Estimation of interfacial interaction of poly(vinylidene fluoride-co-hexafluoro acetone) by contact angle

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Using contact angle data for poly(vinylidene fluoride-co-hexafluoro acetone) with various organic liquids, such as dispersion, polar and hydrogen-bonding liquids, the Good–Girifalco interaction parameter, Φ_G, work of adhesion, W_a, and interfacial tension, γ_{SL}, were calculated. The values of Φ_G, W_a and γ_{SL} were dependent on the surface tension γ_L and the species of liquid.

Introduction

It is well known that the surface tension of polymer solids may be estimated by contact angle using organic liquids[1-6]. In our previous paper[7], the contact angles of dispersion (D), polar (P) and hydrogen-bonding (H) liquids with poly(vinylidene fluoride-co-hexafluoro acetone) [P(VDF–HFA)] were measured. The critical surface tension, γ_C, of P(VDF–HFA) estimated with P liquids was larger than that with D and H liquids. It was suggested that the orientation and rearrangement of P(VDF–HFA) occurred and the plot of $\cos\theta$ and γ_L resulted in essentially a concave curve. The surface tensions of P(VDF–HFA), γ_S, were obtained using the $\log(1+\cos\theta)$ versus $\log(\gamma_L)$ plot. On the other hand, Good and Girifalco[3,4] defined the next equation using parameter Φ_G:

$$W_a = 2\Phi_G(\gamma_S\gamma_L)^{0.5} \tag{1}$$

where W_a is the work of adhesion and is calculated with Young–Dupré's equation:

$$W_a = \gamma_L(1+\cos\theta) \tag{2}$$

The interfacial tension, γ_{SL}, is obtained by means of Dupré's equation as follows:

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \tag{3}$$

W_a and γ_{SL} are very important parameters for wettability and adhesion[8]. In this study, from contact angle data of organic liquids on P(VDF–HFA) as in the previous study[7], the values of Φ_G, W_a and γ_{SL} were examined. The polymer samples were P(VDF–HFA) with HFA contents of 6.5 ($M_n=30\,000$, $M_w/M_n=4.23$), 8.3 ($M_n=11\,600$, $M_w/M_n=4.94$) and 10.4 mol% ($M_n=35\,000$, $M_w/M_n=4.63$). The surface tensions, γ_L, and the dispersion component, X_L^d, of the organic liquids, D, P and H, are shown in *Table 1*.

Discussion

Good and Girifalco[3,4] expressed Φ_G by means of the polarizability, α, ionization potential, I, permanent dipole moment, μ, Boltzmann constant, κ, and temperature, T, in the following equation:

$$\Phi_G = \frac{\dfrac{3}{4}\alpha_1\alpha_2\dfrac{2I_1I_2}{I_1+I_2}+\dfrac{\alpha_1\mu_2^2+\alpha_2\mu_1^2}{2}+\dfrac{\mu_1^2\mu_2^2}{3\kappa T}}{\left(\dfrac{3}{4}\alpha_1^2I_1+\alpha_1\mu_1^2+\dfrac{\mu_1^4}{3\kappa T}\right)^{0.5}\left(\dfrac{3}{4}\alpha_2^2I_2+\alpha_2\mu_2^2+\dfrac{\mu_2^4}{3\kappa T}\right)^{0.5}}$$

$$\tag{4}$$

where subscripts 1 and 2 refer to phases 1 and 2, respectively. The estimation of Φ_G using equation (4) is

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

Species	Liquid	γ_L^d	γ_L^p	γ_L^h	γ_L	X_L^d
	n-Octane	21.8	0	0	21.8	1.00
	n-Nonane	22.9	0	0	22.9	1.00
	n-Decane	23.9	0	0	23.9	1.00
D	n-Undecane	24.7	0	0	24.7	1.00
	n-Dodecane	25.4	0	0	25.4	1.00
	n-Tetradecane	26.7	0	0	26.7	1.00
	n-Hexadecane	27.6	0	0	27.6	1.00
	1,1,2-Trichloroethane	–	–	–	33.6	–
	Hexachlorobutadiene	35.8	0.2	0	36.0	0.994
P	Tetrachloroethane	33.2	3.1	0	36.3	0.915
	1,2-Dibromoethane	–	–	–	38.9	–
	α-Bromonaphthalene	44.4	0.2	0	44.6	0.996
	Tetrabromoethane	44.3	3.2	0	47.5	0.933
	1-Methoxy-2-propanol	–	–	–	27.1	–
	Dipropyleneglycol	29.4	0	4.5	33.9	0.867
	1,3-Butanediol	–	–	–	37.8	–
H	Polyethyleneglycol	29.9	0.1	13.5	43.5	0.687
	Diethyleneglycol	31.7	0	12.7	44.4	0.714
	Ethyleneglycol	30.1	0	17.6	47.7	0.631
	Thiodiglycol	39.2	1.4	13.4	54.0	0.726

[a] Data from ref. 7

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very hard because of various parameters. Saito[9–12] presented two different approaches for estimating Φ_G: from equation (5) with parameter ϕ, and from equation (6) using parameter a as follows:

$$\Phi_G = [(2-\phi)\gamma_C^{0.5} + \phi\gamma_L^{0.5}]/(2\gamma_S^{0.5}) \qquad (5)$$

$$\Phi_G = [(X_L^d X_S^d)^{0.5} + (X_L^p X_S^p)^{0.5}] (\gamma_L/\gamma_S)^a \qquad (6)$$

where ϕ and $0.5-a$ are the intercept of $1+\cos\theta$ at $\gamma_L^{-0.5}=0$ in the $(1+\cos\theta)$ *versus* $1/\gamma_L^{0.5}$ plot and the slope between $\log(1+\cos\theta)$ and $\log(\gamma_L)$, respectively. X_j^d and X_j^p are the dispersion and polarity, respectively, of surface tension of component j. The relationship between Φ_G of P(VDF–HFA) with 10.4 mol% HFA content and γ_L is shown in *Figure 1*. There are few differences between Φ_G obtained with equation (5) and that with equation (6). However, both Φ_G values have similar tendencies in homogeneous liquids. As shown in *Figure 1*, Φ_G decreases with increasing γ_L in D, P and H liquids. In our previous study[13], from the contact angle of various organic liquids on poly(vinyl ethylene-*co*-1,4-butadiene) (V–BR)/terpene resin blends, Φ_G decreased with increasing γ_L in D and H liquids while in P liquids it increased with increasing γ_L. Both V–BR and terpene resin consist of carbon and hydrogen, whereas P(VDF–HFA) includes polar sites such as C–F. Φ_G depends on α, I and μ from equation (4). Consequently, we think that the difference in interaction between V–BR/terpene resin blends and P(VDF–HFA) and organic liquids is due to the polar parameters (α, I, μ).

We can estimate the work of adhesion W_a from Φ_G using equation (1). On the other hand, W_a is directly evaluated with the Young–Dupré equation (2) using the contact angle of liquid on a solid. We can compare W_a calculated from equation (1) and that from equation (2) using the experimental data shown in *Figure 2*. The W_a *versus* γ_L plot is similar using three different estimations. The relationship between W_a and γ_L varies with the species
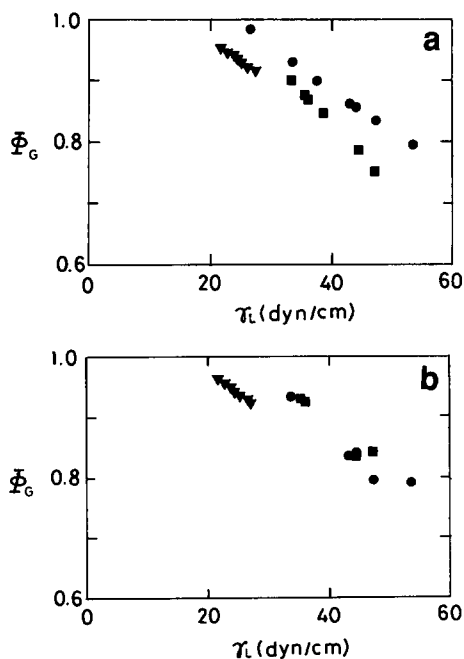
Figure 1 Relationship between Φ_G and γ_L of P(VDF–HFA) with 10.4 mol% HFA content. ●, H liquids; ▼, D liquids; ■, P liquids

(a) $\Phi_G = [(2-\phi)\gamma_C^{0.5} + \phi\gamma_L^{0.5}]/(2\gamma_S^{0.5})$
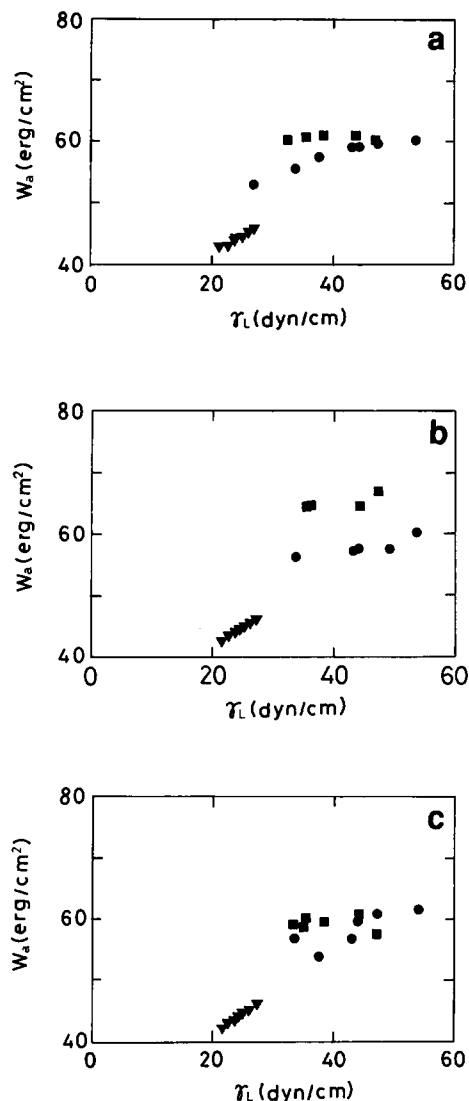(b) $\Phi_G = [(X_L^d X_S^d)^{0.5} + (X_L^p X_S^p)^{0.5}] (\gamma_L/\gamma_S)^a$

Figure 2 Relationship between W_a and γ_L of P(VDF–HFA) with 10.4 mol% HFA content. Symbols as in *Figure 1*

(a) $W_a = 2\Phi_G(\gamma_S\gamma_L)^{0.5}$
$\Phi_G = [(2-\phi)\gamma_C^{0.5} + \phi\gamma_L^{0.5}]/(2\gamma_S^{0.5})$
(b) $W_a = 2\Phi_G(\gamma_S\gamma_L)^{0.5}$
$\Phi_G = [(X_L^d X_S^d)^{0.5} + (X_L^p X_S^p)^{0.5}] (\gamma_L/\gamma_S)^a$
(c) $W_a = \gamma_L(1+\cos\theta)$

of liquid. In D and H liquids, W_a increases with increasing γ_L, whereas in P liquids, it does not change with increasing γ_L. The increase in W_a with increasing γ_L using D liquids is smaller than that using H liquids. It is thought that W_a is influenced by the polar parameters (α, I, μ) of P(VDF–HFA) and each organic liquid. The W_a values calculated with Φ_G are consistent with those calculated using equation (2). Thus, it is clear that the two estimations of Φ_G in this study are available for estimating W_a.

The interfacial tension between solid and liquid, γ_{SL}, is expressed with equation (3) in terms of W_a. *Figure 3* shows the γ_{SL} *versus* γ_L plots for P(VDF–HFA) with 10.4 mol% HFA content. γ_{SL} increases monotonically with increasing γ_L. Gray[14] and Saito[10] pointed out that the relationship between γ_{SL} and γ_L exhibits a concave curve and the minimum in γ_{SL} shows a negative value. If we can find liquids having $\gamma_L < 25$ dyn cm^{-1} and which display positive contact angles on the surface of P(VDF–HFA), a negative value of γ_{SL} can be calculated
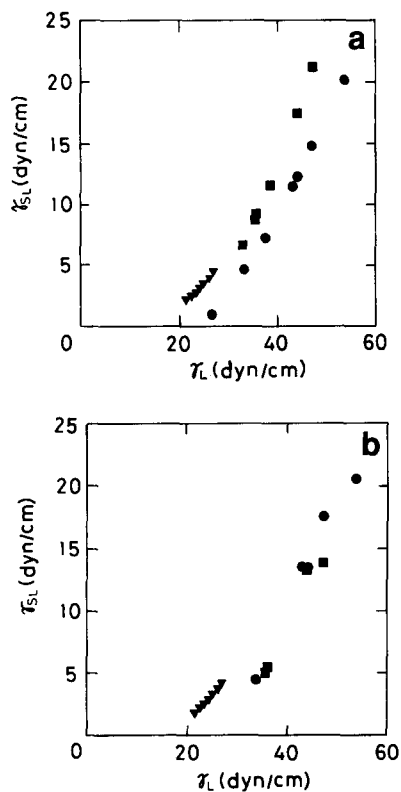
Figure 3 Relationship between γ_{SL} and γ_L of P(VDF–HFA) with 10.4 mol% HFA content. Symbols as in *Figure 1*

(a) $\gamma_{SL} = \gamma_S + \gamma_L - W_a$
$W_a = 2\Phi_G(\gamma_S\gamma_L)^{0.5}$
$\Phi_G = [(2-\phi)\gamma_C^{0.5} + \phi\gamma_L^{0.5}]/(2\gamma_S^{0.5})$

(b) $\gamma_{SL} = \gamma_S + \gamma_L - W_a$
$W_a = 2\Phi_G(\gamma_S\gamma_L)^{0.5}$
$\Phi_G = [(X_L^d X_S^d)^{0.5} + (X_L^p X_S^p)^{0.5}] (\gamma_L/\gamma_S)^a$

with equation (3). From Φ_G, W_a and γ_{SL} *versus* γ_L plots, we expect the parameters ϕ and a can be made available to estimate the interaction between the liquid and solid, such as P(VDF–HFA). The Φ_G, W_a and γ_{SL} *versus* γ_L plots of other P(VDF–HFA) copolymers were similar to that of P(VDF–HFA) with 10.4 mol% HFA content.

Conclusion

The interfacial interaction between P(VDF–HFA) and organic liquids, such as dispersion, polar and hydrogen-bonding liquids, was evaluated using contact angle data. The Good–Girifalco interaction parameter, Φ_G, work of adhesion, W_a, and interfacial tension, γ_{SL}, were calculated. The Φ_G, W_a and γ_{SL} values were dependent on surface tension, γ_L, and species of liquid. Finally, we found the parameters ϕ and a were available for estimating Φ_G, W_a and γ_{SL}.

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