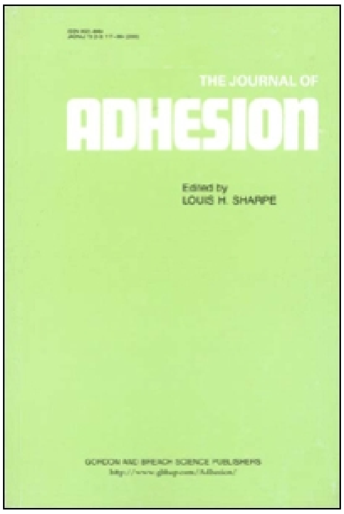

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Yoshihisa Kano[a]; Saburo Akiyama[a]; Hironari Sano[b]; Hiroshi Yui[c]
[a] Department of Chemical Science and Technology, Faculty of Technology, Tokyo University of Agriculture and Technology, Tokyo, Japan [b] Mitsubishi Kagaku Co. Ltd., Yokkaichi-shi, Mie, Japan [c] AMCO Enterprises Incorporated, Tokyo, Japan

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ATR-FTIR and SEM Gradient Study of Poly(2-ethylhexyl acrylate)/Poly (vinylidene fluoride-co-hexafluoro acetone) Blends*

YOSHIHISA KANO[a], SABURO AKIYAMA[a,**],
HIRONARI SANO[b] and HIROSHI YUI[c]

[a]*Department of Chemical Science and Technology, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo 184, Japan;* [b]*Mitsubishi Kagaku Co. Ltd., Yokkaichi-shi, Mie 510, Japan;* [c]*AMCO Enterprises Incorporated, Shibuya-ku, Tokyo 150, Japan*

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The segregation structure and the gradient structure of poly(2-ethylhexylacrylate) (P2-EHA)/poly(vinylidene fluoride-co-hexafluoro acetone) [P(VDF-HFA)] blends were confirmed by ATR-FTIR and SEM. For the P2-EHA/P(VDF-HFA) (50/50) blend, the P(VDF-HFA) and P2-EHA layers were observed at the free surface side and bottom side, respectively. The gradient structure was obtained for the P2-EHA/P(VDF-HFA) (30/70) blend. The domain morphology of a cross section of the P2-EHA/P(VDF-HFA) (50/50) blend was dramatically changed by the thickness of the blend film. Finally, we propose that the segregation structure and gradient structure formed in P2-EHA/P(VDF-HFA) blends were caused by surface tension difference, rate of phase separation, rate of solvent evaporation, and molecular weight difference.

Keywords: Segregation; gradient structure; poly(2-ethylhexylacrylate); fluoro-copolymer; blends; rate of solvent evaporation

1. INTRODUCTION

In the last decade, the controlling morphology of immiscible polymer blends has been reported by several researchers [1–3]. For instance,

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**Corresponding author.

the gradient structure [1] formed in polymer blends is remarkable. In the gradient structure, the concentration of one component in the blend gradually changes from the surface to the bottom of the film. In particular, the concept of gradient structure is very interesting for an aerospace material [4] and for pressure sensitive adhesive (PSA) tape [5]. Gradient structures have been prepared by several methods [5–7], including a dissolution and diffusion method [1], and by controlling the temperature between the surface and the bottom of the mold [7].

On the contrary, in thin films of about 20–30 μm of poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) : P(2EHA-AA-VAc)/poly(vinylidene fluoride-co-hexafluoro acetone) : P(VDF-HFA) blends, the gradient structure [8–14] could be made by coating from THF solution. Since the P(VDF-HFA) component was enriched on the surface and P(2EHA-AA-VAc) precipitated at the bottom, the tack value of the bottom side was remarkably higher than that of the surface side. It was presumed that the gradient structure was formed due to the difference in surface tension between the components, the rate of solvent evaporation and the rate of phase separation. Finally, it was expected that these blends could be utilized as a new type pressure sensitive adhesive (PSA) tape, without a backing.

In general, the acrylate polymers, such as poly(ethyl acrylate): PEA, poly(butyl acrylate): PBA, and poly(2-ethylhexyl acrylate): P2-EHA are utilized as the dominant components of pressure sensitive adhesives. These acrylate polymers, possessing low *Tg* ($< -20°C$) and flexibility at room temperature, are very tacky [15]. Kim and Mizumachi [16–18] have investigated miscibility and PSA properties in blends of acrylate adhesives with various tackifiers. On the other hand, P(VDF-HFA) possesses nontackiness, water repellency, and heat and chemical resistance [8]. Incidentally, the miscibility between acrylate polymer and fluoro polymer increases with decreasing side chain length of acrylate polymer because of the ease of hydrogen bonding. In other words, the lower critical solution temperature (LCST) phase diagram shifts to the high temperature side with decreasing side chain length of acrylate polymer. If gradient structure was influenced by miscibility, we expected that the gradient structure could be formed for blends of the acrylate polymer having long side chain length with P(VDF-HFA).

In a previous study [19], the surface and bottom compositions were examined for P2-EHA having long side chain length/P(VDF-HFA) blends by XPS. In these blends, a P(VDF-HFA) enriched layer and a P2-EHA enriched layer were observed at the surface side and the bottom side, respectively. Thus, the probe tack value of the bottom side was remarkably higher than that of the surface side. We presumed that the segregation structure found in the P2-EHA/P(VDF-HFA) blends was strongly influenced by several factors, such as surface tension difference, rate of phase separation, rate of solvent evaporation, and molecular weight. In addition, the surface composition of the P2-EHA/P(VDF-HFA) (50/50) blend depended on film thickness. However, the gradient structure was not confirmed for P2-EHA/P(VDF-HFA) blends because XPS samples only the top few nm.

In this work, a more detailed characterization of the surface segregation and gradient structure formed in the P2-EHA/P(VDF-HFA) blends is presented. The surface and bottom compositions and cross-sectional layer morphology of the P2-EHA/P(VDF-HFA) blends were examined by ATR-FTIR and SEM, respectively. Particularly, the effects of blend ratio, solvent evaporation rate and molecular weight difference on the gradient structure were examined for these blends.

2. EXPERIMENTAL

2.1. Materials

The P2-EHA was supplied by Nichiban Co., Ltd. (Japan) and synthesized by a solution polymerization at 70–80°C for 15 h, using lauroyl peroxide as an initiator and mixtures of ethyl acetate (70 wt%) with acetone (30 wt%) as a solvent. Molecular weights of P2-EHA were determined using a Hitachi Co. Ltd. Liquid Chromatograph 655A-11 GPC system in 0.3 (wt%) THF solution. The number and weight average molecular weights of P2-EHA and P(VDF-HFA) are represented in Table I. When the P2-EHA having low molecular weight was synthesized, lauryl mercaptan (0.1 phr) was added as chain transfer agent. The notation "*−L*" as shown in Table I means low molecular weights. The P(VDF-HFA) (HFA content: 8.3 mol%) was

TABLE I Molecular weights[a] of polymers

Sample	$\overline{Mn}$	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$
P2-EHA-L	58000	231000	3.98
P2-EHA	106000	813000	7.63
P(VDF-HFA)	12000	57000	4.94

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

supplied by Central Glass Co. Ltd. (Japan). Molecular weights of P(VDF-HFA) were determined using a TOSO Co., Ltd. CP8000 GPC system in 0.1 (wt%) THF solution.

2.2. Sample Preparations

The P2-EHA/P(VDF-HFA) blend solutions were coated onto a PET film or release liner [poly(dimethyl siloxane) (PDMS) having a critical surface tension of wetting, $\gamma = 24$ dyn/cm, is coated onto the liner] using a hand coating bar from 20 (wt%) THF solution. The films of P2-EHA/P(VDF-HFA) blends were dried at 90°C for 1 min, then the films were permitted to stand at room temperature for at least 24 h. The specimens were further dried in a vacuum for 7 days at 40°C. The prepared films of P2-EHA/P(VDF-HFA) blends were 5, 30 or 50 μm thick.

2.3. Measurements

FTIR spectra of P2-EHA/P (VDF-HFA) blends (surface and bottom) were obtained by ATR-FTIR methods using a JEOL Co. Ltd. JIR-WINSPEC50 FTIR analyzer. ATR-FTIR spectra were obtained with ZnSe as a prism at an incidence angle of 45°.

The cross sections of P2-EHA/P(VDF-HFA) blends were observed using a Hitachi Ltd. SEM type S-800. Firstly, all the blend films were embedded in epoxy resin (Ouken Co. Ltd. EPON 812) at 30–40°C for 24 h. Then, the embeded films were cut into about 0.1 μm thick sections at −120° C with an ultra-microtome Reichert ULTRACUT-N (Knife: Diatome). The P2-EHA phase is more heavily stained with ruthenium tetraoxide (RuO_4).

The transmission photographs of the P2-EHA/P(VDF-HFA) blends were obtained using an OPTIPHOT optical microscope of Nikon Co. Ltd.

3. RESULTS AND DISCUSSION

3.1. Effect of Blend Ratio on Gradient Structure

The chemical compositions of the top few μm of both sides of the films were analyzed by means of ATR-FTIR. In the P2-EHA/P(VDF-HFA) (50/50) blend, the ATR-FTIR spectra of the free surface side and the bottom side, at the incidence angle of 45°, are shown in Figures 1a and b, respectively. From the FTIR spectra of the P2-EHA/P(VDF-HFA) (50/50) blend, the C=O absorption of P2-EHA and the C—F absorption of P(VDF-HFA) were observed at 1730 cm^{-1} and 8700 cm^{-1}, respectively. The ATR-FTIR spectra of P2-EHA/P (VDF-HFA) (30/70) blend were similar to those of the (50/50) blend. Using the C—F absorption at 870 cm^{-1} (I_{870}) and the C=O absorption at 1730 cm^{-1} (I_{1730}), the absorbance ratio (I_{870}/I_{1730}) can be

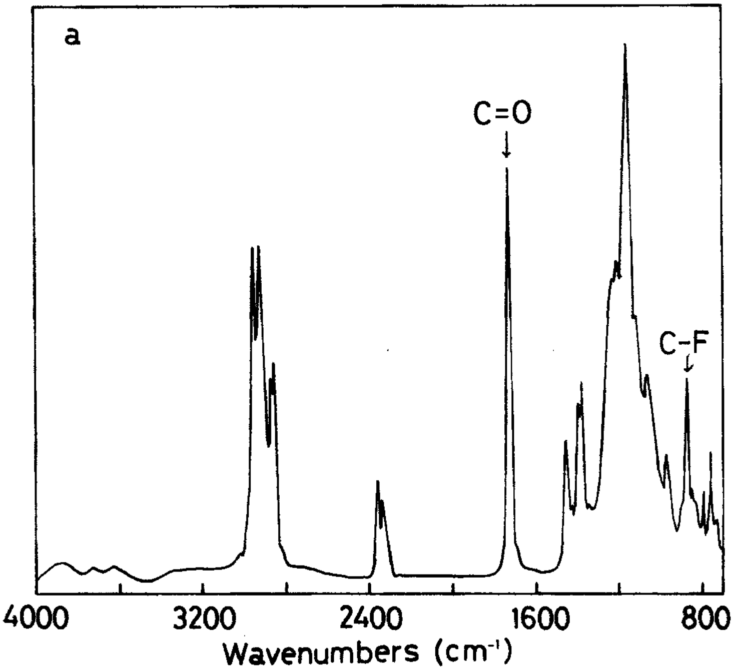

FIGURE 1 Infrared spectra of P2-EHA/P(VDF-HFA) (50/50) blend by ATR-FTIR (45° incidence angle). a) Free surface side, b) Bottom side.

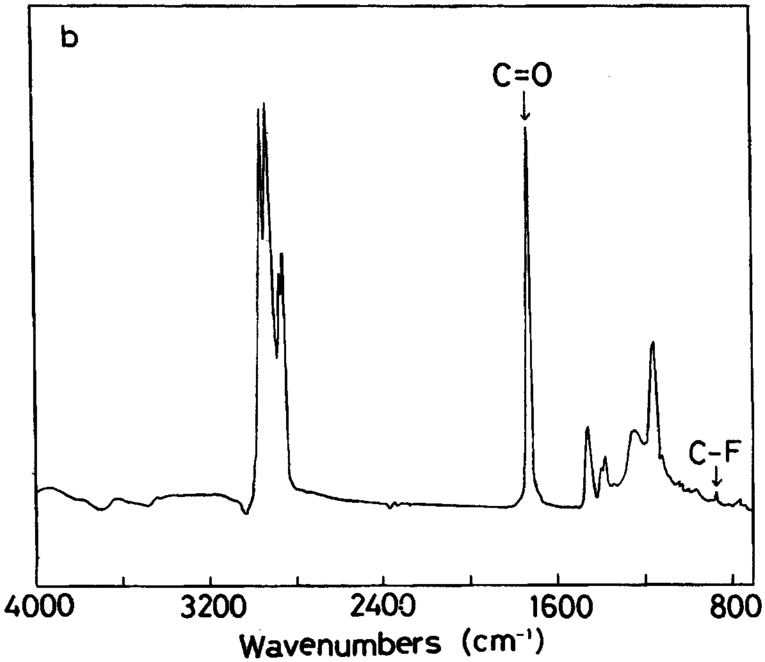

FIGURE 1 (Continued).

calculated. Table II shows the absorbance ratio (I_{870}/I_{1730}) of P2-EHA/P(VDF-HFA) (50/50) and (30/70) blends. The absorbance ratio (I_{870}/I_{1730}) at the free surface side is larger than that at the bottom side, suggesting that in the P2-EHA/P(VDF-HFA) (50/50) and (30/70) blends, there is a difference in composition between the surface and bottom sides. The P(VDF-HFA) is segregated at the free surface to a few µm depth, while the P2-EHA is precipitated at the bottom to a few µm depth of film. Thus, it is expected that the segregation structure or the gradient structure may be formed for P2-EHA/P (VDF-HFA) blends. Figures 2a and b show the ATR-FTIR spectra of the free surface side and the bottom side for the P2-EHA/P(VDF-HFA) (70/30) blend. In the XPS results [19], the surface composition was the same as the bottom composition for the (70/30) blend. Since the ATR-FTIR spectrum at the free surface side is also the same as that of the bottom side, it is expected that the segregation or gradient structure is not formed for the (70/30) blend.

TABLE II I_{870}/I_{1730} for P2-EHA/P(VDF-HFA) blends

P(VDF-HFA) content (wt%)	*50*	*70*
Free Surface Side	0.384	0.794
Bottom Side	0.029	0.049

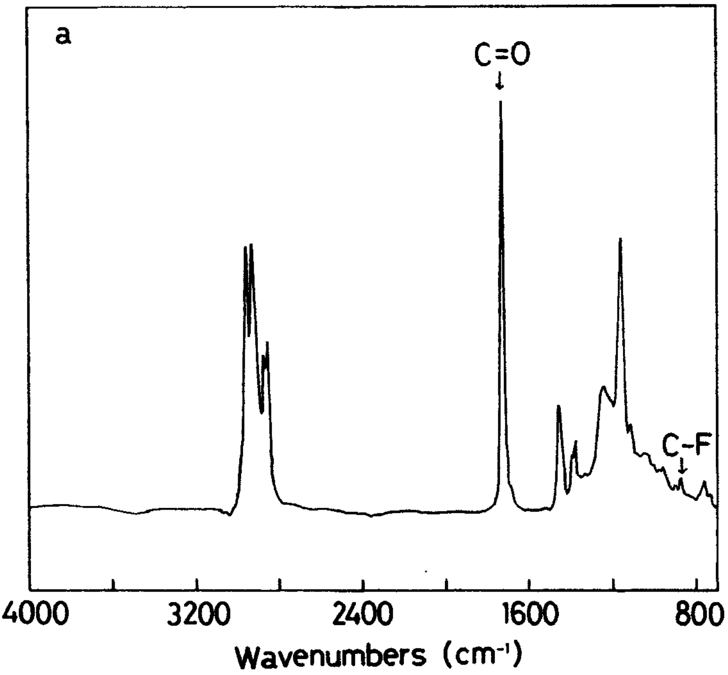

FIGURE 2 Infrared spectra of P2-EHA/P(VDF-HFA) (70/30) blend by ATR-FTIR (45° incidence angle). a) Free surface side, b) Bottom side.

Figure 3 shows the cross-sections of P2-EHA/P(VDF-HFA) (70/30), (50/50) and (30/70) blends. The darker dispersed spherical particles corresponding to P(VDF-HFA) in a P2-EHA matrix were observed for the (70/30) blend. A segregation or gradient structure was not formed in this blend. It was presumed that the phase inversion of matrix from the P2-EHA component to the P(VDF-HFA) component might be related to the formation of segregation and gradient structures. In the P2-EHA/P(VDF-HFA) (50/50) blend, the P(VDF-HFA) and the P2-EHA layers clearly segregate at the free surface side and the bottom side, respectively. In addition, the interface between

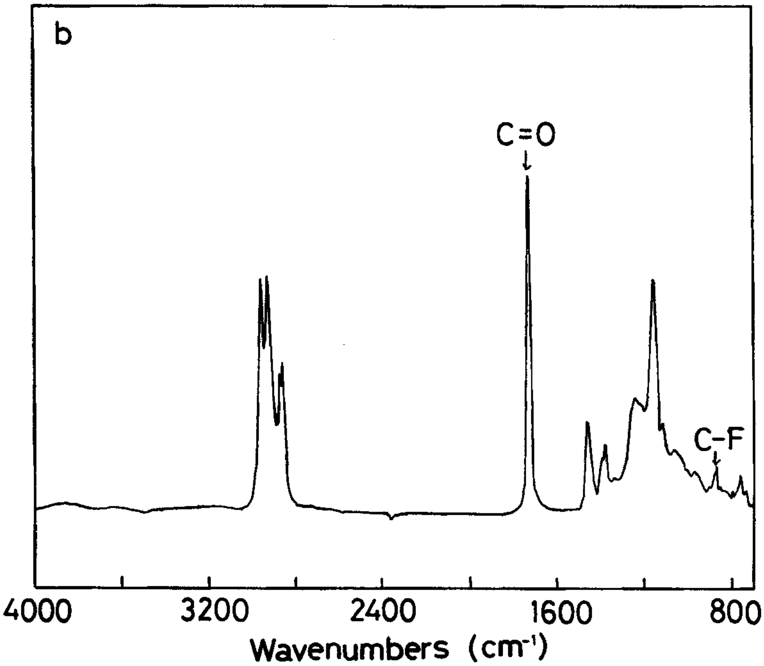

FIGURE 2 (Continued).

the P(VDF-HFA) layer and the P2-EHA layer is separated. The separation at the interface may be due to the difference in the thermal expansion coefficient between P2-EHA and P(VDF-HFA). In fact, the thermal expansion coefficient of P(VDF-HFA) is smaller than that of P2-EHA [19]. Another factor may be the very weak interfacial strength between the layers. In our previous study [20], we presented a model diagram of the gradient structure of the acrylate polymer/P(VDF-HFA) blends formed by various solvent evaporation rates. If the blend film was prepared with a very fast rate of solvent evaporation, it was possible to make the two phases co-continuous because the diffusion of the polymer chains was difficult at this fast evaporation rate. With a decrease in solvent evaporation rate, the size of the dispersed domains increases with increasing depth since the diffusion of the polymer chains occurs more easily. When the blend film was prepared by an even slow evaporation rate, coalescence of the dispersed domains

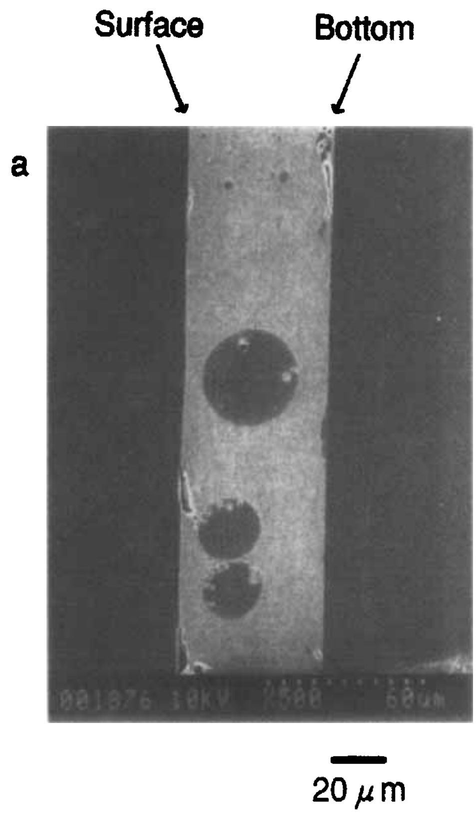

FIGURE 3 SEM micrographs of cross sections of films of P2-EHA/P(VDF-HFA) blends. P(VDF-HFA) content (wt%): a) 30, b) 50, c) 70.

could occur. Then, the acrylate polymer layer could be formed at the bottom side and the gradient structure would be formed. Finally, it is expected that the acrylate polymer/P(VDF-HFA) blend film is separated into two layers (segregation structure). We predicted that the formation process of segregation and gradient structures was influenced by many factors, such as surface tension difference, the rate of phase separation, and also the rate of solvent evaporation. The observed morphology of the cross section of the P2-EHA/P(VDF-HFA) (50/50) blend is similar to that predicted for the slower rate of solvent evaporation. In the P2-EHA/P(VDF-HFA) (30/70) blend, an ellipsoidal domain particle of P2-EHA in the P(VDF-HFA) matrix is

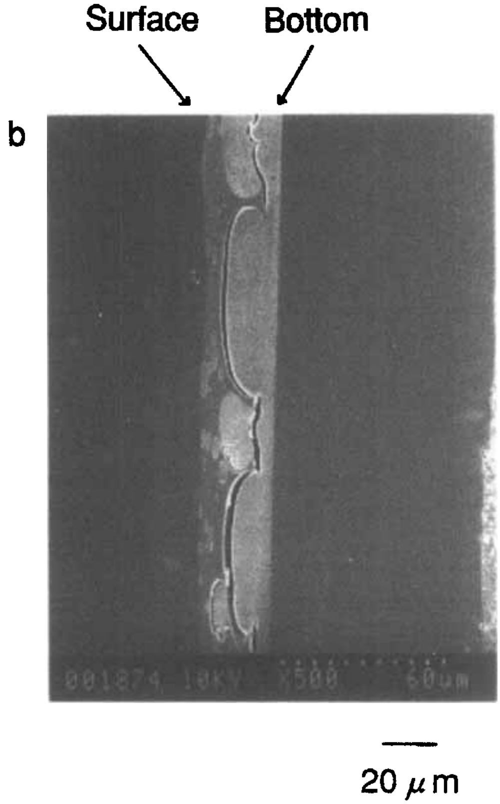

FIGURE 3 (Continued). (50/50).

observed and its size increases from surface to bottom, indicating a typical gradient structure. A P2-EHA layer, about 3 μm thickness, is observed at the bottom side. This cross-sectional layer morphology of the P2-EHA/P(VDF-HFA) (30/70) blend corresponds to that of the P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend reported in our previous paper [14]. It was confirmed that the ellipsoidal domain in the P(2EHA-AA-VAc)/P(VDF-HFA) (30/70) blend was formed during the process of solvent evaporation [21–23]. Thus, the ellipsoidal domain morphology is formed due to the non-equilibrium state. In the P2-EHA/P(VDF-HFA) (30/70) blend, the interface between P(VDF-HFA) matrix and P2-EHA layer is also separated.

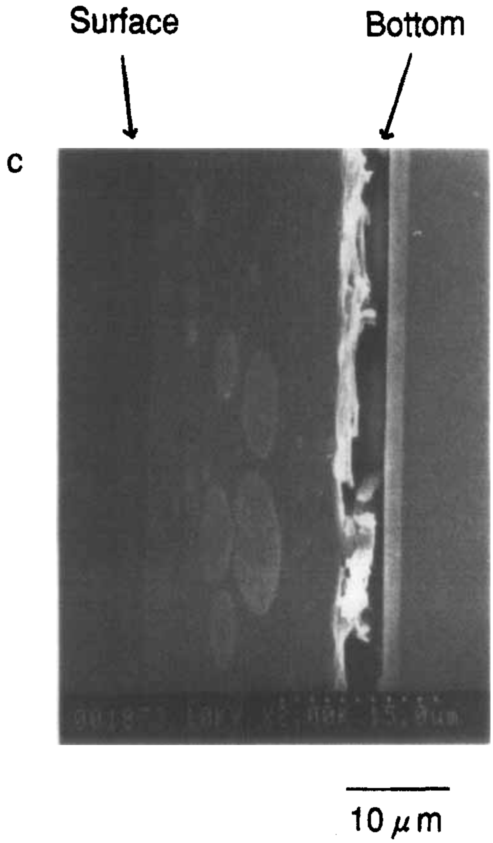

FIGURE 3 (Continued). (30/70).

Incidentally, since the P2-EHA/P(VDF-HFA) (30/70) blend exhibited the typical gradient structure, the tackiness betweeen the free surface and bottom sides is different. In fact, since the probe tack value of the bottom side is remarkably larger than that of the surface side in the 30/70 blend [19], we pointed out that the P2-EHA/P(VDF-HFA) (30/70) blend is applicable as a non-backing pressure sensitive adhesive (PSA) tape.

The transmission photographs of P2-EHA/P(VDF-HFA)(70/30), (50/50) and (30/70) blends are shown in Figure 4. The (70/30) blend exhibits a phase separated structure. The P(VDF-HFA) spherical domains are observed in the P2-EHA matrix and their diameters range

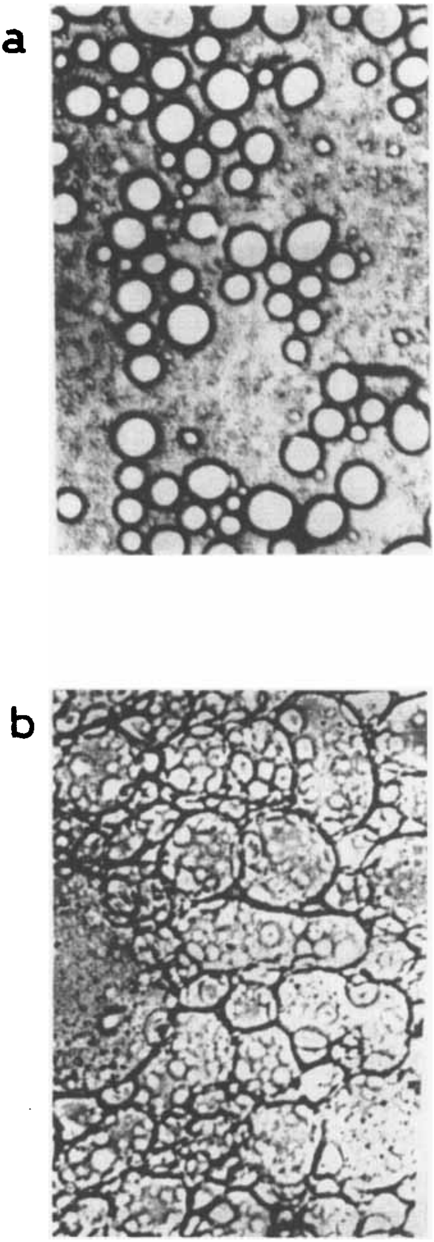

FIGURE 4 Optical photographs of P2-EHA/P(VDF-HFA) blends. P(VDF-HFA) content (wt%): a) 30, b) 50, c) 70.

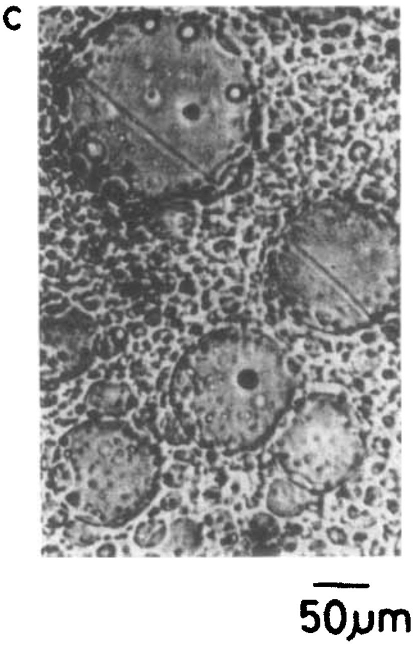

FIGURE 4 (Continued). (30/70).

from about 20–50 μm, similar to that observed by SEM. In the P2-EHA/P(VDF-HFA) (50/50) and (30/70) blends, the morphology observed by optical microscopy is similar to the morphology observed by SEM. In this section, it has been shown that the morphology is considerably changed by the blend ratio.

3.2. Eect of Solvent Evaporation Rate on Gradient Structure

In this section, the effect of the rate of solvent evaporation on the segregation structure of P2-EHA/P(VDF-HFA) (50/50) blend is examined. In the previous section, it was confirmed that these blends formed segregation and gradient structures. When the blend film is prepared by coating from THF solution, the rate of solvent evaporation can be controlled simply by the thickness (coating weight). In other words, the efficiency of solvent evaporation at the free surface side differs from that of the bottom side when blend film is thick. On the contrary, the rate of solvent evaporation at the free surface side is the same as that at the bottom side for a thin blend film.

Figure 5 shows SEM micrographs of cross sections of P2-EHA/P(VDF-HFA) (50/50) blends having various thickness (5 μm, 50 μm). The rate of solvent evaporation in different thickness films could not be estimated quantitatively; however, the rate should be different for each film. When the blend film was 5 μm thick, a fine, discrete phase-separated structure was observed. It is thought that the polymer structure is frozen in the formation of a gradient structure when the solvent evaporation time is very short. In the SEM photograph of the

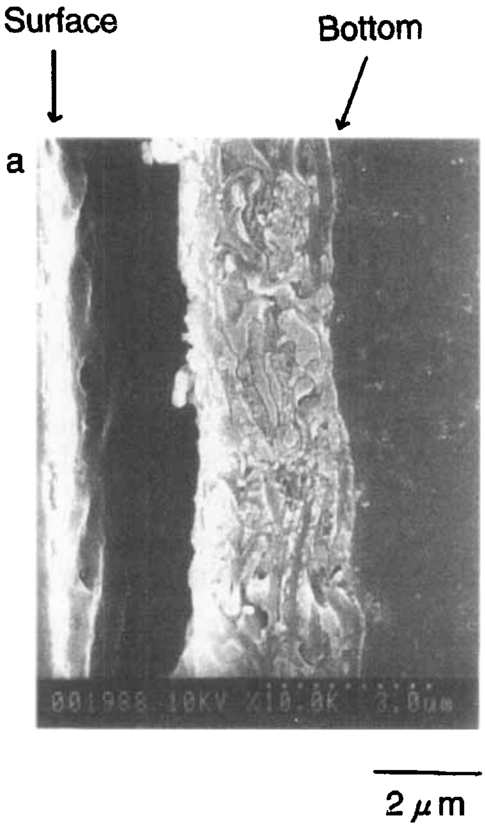

FIGURE 5 SEM micrographs of cross sections of films of P2-EHA/P(VDF-HFA) (50/50) blend having various thickness. (a) 5 μm, (b) 50 μm.

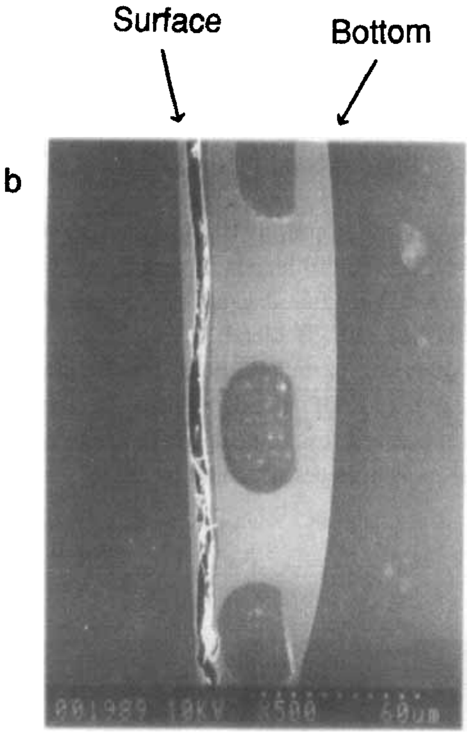

FIGURE 5 (Continued).

cross-sectional layer having 30 µm thickness, the P(VDF-HFA) and the P2-EHA layers segregate at the free surface side and bottom side, respectively, as shown in Figure 3b. The blend film prepared by this solvent evaporation condition could be utilized as a non-backing pressure sensitive adhesive tape. With this solvent evaporation rate, we assume that the formation of the characteristic segregation structure is strongly influenced by the rate of solvent evaporation, the rate of phase separation and the difference in surface tension between components. When the blend film thickness was 50 µm, the P2-EHA matrix and the P(VDF-HFA) spherical domain are observed. In general, the low viscosity component becomes the matrix phase. The viscosity of the acrylate polymer was remarkably lower than that of the P(VDF-HFA). In our previous study [14], the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) thick blend film exhibited a P(2EHA-AA-VAc) matrix and P(VDF-HFA) spherical domains. Therefore, it was thought that the morphology of the (50/50) blend having 50 μm thickness was strongly affected by the difference of viscosity between the components.

The transmission photographs from surface to bottom for the P2-EHA/P(VDF-HFA) (50/50) blends having 5 and 50 μm thickness are shown in Figure 6. Very fine discrete phases are observed in the P2-EHA/P(VDF-HFA) (50/50) blend having 5 μm thickness. On the other hand, spherical particles about 10–30 μm in diameter are observed in the (50/50) blend having 50 μm thickness. The morphologies observed by optical microscopy are similar to the cross-sectional morphologies obtained by SEM.

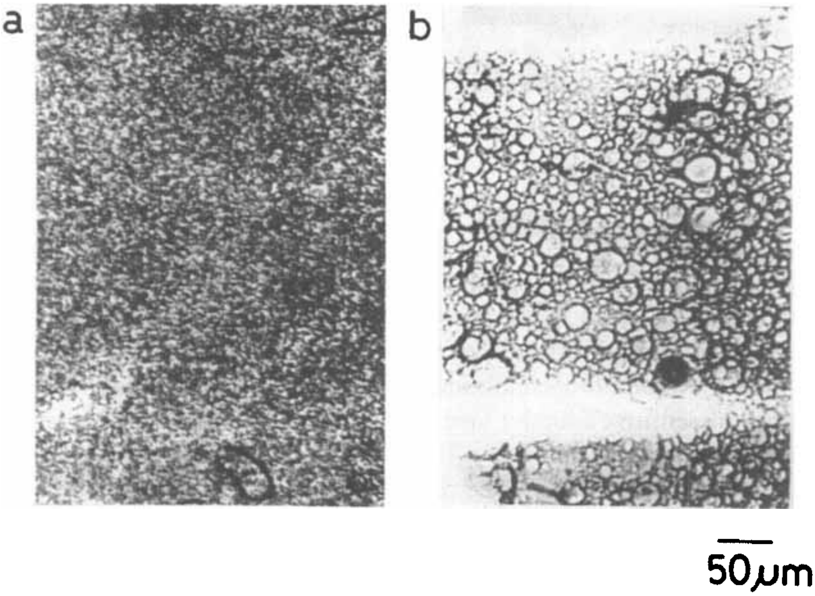

FIGURE 6 Optical photographs of P2-EHA/P(VDF-HFA) (50/50) blend having various thickness. a) 5 μm, b) 50 μm.

3.3. Effect of Molecular Weights on Gradient Structure

Finally, the influence of P2-EHA molecular weight on the gradient structure formation is discussed in this section. Figure 7 shows the cross-sectional morphology for low molecular weight P2-EHA-L/P(VDF-HFA) (50/50) blend having 5 μm thickness. The morphology of the P2-EHA-L/P(VDF-HFA) (50/50) blend is more homogeneous compared with that of the P2-EHA/P(VDF-HFA) (50/50) blend. In our previous DSC study [19], as double *Tg* peaks were observed in all P2-EHA-L, P2-EHA/P(VDF-HFA) blends, it was suggested that both P2-EHA's were immiscible with P(VDF-HFA) on the nm scale.

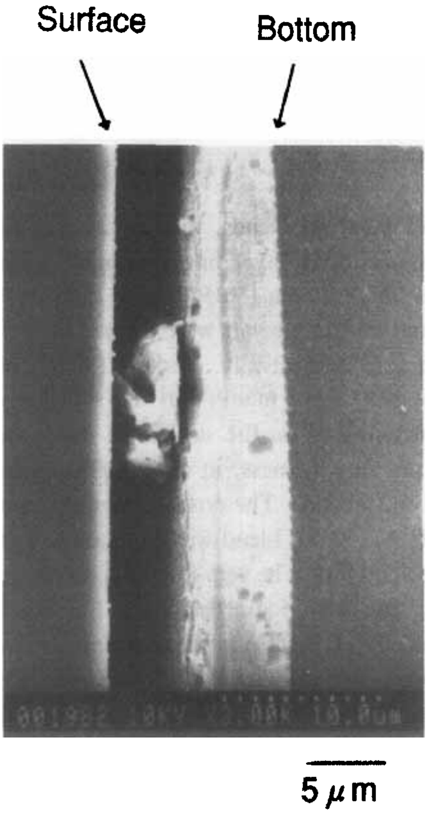

FIGURE 7 SEM micrograph of cross section of film of low molecular weight P2-EHA-L/ P(VDF-HFA) (50/50) blend having 5 μm in thickness.

However, from the results of sectional layer morphology, the affinity of P2-EHA-L/P(VDF-HFA) blends is better than that of P2-EHA/P(VDF-HFA) blends on the μm scale. Therefore, it is considered that the molecular weight may also influence the formation of segregation and gradient structures.

By the way, that gradient structure formed in the blends, we considered that the difference of probe tack between the free surface side and bottom side corresponded to a difference in dynamic mechanical properties. Thus, the dynamic mechanical properties in the vicinity of surface and bottom in the blends will be measured by means of a free decay oscillation method [9] in a future study. Finally, we would like to develop a non-backing PSA tape as a matter of practical utility.

4. CONCLUSIONS

In P2-EHA/P(VDF-HFA) blends, the surface and bottom compositions and cross-sectional layer morphologies were examined by ATR-FTIR and SEM. For a (50/50) blend having 30 μm thickness, P(VDF-HFA) and P2-EHA layers were formed at the free surface side and the bottom side, respectively. For the (30/70) blend, ellipsoidal domain particles of P2-EHA in a P(VDF-HFA) matrix were observed, and their size increased from the surface to the bottom. A P2-EHA layer, about 3 μm in thickness, in the (30/70) blend film was also observed at the bottom side. The cross-sectional morphology of a P2-EHA/P(VDF-HFA) (50/50) blend was dramatically influenced by the thickness of the blend film. The very fine discrete phases were observed for the (50/50) blend with 5 μm thickness. For the thick blend film (50 μm thickness), P(VDF-HFA) spherical domains were observed in the P2-EHA matrix. It is thought that the rates of solvent evaporation and of phase separation and the difference in viscosity between the components should influence the formation of the segregation and gradient structures [23]. Finally, it is suggested that the molecular weight also has very important effects on the sectional layer morphology.

Acknowledgments

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