

Analysis of Surface Segregation in Blends of Acrylate Copolymer with Fluoro-Copolymer

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ABSTRACT: The surface segregation 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 was investigated by FTIR in surface analysis, the miscibility of blends examined by both the Prigogine-Flory-Patterson's theory and the thermo-photometry and surface tension γ_s . From 1 to $\sim 2\mu\text{m}$ of the surface in P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend, the variation in P(VDF-HFA) concentration with increasing distance from the surface was observed by use of ATR-FTIR with incidence angle dependence. It was suggested that the surface segregation of P(VDF-HFA) took place in the blends. The P(2EHA-AA-VAc)/P(VDF-HFA) blends were revealed to be heterogeneous systems by the results of state parameters and thermo-photometry. The γ_s of P(2EHA-AA-VAc) and P(VDF-HFA) were evaluated according to Prigogine's corresponding state theory, as extended for surfaces by Patterson and co-workers. The values of γ_s of P(2EHA-AA-VAc) and P(VDF-HFA) were 28.3 and 20.4 (dyn cm^{-1}), respectively. Therefore, it was expected that surface segregation in P(2EHA-AA-VAc)/P(VDF-HFA) blends may occur, when the blend is immiscible and difference in γ_s between components is large.

KEY WORDS Surface Segregation / Poly(2-ethylhexyl acrylate-*co*-acrylic acid-*co*-vinyl acetate) / Poly(vinylidene fluoride-*co*-hexafluoro acetone) / ATR-FTIR / Blend / Incidence Angle / Miscibility / Prigogine-Flory-Patterson's Theory / Thermo-Photometry / Surface Tension /

In the last decades, research into morphology of immiscible polymer blend has been made in an effort to control the extent of dispersive phase structure. If a thin film of the immiscible blend is prepared with solvent casting from a polymer solution, the morphology of immiscible blend is affected by a rate of solvent casting, an affinity between the polymer and solvent, and a convection in the solution. For instance, the surface segregation of polymer blends is remarkable. The surface segregation occurs as the low surface tension component is preferentially enriched on the surface of film samples according to the difference between the

surface tensions of components¹⁻⁴ in polymer blends, *i.e.*, whether the polymer containing the plasticizer, the graft copolymer and the block copolymer. For example, blends of the silicone polymer (poly(dimethyl siloxane)) possessing the lower surface tension⁵ (the critical surface tension $\gamma_c \approx 24 (\text{dyn cm}^{-1})$) with various polymers underwent phase separation and the silicone polymer enriched on the surface of samples.² These blend samples have been utilized as materials with the various surface properties (water repellent, lower release strength, excellent lubrication).

In recent years, pressure sensitive adhesives

composed of acrylate copolymers have been utilized for the label, surgical dressing, marking film and double-faced tape.⁶ In general, the acrylate copolymer consists of an alkyl ester of 2-ethyl hexyl acrylate, co-monomer of vinyl acetate, and the polar monomer of acrylic acid. The alkyl ester has a low glass transition temperature ($T_g \leq -20^\circ\text{C}$) and the flexibility as a dominant component of pressure sensitive adhesives. The vinyl acetate provides the performance of adhesion and reduces the cohesion of acrylate copolymer.⁷ The acrylic acid provides both cohesion and physical crosslinking.⁸ The pressure sensitive adhesive properties have been controlled with the composition ratio of monomers in acrylate copolymer, the blending of the tackifying resins, and the adding of curing agents.⁷⁻¹⁰

The poly(vinylidene fluoride-*co*-hexafluoro acetone) P(VDF-HFA) possesses excellent properties of water repellent, non-tackiness, heating, weather and chemical protesting.²⁰ The micro structure of P(VDF-HFA) has been examined with IR, NMR, and DSC.¹¹ The miscibility of blends of P(VDF-HFA) with various polymer samples has been studied.¹²⁻¹⁴ Miyata and co-workers¹² found that the P(VDF-HFA)/poly(methyl methacrylate) blends had the lower critical solution temperature around 220°C and the reversible phase transition from the immiscible (cloudy) to miscible states (clear) took place with observable short time (≤ 10 s). Akiyama and Hashimoto¹⁴ made micro-dispersed plastic alloys with P(VDF-HFA) and poly(carbonate) systems in which the polish of silverwhite color was found. They pointed out that the P(VDF-HFA)/poly(carbonate) blends are the phase separated systems and can be utilized as artificial marbles.

In our previous studies, tackiness, viscoelasticity, phase morphology and surface structure of the P(2EHA-AA-VAc)/P(VDF-HFA) blends were investigated.¹⁵⁻²¹ It was suggested that the surface segregation of P(VDF-HFA) took place in the blends with

≥ 50 (wt%) P(VDF-HFA) content.^{17,18}

In the previous paper,²¹ surface segregation was investigated with the prediction of miscibility based on the Flory-Huggins-Scott theory, density and critical surface tension γ_c . The following results were obtained.

1) The P(2EHA-AA-VAc)/P(VDF-HFA) blends were found to be the phase separated systems.

2) The density increased with increasing P(VDF-HFA) content.

3) The value of γ_c of the P(VDF-HFA) was 22 (dyn cm⁻¹). However, since the contact angle of organic liquids on the P(2EHA-AA-VAc) surface decreased exponentially with the passage of contact time, it was impossible to evaluate the absolute value of γ_c .

We should confirm that the surface segregation of P(VDF-HFA) in the P(2EHA-AA-VAc)/P(VDF-HFA) blends is influenced by the variation in γ_c .

In this study, the surface segregation of the P(2EHA-AA-VAc)/P(VDF-HFA) blends was investigated by ATR-FTIR with an incidence angle dependence. The immiscibility of the P(2EHA-AA-VAc)/P(VDF-HFA) blends was expected by the Prigogine-Flory-Patterson's theory. The surface tensions γ_s of copolymers were estimated by Prigogine's corresponding state theory in thermodynamically equilibrium state.

THEORETICAL BACKGROUND

Flory^{22,23} derived the equation of state for the polymer fluid using the Prigogine's corresponding state theory²⁴ as follows:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3}-1} - \frac{1}{\tilde{V}\tilde{T}} \quad (1)$$

where \tilde{P} , \tilde{V} , and \tilde{T} represent the reduced pressure, the reduced volume and reduced temperature, respectively. The reduced parameters are calculated with the thermal expansion coefficient α , the isothermal compressibility β and the thermal pressure

coefficient κ as follows:

$$\tilde{V} = V_{sp}/V^* = \left(\frac{1 + T\alpha}{1 + 4T\alpha/3} \right)^{-3} \quad (2)$$

$$\tilde{P} = P/P^* = P/\tilde{V}^2 T\kappa = \beta P/\tilde{V}^2 T\alpha \quad (3)$$

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

$$V^* = Mv^* \quad (5)$$

The P^* , V^* , and T^* are constant reference parameters and M is the number of repeating units. The V_{sp} and v^* are the specific volume and occupied volume of segment, respectively. Therefore, thermodynamic conditions of polymer were experimentally evaluated by the corresponding state parameters α , β , and κ . The thermal pressure coefficient κ can be estimated from solubility parameter δ as follows²⁵:

$$\kappa = \delta^2/T \quad (6)$$

When Flory's equation of state is applied to the polymer blend, the chemical potential $\mu_1 - \mu_0$ for polymer 1 is expressed by the following equation.²⁶

$$\begin{aligned} \mu_1 - \mu_0 = & RT \{ \ln \phi_1 + (1 - m_1/m_2)\phi_2 \} \\ & + m_1 V_1^* (1/\tilde{V}) X_{12} \xi_2^2 \\ & + m_1 \varepsilon_1^* \{ (1/\tilde{V}_1) - (1/\tilde{V}) \} \\ & + \tilde{P}_1 (\tilde{V} - \tilde{V}_1) + 3\tilde{T}_1 \\ & \times \ln(\tilde{V}_1^{1/3} - 1)/(\tilde{V}^{1/3} - 1) \} \quad (7) \end{aligned}$$

for

$$\begin{aligned} X_{12} = & \frac{S_1}{2(V^*)^2} (\eta_{11} + \eta_{22} - \eta_{12}), \\ \xi_2 = & \frac{S_2 m_2 N_2}{S m N} \\ \varepsilon_1^* = & M_1/m_1 (P_1^* V_1^*{}_{,sp}), \quad \tilde{V} = V/V^* \quad (8) \end{aligned}$$

The \tilde{V}_1 and V_1^* are the reduced volume and constant reference volume for polymer 1. The \tilde{P}_1 and P_1^* are the reduced pressure and constant reference pressure for polymer 1. The \tilde{T}_1 is the reduced temperature for polymer 1. The R is the gas constant, ϕ_1 and ϕ_2 are volume

fractions of the polymers 1 and 2, N_2 is the number of polymer 2 in the system [$N = N_1 + N_2$, $m = m_1 x_1 + m_2 x_2$ (x , mol fraction), m_1 and m_2 are the degrees of polymerization for polymer 1 and polymer 2], M_1 is the molecular weight of polymer 1, S is contacting surface area, S_1 and S_2 are the surface areas of polymers 1 and 2, ε_1^* is the reference parameter of potential energy in polymer 1, $V_1^*{}_{,sp}$ is the occupied volume of segment in polymer 1 and ξ_2 is the site fraction of polymer 2. The X_{12} is the interaction parameter having the unit of pressure, where $X_{12} > 0$ and $X_{12} < 0$ show the repulsion system and attraction system, respectively.

$$X_{12} = q_1/2m_1 V_{seg}^* (\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}) \quad (9)$$

The V_{seg}^* is the occupied volume in segment, ε_{ij} is the interaction potential energy between the segments and q_1 expresses the surface area of polymer 1. The η_{ij} is calculated from ε_{ij} , which represents the mean intermolecular energy between segments as follows.

$$\varepsilon_{ij} = -\eta_{ij}/V \quad (10)$$

EXPERIMENTAL

Materials

The acrylate copolymer [P(2EHA-AA-VAc)] was prepared by means of a solution polymerization at 70°C for 7h, using benzoyl peroxide as an initiator and mixtures of ethyl acetate (95 wt%) with toluene (5 wt%) as a solvent. The fluoro-copolymer P(VDF-HFA) was supplied by Central Glass Co., Ltd. Molecular weights of the copolymers were detected using a TOSO Co., Ltd. CP8000 GPC system in 0.1 (wt%) THF solution. The compositions and molecular weights of copolymers are shown in Table I.

ATR-FTIR

The blend samples used in ATR-FTIR measurements were prepared by using LINTEC Corporation Universal Coating System

Table I. Components and molecular weights^a of copolymers

P(2EHA-AA-VAc)	2-Ethylhexyl acrylate/acrylic acid/vinyl acetate = 85/5/10 (mol%) $M_n = 46000$, $M_w = 315000$
P(VDF-HFA)	Vinylidene fluoride/hexafluoro acetone = 89.6/10.4 (mol%) $M_n = 35000$, $M_w = 162000$

^a Equivalent molecular weight to that of polystyrene by GPC.

at 90°C for 60 s, in which 20 (wt%) THF solutions were coated onto the substrate [poly(ethylene terephthalate) (PET) film; $\gamma_C \approx 43$ (dyn cm⁻¹) and release liner; silicone polymer (dimethyl siloxane, $\gamma_C \approx 24$ (dyn cm⁻¹)) was coated onto the PET film]. The films were seasoned at $23 \pm 3^\circ\text{C}$ and $65 \pm 5\%$ RH for 7 days to get a dry coating film with 30 μm thickness. The surface of blends were measured by using Nicolet Co. Ltd. 20SXB-FTIR spectrometer, with a KRS-5 as a prism and several incidence angles; 30°, 45°, 60°. The ATR-FTIR measurements of top side and bottom side of films were carried out on the blend surfaces in contact with air and release liner, respectively.

The acrylate copolymers, such as P(2EHA-AA-VAc), exhibit high tacky and are very flexible. Thus, when the P(2EHA-AA-VAc) is enriched on the bottom side, the blend surface cannot be separated from the common substrate as the glass plate. Therefore, the ATR-FTIR spectra on the bottom side of blend sample were measured on the surface of a sample in contact with release liner possessing the lower release strength. Also, the migration of the blend samples onto the release liner was not observed by scanning electron microscopy (SEM) at 1 μm order.

Dilatometer²⁷

The thermal expansion coefficient α of copolymers were measured based on the dilatometric method.²⁸ A Pyrex glass dilatometer (length ≈ 50 cm, thickness ≈ 3 mm, inside

diameter ≈ 2 mm) revised with the mercury was used. After the copolymers and mercury were put into the dilatometer, P(2EHA-AA-VAc) and P(VDF-HFA) in the dilatometer were annealed for 2 h at 70°C and 100°C, respectively. The dilatometer was placed in an oil, and the specific volumes of copolymers at the various temperatures (25~180°C) were measured. The heating rate was set 2°C min⁻¹.

Thermo-Photometry

The miscibility for the P(2EHA-AA-VAc)/P(VDF-HFA) blends was assessed with the hand-made thermo-photometer^{29,30} at 25~300°C. The heating rate was set 5°C min⁻¹.

RESULTS AND DISCUSSION

Surface Analysis of Blend Samples by ATR-FTIR Method

The FTIR spectra of P(2EHA-AA-VAc) and P(VDF-HFA) are shown in Figure 1. In the spectrum of P(2EHA-AA-VAc), stretching vibration peaks of C-H and C=O absorption are observed at 3000~2800 cm⁻¹ and both 1160 and 1730 cm⁻¹, respectively. On the other hand, the peaks of C-F absorption³¹ in the spectra of P(VDF-HFA) were observed at 870, 1200, and 1400 cm⁻¹. An absorbance ratio (I_{870}/I_{1730}) in the P(2EHA-AA-VAc)/P(VDF-HFA) blends is taken as a ratio of C=O absorption at 1730 cm⁻¹ (I_{1730}) for P(2EHA-AA-VAc) and C-F absorption at 870 cm⁻¹ (I_{870}) for P(VDF-HFA). In the previous paper,¹⁸ the concentration distribution of P(2EHA-AA-VAc) and P(VDF-HFA) on the blend film surface was analyzed by ATR-FTIR at incidence angle 45°. In blends with above ≥ 50 (wt%) P(VDF-HFA) content, we confirmed that the I_{870}/I_{1730} of blend coated onto the PET [blend surface in contact with air] was enormously larger than that coated onto the release liner [blend surface contacted with substrate]. It was suggested that the surface segregation of P(VDF-HFA) took place in the

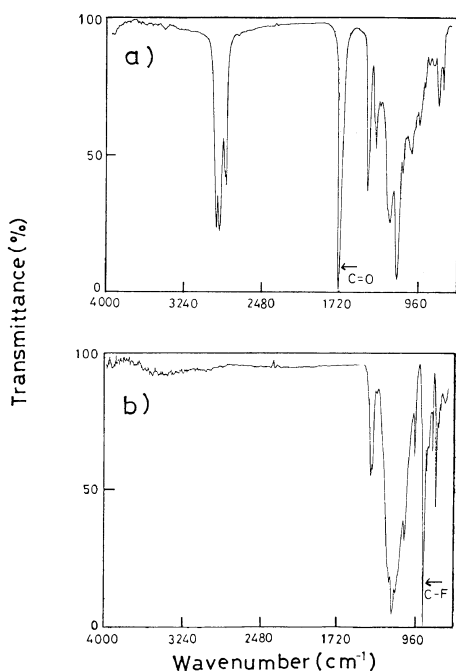


Figure 1. Infrared spectra of copolymers by ATR-FTIR method. a) P(2EHA-AA-VAc); b) P(VDF-HFA).

blends. In the present work, we evaluated the I_{870}/I_{1730} of the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50 by weight %) blend using ATR-FTIR with the several incidence angles (measuring depth). The difference of concentration between surface and bulk for the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend was investigated. The measuring depth (d_p) is expressed as the following equation³²:

$$d_p = \lambda / 2\pi n_A (\sin^2 \theta - n_{BA}^2)^{1/2} \quad (11)$$

where θ is the incidence angle, π is the circular constant, λ is the infrared ray absorption wave length, n_A and n_B are refractive indices for the prism and sample, respectively. The n_{BA} is the relative refractive indices n_B/n_A . Therefore, the measuring depth (d_p) for the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend is $60^\circ \rightarrow 1 \mu\text{m}$, $45^\circ \rightarrow 2 \mu\text{m}$, $30^\circ \rightarrow$ (cannot be calculated because of $\sin^2 \theta - n_{BA}^2 < 0$) using the refractive indices of the sample $n_B \approx 1.45$,³³ KRS-5 $n_A \approx 2.37$,³⁴ and $\lambda = 1300 \text{ cm}^{-1}$.

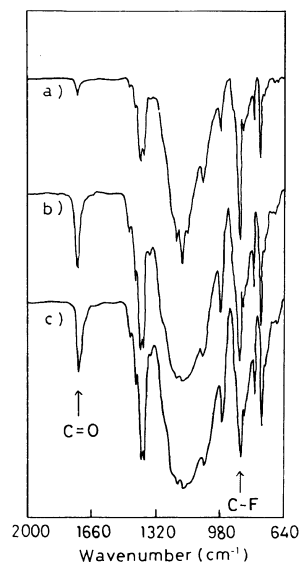


Figure 2. Infrared spectra for the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend surface in contact with air by ATR-FTIR method. Incidence angle: a) 60° ; b) 45° ; c) 30° .

The ATR-FTIR spectra of (50/50) blend coated onto the PET [blend surface in contact with air] at the incidence angles, 60° , 45° , and 30° are shown in Figure 2. The magnitude of C=O absorption I_{1730} increases with decreasing incidence angle, while the magnitude of C-F absorption I_{870} decreases with decreasing the incidence angle. On the other hand, Figure 3 shows the ATR-FTIR spectra at 60° , 45° , and 30° as the incidence angle for the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend coated onto the release liner [blend surface in contact with substrate]. The magnitude of I_{1730} decreases with decreasing the incidence angle, while the magnitude of I_{870} increases with decreasing incidence angle. It is suggested that in the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend, there is a difference of concentration between the surface and bulk. The relationship between the absorbance ratio I_{870}/I_{1730} and incidence angle for the (50/50) blend is shown in Figure 4. The I_{870}/I_{1730} of the blend surface in contact with air decreases with decreasing incidence angle

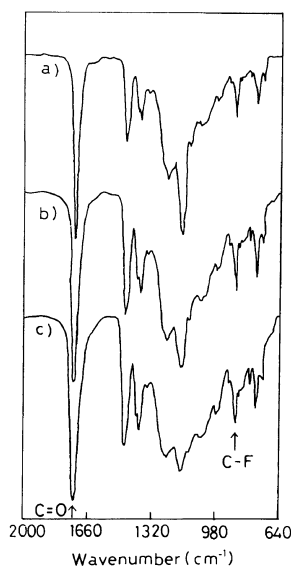


Figure 3. Infrared spectra for the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend surface in contact with substrate by ATR-FTIR method. Incidence angle: a) 60°; b) 45°; c) 30°.

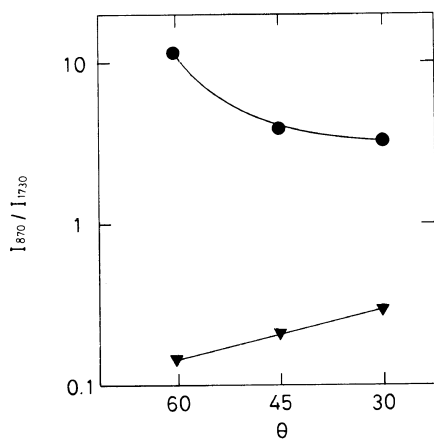


Figure 4. Relationship between I_{870}/I_{1730} and incidence angle θ for the P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend. ●, blend surface in contact with air; ▼, blend surface in contact with substrate.

(increasing the measuring depth), while the I_{870}/I_{1730} of the blend surface in contact with the substrate increases with decreasing incidence angle. The P(VDF-HFA) is segregated at the top to $\approx 1 \mu\text{m}$ depth of air facing surface film, while the P(2EHA-AA-VAc) is pre-

cipitated at the bottom to $\approx 1 \mu\text{m}$ depth of film. Thus, it is expected that the surface segregation of P(VDF-HFA) takes place in the P(2EHA-AA-VAc)/P(VDF-HFA) blends. In general, the surface segregation at the top $\approx 10 \text{ nm}$ surface is analyzed by means of X-ray photo-electron spectroscopy (XPS). Therefore, it is necessary that the thickness of surface segregation of the P(2EHA-AA-VAc)/P(VDF-HFA) blends should be confirmed with XPS. In the previous paper,¹⁸ the value of I_{870}/I_{1730} for blend surface contacted on air with the PET substrate corresponded to that of with the release liner substrate. We consider that the I_{870}/I_{1730} values are changeless because the value of surface tension of the air is much lower than that of the PET and release liner.

Thermodynamic Interpretation of Surface Segregation

Let us attempt a thermodynamic interpretation of miscibility and surface tension for the surface segregation. Patterson and Robard³⁵ reported that the χ_{12} parameter in Flory's equation of state was arranged as follows:

$$\frac{\chi_{12}}{M_1 V_1^*} = \frac{P_1^*}{RT_1^*} \left[\frac{\tilde{V}_1^{1/3}}{(\tilde{V}_1^{1/3} - 1)} (X_{12}/P_1^*) + \frac{\tilde{V}_1^{1/3}}{2\{(4/3) - \tilde{V}_1^{1/3}\}} \tau^2 \right] \quad (12)$$

The first term and second term in [] for eq 12 imply the interaction and free volume, respectively.

$$C_1/M_1 V_1^* = P_1^*/RT_1^*, \quad \tau = 1 - (T_1^*/T_2^*) \quad (13)$$

where M_1 is the molecular weight of polymer 1 and C_1 is the number of segments in polymer 1. If the term of free volume for $T_1^* \neq T_2^*$ using eq 12 and 13 is positive, the incompatibility of polymer blend might be predicted. For large positive value in the free volume term, phase separation of blend could appear to occur. The above Prigogine-Flory-Patterson's

theory gives the prediction of the miscibility as follows.³⁶

1) When χ_{12} is negative or very little positive, miscibility can be achieved for polymer blend. Both UCST and LCST curves in liquid-liquid phase diagram are observed, as χ_{12} is a little positive. When χ_{12} refers a positive value, a sandglass type phase boundary curve lain to overlap LCST and UCST curves is found in the phase diagram. In the χ_{12} being a negative value, the phase diagram indicates the LCST type.

2) The miscibility of polymer blend is enhanced with decreasing degree of polymerization.

3) The miscibility of polymers 1 and 2 is excellent when $T_1^* = T_2^*$ or $\alpha_1 = \alpha_2$.

4) As for $T_1^* > T_2^*$, $P_1^* > P_2^*$ and $\kappa_1 > \kappa_2$, the equation of state enables us to predict the miscibility for the blend.

5) When $T_1^* > T_2^*$ and $P_1^* > P_2^*$, polymer 1 is miscible with polymer 2, whereas polymer 1 is immiscible with polymer 2 as $T_1^* > T_2^*$ and $P_1^* < P_2^*$.

In this study, P(2EHA-AA-VAc) was immiscible with P(VDF-HFA), so that the films of P(2EHA-AA-VAc)/P(VDF-HFA) blends were opaque for an observable temperature range. In order to make the thermodynamic interpretation of surface segregation of P(VDF-HFA) in P(2EHA-AA-VAc)/P(VDF-HFA) blends, we have to evaluate the miscibility of blends by thermodynamics. According to Flory's equation of state theory, one must obtain specific volumes and thermal expansion coefficients α for components.

The specific volumes V_{SP} of P(2EHA-AA-VAc) against temperature are shown in Figure 5. In the plot of V_{SP} versus temperature, straight line was revealed by the least square approximation with higher correlation coefficient >0.999 . The slope of the line represents the thermal expansion coefficient α . The relationship between V_{SP} and temperature for P(2EHA-AA-VAc) is expressed by the least squares as follows:

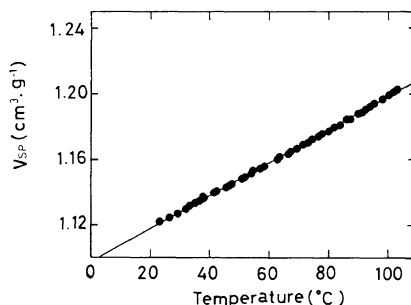


Figure 5. Relationship between specific volume V_{SP} and temperature for P(2EHA-AA-VAc).

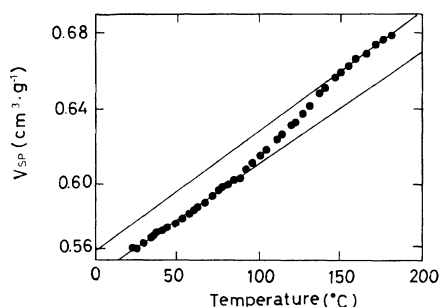


Figure 6. Relationship between specific volume V_{SP} and temperature for P(VDF-HFA).

$$V_{SP} = 1.002 \times 10^{-3} \cdot T(^{\circ}\text{C}) + 1.098 \quad (14)$$

In the previous paper,^{16,17,19} the glass transition temperature T_g of P(2EHA-AA-VAc) was observed at around -50°C by means of DSC,¹⁶ the rubber region could not be observed in the plot of the storage modulus G' and temperature¹⁷ and the amorphous state was confirmed using X-ray diffraction at 25°C .¹⁹ Thus, P(2EHA-AA-VAc) is the liquid state in the range between 25 and 100°C .

Figure 6 shows the V_{SP} against temperature for P(VDF-HFA). The phase transition of P(VDF-HFA) is observed in the range from 90 to 150°C . It is suggested that this phase transition is a solid-liquid phase transition, because this phase transition is the same feature as that around melting point of P(VDF-HFA) obtained by DSC.¹¹ On the other hand, we obtained T_g of P(VDF-HFA) $\approx -15^{\circ}\text{C}$ with DSC¹⁵ and the crystal peak for P(VDF-HFA)

Table II. State parameters for P(2EHA-AA-VAc) and P(VDF-HFA) at 25°C

Copolymer	V_{SP}	$\alpha \times 10^4$	κ	\bar{v}	V^*	T^*	P^*
	$\text{cm}^3 \text{g}^{-1}$	K^{-1}	$\text{J cm}^{-3} \cdot \text{K}^{-1}$		$\text{cm}^3 \text{g}^{-1}$	K	J cm^{-3}
P(2EHA-AA-VAc)	1.123	10.025	1.154	1.248	0.899	5220	536
P(VDF-HFA)	0.753	6.312	0.465	1.167	0.646	6940	189

was confirmed with X-ray diffraction at 25°C.¹⁹ In a plot of V_{SP} versus temperature for P(VDF-HFA), three states were defined: a solid state ($T=25\sim 90^\circ\text{C}$), solid-liquid transition state and liquid state ($150\sim 180^\circ\text{C}$). Two straight lines are drawn in the solid and liquid states by the following equations.

$$V_{SP} = 5.926 \times 10^{-4} \cdot T(^{\circ}\text{C}) + 0.552 \quad (25 \sim 90^{\circ}\text{C}) \quad (15)$$

$$V_{SP} = 6.312 \times 10^{-4} \cdot T(^{\circ}\text{C}) + 0.565 \quad (150 \sim 180^{\circ}\text{C}) \quad (16)$$

The correlation coefficient of the V_{SP} -Temperature line for P(VDF-HFA) was >0.999 .

In order to estimate P^* , the thermal pressure coefficient κ must be evaluated for components. In the case of polymers, κ can be estimated from solubility parameters δ , which themselves are related to the cohesive energy density. The solubility parameters at 25°C can be obtained from the group contributions by using Hoy's table.³⁷ The state parameters (V^* , T^* , P^*) at 25°C for P(2EHA-AA-VAc) and P(VDF-HFA) are shown in Table II. The state parameters for P(VDF-HFA) were calculated using eq 16 in the range from 150 to 180°C, because of the liquid state. Since the ratio of the thermal expansion coefficient α of P(2EHA-AA-VAc) and P(VDF-HFA) gives about 0.4, the value of T^* of P(2EHA-AA-VAc) is smaller than that of P(VDF-HFA). On the other hand, P^* of P(2EHA-AA-VAc) is larger than that of P(VDF-HFA).

As these results correspond to the prediction obtained with Prigogine-Flory-Patterson's theory [3), 4), and 5)], it is expected that the

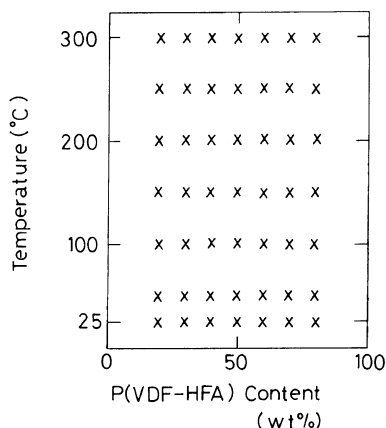


Figure 7. Compatibility of P(2EHA-AA-VAc)/P(VDF-HFA) blends with visual observation by thermo photometry. Heating rate is 5°C min^{-1} and the symbol \times refers opaque.

P(2EHA-AA-VAc)/P(VDF-HFA) blends are the heterogeneous systems. The P(2EHA-AA-VAc)/P(VDF-HFA) blends are immiscible by a thermo-photometer as shown in Figure 7. The films of the P(2EHA-AA-VAc)/P(VDF-HFA) blends are opaque in the temperature range between 25 and 300°C. The phase separation in the blends was shown by the Prigogine-Flory-Patterson's theory and thermo-photometer. We expect that the surface segregation for the P(2EHA-AA-VAc)/P(VDF-HFA) blends is caused by immiscibility on blending.

In order to make a thermodynamic interpretation of surface segregation, we evaluated the surface tension γ_s according to corresponding state theory. Patterson and co-workers³⁸⁻⁴⁰ estimated the surface tension of polymer with the state parameters. They

expressed the surface tension γ_s and reduced surface tension $\tilde{\gamma}_s$ using Prigogine's corresponding state theory as follows:

$$\tilde{\gamma}_s = \gamma_s / \gamma_s^* = \gamma_s / k^{1/3} \cdot P^{*2/3} \cdot T^{*1/3} \quad (17)$$

$$\tilde{\gamma}_s \cdot \tilde{V}^{5/3} = 0.29 - (1 - \tilde{V}^{-1/3}) \times \ln[(\tilde{V}^{1/3} - 0.5) / (\tilde{V}^{1/3} - 1)] \quad (18)$$

where k is the Boltzmann constant and γ_s^* is the constant reference parameter of the surface tension. Stewart and Frankenberg⁴¹ calculated γ_s of poly(ethylene) with the above equations and pointed out that eq 17 and 18 can be applied to the estimation of γ_s for polymers.

In this study, surface tensions γ_s of P(2EHA-AA-VAc) and P(VDF-HFA) were calculated by eq 17 and 18. The γ_s of P(2EHA-AA-VAc) and P(VDF-HFA) are shown in Table III. The γ_s of P(2EHA-AA-VAc) is equal to γ_s [poly(2-ethylhexyl acrylate) ≈ 28.0 (dyn cm⁻¹)] estimated by Kasemura *et al.*⁴² based on the sessile bubble method, because the P(2EHA-AA-VAc) consisted of 2-ethyl hexyl acrylate (85 mol%). On the other hand, γ_c of P(VDF-HFA) is closed to the critical surface tension γ_c value [= 22.7 (dyn cm⁻¹)] evaluated by the contact angle method in the previous paper.⁴³ Therefore, it is expected that the theoretical method using eq 17 and 18 provides a reasonable surface tension value. The γ_s of P(VDF-HFA) is smaller than that of P(2EHA-AA-VAc), and the difference in the value of γ_s between P(2EHA-AA-VAc) and P(VDF-HFA) is about 30%. It is expected that the surface segregation for P(2EHA-AA-VAc)/P(VDF-HFA) blends may be caused by the low surface tension of the P(VDF-HFA) component. Thus, if the extent of miscibility and the variation in γ_s for the various polymer blends can be controlled, new functional material with the surface segregation may be designed.

Recently, Hariharan *et al.*⁴⁴ investigated the effect of the difference between the molecular weights of the polymer chains on the surface

Table III. Surface tension of copolymers

Polymer	P(2EHA-AA-VAc)	P(VDF-HFA)
γ_s /dyn cm ⁻¹	28.3	20.4

segregation with the lattice model. They predicted that the shorter chains were preferentially enriched on the surface because of the entropic effects. In the miscible blends of polystyrene with deuterated polystyrene, Composto *et al.*⁴⁵ found that deuterated polystyrene was segregated on the surface of blend using a forward recoil spectrometry (FRES). In this study, the copolymers were not purified by the reprecipitation method. Therefore, the surface segregation may come from the casting condition of blend films (temperature, drying time), the distribution of molecular weight and difference in γ_s in a compatible system. Those elucidation is necessary and now be conducted.

CONCLUSION

The surface segregation of the P(2EHA-AA-VAc)/P(VDF-HFA) blends was suggested by surface analysis using ATR-FTIR. The immiscibility for the P(2EHA-AA-VAc)/P(VDF-HFA) blends was predicted by Prigogine-Flory-Patterson's theory and confirmed by thermo-photometry. According to the corresponding state theory, γ_s of P(2EHA-AA-VAc) and P(VDF-HFA) were 28.3 and 20.4 (dyn cm⁻¹), respectively. Consequently, the surface segregation of the P(2EHA-AA-VAc)/P(VDF-HFA) blends may be caused by immiscibility on blending and large difference in γ_s between components.

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