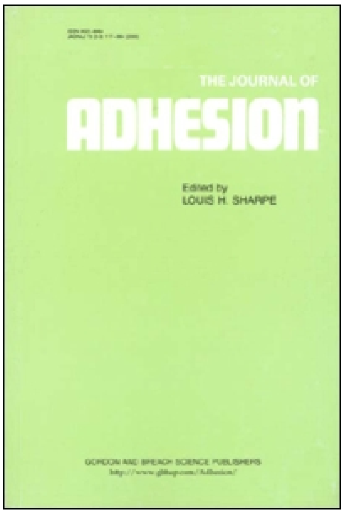

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Yoshihisa Kano[a]; Saburo Akiyama[a]; Shigehiko Kobayashi[b]
[a] Department of Applied Chemistry, Faculty of Engineering, Tokyo University of Agriculture and Technology, Tokyo, Japan [b] Analytical Instruments Division, Nippon Bio-Rad Laboratories, Osaka, Japan

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Study of Interface Segregation Behavior in Acrylate Copolymer/Fluoro-copolymer Blends using FT-IR Phase-modulated Photoacoustic Spectroscopy

YOSHIHISA KANO and SABURO AKIYAMA

Department of Applied Chemistry, Faculty of Engineering, Tokyo University of Agriculture and Technology, 2-24-16, Nakacho, Koganei-shi, Tokyo 184, Japan

SHIGEHIKO KOBAYASHI

Analytical Instruments Division, Nippon Bio-Rad Laboratories, 1-14-11, Shinkitano, Yodogawa-ku Osaka 532, Japan

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The interface segregation was investigated for poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) (P(2EHA-AA-VAc))/poly(vinylidene fluoride-co-hexafluoro acetone (P(VDF-HFA)) blends coated on poly(dimethyl siloxane) (PDMS) by FT-IR phase-modulated photoacoustic spectroscopy (PAS-FTIR). The P(2EHA-AA-VAc) component segregated at the PDMS-polymer interface and its concentration exponentially changed from the interface in the depth direction. The observed PAS-FTIR spectra for respective phase angles corresponded to the magnitude PAS-FTIR spectra for arbitrary phase angles which were calculated with the PAS-FTIR spectra at two phase angles.

KEY WORDS: Acrylate copolymer; fluoro-copolymer; blends; interface segregation; PAS-FTIR; phase angle; depth profile; magnitude spectrum.

1. INTRODUCTION

Recently, investigations of surface segregation, or interface segregation, in polymer blends have been focused on development of various surface analyses. For example, X-ray photoelectron spectroscopy (XPS)[1], secondary ion mass spectrometry (SIMS)[2] and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)[3] are very effective methods to investigate surface segregation structure. Surface segregation and interface segregation behavior is affected by miscibility, difference of surface tension between components and environment conditions. In particular, interface segregation is very important to adhesion because adhesives are applied to various adherends. Tachikake *et al.*[4] studied interface segregation between hot-melt adhesives and four adherends: polypropylene, surface-modified polypropylene, polyethylene terephthalate and aluminium by use of XPS and contact angle measurements. They concluded that interface segregation is influenced by surface tension and compatibility between ethylene-vinyl acetate copolymer and wax which comprise some hot-melt adhesives. We[5] found that poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) (P(2EHA-AA-VAc))/poly(vinylidene fluoride-co-hexafluoro acetone (P(VDF-HFA)) blends showed a surface segregation or functional gradient structure since the P(VDF-HFA) component enriched the surface and the P(2EHA-AA-VAc) component precipitated at the bottom. In these blends, tackiness of the top surface is unexpectedly smaller than that of the bottom. Thus, we pointed out that the P(2EHA-AA-VAc)/P(VDF-HFA) blends could be used as a new type of pressure sensitive adhesive (PSA) tape, without a backing film.[6] It was also concluded that surface segregation behavior or functional gradient structure found in these blends is formed by differences in surface tension, γ, between copolymers and by immiscibility. In our previous study,[7] we constructed the depth profiles from surface to bottom in the P(2EHA-AA-VAc)/P(VDF-HFA) blends using XPS, ATR-FTIR and step-scan FTIR photoacoustic (PAS-FTIR)[8] analyses. From the results, the depth profile of the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend did not show a simple gradient structure but a sharp gradient on the surface and bottom and a plateau in the middle region.

Incidentally, it is well known that step-scan FTIR provides depth profile information due to single modulation frequency which can be applied over all spectral ranges.[9] The measuring depth increases with increasing phase angle. The detailed depth profiles can be also constructed by PAS-FTIR measurements at various modulation frequencies. Dittmar *et al.*[8] reported that the magnitude PAS-FTIR spectra, $S_{\theta}^{\mathrm{calc}}$ for arbitrary phase angles were obtained by the PAS-FTIR spectrum at one phase angle and thePAS-FTIR spectrum at a 90° phase angle from it. Sowa and Mantsch[10] proposed the program calculation to obtain magnitude PAS-FTIR spectra for arbitrary phase angles.

In our previous paper,[7] the depth profiles in these blends were constructed using PAS-FTIR spectra at only two phases (in-phase and quadrature) and ATR-FTIR spectra. Therefore, further research was necessary to get more accurate depth profiles and to confirm a sharp gradient on surfaces and a plateau in the middle region. In this study, to obtain the detailed depth profile of the P(2EHA-AA-VAc)/P(VDF-HFA) blend films, PAS-FTIR spectra at various phase angles were obtained for the bottom (blends/PDMS interface). We also investigated whether the observed PAS-FTIR spectra for respective phase angles corresponded to the magnitude PAS-FTIR spectra for arbitrary phase angles obtained by program calculation.

2. EXPERIMENTAL

The P(2EHA-AA-VAc) was synthesized by a solution polymerization at 70°C for 7 h, using benzoyl peroxide as an initiator and mixtures of ethyl acetate (95 wt%) with toluene (5 wt%) as a solvent. The P(VDF-HFA) was supplied by Central Glass Co., Ltd. (Japan). Molecular weights of copolymers were determined using a TOSO Co., Ltd. CP8000 GPC system in 0.1 (wt%), THF solution. The compositions and molecular weights of copolymers used in this study are shown in Table I. The residual THF in blend films could not be observed by use of the gas detector.

TABLE I
Components and molecular weights[a] of copolymers

P(2EHA-AA-VAc)	2-Ethylhexyl acrylate/acrylic acid/vinyl acetate = 85/5/10 (mol%) $M_n = 46000$, $M_w = 315000$
P(VDF-HFA)	Vinylidene fluoride/hexafluoro acetone = 91.6/8.4 (mol%) $M_n = 78000$, $M_w = 200000$

[a] Molecular weight equivalent to that of polystyrene by GPC.

The blend films used in PAS-FTIR measurements were prepared by a knife coating system at 90°C for 60 s, in which 20 wt% THF solutions were coated onto the release liner [poly(dimethyl siloxane) (PDMS) having a critical surface tension of wetting, $\gamma_c \sim 24$ dyn/cm, is coated onto the liner]. The films were seasoned at 23 ± 3°C and 65 ± 5% RH for 7days to produce a dry coating film 30 μm in thickness. The PAS-FTIR spectra for blend films were determined at the bottom (blend/PDMS interface). In general, polyacrylate adhesives such as P(2EHA-AA-VAc) are very tacky and very flexible. If the P(2EHA-AA-VAc) component segregates at the bottom, the interface between the blend films and common adherends, such as glass plate, stainless steel and plastic films, cannot be separated. The PAS-FTIR spectra on the bottom of the blends should be measured on the bottom in contact with an adherend possessing lower release strength. Therefore, PDMS, having lower release strength, is used as an adherend.

The PAS-FTIR spectra of blends were obtained by a Bio-Rad Laboratories step-scan FTIR spectrometer, type FTS60A/896, at 400 Hz modulation frequency. The PAS cell was an MTEC Co. Ltd. type 200 photoacoustic detector, and regeneration of modulation signals was performed with a Bio-Rad Laboratories Demodulator.[7] A carbon black film was used as the reference material for all spectra. The scanning of the interferogram was performed by the double-sided procedure. The interferograms were obtained at 9° intervals of phase angle. The observed PAS-FTIR spectrum S_θ^{obs} was calculated by the complex Fourier transform of the interferograms.

3. RESULTS AND DISCUSSION

Firstly, the program calculation of the magnitude PAS-FTIR spectra, S_θ^{calc}, for arbitrary phase angles will be explained. In phase-modulated PAS-FTIR measurements, the interferogram for an arbitrary phase angle, I_θ, is calculated from the interferogram at one phase angle, I_0, and the interferogram at 90° phase angle from it, I_{90}, according to the following equation.

$$I_\theta = I_0 \cos\theta + I_{90} \sin\theta \tag{1}$$

The respective interferograms can be obtained simultaneously by use of a two-phase lock-in amplifier.[10] The phase angle, θ, is calculated in the range from $-\pi$ to π radians as the arctangent of the ratio of the real part, Re_θ, and imaginary part, Im_θ, of the complex Fourier transform of the full double-sided interferograms, I_0, and I_{90}:

$$\theta = \arctan(Im_\theta / Re_\theta) \tag{2}$$

Thus, the magnitude PAS-FTIR spectrum, S_θ^{calc}, is calculated from the real and imaginary components of the complex Fourier transform of the full double-sided interferograms according to the following equation:

$$S_\theta^{\text{calc}} = [(Re_\theta)^2 + (Im_\theta)^2]^{1/2} \tag{3}$$

In this study, the calculation of S_θ^{calc} was programmed with the measured double-sided interferograms, I_0 and I_{90}.

The observed PAS-FTIR spectra, S_θ^{obs}, of the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend at various phase angles are shown in Figure 1. As shown in this figure, the stretching vibration peaks of C=O absorption and C-F absorption[11] are observed at 1730 cm^{-1} and 870 cm^{-1}, respectively. These peaks are based on the respective

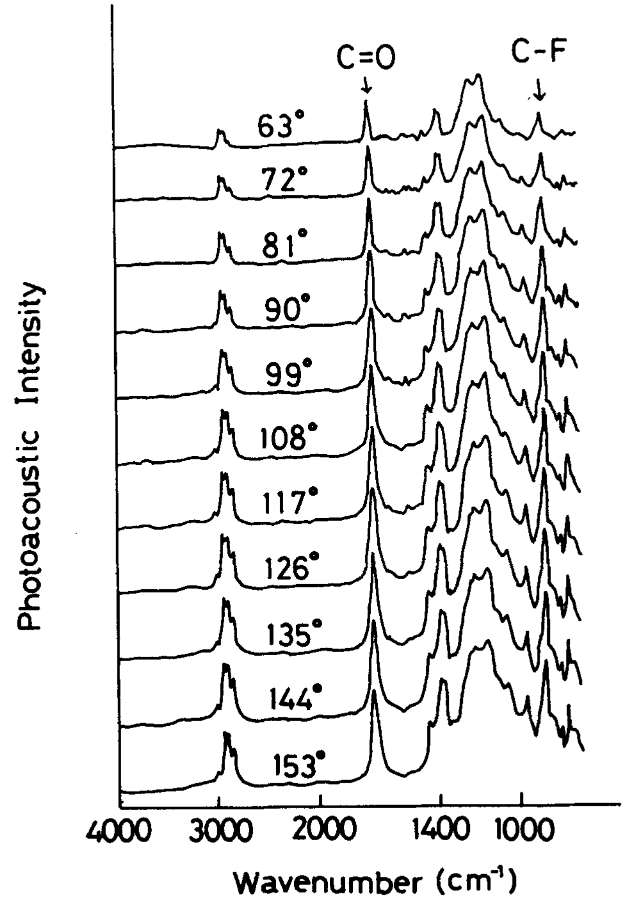

FIGURE 1 PAS-FTIR spectra S_θ^{obs} for P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend.

copolymers. By an absorbance ratio (I_{870}/I_{1730}) of C=O absorption at 1730 cm^{-1} (I_{1730}) for P(2EHA-AA-VAc) and C-F absorption at 870 cm^{-1} (I_{870}) for P(VDF-HFA), the change of the concentration distribution of P(2EHA-AA-VAc) and P(VDF-HFA) can be evaluated for all phase angles (thus, as a function of depth). Since the I_{870}/I_{1730} value increases with increasing phase angle, P(2EHA-AA-VAc) concentration diminishes as a function of depth. Its component must be segregated at the bottom (laminated, blend film/PDMS interface).

On the contrary, the magnitude PAS-FTIR spectra of S_θ^{calc} of the 50/50 blend calculated with equations[1-4] are shown in Figure 2. The delineation of S_θ^{calc} spectra is similar to that of S_θ^{obs} spectra for the intensities of C=O absorption at 1730 cm^{-1}, C-F absorption at 870 cm^{-1}, C-H absorption at 3000 ~ 2800 cm^{-1}, and broad absorption around 1300 ~ 1100 cm^{-1}. It is expected that the S_θ^{obs} spectra for respective phase angles correspond to the S_θ^{calc} spectra of arbitrary phase angles obtained by program calculation for the 50/50 blend.

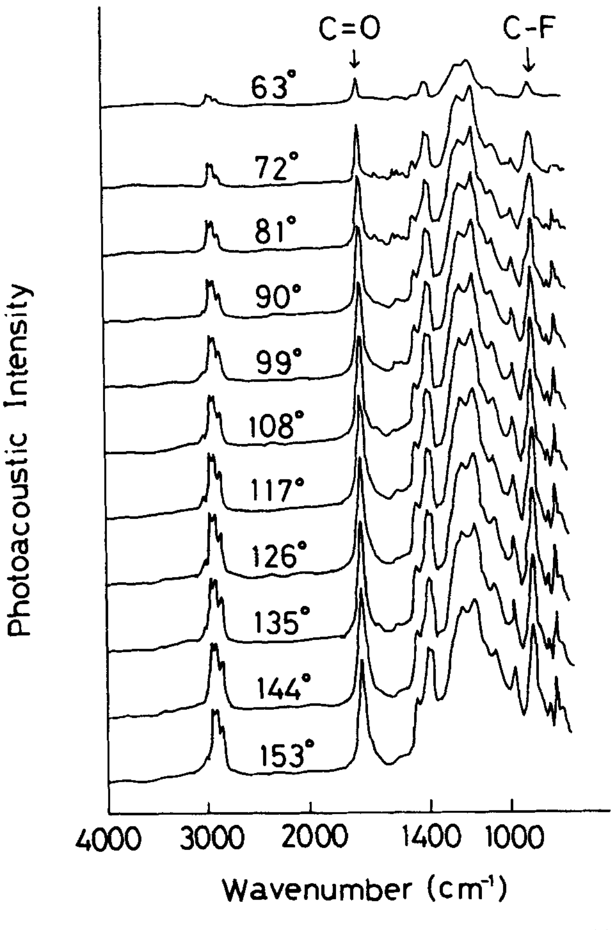

FIGURE 2 PAS-FTIR spectra S_θ^{calc} for P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend. S_θ^{calc} $(I_0 = 153°$, $I_{90} = 63°)$.

The delineation of the S_θ^{obs} spectra and S_θ^{calc} spectra for the 30/70 blend is also very similar. Since the I_{870}/I_{1730} value increases with increasing phase angle, P(2EHA-AA-VAc) concentration also diminishes as a function of depth. This implies that both of these blends form an interface segregation, or gradient structure.

Figure 3 shows the phase angle dependence of the absorbance ratio I_{870}/I_{1730} for the 50/50 blend. In this figure, the obtained I_{870}/I_{1730} values were calculated from two magnitude spectra S_θ^{calc} ($I_0 = 162°$, $I_{90} = 72°$) and S_θ^{calc} ($I_0 = 171°$, $I_{90} = 81°$). The relationship between I_{870}/I_{1730} values and phase angles obtained from S_θ^{obs} spectra and two S_θ^{calc} spectra is similar for delineation, approximately. Therefore, we think that the S_θ^{obs} spectra for the respective phase angles can be expressed with two S_θ^{calc} spectra for arbitrary phase angles obtained by program calculation. The in-phase and quadrature PAS-FTIR spectra measured in the previous study[7] were obtained at 171° and 81° phase angles, respectively. The I_{870}/I_{1730} ratio increases with phase angle exponentially and a constant of I_{870}/I_{1730} value (approximately 0.9) is observed above a phase angle of 100°.

The depth from the inphase spectrum in PAS-FTIR is evaluated as the thermal diffusion length, μ. The μ is defined by the following equation:[8]

$$\mu = [\kappa/(\rho \cdot C_p \cdot \pi \cdot f)]^{0.5} \tag{4}$$

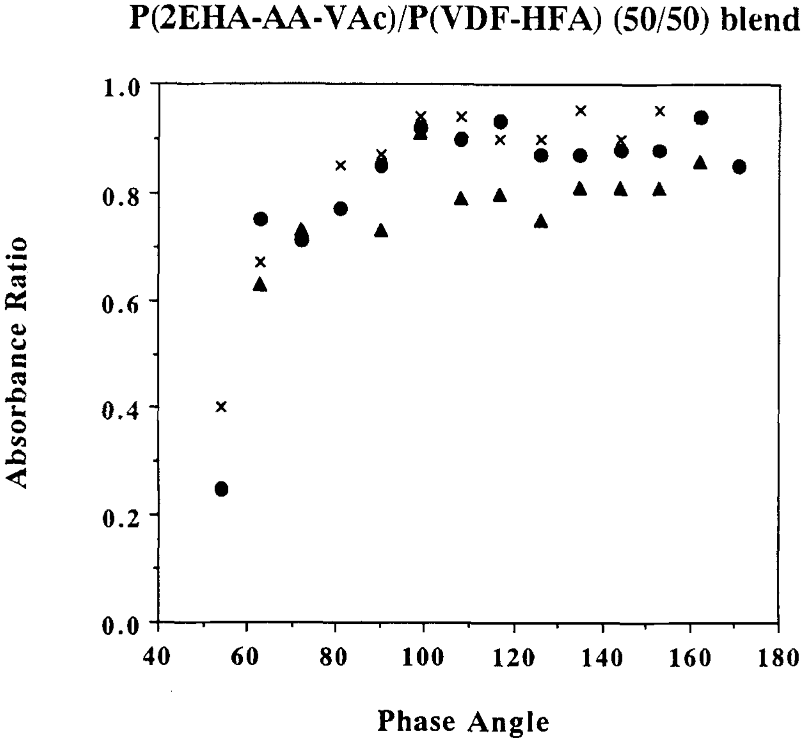

FIGURE 3 Relationship between absorbance ratio, I_{870}/I_{1730}, and phase angle for P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend. ●: S_θ^{obs}, ×: $S_\theta^{calc}(I_0 = 162°, I_{90} = 72°)$, ▲: $S_\theta^{calc}(I_0 = 171°, I_{90} = 81°)$.

where κ is the thermal conductivity, ρ the density, C_p the heat capacity, π the circular constant and f the modulation frequency. The value of μ from the in-phase spectrum was 8 μm (calculated parameter: κ and C_p are the reference values,[8] ρ is the measured value[12] and f is 400 Hz) in our previous study.[7] On the other hand, μ from the quadrature spectrum was about 6 μm on which the curve of depth profiling of the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend fitted. As expressed in Eq. 4, μ depends on the modulation frequency, f. Therefore, it is well known that μ from the quadrature spectrum at 400 Hz corresponds to μ from the in-phase spectrum at >400 Hz. It is suggested that the I_{870}/I_{1730} values are invariant over the depth region from 6 to 8 μm. In other words, the interface segregation between the 50/50 blend and PDMS is affected until this region because the I_{870}/I_{1730} value increases. The relationships between the I_{870}/I_{1730} and phase angle for 30/70 and 55/45 blends are shown in Figures 4 and 5, respectively. In ATR-FTIR measurements in the previous study,[13] since the interface segregation behavior for the surface (blend/air interface) and bottom (blend/PDMS interface) was observed to be above 45 (wt%) P(VDF-HFA) content, a 55/45 blend was investigated by PAS-FTIR analysis. The relationship between I_{870}/I_{1730} values and phase angles obtained from S_θ^{obs} spectra is again similar to that from S_θ^{calc} spectra. In addition, the curves of I_{870}/I_{1730} vs. phase angle for 30/70 and

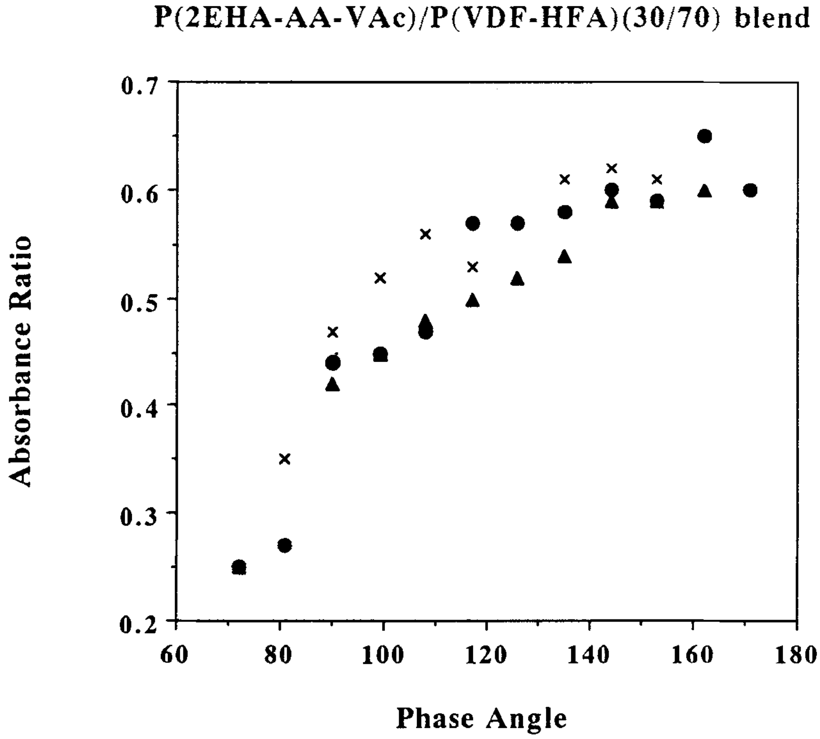

FIGURE 4 Relationship between absorbance ratio, I_{870}/I_{1730}, and phase angle for P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend. ●: S_θ^{obs}, ×: S_θ^{calc} ($I_0 = 162°$, $I_{90} = 72°$), ▲: S_θ^{calc} ($I_0 = 171°$, $I_{90} = 81°$).

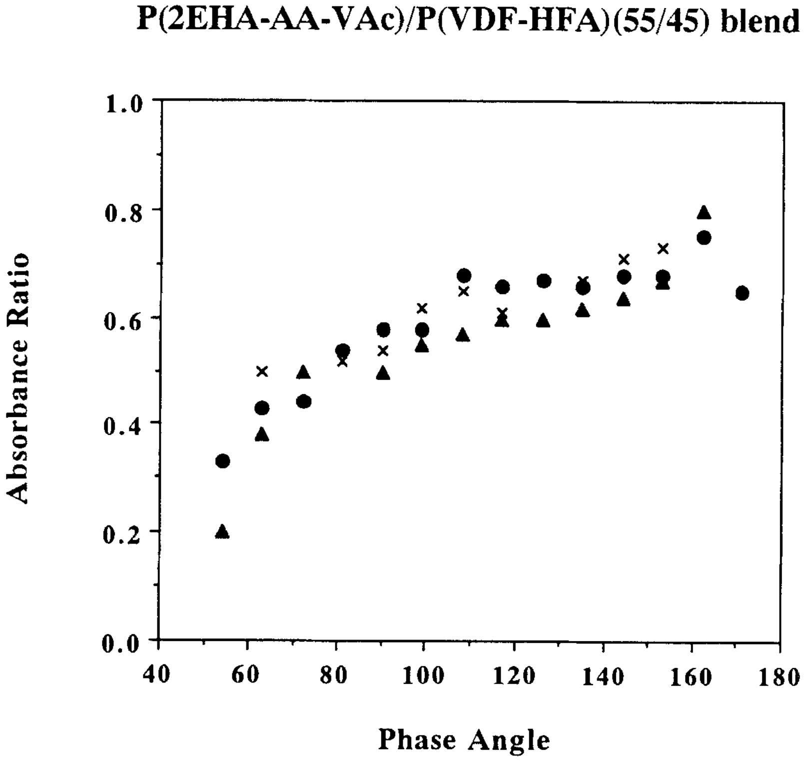

FIGURE 5 Relationship between absorbance ratio, I_{870}/I_{1730}, and phase angle for P(2EHA-AA-VAc)/P(VDF-HFA)(55/45) blend. ●: S_θ^{obs}, ×: S_θ^{calc} ($I_0 = 162°$, $I_{90} = 72°$), ▲: S_θ^{calc} ($I_0 = 171°$, $I_{90} = 81°$).

55/45 blends are divided into two regions, *i.e.*, the exponential increase and the constant of I_{870}/I_{1730} regions at 100° phase angle. These relationships support the results of depth profiles in the previous paper.[7] As the interface segregation for these blends was also confirmed by PAS-FTIR analysis, more detailed depth profiles of the concentration of component against phase angle (depth) should be examined.

The relationship between $\log(I_{870}/I_{1730})$ and P(VDF-HFA) weight fraction, ϕ_1, for P(2EHA-AA-VAc)/P(VDF-HFA) blends obtained by KBr disk was, according to the Lambert-Beer law, as follows:[7]

$$\log(I_{870}/I_{1730}) = 0.0275(\phi_1) - 2.08 \qquad (5)$$

Thus, we can calculate the integrated surface excess as the P(2EHA-AA-VAc) weight fraction, $\phi_2 = (1 - \phi_1)$, obtained by PAS-FTIR analysis using Eq. (5). The ϕ_2 *vs.* phase angle plot for the P(2EHA-AA-VAc)/P(VDF-HFA) 50/50 blend is shown in Figure 6. The ϕ_2 exponentially decreases with increasing phase angle and then exhibits constant ϕ_2 at a phase angle of approximately 100° for the 50/50 blend. As shown in Figures 7 and 8, the delineations of the ϕ_2 *vs.* phase angle plotts for P(2EHA-AA-VAc)/P(VDF-HFA) 30/70 and 55/45 blends are similar to that for the 50/50 blend. It is suggested that the P(2EHA-AA-VAc) component preferentially enriched at the bottom (blend/PDMS

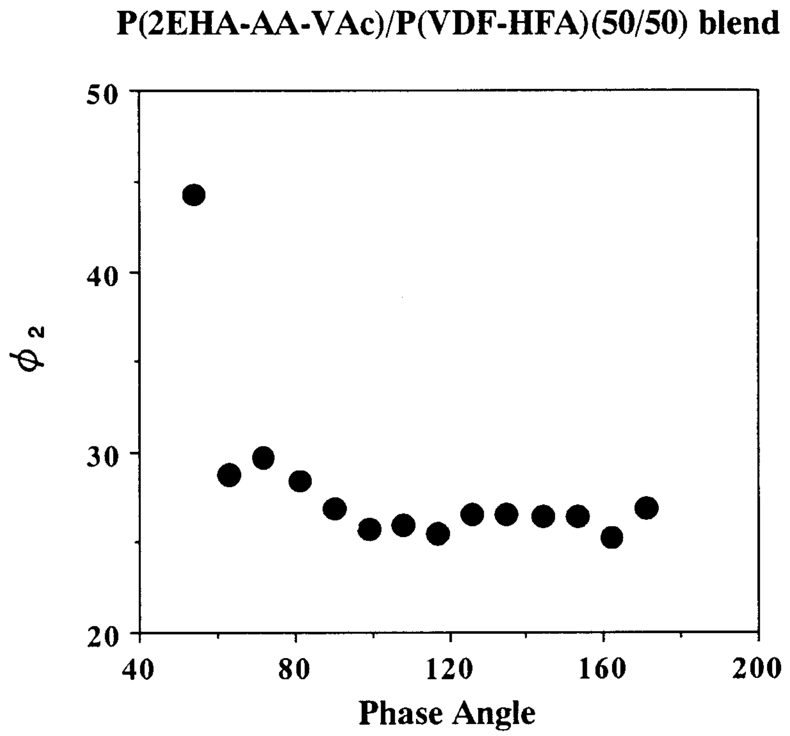

FIGURE 6 Phase angle dependence of interfacial excess of P(2EHA-AA-VAc) component, ϕ_2, for P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend.

interface). Therefore, since the ϕ_2 exponentially decreases with increasing phase angle and exhibits constant ϕ_2 at approximately 100° phase angle, we judge that the depth profiles of 50/50, 30/70 and 55/45 blends show a sharp gradient on the surface and bottom and a plateau in the middle position. In this study, the absorptivity of two peaks (870 and 1730 cm^{-1}) for the blends could not be evaluated. The absorptivity is very important for the construction of more precise depth profiles. We should evaluate these absorptivities in a future study.

The surface enrichment of the low surface tension component is caused by the difference in surface tension between the components of the blends. For example, the surface enrichment of poly(styrene)/poly(ethylene oxide) blends[14] and poly(styrene)/poly(vinylmethylether) blends[15] is well known as an example of preferential surface enrichment by a low surface tension component. In the P(2EHA-AA-VAc)/P(VDF-HFA) blends, the surface enrichment of the P(VDF-HFA) component, possessing low surface tension compared with P(2EHA-AA-VAc), was observed by XPS, ATR-FTIR and PAS-FTIR analyses.[7] However, it was confirmed that the P(2EHA-AA-VAc) component was enriched at the bottom by the results of XPS, ATR-FTIR and PAS-FTIR.

We should explain why the P(2EHA-AA-VAc) component (high surface tension) was enriched at the interface of the blends with PDMS. Takahara *et al.*[16] reported that

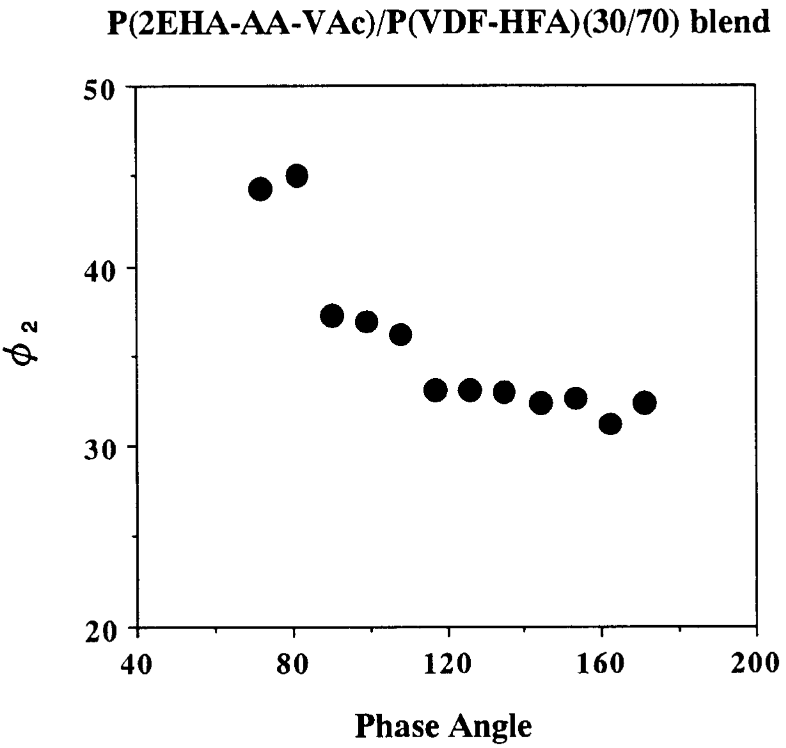

FIGURE 7 Phase angle dependence of interfacial excess of P(2EHA-AA-VAc) component, ϕ_2, for P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend.

poly(styrene)/poly(ethylene oxide) blends exhibited enrichment by the poly(ethylene oxide) component (with higher surface tension) at the surface, in a hydrated state, by XPS analysis. Their data indicate a result opposite to the report by Thomas and O'Malley.[14] This discrepancy is attributed to the interfacial environment (sample/air interface or sample/water interface). That is to say, the rearrangement of the hydrated component for the blends took place in the hydrated state. Lewis *et al.*[17] observed rearrangement behavior for hydroxyethyl methacrylate grafted onto a silicone elastomer in the hydrated state. Nakamae *et al.*[18] and Kasemura *et al.*[19] have also observed rearrangement behavior in polymer alloys using the contact angle technique. The rearrangement is caused by compatibility between the sample and the interfacial environment. It is expected that the interfacial segregation of the P(2EHA-AA-VAc) component at the bottom is caused by the rearrangement. This occurs because the compatibility of PDMS with acrylate polymer is superior to that of PDMS to fluoride polymer. Since P(2EHA-AA-VAc)/P(VDF-HFA) blends exhibited a complex segregation structure (a sharp gradient on the surface and bottom and a plateau in the middle position), we presume that the characteristic depth profiles for these blends were formed by the balance of several factors, such as surface tension, miscibility, density (the density of P(VDF-HFA) is higher than that of P(2EHA-AA-VAc)), molecular weight (and its distribution) and environment conditions (polarity, compatibility).

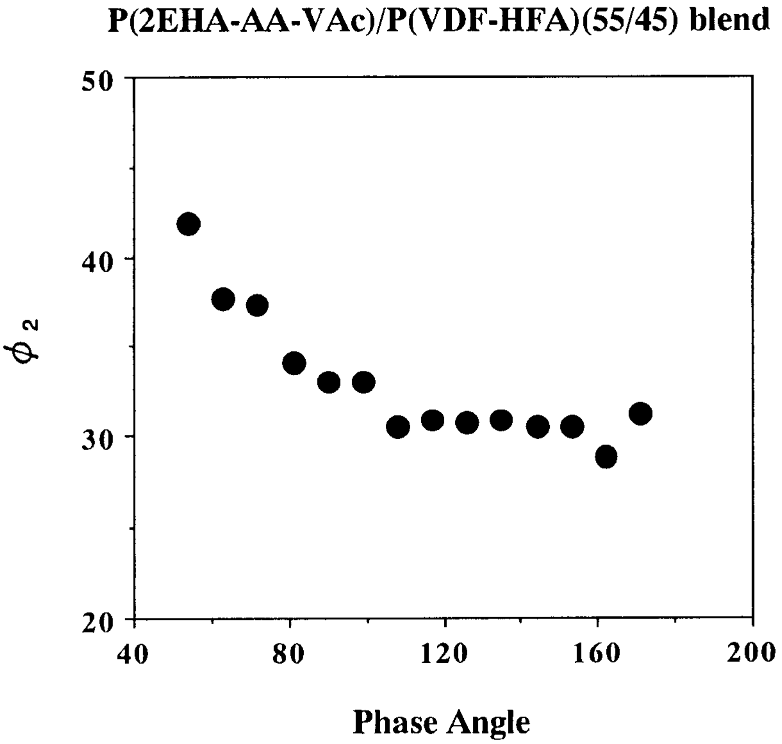

FIGURE 8 Phase angle dependence of interfacial excess of P(2EHA-AA-VAc) component, ϕ_2, for P(2EHA-AA-VAc)/P(VDF-HFA) (55/45) blend.

We are undertaking the construction of a sectional view for P(2EHA-AA-VAc)/P(VDF-HFA) blends by transmittance electron microscopy (TEM), since the depth profilings of these blends were completed using XPS, ATR-FTIR and PAS-FTIR analyses. TEM observations in these blends may be very difficult because of tackiness and flexibility of the acrylate copolymer. Moreover, it is also necessary to clarify the factors producing this complex segregation behavior and to examine the effect of the environment conditions (blends/polytetrafluoroethylene (PTFE) interface) on the segregation behavior of P(2EHA-AA-VAc)/P(VDF-HFA) blends.

CONCLUSIONS

PAS-FTIR is a very effective technique for construction of more detailed depth profiles for P(2EHA-AA-VAc)/P(VDF-HFA) blends[20] coated on poly(dimethyl siloxane) (PDMS). In the PAS-FTIR method, the interferogram for an arbitrary phase angle, I_θ, was calculated from the interferogram at one phase angle, I_0, and the interferogram at 90° using the equation, $I_\theta = I_0 \cos\theta + I_{90} \sin\theta$. It was confirmed that the P(2EHA-AA-VAc) component for P(2EHA-AA-VAc)/P(VDF-HFA) 50/50, 30/70 and 55/45 blends was segregated at the PDMS-polymer interface. Its concentration exponentially changed from the interface in the depth direction and became constant at an approximately 100° phase angle. We presumed that the segregation structures were formed by the rearrangement of blends on the PDMS substrate.

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