

## Estimation of the Surface Free Energy of Polymers

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### Synopsis

A method for measuring the surface energy of solids and for resolving the surface energy into contributions from dispersion and dipole-hydrogen bonding forces has been developed. It is based on the measurement of contact angles with water and methylene iodide. Good agreement has been obtained with the more laborious  $\gamma_c$  method. Evidence for a finite value of liquid-solid interfacial tension at zero contact angle is presented. The method is especially applicable to the surface characterization of polymers.

### INTRODUCTION

Many important applications of polymers require that they adhere well to other substances. Adhesion is a manifestation of the attractive forces that exist between all atoms and which fall into three broad categories: primary (chemical); quasi-chemical (hydrogen bond); and secondary (van der Waals). In the last category are the Keesom forces<sup>1</sup> arising from molecules with permanent dipoles, Debye forces<sup>2</sup> caused by a molecule with a permanent dipole inducing a dipole in a neighboring molecule by polarization, and London dispersion forces<sup>3</sup> arising from instantaneous dipoles produced by the motion of electrons within the molecule. The London forces are ubiquitous and account for a major part if not all of the strength of such polymers as polyethylene.

It is generally agreed in theory that attraction due only to secondary forces and hydrogen-bonding is sufficient to produce adhesive joints between polymers of strength equal to that of the polymers themselves without the need for chemical bonds. Since these forces decrease as the inverse sixth power of the distance between molecules, it is apparent that surfaces to be adhered must come into intimate, wetting contact.

It has been recognized for many years that wetting of surfaces by adhesives is a necessary, though sometimes insufficient, requirement for developing strong adhesive joints.<sup>4</sup> Thermodynamic wetting (small or zero contact angle,  $\theta$ , between liquid and solid) is a function of four parameters given by the well-known Young equation,

$$\cos \theta \gamma_{lv} = \gamma_{sv} - \gamma_{sl} - \pi_e \quad (1)$$

where  $\gamma_{lv}$ ,  $\gamma_{sv}$ , and  $\gamma_{sl}$  are the free energies of the liquid and solid against

their saturated vapor and of the interface between liquid and solid, respectively, and  $\pi_e$  is the equilibrium pressure of adsorbed vapor of the liquid on the solid. It is evident that wetting is favored by low interfacial free energy, high solid surface free energy and low liquid surface free energy. Unfortunately, only  $\gamma_{lv}$  and  $\theta$  are susceptible to direct experimental determination. In order to understand and predict the adhesion of polymers, however, it is essential that something be known about  $\gamma_{sv}$  and  $\gamma_{sl}$ .

Zisman and his coworkers have made a useful approach to this problem.<sup>5</sup> They have found that a plot of  $\cos \theta$  vs.  $\gamma_{lv}$  for homologous series of liquids on a given solid is generally a straight line and have introduced the concept of critical surface tension of wetting ( $\gamma_c$ ). This empirical quantity is defined as the value of  $\gamma_{lv}$  at the intercept of the plot of  $\cos \theta$  vs.  $\gamma_{lv}$  with the horizontal line,  $\cos \theta = 1$ . Liquids of  $\gamma_{lv}$  less than  $\gamma_c$  would be expected to spread on the solid surface.

From eq. 1 it follows that

$$\cos \theta \gamma_{lv} = (1) \gamma_c = \gamma_{sv} - \gamma_{sl} - \pi_e \quad (2)$$

Although many workers have been inclined to identify  $\gamma_c$  with  $\gamma_{sv}$ , Zisman has been careful to point out that  $\gamma_c$  is symbatic with, but not necessarily equal to the solid surface free energy because it is not certain that  $\gamma_{sl}$  and  $\pi_e = 0$  when  $\theta = 0$ . In fact it will be shown that  $\gamma_{sl}$  is usually not zero when  $\theta = 0$ . The concept has nevertheless proved extremely useful and has been related to adhesion and to friction by many workers.<sup>4</sup>

Fowkes<sup>6</sup> in a theoretical consideration of attractive forces at interfaces has suggested that the total free energy at a surface is the sum of contributions from the different intermolecular forces at the surface. Thus the surface free energy of water could be written

$$\gamma_{lv} = \gamma_l^d + \gamma_l^h \quad (3)$$

where the superscripts  $h$  and  $d$  refer to the hydrogen bonding and dispersion force components.

By assuming that  $\pi_e = 0$  and

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2 \sqrt{\gamma_s^d \gamma_l^d} \quad (4)$$

Fowkes has derived from the Young equation an expression for the contact angle of a liquid on a solid in terms of the dispersion force contributions of each:

$$1 + \cos \theta = 2 \sqrt{\gamma_s^d} \left( \frac{\sqrt{\gamma_l^d}}{\gamma_{lv}} \right) \quad (5)$$

Since values of  $\gamma_l^d$  have been published for many liquids,<sup>6</sup> it is possible to approximate  $\gamma_s^d$  from a single measurement of  $\theta$  by the use of eq. 5 in cases where only dispersion forces operate (i.e., the liquid or solid is nonpolar).

For cases where both forces operate, assume that eq. 4 has the more general form

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_s^d \gamma_l^d} - 2\sqrt{\gamma_s^h \gamma_l^h} \quad (6)$$

which can be expressed alternatively as

$$\gamma_{sl} = (\sqrt{\gamma_s^d} - \sqrt{\gamma_l^d})^2 + (\sqrt{\gamma_s^h} - \sqrt{\gamma_l^h})^2 \tag{6a}$$

$\gamma^h$  denotes the component of surface energy due to hydrogen bonding and dipole-dipole interactions. Although hydrogen bonding interactions are more specific than implied by the  $\sqrt{\gamma_s^h \gamma_l^h}$  term in eq. 6, the dipole-dipole interactions (to which hydrogen bonding is similar) take the form of a geometric mean.<sup>1</sup>

In the more general form of eq. 6, eq. 5 then can be written:

$$1 + \cos \theta = 2\sqrt{\gamma_s^d} \left( \frac{\sqrt{\gamma_l^d}}{\gamma_{lv}} \right) + 2\sqrt{\gamma_s^h} \left( \frac{\sqrt{\gamma_l^h}}{\gamma_{lv}} \right) \tag{7}$$

TABLE I  
Components of Surface Energy for Various Solids

Surface	Contact angle°		ergs/cm <sup>2</sup>			dynes/cm $\gamma_c$
	Water	Methylene iodide	$\gamma_s^d$	$\gamma_s^h$	$\gamma_s$	
Polyethylene (low density)	94	52	32.0	1.1	33.1	31
	<sup>a</sup> (104)	<sup>a</sup> (53)	<sup>a</sup> (33.2)	<sup>a</sup> (0.0)	<sup>a</sup> (33.2)	
Poly(vinyl chloride)	87	36	40.0	1.5	41.5	39
Poly(vinylidene chloride)	80	29	42.0	3.0	45.0	40
Poly(vinyl fluoride)	80	49	31.3	5.4	36.7	28
Poly(vinylidene fluoride)	82	63	23.2	7.1	30.3	25
Poly(trifluoroethylene)	92	71	19.9	4.0	23.9	22
Poly(tetrafluoroethylene)	108	88	12.5	1.5	14.0	18.5
	<sup>a</sup> (108)	<sup>a</sup> (77)	<sup>a</sup> (18.6)	<sup>a</sup> (0.5)	<sup>a</sup> (19.1)	
Poly(ethylene terephthalate)	81	38	37.8	3.5	41.3	43
	<sup>a</sup> (76)	<sup>a</sup> (24)	<sup>a</sup> (43.2)	<sup>a</sup> (4.1)	<sup>a</sup> (47.3)	
Poly(methyl methacrylate)	80	41	35.9	4.3	40.2	39
Nylon 6-6	70	41	34.1	9.1	43.2	46
	<sup>a</sup> (72)	<sup>a</sup> (28)	<sup>a</sup> (40.8)	<sup>a</sup> (6.2)	<sup>a</sup> (47.0)	
Polystyrene	91	35	41.4	0.6	42.0	43
						(35)p
n-Hexatriacontane	111	77	18.9	0.2	19.1	21
						(11)p
Paraffin	108	66	25.4	0.0	25.4	23
						(15)p
Pentaerythritol tetranitrate (single crystal)						
110 face	77	41	35.4	5.5	40.9	40
101 face	72	31	39.5	6.6	46.1	45
Fluorinated methacrylic polymer A	120	98	9.1	0.3	9.4	10.6
polymer S	118	97	9.3	0.5	9.8	11.1
Vinylidene chloride- acrylonitrile copolymer 80/20	81	27	43.1	2.6	45.7	38-44

<sup>a</sup> ( )—Measurements by the authors.  
( ) p— $\gamma_c$  from polar liquids.

The value of  $\gamma_i^h$  can be determined from available values of  $\gamma_{i_0}$  and  $\gamma_i^d$  by eq. 3. By measuring  $\theta$  of two different liquids against a solid, simultaneous equations are obtained which can be solved for  $\gamma_s^d$  and  $\gamma_s^h$ . Thus the components of surface free energy due to various forces can be approximated, and the sum of these components by analogy with eq. 3 should yield a reasonable approximation of the total solid surface energy  $\gamma_s$ . The use of the more general subscript  $s$  instead of  $sv$  assumes that the vapor pressure of the solid is negligible.

For purposes of discussion and data analysis, it will be convenient to combine eq. 2 with eq. 6a to give:

$$\gamma_c = \gamma_s - [(\sqrt{\gamma_s^d} - \sqrt{\gamma_i^d})^2 + (\sqrt{\gamma_s^h} - \sqrt{\gamma_i^h})^2] \quad (8)$$

The term in brackets is the interfacial tension  $\gamma_{si}$  which equals  $\gamma_s - \gamma_c$ .

Equation 7 was tested by taking contact angle values for two liquids of widely different properties on various surfaces and calculating  $\gamma_s^d$ ,  $\gamma_s^h$ , and  $\gamma_s$ .  $\gamma_s$  was compared with reported values of  $\gamma_c$ . The properties of the liquids at 20°C are given below.

Liquid	$\gamma_i^d$	$\gamma_i^h$	$\gamma_{i_0}$ (ergs/cm <sup>2</sup> )
Water	21.8 ± 0.7	51.0	72.8
Methylene iodide	49.5	1.3	50.8

The values for water were taken from Ref. 6; the values for methylene iodide given in this reference contained a large uncertainty ( $\pm 9$  ergs/cm<sup>2</sup>). The properties of methylene iodide shown above were calculated from the given water values and the published water-methylene iodide interfacial tension of 41.6 dynes/cm<sup>7,8,9</sup> by the use of eq. 6. The uncertainty in  $\gamma_i^d$  for methylene iodide by this method is probably less than 1 erg/cm<sup>2</sup>.

The results for a variety of solids using water and methylene iodide

TABLE II  
Components of Surface Energy for Various Monolayers

Monolayer	Contact angle°		ergs/cm <sup>2</sup>			dynes/-
	Water	Methylene iodide	$\gamma_s^d$	$\gamma_s^h$	$\gamma_s$	cm
						$\gamma_c$
17-(perfluoroheptyl)-heptadecanoic acid	115	101	7.4	1.3	8.7	8.0
17-(perfluoropentyl)-heptadecanoic acid	110	94	9.9	1.7	11.6	11.4
17-(perfluoropropyl)-heptadecanoic acid	106	86	13.3	1.7	15.0	16.4
17-(perfluoroethyl)-heptadecanoic acid	105	83	14.7	1.6	16.3	16.0
11-(perfluorodecyl)-undecanoic acid	118	101	7.7	0.8	8.5	7.8
11-(perfluoroheptyl)-undecanoic acid	115	98	8.6	1.0	9.6	11.7
11-(perfluorobutyl)-undecanoic acid	108	82	15.6	0.9	16.5	15.8
11-(perfluoroethyl)-undecanoic acid	105	79	16.9	1.2	18.1	18.8
$\omega$ -Monohydroperfluoroundecanoic acid	97	88	11.3	5.2	16.5	15
Octadecylamine	101	68	23.0	1.0	24.0	21.5
Trinitrobutyric acid	73	40	35.1	7.3	42.4	42
Poly(dimethyl siloxane)	101	70	21.7	1.1	22.8	24

contact angles published by Shafrin and Zisman<sup>10</sup> are shown in Table I. Similar results for various monolayers<sup>10</sup> are shown in Table II.

### Discussion

In general there is reasonable agreement between  $\gamma_c$  and  $\gamma_s$ . In the case of polyethylene, the calculated value of 33.1 ergs/cm<sup>2</sup> for  $\gamma_s$  agrees better with the value of 34.3 ergs/cm<sup>2</sup> obtained by Dettre and Johnson<sup>11</sup> by extrapolating surface tension data for molten low density polyethylene to 20°C than it does with  $\gamma_c$ . The polyethylene used by Shafrin and Zisman also exhibits a small amount of hydrogen bonding ability. Adam<sup>12</sup> in commenting on the difference in water contact angle between polyethylene and paraffin has speculated that even the best samples of polyethylene appear to have traces of polar substances in their surfaces. Various samples differ in this respect as shown by the parenthetical values in Table I which are the authors' measurements on a very carefully prepared sample of low-density polyethylene. In this case  $\gamma_s^h = 0$ .

Substitution of the hydrogen atoms in polyethylene by chlorine leads to a large increase in the dispersion force component and a small increase in hydrogen-bonding ability. This is reasonable in view of the large polarizability and weak hydrogen-bonding ability of the covalent chlorine atom.<sup>13</sup> Fluorine substitution gives a particularly interesting result. While the dispersion force component decreases in an essentially linear manner with increasing fluorine substitution, the hydrogen-bonding component goes through a maximum at 50-atom per cent substitution. Ellison and Zisman<sup>14</sup> have noted the increase in wettability by water of surfaces in the range 0-25-atom percent fluorine substitution and have explained the increase on the basis of hydrogen-bonding between fluorine and water due to the relatively high electronegativity of the fluorine atom. The degree of electronegativity of the fluorine atom attached to a carbon atom will depend on other substitutions on the same carbon atom. They have concluded that the relative electronegativity of a fluorine substituent will decrease with additional fluorine substitution. Our calculations support this conclusion except we find that the hydrogen-bonding ability of fluorinated polymers does not decrease until fluorine content exceeds 50-atom percent.

From eq. 8 it is apparent that  $\gamma_s - \gamma_c \geq 0$ . Three cases of measurement of  $\gamma_c$  are of interest.

*I. Nonpolar liquid,  $\gamma_i^h = 0$ .* Then  $\gamma_s^d = \gamma_i^d = \gamma_c$ , i.e., the use of nonpolar liquids to determine  $\gamma_c$  leads to a value equal to the dispersion component of  $\gamma_s$ .

*II. Polar liquid on nonpolar solid,  $\gamma_i^h \neq 0$  but  $\gamma_s^h = 0$ .* Then  $\gamma_s^d = \gamma_s > \gamma_i^d$  and  $\gamma_s - \gamma_c = (\sqrt{\gamma_s^d} - \sqrt{\gamma_i^d})^2 + \gamma_i^h$ , i.e., the use of polar liquids to determine  $\gamma_c$  on nonpolar solids leads to a value considerably less than  $\gamma_s$ . The interfacial tension  $\gamma_s - \gamma_c$  will have a positive value.

*III. Nonpolar liquid on polar solid,  $\gamma_i^h = 0$  but  $\gamma_s^h \neq 0$ .* Then  $\gamma_s - \gamma_c = (\sqrt{\gamma_s^d} - \sqrt{\gamma_i^d})^2 + \gamma_s^h$ , i.e., the results are the same as Case II.

TABLE III  
Comparison of Surface Energy Measurements from Table I

Surface	$\gamma_c$	$\gamma_s^{d'}$	$\gamma_s - \gamma_c$	$\gamma_s^d - \gamma_s^{d'}$
Polyethylene (low density)	31	$34.6 \pm 2.3$	2.1 *(2.2)	-2.6 *(-1.4)
Poly(vinyl chloride)	39	$41.7 \pm 2.0$	2.5	-1.7
Poly(vinylidene chloride)	40	$43.0 \pm 2.4$	5.0PS	-1.0
Poly(vinyl fluoride)	28	$34.8 \pm 2.8$	8.7PS	-3.5
Poly(vinylidene fluoride)	25	$25.0 \pm 0.3$	5.2PS	-1.8
Poly(trifluoroethylene)	22	$22.3 \pm 0.3$	1.9PS	-2.4
Poly(tetrafluoroethylene)	18.5	$19.65 \pm 0.2$	-4.5 *(0.6)	-7.15 *(-1.05)
Poly(ethylene terephthalate)	43	$43.2 \pm 0.2$	-1.7 *(4.3)PS	-5.4 *(0.0)
Poly(methyl methacrylate)	39	—	1.2	—
Nylon 6-6	46	$42.9 \pm 0.0$	-2.8 *(1.0)PS	-8.7 *(-2.1)
Polystyrene	43 (35)p	$43.1 \pm 0.8$	-1.0 (7.0)PL	-1.7
n-Hexatriacontane	21 (11)p	$20.8 \pm 0.4$	-1.9 (8.1)PL	-1.9
Paraffin	23 (15)p	$24.2 \pm 0.5$	2.4 (10.4)PL	+1.2
* (—) — Measurements by the authors.		Average	$(\gamma_s - \gamma_c)$	$(\gamma_s^d - \gamma_s^{d'})$
( ) p — $\gamma_c$ from polar liquids.		Nonpolar	$\bar{X} = 0.4$	Overall
PS — polar surface.		liquid	$\sigma(X) = 2.4$	average
PL — polar $\gamma_c$ liquids on non-polar surface.				$\bar{X} = -2.6$
				$\sigma(X) = 2.5$
		PS	$\bar{X} = 2.0$	
			$\sigma(X) = 4.1$	
		PL	$\bar{X} = 8.5$	
			$\sigma(X) = 1.7$	

The third column of Table III shows values of interfacial tension ( $\gamma_s - \gamma_c$ ). Statistics of the above three cases are given at the bottom of the table ( $\bar{X}$  is the average  $\gamma_s - \gamma_c$  and  $\sigma(X)$  is the standard deviation). For nonpolar liquids on nonpolar solids (Case I)  $\bar{X} \sim 0$ . For Case II (polar solid) and Case III (polar liquid)  $\bar{X}$  is positive, particularly in Case III where it is apparent that polar liquids seriously underestimate the true surface energy of nonpolar solids. Obviously the interfacial tension at  $\theta = 0$  can be fairly large, e.g., 10.4 ergs/cm<sup>2</sup> in the case of paraffin.

Poly(tetrafluoroethylene) appears to be an exception to eq. 8 with  $\gamma_s$  considerably lower than  $\gamma_c$ . The reported contact angle of 88° for methylene iodide on this substance is, however, suspect. Angles on fluorinated monolayers of equal or slightly lower  $\gamma_c$  than poly(tetrafluoroethylene) have been reported in the range of 79°–83° (See Table II). The best measurements by the authors are in agreement with the reported water contact angle, but give a methylene iodide contact angle of 77°. The highest angle obtained on several different specimens of poly(tetrafluoroethylene) was

79°. When these values are used in eq. 7 the parenthetical energies shown in Tables I and III were obtained, and poly(tetrafluoroethylene) is not an exception to eq. 8.

A further test of the validity of eq. 7 can be made by comparing  $\gamma_s^d$  from H<sub>2</sub>O—CH<sub>2</sub>I<sub>2</sub> data (Table I) with  $\gamma_s^{d'}$  which has been calculated from eq. 5 by using Zisman's  $\gamma_c$  data<sup>5,14</sup> for nonpolar liquids. The comparison  $\gamma_s^d - \gamma_s^{d'}$  is shown in Table III. Agreement is good but consistently negative. We cannot account for this difference except to suggest that it is due either to the large size of the iodine atoms in methylene iodide which causes the geometric mean estimate of interaction energy (eq. 4) to be too large (see ref. 6 and 15) or to the assumption that  $\pi_e = 0$ .

### Conclusions

A method for approximating the surface free energy of solids has been developed. It depends simply on the measurement of water and methylene iodide contact angles. The resulting free energy is resolved into two components, dispersion and hydrogen bonding-dipole. Comparison of results with Zisman's  $\gamma_c$  and Fowkes'  $\gamma^d$  values shows reasonable agreement.

The simplicity of the method and its ability to resolve surface energy into components make it a useful tool in any study where surface interactions are important. Since  $\gamma_s^d$  and  $\gamma_s^h$  values are sensitive to surface composition, this method should also be useful as a semiquantitative measure of surface composition.

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