Surface Free Energy Analysis of Polymers and its Relation to Surface Composition

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Synopsis

The dispersion force component of surface free energy, γ_S^d, and the nondispersive interaction free energy between solid and water, I_{SW}^n, were determined by the two-liquid contact-angle method, i.e., by the measurement of contact angles of water drops on plain solids in hydrocarbon, for commercially available organic polymers such as nylons, halogenated vinyl polymers, polyesters, etc. A method to estimate the I_{SW}^n values from the knowledge of the polymer composition is also proposed, on the basis of the assumption of the spherical monomer unit and the sum of interactions between functional groups and water molecules at the surface.

INTRODUCTION

Since Fowkes had proposed experimental methods for doing so,[1] many investigations have been conducted to evaluate the components of surface and interfacial free energies due to intermolecular forces in order to understand interfacial phenomena of organic polymers. The surface and interfacial tensions mainly for molten polymers has recently been reviewed by Wu.[2] For solids, unfortunately, an intrinsically correct method has not yet been elucidated.

As an extension of Fowkes' approach, the dispersion force component as well as the po term of surface free energy have been approximated by contact angle measurement of polar and nonpolar liquids in air (the one-liquid contact-angle method).[3-6] Another extension of Fowkes approach has been proposed by Tamai et al.[7] from contact angle measurement of water drops on solids in hydrocarbon (the two-liquid contact-angle method).

A different approach from the solubility parameters has also been reported to evaluate the dispersion and the polar components.[8] The dispersion force component of surface free energy γ_S^d obtained by Tamai et al.[7] seems to be comparatively larger than others, as pointed out by Panzer.[8] There may be many yet unknown factors for this discrepancy, but one possible reason may be that the neglect of the surface pressure in the one-liquid method could have given the apparently smaller γ_S^d values, as discussed elsewhere in detail.[9]

In this investigation, the two-liquid method was applied to commercially available organic polymers, and γ_S^d and I_{SW}^n (the nondispersive interaction free energy beιween solid and water) were determined. A method of estimation of I_{SW}^n from the surface composition of polymers is also proposed. Since I_{SW}^n values can give useful surface energy information on polar terms, it may be of value for

such applications as adhesion phenomena if the I^n_{SW} values can be estimated from the knowledge of polymer composition.

EXPERIMENTAL

Materials

Isooctane and cyclohexane of absorption-spectoscopic grade were used as saturated hydrocarbons. Water was redistilled from alkaline permanganate solution in a Pyrex glass apparatus.

Most polymers were commercially available plates as follows:

Nylon 6, CM-1031, Toray Industries Inc.

Nylon 6,6, "Zytel" 101; Nylon 6,12, "Zytel" 151, E.I. du Pont Far East Co.

Poly(vinylidene Fluoride) (PVDF), Kureha Chemical Industries Co.

Poly(trifluoromonochloroethylene) (PFCE), "Daiflon," and poly(tetrafluoroethylene–hexafluoropropylene) copolymer (PFEP$_{cop}$), "Neoflon," Daikin Kogyo Co.

Poly(oxymethylene) (POM), "Delrin" 5000, E.I. du Pont Far East Co.

Poly(ethylene terephthalate) (PET), "Lumilar" 100, Toray Industries Inc.

Polycarbonate (PC), Polycarbonate A-3000, Idemitsu Petrochemical Co.

Phenol (PPh) and Melamine (PMe) resin laminated plates, Sumitomo Bakelite Co.

The densities[d], determined from their sizes and weights, and the characteristics of the crystal structures, investigated by x-ray diffractometer (Shimadzu Seisakusho, VD-1), for these plate samples were as follows: PVDF: $d = 1.76$, small peaks of (010) and (200) of orthogonal structure. PFCE: $d = 2.10$, small peak of hexagonal (100). PFEP: $d = 2.07$, sharp peak of poly(tetrafluoroethylene). POM: $d = 1.39$, large and sharp peak of orthogonal structure. PC: $d = 1.19$, very broad peak. PET: $d = 1.38$, large peak of triclinic (100). Nylon 6: $d = 1.19$. Nylon 6,6: $d = 1.14$. Nylon 6,12: $d = 1.05$.

The x-ray diffraction patterns for nylons will be discussed later. Since phenol and melamine resins are laminated, their densities could not be determined.

Surface Preparation and Measurement of Contact Angles

The size of the sample plates was about 1×3 cm. Thicknesses were from 1 to 5 mm according to polymers, except PET, which was 0.1 mm thick.

These samples were cleaned before each measurement, by slight rubbing with a piece of gauze soaked in detergent solution and then thoroughly washing with distilled water. After drying for 1 hr in a desiccator with phosphorus pentoxide, these samples were transferred to an optical cell and covered with hydrocarbon.

The contact angles of water drops on the polymers were measured with a goniometer–telescope system at $20 \pm 0.5°$C. For each measurement, 12 to 18 contact angles were averaged, changing the size and place of the water drops.

The surface and interfacial tensions of liquids were measured by the Wilhelmy plate method.

TABLE I
Contact Angles and Analytical Results (20°C)a

Polymers	θ, degrees		γ_S^d, erg/cm²	I_{SW}^n, erg/cm²	γ_S^p, erg/cm²	γ_S, erg/cm²
	c-Hex	i-Oct				
Nylon 6	105.6 ± 0.5	99.4 ± 0.6	78' ± 7	37.8 ± 0.3	7.2	85
Nylon 6,6	94.1 ± 0.6	87.6 ± 0.6	81 ± 7	47.8 ± 0.3	11.5	93
Nylon 6, 12	113.9 ± 1.0	109.0 ± 0.8	62 ± 9	30.7 ± 0.4	4.7	67
PVCb	139.9 ± 1.5	134.2 ± 1.0	56 ± 5	12.5 ± 0.3	0.8	57
PVDF	125.7 ± 1.1	123.2 ± 0.8	40 ± 4	21.1 ± 0.3	2.3	42
PFCE	170.4 ± 0.9	164.6 ± 0.6	36 ± 3	0.9 ± 0.1	0.0	36
PTFEb	174.7 ± 0.9	173.4 ± 0.8	25 ± 2	0.1 ± 0.1	0.0	25
PFEPcop	174.2 ± 0.5	175.4 ± 0.6	26 ± 2	0.1 ± 0.1	0.0	26
POM	123.7 ± 1.1	117.6 ± 1.2	71 ± 6	23.4 ± 0.3	2.7	74
PET	118.8 ± 0.5	114.5 ± 1.0	56 ± 5	26.7 ± 0.3	3.6	60
PC	143.2 ± 0.4	137.9 ± 1.0	54 ± 5	10.6 ± 0.3	0.6	55
PPh	102.1 ± 1.0	95.6 ± 0.9	81 ± 7	40.9 ± 0.4	8.4	89
PMe	111.1 ± 0.7	106.8 ± 0.5	57 ± 5	32.8 ± 0.4	5.4	62

a Surface and interfacial tensions for liquids at 20°C: $\gamma_{c\text{-Hex}} = 25.0$, $\gamma_{i\text{-Oct}} = 18.9$, $\gamma_{c\text{-Hex}/W} = 50.0$; $\gamma_{i\text{-Oct}/W} = 49.3$, $\gamma_W = 72.7$, $\gamma_W^d = 23.0$ dynes/cm.
b From ref. 9.

RESULTS AND DISCUSSION

The analysis of the two-liquid contact-angle method is according to Tamai et al.[7]

The Young-Dupré equation of the contact angle θ of water drops (W) on plain solid (S) in hydrocarbon (H) is

$$\gamma_{SH} = \gamma_{SW} + \gamma_{HW} \cos \theta \qquad (1)$$

where γ is the surface or interfacial free energy and the subscripts SH, SW, and HW mean the interface of solid/hydrocarbon, solid/water, and hydrocarbon/water, respectively.

According to Fowkes' theory for the expansion of surface free energy in regard to intermolecular forces and the geometric mean assumption for the dispersive interaction free energy at the interface, eq. (1) can be rearranged:

$$I_{SW}^n - 2(\gamma_S^d)^{1/2}[(\gamma_H)^{1/2} - (\gamma_W^d)^{1/2}] = \gamma_W - \gamma_H + \gamma_{HW} \cos \theta \qquad (2)$$

where I_{SW}^n is the nondispersive interaction free energy between solid and water. The two unknowns, γ_S^d and I_{SW}^n, in eq. (2) can be solved by measurement of contact angles in two different hydrocarbons.

The accuracy of the γ_S^d determination by the two-liquid method is not very high, estimated about ±10%, because of its high sensitivity to the error in contact angle measurement. However, the accuracy of I_{SW}^n is considered to be sufficiently adequate, within around ±0.3 erg/cm².

The contact angles and their analytical results by the two-liquid method are listed in Table I. The sign ± for contact angles indicates the standard deviations, and those for γ_S^d and I_{SW}^n represent the 90% confidence limits of accuracy. The surface and interfacial tensions for liquids are shown in this table. The dis-
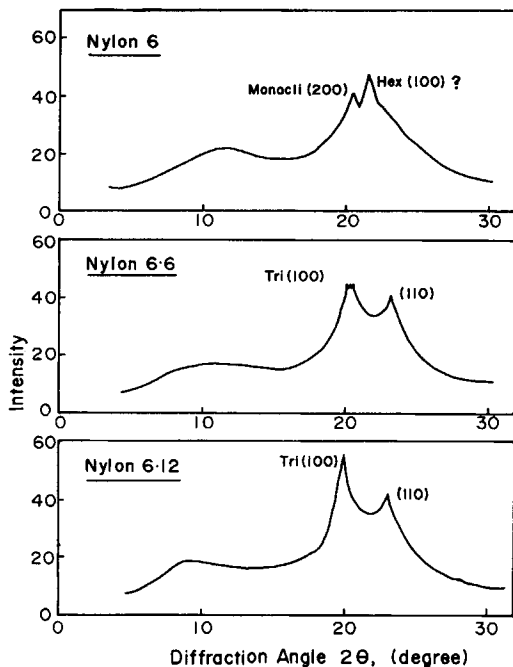
Fig. 1. X-ray diffraction patterns for nylons (Cu $K\alpha$).

persion component of the surface tension of water γ_W^d was calculated according to Fowkes' method from the interfacial tensions between the hydrocarbon and water interfaces. Although Fowkes has given 21.8 dynes/cm as the average value of γ_W^d, 23.0 dynes/cm was adopted in this paper from the interfacial tensions obtained here and in the previous study.[9]

Nylons

Since nylon 6,6 has a larger amount of amide groups than nylon 6,12, the former may well have a larger I_{SW}^n value. Moreover, that γ_S^d of nylon 6,6 is larger may be reasonable, because the functional groups such as amides, hydroxyls, carboxyls, etc., have larger polarizabilities than C—H or C—C bonds,[10] which should contribute to an increase in the dispersion force, if other factors remain constant.

Nylon 6 and nylon 6,6 have different I_{SW}^n values, even though their γ_S^d values are almost equal. This difference may be somewhat unexpected, considering that these nylons have equal amounts of amide groups though different arrangements in the polymer chains.

According to Fort,[11] nylon 6 and nylon 6,6 have similar wetting behavior and equal critical surface tensions γ_c, 42 dynes/cm. Baier and Zisman,[12] however, have indicated that γ_c of nylon 11 was sometimes even larger than that of nylon 6 according to their preparation methods.

The difference in crystal structure of these polymers might affect their surface properties. The x-ray diffraction patterns are shown in Figure 1. Although nylon 6,6 and 6,12 present similar patterns of stable triclinic crystals, nylon 6

display a diffraction peak of stable monoclinic crystals as well as that due to some quasi-stable structure.

This difference in bulk structure might affect the surface structure and the configuration or conformation of functional groups at the surface, and consequently the I_{SW}^n values.

Halogenated Vinyl Polymers

The γ_S^d values of halogenated vinyl polymers are comparatively larger than reported values. For example, γ_S^d values reported are 32.0 erg/cm^2 for PVC,[3] 14.5 erg/cm^2 for PTFE,[4] and 26.2 erg/cm^2 for PVDF.[4]

However, γ_S^d values obtained here for PTFE and PFCE, 25 and 36 erg/cm^2, respectively, correspond very well to the surface free energies theoretically calculated by Good,[14] 24 and 38 erg/cm^2 respectively. As these polymers have very small polarities, as shown in Table I, γ_S^d should be considered to be almost equal to γ_S. There may be many reasons for the disagreement between the results of the two-liquid method and other experimental methods. For one, this discrepancy may be due, at least partly, to the neglect of the surface pressure effect (π) in the one-liquid method. A detailed discussion of this point has been reported elsewhere.[9]

In comparison with those of investigated molten polymers,[2] the γ_S^d values for all polymers investigated here seem to be larger. However, since a correct, reliable method to determine surface free energies for solids is not yet available and some discontinuity of surface free energy between solid and liquid might still possibly exist, it cannot be claimed at present which results are accurate.

Polyesters and Other Polymers

The polyesters, such as PET and PC, and those polymers in the lower part of Table I have, in general, many functional groups, and so it would be natural that I_{SW}^n as well as γ_S^d are comparatively large, as discussed above for nylons.

Estimation of I_{SW}^n from the Composition of Polymers

In the one-liquid method, the nondispersive interaction free energy between solid and polar liquids have been frequently used to obtain the polar surface free energy γ_S^p, assuming the geometric mean for the interfacial force[3,4,5,6] or the harmonic mean.[15]

For the results of the two-liquid method, Kaelble[16] has shown that the geometric mean rule would be applicable. He has rearranged eq. (2) into the following form:

$$\frac{W_{23} + \gamma_{2V} - \gamma_{1V} - \gamma_{12}}{2(\beta_2 - \beta_1)} = \beta_3 + \alpha_3 \left(\frac{\alpha_2 - \alpha_1}{\beta_2 - \beta_1}\right) \tag{3}$$

where the subscripts 1, 2, 3, and V are hydrocarbon, water, solid, and vapor, respectively, and W is the work at the interface, and α and β are the square roots of the dispersion and polar component of the surface tension of each phase, respectively. By application of this equation to Tamai and co-workers' data, Kaelble obtained a linear line for each solid, which should mean that the geo-

TABLE II
Estimation of I_{SW}^{n} from Polymer Structure

Polymer	x	$I/_{SW}^{n}(x)^a$	$s(x)^b$	$I/_{SW}^{n}(x) \cdot s(x)$, erg/cm^2	$I/_{SW}^{n}$, erg/cm^2 Calcd.	$I/_{SW}^{n}$, erg/cm^2 Obsd.
Nylon 6	—CONH—	17	2.7[c]	45.9	45.9	37.8
Nylon 6, 6	—CONH—	17	2.7[c]	45.9	45.9	47.8
Nylon 6, 12	—CONH—	17	1.8[c]	30.6	30.6	30.7
PMMA[d]	—COO—	4.5	3.7	16.7	16.7	27.4
PSt[e]	—Benz.	1	3.3	3.3	3.3	5.9
PVC[d]	—Cl	2	5.7	11.4	11.4	12.5
PVDF	—F$_2$	3	6.5	19.5	19.5	21.1
PET	—COO—	4.5	5.3	23.9	26.5	26.7
	—Benz.	1	2.6	2.6		
PC	—COO—	4.5	2.1	9.5	13.7	10.6
	—Benz.	1	4.2	4.2		
POM	—O—	2.5	9.2	23.0	23.0	23.4
PPh[f]	—OH	10	3.7	37.0	40.7	40.9
	—Benz.	1	3.7	3.7		

[a] In units of 10^{-14} erg/molecule.

[b] In units of 10^{14} cm^{-2}.

[c] Only for nylons, $s(x)$ was calculated assuming the nylon chains to be rod-like, not spherical. Then, since the volume of one monomer unit can be obtained as $v = (M/dN)$, the occupied surface area by one monomer unit a is given as $a = l(v/l)^{1/2} = (lv)^{1/2}$, if polymer chains lie parallel to the surface plane, where l is the length of monomer unit along the polymer chain, 8.7, 8.7, and 13.1 Å for nylon 6, 6, 6, and 6, 12, respectively.

[d] $I/_{SW}^{n}$ values from ref. 9.

[e] Unpublished data.

[f] For phenol resin, a network-structured polymer, an average monomer unit was assumed as $\text{+C}_6\text{H}_3\cdot(\text{OH})\cdot\text{CH}_2\text{+}_n$, and $d = 1.27$ was adopted as the bulk density. Melamine resin was excluded, because its average monomer unit is considered more vague.

metric mean rule is applicable to the polar terms, and could obtain $\alpha_3 (= \gamma_S^d)$ and $\beta_3 (\gamma_S^h)$ values. Therefore, applying this idea to I_{SW}^{n} values here obtained, γ_S^h values were calculated for the present polymers which are also listed in Table I with the total surface free energy γ_S, the sum of γ_S^d and γ_S^h.

However, as Tsutsumi has revealed,[16] the nondispersive interaction energy between mica and water deviates from the geometric mean, although those between mica and several organic polar liquids obey rather well the geometric mean assumption. At any rate, since I_{SW}^{n} itself can be used as a measure of surface polarities, the estimation of I_{SW}^{n} values from the surface composition of polymers has been attempted.

I_{SW}^{n} is considered to be mainly due to hydrogen bonding, and in some cases also due to dipole–dipolde interaction, between functional groups on a given surface and water molecules. Because of the short-range characteristics of hydrogen bonding, effective interaction may be restricted to that between the functional groups and tlhe nearest water molecules. If this is the case, I_{SW}^{n} may be estimated from the kinds and amounts of functional groups as the sum of the interactions, as follows.

$$I_{SW}^{n} = \sum_{x} I_{SW}^{n}(x) \cdot s(x) \qquad (4)$$

where x denotes functional groups, $I_{SW}^n(x)$ is the contribution of one x group to I_{SW}^n, and $s(x)$ is the surface density of x. This equation means that a functional group x may similarly contribute to I_{SW}^n in any polymer, regardless of its specific properties in each polymer. Even with this assumption, it is difficult to know exactly the surface density $s(x)$.

As a first approximation, $s(x)$ was calculated assuming the spherical monomer unit of a given polymer as

$$s(x) = k(M/dN)^{-2/3} \tag{5}$$

where k is the number of x in one monomer unit, M is the molecular weight of the monomer unit, d is the bulk density, and N is Avogadro's number.

The I_{SW}^n values so calculated are listed in Table II and compared with observed values. The contribution of each functional group $I_{SW}^n(x)$ was appropriately chosen so that the calculated values should agree with the observed ones as far as possible.

These $I_{SW}^n(x)$ values seem to be rather reasonable in two ways. The first is that some $I_{SW}^n(x)$ values such as those for ester and aromatic groups can be used for several polymers, as seen in Table II. The second is that the $I_{SW}^n(x)$ values may be considered reasonable when compared with that for water surface. Since the interaction free energy between the imaginary water/water interface I_{WW}^n is calculated to be 99.6 erg/cm^2 (as $I_{WW}^n = 2(\gamma_W - \gamma_W^d)$), and the surface density $s(H_2O)$ by eq. (5) is 10.4×10^{14} cm^{-2}, $I_{WW}^n(H_2O)$ is obtained as 10×10^{-14} erg/molecule. This value corresponds well to that of the OH group, $I_{SW}(OH)$. Moreover, the $I_{SW}^n(x)$ for ester and ether groups, about $\frac{1}{2}$ and $\frac{1}{4}$ of $I_{SW}^n(OH)$, respectively, may be reasonable. For instance, the solubilities in water of polar organic compounds consisting of similar alkyl chain structures, 2-pentanol ($C_2H_4OHC_3H_7$), butyl acetate ($CH_3COOC_4H_9$), and ethyl propyl ether ($C_2H_5OC_3H_7$) are 0.54, 0.37, and 0.21 mole/kg H_2O at 25°C, respectively.[18]

To refine this approach, however, further research for many polymers should be done, and if in some cases specific information on functional groups at the given polymer surface can be added for $I_{SW}^n(x)$, more accurate and applicable I_{SW}^n values would be obtained.

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