and PVC homopolymers, by contact-angle technique, yielded values of 42.9[23] and 44.0 dyn/cm,[23,24] respectively. Although the solid surface tension is not an exact measure of the surface free energy, comparison of the two values can provide an empirical measure of the surface energetics. Even if polymer blends are completely miscible in the bulk, a difference in surface free energies of 0.1 dyn/cm can lead to an enrichment of the lower surface energy component at the polymer/air interface.[25] Because of the difference in solid surface tensions for these homopolymers, it is not surprising that PCL dominates the surface of the blends in this concentration range.

From the ESCA results, it is not clear why 50 wt % is a critical concentration for excess PCL, except that crystalline PCL is detected at this concentration by IR and DSC. The preference of the semicrystalline PCL, with its amorphous component, for the surface region of the blend can be seen by comparing the ESCA results to Table II. From Table II, the 50 and 60 wt % PCL blends contain only 23.9% and 28.1% crystalline PCL, respectively, while the ESCA results indicate an increase of PCL at the polymer/air interface of ≈15 wt % for the 50 wt % PCL blend and ≈40 wt % for the 60 wt % blend. This observation would support the ATR-FTIR results that the near surface region of these blends contains a higher concentration of semicrystalline PCL.

An exception to this data is the surface composition of the 90 wt % PCL blend. ESCA analysis of this blend shows the surface composition of this blend was 65/35 PCL/PVC. In comparison to the amorphous PCL/PVC concentration of 83/17, calculated from DSC results, the surface composition of this blend contains a higher concentration of the blended phase than does the bulk.

Discussion and Conclusions

In this work we used quantitative angle-dependent ESCA coupled with infrared spectroscopy and DSC measurements to investigate the compatibility of PCL and high molecular weight PVC. It was found that blends of PCL and high molecular weight PVC are miscible (in the bulk and surface region) between the 10 and 40 wt % PCL range. This conclusion is based on (i) these blends producing an optically clear film, (ii) the observance of a single T_g and no T_m, (iii) the infrared spectra showing peak shifts and the presence of amorphous PCL, (iv) the ATR-FTIR and transmission infrared spectra showing the blends are homogeneous, and (v) the ESCA results showing that the blend surface composition is equivalent to the bulk composition. These results taken together indicate miscibility is on a molecular scale, with domain sizes no greater that tens of angstroms. In addition, it may be concluded that the thermodynamics of mixing overcome surface energetic driving forces for surface excess in this composition range.

The blends fabricated with ≥50 wt % PCL were found to be immiscible. These blends were opaque. The observance of a crystalline melting temperature at 54 °C in the DSC measurements for blends in this range indicate the presence of crystalline PCL. Although a single glass transition temperature is observed for these blends, one must conclude that there are at least two different phases of PCL present, and they are not completely miscible. The transmission IR spectra for the blends in this composition range show the PCL is present only in a semicrystalline form; however, the sensitivity of the IR to amorphous PCL in comparison to the crystalline PCL is greatly reduced. Ge and KRS-5 ATR-FTIR spectra of the 50 and 60 wt % PCL blends indicate that the semicrystalline PCL is located in the surface region of the blend, and the relative concentration of the amorphous or blended PCL to semicrystalline PCL increases with greater sampling depths. The surface composition for the blends with semicrystalline PCL present shows a surface excess of one of the polymers. PCL dominates the surface composition for blends with $50 \leq$ wt % PCL ≤ 90 concentrations. This result is consistent with simple surface energetic considerations of semicrystalline PCL and PVC. ESCA analysis of the 90 wt % PCL blend indicates the surface composition contains an enrichment of blended amorphous PCL/PVC when compared to the bulk DSC results.

An overall view of the data shows that blends of PCL and this particular molecular weight PVC are miscible in the <50 wt % PCL range. Above this concentration of PCL the blends were found to contain a miscible PCL/PVC phase and immiscible crystalline PCL phase. In addition, it was shown that calculating the surface composition from the ESCA peak area ratios and curve-fitting the carbon 1s spectra are complementary methods in calculating the surface composition of a polymer blend. Blends of PCL/PVC, with <50 wt % PCL, are homogeneous over the first 80 Å as shown by ESCA. From the ESCA results, if microdomains exist, the domain sizes are larger than 100 Å in diameter. ATR-FTIR results were found to be equivalent to the bulk transmission spectra for blends with <50 wt % PCL. There was a detectable relative increase in the amorphous PCL band, at 1160 cm^{-1}, in the 50 and 60 wt % PCL blends in the KRS-5 ATR-FTIR spectra compared to the Ge ATR-FTIR spectra. Finally, it was shown that surface analytical techniques may be used to evaluate the effects of crystallinity on the surface composition and miscibility of polymers in a blend system.

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Registry No. PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4; PVC, 9002-86-2.

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