

Surface Segregation and Tackiness in Blends of Poly(Vinylidene Fluoride-co-Hexafluoro Acetone) with Poly(2-Ethylhexyl Acrylate-co-Acrylic Acid-co-Vinyl Acetate)

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SYNOPSIS

In the blends of poly(vinylidene fluoride-co-hexafluoro acetone) P(VDF-HFA) with poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) P(2EHA-AA-VAc), the surface composition was investigated with X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), and the tackiness was evaluated using the J. Dow ball tack and dynamic mechanical analysis. From surface to a few nm in depth, in the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend, the variation in P(VDF-HFA) concentration, with increasing distance from the surface, was found by means of XPS with take-off angle dependence. It was confirmed that surface segregation of P(VDF-HFA) in the P(VDF-HFA)/P(2EHA-AA-VAc) blends took place. The value of J. Dow ball tack of the surface side in the P(VDF-HFA)/P(2EHA-AA-VAc) blends was smaller than that of bottom side in blends. The delineation of dynamic loss factor Δ vs. the temperature curve of the surface side in a (50/50) blend differed from that of the bottom side. It was suggested that surface segregation affected the difference in tackiness between the surface side and the bottom side. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Surface segregation has been found in polymer blends, graft copolymer, and block copolymer using X-ray photoelectron spectroscopy (XPS), ATR-FTIR, and scanning electron microscopy (SEM). The surface segregation in polymer blends will take place when the low surface tension component is preferentially enriched on the surface of blend films according to the difference between the surface tensions of components.^{1,2}

In the polystyrene/sulfone-siloxane-sulfone block copolymer blends, Patel et al.,³ using XPS, reported the surface segregation of a siloxane block to occur. Miki et al.⁴ also confirmed surface segre-

gation in blends of poly(trifluoroethyl methacrylate) with acrylate resin with XPS. Surface segregation phenomena have been applied in the medical,⁵ plastic,^{6,29} and adhesive⁷ fields.

In the pressure sensitive adhesives (PSA) industry, the surface segregation is important in controlling tackiness. Poly(vinylidene fluoride-co-hexafluoro acetone) P(VDF-HFA) possesses excellent water repellency, nontackiness, heating, weather, and chemical resistance properties.⁸ Maeda et al.⁹ investigated the microstructure and melting point, T_m , of P(VDF-HFA) using IR, NMR, and DSC. In the studies of miscibility between P(VDF-HFA) and various dissimilar polymers, Kobayashi et al.¹⁰ found the P(VDF-HFA)/poly(methyl methacrylate) blends to have a lower critical solution temperature at 220°C and the rapid reversible phase transition from the miscible to immiscible states (≤ 10 s). Akiyama and Hashimoto¹¹ also reported that P(VDF-

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HFA)/poly(carbonate) blends exhibited heterogeneous morphology and could be utilized as artificial marbles. Since the surface tension, γ_s , of P(VDF-HFA) was lower than that of poly(vinylidene fluoride),^{12,13} it is expected that P(VDF-HFA) could easily induce surface segregation in P(VDF-HFA)/dissimilar polymer blends. It is well known that the acrylate copolymers have excellent pressure sensitive adhesive properties because of their lower glass transition temperatures ($T_g \leq -20^\circ\text{C}$) and flexibility at room temperature. In particular, the high tackiness of the copolymer of 2-ethylhexyl acrylate, acrylic acid, and vinyl acetate P(2EHA-AA-VAc) is confirmed with the fluorescence probe method,¹⁴⁻¹⁶ contact angle method,¹⁷ and peeling morphology observation.¹⁸

In the blends of P(VDF-HFA) with P(2EHA-AA-VAc), surface segregation of P(VDF-HFA) occurred by the use of ATR-FTIR and SEM measurements.^{2,19-23} It was then suggested that surface segregation in the P(VDF-HFA)/P(2EHA-AA-VAc) blends was influenced by the immiscibility and the difference in the surface tension, γ_s , between components. In this study, surface segregation of the P(VDF-HFA)/P(2EHA-AA-VAc) blends was confirmed by XPS in surface analysis and tackiness, investigated using the J. Dow ball tack method and dynamic mechanical analysis.

EXPERIMENTAL

Materials

The P(VDF-HFA) was supplied by Central Glass Co., Ltd. The P(2EHA-AA-VAc) was prepared by means of 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. Molecular weights of the copolymers were detected using a Tosoh Co., Ltd., CP8000 GPC system

Table I Component and Molecular Weight* of Copolymers

P(2EHA-AA-VAc)	2-Ethylhexyl Acrylate/Acrylic Acid/Vinyl Acetate = 85/5/10 (mol %) $M_n = 46,000$; $M_w = 315,000$
P(VDF-HFA)	Vinylidene Fluoride/Hexafluoro Acetone = 91.6/8.4 (mol %) $M_n = 78,000$, $M_w = 200,000$

* Equivalent molecular weight to that of poly(styrene) by GPC.

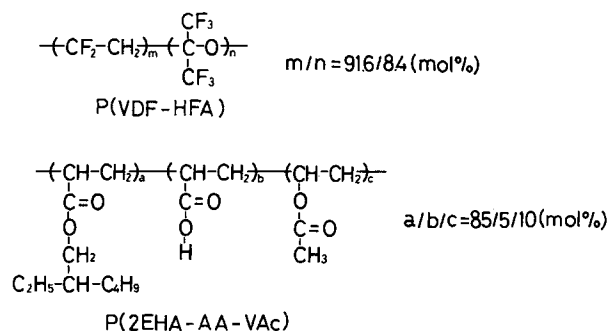


Figure 1 Structures of P(VDF-HFA) and P(2EHA-AA-VAc).

in 0.1 wt % THF solution. The composition and molecular weights of the copolymers are shown in Table I. The structures of P(VDF-HFA) and P(2EHA-AA-VAc), used in this study, are presented in Figure 1.

The blend samples in weight ratio were prepared using the knife coating system at 90°C for 60 s, in which 20 wt % THF solutions were coated onto the release liner {dimethyl siloxane [$\gamma_c = 24$ (dyncm⁻¹)], coated onto liner}. The γ_c is the critical surface tension. The films were seasoned at $23 \pm 3^\circ\text{C}$ and $65 \pm 5\%$ RH for 7 days to produce a dry coating film with 30 μm thickness. The surface of blend samples was covered by the release liner.

XPS

The components of surface of blends were analyzed with a Shimadzu Manufacturing, Ltd., ESCA model 850 X-ray photoelectron spectrometer (X-ray voltage: 8 kV, current: 30 mA), using take-off angles of 15° , 45° , and 90° . Because fluoride is an insulator, the charge shift occurs. Thus, the charge correction was carried out as the peak of F_{1s} appears at 689 eV.

The XPS measurements of the top and the bottom of blend films were performed on the blend surface, in contact with air, and were coated onto release liner, respectively. As the P(2EHA-AA-VAc) possesses high tackiness and flexibility, when the P(2EHA-AA-VAc) is enriched on the bottom side, the blend surface cannot be separated from a common substrate, such as a glass plate. Therefore, the XPS spectrum on the bottom side of the blend film was measured on the surface of a sample in contact with the release liner, having a lower release strength. Also, migration of the silicone polymer into the blend films was not detected on the Si_{2p} spectrum by XPS analysis.

SEM

The surface morphology of the P(VDF-HFA)/P(2EHA-AA-VAc) 50/50 blend was investigated with scanning electron microscopy (SEM). The surface of the blends was treated by vacuum evaporation with Au, using an Eiko Engineering Co., Ltd., IB-3 ion coater. The surface of the blend films was observed using a Hitachi, Ltd., SEM S-430.

Tack Measurement

The tack was measured by means of the J. Dow ball tack method [which obeyed the JIS-Z0237 (Japanese Industry Standard)] at 23°C. The ball was made of stainless steel. Both the surface side and the bottom side of P(VDF-HFA)/P(2EHA-AA-VAc) blends were evaluated with poly(ethylene terephthalate) (PET) film (thickness = 50 μm) as the backing.

Dynamic Mechanical Analysis

The dynamic loss factor, Δ , of P(VDF-HFA)/P(2EHA-AA-VAc) (50/50 by wt %) blend film is measured by means of the free decay oscillation method, using an Orientec Co., Ltd., rigid body pendulum-type dynamic mechanical property apparatus, model DDV-OPAIH, at $-100 \sim 50^\circ\text{C}$. The heating rate was $5^\circ\text{C}/\text{min}$. The dynamic mechanical property apparatus in this study is shown in Figure 2. The pendulum with the knife edge, put on in contact with the sample, was used for dynamic mechanical measurement. The dynamic mechanical model, between the sample and the pendulum, is shown in Figure 3. The dynamic mechanical properties are expressed with elasticity (spring) and viscosity (dashpot).

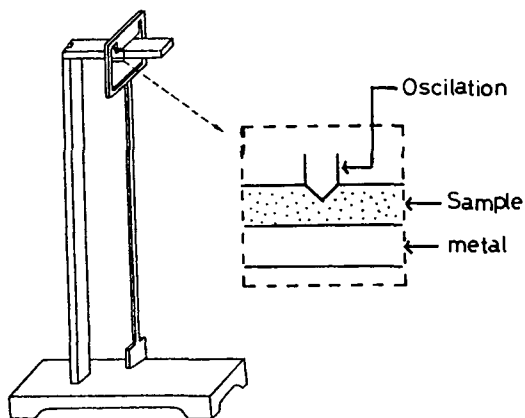


Figure 2 Rigid body pendulum-type dynamic mechanical property apparatus.

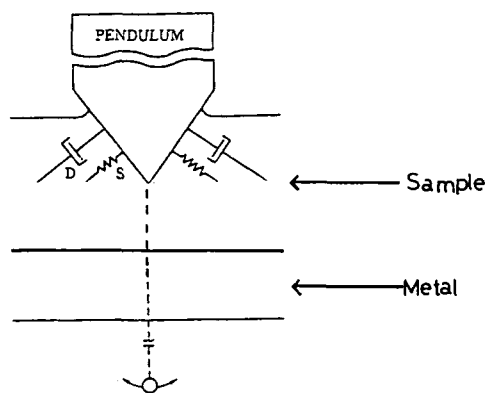


Figure 3 Schematic diagram of a dynamic mechanical model between the sample and the pendulum.

RESULTS AND DISCUSSION

In the previous article,² we investigated an absorbance ratio (I_{870}/I_{1730}) of P(VDF-HFA)/P(2EHA-AA-VAc) (50/50 in weight ratio) blend, by the use of ATR-FTIR with the several incidence angles, where I_{870} is the C-F absorption at 870 cm^{-1} for P(VDF-HFA) and I_{1730} is the C=O absorption at 1730 cm^{-1} for P(2EHA-AA-VAc). The I_{870}/I_{1730} of the surface side of the (50/50) blend decreased with decreasing incidence angle (increasing the measuring depth), whereas the I_{870}/I_{1730} of the bottom side of the (50/50) blend increased with decreasing incidence angle. It is suggested that P(VDF-HFA) is enriched at the top to $\sim 1\text{ }\mu\text{m}$ of the depth of the surface side, while P(2EHA-AA-VAc) is precipitated at the bottom to $\sim 1\text{ }\mu\text{m}$ of the depth of the sample. Therefore, we expected that surface segregation of P(VDF-HFA) took place in the P(VDF-HFA)/P(2EHA-AA-VAc) blends. It is well known that the surface segregation at the top $\sim 10\text{ nm}$ of the surface can be detected by means of XPS, using the take-off angle dependence. In this study, the surface segregation in the P(VDF-HFA)/P(2EHA-AA-VAc) blend was investigated with XPS analysis.

The XPS spectrum of the $\text{C}_{1\text{S}}$ of the surface in P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend, with 15° being the take-off angle, is shown in Figure 4. The peaks of CF_3 and CF_2 are observed at 295.3 eV and 292.5 eV (peak number: 4 and 3), respectively.²⁴ On the other hand, as the shoulder peak existed at 288 eV, the wave analysis of the XPS spectrum was carried out in the range of 284 to 290 eV. The peaks, based on CH_2 and COC, are then observed at 286.5 eV and 288.1 eV, respectively. It is assumed that the COC peak, at 288.1 eV, depends on the HFA group in P(VDF-HFA). According to the magnitude of the CF_3 peak at 295.3 eV and the

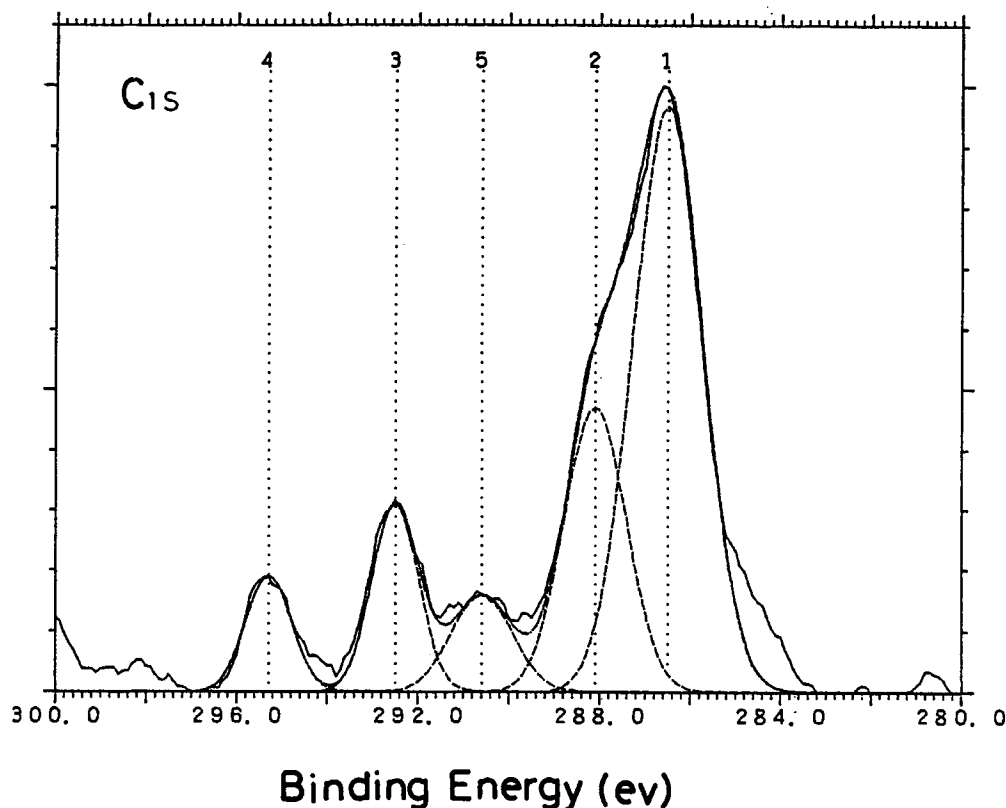


Figure 4 XPS spectrum of C_{1s} on the surface of a P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend at a take-off angle of $\theta = 15^\circ$.

CF_2 peak at 292.5 eV in the XPS spectrum of C_{1s} , it is expected that the surface segregation of P(VDF-HFA) in P(VDF-HFA)/P(2EHA-AA-VAc) blends is observed with take-off angle dependence. Figure 5 shows the XPS spectra of the C_{1s} of the surface side at 15° , 45° , and 90° being the take-off angle and shows the bottom side at a take-off angle of 90° in the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend. The relationship between the measuring depth, $d(\theta)$, and the take-off angle, θ , is expressed in the following equation:

$$d(\theta) = d \times \sin \theta \quad (1)$$

where d is the measuring depth at $\theta = 90^\circ$. Thus, the measuring depth at $\theta = 15^\circ$ is almost a quarter of the depth of $\theta = 90^\circ$. On the surface side of the (50/50) blend, the CF_3 peak (295.3 eV) and the CF_2 peak (292.5 eV) are observed in the XPS spectrum of C_{1s} , whereas the CF_3 and the CF_2 peaks on the XPS spectrum of C_{1s} cannot be detected for the bottom side of the (50/50) blend. For the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend, it is suggested that the P(VDF-HFA) component is segre-

gated at the top side to a few nm in depth of the surface side and the P(2EHA-AA-VAc) component is segregated at the top side to a few nm in depth of the bottom side. The magnitude of the CF_3 (295.3 eV) and the CF_2 (292.5 eV) peaks decreases with increasing take-off angle (increasing measuring depth). The depth dependence of the P(VDF-HFA) concentration is observed at the top side to a few nm in depth of the surface side. The relationship between the atomic ratio of F to C = 1 for P(VDF-HFA)/P(2EHA-AA-VAc) 50/50 blend and take-off angle is shown in Figure 6. The atomic ratio decreases with increasing take-off angle on the surface side and the atomic ratio on the bottom side is much too small, as compared to the atomic ratio on the surface side. The P(VDF-HFA) component was segregated on surface side and the P(2EHA-AA-VAc) component was precipitated on bottom side in the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend.

In the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend, surface morphology on the surface side and bottom side, under SEM observation, is shown in Figure 7. The photographs are not clear, however,

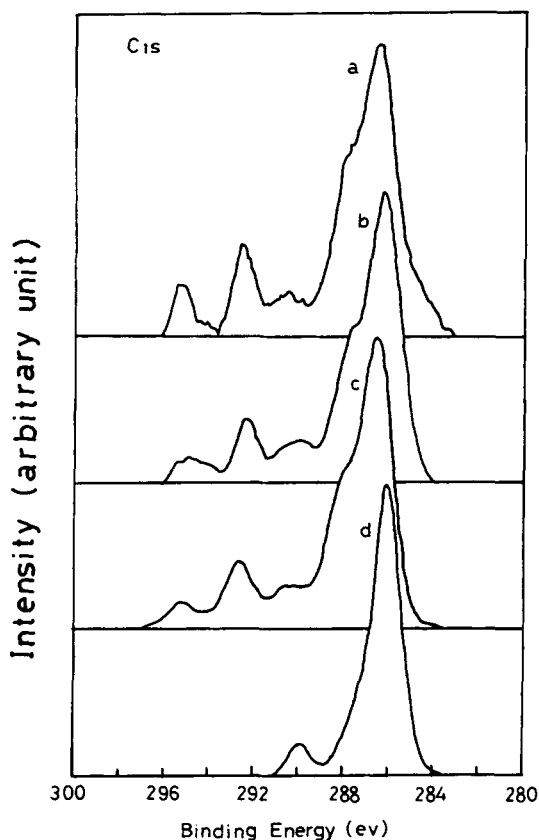


Figure 5 XPS spectra of C_{1s} for the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend. Take-off angle: (a) 15° , (b) 45° , (c) 90° on the surface side of the sample, and (d) 90° on the bottom side of sample.

the smooth morphology is observed on the surface side of blend film, while the wrinkled morphology is observed on the bottom side. In general, the flexible polymer at room temperature, such as acrylate polymer P(2EHA-AA-VAc), exhibits the wrinkled morphology on the SEM photogram.¹⁹ Consequently, in P(VDF-HFA)/P(2EHA-AA-VAc) blends, the P(2EHA-AA-VAc) component is precipitated on the bottom side and the P(VDF-HFA) component is enriched on the surface side, at the nm order, by use of the XPS and SEM methods. In our previous study,² the variation in the P(VDF-HFA) concentration, with increasing distance from the surface (μm order), was observed by the use of an ATR-FTIR with incidence angle dependence. It is assumed that the P(VDF-HFA) concentration of the P(VDF-HFA)/P(2EHA-AA-VAc) blend changes from surface to bottom. This interesting composition is called *functionally gradient material*.²⁵

We² explained that the surface segregation in P(VDF-HFA)/P(2EHA-AA-VAc) blends resulted

from the immiscibility of P(VDF-HFA) and P(2EHA-AA-VAc) and the difference in surface tension γ_s between components. The immiscibility in the P(VDF-HFA)/P(2EHA-AA-VAc) blends was predicted by the thermodynamic theoretical interpretation, using the interaction parameter χ_{12} , according to the solubility parameter δ^{22} and the state parameters, based on Prigogine-Flory-Patterson's theory,^{2,23} and the immiscibility was confirmed by experimental results, such as differential scanning calorimetry (DSC),²³ thermophotometry,²³ and SEM observation.¹⁹ On the other hand, the surface tension γ_s of copolymers was evaluated according to Prigogine's corresponding state theory, as extended for surfaces by Siow and Patterson,²⁶ according to the following equation

$$\tilde{\gamma}_s = \gamma_s/k^{1/3} \times P^{*2/3} \times T^{*1/3} \quad (2)$$

$$\tilde{\gamma}_s \times \tilde{v}^{5/3} = 0.29 - (1 - \tilde{v}^{-1/3})$$

$$\times \ln[(\tilde{v}^{1/3} - 0.5)/(\tilde{v}^{1/3} - 1)] \quad (3)$$

where $\tilde{\gamma}_s$ is the reduced surface tension, k is the Boltzmann constant, P^* is the constant reference pressure, T^* is the constant reference temperature, and \tilde{v} is the reduced volume. These parameters (T^* , P^* , \tilde{v}) are calculated by the following equations.

$$\tilde{v} = [(1 + T\alpha)/(1 + 4T\alpha/3)]^{-3} \quad (4)$$

$$P^* = \tilde{v}^2 T \kappa \quad (5)$$

$$T^* = \tilde{v}^{4/3} \times T/(\tilde{v}^{1/3} - 1) \quad (6)$$

The α and κ are the thermal expansion coefficient and the thermal pressure coefficient, respectively.

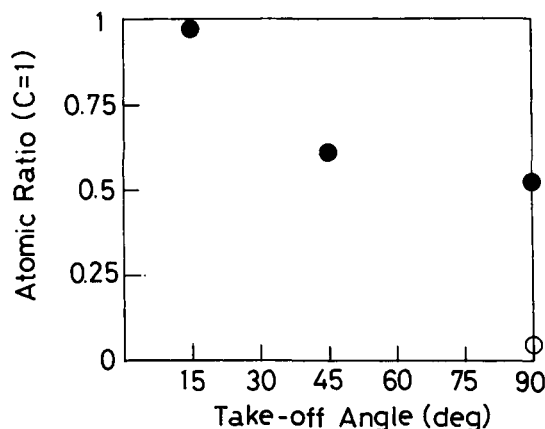


Figure 6 The relationship between atomic ratio F to $C = 1$ for the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend and take-off angle. (●) surface side, (○) bottom side.

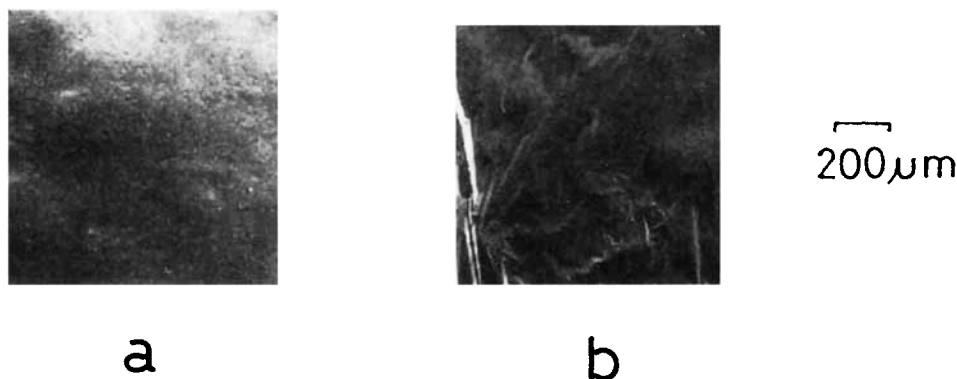


Figure 7 SEM photographs of the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend. (a) surface side, (b) bottom side.

The α is obtained as the slope of the specific volume vs. temperature plot and κ can be estimated with the solubility parameter δ as follows

$$\kappa = \delta^2/T \quad (7)$$

Using parameters (α , κ) of P(VDF-HFA) and P(2EHA-AA-VAc), obtained in our previous study,²³ and using eq. (2), the values of γ_S of P(VDF-HFA) and P(2EHA-AA-VAc) are calculated to be 19.4 and 28.3 (dyn/cm), respectively. Consequently, we assumed that surface segregation in the P(VDF-HFA)/P(2EHA-AA-VAc) blends took place, as the blend is immiscible and the difference in γ_S between components is large. Additionally, it is well known that a water and oil mixture separates because of the immiscibility and the difference in density ρ between components. We²² investigated the effect of density ρ on the surface segregation in P(VDF-HFA)/P(2EHA-AA-VAc) blends. The γ_S and density ρ of P(VDF-HFA) and P(2EHA-AA-VAc) are represented in Table II. The density of P(VDF-HFA) is greater than that of P(2EHA-AA-VAc). Thus, we presumed that the surface segregation in P(VDF-HFA)/P(2EHA-AA-VAc) blends was not influenced by the difference in ρ between components. Hariharan et al.²⁷ reported that surface segregation was influenced by the difference between the molecular weights of the polymer chains using the lattice model. They then presumed that the shorter chain component was pre-

Table II Surface Tension (γ_S) (dyn/cm) and Density (ρ) (g/cm³) of Copolymers

	γ_S	ρ
P(2EHA-AA-VAc)	28.3	0.89
P(VDF-HFA)	19.4	1.75

ferentially segregated on the surface because of the entropic effects. In our study the copolymers were not purified by the reprecipitation method. In future studies, the effect of molecular weight on the surface segregation in the P(VDF-HFA)/P(2EHA-AA-VAc) blends should be investigated.

The P(2EHA-AA-VAc) is tacky because of flexibility and low glass transition temperature ($T_g \leq -20^\circ\text{C}$), whereas the P(VDF-HFA) is nontacky. As P(VDF-HFA) segregates on the surface side and P(2EHA-AA-VAc) precipitates on the bottom side in the P(VDF-HFA)/P(2EHA-AA-VAc) blends, the tack value of the surface side should be less than that of the bottom side. This is of interest, because a backing of pressure-sensitive adhesive tape will be unnecessary if one takes advantage of this phenomena. In the P(VDF-HFA)/P(2EHA-AA-VAc) blends, the J. Dow ball tack of the surface side and the bottom side is presented in Table III. In the P(VDF-HFA)/P(2EHA-AA-VAc) blends with P(VDF-HFA) contents of 30, 40, and 50 wt %, the values of the J. Dow ball tack of the bottom side are larger than those of the surface side. Therefore, it is possible that the P(VDF-HFA)/P(2EHA-AA-VAc) blends can be used as a new type of pressure-sensitive adhesive. In general, the tack value is influenced by the dynamic mechanical properties of bulk and the tack value is dependent on the storage modulus G' , the loss modulus G'' and the glass transition temperature T_g .²⁸ The dynamic mechanical

Table III J. Dow Ball Tack of P(2EHA-AA-VAc)/P(VDF-HFA) Blends

P(VDF-HFA) Content (wt %)	30	40	50
Surface Side	2 >	2 >	2 >
Bottom Side	8	7	9

property in the vicinity of the surface side differs from that of the bottom side in the P(VDF-HFA)/P(2EHA-AA-VAc) blends. Figure 8 shows the temperature dependence of the dynamic loss factor, Δ , for the vicinity of the surface side and the bottom side in the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend by means of the free decay oscillation method. The delineation of the curve of loss factor, Δ , and temperature for the surface side differs from the bottom side remarkably. In addition, the loss factor, Δ , for the bottom side is larger than that for the surface side. Therefore, we expect that the difference in tack value, between the surface side and the bottom side, is influenced by the difference in the dynamic mechanical property. Since the P(VDF-HFA)/P(2EHA-AA-VAc) blends possess unique tackiness, the deepened interpretation of surface segregation is important, and we leave it for future study.

CONCLUSIONS

The surface segregation in the P(VDF-HFA)/P(2EHA-AA-VAc) 50/50 blend was determined by the XPS and SEM methods. The tack value of surface side is lower than that of bottom side in the P(VDF-HFA)/P(2EHA-AA-VAc) blends. It is suggested that the difference in tack value between the surface side and the bottom side was affected by dynamic mechanical property in the vicinity of the surface side and bottom side of blend films. We expect that the P(VDF-HFA)/P(2EHA-AA-VAc) blends will be utilized as a new type of pressure-sensitive adhesive tape, using no backing polymer.

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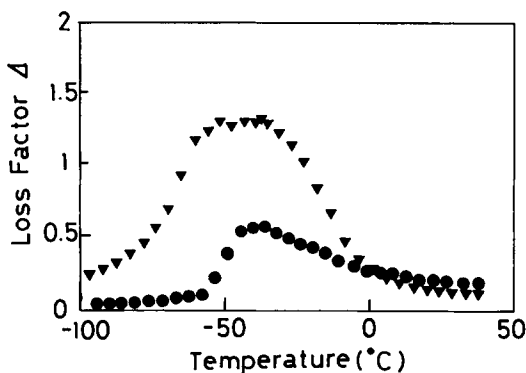


Figure 8 Temperature dependence of dynamic loss factor, Δ , for the P(VDF-HFA)/P(2EHA-AA-VAc) (50/50) blend. (●) surface side, (▼) bottom side.

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