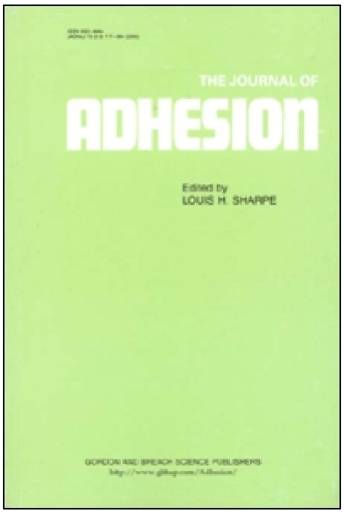

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Physico-Chemical Criteria for Maximum Adhesion. Part II: A New Comprehensive Thermodynamic Analysis

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In this paper, two parameters defined as the relative work of adhesion $[W_A/\gamma_L]$ and the relative interfacial energy $[\gamma_{SL}/\gamma_L]$ have been examined for their assumed usefulness in correlating the thermodynamic properties of the components of the system substrate/adhesive with its practical performance (strength). It is shown that the minimum value of $[\gamma_{SL}/\gamma_L]$ relevant to conditions for the maximum adhesion becomes zero only for those systems (relatively rare) for which interaction factor Φ_0 is equal to 1.0.

Several transition points were identified for boundary conditions acquired at $\theta = 0°$ and $\theta = 90°$ which can be used to predict the properties and performance of an adhesive joint. These transition points are: a_{MIN}—energy modulus of the system (E.M.S.), relevant to the minimum interfacial energy; a_S—E.M.S. where self-spreading of adhesive occurs; a_{CRIT}—E.M.S. relevant to conditions under which the thermodynamic work of adhesion becomes negative and the system exhibits a tendency for self-delaminating or has "zero-strength"; a_{CT}—E.M.S. beyond which the geometry of the interface at any interfacial void or boundary of the joint may be regarded as a crack tip.

It is shown that only in those systems for which $\Phi_0 = 1.0$ can a minimum contact angle of 0° indicate a condition for the maximum strength. If Φ_0 is known, the optimum contact angle can be estimated and hence the optimum surface energy of the substrate (adjusted by surface treatment, etc.) for the maximum adhesion.

KEYWORDS: Adhesion, Surface energy, Energy modulus, Adhesive joints, Performance criteria, Contact angle.

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1. INTRODUCTION

In Part I of this study[1] various relations between joint strength and properties of adhesives and substrates were reviewed and basic criteria were defined. In this paper a more comprehensive treatment of the criteria is presented by introducing new dimensionless quantities.

Physical equations can be better analyzed when transformed into a dimensionless form. This strictly mathematical operation is recognized as a useful analytical tool, which in the present case allows a reduction in the number of variables. When new dimensionless quantities are introduced, all analytical conclusions retain the same validity as those drawn from the original equations, providing that all physical limitations are taken into account when performing the algebraic operations. The nomenclature used in this paper is given in the Appendix.

2. DIMENSIONLESS ANALYSIS OF THERMODYNAMIC PHENOMENA AT INTERFACES

Dividing the Young-Dupré equation for the thermodynamic work of adhesion by γ_L, gives the following:

$$[W_A/\gamma_L] = 1 + \cos\theta. \tag{1}$$

Rearranging the Young's equation further and dividing through by γ_L we obtain:

$$[\gamma_{SL}/\gamma_L] = \gamma_S/\gamma_L - \cos\theta. \tag{2}$$

The dimensionless quantities will be called:
$[W_A/\gamma_L] \rightarrow$ "relative work of adhesion";
$[\gamma_{SL}/\gamma_L] \rightarrow$ "relative interfacial energy"; and
$[\gamma_S/\gamma_L] \rightarrow$ "energy modulus of the system".

The presence of $\cos\theta$ in equations (1) and (2) emphasizes its importance in regard to the accuracy of estimation of the relative interfacial energy and thermodynamic work of adhesion.

Two expressions were introduced[1] to estimate the value of $\cos\theta$, depending upon conditions at the interface, *e.g.*

(a) for a rectilinear relationship $\cos\theta = f(\gamma_L)$.

$$\cos\theta = 2 - (\gamma_L/\Phi_0^2.\gamma_S); \text{ and} \tag{3}$$

(b) for a curvilinear relationship $\cos\theta = f(\gamma_L, \Phi)$

$$\cos\theta = 2\,\Phi(\gamma_S/\gamma_L)^{1/2} - 1. \tag{4}$$

It might be supposed that knowledge of eqn (4) is not necessary, since Good's definition[2] of the interaction factor:

$$\Phi = [\gamma_S + \gamma_L - \gamma_{SL}]/[2(\gamma_S \cdot \gamma_L)^{1/2}], \tag{5}$$

does not contain $\cos\theta$ and the relative interfacial energy could be derived from eqn (5) as follows:

$$[\gamma_{SL}/\gamma_L] = \gamma_S/\gamma_L - [2\Phi(\gamma_S/\gamma_L)^{1/2} - 1]. \tag{6}$$

However, it is evident from eqn (4) that $\cos\theta$ is involved implicitly in the expression (6) in the brackets.

From equations (1), (2) and (6) the importance of the definition of the true relation $\cos\theta = f(\gamma_L)$ is seen as the basis of any physical equation describing interfacial phenomena—either in explicit or implicit form.

Combining equations (3) and (4) with (1) and (2), and introducing "a" for the energy modulus of the system (where $a = \gamma_S/\gamma_L$), we obtain dimensionless equations describing the relative interfacial energy $(\gamma_{SL}/\gamma_L]$ and relative thermodynamic work of adhesion $[W_A/\gamma_L]$.

These equations are as follows:

(a) for a rectilinear case (see eqn 3) of $\cos\theta = f(\gamma_L)$,

$$[\gamma_{SL}/\gamma_L] = a + (1/a).(1/\Phi_0^2) - 2 \tag{7}$$

and

$$[W_A/\gamma_L] = 3 - (1/a).(1/\Phi_0^2);\text{ and} \tag{8}$$

(b) for a curvilinear case (see eqn 4) of $\cos\theta = f(\gamma_L, \Phi)$,

$$[\gamma_{SL}/\gamma_L] = (a + 1) - 2\Phi.a^{1/2} \tag{9}$$

and

$$[W_A/\gamma_L] = 2\Phi.a^{1/2}. \tag{10}$$

These equations describing interfacial phenomena have a very simple, two-dimensional format. This facilitates the analysis, because both $[\gamma_{SL}/\gamma_L]$ and $[W_A/\gamma_L]$ become dependent only on the energy modulus of the system $[a]$ and the interaction factor Φ. The other reasons explaining the usefulness of the above equations are given in Sections 3, 4 and 5.

The conditions of existence of the curvilinear and rectilinear cases of the relationship cos θ *v.* γ_L have been previously described.[1] It has been explained that a curvilinear relation expressed by eqn (3) can very rarely be obtained in practice, as it is a very peculiar case dependent upon the interaction factor Φ being constant which can be achieved *only* if the following conditions are simultaneously satisfied:

(a) Surface energy of the substrate and its dispersive/polar structure remain constant; *i.e.* γ_s = constant, d_s = constant, and p_s = constant.

(b) All test liquids utilized during the experimental procedure of determining the characteristic cos $\theta = f(\gamma_L)$ exhibit at the same time the following:

  (i) different total surface energies, *e.g.*

$$\gamma_L^{(1)} \neq \gamma_L^{(2)} \neq \ldots \neq \gamma_L^{(3)}; \text{ and}$$

  (ii) equal polar and dispersive fractions of total surface energies *e.g.*

$$d_L^{(1)} = d_L^{(2)} = \ldots = d_L{}^{(n)}$$

$$p_L^{(1)} = p_l^{(2)} = \ldots = p_L^{(n)}$$

$$\text{where } p + d = 1.0.$$

It has also been mentioned[1] that within the region in which cos $\theta \simeq 0.6$ to 1.0 (which has engineering importance), the experimental results can be well approximated by a straight line. Therefore, the criteria for maximum adhesion will be developed in this paper based on this rectilinear case of the relationship cos $\theta = f(\gamma_L)$.

2. RELATIVE INTERFACIAL ENERGY OF THE SYSTEM

2.1 *Rectilinear Case of cos $\theta = f(\gamma_L)$. Properties of the Solid Expressed by γ_S*

For the rectilinear case of cos $\theta = f(\gamma_L)$ (see eqn 3), the expression for the relative interfacial energy has been described by eqn (7).

To obtain the solution of this equation, the following physical limitations have to be taken into consideration:

(a) for the conditions in which $\gamma_L > \gamma_C$, the contact angle has the value of $\theta > 0$ deg., so that $1.0 > \cos\theta > -1$; and

(b) when $\gamma_L \leqq \gamma_C$, the contact angle equals zero, so that cos $\theta = 1.0$.

For condition (b), eqn (3) takes the following form:

$$\left.\begin{array}{l}\gamma_L/(\gamma_S.\Phi_0^2) = 1.0 \\ \text{and further:} \\ \gamma_L/\gamma_S = \Phi_0^2\end{array}\right\} \text{ for any } \gamma_L \leqq \gamma_C.$$

From the above, a transition value of the energy modulus is achieved, relevant to the conditions at which the liquid starts to spread spontaneously over the surface of the solid, *i.e.*

$$\left.\begin{array}{l}a = a_S \\ a_S = 1/\Phi_0^2.\end{array}\right\} \qquad (11)$$

Values of "a_S" for different values of the interaction factor Φ_0 are shown in Table I.

TABLE I

Values of energy modulus $a_S = \gamma_S/\gamma_L$ where liquid starts to spread spontaneously over the solid surface

Φ_0	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
a_S	1.0	1.23	1.56	2.04	2.77	4.0	6.25	11.11	25.0	100	∞

Substituting the transition value a_S (eqn 11) into equation (7) we obtain the solution for those conditions under which $\cos\theta = 1.0$, *i.e.* where $\gamma_L \leqq \gamma_C$. This is as follows:

$$[\gamma_{SL}/\gamma_L]_S = a_S - 1. \qquad (12)$$

The minimum value of the relative interfacial energy $[\lambda_{SL}/\lambda_L]_{\text{MIN}}$ can be determined by differentiating eqn (7). The point at which $[\gamma_{SL}/\gamma_L]_{\text{MIN}}$ is acquired is described by the modulus $a = a_{\text{MIN}}$, so that differentiating eqn (7) and incorporating a_{MIN} we obtain:

$$d[\gamma_{SL}/\gamma_L]/da = 1 - (1/a^2{}_{\text{MIN}}.\Phi_0^2)$$

$$a_{\text{MIN}} = 1/\Phi_0. \qquad (13)$$

Substituting further the condition (13) into eqn (7) we can obtain the value of the minimum relative interfacial energy $[\gamma_{SL}/\gamma_L]_{\text{MIN}}$ at the point where $a_{\text{MIN}} = 1/\Phi_0$, so that:

$$[\gamma_{SL}/\gamma_L]_{\text{MIN}} = (2/\Phi_0) - 2. \qquad (14)$$

Cos θ has the value of unity for any $a \geqq a_S$. Thus eqn (2) and furthermore (7) over this range of the energy moduli have a different form from that where $0 \leqq a \leqq a_S$ (compare eqn 7), *e.g.*

$$[\gamma_{SL}/\gamma_L] = \text{a} - 1. \qquad (15)$$

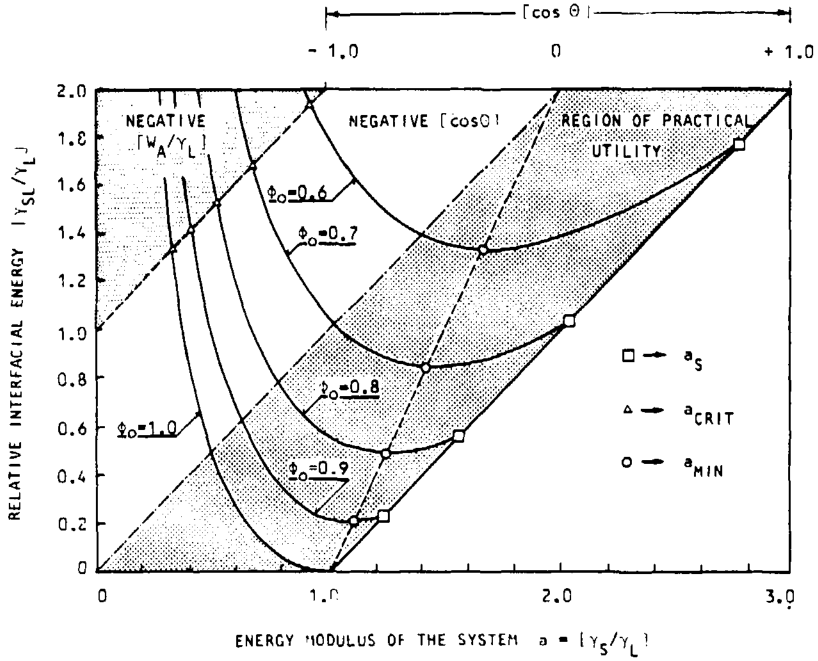

FIGURE 1 Relationship between relative interfacial energy and energy modulus of the system expressed by equations (7) and (15); $(\gamma_{SL}/\gamma_L] = a + (1/a.\Phi_0^2) - 2$ for $0 \leqq a \leqq a_S$ and $a \geqq a_S$. Surface properties of the solid expressed by $[\gamma_S]$ [rectilinear case: $\cos\theta = f(\gamma_L)$].

Summarizing the above analysis, it can be seen that there are two different equations describing the relative interfacial energy, depending upon the boundary conditions, *i.e.*

$$[\gamma_{SL}/\gamma_L] = \begin{cases} a + (1/a.\Phi_0^2) - 2 \text{ for } \leqq a \leqq a_S & (7) \\ a - 1 \qquad \text{for } a \geqq a_S, \text{ where } \cos\theta = 1.0. & (15) \end{cases}$$

The graphical solution of eqns (7) and (15) has been presented in Figure 1.

Interpretation of Figure 1 and eqns (7) and (15) explains the following:

(a) In the area where $0 \leqq a \leqq a_S$, the relative interfacial energy $[\gamma_{SL}/\gamma_L] = f(a)$ has the character of a quadratic equation.

(b) In the area where $a \geqq a_S$, the relative interfacial energy $[\gamma_{SL}/\gamma_L]$ has a rectilinear relationship to energy modulus of the system $[a]$ and constitutes a representation of the points where self-spreading of an adhesive over the substrate occurs.

(c) The system substrate-adhesive acquires its minimum relative interfacial energy not for this condition in which self-spreading of adhesive occurs ($\cos\theta = 1.0$ for $a \geqq [a_S = 1/\Phi_0^2]$) but for the energy modulus of the system, in which $a = a_{MIN} = 1/\Phi_0$.

Equations (7) and (15) throw a completely new light on practical interpretations of interfacial phenomena. Previously the opinion has prevailed that conditions under which the contact angle becomes zero (at $\gamma_L = \gamma_C$) correspond with the optimum conditions for adhesion. However, not all the experiments confirm this view[3] and now the above theory refutes it. Analysis of eqns (7) and (15) explains why the point at which the surface energy of liquid (γ_L) equals the critical wetting tension (γ_C) seldom coincides with the condition for the minimum interfacial energy. Maximum strength of the joint is achieved for the condition corresponding to the minimum relative interfacial energy.

Equation (13) enables estimation of the optimum surface energy of the adhesive for minimum interfacial energy (as the condition of maximum strength of adhesive joint), *i.e.*

$$a_{MIN} = \gamma_S/(\gamma_L)_{OPT} = 1/\Phi_0, \text{ hence}$$

$$(\gamma_L)_{OPT} = \Phi_0 . \gamma_S. \tag{16}$$

It can be easily shown that eqn (13) for minimum interfacial energy differs from that for self-spreading of the liquid over the substrate, since from (11) we can obtain:

$$(\gamma_L)_{\text{Self-spreading}} = \Phi_0^2 . \gamma_S \text{ for } a = a_S. \tag{17}$$

Summarizing the above it can be shown that *the only case* in which the condition $\cos\theta = 1$ ($\theta = 0$ degrees) produces optimum adhesion is obtained in systems whose interaction factor $\Phi_0 = 1.0$. Unfortunately it seldom occurs in practice that both the solid and adhesive have the same polar-dispersion ratios, giving $\Phi_0 = 1.0$ (*i.e.* soldering of the same materials by basic material, etc). Therefore to obtain the condition that provides the minimum interfacial energy of the system, equation (16) has to be satisfied.

From eqn (2), we can calculate the value of the contact angle that exists at the optimum point relevant to the conditions for maximum adhesion, *i.e.* that of the minimum relative interfacial energy:

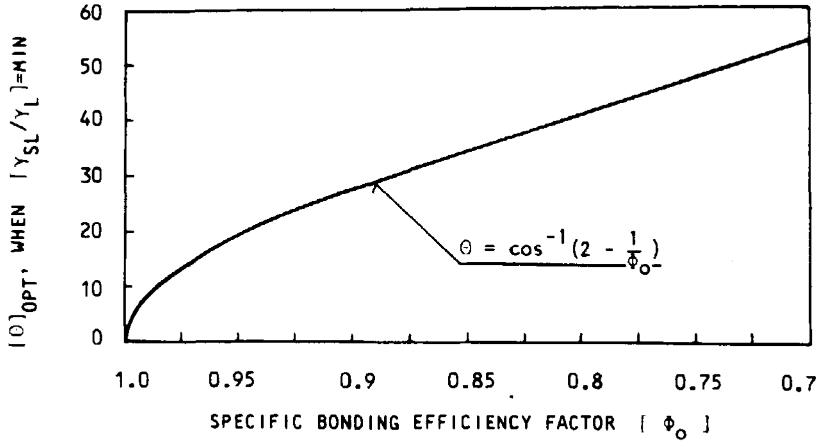

FIGURE 2 Equilibrium contact angle $[\theta_{OPT}]$ corresponding to the condition in which the system solid/liquid acquires its minimum interfacial energy $[\gamma_{SL}/\gamma_L]_{MIN}$ for the rectilinear case of relationship $\cos\theta = f(\gamma_L)$.

$$[\cos\theta]_{OPT} = [\gamma_S/\gamma_L]_{OPT} - [\gamma_{SL}/\gamma_L]_{MIN}. \tag{18}$$

Thus, introducing condition (16) instead of $[\gamma_S/\gamma_L]_{OPT}$ and (14) instead of $[\gamma_{SL}/\gamma_L]_{MIN}$ in eqn (18), we obtain the following:

$$\theta_{OPT} = \cos^{-1}(2 - 1/\Phi_0). \tag{19}$$

Values of θ_{OPT} have been calculated and plotted as a function of Φ_0 in Figure 2. It should be noted how rapidly θ_{OPT} increases as Φ_0 decreases from unity.

It is clear from equation (19) that now the contact angle θ can be utilized as a useful tool for indicating when the surface properties of the substrate have reached the optimum (*e.g.* after etching and/or other treatment). However, it is necessary to stress here the need for extremely accurate determination of the interaction factor Φ_0.

By definition,[1] Φ_0 represents a particular case of Φ which is obtained for this condition where $\cos\theta = 1.0$ and $\gamma_L = \gamma_C$, so that

$$\Phi_0 = (\gamma_C/\gamma_S)^{1/2}. \tag{20}$$

The magnitude of the influence of any error in estimation of Φ_0 on the value of θ_{OPT} depends on the nominal value of Φ_0. If for instance the true value of $\Phi_0 = 1.0$, but experiments give $\Phi_0 = 0.995$ (error of only 0.005), the difference in optimum contact angles reaches a value as high as 5°45′. In the range of $0.7 \leqq \Phi_0 \leqq 0.9$ an error of 0.01 in estimating Φ_0 (e.g. 0.89 or 0.91 instead of 0.90) repesents a difference in θ_{OPT} of only ±1.5°.

2.2 *Rectilinear Case of cos θ = f(γ_L). Properties of the Solid Expressed by γ_C*

The graphical solution of the basic eqns (7) and (15) for the relative interfacial energy (compare Figures 1 and 3) may be clearer for practical purposes if γ_C replaces γ_S. Therefore, the case will be considered when the surface energy of the solid has been expressed in the implicit form by γ_C.

It is known from eqn (20) that:

$$\gamma_S = \gamma_C/\Phi_0^2. \tag{21}$$

Combining eqns (21) and (7) we can obtain the following expression for $[\gamma_{SL}/\gamma_L]$:

$$[\gamma_{SL}/\gamma_L] = (a^*/\Phi_0^2) + (1/a^*) - 2. \tag{22}$$

From eqn (3), we can also determine the transition value of the energy modulus, a_S^*, at which spontaneous wetting of the solid occurs, *i.e.*

$$a_S^* = \gamma_C/\gamma_L = 1.0. \tag{23}$$

It is now clear that utilizing γ_C instead of γ_S to describe the energy properties of the substrate, the transition value a_S^* always remains unity regardless of the value of the interaction factor Φ_0.

Incorporating condition (23) into (22) we obtain the solution of (22) for any value of the energy modulus a* of the system:

$$[\gamma_{SL}/\gamma_L] = \begin{cases} (a^*/\Phi_0^2) + (1/a^*) - 2 & \text{for } 0 \leqq a^* \leqq 1.0 \qquad (24) \\ (a^*/\Phi_0^2) - 1 & \text{for } a^* \geqq 1.0, \text{ where } \cos\theta = 1.0. \qquad (25) \end{cases}$$

Further substitution of (23) into equation (24) or (25) leads to the expression for the relative interfacial energy at the transition point a_S^*, *i.e.*

$$[\gamma_{SL}/\gamma_L]_S = (1/\Phi_0^2) - 1. \tag{26}$$

The above indicates that for the range where $a^* \geqq a_S^*$, values of the relative interfacial energy remain on the straight line starting from $a^* = 1.0$, with the slope of $1/\Phi_0^2$.

Coordinates of the point where the minimum interfacial energy occurs can be obtained by differentiating equation (24), *i.e.*

$$d[\gamma_{SL}/\gamma_L]/da^* = (1/\Phi_0^2) - (1/a^{*2}_{\mathrm{MIN}}) = 0$$

Consequently we obtain a value of the energy modulus a^*_{MIN} relevant to conditions giving $[\gamma_{SL}/\gamma_L]_{\mathrm{MIN}}$, *i.e.*

$$a^*_{\mathrm{MIN}} = \Phi_0. \tag{27}$$

Further substitution of parameter (27) into eqn (24) provides an expression for the minimum relative interfacial energy obtainable by a given system:

$$[\gamma_{SL}/\gamma_L]_{\mathrm{MIN}} = (2/\Phi_0) - 2. \tag{28}$$

Graphical representation of the equations (24) and (25) showing particularly the values of $[\gamma_{SL}/\gamma_L]$ for the important values of the energy moduli, namely: $a^* = a^*_{\mathrm{MIN}}$ and $a^* = 1.0$, are given in Figure 3.

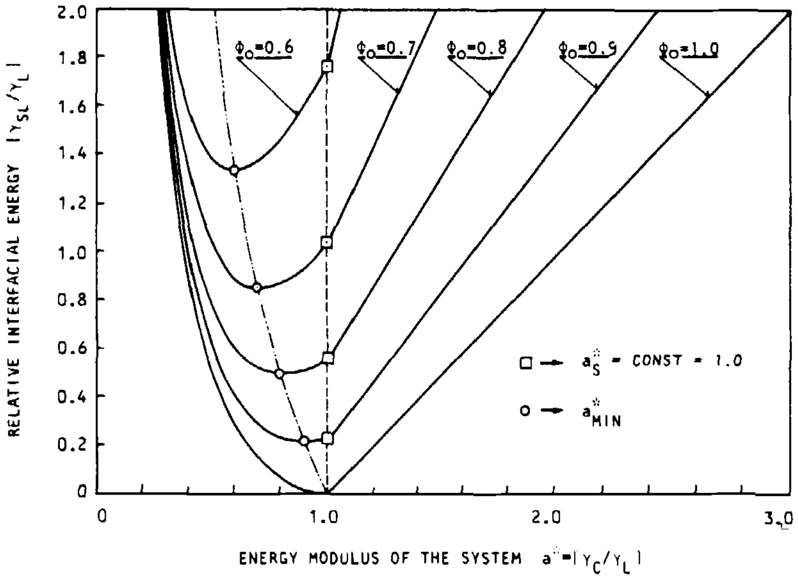

FIGURE 3 Relationship between relative interfacial energy and energy modulus of the system, expressed by equations (24) and (25); $[\gamma_{SL}/\gamma_L] = (a^*/\Phi_0^2) + (1/a^*) - 2$ for $0 \leq a^* \leq 1.0$ and $a^* \geq [a^*_S = 1.0]$. Surface properties of the solid expressed by $[\gamma_C]$ [rectilinear case: $\cos\theta = f(\gamma_L)$].

In the case when "γ_C" has been used to describe the surface properties of the solid, the minimum interfacial energy can be obtained if condition (27) has been fulfilled. Thus,

$$a^*_{\mathrm{MIN}} = \gamma_C/(\gamma_L)_{\mathrm{OPT}} = \Phi_0.$$

Then, the minimum interfacial energy is obtained for the surface energy of the liquid $(\gamma_L)_{\mathrm{OPT}}$, as calculated by the following formula:

$$(\gamma_L)_{\mathrm{OPT}} = \gamma_C/\Phi_0. \tag{29}$$

Substitution of equations (28) and (23) into formula (18) for the contact angle at the point where the interfacial free energy becomes minimum leads back to (19), namely:

$$(\theta)_{\mathrm{OPT}} = \cos^{-1}(2 - 1/\Phi_0).$$

3. RELATIVE THERMODYNAMIC WORK OF ADHESION

In its original form, the Young-Dupré equation for the thermodynamic work of adhesion does not allow analysis of interfacial phenomena in regard to their further design and engineering applications.

The analysis presented below makes possible interpretation of the dimensionless equations for thermodynamic work of adhesion in order to identify a series of transition values of energy moduli "a", as summarized in Section 5. Coordinates of these transition points indicate specific limits in performance of adhesive joints.

The relative thermodynamic work of adhesion for systems relevant to a rectilinear case $\cos\theta = f(\gamma_L)$ has been described by eqn (8):

$$[W_A/\gamma_L] = 3 - (1/a).(1/\Phi_0^2). \tag{8}$$

It should be remembered here that $\cos\theta$ has values $-1 \leqq \cos\theta \leqq 1.0$ in the region of $0 \leqq a \leqq a_S$. Then equations (8) and (10) are valid only for the region in which $a \leqq a_S = 1/\Phi_0^2$.

Under those conditions where $a \geqq a_S$, $\cos\theta$ reaches a value of 1.0 and at this specific point the work of adhesion acquires its maximum value, *i.e.*

$$\left.\begin{aligned}[W_A]^{\mathrm{MAX}} &= 2/\gamma_L\\ [W_A/\gamma_L]^{\mathrm{MAX}} &= 2.0\end{aligned}\right\} \text{for any } +\infty \geqq a \geqq a_S. \tag{30}$$

Analysis of equation (8) identifies the region where the relative thermodynamic work of adhesion becomes negative. This is relevant to the critical condition in which the system has a tendency to delaminate without the influence of external forces. In other words, the conditions under which $[W_A/\gamma_L] = 0$ should coincide with "zero-strength" of an adhesive joint.

At this critical point, eqn (8) takes the following form:

$$[W_A/\gamma_L] = 3 - (1/\Phi_0^2)(1/a_{\text{CRIT}}) = 0. \tag{31}$$

Consequently the value of a_{CRIT}, at which $[W_A/\gamma_L]$ becomes negative can be determined as follows:

$$a_{\text{CRIT}} = 1/3\Phi_0^2. \tag{32}$$

Values of a_{CRIT} as a function of the interaction factor Φ_0 are shown in Table II.

TABLE II
Values of ratio a_{CRIT}, where relative work of adhesion $[W_A/\gamma_L]$ becomes negative

Φ_0	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
a_{CRIT}	0.333	0.411	0.521	0.68	0.98	1.333	2.08	3.70	8.33	33.33

Graphical solutions of equations (31) or (8) respectively are shown in Figure 4.

It is necessary to stress that the graph of $W_a = f(a)$ for $\Phi_0 = 1.0$ represents also the solution of equation (8) where the ratio $a^* = \gamma_C/\gamma_L$ has been used instead of $a = \gamma_S/\gamma_L$. For this case then,

$$[W_A/\gamma_L] = 3 - 1/a^*. \tag{33}$$

4. LIMITS TO THE THERMODYNAMIC WORK OF ADHESION WHERE MICROCRACKS OCCUR AT THE INTERFACE

Let us consider the performance of a substrate/adhesive system for three typical equilibrium contact angles: $\theta < 90°$; $\theta = 90°$ and $\theta > 90°$. Figure 5 illustrates the above for the two main steps of a gluing procedure, *e.g.*, before and after assembly.

When the hydrophobic adhesive is still in a liquid state and substrates are of hydrophilic nature (*e.g.* metal oxides), there is a tendency for the contact angles to increase when the system is exposed to the humidity or vapour of other liquids. This occurs due to adsorption of molecules

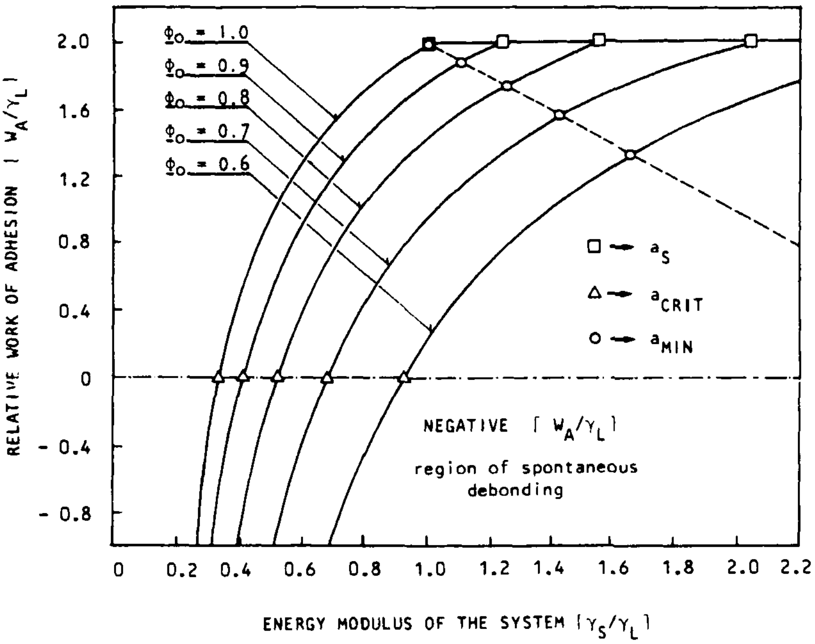

FIGURE 4 Graphical repesentation of the relationship between relative work of adhesion and energy modulus of the system expressed by equation (8): $[W_A/\gamma_L] = 3 - (1/a)(1/\Phi_0^2)$ [rectilinear case: $\cos\theta = f(\gamma_L)$].

(*e.g.* water) from the atmosphere on the solid's surface[4] which results in the displacement of the organic liquid (adhesive) from a peripheral area. This phenomenon is illustrated in Figure 6 based on experimental data[4,5] for the following contact angles: $\theta = 90°$; $\theta = 90°$; $\theta > 90°$ (see also Table III).

It is clear from Figure 6 that the term "equilibrium" has to be considered under constant conditions—in respect of the temperature, humidity and pressure. Surface properties for bonding identified as the optimum for a given temperature and humidity no longer remain the optimum if manufacturing conditions themselves change. This is stressed because there is a "jump" from the contact angle of, for instance, 42° at 7% RH to 86° when the RH is raised to 88% or higher (as Figure 6 explains).

If the energy properties of the solid and liquid adhesive produce an equilibrium contact angle much greater than 90 degrees, prior to the curing process, then the geometry of the joint in the vicinity of the

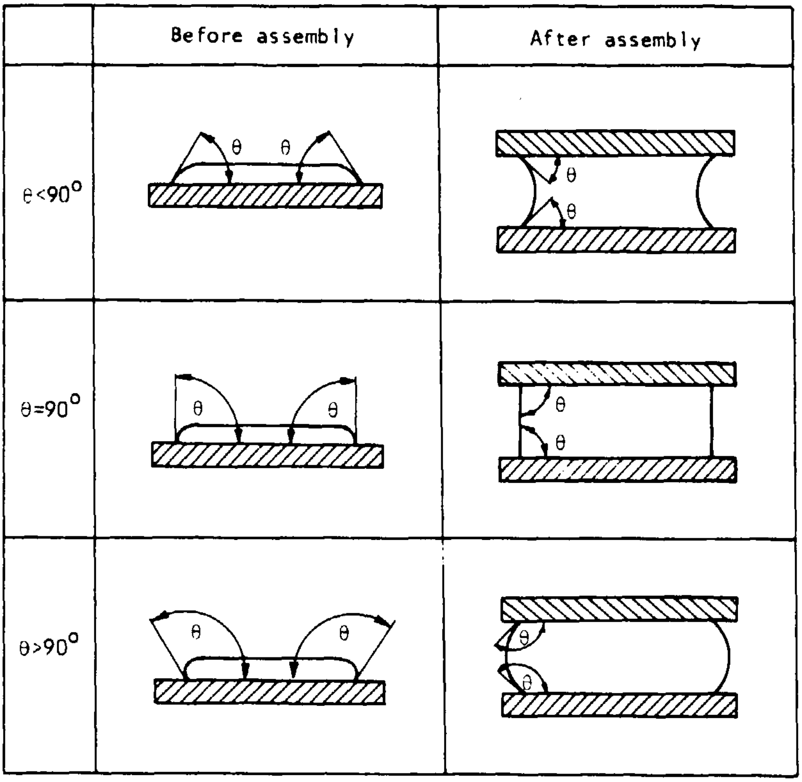

FIGURE 5 Performance of adhesive in an adhesive joint depending upon the contact angle at thermodynamic equilibrium.

TABLE III
Influence of ambient humidity on the equilibrium contact angle [deg]

Substrate/liquid	Relative humidity								Reference
	0.6%	7%	16%	35%	56%	80%	88%	95%	
Steel/water	—	66	69	76	—	>90	>90	>90	5
Steel/glycerol	—	42	48	61	67	83	86	—	5
Pyrex/p-octadecyl toluene	5	—	—	—	—	—	—	28	4
Glass/ tetrabromoethane	17	—	—	—	—	—	—	35	4
Al/tetrabromoethane	8	—	—	—	—	—	—	35	4
Zr/tetrabromoethane	18	—	—	—	—	—	—	30	4
Cr/tetrabromoethane	8	—	—	—	—	—	—	30	4
Ni/tetrabromoethane	10	—	—	—	—	—	—	34	4
Au/tetrabromoethane	8	—	—	—	—	—	—	16	4

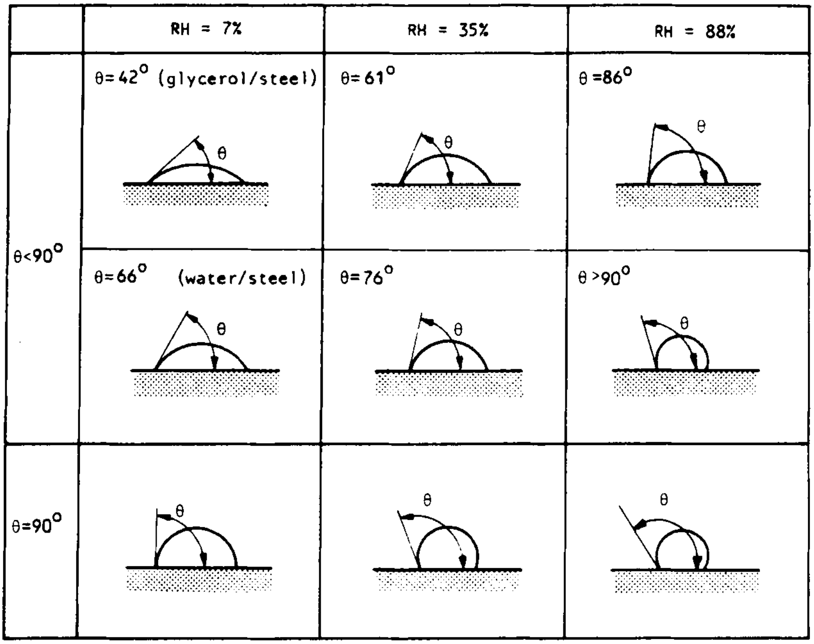

FIGURE 6 Changes in equilibrium contact angle due to variable ambient humidity. Data from Gledhill *et al.*[5]

contact line remains as shown in Figure 7. This may be regarded as a crack tip at the interface. Whilst in vacuum, such geometry does not produce problems, however the situation may change dramatically in the real environment, *e.g.* in humid air, water or other liquid. The fact is known[6] that adsorption of polar molecules (*e.g.* of water, surfactants, etc.) at the crack tip results in stresses that decrease the strength and provide a delaminating tendency. Microvoids at the interface aggravate the problem, as the situation at each interfacial void is similar to that in Figure 7.

The phenomenon described does not occur when the equilibrium contact angle at the curing is less than 90°. Thus, it may be proposed that the contact angle of 90° provides another practical limit to the thermodynamic work of adhesion. This requires an experimental confirmation.

Relative work of adhesion is expressed by eqn (1), *i.e.*:

$$[W_A/\gamma_L] = 1 + \cos\theta$$

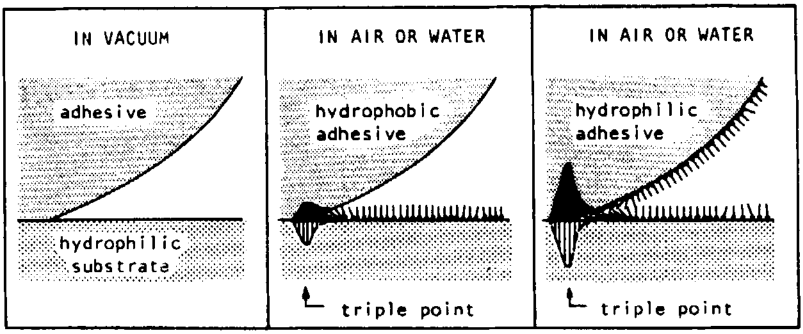

FIGURE 7 Geometry of an adhesive joint and stress distribution at the tip as a result of water adsorption (for equilibrium contact angle $\theta \gg 90°$).

If $\theta = 90°$ is assumed to be a maximum in regard to avoiding crack tip formation at the interface, the relevant value of $[W_A/\gamma_L]$ equals unity. For any $\theta > 90°$, $[W_A/\gamma_L]$ takes values less than 1.0.

Thus, in order to avoid any tendency for spontaneous crack formation at the interface, the following condition should be satisfied:

$$[W_A/\gamma_L]_{\mathrm{MIN}} \geqq 1.0 \tag{34}$$

Substituting equations (8) or (10) into (34) the following is obtained:

$$[W_A/\gamma_L]_{\mathrm{MIN}} = 3 - (1/\Phi_0^2)(1/a_{\mathrm{CF}}) \geqq 1.0, \tag{35}$$

for rectilinear case of $\cos\theta = f(\gamma_L)$.

Symbol "a_{CF}" describes the energy modulus at which the system acquires the capacity to develop the crack geometry as a consequence of the condition $\theta > 90°$, which may be derived from eqn (35):

$$a_{\mathrm{CF}} = 1/2\Phi_0^2. \tag{36}$$

Ultimately, to avoid the tendency for crack generation in the system, condition (35) has to be fulfilled, which means that the energy modulus of a real system,

$$a \geqq a_{\mathrm{CF}}. \tag{37}$$

Incorporating (36) into (37) the following condition is found:

$$a \geqq 1/2\Phi_0^2. \tag{38}$$

Values of ratio "a_{CF}" depending upon the interaction factor Φ_0 are presented in Table IV.

TABLE IV
Values of ratio a_{CF} where system liquid-solid exhibits a tendency for crack generation

Φ_0	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
a_{CF}	0.5	0.619	0.781	1.02	1.288	2.0	3.125	5.55	12.5	50

5. LIMITS TO THE PRACTICAL UTILITY OF EXPRESSIONS FOR THERMO-DYNAMIC WORK OF ADHESION AND INTERFACIAL FREE ENERGY

As previously described, it is possible to indicate limits to the optimum utility of formulae for the work of adhesion and interfacial energy in terms of transition values of the energy modulus, $[a]$, as follows:

(a) a_{CRIT}, the critical value of $a = \gamma_S/\gamma_L$ at which the thermodynamic work of adhesion becomes negative (eqn 32);

(b) a_{CF}, this is the value of $a = \gamma_S/\gamma_L$ at which physical conditions at the interface produce conditions relevant to a crack tip at the boundary of an adhesive joint or at interfacial micro-voids (eqn 36);

(c) a_{MIN}, the value of ratio $a = \gamma_S/\gamma_L$ at which interfacial free energy acquires a minimum for a given solid-adhesive system (see eqns 13, 27); and

(d) a_S, the value of ratio $a = \gamma_S/\gamma_L$ at which adhesive exhibits the tendency for spontaneous self-spreading over the solid's surface (see eqn 11).

These characteristic points have been indicated in Figure 8.

A negative value of the work of adhesion indicates that an adhesive joint with $a \leqq a_{CRIT}$ has a tendency to delaminate even if no external force has been applied.

Since the value of $[\cos\theta]$ can be calculated as follows:

$$\cos\theta = [W_A/\gamma_L] - 1, \tag{39}$$

it can be related directly to the characteristics $[W_A/\gamma_L] = f(a)$ or $[W_A/\gamma_L] = f(a^*)$, and included as an ordinate in Fig. 8.

As $\cos\theta$ becomes negative, an adhesive joint will develop a crack-like profile at the interface due to the mechanism explained in Section 4 and illustrated in Figures 5 to 7.

Therefore conditions under which

$$2.0 \geqq [W_A/\gamma_L] \geqq 1.0, \tag{40}$$

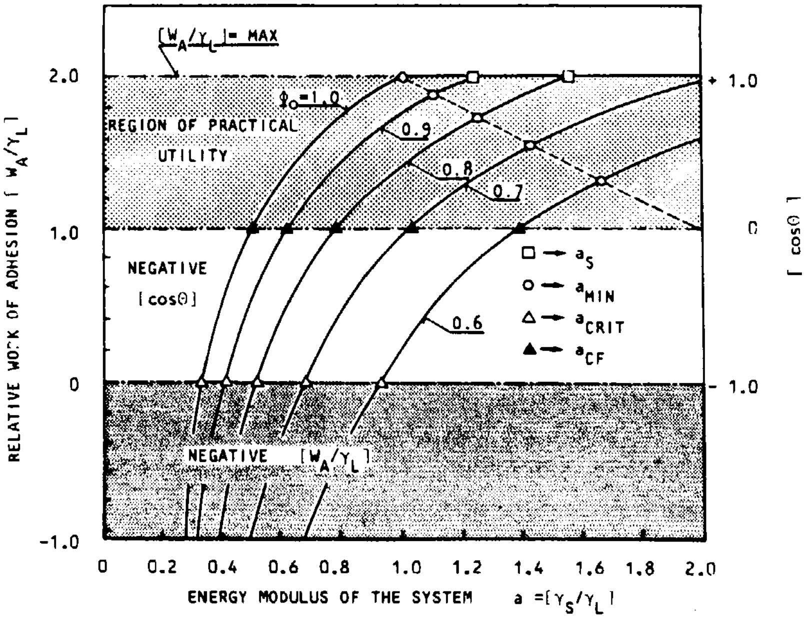

FIGURE 8 Relationship between relative work of adhesion and energy modulus of the system with the indication of transition points and specific areas related to the performance of adhesive joint.

are recommended for obtaining the best practical performance of an adhesive joint (region of optimum utility).

6. CONCLUSIONS

1. The physico-chemical criteria for maximum adhesion between a liquid and solid can be analytically determined, based on the thermodynamic relations between the components of the system, which are expressed by eqns (7), (8) and (15).

2. If it is assumed that maximum adhesion, as measured by the strength of the joint, occurs at the point of minimum interfacial energy of the system then the parameters for this condition are as follows:

$$a_{\text{MIN}} = [\gamma_S/\gamma_L] = 1/\Phi_0$$

$$\gamma_{SL} \rightarrow \text{MIN}$$

$$[\gamma_{SL}/\gamma_L]_{\text{MIN}} = (2/\Phi_0) - 2.$$

3. A zero contact angle θ DOES NOT coincide with conditions for the minimum interfacial energy (and thus for the maximum strength of the system) with the exception of systems having the specific interaction factor $\Phi_0 = 1.0$.

Interfacial free energy at the point where the contact angle becomes zero ($\cos\theta = 1.0$) is always greater than at the point where $(\gamma_{SL})_{MIN}$ occurs, except for systems in which $\Phi_0 = 1.0$. Therefore the strength to be expected when $\cos\theta = 1.0$ (then, for $\theta = 0°$) should be less than the maximum obtainable for the system (except an ideal situation where $\Phi_0 = 1.0$).

4. The value of the optimum contact angle under conditions where the minimum interfacial energy occurs can be determined as

$$\theta_{OPT} = \cos^{-1}(2 - 1/\Phi_0).$$

5. A zero contact angle, indicating a condition for self-spreading of a liquid, is reached for the following condition:

$$a_S = [\gamma_S/\gamma_L] = 1/\Phi_0^2.$$

6. At the point where the relative thermodynamic work of adhesion becomes negative (for $a \leqq a_{CRIT}$), a tendency for the system to delaminate has to be expected which is also relevant to the zero-strength of an adhesive joint.

7. For the case in which $\cos\theta$ v. γ_L remains rectilinear, the transition point from $[+W_A]$ to $[-W_A]$ may be determined theoretically.

8. The critical point for $[W_A/\gamma_L]$ becoming NEGATIVE is obtained for the condition in which the energy modulus of the system becomes:

$$a \leqq [a_{CRIT} = 1/3\Phi_0^2].$$

9. The conditions where the contact angle exceeds 90 degrees produce a tendency for the systems to generate cracks at the interface around any interfacial void (including the periphery of the joint). This tendency will be expected for the condition in which the energy modulus of the system becomes:

$$a < [a_{CF} = 1/2\Phi_0^2].$$

10. The region of practical usefulness in order to obtain an acceptable performance of an adhesive joint is indicated by those limiting parameters of solid-liquid system, for which:

$$1.0 \leqq [W_A/\gamma_L] \leqq 2.0.$$

This means that the condition:

$$a > a_{CF},$$

has to be met by the system.

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APPENDIX: NOMENCLATURE

γ_L, γ_S	surface free energy of liquid and solid respectively
γ^P, γ^D	polar (P) and dispersion (D) components of surface energy
γ_{SL}	interfacial free energy
γ_C	critical surface tension for wetting
W_A	thermodynamic work of adhesion
Φ	interaction factor
Φ_0	maximum value of the interaction factor Φ for a given solid obtainable for the condition in which $\cos\theta = 1.0$; $\gamma_L = \gamma_C$ (specific bonding efficiency factor)
d,p	dispersion and polar fraction of surface energy
θ	equilibrium contact angle
θ_{OPT}	equilibrium contact angle for minimum interfacial energy
$[\gamma_{SL}/\gamma_L]$	relative interfacial energy
$[W_A/\gamma_L]$	relative thermodynamic work of adhesion
$a;a^*$	energy modulus of the system $a = \gamma_S/\gamma_L$ $a^* = \gamma_C/\gamma_L$
a_S	energy modulus for spontaneous wetting
a_{MIN}	energy modulus for minimum interfacial energy
a_{CRIT}	critical energy modulus for negative work of adhesion
a_{CF}	energy modulus at which crack geometry becomes relevant
$a^*_S, a^*_{MIN}, a^*_{CRIT}, a^*_{CF}$	$\Big\{$ the above moduli calculated when equations contain γ_C instead of γ_S (for $a^* = \gamma_C/\gamma_L$)