Critical surface tension of poly(vinylidene fluoride-*co*-hexafluoroacetone) by the contact angle method

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The contact angles θ of dispersion (D), polar (P) and hydrogen bonding (H) liquids on poly(vinylidene fluoride-*co*-hexafluoroacetone) (P(VDF-HFA); HFA content 6.5, 8.3 and 10.4 mol%) were measured. The critical surface tensions γ_c of P(VDF-HFA) were evaluated by the Zisman plot ($\cos\theta$ *versus* γ_L), Young–Dupre–Good–Girifalco plot ($1 + \cos\theta$ *versus* $1/\gamma_L^{0.5}$) and the $\log(1 + \cos\theta)$ *versus* $\log(\gamma_L)$ plot. The following results were obtained: the γ_c values of P(VDF-HFA) evaluated for the P liquids were larger than those for the D and H liquids; the γ_c values estimated by the Zisman plot were smaller than those obtained by the other plots; the surface tension γ_s values of P(VDF-HFA) revealed a minimum at the HFA content of 8.3 mol%. It was expected that P(VDF-HFA) with HFA = 8.3 mol% induced surface segregation most easily.

(Keywords: P(VDF-HFA); Zisman plot; Young–Dupre–Good–Girifalco plot; critical surface tension; surface segregation)

INTRODUCTION

Poly(vinylidene fluoride-*co*-hexafluoroacetone), P(VDF-HFA), possesses excellent properties of resistance to heating, weather and chemicals, water repellency and non-tackiness. Recent studies have investigated the miscibility of P(VDF-HFA) with poly(methyl methacrylate) (PMMA)[1], poly(ethylene-*co*-vinyl acetate) (EVAc)[2] and poly(carbonate) (PC)[3].

The surface properties (water repellency, non-tackiness) of P(VDF-HFA) are closely related to the surface tension γ_s. Estimation of γ_s of the polymer solid has generally been made by the contact angle method[4–11]. Zisman[4,5] measured the contact angles θ of organic liquids on various polymer solids. He found that the relationship between $\cos\theta$ and the surface tension of liquid γ_L gave rise to a good straight line. He named the critical surface tension γ_c, which was the value of γ_L at $\cos\theta = 1$ by extrapolating the straight line.

Good and Girifalco[6] defined the interaction parameter Φ_G using the work of adhesion W_a and the work of cohesion W_c:

$$\Phi_G = W_a/(W_{c1}W_{c2})^{0.5} \quad (1)$$

They presented the following equation:

$$W_a = 2\Phi_G(\gamma_s\gamma_L)^{0.5} \quad (2)$$

Using equation (2) and Young–Dupre's equation

$$W_a = \gamma_L(1 + \cos\theta) \quad (3)$$

the equation of Young–Dupre–Good–Girifalco was expressed as:

$$1 + \cos\theta = 2\Phi_G(\gamma_s/\gamma_L)^{0.5} \quad (4)$$

Good and Girifalco[6] measured the contact angles θ of poly(tetrafluoroethylene) (PTFE) with organic liquids. They evaluated the Φ_G and the γ_s by use of the $1 + \cos\theta$ *versus* $1/\gamma_L^{0.5}$ plot. However, we[7–11] have found that the γ_s values of various polymers can be estimated by the $\log(1 + \cos\theta)$ *versus* $\log(\gamma_L)$ plot.

We investigated the miscibility, adhesive properties, viscoelastic properties and surface structure for poly(2-ethyl hexyl acrylate-*co*-acrylic acid-*co*-vinyl acetate) (PEHA/P(VDF-HFA)) blends[12–18]. The following results were obtained. It was confirmed that PEHA and P(VDF-HFA) were enriched at the interface of blend and substrate and at the surface of blends, respectively, in blends with the P(VDF-HFA) component over 50 wt% by the ATR-*FT*i.r. method (*Figure 1*)[15]. I_{870} is the C–F absorbance for P(VDF-HFA) at 870 cm^{-1} and I_{1730} is the C=O absorbance for PEHA at 1730 cm^{-1}. It was suggested that the surface segregation[19,20] of the low surface energy component (P(VDF-HFA)) occurred on the surface of the blend in contact with air[18].

In the present paper, the contact angles θ of P(VDF-HFA) (with HFA content of 6.5, 8.3 and 10.4 mol%) with dispersion (D), polar (P) and hydrogen bonding (H) liquids were measured. The critical surface

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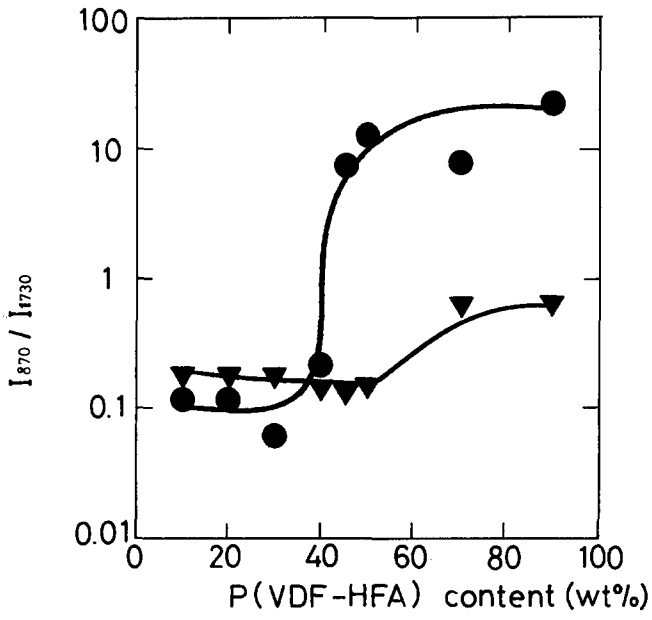

Figure 1 Variation of absorbance ratio of PEHA/P(VDF-HFA) blends. ●, Surface of blends; ▼, interface of blends and substrate

tensions γ_c of P(VDF-HFA) were estimated by the Zisman plot ($\cos\theta$ *versus* γ_L), the Young–Dupre–Good–Girifalco plot ($1+\cos\theta$ *versus* $1/\gamma_L^{0.5}$) and the $\log(1+\cos\theta)$ *versus* $\log(\gamma_L)$ plot[7–11]. The surface segregation for the PEHA/P(VDF-HFA) blends was investigated with γ_s.

THEORETICAL BACKGROUND

Young–Dupre–Good–Girifalco plot

The $1+\cos\theta$ *versus* $1/\gamma_L^{0.5}$ plot obtained by the contact angles θ of homogeneous liquids on a polymer solid gives rise to a good straight line with the experimental data. However, in many cases the straight line greatly deviated from the origin with the polarity of the liquids[11]. In such cases, the straight line can be expressed as:

$$1+\cos\theta = \lambda\gamma_L^{-0.5} + \phi \tag{5}$$

where λ and ϕ are the slope and the intercept of $1+\cos\theta$ at $1/\gamma_L^{0.5}=0$ in the $1+\cos\theta$ *versus* $1/\gamma_L^{0.5}$ plot, respectively. These parameters are constant with homogeneous liquids. The critical surface tension γ_c is defined as the value of γ_L at $\theta\to 0$. The relationship between λ and ϕ is expressed in the following equation by the use of γ_c:

$$\lambda = (2-\phi)\gamma_C^{0.5} \tag{6}$$

$$\lambda < 0, \quad \phi < 2 \quad \text{for } \mathrm{d}\cos\theta/\mathrm{d}\gamma_L < 0 \tag{6a}$$

Using equation (5), Young–Dupre's equation (3) and Good–Girifalco's equation (2), and neglecting the spreading pressure π_e, the Good–Girifalco interaction parameter Φ_G is expressed as:

$$\Phi_G = (1/2\gamma_S^{0.5})[(2-\phi)\gamma_C^{0.5} + \phi\gamma_L^{0.5}] \tag{7}$$

where γ_s is the surface tension of solid. The parameter Φ_G^0, defined as Φ_G at $\theta\to 0$, is expressed as follows:

$$\Phi_G^0 = (\gamma_c/\gamma_s)^{1/2} \tag{8}$$

The $\log(1+\cos\theta)$ versus $\log(\gamma_L)$ plot

As the interaction between liquid and solid is approximated by use of the geometric mean law, Φ_0 is defined as the indication of polarity in Φ_G. Furthermore, we also took account of an adjustable parameter (X_{LS}) within Φ_G as a departure from the interaction estimated by the geometric law[11]. Thus, Φ_G is expressed as:

$$\Phi_G = (X_L^d X_s^d)^{0.5} + (X_L^p X_s^p)^{0.5} + X_{LS} = \Phi_0 + X_{LS} \tag{9}$$

where X_j^d and X_j^p are the dispersion and the polarity of the j component.

Wu[21] reported that the polarity X_j^p was estimated with the solubility parameter δ and the polarity component of solubility parameter δ^p by the following equation:

$$X_s^p = (\delta^p/\delta)^2 \tag{10}$$

Also, the parameter a, determined with the polarity and X_{LS}, is introduced into Φ_G as follows:

$$\Phi_G = \Phi_0(\gamma_L/\gamma_s)^a$$

$$a = \left[\log\left(\frac{\Phi_0 + X_{LS}}{\Phi_0}\right)\right] \Big/ \log(\gamma_L/\gamma_s)$$

$$a < 0.5 \quad \text{for } \mathrm{d}\cos\theta/\mathrm{d}\gamma_L < 0 \tag{11}$$

The Φ_0 is equal to the bonding efficiency parameter of Kaelble and Uy[22]. Therefore, Φ_G^0 is expressed by:

$$\Phi_G^0 = [(X_c^d X_s^d)^{0.5} + (X_c^p X_s^p)^{0.5}](\gamma_c/\gamma_s)^a \tag{12}$$

where X_c^d is the ratio of γ_c obtained with D liquids and γ_c obtained with P or H liquids[11]. The surface tension γ_s is obtained from equations (8) and (12) as follows:

$$\gamma_s = \gamma_c[(X_c^d X_s^d)^{0.5} + (X_c^p X_s^p)^{0.5}]^{2/(2a-1)} \tag{13}$$

Also, the reversible work of adhesion W_a is expressed by:

$$W_a = 2\Phi_0(\gamma_s^{0.5-a}\gamma_L^{0.5+a}) \tag{14}$$

Consequently, the combination of equation (14) and Young–Dupre's equation (3) leads to:

$$\log(1+\cos\theta) = -\psi\log(\gamma_L) + \log(2\Phi_0\gamma_s^{0.5-a}) \tag{15}$$

Using equation (15), the parameter a is determined with the slope $\psi = (0.5-a)$ in the plot of $\log(1+\cos\theta)$ *versus* $\log(\gamma_L)$ and γ_c is obtained from the value of γ_L at $\log(1+\cos\theta) = \log 2$ by extrapolating the straight line.

EXPERIMENTAL

Materials

The structure of P(VDF-HFA) used in this study is shown in *Figure 2*; the HFA contents and the molecular weights of P(VDF-HFA) are shown in *Table 1*. The molecular weights of P(VDF-HFA) were measured by gel permeation chromatography using a Toso G-HXL column with 0.4 mol% DMF at 40°C. The P(VDF-HFA) films used in contact angle measurements were

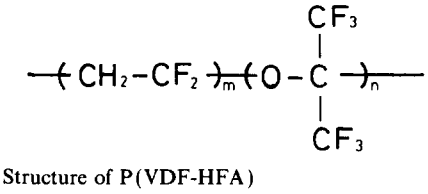

Figure 2 Structure of P(VDF-HFA)

prepared by coating with 20 wt% THF solution onto poly(ethylene terephthalate) (PET) film using LINTEC Universal Coating system. The P(VDF-HFA) films were dried at 90°C for 60 s, then laminated with the release liner. The P(VDF-HFA) films were then seasoned at 23 ± 3°C and 65 ± 5% r.h. for 7 days. The films were 30 μm thick in their dry states.

Contact angle measurement

The contact angles of P(VDF-HFA) films with various liquids were measured by Kyowa Kaimen Kagaku CA-D type. The 1.5–2.0 mm diameter drops of liquids were prepared with a microsyringe, and they were dropped on the surface of P(VDF-HFA) films at 20°C. The surface tensions γ_L and the polarity X_L^p of the organic liquids, D, P and H, are shown in *Table 2*.

RESULTS

The Zisman plots ($\cos\theta$ *versus* γ_L) for P(VDF-HFA) (HFA content 10.4 mol%) with the organic liquids are shown in *Figure 3*. The critical surface tensions γ_c of P(VDF-HFA) evaluated by Zisman's linear approximation have various values with varying polarity of liquids. The magnitude of the critical surface tension γ_c for P(VDF-HFA) film increases in the order: D < H < P liquids. Substituting equation (3) into (2), the relationships between $1 + \cos\theta$ and $1/\gamma_L^{0.5}$ are shown in *Figure 4*. The γ_c values of P(VDF-HFA) evaluated with the $1 + \cos\theta$ *versus* $1/\gamma_L^{0.5}$ plot also have various values with varying polarity of liquids used. The magnitude of γ_c also increases in the order: D < H < P liquids. The straight lines between $1 + \cos\theta$ and $1/\gamma_L^{0.5}$ approximated by the method of least squares greatly deviated from the origin. The $\log(1 + \cos\theta)$ *versus* $\log(\gamma_L)$ plots are shown in *Figure 5*. The order of magnitude of γ_c evaluated with this plot is similar to those on the other plots.

The γ_c values of P(VDF-HFA) films obtained by all the plots, the intercept ϕ of $1 + \cos\theta$ at $1/\gamma_L^{0.5} = 0$ in the $1 + \cos\theta$ *versus* $1/\gamma_L^{0.5}$ plot and the slope $-\psi$ on the $\log(1 + \cos\theta)$ *versus* $\log(\gamma_L)$ plot are shown in *Table 3*. The γ_c values estimated by the Zisman plot are smaller than those estimated by other plots. ϕ decreases with increasing HFA content in P(VDF-HFA) and it has a minimum with the P liquids. The slope $-\psi$ decreases

Table 1 Hexafluoroacetone (HFA) contents and molecular weights of fluorocopolymers

HFA content (mol%)	M_n	M_w	M_w/M_n
6.5	30000	127000	4.23
8.3	11600	57300	4.94
10.4	35000	162000	4.63

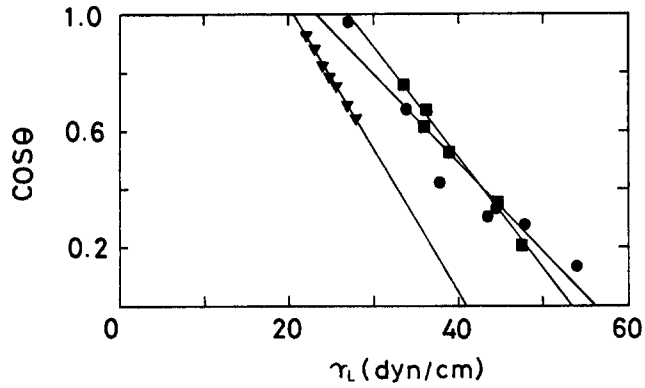

Figure 3 Zisman plots for P(VDF-HFA) with 10.4 mol% HFA content. ●, H liquids; ▼, D liquids; ■, P liquids

Table 2 The surface tensions and polarity (X_L^p) of liquids at 20°C (in dyn cm^{-1}) from ref. 31

Species	Liquid	γ_L^d	γ_L^p	γ_L^h	γ_L	X_L^p
D	n-Octane	21.8	0	0	21.8	0
	n-Nonane	22.9	0	0	22.9	0
	n-Decane	23.9	0	0	23.9	0
	n-Undecane	24.7	0	0	24.7	0
	n-Dodecane	25.4	0	0	25.4	0
	n-Tetradecane	26.7	0	0	26.7	0
	n-Hexadecane	27.6	0	0	27.6	0
P	1,1,2-Trichloroethane[a]	–	–	–	33.6	–
	Hexachlorobutadiene[a]	35.8	0.2	0	36.0	0.006
	Tetrachloroethane	33.2	3.1	0	36.3	0.085
	1,2-Dibromoethane[a]	–	–	–	38.9	–
	α-Bromonaphthalene	44.4	0.2	0	44.6	0.004
	Tetrabromoethane	44.3	3.2	0	47.5	0.067
H	1-Metoxy-2-propanol[a]	–	–	–	27.1	–
	Dipropyleneglycol	29.4	0	4.5	33.9	0.133
	1,3-Butanediol[a,b]	–	–	–	37.8	–
	Polyethyleneglycol	29.9	0.1	13.5	43.5	0.313
	Diethyleneglycol	31.7	0	12.7	44.4	0.286
	Ethyleneglycol	30.1	0	17.8	47.7	0.369
	Thiodiglycol	39.2	1.4	13.4	54.0	0.274

[a]Data from ref. 32
[b]Surface tension of 1,3-butanediol at 25°C

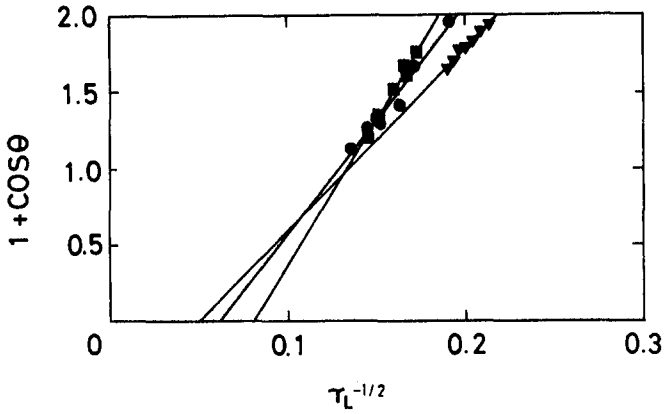

Figure 4 Young–Dupre–Good–Girifalco plots for P(VDF-HFA) with 10.4 mol% HFA content. ●, H liquids; ▼, D liquids; ■, P liquids

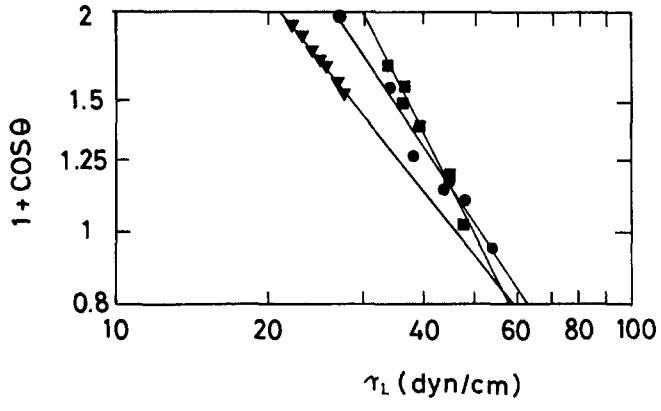

Figure 5 Log(1 + cos θ) *versus* log(γ_L) plots for P(VDF-HFA) with 10.4 mol% HFA content. ●, H liquids; ▼, D liquids; ■, P liquids

with increasing HFA content in P(VDF-HFA) and it also has a minimum with the P liquids.

DISCUSSION

On the Zisman plot, the relationship between cos θ and γ_L displays a favourable straight line when the value of γ_L is in the vicinity of γ_c. On the other hand, it displays a downwardly convex curve[23] when γ_L has a value much larger than γ_c, because a liquid with γ_L much greater than γ_c generally possesses the specific interaction (hydrogen bonding[24]). Gutowski[25] defined the following equation:

$$1 + \cos\theta = 2\Phi_G\left(\frac{\gamma_s}{\gamma_L}\right)^{0.5} \quad (16)$$

Equation (16) is derived from substituting Young–Dupre's equation (3) into Good–Girifalco's equation (2). Gutowski[25] pointed out that the Zisman plot (cos θ *versus* γ_L) essentially demonstrated a downwardly convex curve with equation (16).

In this study, the Zisman plot and the critical surface tensions γ_c of P(VDF-HFA) are discussed by use of the intercept ϕ of $1 + \cos\theta$ at $1/\gamma_L^{0.5} = 0$ in the $1 + \cos\theta$ *versus* $1/\gamma_L^{0.5}$ plot and the slope $-\psi$ in the log(1 + cos θ) *versus* log(γ_L) plot. The relationship between cos θ and γ_L can be defined with the ϕ or ψ by the following equations: from equation (7) and equation (16):

$$\cos\theta = (2 - \phi)(\gamma_c/\gamma_L)^{0.5} + (\phi - 1) \quad (17)$$

from equation (11) and equation (16):

$$\cos\theta = 2\Phi_0(\gamma_s/\gamma_L)^{\psi - 1} \quad (18)$$

Therefore, the relationship between cos θ and γ_L obtained using equation (17) (for $\phi < 2$) illustrates a downwardly convex curve. The γ_c values estimated by the Zisman plot and equation (17) are provided as γ_c^E and γ_c^T, respectively. As the polarity X_L^p of respective liquids in the P and H liquids differ remarkably (*Table 2*), it is suggested that the Φ_0 also depends on the liquid. Thus, the relation on the Zisman plot and the γ_c in this study is discussed with equation (17).

As can be seen in *Table 3*, the parameters ϕ of all P(VDF-HFA) films have negative values. The relationship between cos θ and γ_L for P(VDF-HFA) with 10.4 mol% HFA content, evaluated with the ϕ and γ_c in *Table 3*, is expressed with equation (17) as follows:

$$\text{for D} \quad \cos\theta = 11.81(\gamma_L)^{-0.5} - 1.59$$
$$\text{for P} \quad \cos\theta = 19.08(\gamma_L)^{-0.5} - 2.53$$
$$\text{for H} \quad \cos\theta = 14.95(\gamma_L)^{-0.5} - 1.92$$

Both the relationship between cos θ and γ_L obtained from equation (17) and the straight line on the Zisman plot expressed by the method of least squares are shown in *Figure 6*. For the D liquids, γ_c^E is nearly equal to γ_c^T. On the other hand, γ_c^E is obviously smaller than γ_c^T for the P and the H liquids. Also, the relationship between cos θ and γ_L (experimental data) is approximately fitted with the theoretical curve calculated by equation (17). Consequently, we can presume that the Zisman plot is essentially a downwardly convex curve with the P and H liquids having $\gamma_c \ll \gamma_L$. This result is consistent with that of Gutowski[25].

When the liquid contacts the polymer solid, it is known that the orientation of the polar groups[26] and the rearrangement of the side chain of the polymer[10,11] occur near the interface. In this case, the surface tension γ_s of polymer solid and the theoretical surface tension γ_c^T are changed with varying the polarity of the liquids. The polarity X_s^p and γ_s of P(VDF-HFA) evaluated by the slope $-\psi$ of the log(1 + cos θ) *versus* log(γ_L) plot are

Table 3 The critical surface tensions γ_c of fluorocopolymers and the constants determined from various plots

Constant	Species	HFA content (mol%) 6.5	8.3	10.4
γ_c: critical surface tension by Zisman plot cos θ *versus* γ_L	D	21.2	19.9	20.4
	P	27.9	24.4	26.9
	H	22.7	22.6	23.1
γ_c: critical surface tension by (1 + cos θ) *versus* $1/\gamma_L^{0.5}$ plot	D	21.4	20.4	20.8
	P	29.8	27.8	29.2
	H	27.5	25.9	26.2
γ_c: critical surface tension by log(1 + cos θ) *versus* log(γ_L) plot	D	21.5	20.6	20.9
	P	30.3	28.5	30.0
	H	28.1	26.0	26.4
ϕ: intercept of (1 + cos θ) axis in the plot of (1 + cos θ) *versus* $1/\gamma_L^{0.5}$	D	−0.07	−0.44	−0.59
	P	−0.88	−0.97	−1.53
	H	−0.41	−0.74	−0.92
$(-\psi) = -(0.5 - a)$: slope $(-\psi)$ in the plot of log(1 + cos θ) *versus* log(γ_L)	D	−0.52	−0.63	−0.67
	P	−0.79	−0.82	−1.04
	H	−0.65	−0.73	−0.79

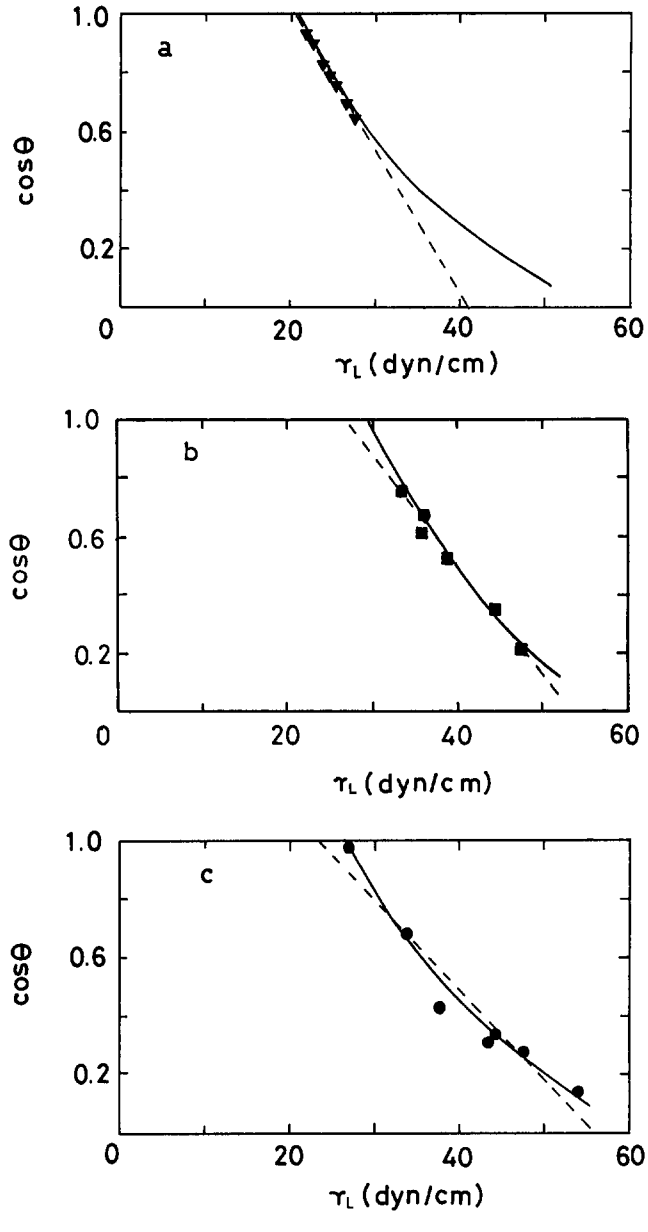

Figure 6 Theoretical curves of cos θ *versus* γ_L based on the equation $\cos\theta = (2-\phi)(\gamma_c/\gamma_L)^{0.5} + (\phi - 1)$. (a) D liquids; (b) P liquids; (c) H liquids

Table 4 The surface tensions γ_s and the polarity X_s^p of fluorocopolymers

HFA content (mol%)	X_s^p	γ_s[a]		
		D	P	H
6.5	0.055	22.7	32.5	29.7
8.3	0.072	21.9	29.9	26.7
10.4	0.089	22.7	33.6	26.9

[a] γ_s is calculated from the equation:

$$\gamma_s = \gamma_c[(X_c^d X_s^d)^{0.5} + (X_c^p X_s^p)^{0.5}]^{2/(2a-1)}$$

shown in *Table 4*. The γ_s value is close to the γ_c estimated by the $\log(1 + \cos\theta)$ *versus* $\log(\gamma_L)$ plot. Also the γ_s has a maximum for the P liquids. It is suggested that the orientation of the polar group and the rearrangement of the side chain in P(VDF-HFA) take place near the polymer surface in contact with the liquid.

In the polymer blend and the polymer containing plasticizer, surface segregation has occurred as the low surface energy component has been preferentially enriched on the surface of the sample by the difference between the surface energies of components[19,20,27,28]. Patel and co-workers[20] confirmed by X-ray photoelectron spectroscopy that the siloxane blocks having low surface energy in the polystyrene/poly(sulphone-siloxane-sulphone) block copolymer blends are enriched on the surface of blends. We found out that surface segregation occurred in the PEHA/P(VDF-HFA) blends[13,15,16,18]. In a previous paper[18], it was suggested that the origins of the surface segregation came from the immiscibility of the P(VDF-HFA) and the PEHA and the significantly low surface tension γ_s of P(VDF-HFA). In this paper, the surface segregation for the PEHA/P(VDF-HFA) blends was interpreted with γ_s and miscibility observed by thermophotometry[29,30]. *Figure 7* shows the miscibility for the PEHA/P(VDF-HFA) (HFA content 10.4 mol%) blends observed by means of thermophotometry. The blend samples displayed opacity in the range 25–300°C. The opacity for blends of PEHA/P(VDF-HFA) (HFA content 6.5 and 8.3 mol%) was also observed in the temperature range 25–300°C. Thus, it is suggested that the blends of PEHA with P(VDF-HFA) (HFA content 6.5, 8.3 and 10.4 mol%) are remarkably immiscible. The relationships between γ_s obtained by equation (13) and the HFA contents of P(VDF-HFA) are shown in *Figure 8*. The γ_s values of P(VDF-HFA) (HFA content 8.3 mol%) are smaller than those of P(VDF-HFA) with other contents about 1–4 dyn cm^{-1}. Therefore, it is predicted that P(VDF-HFA) with 8.3 mol% HFA content, which has the minimum γ_s value, most easily induced surface segregation.

CONCLUSION

The contact angles of organic liquids on P(VDF-HFA) films were measured. The γ_c values of P(VDF-HFA)

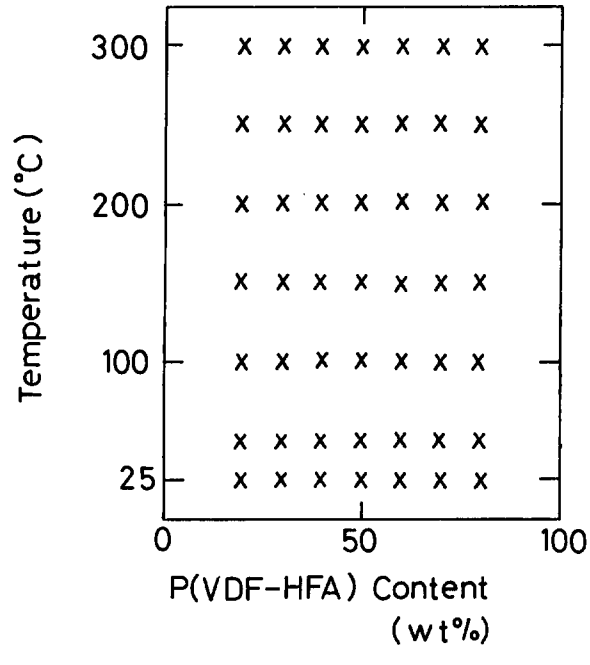

Figure 7 Miscibility in PEHA/P(VDF-HFA) blends (HFA content 10.4 mol%) with visual observation by thermophotometry. The symbol × indicates opacity. Heating rate 5°C min^{-1}

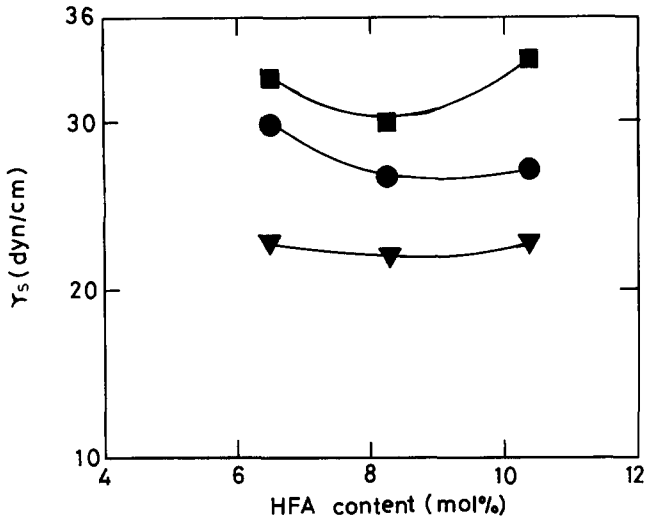

Figure 8 Relationship between the surface tension γ_s and HFA content of P(VDF-HFA). γ_s is calculated using equation (13). ●, H liquids; ▼, D liquids; ■, P liquids

films obtained with the Zisman plot ($\cos\theta$ *versus* γ_L) were smaller than those obtained with either the $1 + \cos\theta$ *versus* $1/\gamma_L^{0.5}$ plot or the $\log(1 + \cos\theta)$ *versus* $\log(\gamma_L)$ plot. It was found that the Zisman plot resulted in essentially a downwardly convex curve. The γ_s evaluated by the $\log(1 + \cos\theta)$ *versus* $\log(\gamma_L)$ plot and equation (13) had a maximum for the P liquids. Thus, we considered that orientation and rearrangement of P(VDF-HFA) occurred. Also, the surface tension of P(VDF-HFA) γ_s revealed a minimum at the HFA content of 8.3 mol%. Therefore, we can expect that the P(VDF-HFA) with 8.3 mol% HFA most easily induced the surface segregation.

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