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Effect of substrate on gradient domain morphology formed in acrylate copolymer/ fluoro-copolymer blends

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The effect of the substrate on the gradient domain morphology was investigated for immiscible blends of poly(2-ethylhexyl acrylate-co-acrylicacid-co-vinylacetate) [P(2EHA-AA-VAc)] and poly(vinylidene fluoride-co-hexa-fluoro acetone) [P(VDF-HFA)]. The blends were prepared on substrates of poly(dimethyl siloxane) (PDMS) coated on a liner and of poly(tetrafluoro ethylene) (PTFE) from a THF solution by coating. The chemical compositions and the cross-sectional morphology of the surface (surface in contact with air) and bottom (surface in contact with substrate) sides were examined by attenuated total reflection Fourier transform infrared spectroscopy and scanning electron microscopy. The P(2EHA-AA-VAc)/P(VDF-HFA) (50/50), (30/70) blends prepared on PDMS revealed a gradient domain morphology, whereas the (50/50) and (30/70) blends prepared on PTFE formed a sea-island type of phase separation structure. On the other hand, when the P(2EHA-AA-VAc)/ P(VDF-HFA) (70/30) blend was prepared on PTFE, P(2EHA-AA-VAc) and P(VDF-HFA) components segregated at the surface and the bottom, respectively. We concluded that the affinity between P(VDF-HFA) and the substrates strongly influenced the formation of the gradient domain morphology and the surface segregation of P(2EHA-AA-VAc). © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: ATR-FTIR; contact angle; gradient domain morphology)

INTRODUCTION

In recent decades, several advanced studies of the surface of polymer alloys, such as polymer blends, block copolymers, and graft copolymers, have been performed[1–3]. The reason is that various surface analysis techniques, e.g. X-ray photoelectron spectroscopy (XPS)[4] and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)[5] for surface chemical composition, contact angle measurement[6] for surface tension estimation, dynamic contact angle (DCA) measurement[7] for surface molecular mobility, scanning electron microscopy (SEM)[8] and atomic force microscopy (AFM)[9] for observation have been developed and applied to polymer alloys. These techniques are particularly effective in identifying surface segregation[10] and gradient structure[11] formed in polymer blends. In binary polymer blends, surface segregation occurs owing to the difference in surface tension between the pure components and the component of lower surface tension enriched on the surface of the blends. For the gradient structure in polymer blends, the concentration of one component gradually changes from the surface to the bottom.

We[12–23] observed surface segregation or the gradient domain morphology in the acrylate adhesive polymer/ poly(vinylidene fluoride-co-hexafluoro acetone) [P(VDF-HFA)] blends prepared on substrates of poly(dimethyl siloxane) (PDMS) and of poly(ethylene terephthalate) (PET) by coating from a THF solution. In miscible blends

of poly(ethyl acrylate) (PEA)[12–14] or poly(butyl acrylate) (PBA)[15,16] with P(VDF-HFA), the surface segregation was confirmed by XPS. In contrast, using XPS, ATR-FTIR, and electron microscopy, we confirmed that a gradient domain morphology was formed in immiscible blends of poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) [P(2EHA-AA-VAc)/P(VDF-HFA)][17–22]. In (50/50) and (30/70) blends, the characteristic gradient domain morphology was confirmed by the observation of a sectional layer by transmission electron microscope (TEM) and SEM, i.e. the ellipsoidal domain corresponding to P(2EHA-AA-VAc) was observed, its size increased from the surface (surface in contact with air) to the bottom and a P(2EHA-AA-VAc) layer was also observed in the bottom side (surface in contact with substrate PDMS, PET)[20,22]. P(2EHA-AA-VAc) was immiscible with P(VDF-HFA) and the surface tension of P(VDF-HFA) was lower than that of P(2EHA-AA-VAc)[17]. Therefore, we considered that the gradient domain morphology found in the P(2EHA-AA-VAc)/ P(VDF-HFA) blends was formed by the difference in surface tension between the components. In our previous papers[22,23], it was also suggested that the gradient domain morphology formed in these blends was moderated by the rate of solvent evaporation and solution concentration. Therefore, the clarification of the factors leading to a gradient domain morphology in these blends is very difficult because many factors influence the form of the gradient domain morphology.

When a blend film is prepared on a substrate from solution by casting, the chemical composition of the bottom

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side of the blend film in contact with the substrate is changed markedly by the substrate[24,25]. In general, the component that minimizes interfacial tension between the blend and the substrate is segregated on the substrate. For example, Miki et al.[24] measured the surface chemical composition of injection-moulded multicomponent polyesters using XPS. They found that the chemical composition was changed by the moulding conditions (contacting substrates, such as air, water, and the metal). Thus, the effect of the substrate on the surface chemical composition is marked. We noted that the gradient domain morphology formed in the P(2EHA-AA-VAc)/P(VDF-HFA) blends would be changed by the substrates. If the blends were prepared on poly(tetrafluoro ethylene) (PTFE), the P(VDF-HFA) component would be segregated at the bottom because of the affinity between PTFE and P(VDF-HFA).

In this study, surface chemical compositions and morphologies of the surface, bottom, and a cross-section for P(2EHA-AA-VAc)/P(VDF-HFA) blends prepared on PTFE or PDMS were investigated by ATR-FTIR and SEM, respectively. To determine the effect of the substrate on the formation of a gradient domain morphology, we calculated the interfacial tension between the substrates and P(VDF-HFA).

EXPERIMENTAL

Materials

The P(2EHA-AA-VAc) and P(VDF-HFA) were synthesized by Mitsubishi Kagaku Co. Ltd. and Central Glass Co. Ltd., respectively. The molecular characteristics of the copolymers are presented in *Table 1*. Under nitrogen gas, the P(2EHA-AA-VAc)/P(VDF-HFA) blends were prepared on substrates using a hand coating bar from 20 wt.% THF solution. PDMS (having a critical surface tension $\gamma_C \approx 24$ dyn cm^{-1} and coated on paper) and PTFE (Nichiasu Co. Ltd., Nafuron) were used as substrates. After the coating film had dried at 23°C for 1–2 h, the film was allowed to dry further in a vacuum at 23°C for 7 days. The film was about 15–20 μm thick. Since the gradient domain morphology formed in the P(2EHA-AA-VAc)/P(VDF-HFA) blends was prepared by coating from THF solution in our previous study[20], the influence of water must be considered because THF easily absorbs water. This is the reason why we prepared the blend films under nitrogen gas (water excluded).

Measurements

The surface and the bottom of the P(2EHA-AA-VAc)/P(VDF-HFA) blends were measured using a Jeol JIR-WINSPEC50 FTIR analyser. ATR-FTIR spectra were obtained with ZnSe as a prism at incidence angle of 45°.

The P(2BHA-AA-VAc)/P(VDF-HFA) blends were treated by vacuum evaporation with Au using an Eiko Engineering IB-3 ion coater. The surface and bottom morphologies of P(2EHA-AA-VAc)/P(VDF-HFA) blends were observed using a Hitachi scanning electron microscope of type S-2100.

Table 1 Components and molecular weights[a] of copolymers

P(2EHA-AA-VAc)	2-Ethylhexyl acrylate/acrylic acid/vinyl acetate = 85/5/10 (mol.%) Mn = 45500, Mw = 372000
P(VDF-HFA)	Vinylidene fluoride/hexafluoro acetone = 92/8 (mol,%) Mn = 52000, Mw = 130000

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

The cross-sectional layers of the P(2EHA-AA-VAc)/P(VDF-HFA) blends were observed using Hitachi scanning electron microscope of type S-800. Firstly, the blends were embedded in epoxy resin (Ouken EPON 812) at 30–40°C for 24 h. The embedded blends were stained with ruthenium tetraoxide (RuO$_4$) because P(2EHA-AA-VAc) is very flexible. Then, the blends were cut into about 0.1 μm section at -120°C with an ultra-microtome Reichert ULTRACUT-N (Knife: Diatome). The optical micrograph for the (50/50) blend prepared on PTFE was observed using an OPTIPHOT optical microscope of Nikon.

The contact angles of dispersion liquids on substrates were measured using a Kyowa Kaimen Kagaku contact angle measurement apparatus of type CA-D. The drops of liquids were deposited using a microsyringe onto the surfaces of blend films at 23°C. The surface tensions γ_L of dispersion liquids used in this study are listed in *Table 2*.

RESULTS AND DISCUSSION

The penetration depth (d_p) in the ATR-FTIR method is expressed by following equation:

$$d_p = \lambda/2\pi n_A (\sin^2\theta - n_{BA}^2)^{0.5} \qquad (1)$$

where θ is the incidence angle, π the circular constant, λ the infrared ray absorption wavelength, and n_A the refractive index of prism. n_{BA} is the refractive index n_B/n_A (n_B is refractive index of sample). According to equation (1) d_p varies with θ and λ. In this study, d_p for the P(2EHA-AA-VAc)/P(VDF-HFA) blends was 1 μm at 1730 cm^{-1} (C=O absorption) and 2 μm at 870 cm^{-1} (C–F absorption) when $\theta = 45°$, $n_A = 2.42$, $n_B = 1.4$[26]. Thus, we did not determine the depth profile of the chemical composition, although a comparison of chemical composition between the surface and bottom sides in the P(2EHA-AA-VAc)/P(VDF-HFA) blends was obtained qualitatively using the ATR-FTIR method.

The ATR-FTIR spectra at the surface side and bottom side for the P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend are shown in *Figure 1*. When the (30/70) blend was prepared on PDMS, the magnitude of I_{870} at the surface side is greater than that at the bottom side, whereas the magnitude of I_{1730} at the surface side is markedly less than that at the bottom side. Here I_{870} and I_{1730} refer to the C–F absorption at 870 cm^{-1} and the C=O absorption at 1730 cm^{-1}, respectively. Obviously, P(2EHA-AA-VAc) and P(VDF-HFA) components segregate at the bottom side and the surface side, respectively. In contrast, for the (30/70) blend prepared on PTFE, it is suggested that P(2EHA-AA-VAc) and P(VDF-HFA) components also segregate at the bottom side and the surface side, respectively. However, as the magnitude of I_{870} at the bottom for the (30/70) blend prepared on PTFE is greater than that for the (30/70) blend prepared on PDMS, the

Table 2 Surface tensions of liquids at 20°C (dyn cm^{-1})[a]

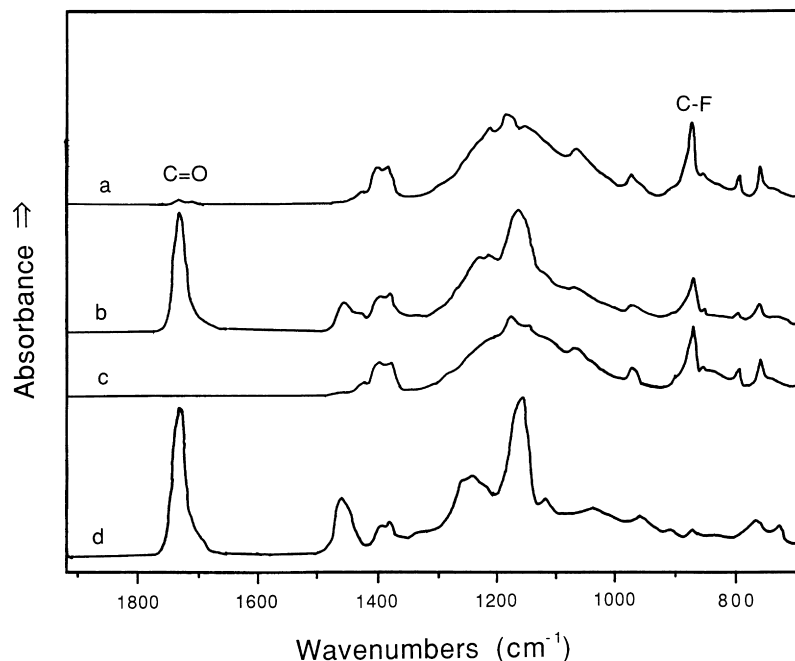| Liquid	γ_L
n-Nonane	22.9
n-Decane	23.9
n-Undecane	24.7
n-Dodecane	25.4
n-Tetradecane	26.7
n-Hexadecane	27.6
trans-Decalin	29.9
cis-Decalin	32.2

[a]Ref. [34].

Figure 1 ATR-FTIR spectra of P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend prepared on PDMS or PTFE: (a) PTFE, surface side; (b) PTFE, bottom side; (c) PDMS, surface side; (d) PDMS, bottom side

substrate clearly influences the chemical composition at the bottom. Presumably the affinity between PTFE and P(VDF-HFA) acts as a driving force for segregation of P(VDF-HFA) at the bottom. As shown in *Figure 2*, the surface and bottom morphologies of the P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend prepared on PDMS were observed by SEM. The surface of the (30/70) blend exhibited a smooth morphology, while a wrinkled morphology was observed at the bottom. From the previous result[18], since an acrylate polymer possesses good flexibility at room temperature, it was judged that the wrinkled morphology was formed during vacuum evaporation coating with Au. Therefore, the smooth morphology and the wrinkled morphology for the (30/70) blend prepared on PDMS correspond to P(VDF-HFA) and P(2EHA-AA-VAc), respectively. As shown in *Figure 3*, the surface and bottom morphologies of the (30/70) blend prepared on PTFE clearly differ from those of the (30/70) blend prepared on PDMS. On the surface side, a heterogeneous morphology is observed, whereas the wrinkled morphology is not confirmed. On the other hand, as the heterogeneous and wrinkled morphologies are observed at the bottom, we presumed that P(2EHA-AA-VAc) and P(VDF-HFA) components coexist. The results of SEM photographs support the ATR-FTIR results for the (30/70) blend.

Figure 4 shows the ATR-FTIR spectra of the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend prepared on PDMS and PTFE. When the (50/50) blend film is prepared on PDMS, the magnitude of I_{1730} at the surface is markedly less than that at the bottom, whereas the magnitude of I_{870} at the surface is greater than that at the bottom. In the (50/50) blend prepared on PDMS, it is suggested that the P(VDF-HFA) and P(2EHA-AA-VAc) segregate at the surface and the bottom, respectively. In the (50/50) blend, a smooth morphology and a wrinkled morphology were also observed at the surface side and the bottom side, respectively. In other words, SEM observations confirmed that the P(VDF-HFA) segregated at the surface and the P(2EHA-AA-VAc) precipitated at the bottom in the (50/50) blend prepared on
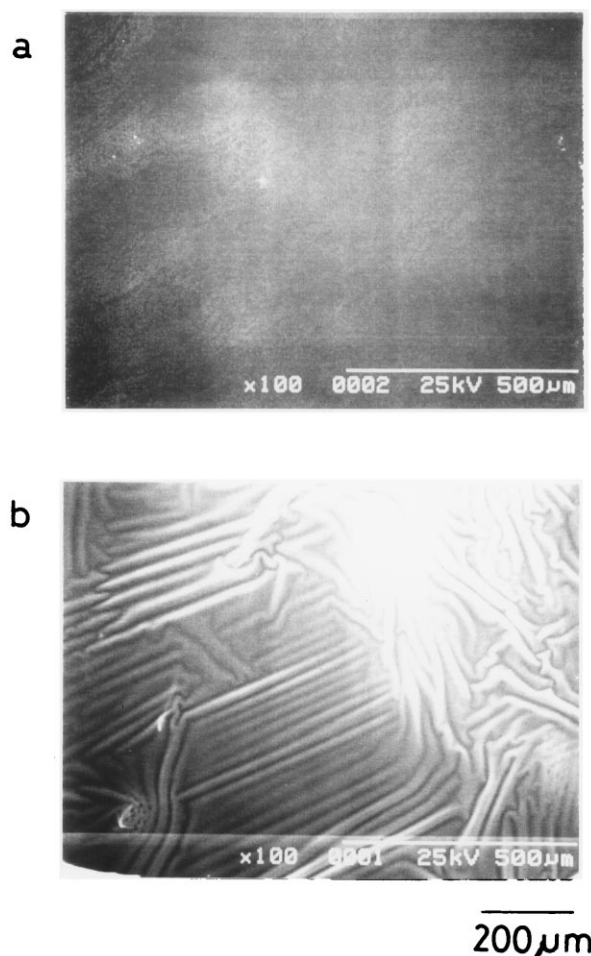

Figure 2 SEM photographs of P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend prepared on PDMS: (a) surface side; (b) bottom side
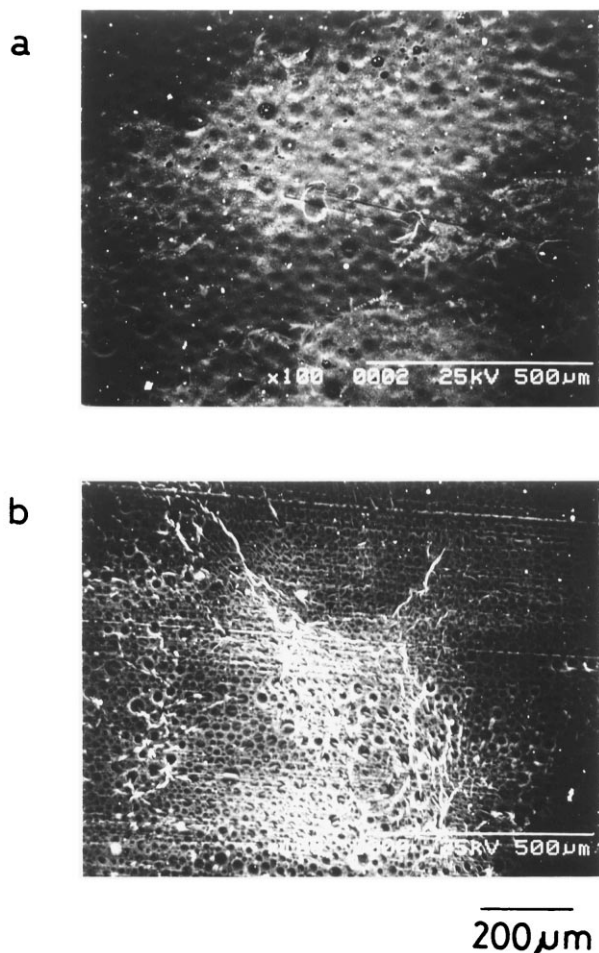
Figure 3 SEM photographs of P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend prepared on PTFE: (a) surface side; (b) bottom side

PDMS. Although the photographs are not shown here, these morphologies were similar to those reported in our previous study[27]. Evidently, the delineations of ATR-FTIR spectra of the (50/50) blend prepared on PTFE differ from those of the (50/50) blend prepared on PDMS. Since the magnitude of the I_{1730} and I_{870} peaks in the ATR-FTIR spectrum from the surface side almost equals that at the bottom side for the (50/50) blend prepared on PTFE, no segregation or gradient domain morphology occurs in the blend film. SEM photographs of the (50/50) blend prepared on PTFE are shown in *Figure 5*. A sea-island type of phase separation structure is observed at the surface and bottom sides and the diameter of the domain is about 50–200 μm. Since the morphology at the surface side completely corresponds to that at the bottom side, the SEM results support the ATR-FTIR results for the (50/50) blend prepared on PTFE. We think that the affinity between PTFE and P(VDF-HFA) also contributes the surface and bottom morphologies of the (50/50) blend.

ATR-FTIR spectra of the P(2EHA-AA-VAc)/P(VDF-HFA) (70/30) blend prepared on PDMS and PTFE are shown in *Figure 6*. When the (70/30) blend was prepared on PDMS, the delineation of the ATR-FTIR spectrum of the surface side was similar to that for the bottom side. It is suggested that no segregation or gradient domain morphology occurred for the (70/30) blend prepared on PDMS. In our previous study[19,22], the (70/30) blend did not exhibit either segregation or gradient domain morphology. However, in the (70/30) blend prepared on PTFE, the magnitude of I_{1730} at the surface side is much greater than that at the bottom side, while the magnitude of I_{870} at the surface side is less than that at the bottom side. *Figure 7* shows SEM photographs of the (70/30) blend prepared on PTFE. A smooth morphology and a wrinkled morphology are observed at the bottom side and the surface side, respectively. Presumably the particles corresponding to P(VDF-HFA) are also observed at the surface side. ATR-FTIR and SEM analyses confirmed that P(2EHA-AA-VAc)
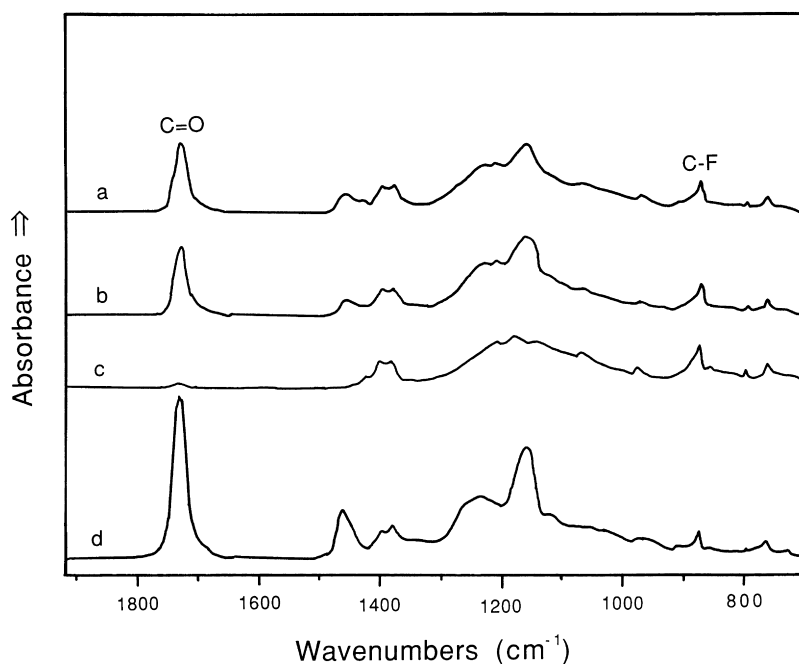

Figure 4 ATR-FTIR spectra of P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend prepared on PDMS or PTFE: (a) PTFE, surface side; (b) PTFE, bottom side; (c) PDMS, surface side; (d) PDMS, bottom side
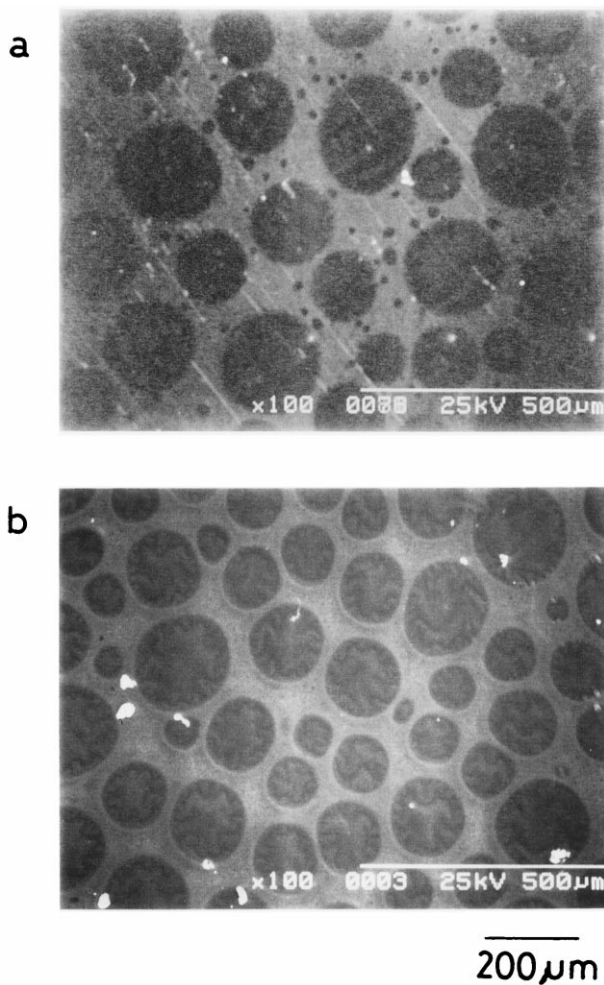
Figure 5 SEM photographs of P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend prepared on PTFE: (a) surface side; (b) bottom side

segregated at the surface and P(VDF-HFA) precipitated at the bottom for the (70/30) blend prepared on PTFE. The surface segregation of P(2EHA-AA-VAc) is very interesting because the surface tension of P(2EHA-AA-VAc) is higher than that of P(VDF-HFA).

As noted above, it was confirmed that the surface and bottom chemical compositions of the P(2EHA-AA-VAc)/ P(VDF-HFA) blends were altered by the substrates (PDMS, PTFE). However, the effect of the substrate on the gradient domain morphology formed in the P(2EHA-AA-VAc)/ P(VDF-HFA) blends was not identified. We observed the cross-sectional morphology of the blends to clarify the influence of the substrate on the formation of a gradient domain morphology.

Figure 8 shows SEM photographs of cross-sectional layers for the P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend prepared on PDMS or PTFE. When the (30/70) blend was prepared on PDMS, an ellipsoidal domain corresponding to P(2EHA-AA-VAc) was observed in a P(VDF-HFA) matrix and its size increased from the surface to the bottom and a P(2EHA-AA-VAc) layer 5–8 μm thick was also observed at the bottom side, i.e. a typical gradient domain morphology was revealed. On the other hand, when the (30/70) blend was prepared on PTFE, an ellipsoidal domain corresponding to P(2EHA-AA-VAc) was also observed. However, the gradient domain morphology formed in the (30/70) blend prepared on PDMS was completely moderated. Therefore, we found for the first time that the gradient domain morphology formed in the (30/70) blend could be controlled by substrate (PTFE).

SEM photographs of cross-sectional layers for the (50/50) blend prepared on PDMS or PTFE are shown in *Figure 9*. In the (50/50) blend prepared on PDMS, a P(2EHA-AA-VAc) layer about 10 μm thick is observed at the bottom side and a domain corresponding to P(2EHA-AA-VAc) is observed at the surface side. That is to say, the (50/50) blend prepared on PDMS reveals a gradient domain morphology. When the (50/50) blend was prepared on PTFE, fine dispersed
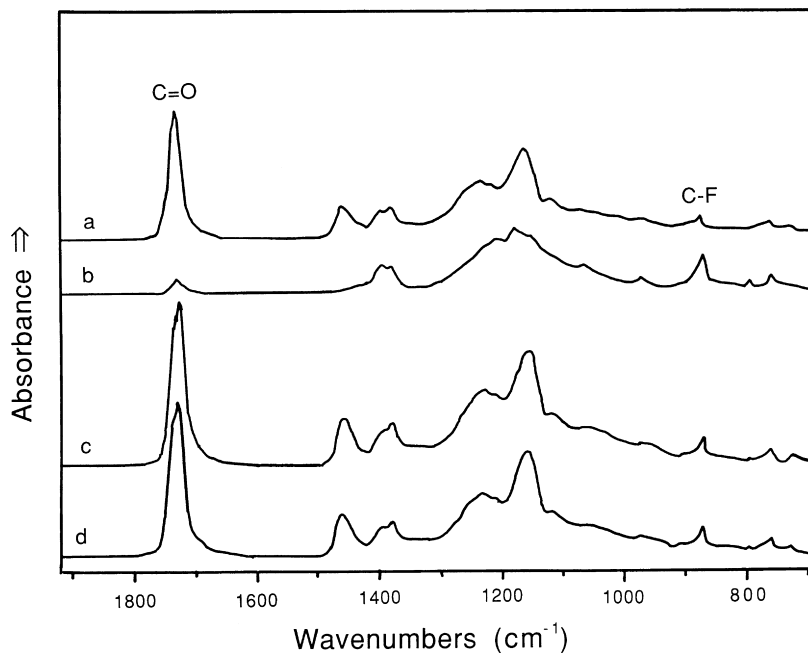

Figure 6 ATR-FTIR spectra of P(2EHA-AA-VAc)/P(VDF-HFA) (70/30) blend prepared on PDMS or PTFE: (a) PTFE, surface side; (b) PTFE, bottom side; (c) PDMS, surface side; (d) PDMS, bottom side
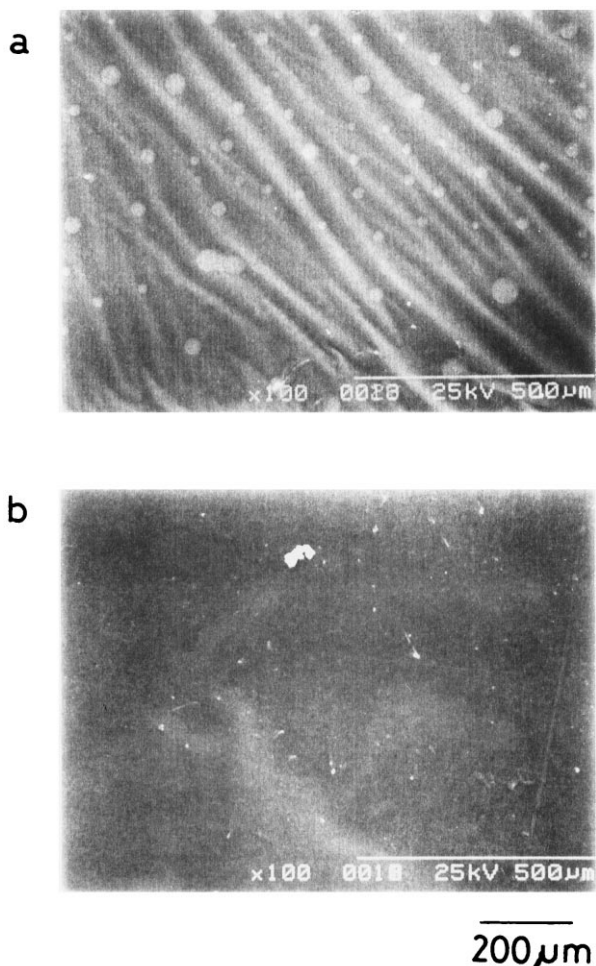
Figure 7 SEM photographs of P(2EHA-AA-VAc)/P(VDF-HFA) (70/30) blend prepared on PTFE: (a) surface side; (b) bottom side
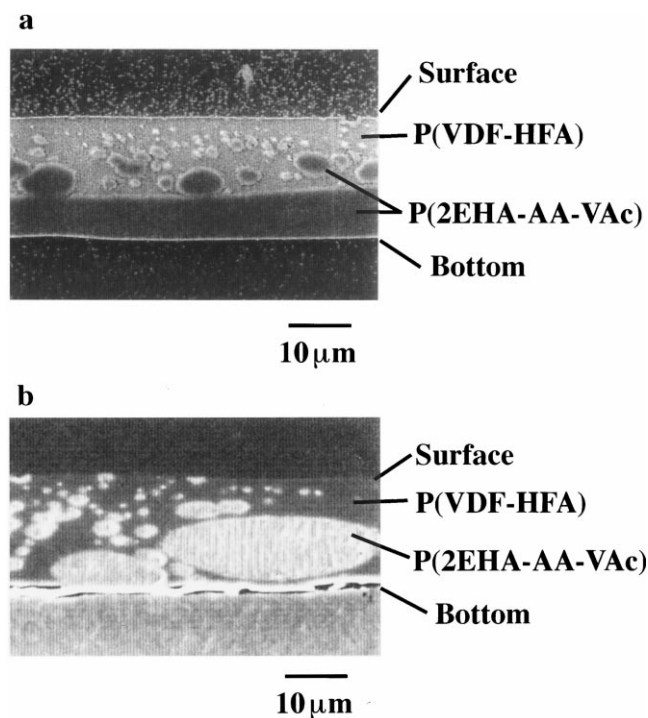

Figure 8 SEM photographs of cross-sectional layer of P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend prepared on PDMS or PTFE: (a) PDMS; (b) PTFE

particles corresponding to P(2EHA-AA-VAc) in a P(VDF-HFA) matrix and a large grown P(2EHA-AA-VAc) domain are observed in the cross-sectional layer. Clearly the cross-sectional morphology of the (50/50) blend prepared on PTFE is very different from that of the (50/50) blend prepared on PDMS. *Figure 10* shows an optical micrograph of the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend prepared on PTFE. Since the domain corresponding to P(2EHA-AA-VAc) was 100–500 μm in diameter, the (50/50) blend prepared on PTFE revealed a sea-island type of phase separation structure. Thus, it is judged that the domain observed in *Figure 5* corresponds to P(2EHA-AA-VAc). The gradient domain morphology was moderated for the (50/50), (30/70) blends prepared on PTFE. We speculate that the affinity between P(VDF-HFA) and PTFE greatly contributed to the disappearance of the gradient domain morphology.

Figure 11 shows an SEM photograph of a cross-sectional layer for the (70/30) blend prepared on PTFE. A P(2EHA-AA-VAc) layer about 12.5 μm thick is observed at the surface side and contains spherical domains corresponding to P(VDF-HFA) 0.5–1 μm in diameter. In contrast, a
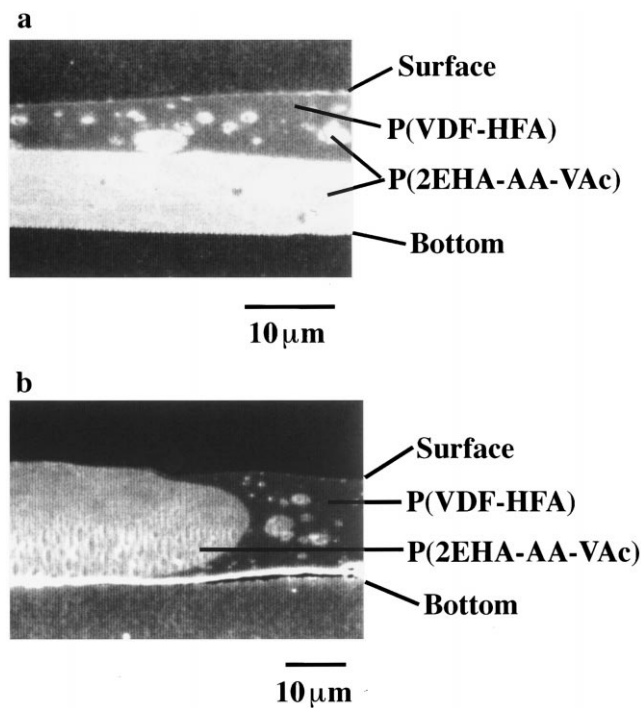

Figure 9 SEM photographs of cross-sectional layer of P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend prepared on PDMS or PTFE: (a) PDMS; (b) PTFE
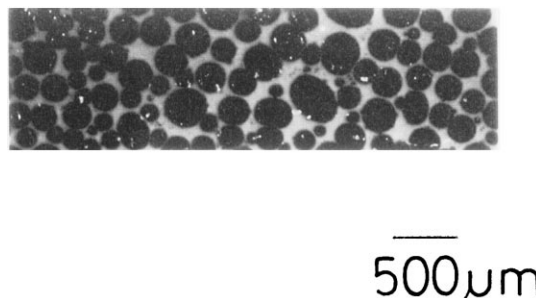

Figure 10 Optical micrograph of P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend prepared on PTFE

P(VDF-HFA) layer 2.5 μm thick is observed at the bottom side and contains ellipsoidal domains corresponding to P(2EHA-AA-VAc). The interface between the P(2EHA-AA-VAc) layer and P(VDF-HFA) layer is very flat. In our previous study[22], when the (70/30) blend was prepared on PDMS, a sea-island structure was formed (matrix of P(2EHA-AA-VAc)). Thus, we found that the morphology of the cross-sectional layer for the P(2EHA-AA-VAc)/P(VDF-HFA) blends is changed markedly by the substrates.

It is well known that surface segregation in polymer blends occurs as a low surface tension component is preferentially enriched on the surface of samples according to differences in surface tension of the components. Since the surface tension of P(VDF-HFA) is lower than that of P(2EHA-AA-VAc)[17], it is reasonable that the segregation of P(VDF-HFA) at the surface side occurred in the P(2EHA-AA-VAc)/P(VDF-HFA) blends. However, when the (70/30) blend was prepared on PTFE, it is surprising that the P(2EHA-AA-VAc) component having a high surface tension than P(VDF-HFA) was preferentially segregated at the surface side in the blend film 20 μm in thickness. Probably the affinity between PTFE and P(VDF-HFA) influences the characteristic segregation behaviour.

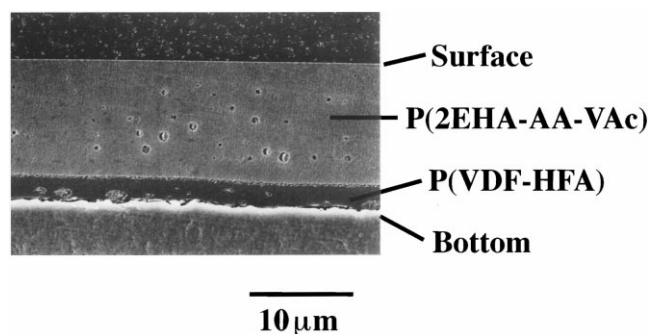In general, the affinity can be evaluated as the interfacial

Figure 11 SEM photograph of cross-sectional layer of P(2EHA-AA-VAc)/P(VDF-HFA) (70/30) blend prepared onto PTFE

tension between components (1 and 2) γ_{12}. γ_{12} is calculated from the surface tensions of components as follows

$$\gamma_{12} = (\gamma_1^{0.5} - \gamma_2^{0.5})^2 \qquad (2)$$

where γ_1 and γ_2 are the surface tensions of components 1 and 2. If γ_1 and γ_2 are known, γ_{12} can be calculated from equation (2). In this study, the surface tensions of the substrates (PDMS, PTFE) were estimated from the contact angles of the dispersion liquids on substrates. Saito[28,35,36] has proposed a new equation relating contact angle θ and γ_L (surface tension of liquid) which is expressed as follows

$$\log(1 + \cos\theta) = -\psi \log(\gamma_L) + \log(2\phi_0\gamma_S^{0.5-a}) \qquad (3)$$

where the parameter a is determined from the slope ($\psi = 0.5 - a$) in the $\log(1 + \cos\theta)$ *versus* $\log\gamma_L$ plots, γ_C is obtained as the γ_L value at $\log(1 + \cos\theta) = \log 2$ by extrapolating the straight line and ϕ_0 is calculated as follows

$$\phi_0 = (X_L^d X_S^d)^{0.5} + (X_L^p X_S^p)^{0.5} \qquad (4)$$

where X_j^d and X_j^p denote the dispersion and the polarity of component j, respectively. The parameters X_j^d and X_j^p are obtained from following equation.

$$X_j^d + X_j^p = 1 \qquad (5)$$

Therefore, the X_L^d and X_L^p values of the dispersion liquids used in this study are 1.0 and 0. On the other hand, the X_S^p values of PDMS and PTFE were determined using the solubility parameter δ and its polarity component δ^p according to the equation[29]

$$X_S^p = (\delta^p/\delta)^2 \qquad (6)$$

We have already verified that the $\log(1 + \cos\theta)$ versus $\log\gamma_L$ plot gave a reasonable critical surface tension γ_C for P(VDF-HFA)[30], blends of poly(vinyl ethylene-co-1, 4-butadiene) with terpene resin[31] and hydrogenated terpene resin[32].

The $\log(1 + \cos\theta)$ *versus* $\log\gamma_L$ plots of the dispersion liquids and PDMS or PTFE are shown in *Figure 12*. Since the plots of $\log(1 + \cos\theta)$ *versus* $\log\gamma_L$ for PDMS and
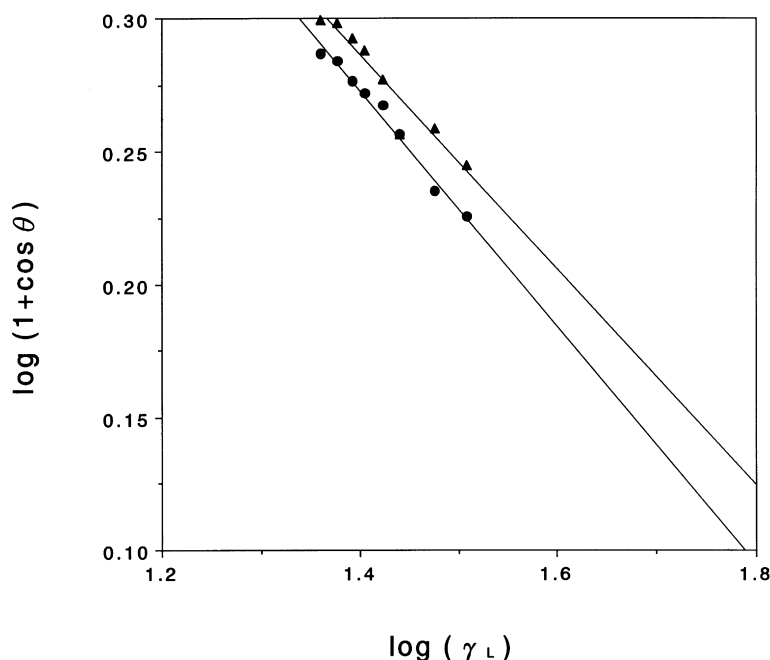

Figure 12 Plots of $\log(1 + \cos\theta)$ *versus* $\log\gamma_L$ obtained from contact angles of the substrates on dispersion liquids: ▲, PDMS; ●, PTFE

PTFE are straight lines, the γ_C values can be estimated as the γ_L values at $\log(1 + \cos\theta) = \log 2$ by extrapolating the straight lines. The γ_C values of PDMS and PTFE were 23.1 and 21.7 dyn cm^{-1}. On the other hand, we have already reported that the γ_C values of P(VDF-HFA) is 20.8 dyn cm^{-1} [33]. Using these γ_C values, the interfacial tensions γ_{12} between P(VDF-HFA) and PDMS or PTFE were calculated using equation (2). The γ_{12} values of PDMS and PTFE against P(VDF-HFA) were 0.0603 and 0.0095 dyn cm^{-1}, respectively. As the γ_{12} value between PTFE and P(VDF-HFA) is lower than that between PDMS and P(VDF-HFA), it is presumed that PTFE possesses an affinity for P(VDF-HFA) superior to that of PDMS. Thus, we presume that the affinity between P(VDF-HFA) and PTFE induces the segregation toward the surface side of P(2EHA-AA-VAc) having higher surface tension than P(VDF-HFA) for P(2EHA-AA-VAc)/P(VDF-HFA) blends. However, since the γ_{12} values in this study was calculated using equation (2), the γ_{12} value should be also evaluated by the contact angle (sessile bubble) method.

We should examine in detail why the segregation toward the surface side of P(2EHA-AA-VAc) occurred for the (70/30) blend prepared on PTFE. One reason is the above-mentioned affinity or interfacial tension γ_{12} between PTFE and P(VDF-HFA) as the driving force. We speculate that the rate of solvent evaporation as the other correlates the segregation towards the surface of P(2EHA-AA-VAc) because the blend film was prepared by coating from THF solution and the prepared blend was 20 μm thick. When the rate of solvent evaporation was very fast, no segregation of P(2EHA-AA-VAc) occurred in the blend film because the polymer chains were quickly frozen before the start of the segregation towards the surface side of P(2EHA-AA-VAc). In this study, since the preparation of blend films was performed at 23°C, the rate of solvent evaporation was presumably very slow. Therefore, we presume that the segregation towards the surface side of P(2EHA-AA-VAc) was caused by the affinity between PTFE and P(VDF-HFA) and by the slow solvent evaporation rate.

CONCLUSIONS

The chemical compositions and morphologies of the surface, bottom and cross-sections for P(2EHA-AA-VAc)/P(VDF-HFA) blends prepared on the PDMS and the PTFE were investigated by ATR-FTIR and SEM. The surface and bottom chemical compositions and cross-sectional morphology of the blends prepared on PTFE differed from that of the blends prepared on PDMS. The P(2EHA-AA-VAc)/P(VDF-HFA) (50/50), (30/70) blends prepared on PDMS exhibited a typical gradient domain morphology, while the blends prepared on PTFE formed a sea-island type of phase separation structure. In contrast, when the (70/30) blend was prepared on PTFE, P(2EHA-AA-VAc) was markedly segregated at the surface side. We concluded that the affinity between P(VDF-HFA) and substrates influenced

the formation of the gradient domain morphology and the surface segregation of P(2EHA-AA-VAc).

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