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Estimation of surface tension and surface segregation of poly(ethyl acrylate)/poly(vinylidene fluoride-*co*-hexafluoro acetone) blends

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The surface tensions (γ) of poly(ethyl acrylate) (PEA)/poly(vinylidene fluoride-*co*-hexafluoro acetone) (P(VDF–HFA)) blends were estimated by means of the contact angles with organic liquids Θ and bulk pressure–volume–temperature (PVT) properties. Two methods of estimation provided different γ values related to the surface segregation behaviour and the rearrangement. The change of γ against volume fraction of P(VDF–HFA) for PEA/P(VDF–HFA) blends was calculated using thermodynamic theory on γ of miscible polymer blends presented by Kammer. Finally, the surface segregation behaviour of P(VDF–HFA) component could also be expressed with the experimental data of γ and the Kammer theory. Copyright © 1996 Elsevier Science Ltd.

(Keywords: bulk PVT properties; contact angle; polymer blends)

INTRODUCTION

Evaluating surface tension for binary polymer blends is significantly important when surface composition differs from bulk composition. In general, this behaviour found in polymer blends is called 'surface segregation' or 'surface enrichment'. Surface segregation for polymer blends is caused by the difference of surface tension between pure components and the lower surface tension component enriched on the surface of blend films. The surface segregation behaviour for various blend systems has been found by several researchers. For example, Thomas and O'Malley[1] found surface segregation of the poly(styrene) component in poly(styrene)/poly(ethylene oxide) blends using X-ray photoelectron spectroscopy (X.p.s.). Similar results were reported for poly(vinyl methyl ether)/poly(styrene) blends[2] and poly(methyl methacrylate)/poly(vinyl chloride) blends[3]. We [4-8] have also found surface segregation in the blends of acrylate adhesive polymers with poly(vinylidene fluoride-*co*-hexafluoro acetone) (P(VDF–HFA)). The gradient structure was formed for immiscible blends of poly(2-ethylhexyl acrylate-*co*-acrylic acid-*co*-vinyl acetate) (P(2EHA–AA–VAc)) and P(VDF–HFA) since P(VDF–HFA) concentration gradually changed from the surface to the bottom[4–6]. On the other hand, the poly(ethyl acrylate) (PEA)/P(VDF–HFA) blends exhibited surface segregation behaviour from the top to about 10 nm depth[7,8]. From these results, we concluded that the formation of surface segregation depended on miscibility, and differences of surface tension and density between the components.

Recently, Kammer[9] presented the estimation method of surface tension for miscible polymer blends using thermodynamic theory. He calculated the surface tension of poly(vinyl methyl ether)/poly(styrene) miscible blends[2] exhibiting surface segregation. The calculated surface tensions of blends agree with the experimental data. Finally, the change of the calculated surface tension against volume fraction of poly(styrene) (higher surface tension component) for this blend system exhibited a concave curve. It is presumed that this concave curve is caused by surface segregation because surface tension is proportional to the volume fraction of the higher surface tension component at the surface for miscible blends. Thus, if the surface tension of the blends was known, the change of surface segregation behaviour against volume fraction of component could be estimated with surface tension in Kammer's thermodynamic theory.

It is well known that surface tension for polymer or polymer blends is evaluated by means of several methods, such as the weighted group contribution method[10], the calculation with solubility parameter δ[11], the contact angle method[12] and the estimation using bulk pressure–volume–temperature (PVT) properties[13]. In these methods, the contact angle method and estimation using bulk PVT properties is very useful to estimate the surface tension for miscible binary blends exhibiting surface segregation. The contact angle method gives information about the top surface. On the other hand, estimation using bulk PVT properties provides information about the bulk. Therefore, the comparison of surface tension values obtained by these two methods is significant to discussion of the surface segregation found in miscible polymer blends.

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In this paper, surface tensions of PEA/P(VDF–HFA) blends were estimated by two approaches, the contact angle method and bulk PVT properties. Next, the change of surface tension against volume fraction of P(VDF–HFA) for PEA/P(VDF–HFA) blends was calculated using Kammer's theory. Finally, the surface segregation behaviour found in PEA/P(VDF–HFA) blends was expressed with the experimental data of surface tension and Kammer's theory.

THEORETICAL BACKGROUND

Kammer[9] determined surface tension of miscible polymer blends according to thermodynamic theory. Firstly, the thermodynamic properties of bulk and surface are defined as the following equations, respectively:

$$\sum_{i=1}^{n} \phi_i d\mu_i = 0$$

$$A d\gamma = -\sum_{i=1}^{n} \phi_i^{s} d\mu_i \qquad (1)$$

where summations are over all components i. A is the molar surface area, γ is the surface tension, μ is the chemical potential of component i, ϕ_{i} is the volume fraction of component i and $\phi_{\mathrm{i}}^{\mathrm{s}}$ the volume fraction of component i in the surface region. Equations (1) are combined as follows:

$$A d\gamma = \sum_{i=1}^{n} (\phi_i - \phi_{\mathrm{i}}^{\mathrm{s}}) d\mu_{\mathrm{i}} \qquad (2)$$

The change of chemical potential in bulk concentrations is expressed as

$$d\mu_{\mathrm{i}} = \sum_{k=1}^{n-1} G_{ik} d\phi_{\mathrm{k}} \qquad (3)$$

The G_{ik} is the second derivative of the Gibbs free energy related to composition ϕ_i and ϕ_k. By inserting equation (3) into equation (2)

$$A d\gamma = \sum_{i,k=1}^{n-1} (\phi - \phi^{\mathrm{s}}) G_{\mathrm{ik}} d\phi_{\mathrm{k}} \qquad (4)$$

is obtained. For binary mixtures, equation (4) is simplified as follows:

$$A d\gamma = (\phi - \phi^{\mathrm{s}}) G_{11} d\phi_1 \qquad (5)$$

He assumed that the ϕ^{s} is expressed by a Langmuir-type function:

$$\phi^{\mathrm{s}} = k\phi/[1 + (k-1)\phi] \qquad (6)$$

where k is a constant. He also defined that the G_{11} is expressed with a Flory–Huggins type expression for the free energy[14] in binary polymer blends.

$$G_{11}/RT = 1/[r_1\phi] + 1/[r_2(1-\phi)] - 2X \qquad (7)$$

where X is a free energy parameter[14] calculated with the bulk PVT parameters and r_i the degree of polymerization of component i. After equations (5) and (6) are inserted into equation (7), the integrated equation is expressed as follows:

$$A(\gamma - \gamma_2)/RT = B\ln[1 - (1-k)\phi] + \phi(1/r_1 - 1/r_2) - X\phi[2k/(1-k) + \phi] \qquad (8)$$

$$B = -(r_1 - r_2 k)/[r_1 r_2 (1-k)] - 2Xk/(1-k)^2 \qquad (9)$$

The surface tension of blend is also expressed as the following equation

$$\gamma = \gamma_1\phi + \gamma_2(1-\phi) + \Delta\gamma \qquad (10)$$

Eventually, Kammer determines the surface tension of miscible polymer blend as the following equation

$$A\Delta\gamma/RT = B[\ln\{1 - (1-k)\phi\} - \phi\ln k] + X\phi(1-\phi) \qquad (11)$$

EXPERIMENTAL

The PEA was prepared by the solution polymerization method at 70°C for 8 h using benzoyl peroxide as an initiator in the solvent mixture of ethyl acetate (95 wt%) and toluene (5 wt%). The number–average molecular weight $\bar{M}_{\mathrm{n}}$ and weight–number molecular weight $\bar{M}_{\mathrm{w}}$ of PEA were 46 700 and 312 000, respectively. The P(VDF–HFA) with 8 mol% HFA content was supplied by Central Glass Co. Ltd. (Japan). The $\bar{M}_{\mathrm{n}}$ and $\bar{M}_{\mathrm{w}}$ of P(VDF–HFA) were 52 000 and 130 000, respectively. The PEA/P(VDF–HFA) blends were stirred overnight in about 20 wt% tetrahydrofuran (THF) solution in the various ratios. The blend films used for contact angle measurement were prepared by solution casting onto poly(ethylene terephthalate) (PET) film using the knife coating system. After the blend films were dried at 90°C for 2 min, they were kept at 23 ± 3°C, and 65 ± 5% relative humidity (RH) for a week. The blends were 30 μm thick in their dry state.

In our previous study[8], the PEA/P(VDF–HFA) blends exhibited LCST (least critical solution temperature) phase behaviour with a critical temperature of 150°C. Since the transition temperature from miscible to immiscible (T_{d}) was higher than the melting temperature ($T_{\mathrm{m}} = 110$–130°C), the PEA/P(VDF–HFA) blends were a liquid–liquid phase separation system. Therefore, we concluded that the PEA/P(VDF–HFA) blends are not crystalline and are liquid state at 140°C. Thus, the samples for contact angle measurement and X.p.s. analysis were further allowed to dry in a vacuum for 7 days at 40–60°C, and then samples were annealed at 140°C for 1 h and quenched in liquid nitrogen. As all PEA/P(VDF–HFA) blends were liquid state at 140°C, we can discuss the surface segregation by comparing the results of X.p.s. with the surface tension for the liquid state.

The surface of PEA/P(VDF–HFA) blends was analysed with Shimadzu Manufacturing Ltd ESCA model 850 X-ray photoelectron spectrometer (X-ray: MgK α-ray, voltage: 8 kV, current: 30 mA) using take-off angles of 15° and 90°.

The contact angles of various organic liquids on blend films were measured by Kyowa Kaimen Kagaku Co. Ltd. contact angle measurement apparatus type CA-D. 1.5–2.0 mm diameter drops of liquids were deposited using a microsyringe on the surface of blend films at 20°C. The surface tensions γ_{L} and the polar parts of liquid's surface tension $X_{\mathrm{L}}^{\mathrm{P}}$ used in this study are listed in

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

Liquid series[b]	Liquid	γ_L^d	γ_L^p	γ_L^h	γ_L	X_L^p[c]
	n-Nonane	22.9	0.0	0.0	22.9	0.0
	n-Decane	23.9	0.0	0.0	23.9	0.0
D	*n*-Undecane	24.7	0.0	0.0	24.7	0.0
	n-Dodecane	25.4	0.0	0.0	25.4	0.0
	n-Tetradecane	26.7	0.0	0.0	26.7	0.0
	n-Hexadecane	27.6	0.0	0.0	27.6	0.0
	trans-Decalin	29.9	0.0	0.0	29.9	0.0
	cis-Decalin	32.2	0.0	0.0	32.2	0.0
H	Dipropyleneglycol	29.4	0.0	4.5	33.9	0.133
	1,3-Butanediol[d,e]	–	–	–	37.8	–
	Polyethyleneglycol	29.9	0.1	13.5	43.5	0.313
	Diethyleneglycol	31.7	0.0	12.7	44.4	0.286
	Ethyleneglycol	30.1	0.0	17.6	47.7	0.369
	Thiodiglycol	39.2	1.4	13.4	54.0	0.274

[a] Y. Kitazaki and T. Hata, *Nippon Setchaku Gakkaishi* 1972, **8,** 133

[b] D: Dispersion liquid, H: Hydrogen bonding liquid

[c] The X_L^p is calculated with: $X_L^p = 1 - (\gamma_L^d/\gamma_L)$

[d] Yozai Handbook, p. 407. Kodansha, Tokyo, 1976

[e] Surface tension of 1,3-butanediol at 25°C

Table 1. The γ_L^d, γ_L^p and γ_L^h are dispersion, polar and hydrogen bonding parts of liquid's surface tension, respectively. The contact angle data for the PEA/P(VDF–HFA)(100/0), (90/10), (80/20), (70/30), (60/40) and (50/50 wt ratio) blends were reused as the results measured in our previous paper[7].

The temperature dependence of volume for PEA/P(VDF–HFA) blends was measured by a Perkin Elmer Co. Ltd. 7 Series thermal analysis system with quartz glass. After blend samples and silicone oil (Shin-etsu Silicone Co. Ltd. KF96) were put into the quartz glass, annealed for 2h at 70°C or more than the melting temperatures of the respective blend samples. The heating rate was 2°C min^{-1}.

RESULTS AND DISCUSSION

Critical surface tension

Fox and Zisman[12] measured the contact angles θ of various organic liquids on the surface of polymer films. They found that the plots of $\cos\theta$ and surface tension of liquids γ_L exhibited the good straight line. Then they determined the critical surface tension γ_c which was the γ_L value at $\cos\theta = 1$ by extrapolating the straight line. Since their investigation, the critical surface tension γ_c of various polymer films was estimated using the contact angle method.

Saito[15] presented a new relation of $\cos\theta$ and γ_L which was expressed using the interfacial interaction of solid and liquid as follows:

$$\log(1+\cos\theta) = -\psi\cdot\log(\gamma_L) + \log(2\Phi_o\cdot\gamma_s^{0.5-a}) \quad (12)$$

where the parameter a is determined as the slope $\psi = 0.5 - a$ in the plots of $\log(1+\cos\theta)$ and $\log(\gamma_L)$, γ_c is obtained as the γ_L value at $\log(1+\cos\theta) = \log(2)$ by extrapolating the straight line and Φ_o is calculated by the following equation:

$$\Phi_o = (X_L^d\cdot X_S^d)^{0.5} + (X_L^p\cdot X_S^p)^{0.5} \quad (13)$$

where X_j^d and X_j^p denote the dispersion and the polarity of the j component, respectively. The polarity of the solid X_S^p is determined using the solubility parameter δ and its polarity component δ^p according to the next equation[16].

$$X_S^p = (\delta^p/\delta)^2 \quad (14)$$

We have already verified that the $\log(1+\cos\theta)$ vs $\log(\gamma_L)$ plot gave a reasonable critical surface tension γ_c for P(VDF–HFA)[17], PEA/P(VDF–HFA) blends with P(VDF–HFA) contents varied from 0 to 50 wt% resin[7], blends of poly(vinylethylene-*co*-1,4-butadiene) with terpene resin[18] and hydrogenated terpene resin[19].

The plots of $\log(1+\cos\theta)$ against $\log(\gamma_L)$ for the PEA/P(VDF–HFA) (20/80) blend using dispersion (D) liquids and hydrogen bonding (H) liquids are shown in

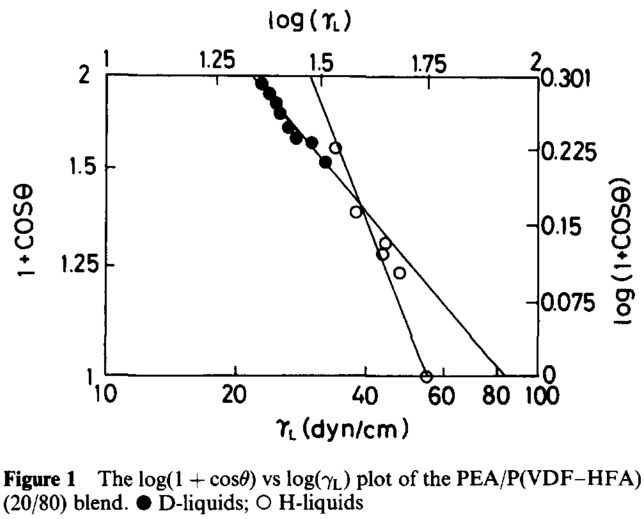

Figure 1 The $\log(1+\cos\theta)$ vs $\log(\gamma_L)$ plot of the PEA/P(VDF–HFA) (20/80) blend. ● D-liquids; ○ H-liquids

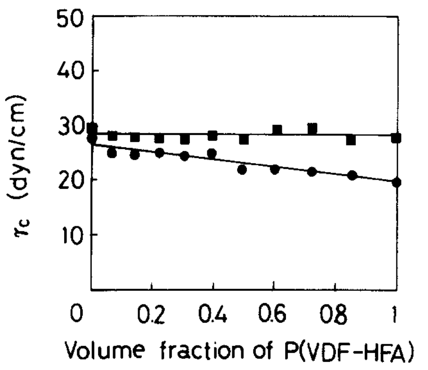

Figure 2 Relationship between the critical surface tension γ_c and volume fraction of P(VDF–HFA) of PEA/P(VDF–HFA) blends. ● D-liquids; ■ H-liquids

Figure 1. The critical surface tension γ_c of (20/80) blend estimated by extrapolating the straight line shows different values for two homogeneous liquids. The magnitude of γ_c with the (H) liquids is larger than that with the (D) liquids. The relationship between γ_c obtained by use of (D) and (H) liquids and volume fraction of P(VDF–HFA) is shown in *Figure 2*. The γ_c values in the blends estimated with the (H) liquids are little changed against volume fraction of P(VDF–HFA). On the other hand, with the (D) liquids the γ_c values decrease with increasing volume fraction of P(VDF–HFA). In this study, we cannot interpret this characteristic γ_c behaviour. However, it is well known that the γ_c has various values according to the kind used or liquids, such as dispersion, polar hydrogen bonding liquids[20]. Therefore, to simulate surface tension γ and surface segregation, we estimated γ with bulk PVT properties.

Surface tension estimated by bulk PVT properties

It is well known that the surface tension γ of polymer is also evaluated with the bulk PVT properties[12,13]. Patterson and Rastogi[13] calculated γ using the PVT parameters as the following equation

$$\tilde{\gamma} = \gamma/\kappa^{1/3} \cdot P^{*2/3} \cdot T^{*1/3} \tag{15}$$

$$\tilde{\gamma} \cdot \tilde{V}^{5/3} = 0.29 - (1 - \tilde{V}^{1/3}) \times \ln[(\tilde{V}^{1/3} - 0.5)/(\tilde{V}^{1/3} - 1)] \tag{16}$$

where $\tilde{\gamma}$ and $\tilde{V}$ are the reduced values for surface tension and volume, P^* and T^* are the reference parameters for pressure and temperature and κ is the Boltzman constant. These PVT parameters are determined by means of Flory's equation of state[22, 23] as follows:

$$(\tilde{P}\tilde{V}/\tilde{T}) = \{\tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1)\} - (1/\tilde{V}\tilde{T}) \tag{17}$$

where $\tilde{P}$ and $\tilde{T}$ are the reduced parameters of pressure and temperature, respectively. The reduced parameters are calculated using the thermal expansion coefficient α and the thermal pressure coefficient β as follows:

$$\tilde{V} = V_{SP}/V^* = \{(1 + T\alpha)/[1 + (4T\alpha/3)]\}^{-3} \tag{18}$$

$$\tilde{P} = P/P^* = P/(V^2T\beta) \tag{19}$$

$$\tilde{T} = T/T^* = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3} \tag{20}$$

where V^* and V_{SP} are reference volume and specific volume. Equations (18)–(20) were approximated for the case of $P = 0$. α is obtained as the slope of the V_{SP} vs temperature plot and β can be estimated using the solubility parameter δ as follows[24]:

$$\beta = \delta^2/T \tag{21}$$

Figure 3 and *Figure 4* show the temperature dependences of V_{SP} for PEA/P(VDF-HFA) (80/20), (20/80) blends, respectively. In the plot of V_{SP} vs temperature for the (80/20) blend, the straight line is revealed by the least square approximation and is expressed as follows:

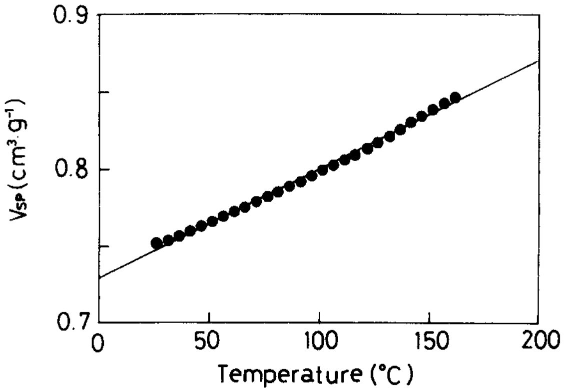

Figure 3 Relationship between specific volume V_{SP} and temperature for the PEA/P(VDF–HFA) (80/20) blend

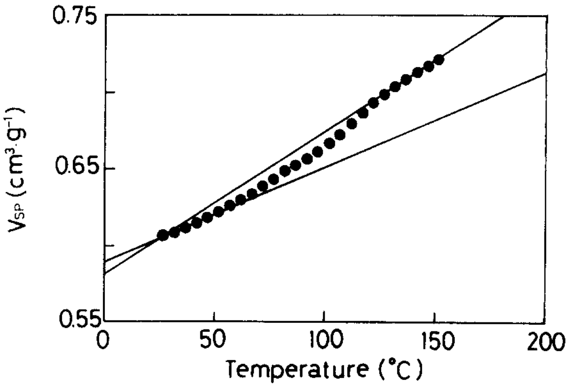

Figure 4 Relationship between specific volume V_{SP} and temperature for the PEA/P(VDF–HFA) (20/80) blend

$$V_{SP} = 7.02 \times 10^{-4} \cdot T(°\mathrm{C}) + 0.730 \tag{22}$$

On the contrary, for the (20/80) blend, the solid–liquid transition is observed in the range from 50 to 125°C. Therefore, three states were determined for the (20/80) blend: solid state (25–50°C), solid–liquid transition state, and liquid state (125–150°C). Two straight lines are drawn in the solid and liquid states, following respectively the equations

$$V_{SP} = 6.18 \times 10^{-4} \cdot T(°\mathrm{C}) + 0.589(25\text{–}50°\mathrm{C}) \tag{23}$$

$$V_{SP} = 9.32 \times 10^{-4} \cdot T(°\mathrm{C}) + 0.581(125 - 150°\mathrm{C}) \tag{24}$$

The thermal expansion coefficient α can be obtained as the slope of V_{SP} and temperature. On the other hand, the thermal pressure coefficient β should be estimated with the solubility parameter δ as shown in equation (21). We calculated the δ with the molar attraction constant by means of Hoy's table[25]:

$$\delta = \Sigma F_i / V \tag{25}$$

where F_i and V are a molar constant and molar volume, respectively. Thus, the surface tension γ for PEA/P(VDF–HFA) blends can be obtained with the PVT parameters according to equations (15) and (16). In this study we determined the bulk PVT properties at 140°C using α in the liquid state for PEA/P(VDF–HFA) blends because P(VDF–HFA) is a crystalline component.

Figure 5 shows the relationship between the surface tension, γ, calculated with the PVT parameters at 140°C and the volume fraction of P(VDF–HFA) for PEA/P(VDF–HFA) blends. The surface tension, γ, decreases with increasing the volume fraction of P(VDF–HFA). A straight line was revealed by least square approximation as follows:

$$\gamma = -17.29(\phi_1) + 35.96 \tag{26}$$

where ϕ_1 is the volume fraction of P(VDF–HFA). Since γ is proportional to ϕ_1 it is judged that γ calculated with the PVT properties expresses the mean γ value in bulk. The γ obtained by the equation of state includes some errors, as shown in *Figure 5*. However, in this study we discuss the relation between the volume content of P(VDF–HFA) on the surface and γ simulated by equation (26) since the γ_c values showed different values for two homogeneous liquids.

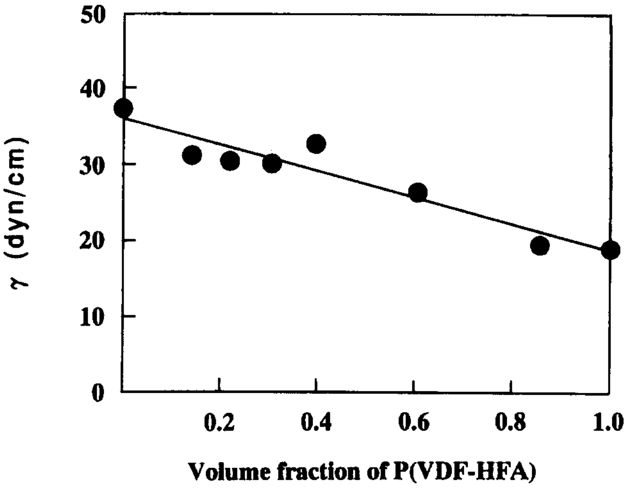

Figure 5 Relationship between surface tension γ estimated by PVT properties at 140°C and volume fraction of P(VDF–HFA) for PEA/P(VDF–HFA) blends

Fitting of γ and surface segregation

As represented in *Figure 6*, the volume fraction of P(VDF–HFA) on the surface obtained by X.p.s. at 15° (≈ 2 nm) of take-off angle is higher than the volume fraction of P(VDF–HFA) in bulk for PEA/P(VDF–HFA) blends. On the other hand, the volume fraction of P(VDF–HFA) at surface (is measured at 90° take-off angle (6–8 nm)) is approximately consistent with that at bulk.

Therefore, at a depth of 6–8 nm, the surface segregation was not observed by X.p.s. measurements. If the

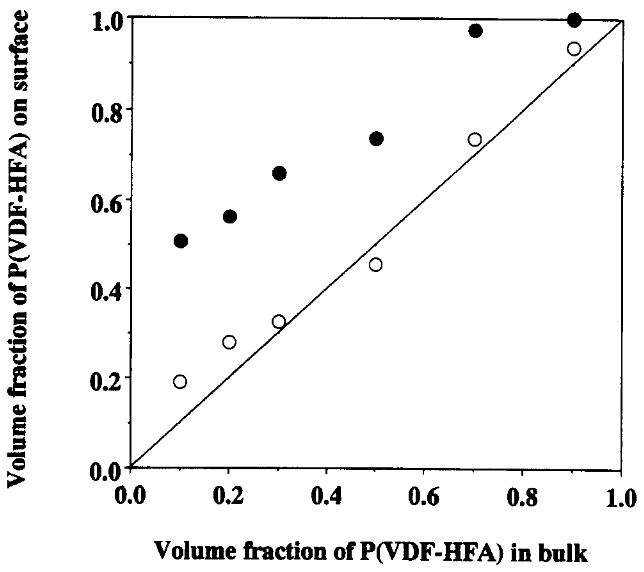

Figure 6 Relationship between volume fraction of P(VDF–HFA) on surface and volume fraction of P(VDF–HFA) in bulk for PEA/P(VDF–HFA) blends. Take-off angles: ●, 15°; ○, 90°

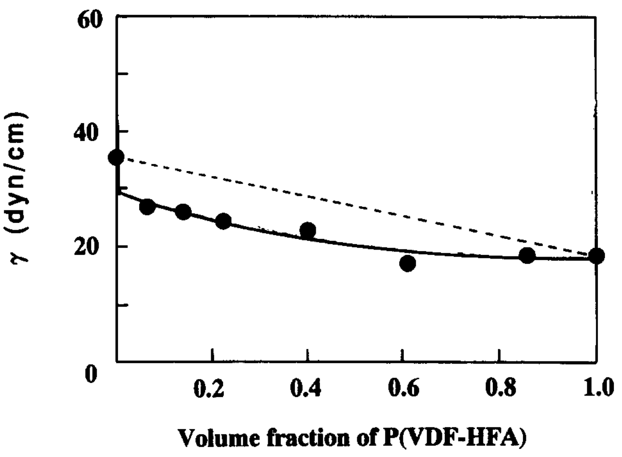

Figure 7 Relationship between surface tension, γ, calculated using equation (26) and volume fraction of P(VDF–HFA). The γ was calculated using the X.p.s. results of take-off angle 15°. The solid line refers to the surface tension calculated by thermodynamic theory ($k = 10^{-40}$, $X = 200$). The broken line refers to additivity behaviour

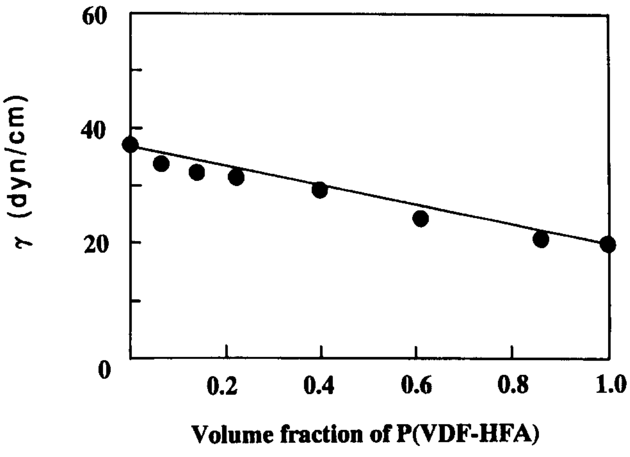

Figure 8 Relationship between surface tension , γ, calculated using equation (26) and volume fraction of P(VDF–HFA). The γ was calculated using the X.p.s. results of take-off angle 90°. The solid line refers to additivity behaviour

volume fraction of P(VDF–HFA) in the surface region obtained by X.p.s. data was introduced as the volume fraction of P(VDF–HFA) ϕ_1, the surface tension, γ, in the surface region (the top to a few nm depth) is calculated using equation (26). *Figures 7* and *8* show the relationships between the γ calculated using equation (26) and the volume fraction of P(VDF–HFA). Using the X.p.s. data measured at a 90° take-off angle, the plots of γ and ϕ_1 corresponded to the straight line (additivity behaviour). This is because the volume fraction of P(VDF–HFA) in the surface region obtained at 90° take-off angle is equal to that in bulk. However, the relation of γ at 15° take-off angle and ϕ_1 reveals a concave curve. We concluded that this relation is caused by the difference of P(VDF–HFA) concentration between surface and bulk.

According to Kammer's thermodynamic theory, the relation between γ and ϕ is expressed with equations (8)–(11) using parameter X. In fact, he carried out the plots of γ and ϕ for the poly(vinyl methyl ether)/polystyrene exhibiting surface segregation. We estimate the relation of γ and ϕ for the PEA/P(VDF–HFA) blends based on the theory. The plots of γ at 15° take-off angle and ϕ_1 are also represented as the solid line in *Figure 7*. Where the solid line refers to the surface tension calculated by thermodynamic theory ($k = 10^{-40}$, $X = 200$) and the molar surface area A of the PEA/P(VDF–HFA) blends are 46–48 m^2 (the molar volume, V = 70–100 cm^3 mol^{-1}; molar volume of monomer unit for PEA/P(VDF–HFA) blends, and the depth of the surface region $d = 1.5$–2.0 nm). We determined the parameters k and X as values at which the experimental results are approximately fitted to the calculated curve. The coefficient for a Langmuir-type function k was very small value for the PEA/P(VDF–HFA) blends. This is because the difference in surface tensions of components is very large (≈ 20 dyn cm^{-1}) as reported by Kammer[9]. The γ vs ϕ_1 plots are fitted on the solid curve evaluated using equations (8)–(11). Since the relationship between γ and ϕ_1 was obtained by the theory, we simulated the relationship between volume fraction of P(VDF–HFA) on the surface and volume fraction of P(VDF–HFA) in the bulk for PEA/P(VDF–HFA) blends using equation (26). *Figure 9* represents the volume fraction on the surface and that in the bulk for P(VDF–HFA). The solid line refers to the fitting curve estimated using γ data by his theory. Naturally, the surface segregation behaviour found in PEA/P(VDF–HFA) blends is very well fitted to the calculated convex curve because the γ vs ϕ_1 plots are well fitted to the curve as shown in *Figure 7*. Therefore, we think that surface segregation behaviour in binary polymer blends (plots of volume fraction on surface and volume fraction in bulk) can be evaluated using the γ values of blends estimated by PVT properties according to Kammer's thermodynamic theory. However, in fact, two problems existed in this evaluation of the PEA/P(VDF–HFA) blends. One is the implication of parameters X and k. The other is that the depth profile of surface segregation behaviour for polymer blends cannot be simulated with Kammer's theory. In our previous study[8], the depth profiles of PEA/P(VDF–HFA) (90/10), (80/20) blends were constructed with the X.p.s. data of take-off angle dependence. Thus, in our future study, the calculation of depth profile is necessary to interpret the effects of other factors on surface segregation behaviour for polymer blends.

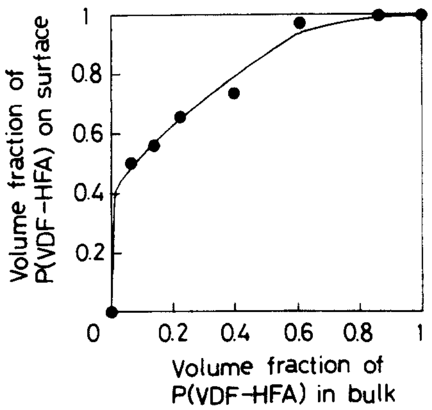

Figure 9 Relationship between volume fraction of P(VDF–HFA) on surface at 15° take-off angle and volume fraction of P(VDF–HFA) in bulk for PEA/P(VDF–HFA) blends. The solid line refers to fitting curve estimated using γ data

CONCLUSIONS

The surface tension, γ, and the surface segregation for PEA/P(VDF–HFA) blends was evaluated by means of Kammer's thermodynamic theory using the parameter for a Langmuir-type function k and a free energy parameter X. The surface tensions of PEA/P(VDF–HFA) blends were estimated by two methods, contact angle and bulk PVT properties. Since the relationship between γ obtained with bulk PVT properties and volume fraction of PEA/P(VDF–HFA) exhibited a straight line, the calculation of surface tension and surface segregation against volume fraction of P(VDF–HFA) for PEA/P(VDF–HFA) blends was performed using equation (26). When the parameters were $k = 10^{-40}$ and $X = 200$, the changes of surface tension and volume fraction of P(VDF–HFA) on the surface region against volume fraction of P(VDF–HFA) were very well fitted to the calculated curves. Therefore, we expected that surface segregation behaviour found in the PEA/P(VDF–HFA) blends (the change of volume fraction on surface against volume fraction in bulk) could be estimated using the experimental γ values of blends according to Kammer's thermodynamic theory.

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