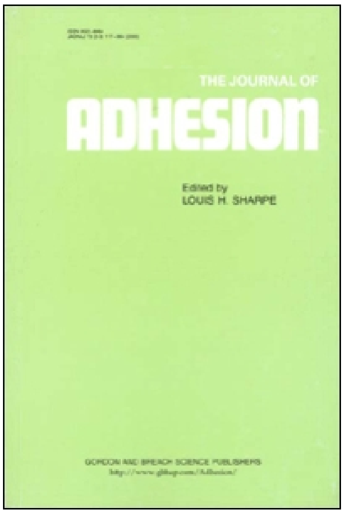
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Segregation Behavior Found in Poly(2-ethylhexyl acrylate)/Poly-(vinylidenefluoride-co-hexafluoro acetone) Blends

Yoshihisa Kano[a]; Yuichi Katayama[a]; Saburo Akiyama[a]; Yasuaki Kitazaki[b]; Tomoyuki Kasemura[c]
[a] Department of Chemical Science and Technology, Faculty of Technology, Tokyo, University of Agriculture and Technology, Tokyo, Japan [b] Nichiban Co. Ltd., Saitama, Japan [c] Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu, Japan

To cite this Article Kano, Yoshihisa , Katayama, Yuichi , Akiyama, Saburo , Kitazaki, Yasuaki and Kasemura, Tomoyuki(1997) 'Segregation Behavior Found in Poly(2-ethylhexyl acrylate)/Poly-(vinylidenefluoride-co-hexafluoro acetone) Blends', The Journal of Adhesion, 62: 1, 75 — 92

To link to this Article: DOI: 10.1080/00218469708014563

URL: http://dx.doi.org/10.1080/00218469708014563

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1997, Vol. 62, pp. 75–92
Reprints available directly from the publisher
Photocopying permitted by license only

Segregation Behavior Found in Poly(2-ethylhexyl acrylate)/Poly-(vinylidene fluoride-co-hexafluoro acetone) Blends

YOSHIHISA KANO[a], YUICHI KATAYAMA[a], SABURO AKIYAMA[a,*], YASUAKI KITAZAKI[b] and TOMOYUKI KASEMURA[c]

[a]*Department of Chemical Science and Technology, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo 184, Japan;*
[b]*Nichiban Co. Ltd., Iruma-shi, Saitama 350-12, Japan;*
[c]*Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu-shi, Gifu 501-11, Japan*

(Received 8 July 1996; In final form 30 August 1996)

The surface and bottom compositions of poly(2-ethylhexyl acrylate) (P2EHA)/poly-(vinylidene fluoride-co-hexafluoro acetone) [P(VDF-HFA)] blends were investigated by XPS analysis. In these blends, the enriched P(VDF-HFA) layer was observed from the top surface to a few nm depth, while the P2EHA component segregated at the bottom (the surface in contact with release liner). The probe tack values of the bottom side were remarkably larger than those of the surface side for the P2EHA/P(VDF-HFA) blends because the characteristic segregation structure was formed. We expected that the P2EHA/P(VDF-HFA) blends could be utilized as a non-backing pressure sensitive adhesive (PSA) tape. The effects of the film thickness of the blends and the molecular weights of P2EHA on the segregation structure were also examined. We thought that segregation behavior found in P2EHA/P(VDF-HFA) blends was caused by several factors, such as surface tension, miscibility, density, and rate of solvent casting.

Keywords: Poly(2-ethylhexyl acrylate); fluoro-copolymer; blends; segregation; XPS; surface tension; miscibility; pressure sensitive adhesive

---

[*] Corresponding author.

1. INTRODUCTION

Pressure sensitive adhesive (PSA) tape is prepared by coating an adhesive polymer solution onto a backing film. Generally, PSA tapes consisting of adhesive polymer and backing are used in various industries, such as label, decal, medical, electrical, packaging, and automobile [1–4]. If the coating process could be eliminated in the manufacture of PSA tapes, more efficient and less costly processes could result.

Recently, studies on surface segregation [5,6] and gradient structure [7] have been reported by many researchers. Surface segregation in polymer blends occurs when there is a difference of the surface tension between components. Usually the lower surface tension component is preferentially segregated on the surface of the blend film. For example, surface segregation of the lower surface tension component is found in binary polymer blends, such as poly(styrene)/poly(vinyl methyl ether) [5, 6, 8–10], poly(styrene)/poly(ethylene oxide) [11,12], poly(methyl methacrylate)/poly(vinyl chloride) [12, 13] and poly(methyl methacrylate)/poly(vinylidene fluoride) [14]. On the other hand, in the gradient structure, the concentration of one component in the mixture gradually changes from the surface to the bottom of the film. Functional gradient structures consisting of blends of metal and ceramics have been developed as aerospace materials. When surface segregation or gradient structure is applied to PSA tape, a non-backing PSA tape can be prepared.

We have examined the surface segregation or gradient structure formed 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 [15–20]. The surface and bottom compositions and depth profile of P(2EHA-AA-VAc)/P(VDF-HFA) blends were determined using XPS, ATR-FTIR and PAS-FTIR analyses. It was confirmed that the surface was enriched in P(VDF-HFA) and P(2EHA-AA-VAc) segregated at the bottom. For the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend, the P(2EHA-AA-VAc) layer of about 0.5μm in thickness at the bottom was also observed by TEM [18]. Thus, as the tackiness of bottom side was remarkably larger than that of the surface side for the (50/50) blend, we expected that the P(2EHA-AA-VAc)/P(VDF-HFA) blends could be utilized as a non-backing PSA tape. We presumed that this characteristic segregation structure resulted from such factors as miscibility, surface tension, desity, and rate of solvent evaporation.

In this study, the surface and bottom compositions of poly(2-ethyl hexyl acrylate) (P2EHA)/P(VDF-HFA) blends were determined by XPS analysis. To elucidate the factors influencing the formation of the segregation structure, the miscibility, surface tension and density were investigated. The effects of the molecular weights of P2EHA and the film thickness of the blends on the degree of segregation were also examined for P2EHA/P(VDF-HFA) blends.

2. EXPERIMENTAL

2.1. Materials

Two P2EHA were 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 P2EHA were determined using a Hitachi Co. Ltd. Liquid Chromatograph 655A-11 GPC system in 0.3 (wt%) THF solution. The molecular weights and distributions of P2EHA and P(VDF-HFA) are represented in Table I. When the P2EHA having low molecular weight was synthesized, lauryl mercaptan (0.1phr) as chain transfer agent was added. The P(VDF-HFA) (HFA content: 8.3 mol%) was supplied by Central Glass Co. Ltd. (Japan). Mole- cular weights of P(VDF-HFA) was determined using a TOSO Co., Ltd. CP8000 GPC system in 0.1 (wt%) solution.

TABLE I Molecular weights[a] of polymers

Sample	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
P2EHA-L	58000	231000	3.98
P2EHA-H	106000	813000	7.63
P(VDF-HFA)	12000	57000	4.94

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

2.2. Measurements

Films of P2EHA/P(VDF-HFA) blends were prepared on PET film and release liner [poly(dimethyl siloxane) (PDMS) having a critical surface tension of wetting, $\gamma \sim 24$ dyn/cm, is coated on the liner] using a hand coating bar, from 20 (wt%) THF solution. The films of P2EHA/P(VDF-HFA) blends were dried at 90°C for 1 min, then the coated films were permitted to stand at room temperature for at least 24 h. The specimens were further allowed to dry in a vacuum for 7days at 40°C. The P2EHA/P(VDF-HFA) blends were 10, 30 and 50 μm thick.

The XPS and probe tack measurements of the surface and bottom of the blend films were carried out on the blend surfaces in contact with air and release liner, respectively. It is well known that P2EHA is very tacky and very flexible. If the P2EHA component segregates at the bottom, the interface between the blends and common adherends, such as glass plate, stainless steel and plastic films, cannot be separated. Therefore, a release liner having lower release strength was used as an adherend.

To evaluate the miscibility between components, the glass transition temperatures (*Tg*) of P2EHA/P(VDF-HFA) blends were determined using a 910 DSC with Du Pont 990 system at a heating rate of 10°C/min under nitrogen gas.

The XPS spectra of the surface and bottom for P2EHA/P(VDF-HFA) blends were measured by a Shimadzu Manufacturing Ltd. ESCA model 850 X-ray photoelectron spectrometer (X-ray: Mg-Kα, voltage: 8 kV, current: 30 mA) using take-off angles of 15°, 30°, 45°, 60° and 90°.

FTIR spectra of P2EHA/P(VDF-HFA) blends were measured by the IR-RAS method using a JEOL Co. Ltd. JIR-WINSPEC50 FTIR analyzer.

The surface and bottom of the P2EHA-H/P(VDF-HFA) (30/70) blend was observed using a Hitachi Ltd. scanning electron microscope (SEM), Type S-2100. The surface and bottom of the (30/70) blend was treated by vacuum evaporation with Au using an Eiko Engineering Co. Ltd. IB-3 ion coater.

The tack was measured by means of the probe tack test at 23°C, using a Nichiban Co. Ltd. probe tack tester and a stainless steel probe. The thickness of the P2EHA/P(VDF-HFA) blends was 30 μm and the backing was PET film.

The density, ρ, of the polymers was measured using a Shimadzu Co. Ltd. gas pycnometer, Type accupyc 1330-01.

To calculate surface tension, γ, of P2EHA using state parameters, the thermal expansion coefficient, α, was estimated based on a dilatometric method. Temperature dependence of volume for P2EHA was measured using a PERKIN ELMER Co. Ltd. 7 series thermal analysis system with quartz glass. After samples and phenyl methyl silicone oil (Ohio Valley Speciality Chemical Inc., OV-17 25GMS) were put into the quartz glass and annealed for 2 h at 100°C to remove the thermal hysteresis, the annealed samples were cooled to room temperature without quenching. The heating rate was 2°C/min.

3. RESULTS AND DISCUSSION

The DSC thermograms of P2EHA-L/P(VDF-HFA) blends are shown in Figure 1. The signs -L and -H as shown in Table I mean low molecular weights and high molecular weights, respectively. The T_g peaks of

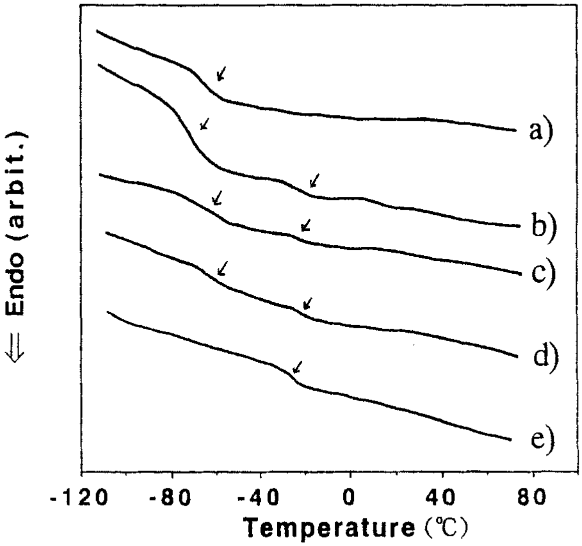


FIGURE 1 DSC thermograms of P2EHA-L/P(VDF-HFA) blends. P(VDF-HFA) content (wt%): a) 0, b) 30, c) 50, d) 70, and e) 100.

P2EHA-L and P(VDF-HFA) are observed at −50°C and −25°C, respectively. As double T_g peaks are clearly observed in all blends, the P2EHA-L is found to be immiscible with P(VDF-HFA). Double T_g peaks are also observed on the DSC thermograms of P2EHA-H/P(VDF-HFA) blends. Generally, the miscibility of acrylate polymer and fluoro polymer is enhanced with decreasing side chain length of the acrylate polymer because of the increased ease of making hydrogen bonds. We considered that the hydrogen bonding was occurring between acrylate carbonyl groups (C=O) and C—H groups in P(VDF-HFA)[21]. In our previous study [21,22], the miscibility between P(VDF-HFA) with both poly(ethylacrylate) (PEA) and poly-(butyl acrylate) (PBA) was examined by cloud point measurement. The PEA/P(VDF-HFA) blends were miscible at room temperature and exhibited LCST phase behavior with a critical temperature $Tc = 150°C$. On the other hand, PBA/P(VDF-HFA) blends were found to be inferior to PEA/P(VDF-HFA) blends in miscibility since the cloud points of PBA/P(VDF-HFA) blends were lower than those of PEA/P(VDF-HFA) blends. Therefore, the effect of the side chain length of the acrylate polymer on miscibility with P(VDF-HFA) was confirmed because P2EHA/P(VDF-HFA) blends were immiscible at room temperature. If the miscibility between acrylate polymer and P(VDF-HFA) greatly influences the surface segregation, the inclination of P2EHA/P(VDF-HFA) blends to surface segregate may be larger than that of P(VDF-HFA) and PEA or PBA blends.

The XPS spectra of C_{1S} at a 90° take-off angle for the P2EHA-L/P(VDF-HFA) (30/70) blend are shown in Figure 2. In the XPS spectrum of the surface side, the peaks based on CF_3 and CF_2 groups are apparently observed at 295.3 eV and 292.5 eV [23], respectively. The peaks at 286.5 eV and 288.1 eV correspond to CH_2 and COC groups, respectively. On the contrary, on the bottom side of the (30/70) blend, CF_3 and CF_2 peaks can hardly be detected in the XPS spectrum. At the top to a few nm depth, the P(VDF-HFA) and P2EHA-L are confirmed to be segregated at the surface side and the bottom side, respectively. Similar C_{1S} XPS spectra at a 90° take-off angle for the P2EHA-H/P(VDF-HFA) (30/70) blend are shown in Figure 3. The peaks at 290.5–291 eV, as shown in Figures 2 and 3, are related to the —CF— group [24]. The CF_3 and CF_2 peaks are also observed on the surface side, whereas these peaks can not be observed

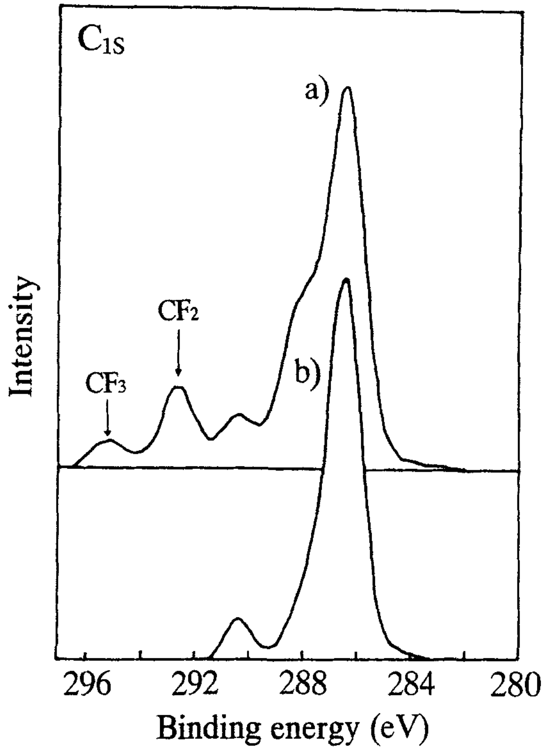


FIGURE 2 XPS spectra of C_{1s} for P2EHA-L/P(VDF-HFA) (30/70) blend using 90° take-off angle. The thickness of (30/70) blend is 30 μm. a) surface side, b) bottom side.

on the XPS spectrum of the bottom side. Particularly, the magnitude of the CF_3 and CF_2 peaks for the P2EHA-H/P(VDF-HFA) (30/70) blend is remarkably larger than those for the P2EHA-L/P(VDF-HFA) (30/70) blend. The influence of molecular weight of P2EHA on the inclination of P(VDF-HFA) to segregate on the surface are clearly suggested by these XPS results. However, this interpretation is made more difficult because it is well known that the low molecular component easily segregates on the surface [5, 6].

The relationship between the atomic ratio of F to C for the P2EHA/P(VDF-HFA) (30/70) blend and the take-off angle are shown in Figure 4. In both blends, the atomic ratio on the bottom side is much lower than that on the surface side and the atomic ratios do not change with increasing take-off angle (measuring depth) on the surface

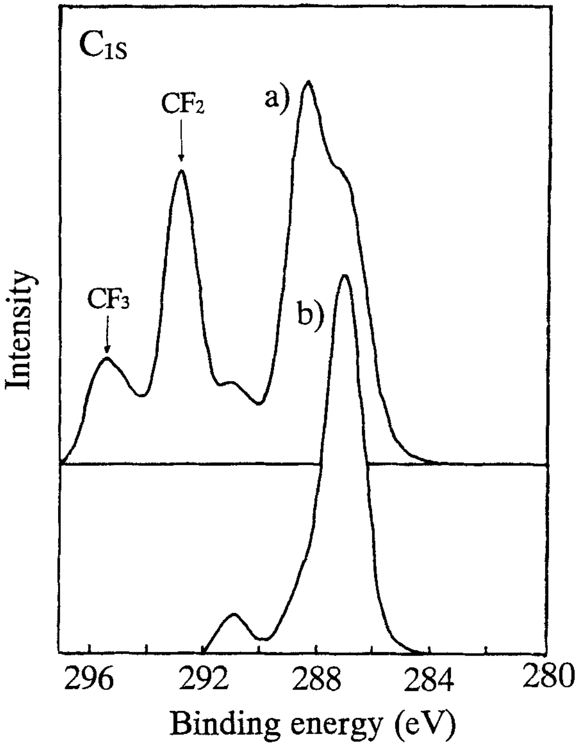


FIGURE 3 XPS spectra of C_{1S} for P2EHA-H/P(VDF-HFA) (30/70) blend using 90° take-off angle. The thickness of (30/70) blend is 30μm. a) surface side, b) bottom side.

side. For both P2EHA/P(VDF-HFA) (30/70) blends, it is presumed that the enriched P(VDF-HFA) layers exist from the top surface to a few nm in depth.

The bulk chemical compositions of P2EHA/P(VDF-HFA) blends were measured by an IR-RAS method. From the FTIR spectra of the P2EHA/P(VDF-HFA) blends, the C=O absorption of P2EHA and the C—F absorption of P(VDF-HFA) were observed at 870 cm^{-1} and 1730 cm^{-1}, respectively. 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 calculated. Figure 5 shows the absorbance ratio (I_{870}/I_{1730}) *vs.* P(VDF-HFA) weight content plots for P(2EHA-H/P(VDF-HFA) blends. The relationship between I_{870}/I_{1730} and P(VDF-HFA) weight content fits on a straight line by least squares

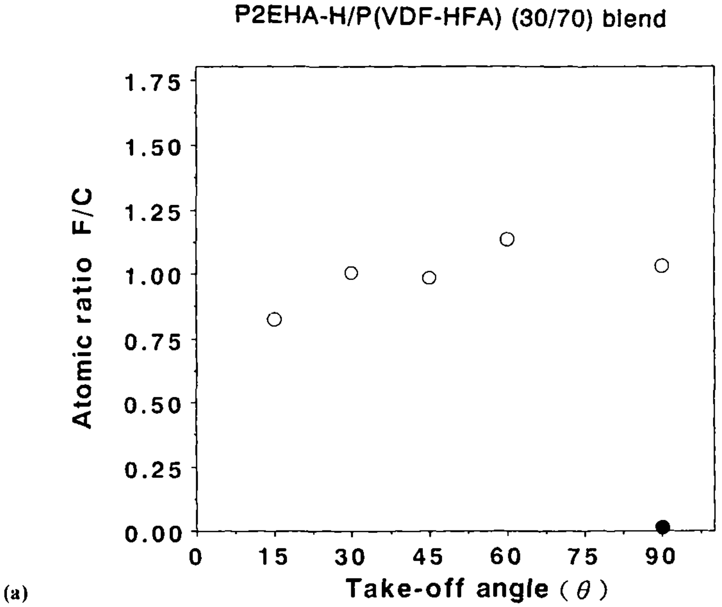


FIGURE 4 Relationship between atomic ratio F to C (F/C) and take-off angle (θ) for P2EHA/P(VDF-HFA) (30/70) blend. The thickness of (30/70) blend is 30 μm: a) high mol. wt. (P2EHA-H); b) low mol. wt. (P2EHA-L) ○) surface side, ●) bottom side.

analysis as the following equation:

$$\log\left(I_{870}/I_{1730}\right) = 0.0183\,(W_1) - 1.214 \tag{1}$$

where W_1 is the weight fraction of P(VDF-HFA). The relationship between I_{870}/I_{1730} and P(VDF-HFA) weight content for P2EHA-L/P(VDF-HFA) blends was also expressed by following equation:

$$\log(I_{870}/I_{1730}) = 0.0137(W_1) - 0.923 \tag{2}$$

Therefore, these relations fit the Lambert-Beer law.

On the other hand, the relationship between the atomic ratio (F/C) and P(VDF-HFA) weight content for the P2EHA-H/P(VDF-HFA) blends are shown in Figure 6. The F/C values for the surface are much larger than those for the bottom in P2EHA-H/P(VDF-HFA) (50/50), (30/70) and (10/90) blends. This behavior corresponds to the ATR-FTIR

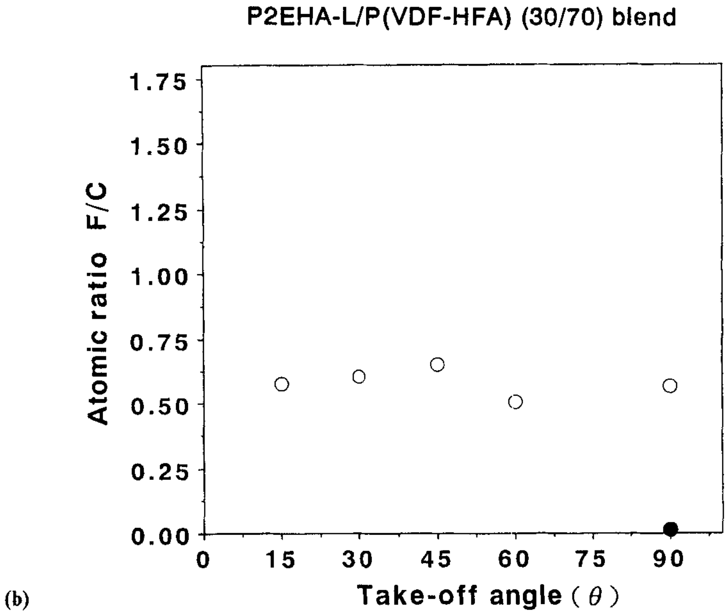


FIGURE 4 (Continued).

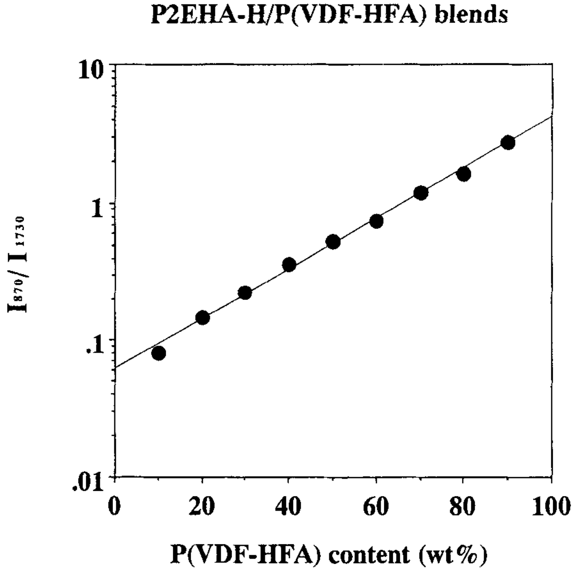


FIGURE 5 Relationship between absorbance ratio (I_{870}/I_{1730}) and P(VDF-HFA) content for P2EHA-H/P(VDF-HFA) blends by FTIR analysis.

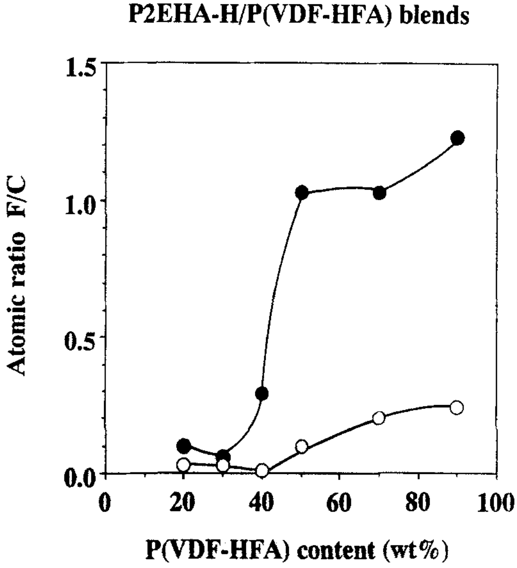


FIGURE 6 Relationship between F/C ratio obtained using 90° take-off angle and P(VDF-HFA) content for P2EHA-H/P(VDF-HFA) blends. The thickness of blends is 30 μm. ●) surface side, ○) bottom side.

results in our previous study [17]. We measured the probe tack of the surface and bottom for P2EHA-H/P(VDF-HFA) (50/50), (30/70) and (10/90) blends, since it is thought that the segregation behavior or gradient structure occurs in these blends.

The P2EHA is very tacky because of flexibility and having a low T_g, whereas P(VDF-HFA) is non-tacky. As P(VDF-HFA) and P2EHA segregated at the surface side and the bottom side, respectively, the tack value of the surface side should be less than that of the bottom side. The probe tack values of the surface side and bottom side in P2EHA/P(VDF-HFA) (50/50), (30/70) and (10/90) blends are shown in Table II. The probe tack values of the bottom side are larger than those of the surface side in both (50/50) and (30/70) blends. Especially, the difference of probe tack value between surface and bottom sides is very large in the P2EHA-H/P(VDF-HFA) (30/70) blend. Therefore, we expect that the P2EHA-H/P(VDF-HFA) (30/70) blend is most appropriate as a non-backing pressure sensitive adhesive (PSA) tape in these blends. In general, the tack value depends on the surface chemical compositions

TABLE II Probe tack (N/5mmϕ) of P2EHA/P(VDF-HFA) blends

P(VDF-HFA)	content (wt%)	50	70	90
P2EHA-L	Surface side	0.602	0.714	0.133
	Bottom side	1.571	1.418	0.184
P2EHA-H	Surface side	0.347	0.112	0.143
	Bottom side	1.959	3.531	0.133

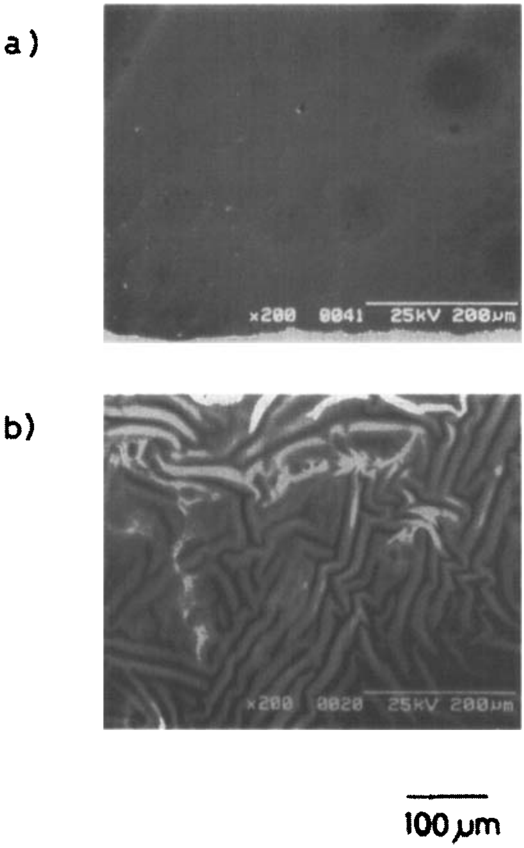


FIGURE 7 SEM photographs of P2EHA-H/P(VDF-HFA) (30/70) blend. The thickness of the (30/70) blend is 30 µm. a) surface side, b) bottom side.

and the bulk mechanical properties of the adhesive polymer. The P2EHA-H/P(VDF-HFA) (30/70) blend may exhibit favorable surface chemical composition and bulk mechanical properties for tackiness. In both P2EHA/P(VDF-HFA) (10/90) blends, probe tack values of both surface and bottom sides are very small. This is because the P2EHA/P(VDF-HFA) (10/90) blends have a high fluoro content even in the bottom side.

The surface and bottom morphologies of the P2EHA-H/P(VDF-HFA) (30/70) blend exhibiting the excellent tack property are shown in Figure 7. The surface of the (30/70) blend exhibits a smooth morphology, whereas the bottom exhibits a wrinkled morphology. In general, an acrylate polymer that is very flexible at room temperature often forms the wrinkled morphology, as revealed by vacuum evaporation with Au [18]. In fact, as the wrinkled morphology was observed for P(2EHA-AA-VAc) [25], it is considered that this morphology in this blend corresponds to the P2EHA-H component. Thus, by SEM analysis we can judge that the P(VDF-HFA) and P2EHA-H components are segregated at the surface and bottom, respectively.

Next, we explain why the characteristic segregation structures were formed in P2EHA/P(VDF-HFA) blends. In the previous studies [15–20], we reported that the segregation behavior or gradient structure, occurs as a result of various factors, such as surface tension, miscibility, density, and rate of solvent evaporation. Particularly, it was presumed that the gradient structure found in immiscible acrylate adhesive/fluoro-copolymer blends is strongly influenced by the rate of solvent evaporation [20]. Thus, the effects of surface tension, density, and rate of solvent evaporation on segregation behavior were investigated in P2EHA/P(VDF-HFA) blends.

The surface tension, γ, of P2EHA was estimated with the state parameters according to Patterson's theory [26] as follows:

$$\gamma = \tilde{\gamma} \cdot \kappa^{1/3} \cdot P^{*2/3} \cdot T^{*1/3} \tag{3}$$

$$\tilde{\gamma} = \{0.29 - (1 - \tilde{V}^{-1/3}) \times \ln[(\tilde{V}^{1/3} - 0.5)/(\tilde{V}^{1/3} - 1)]\}/\tilde{V}^{5/3} \tag{4}$$

where $\tilde{\gamma}$ is reduced surface tension, κ is the Boltzmann constant, P^* and T^* are the constant 1reference parameters for pressure and temperature, respectively, and $\tilde{V}$ is the reduced volume. These state parameters can be obtained from the thermal expansion coefficient, α, and solubility parameter, δ, as follows:

$$\tilde{V}=[(1+T\alpha)/(1+4T\alpha/3)]^{-3} \tag{5}$$

$$P^{*}=\tilde{V}^{2}Tk=(\tilde{V}\delta)^{2} \tag{6}$$

$$T^{*}=\tilde{V}^{4/3}T/(\tilde{V}^{1/3}-1) \tag{7}$$

where T is the absolute temperature. The α of P2EHA is obtained as the slope of specific volume V_{SP} *vs.* temperature plots according to the dilatometric method. The relationship between V_{SP} and temperature for P2EHA-H is shown in Figure 8. As shown in this figure, the V_{SP} *vs.* temperature plots fit a straight line derived by least squares analysis, as follows:

$$V_{SP}=6.33\times10^{-4}\cdot T+1.005 \quad (25\sim90^{\circ}\mathrm{C}) \tag{8}$$

The correlation coefficient of V_{SP} *vs* temperature plots for P2EHA-H was >0.99. On the other hand, the relationship between V_{SP} and temperature for P2EHA-L could be expressed with the following equation:

$$V_{SP}=6.23\times10^{-4}\cdot T+1.013 \quad (25\sim90^{\circ}\mathrm{C}) \tag{9}$$

The solubility parameter, δ, of P2EHA was calculated by the group contribution method by using Hoy's table [27]. In our previous study [28], the critical surface tension of P2EHA could not be estimated by the classical contact angle method because the contact angles of organic liquids on P2EHA films depended on elapsed time. Thus, the γ values in this study were calculated with state parameters. We have already confirmed that the theoretical method using Eqs. (3) and (4) provided a reasonable surface tension value in our previous papers [15, 29].

The surface tension, γ, and density of the polymers are presented in Table III. The γ values of P2EHA calculated by Eqs. (3) and (4) with the state parameters were about 35 (mN/m). As the γ values of P2EHA are larger than that of P(VDF-HFA), we judged that the

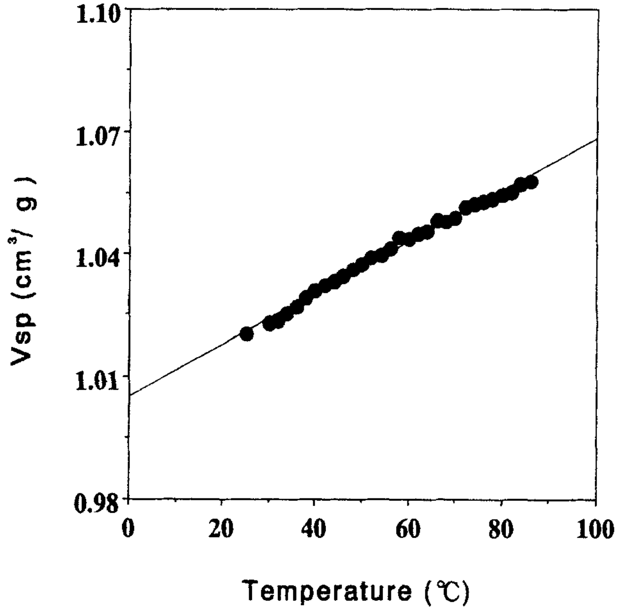


FIGURE 8 Relationship between specific volume, V_{sp}, and temperature for P2EHA-H.

TABLE III Surface tension, γ, and density, ρ, of the polymers

Sample	$\gamma\,(mN/m)$	$\rho\,(g/cm^3)$
P2EHA-L	35.6	0.98
P2EHA-H	35.1	0.97
P(VDF-HFA)	19.1	1.80

difference of surface tension, γ, between components strongly influences the segregation structure for P2EHA/P(VDF-HFA) blends. On the other hand, the densities, ρ, of the P2EHA are remarkably lower than that of P(VDF-HFA). If the difference of ρ has an effect on the segregation structure, P2EHA and P(VDF-HFA) should enrich the surface and bottom sides, respectively. However, in this study, P(VDF-HFA) segregated at the surface and P2EHA precipitated at the bottom.

Finally, the effect of the solvent evaporation rate on segregation behavior for P2EHA/P(VDF-HFA) blends was examined. When the blend film is prepared by the coating method from THF solution, the solvent evaporation rate can be controlled by the thickness of the applied film (coating weight). In other words, the solvent evaporation rate of a thin film is faster than that of a thick film. The relationships between F/C and film thickness for the P2EHA-H/P(VDF-HFA) (50/50) blend are shown in Figure 9. On the surface side, the maximum of F/C is observed at 30μm in thickness. However, on the bottom side, the F/C value does not change with film thickness. The inclination of the P(VDF-HFA) component to segregate on the surface of the blend film is also influenced by the rate of solvent evaporation (film thickness). In P2EHA-H/P(VDF-HFA) (50/50) blends of 10, 30 and 50μm in thickness, F/C values of the surface side are remarkably larger than those of the bottom side. We think that the characteristic segregation behavior found in P2EHA/P(VDF-HFA) blends occurs as a result of various factors, such as surface tension, miscibility, molecular weight, density, and rate of solvent casting. We

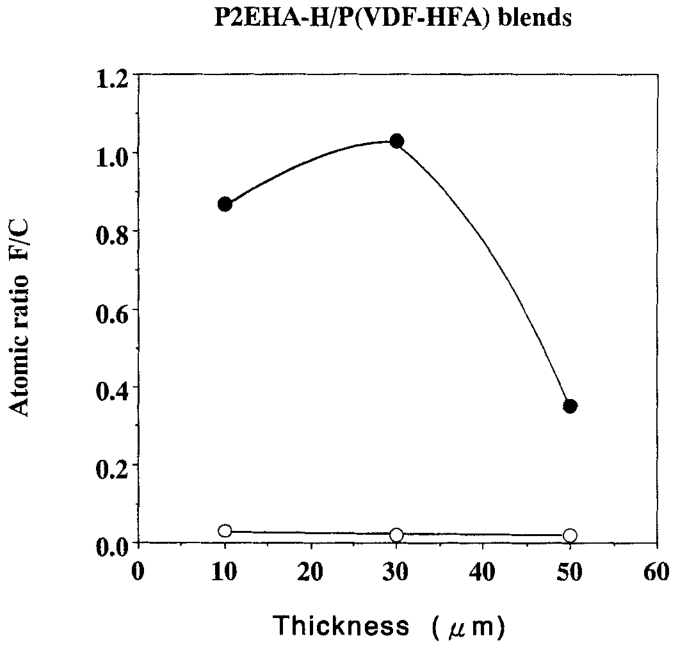


FIGURE 9 Plots of F/C ratio obtained 90° take-off angle *vs.* thickness of P2EHA-H/P(VDF-HFA) (50/50) blend. ●) surface side, ○) bottom side.

intend to investigate the sectional layering of P2EHA/P(VDF-HFA) blends by transmission electron microscopy (TEM) in future studies.

4. CONCLUSIONS

The segregation structure of P2EHA/P(VDF-HFA) blends was found by XPS analysis. In these blends, an enriched P(VDF-HFA) layer was observed at the surface side, whereas the P2EHA component segregated at the bottom. Because the characteristic segregation structure was formed, the probe tack values of the bottom side were remarkably larger than those of the surface side for the P2EHA/P(VDF-HFA) blends. We judged that the P2EHA-H/P(VDF-HFA) (30/70) blend is most appropriate as a non-backing PSA tape because the difference of probe tack between the surface and bottom is largest in this blend. The inclination to segregate of P(VDF-HFA) for the P2EHA-H series is found to be larger than that for the P2EHA-L series. From the film thickness *vs.* F/C plots obtained by XPS analysis, the maximum of the F/C value was obtained at 30μm thickness. We presumed that the segregation structure found in P2EHA/P(VDF-HFA) blends was influenced by several factors, such as surface tension, miscibility, molecular weight, density, and rate of solvent casting. This characteristic segregation structure should be examined sectionally by TEM for P2EHA/P(VDF-HFA) blends in future studies.

Acknowledgments

The authors express their thanks to Dr. K. Maeda of Central Glass Co. Ltd. for supplying P(VDF-HFA), Mr. Y. Fujita of Hitachi Kasei Polymer Co. Ltd. for the SEM observations, Shimadzu Co. Ltd. for density measurement and PERKIN ELMER Co. Ltd. for thermal analysis. One of the authors, Y. Kano, is a research fellow of the Japan Society for the Promotion of Science of the Ministry of Education.

References

[1] Satas, D., *Handbook of Pressure Sensitive Adhesive Technology*, 2nd ed. (Van Nostrand Reinhold, New York, 1989).
[2] Toyama, M., *Kanatsu Setchakuzai* (Kobunshi Kankokai, Kyoto, 1991).

[3] Fukuzawa, K., *Nenchaku Gijyutsu* (Kobunshi Kankokai, Kyoto, 1987).
[4] Krenceski, M. A., Johnson, J. F. and Temin, S. C., *Rev. Macromol. Chem. Phys.* **C26**(1), 143 (1986).
[5] Pan, D. H. and Prest Jr, W. M., *J. Appl. Phys.* **58**, 2861 (1985).
[6] Bhatia, Q. S., Pan, D. H. and Koberstein, J. T., *Macromolecules* **21**, 2166 (1988).
[7] Shioda, K., *Kagaku* **46**, 131 (1991).
[8] Cowie, J. M. G., Devlin, B. G. and McEwen, I. J., *Polymer* **34**, 501 (1993).
[9] Cowie, J. M. G., Devlin, B. G. and McEwen, I. J., *Polymer* **34**, 4130 (1993).
[10] Cowie, J. M. G., Devlin, B. G. and McEwen, I. J., *Macromolecules* **26**, 5628 (1993).
[11] Thomas, H. R. and O'Malley, J. J., *Macromolecules* **14**, 1316 (1981).
[12] Takahara, A., Korehisa, K., Takahashi, K. and Kajiyama, T., *Kobunshi Ronbunshu* **49**, 275 (1992).
[13] Schmidt, J. J., Gardella Jr, J. A. and Salvati Jr, L., *Macromolecules* **22**, 4489 (1989).
[14] Chujo, R., Nishi, T., Sumi, Y., Adachi, T., Naito, H. and Frentzel, H., *J. Polym. Sci., Polym. Lett. Ed.* **21**, 487 (1983).
[15] Kano, Y., Ishikura, K., Kawahara, S. and Akiyama, S., *Polym. J.* **24**, 135 (1992).
[16] Kano, Y., Akiyama, S. and Kasemura, T., *J. Appl. Polym. Sci.* **50**, 1619 (1993).
[17] Kano, Y., Akiyama, S., Kasemura, T. and Kobayashi, S., *Polym. J.* **27**, 339 (1995).
[18] Kano, Y., Akiyama, S., Sano, H. and Yui, H., *J. Electron Microsc.* **44**, 344 (1995).
[19] Kano, Y., Akiyama, S. and Kobayashi, S., *J. Adhesion* **35**, 261 (1996).
[20] Kano, Y., Akiyama, S., Sano, H. and Yui, H., *Nippon Setchaku Gakkaishi* **32**, 164 (1996).
[21] Kano, Y., Akiyama, S. and Kasemura, T., *Int. J. Adhesion and Adhesives* **15**, 219 (1995).
[22] Kano, Y., Akiyama, S. and Kasemura, T., *J. Adhesion Sci. Technol.* in press.
[23] Kasemura, T., Okada, Y. and Fujii, M., *Nippon Setchaku Gakkaishi* **26**, 106 (1990).
[24] Kano, Y., Akiyama, S. and Kasemura, T., *Nippon Setchaku Gakkaishi* **31**, 152 (1995).
[25] Kano, Y. and Akiyama, S., *Nippon Setchaku Gakkaishi* **26**, 173 (1990).
[26] Patterson, D. and Rastogi, A. K., *J. Phys. Chem.* **74**, 1067 (1970).
[27] Hoy, K. L., *J. Paint. Technol.* **42**, 76 (1970).
[28] Kano, Y. and Akiyama, S., *Polymer* **34**, 376 (1993).
[29] Kano, Y., Kawahara, S. and Akiyama, S., *Polym. Commun.* **33**, 3753 (1992).