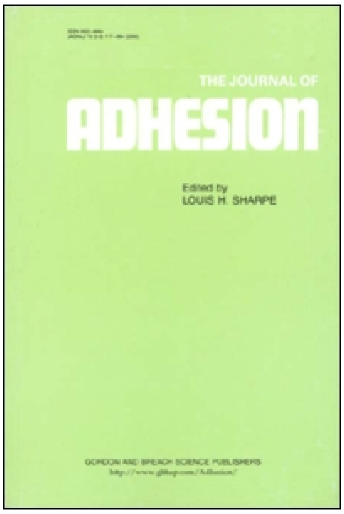

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Polar and Nonpolar Interactions in Adhesion

Souheng Wu[a]
[a] Fabrics and Finishes Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.

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Polar and Nonpolar Interactions in Adhesion[†]

SOUHENG WU

Fabrics and Finishes Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898, U.S.A.

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Equations for polar and nonpolar interactions across the interface are developed by using energy additivity concept in a semi-continuum model. Interfacial and surface tensions of molten polymers are measured directly and used to test the resulting equations:

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1{}^d\gamma_2{}^d}{\gamma_1{}^d + \gamma_2{}^d} - \frac{4\gamma_1{}^p\gamma_2{}^p}{\gamma_1{}^p + \gamma_2{}^p}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1{}^d\gamma_2{}^d)^{0.5} - \frac{4\gamma_1{}^p\gamma_2{}^p}{\gamma_1{}^p + \gamma_2{}^p}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1{}^d\gamma_2{}^d)^{0.5} - 2(\gamma_1{}^p\gamma_2{}^p)^{0.5}$$

The first expression may be called the harmonic-mean equation preferred for low energy systems such as organic liquids, water, polymers, and organic pigments. The second may be called the geometric-harmonic-mean equation preferred for high energy systems such as mercury, glass, metal oxides and graphite. The third may be called the geometric mean equation which is found unsatisfactory. The harmonic-mean equation is used to obtain the "optimum" wettability condition for adhesion. The importance of polar interactions and matching of the polarity are analyzed and emphasized.

INTRODUCTION

We would like to develop equations for the polar and nonpolar (dispersion) components of the interfacial energies by using the energy additivity concept in a semicontinuum model. The present approach bridges and extends the

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methods of Fowkes[1] and of Girifalco and Good[2]. The resulting equations are then used to express the "optimum" wettability condition for adhesion in terms of polarity and surface energy.

To test the validity of these equations, interfacial and surface tensions of molten polymers are measured directly[3-5] and used. Molten polymers are especially suitable for this purpose, because they are immiscible, unlike ordinary liquids. The contact angles of ordinary liquids on polymer solids are not suitable, because the interfacial and surface tensions can only be obtained indirectly by using some theoretical or empirical equations in this method. It is precisely these equations that we have yet to establish.

ENERGY ADDITIVITY AND SEMI-CONTINUUM MODEL

We assume that interfacial energies can be resolved into nonpolar (dispersion) and polar components:

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

where the superscripts d and p refer to nonpolar (dispersion) and polar, respectively. This energy additivity concept has been used by Fowkes[1] in interfacial energies, and by Gardon[6], Hansen and Beerbower[7], and Meyer and co-workers[8], among others, in cohesive energies. The polar component includes various dipole interactions and hydrogen bonding. For simplicity, they are combined into one single term in the present work.

Applying this concept to the work of adhesion, we have from the definition of the work of adhesion,

$$\gamma_{12} = \gamma_1 + \gamma_2 - W^d_{a12} - W^p_{a12} \tag{2}$$

where γ_{12} is the interfacial tension; γ_1 and γ_2 are the surface tensions; W^d_{a12} and W^p_{a12} the nonpolar and polar components of the work of adhesion, $W_{a12} = W^d_{a12} + W^p_{a12}$. Equation (2) is quantitative. In this work, we will convert it into a more useful form by expressing the components of the work of adhesion in terms of the components of the works of cohesion.

Using a semi-continuum model, the works of adhesion and cohesion can be expressed in terms of the molecular properties by [2]

$$W_{a12} = \frac{n_1 n_2 A_{12}}{6d_{12}^2}\left(\frac{1}{2} - \frac{1}{m-4}\right) \tag{3}$$

$$W_{c1} = \frac{n_1^2 A_{11}}{6d_{11}^2}\left(\frac{1}{2} - \frac{1}{m-4}\right) \tag{4}$$

where W_c is the work of cohesion; n the density in molecules per unit volume; d the equilibrium separation of the two phases; A and m are the attraction constant and the repulsive exponent in the Lennard-Jones potential function, respectively. In the following, we will resolve the attraction constants into nonpolar and polar parts

$$A_{ij} = A_{ij}{}^{d} + A_{ij}{}^{p} \tag{5}$$

and then relate the components of the work of adhesion to the components of the works of cohesion.

NONPOLAR (DISPERSION) INTERACTION

The nonpolar part of the attraction constant can be given in terms of the London's theory by

$$A_{12}{}^{d} = \left(\frac{3}{2}\right) h \left(\frac{\nu_1 \nu_2}{\nu_1 + \nu_2}\right) \alpha_1 \alpha_2 \tag{6}$$

$$A_{11}{}^{d} = (\tfrac{3}{4}) h \nu_1 \alpha_1{}^{2} \tag{7}$$

where h is the Planck's constant; ν the electronic vibrational frequency; α the polarizability. $A_{12}{}^{d}$ may be expressed in terms of $A_{11}{}^{d}$ and $A_{22}{}^{d}$ by either the harmonic mean or the geometric mean relations as shown below.

Eliminating ν from Eq. (6) by using Eq. (7), we have

$$A_{12}{}^{d} = \frac{2A_{11}{}^{d} A_{22}{}^{d}}{A_{11}{}^{d}(\alpha_2/\alpha_1) + A_{22}{}^{d}(\alpha_1/\alpha_2)} \tag{8}$$

Thus, if $\alpha_1 \cong \alpha_2$, we have

$$A_{12}{}^{d} \cong \frac{2A_{11}{}^{d} A_{22}{}^{d}}{A_{11}{}^{d} + A_{22}{}^{d}} \tag{9}$$

By using the geometric-mean combining rule for the intermolecular distances[5,9]

$$d_{12} \cong (d_{11}\, d_{22})^{0.5} \tag{10a}$$

and assuming

$$n_1/d_{11} \cong n_2/d_{22} \tag{10b}$$

we thus obtain from Eqs. (3)–(5) and (9)–(10) the following

$$W_{a12}^{d} \cong \frac{2W_{c1}{}^{d}W_{c2}{}^{d}}{W_{c1}{}^{d} + W_{c2}{}^{d}} \tag{11a}$$

$$= \frac{4\gamma_1{}^{d}\gamma_2{}^{d}}{\gamma_1{}^{d} + \gamma_2{}^{d}} \tag{11b}$$

since $W_{ci}{}^{d} = 2\gamma_i{}^{d}$. This is the harmonic-mean approximation.†

Alternatively, we may eliminate α from Eq. (6) by using Eq. (7). In this case, we have

$$A_{12}{}^{d} = \frac{2(v_1 v_2)^{0.5}}{v_1 + v_2}(A_{11}{}^{d}A_{22}{}^{d})^{0.5} \tag{12}$$

Thus, if $v_1 \cong v_2$, we have

$$A_{12}{}^{d} \cong (A_{11}{}^{d}A_{22}{}^{d})^{0.5} \tag{13}$$

Again, by using Eq. (10), we have

$$W_{a12}^{d} \cong (W_{c1}{}^{d}W_{c2}{}^{d})^{0.5} \tag{14a}$$

$$= 2(\gamma_1{}^{d}\gamma_2{}^{d})^{0.5} \tag{14b}$$

This is the geometric-mean approximation.

POLAR INTERACTIONS

Polar interactions include, among others, dipole-dipole, dipole-induced dipole, and hydrogen bonding interactions. For simplicity, we combine all types of polar energies into one single term in this treatment. We realize that separate treatment of each type of polar energies might give further improvement. The polar component of surface energy may be written as

$$\gamma^{p} = \gamma^{pp} + \gamma^{pi} + \gamma^{h} \tag{15}$$

where γ^{pp} is the dipole-dipole component, γ^{pi} the dipole-induced dipole component, and γ^{h} the hydrogen bonding component.

The polar part of the attraction constant can be given in terms of the

† Previously, we called it the "reciprocal-mean" approximation[5].

Debye-Keesom theories by

$$A_{12}{}^{p} = \frac{2\mu_1{}^2\mu_2{}^2}{3kT} + (\alpha_1\mu_2{}^2 + \alpha_2\mu_1{}^2) + A_{12}{}^{h} \tag{16}$$

$$A_{11}{}^{p} = \frac{2\mu_1{}^4}{3kT} + 2\alpha_1\mu_1{}^2 + A_{11}{}^{h} \tag{17}$$

where the first term is for dipole-dipole interaction, the second term for dipole-induced dipole interaction, and the last term for the hydrogen bonding interaction. The symbols used have their usual meanings: μ the permanent dipole moment, k the Boltzmann constant and T the temperature.

Using Eq. (10) and assuming $\alpha_1 \cong \alpha_2$ for the dipole-induced dipole term, we obtain from Eqs. (3)–(5) and (16)–(17) the following

$$W_{a12}^{p} = 2(\gamma_1{}^{pp}\gamma_2{}^{pp})^{0.5} + (\gamma_1{}^{pi} + \gamma_2{}^{pi}) + W_{a12}^{h} \tag{18}$$

noting that $W_{ci}{}^{p} = 2\gamma_i{}^{p}$, $W_{ci}{}^{pp} = 2\gamma_i{}^{pp}$ and $W_{ci}{}^{pi} = 2\gamma_i{}^{pi}$.

Two special cases deserve mention here. When dipole-dipole interaction is predominant, Eq. (18) reduces to:

$$W_{a12}^{p} = 2(\gamma_1{}^{p}\gamma_2{}^{p})^{0.5} \tag{19}$$

On the other hand, when dipole-induced dipole interaction predominates, Eq. (18) reduces to:

$$W_{a12}^{p} = \gamma_1{}^{p} + \gamma_2{}^{p} \tag{20}$$

Meyer and coworkers[8] have reported cases where dipole-induced dipole interaction is predominant. We have found empirically that harmonic-mean expression can be used in place of Eq. (18) rather well in many cases[5]:

$$W_{a12}^{p} = \frac{4\gamma_1{}^{p}\gamma_2{}^{p}}{\gamma_1{}^{p} + \gamma_2{}^{p}} \tag{21}$$

POLARITY AND INTERFACIAL ENERGY

The equations developed above can be combined with Eq. (2) to give several theoretical and semi-empirical equations relating the interfacial tension to the polarity and the surface tension of the individual phases. Three of them will be discussed below shortly.

Girifalco and Good[2] proposed an equation containing an interaction parameter ϕ,

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\phi(\gamma_1\gamma_2)^{0.5} \tag{22}$$

The utility of this equation is limited, because ϕ is an empirical parameter whose value is not known before experiments. Good and Elbing[10] showed that ϕ may be estimated from molecular properties for ordinary liquids. Besides complexity, such calculations for polymers remain untenable. We will develop readily usable expressions for ϕ in terms of the macroscopic properties of the individual phases, i.e. the polarity.

Harmonic-mean Equation

Using Eqs. (11) and (21) in Eq. (2), we obtain

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p} \tag{23}$$

This is the harmonic-mean equation[5] preferred for low energy systems such as water, organic liquids, polymers and organic pigments[5,11]. Applications to molten polymers will be discussed later.

Comparing Eqs. (22) and (23), we obtain

$$\phi = 2\left[\frac{x_1^d x_2^d}{g_1 x_1^d + g_2 x_2^d} + \frac{x_1^p x_2^p}{g_1 x_1^p + g_2 x_2^p}\right] \tag{24}$$

where x_i^p is the polarity and x_i^d is the nonpolarity of phase i defined by

$$x_i^p = \gamma_i^p/\gamma_i \tag{25a}$$

$$x_i^d = \gamma_i^d/\gamma_i \tag{25b}$$

The surface tension ratios g_1 and g_2 are defined by

$$g_1 = \gamma_1/\gamma_2 \tag{26a}$$

$$g_2 = \gamma_2/\gamma_1 \tag{26b}$$

It is obvious that $x_i^d + x_i^p = 1$ and $g_1 g_2 = 1$.

Geometric-harmonic-mean Equation

Using Eqs. (14) and (21) in Eq. (2), we obtain

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{0.5} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p} \tag{27}$$

This is the geometric-harmonic-mean equation[5] preferred for high energy systems such as mercury, glass, metal oxides, and graphite. Comparing Eqs. (22) and (27), we have

$$\phi = (x_1^d x_2^d)^{0.5} + \frac{2x_1^p x_2^p}{g_1 x_1^p + g_2 x_2^p} \tag{28}$$

Geometric-mean Equation

Using Eqs. (14) and (19) in Eq. (2), we obtain

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1{}^d\gamma_2{}^d)^{0.5} - 2(\gamma_1{}^p\gamma_2{}^p)^{0.5} \tag{29}$$

This is the geometric-mean equation which we proposed before[4,12]. Owens and Wendt[13] and Kaelble and Uy[14] have used this equation. We have shown, however, that this equation is not satisfactory[5]. This will be discussed later. Comparing Eqs. (22) and (29), we have

$$\phi = (x_1{}^d x_2{}^d)^{0.5} + (x_1{}^p x_2{}^p)^{0.5} \tag{30}$$

Fowkes' equation[1] is a special case of Eq. (27) or (29), when the polar term is neglected. This is applicable only to nonpolar/nonpolar and nonpolar/polar systems. Most materials are, however, polar to various degrees, and the polar term may in fact be the major factor[5]. Therefore, the polar term should never be neglected without a proper justification. This will be discussed further later. Equation (23), the harmonic-mean equation, is distinct. We note that other useful equations may be obtained readily by suitable combinations of Eqs. (2)–(21).

APPLICATIONS TO MOLTEN POLYMERS

The harmonic-mean equation can be used quite well with molten polymers[5], solid polymers[5], organic pigments[11], and contact angles[5,11]. The geometric-

TABLE I

Surface Tensions of Polymers Measured by the Pendent Drop Method

Polymers	Surface tension, dynes/cm[d] 20°C[b]	140°C	180°C
Polychloroprene (PCP)[a]	43.6	33.2	29.8[c]
Polystyrene (PS)	40.7	32.1	29.2
Poly(methyl methacrylate) (PMMA)	41.1	32.0	28.9
Poly(vinyl acetate) (PVAc)	36.5	28.6	25.9
Poly(*n*-butyl methacrylate) (PnBMA)	31.2	24.1	21.7
Poly(*i*-butyl methacrylate) (PiBMA)	30.9	23.7	21.3
Poly(*t*-butyl methacrylate) (PtBMA)	30.5	23.3	21.0
Polytetrahydrofuran (PTHF)	31.9	24.6	22.2
Polydimethylsiloxane (PDMS)	19.8	14.1	12.2
Linear polyethylene (L-PE)	35.7	28.8	26.5
Branched polyethylene (B-PE)	35.3	27.3	24.6

[a] Polychloroprene = poly(2-chloro-1,3-butadiene).

[b] Values at 20°C are extrapolated ones. See text.

[c] Measurements on PCP were made in the range 60–150°C. The values at 20°C and 180°C were extrapolated.

[d] Values between 20°C and 180°C can be obtained by linear interpolation.

mean equation is, however, not satisfactory[5]. The applications to molten polymers are discussed below.

Interfacial properties of molten polymers

The interfacial and surface tensions of molten polymers were measured directly by a pendent drop method[3-5]. Tables I and II list some values at 20°, 140° and 180°C. The values at 20°C for solid polymers were obtained by linear extrapolation from the molten range. This is justified below.

TABLE II

Interfacial Tensions between Polymers Measured by the Pendent Drop Method

Polymer pairs[a]	Interfacial tension, dynes/cm[b] 20°C	140°C	180°C
Polar/nonpolar systems			
PCP/B-PE	4.6	3.7	3.4
PVAc/L-PE	14.5	11.3	10.2
PMMA/L-PE	11.9	9.7	9.0
PnBMA/L-PE	7.1	5.3	4.7
PiBMA/B-PE	5.5	4.3	3.9
PtBMA/B-PE	5.9	3.8	3.4
PS/L-PE	8.3	5.9	5.1
PTHF/B-PE	5.0	4.2	3.9
PDMS/B-PE	5.3	5.1	5.0
Polar/polar systems			
PVAc/PDMS	8.4	7.4	7.1
PCP/PDMS	7.1	6.5	6.3
PTHF/PDMS	6.4	6.3	6.2
PnBMA/PDMS	4.2	3.8	3.6
PtBMA/PDMS	3.6	3.3	3.2
PCP/PnBMA	—	1.6	—
PCP/PS	—	0.5	—
PVAc/PS	4.2	3.7	3.5
PVAc/PnBMA	4.2	2.9	2.5
PMMA/PnBMA	3.4	1.9	1.5
PMMA/PtBMA	3.0	2.3	2.2
PMMA/PS	3.1	1.7	1.2

[a] See Table I for the meanings of the abbreviations.

[b] Values between 20°C and 180°C can be obtained by linear interpolation.

Table III shows that the surface tensions calculated by the parachor and the density agree well with the measured values. The parachor calculation is done by

$$\gamma = (\rho P/M)^4_{\text{repeat unit}} \tag{31}$$

where ρ is the density, P the parachor and M the molecular weight of the

TABLE III

Comparison between Measured and Calculated Surface Tension Values

	Surface tension, dynes/cm					
	measured			calculated from parachor[a]		
Polymers	20°C	140°C	180°C	20°C	140°C	180°C
Polychloroprene	43.6	33.2	29.8	44.2	32.4	29.0
Polystyrene	40.7	32.1	29.2	37.5	30.9	28.5
Poly(methyl methacrylate)	41.4	32.0	28.9	41.1	32.0	28.9
Poly(vinyl acetate)	36.5	28.6	25.9	38.8	27.7	24.8
L-Polyethylene	35.7	28.8	26.5	35.3	25.0	22.4

[a] The density values required for the calculation of the surface tensions from parachors have been reported in references (3) and (4), except for polychloroprene. The density of polychloroprene is given by $\rho = 1.201 - 7.60 \times 10^{-4} (t - 50)$, where ρ is the density in g/cc and t is the temperature in °C.

repeat unit. Since the parachor is independent of the temperature, differentiation of Eq. (31) with respect to the temperature gives

$$\frac{d\gamma}{dT} = 4\left(\frac{P}{M}\right)^4 \rho^3 \frac{d\rho}{dT} \tag{32}$$

The density is usually "piece-wise" linear within the present temperature range with changes in slope at secondary transition points. Therefore, the surface tension should also behave similarly. However, since the extrapolation is short, simple linearity gives virtually the same results. Linear extrapolation from the molten range is justified for semi-crystalline polymers such as polyethylene and polychloroprene, because the surfaces of semicrystalline polymers are amorphous when "melt-crystallized" as shown by Schonhorn and Ryan[15].

Table IV lists some interfacial energetic functions at 140°C for some polymer pairs. The works of adhesion and cohesion are calculated from the interfacial and surface tensions. The contact angle θ_{12} of phase 1 on phase 2 is calculated by

$$\cos \theta_{12} = (\gamma_2 - \gamma_{12})/\gamma_1 \tag{33}$$

where we assume that the substrate phase does not deform. The spreading coefficient λ_{12} of phase 1 on phase 2 is calculated by

$$\lambda_{12} = \gamma_2 - \gamma_1 - \gamma_{12} \tag{34}$$

Inspection of Table IV reveals several characteristics of the wettability of molten polymers:

(a) The wettability of 1 on 2 is generally different from that of 2 on 1. This is evident from Eqs. (33) and (34).

TABLE IV

Some Derived Interfacial Energetic Quantities for Some Polymer Pairs at 140°C

Polymer pairs[a],[b]	Interfacial tension γ_{12} dynes/cm	Work of adhesion W_{a12} ergs/cm^2	Work of cohesion W_{c1} ergs/cm^2	W_{c2}	Contact angle θ_{12} degrees	θ_{21}	Spreading coefficient λ_{12} ergs/cm^2	λ_{21}
Polar/nonpolar pairs								
PCP/B-PE	3.7	56.8	66.4	54.6	44	0	− 9.6	+ 2.2
PMMA/L-PE	9.7	51.1	64.0	57.6	53	39	−12.9	− 6.5
PnBMA/L-PE	5.3	47.6	48.2	57.6	13	51	− 0.6	−10.0
PS/L-PE	5.9	55.0	64.2	57.6	45	24	− 9.2	− 2.6
PVAc/L-PE	11.3	46.2	57.2	57.6	52	53	−11.1	−11.5
Polar/polar pairs								
PCP/PnBMA	1.6	55.7	66.4	48.2	47	0	−10.7	+ 7.5
PCP/PDMS	6.5	40.8	66.4	28.2	76	0	−25.6	+12.6
PCP/PS	0.5	64.8	66.4	64.2	18	0	− 1.6	+ 0.6
PMMA/PnBMA	1.9	54.2	64.0	48.2	44	0	− 9.8	+ 6.0
PMMA/PS	1.7	62.4	64.0	64.2	18	19	− 1.6	− 1.8
PVAc/PnBMA	2.9	49.8	57.2	48.2	42	0	− 7.4	+ 1.6

[a] For the full names of the polymers, see Table I.

[b] All data at 140°C.

(b) The polymer having lower surface tension may not necessarily spread on the polymer having higher surface tension. When one phase will spread on the other phase, we have $\lambda_{12}\lambda_{21} \leqq 0$. When neither phase will spread on the other phase, we have $\lambda_{12}\lambda_{21} > 0$.

(c) Interfacial tension plays a decisive role in wettability. For instance, neither PMMA nor PS will spread on the other, because the interfacial tension 1.7 dynes/cm is greater than the difference between the two surface tensions, i.e. 0.1 dynes/cm at 140°C.

(d) Polarity plays a key role in wettability, because the interfacial tension is determined largely by the polarity. This can be seen from Eqs. (23)–(30) and will be elaborated later.

(e) The contact angle may either increase or decrease with increasing temperatures. This has been discussed before[4].

(f) The interaction parameter ϕ is independent of the temperature, $d\phi/dT = 0$. This has been discussed before[4].

Polarity of polymers

We will calculate the polarity of polymers as defined in Eq. (25) by using the harmonic-mean equation, i.e. Eq. (23). We use the interfacial and surface tensions of the polar polymers against the nonpolar polyethylene. Since the polar term drops out in this case, the nonpolar part of the surface tension of the polar polymer can be obtained directly. The polar part is then obtained by difference. The polarity values obtained are listed in Table V. The polarity values are found to be independent of temperature,

TABLE V

Polarity Values for Some Polymers Calculated by the Harmonic-Mean Equation, i.e. Eq. (23) Using the Interfacial Tension Values from the Pendent Drop Measurements

Polymers	Surface tensions, dynes/cm at 140°C γ	γ^d	γ^p	Polarity[a] x^p
Polychloroprene	33.2	29.6	3.6	0.11
Polystyrene	32.1	26.7	5.4	0.17
Poly(methyl methacrylate)	32.0	23.0	9.0	0.28
Poly(vinyl acetate)	28.6	19.2	9.4	0.33
Poly(*n*-butyl methacrylate)	24.1	20.3	3.8	0.16
Poly(isobutyl methacrylate)	23.7	20.4	3.3	0.14
Poly(*t*-butyl methacrylate)	23.3	20.5	2.8	0.12
Polytetrahydrofuran	24.6	21.1	3.5	0.14
Polydimethylsiloxane	14.1	13.5	0.6	0.04

[a] Polarity is independent of temperature. See text.

$$\frac{dx^p}{dT} = 0 \tag{35}$$

We can see that the polarity of organic polymers are by no means negligible. For instance, poly(vinyl acetate) is as much as 33% polar; poly(methyl methacrylate) 28%; polychloroprene 11%. It is because of the high polarity that poly(vinyl acetate) has an interfacial tension as high as 11.3 dynes/cm against polyethylene at 140°C. If poly(vinyl acetate) were nonpolar, the interfacial tension against polyethylene would have been nearly zero.

The polarity values thus obtained agree well with those estimated from solubility parameters. The polarity may also be defined by

$$x^p = E^p/E = (\delta_p/\delta)^2 \tag{36}$$

where E is the cohesive energy; E^p the polar component. δ is the solubility parameter; δ_p the polar component. The polarity values obtained by Eq. (36) using Hansen's empirical solubility parameters[16] agree well with the values obtained from the interfacial tensions, as can be seen in Table VI.

TABLE VI

Comparison between the Polarity Values Obtained from the Interfacial Tensions of Molten Polymers and from the Solubility Parameters

Polymers	Polarity, x^p	
	From interfacial tension and Eq. (23)	From solubility parameter and Eq. (36)
Poly(vinyl acetate)	0.33	0.33
Poly(methyl methacrylate)	0.28	0.31
Poly(vinyl chloride)	0.15[a]	0.11
Polystyrene	0.17	0.14[b]

[a] From reference (5) using contact angle data and Eq. (23).

[b] The average using both Hansen's[16] and Hoy's[21] solubility parameter data for styrene.

Estimation of interfacial tensions by the Harmonic-mean Equation

Interfacial tensions can be calculated by using the polarity values as obtained above and the surface tensions of the individual phases in the harmonic-mean equation, i.e. Eq. (23). The geometric-mean equation, i.e. Eq. (29) is, however, found unsatisfactory. This can be seen in Table VII.

Polar interactions have a major effect on the interfacial tension. For instance, if we assume that both poly(vinyl acetate) and poly(n-butyl methacrylate) are nonpolar, the calculated interfacial tension will be only 0.4 dynes/cm at 140°C. However, when polarities are considered, the calculated interfacial tension is 2.9 dynes/cm, in agreement with the measured value of 2.4 dynes/cm. A more conspicuous example of poly(vinyl acetate) and polyethylene has been cited before.

"OPTIMUM" WETTABILITY CONDITION FOR ADHESION

The importance of spreading in adhesion has been implied by Zisman[17] in his wettability studies and discussed by Sharpe and Schonhorn[18]. The kinetics of spreading has been discussed by VanOene[19] among others. We will establish the "optimum" thermodynamic condition for wetting by using the harmonic-mean equation.

Substituting Eq. (23) into Eq. (34), we have

$$\lambda_{as} = 4\left[\frac{\gamma_a^d \gamma_s^d}{\gamma_a^d + \gamma_s^d} + \frac{\gamma_a^p \gamma_s^p}{\gamma_a^p + \gamma_s^p} - \frac{\gamma_a}{2}\right] \tag{37}$$

TABLE VII

Comparison between Estimated and Measured Interfacial Tension Values of Polar Polymer Pairs at 140°C

	Interfacial tension, dynes/cm at 140°C		
		Calculated by	
Polymer pairs[a]	Measured	Harmonic-mean[b] equation, i.e. Eq. (23)	Geometric-mean[c] equation, i.e. Eq. (29)
PVAc/PDMS	7.4	8.5	3·6
PCP/PDMS	6.5	8.2	4.1
PTHF/PDMS	6.3	3.8	1.5
PnBMA/PDMS	3.8	3.7	1.4
PtBMA/PDMS	3.3	2.9	1.2
PCP/PnBMA	1.6	1.7	0.9
PCP/PS	0.5	0.5	0.4
PVAc/PS	3.7	2.3	1.2
PVAc/PnBMA	2.9	2.4	1.2
PMMA/PnBMA	1.9	2.2	1.0
PMMA/PtBMA	2.3	3.4	1.6
PMMA/PS	1.7	1.2	0.5

[a] For the full names of the polymers, see Table I.

[b] The polarity values used are those calculated by the harmonic-mean equation and listed in Table V.

[c] The polarity values used are those calculated by the geometric-mean equation.

where λ_{as} is the spreading coefficient of the adhesive a on the substrate s. This equation expresses the spreading coefficient in terms of the polarity and the surface tensions of the adhesive and the substrate.

For a given substrate, γ_s^d and γ_s^p are fixed. We define $k = \gamma_a/\gamma_s$, $\beta = \gamma_s^p/\gamma_s = x_s^p$ and $x = \gamma_a^p/\gamma_a = x_a^p$, in which β is the polarity of the substrate and x the polarity of the adhesive. Using these in Eq. (37) and rearranging, we have

$$\begin{aligned} Q &= (1/4k\gamma_s)(\lambda_{as} + 2\gamma_a) \\ &= \frac{(1-\beta)(1-x)}{k(1-x)+(1-\beta)} + \frac{\beta x}{kx+\beta} \end{aligned} \tag{38}$$

where Q may be termed a "reduced" spreading coefficient. To obtain the optimum wetting condition, we let

$$\left(\frac{\partial Q}{\partial x}\right)_{k,\beta} = 0 \tag{39}$$

which gives the following quadratic equation

$$k(2\beta - 1)x^2 - 2\beta[\beta(k - 1) + 1]x + \beta^2[(k + 1) - (2\beta - 1)] = 0 \quad (40)$$

This gives a significant root at

$$x = \beta \quad (41)$$

Thus, we conclude that the "optimum" thermodynamic wettability condition is when the polarities of the adhesive and the substrate are exactly the same. The greater the disparity between the two polarities, the poorer the wettability will tend to be. This explains the de Bruyne's empirical statement[20] that polar/non-polar pairs will never form strong joints.

However, de Bruyne's rule is only partially correct. When the surface tensions of the two phases have similar values, matching of the polarity is very important. But, when the surface tensions of the two phases are widely different, matching of the polarity becomes less important. In this case, the system can tolerate a greater disparity in the polarity and still wet each other well. This is evident from Eq. (34) by noting that the interfacial tensio c increases with increasing disparity in the polarities. The thermodynamin condition for spreading or complete wetting is given by $\lambda_{as} \geqq 0$ or $2Q \geqq 1$c

Figure I gives a plot of Q vs. x at several different k values for the ase. $\beta = 0.3$. It shows that Q values increase as k values decrease, i.e. γ_s becomes

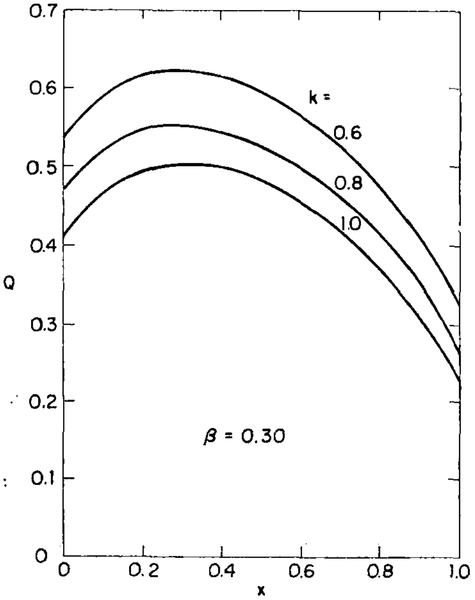

FIGURE 1 A graphical representation of Eq. (38) for the optimum energetics of wetting for the case $\beta = 0.30$ and $k = 1.0$, 0.8 and 0.6.

increasingly greater than γ_a. In other words, when the surface tension of the adhesive is much smaller than that of the substrate, complete wetting may still occur, although the polarities are relatively widely apart. But, when the surface tension of the adhesive is similar to that of the substrate, close matching of the polarities is necessary for complete wetting. In any case, the "optimum" wettability condition is given by exact matching of the polarities, i.e. $x = \beta$.

Table VIII shows the correlation between the spreading coefficient and the adhesion. Because both phases are mobile at the bonding temperature of 140°C, the phase of lower surface tension is taken as the adhesive. If spreading will occur, the phase of higher surface tension will naturally act as the substrate phase, but not the reverse. The table also shows that the work of adhesion does not correlate with adhesion. We expect such correlation, for instance, when comparing the adhesion of a given adhesive on different substrates. This is because for a given adhesive, $W_{c(a)}$ is constant and so $W_{a(as)}$ is directly proportional to λ_{as}, since $\lambda_{as} = W_{a(as)} - W_{c(a)}$. In this special case, if furthermore, the interfacial tension is relatively small, so that the surface tension is proportional to the work of adhesion, then we would also expect a correlation between adhesion and the surface tension of the substrates, such as reported by Levine and coworkers[22]. This is, however, only a special case. We would like to stress that spreading coefficient has a more general and basic relationship to adhesion through its role in wetting energetics.

TABLE VIII

Correlation between Spreading Coefficient and Adhesion of Some Polymer Pairs

Polymer pairs[a]	Spreading coefficient[b], λ, ergs/cm^2 at 140°C	Work of adhesion, W_a, ergs/cm^2 at 140°C	Adhesion[c]
PMMA/L-PE	− 6.5	51.1	poor
PMMA/PS	− 1.6	62.4	poor
PVAc/PS	− 0.2	57.0	fair
PVAc/PnBMA	+ 1.6	49.8	fair
PMMA/PnBMA	+ 6.0	54.2	good
PCP/PDMS	+12.0	40.8	good

[a] For the full names of the polymers, see Table I.

[b] The spreading coefficient is the larger of the two values λ_{12} and λ_{21} at the bonding temperature of 140°C. See text for details.

[c] The polymer pairs were bonded at 140°C. The adhesion was evaluated at the room temperature and rated qualitatively.

This work discusses polar and nonpolar energies at the interface and wetting energetics. We would like to point out that a complete analysis of adhesion should also cover kinetics, rheology and fracture mechanics.

NOMENCLATURE

A	Attraction constant in the Lennard-Jones potential function.
d	Intermolecular distance.
E	Cohesive energy.
g	Surface tension ratio defined by Eq. (26).
k	Ratio of adhesive surface tension to substrate surface tension.
M	Molecular weight of a repeat unit of a polymer.
m	Repulsive exponent in the Lennard-Jones potential function.
n	Molecules per unit volume.
P	Parachor.
Q	Reduced spreading coefficient.
T	Temperature.
W_{a12}	Work of adhesion between phases 1 and 2.
W_{c1}	Work of cohesion of phase 1.
x^p	Polarity defined by Eq. (25a).
x^d	Nonpolarity defined by Eq. (25b).

Greek letters

α	Polarizability.
β	Polarity of the substrate.
γ	Interfacial or surface tension.
δ, δ_p	Solubility parameter and its polar component.
θ_{12}	Contact angle of phase 1 on phase 2.
λ_{12}	Spreading coefficient of phase 1 on phase 2.
μ	Permanent dipole moment.
ν	Electronic vibrational frequency.
ρ	Density.
ϕ	Interaction parameter of Good and Girifalco.

Superscripts

d	Refers to the nonpolar (dispersion) component.
h	Refers to the hydrogen-bonding component.
p	Refers to the polar component.
pp, pi	Refers to the dipole-dipole and dipole-induced dipole components.

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