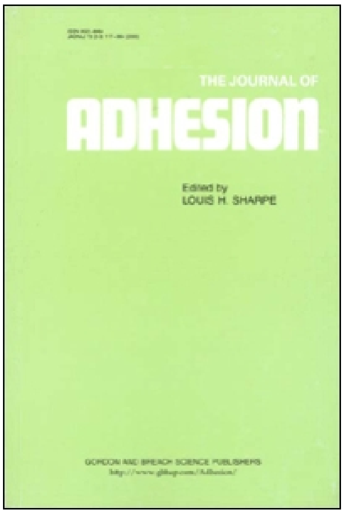

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Physico-Chemical Criteria for Maximum Adhesion. Part I: Theoretical Concepts and Experimental Evidence

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This paper presents an analysis of the literature with the aim of defining basic criteria and developing a general model to describe joint strength. Two particular cases of the relationship: $\cos\theta = f(\gamma_L)$ have been identified as prerequisites for further analysis of interfacial phenomena and conditions governing their existence were discussed.

The fact has been pointed out, based on available experimental results, that for the most important case in practice where $0.6 \leq \cos\theta \leq 1.0$, the relation $\cos\theta = f(\gamma_L)$ can be treated as rectilinear. This finding will be utilized in the comprehensive development of criteria defining joint performance in Part II.

Variability of the interaction factor Φ for various systems has been investigated in relation to $\cos\theta$, for the identified particular cases of the relationship $\cos\theta = f(\gamma_L)$. A special value of the interaction factor, Φ_0, was found. The importance of the rectilinear particular case of $\cos\theta = f(\gamma_L)$ was shown, which involves constant factor Φ_0 instead of variable Φ.

KEYWORDS: Adhesion, Performance criteria, Contact angle, Interaction factor, Specific bonding efficiency factor, Surface energy.

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1. INTRODUCTION

The purpose of an adhesive is to hold two solid surfaces together in a joint having mechanical properties adequate for the intended purpose. In the case of structural adhesives, increasing the strength of the joint up to the strength of the components themselves is usually the objective.

The measured strength of the joint would be dependent on the forces of adhesion acting throughout an interface between the adhesive and substrates. Selection of adhesives or changing the properties of the substrate by surface treatment to maximize these forces, are ways of seeking to improve joint strength.

Two problems immediately arise. One is to choose the most appropriate method for defining in physico-chemical terms the parameter giving the best correlation with measured joint strength. The other is to choose the most appropriate test conditions to be employed for the experimental determination of joint strength.

An obvious starting point for dealing with the first problem is to use the thermodynamics of surfaces for defining the theoretical adhesion parameter. However, it must be remembered that interfacial properties affect not only the interfacial forces directly, but, in many real substrates with rough or heterogeneous surfaces, the completeness of wetting of the surface by the liquid adhesive, as well. In any study of the relationship between theoretical adhesion and observed strength, it will be necessary to consider only those systems for which it is safe to assume that the substrate is completely wetted by the liquid adhesive even if the contact angle is not zero.

Other assumptions necessary at this stage of the study are as follows:

(a) Substrate surfaces are non-porous, homogeneous, stable and reproducible.

(b) The following basic relations are valid (see the Appendix for definition of symbols)

—equation for the thermodynamic work of adhesion

$$W_A = \gamma_L(1 + \cos\theta), \tag{1}$$

—equations for the equilibrium which exists at the contact line

$$\cos\theta = (\gamma_S - \gamma_{SL})\gamma_L, \text{ and} \tag{2}$$

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

(c) The interaction factor defined by Good[1], which relates to the intermolecular forces acting throughout an interface is expressed, as follows:

$$\Phi = [\gamma_S + \gamma_L - \gamma_{SL}]/[2(\gamma_S \cdot \gamma_L)^{1/2}]. \quad (4)$$

2. ANALYSIS OF THE LITERATURE

Four quantities describing thermodynamic properties of an adhesive joint have been variously claimed as determinants of the strength of an adhesive joint:

1. Thermodynamic work of adhesion (W_A);
2. Free interfacial energy (γ_{SL});
3. Critical surface tension for wetting (γ_C); and
4. Solubility parameter (δ).

Results of analyses of the possible relationships between these factors and experimentally measured joint strengths have been based on a single factor without considering the others and has led to different and sometimes divergent conclusions, as discussed in the following.

2.1 Relationship between Thermodynamic Work of Adhesion and Strength of the Joint

Some researchers (DeBruyne[2], Raraty & Tabor[3], Barbaris[4], Mittal[5]) claim that, based on experimental results, there is a strictly rectilinear relation between strength of the joint and work of adhesion (W_A). The general conclusion by this group of researchers was that practical adhesion as measured by joint strength can be increased by better wetting of the substrate by the adhesive (the lower θ, the higher strength).

On the other hand Mittal[5], utilizing Dyckerhoff's[6] experimental data, found that practical adhesion, measured in terms of joint strength, increases up to a maximum value (see Figure 1) and then starts to decline with further increase of W_A as calculated by eqn (1). The optimum value of W_A was found to be different for different adhesives and substrates.

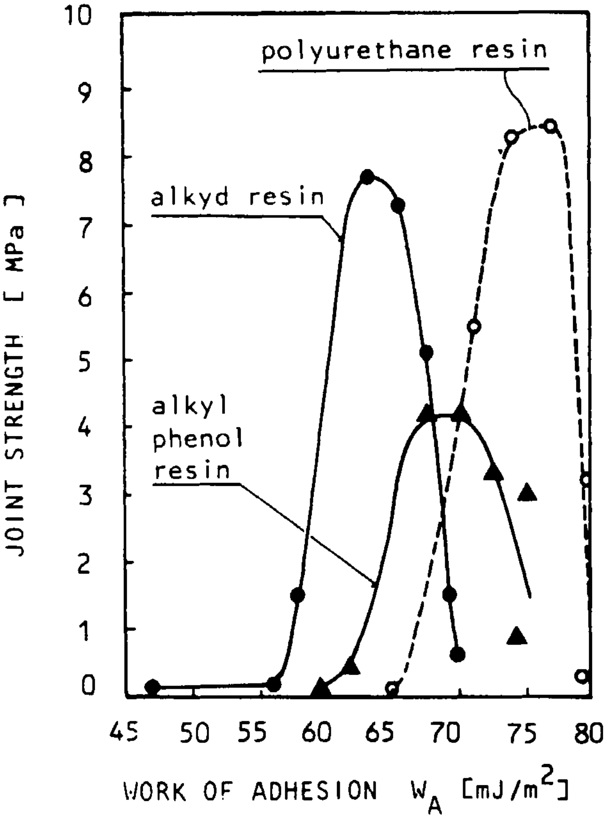

FIGURE 1 Relationship between joint strength and thermodynamic work of adhesion Mittal[5].

2.2 Relationship between Interfacial Free Energy and Strength of the Joint

Interfacial free energy (γ_{SL}) has been claimed by Levine[7], Mittal[5], and Dyckerhoff[6] to be the most significant factor determining the strength of the joint. The maximum strength of the joint is achieved (see Figure 2) for those systems that exhibit the minimum (zero) interfacial free energy. Mittal, utilizing Levine's data, has suggested that there is a rectilinear relationship between the strength of the system and γ_{SL} (see Figure 2a).

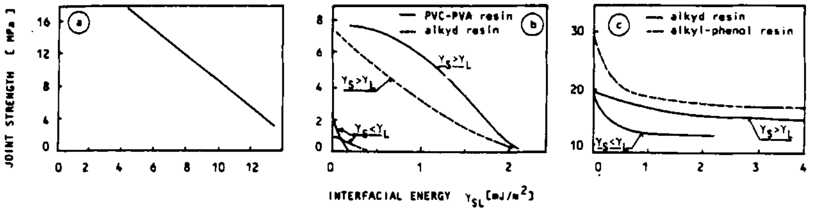

FIGURE 2 Relationship between joint strength and interfacial energy. (a) Mittal's[5] interpretation based on Levine's[7] experimental data; (b) Dyckerhoff's[6] results for plastics; (c) Dyckerhoff's[6] results for steel.

But Dyckerhoff, working with a much wider selection of adhesives and substrates, has obtained curvilinear relationships (Figures 2b, 2c) and was the first researcher to claim the following:

(a) The maximum strength of the joint is to be expected for systems in which the surface energies of adhesive and substrate are equal (see also Figures 4b and 4c).

(b) When surface energies of components are not equal, the decrease in strength is less for those systems in which the surface energy of the substrate is higher than the surface energy of liquid, compared with those systems in which it is lower (see also Figure 4c).

2.3 Relationship between Surface Energy of Solid or Critical Surface Tension for Wetting and Strength of the Joint

Levine[7] and Mittal[5] in their considerations claimed (see Figure 3) that there is a rectilinear relationship between the strength of the joint and the critical surface tension for wetting of the substrate (γ_C). However, it would appear that it is not as simple as they have indicated.

Kitazaki and Hata[8] have re-interpreted Levine's[7] and Schonhorn's[9] data, plotting the strength of the adhesive joint relative to γ_C^C of the adherends (see Figure 4a). (γ_C^C-critical surface tension for wetting obtained using hydrogen-bonding liquids).

They concluded that the optimum adhesion occurs at the minimum interfacial tension and therefore equality of γ_L with γ_C^C (nearest to γ_S) gives the condition for maximum strength. This conclusion is the same as that reached by Dyckerhoff, as illustrated in Figure 4b, c and Figure 2b, c.

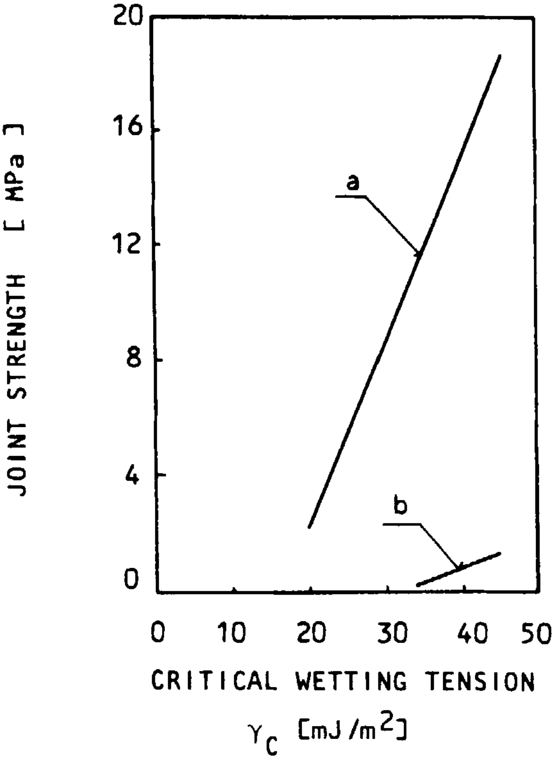

FIGURE 3 Rectilinear interpretation of the relationship between joint strength and critical wetting tension [γ_C] of substrate. (a) Mittal's[5] interpretation of Levine's[7] experimental data; (b) Barbaris'[14] results for polyethylene (γ_C increased by different treatment).

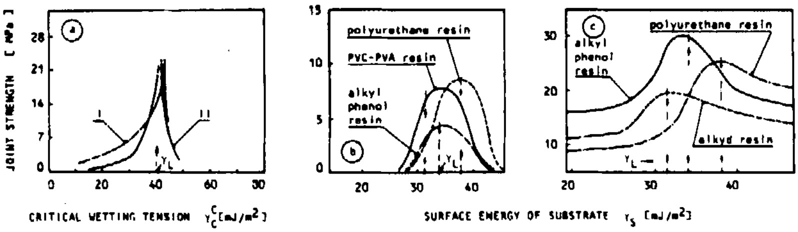

FIGURE 4 Curvilinear relationship between joint strength and energetic properties of the substrate expressed by [γ_S] or [γ_C^C]. (a) Kitazaki and Hata's[8] data for plastics; (b) Dyckerhoff's results for plastics (Dyckerhoff and Sell[6]); (c) Dyckerhoff's results for steel (Dyckerhoff and Sell[6]).

2.4 Relationship Between Solubility Parameter and Strength of the Joint

Plueddemann[10] in his research on the influence of silane coupling agents on the strength of glass-fibre laminates examined his concept of a correlation between the strength and the solubility parameter (δ) of the matrix and the silanes. He found no correlation in the case of a polyester based matrix but confirmed some dependency when polystyrene was used instead (see Figures 5a and 5b). In the latter, the maximum strength was achieved when the solubility parameters of substrate and adhesive were equal.

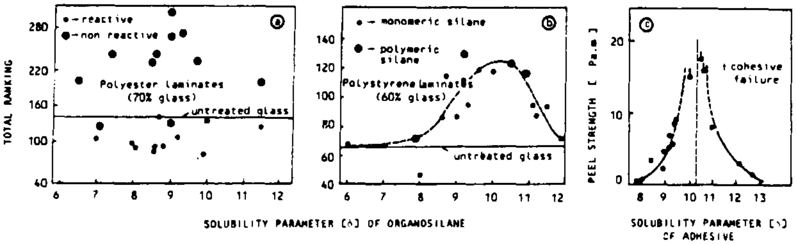

FIGURE 5 Relationship between solubility parameter and strength of the joint. (a) organosilanes in the system: polyester matrix +70% glass fibre (Plueddeman[10]); (b) organosilanes in the system: polystyrene matrix +60% glass fibre (Plueddeman[10]); (c) Mylar–adhesive–Mylar (Iyenger and Erickson[11]).

Iyenger and Erickson[11] confirmed a similar dependency (see Figure 5c) between strength of joint and solubility parameter. They also found that the maximum strength of the joint occurred when the solubility parameters of the substrate and adhesive were equal.

3. BASIC RELATIONS DESCRIBING INTERACTION BETWEEN SOLID SUBSTRATE AND LIQUID ADHERENT

3.1 Interaction Factor as Variable Parameter

The interaction factor Φ defined by equation (4) can be represented in the following form:

$$\Phi = 0.5(1 + \cos\theta)(\gamma_L/\gamma_S)^{1/2}. \tag{5}$$

This form is more useful for analytical and practical purposes than equation (4) for the following reasons:

(a) Φ is now explicitly given in terms of the two variables, instead of three in the case of equation (4), namely $\cos\theta$ and the dimensionless ratio γ_L/γ_S, and

(b) the variability of parameter Φ, upon $\cos\theta$ and γ_L/γ_S is evident.

Therefore the general fact has to be emphasized that the interaction parameter Φ can no longer be considered a constant.

Under conditions for self-spreading of liquid over a substrate it is assumed that the following definitions apply:

$$\left.\begin{array}{ll}\text{(a)} & \cos\theta = 1.0, \\ \text{(b)} & \gamma_L = \gamma_C, \text{ and} \\ \text{(c)} & \Phi = \Phi_0. \end{array}\right\} \tag{6}$$

An incorporation of conditions (6), into equation (5) leads to the definition of Φ_0, which is constant for a given system, *i.e.*

$$\Phi_0 = (\gamma_C/\gamma_S)^{1/2}. \tag{7}$$

For other conditions (where $\cos\theta \neq 1.0$ and $\gamma_L \neq \gamma_C$) parameter Φ varies depending upon values of $\cos\theta$ and ratio γ_L/γ_S as equation (4) explains.

3.2 Particular Cases in the Relationship between cos θ and γ_L

Fox and Zisman[12] provided overwhelming experimental evidence to suggest that the scatter of the results relating $\cos\theta$ to γ_L permits a rectilinear approximation of this relationship, as illustrated in Figure 6. Thus the contact angle θ for any liquid on a given substrate can be calculated using the following empirical formula[12]:

$$\cos\theta \cong 1 - b(\gamma_L - \gamma_C), \tag{8}$$

where $(-b)$ = slope of the graph of $\cos\theta$ *v.* γ_L.

Experimental determination of the slope "b" and therefore of "γ_C" with accuracy is, however, very difficult[5,8,13,14].

An analysis presented below allows determination of values of parameters "b" and "γ_C" in equation (8) and leads to the definition of some basic terms which will be utilized further in order to develop the criteria of joint performance.

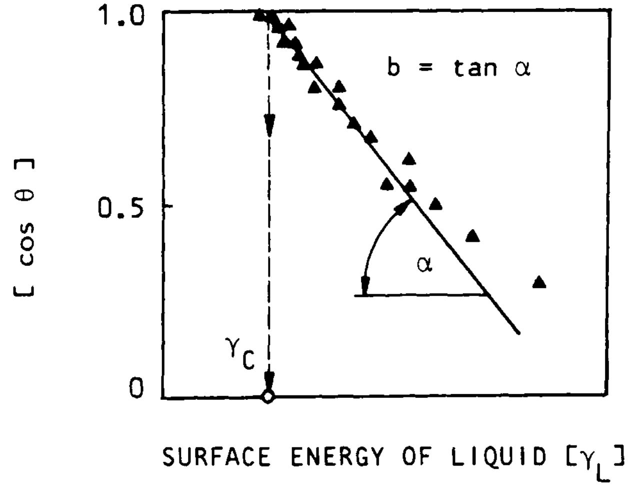

FIGURE 6 Zisman's[17] rectilinear interpretation of the relationship: cos $\theta = f(\gamma_L)$.

A theoretical relationship defining the cosine of the contact angle is expressed by equation (2) and can also be obtained by rearrangement of equation (5), *e.g.*

$$\cos\theta = (\gamma_S - \gamma_{SL})/\gamma_L, \text{ and} \tag{2}$$

$$\cos\theta = 2\Phi(\gamma_S/\gamma_L)^{1/2} - 1. \tag{9}$$

Equation (2) and (9) are equivalent, which is apparent if γ_{SL} calculated from equation (4) is substituted in equation (2).

Thus, equation (9) will be analysed further as a basic expression for the cosine of the contact angle, in which cos θ is a function of two variables, *i.e.* Φ and γ_S/γ_L.

Equation (9) is represented in Figure 7 by the upper curve, and will be called hence-forth the "curvilinear case" of the relationship between cos θ and γ_L.

It will be explained further (see Section 4) that equation (9) is valid only in the case when Φ is constant.

In practice, the scatter of experimental results in the vicinity of cos $\theta = 1.0$ is approximated well by a straight line. At this stage it is assumed that this line is represented by the tangent to the curve described by equation (9) at the point where $\gamma_L = \gamma_C$ (see Figure 7). Based on the above assumption, an experimental approximation of

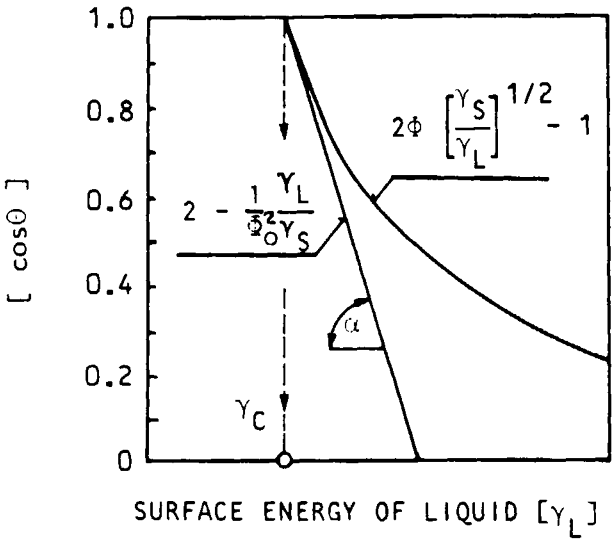

FIGURE 7 Graphical representation of equations (9) and (15a, b) which represent the particular rectilinear and curvilinear cases of the relationship cos $\theta = f(\gamma_L)$.

the relationship between cos θ and γ_L can be expressed by equation (8).

The slope $b \rightarrow b_0$ is obtained in this case by taking the derivative of equation (9) at the point where $\gamma_L \rightarrow \gamma_C$. This particular case will be called the "rectilinear case" of the relationship between cos θ and γ_L. It can be concluded further (see Section 4) that this approach allows a reconciliation between Fox and Zisman's relationship for cos θ *v*. γ_L.

The tangent to the curve (9) at any point is given by:

$$b = d\,(\cos\theta)/d\gamma_L. \tag{10}$$

that is,

$$b = -\Phi(\gamma_S/\gamma_L^3)^{1/2} + 2(\gamma_S/\gamma_L)^{1/2}.(d\Phi/d\gamma_L), \text{ or} \tag{11}$$

$$b = -(1 + \cos\theta)/2\gamma_L + 2(\gamma_S/\gamma_L)^{1/2}.(d\Phi/d\Phi_L). \tag{12}$$

The interaction factor Φ apparent in equations (11) and (12) is variable in a general case, as equation (5) explains. Thus, the second member of equations (11) and (12), which expresses a derivative of Φ in respect to γ_L, cannot be neglected.

Under circumstances which permit Φ = constant (see Section 4), the derivative $d\Phi/d\gamma_L$ becomes zero, so that:

$$b = -\Phi(\gamma_S/\gamma_L^3)^{1/2} \qquad \textit{if} \qquad \Phi = \text{const} \tag{13}$$

From the definition of the "rectilinear particular case" of cos θ *v.* γ_L, the tangent "*b*" has to be determined in the vicinity of the point where self-spreading occurs, *i.e.* in which $b \to b_0$. At this point conditions (6) apply in which $\Phi = \Phi_0$ where Φ_0 is constant. Therefore the tangent to the curve (9) and respectively equations (11) and (12) have the following value:

$$\left.\begin{array}{l} b = b_0, \\ \text{so that: } b_0 = -1/\gamma_C \end{array}\right\} \text{ for } \cos\theta = 1.0. \tag{14}$$

Having determined the theoretical value of "b_0" and incorporating it into equation (8) instead of "*b*", we obtain the formula for rectilinear approximation of the relationship cos θ *v.* γ_L, *e.g.*

$$\cos\theta = 2 - (\gamma_L/\gamma_C), \text{ or} \tag{15a}$$

$$\cos\theta = 2 - (\gamma_L/\gamma_S).(1/\Phi_0^2). \tag{15b}$$

Thus, equations (15a) and (15b) express the "rectilinear particular case" of the relationship $\cos\theta = f(\gamma_L)$.

Table I comprises published data covering various materials with different values of γ_C, for which parameter "*b*" has been determined experimentally from graphs: cos θ *v.* γ_L, and those where "b_0" was calculated using equation (14).

It must be emphasized that all relationships describing interfacial phenomena which are based on equation (9) [relevant to the curvilinear

TABLE I

Comparison of experimentally* determined parameter "*b*" with its theoretical value [b_0] for a variety of materials (equation 14)

	Material	γ_C	Slope Experimental*	Theoretical
1	Poly (tetrafluoroethylene)	18.5	0.036	0.054
2	Poly (ethylene)	31	0.025	0.032
3	Poly (styrene)	33	0.028	0.030
4	Poly (vinyl chloride)	39	0.0355	0.026
5	Poly (vinylidene chloride)	40	0.027	0.025
6	Poly (ethylene terephalate)	43	0.030	0.023
7	Poly (hexamethylene adipamide)	46	0.027	0.022

* taken from reference [6]

case of the relationship cos θ *v.* γ_L], contain cos θ as a function of two variables: Φ and ratio γ_S/γ_L.

In the general case, ***parameter* Φ *must not be treated as a constant***, as equation (5) explains. Particular conditions under which Φ is constant are described in Section 4.

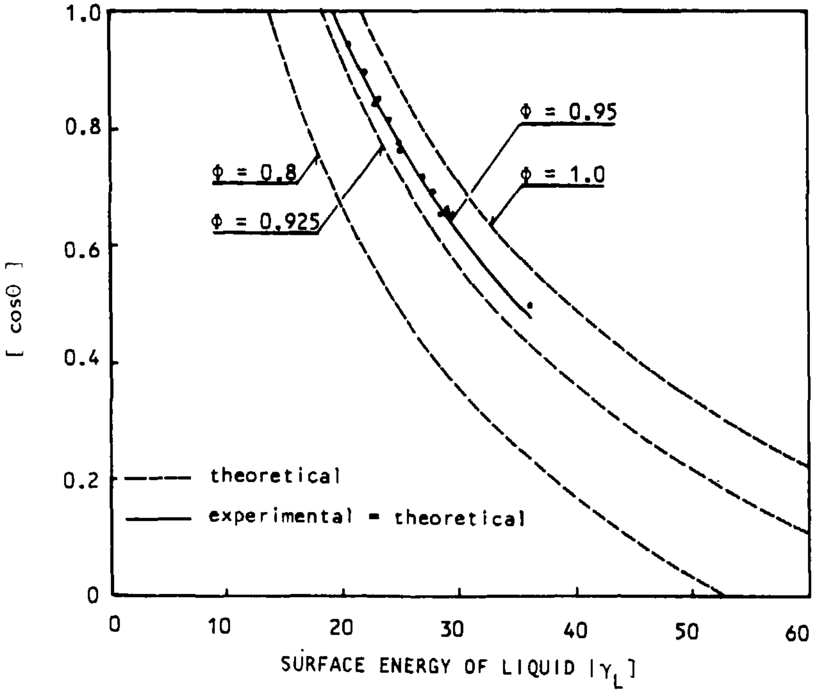

FIGURE 8 Graphical representation of the loci of points which permit Φ = constant in the relationship cos $\theta = f(\gamma_L)$ for polytetrafluoroethylene (Kaelble and Uy[14]) $\gamma_S = 21.6$ mJ/m^2, $d_S = 0.907$).

Equations describing interfacial phenomena which are based on the rectilinear approximation of the relationship between cos θ and γ_L involve expression (15b), which contains Φ_0 instead of Φ. Parameter Φ_0 in this case represents the constant that is a particular case of Φ for the conditions where $\cos\theta = 1.0(\Phi_0^2 = \gamma_C/\gamma_S$; see equation 7).

Thus, the interaction parameter Φ is not involved as a variable in any equation describing interfacial phenomena which is based on the rectilinear approximation of the relationship between cos θ and γ_L.

4. FACTORS INFLUENCING WETTABILITY CHARACTERISTIC OF THE SOLID

For those conditions in which the interaction factor Φ remains constant, the characteristic $\cos\theta = f(\gamma_L)$ has a curvilinear form as illustrated in Figure 8. Each curve corresponds to a given value of Φ.

The surface energy of a liquid, γ_L may generally be expressed by the sum of two main components, *e.g.*

$$\gamma_L = \gamma_L^d + \gamma_L^\sigma. \tag{16}$$

The same remains valid for the total surface energy of a solid.

Kaelbleand Uy[14] developed the alternative [comparing with equation (4)] formula for the interaction factor Φ expressed in terms of the

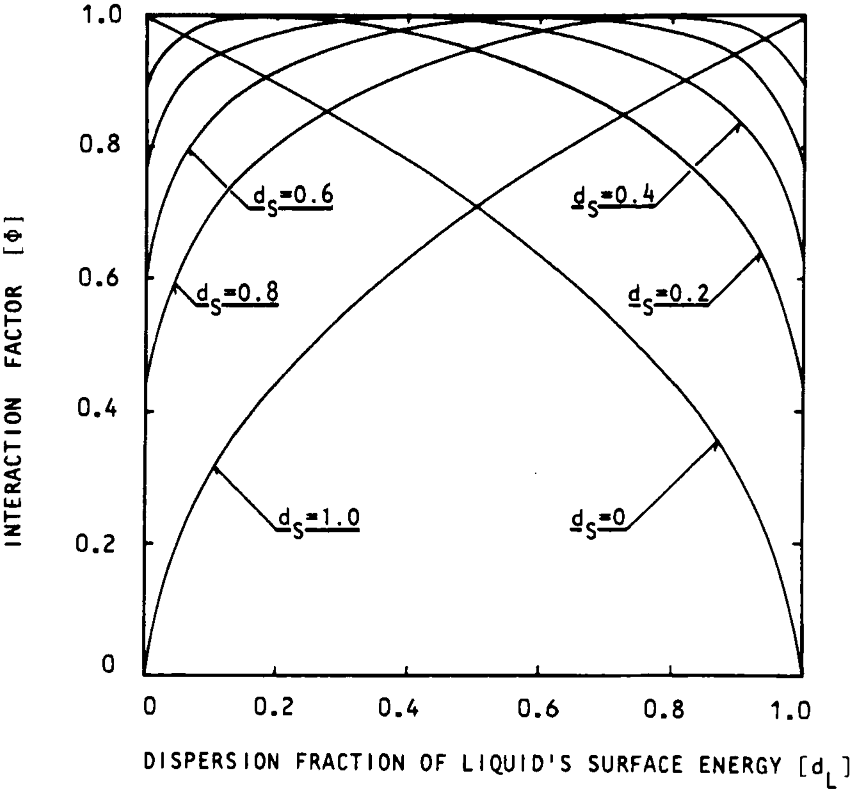

FIGURE 9 Variability of the interaction factor Φ depending upon dispersive component "d_L" of the test liquid and solid; "d_S".

dispersive/polar structure of two materials in direct contact, *i.e.*

$$\Phi = (d_L \times d_S)^{1/2} + (p_L \times p_S)^{1/2}. \tag{17}$$

Here, $d_{L(S)}$ and $p_{L(S)}$ express the dispersive and polar components in total surface energy, *e.g.*

$$\begin{aligned} d_{L(S)} &= \gamma^d_{L(S)}/\gamma_{L(S)}, \\ p_{L(S)} &= \gamma^p_{L(S)}/\gamma_{L(S)}, \text{ and} \\ p + d &= 1.0. \end{aligned} \tag{18}$$

Incorporating conditions (18) into (17), the following expression for the interaction factor can be obtained:

$$\Phi = d_S^{1/2}.d_L^{1/2} + (1 - d_S)^{1/2}.(1 - d_L)^{1/2}. \tag{19}$$

Relationship (19) is illustrated in Figure 9, where the value of Φ is represented as a function of the dispersivity "d_L" of the liquid for given values of the dispersive component "d_S" of the solid.

Conditions for a maximum value of Φ can be determined by differentiating equation (19), *e.g.*

$$d\Phi/d(d_L) = d/d(d_L)[d_S^{1/2}.d_L^{1/2} + (1 - d_S)^{1/2}.(1 - d_L)^{1/2}],$$

from which the following is obtained:

$$\Phi = \text{MAX, } i.e.\ \Phi = 1.0 \quad \text{when } \begin{cases} d_L = d_S, \\ p_L = p_S. \end{cases} \tag{20}$$

Thus, the interaction factor acquires its maximum value equal to unity for a given system solid/liquid, when both solid and liquid have the same polar/dispersive structure indicated by $d_{L(S)}$ and $p_{L(S)}$. The above coincides with conclusions gained by Wu[15] and Cherry[16].

Consideration of the above analysis leads to the following conclusion. The true curvilinear relationship between cos θ and γ_L [as expressed by equation (9) and Figure 8] can be obtained *only* if the test liquids used in the experimental procedure have different total surface energies γ_L, but all exhibit equal dispersive and polar fractions of the total surface energy, *i.e.*

$$\left.\begin{aligned} &\text{(a)} \quad \gamma_L^{(1)} \neq \gamma_L^{(2)} \neq \ldots \neq \gamma_L^{(n)}, \\ &\text{(b)} \quad d_L^{(1)} = d_L^{(2)} = \ldots = d_L^{(n)}, \text{ and} \\ &\qquad p_L^{(1)}\ p_L^{(2)} = \ldots = p_L^{(n)}. \end{aligned}\right\} \tag{21a}$$

It is also necessary that the surface energy of a solid and its polar/

dispersive structure are constant for every stage of the experimental procedure, *i.e.*

$$\left.\begin{array}{ll}\text{(c)} & \gamma_s = \text{constant,} \\ \text{(d)} & d_s = \text{constant, and} \\ & p_s = \text{constant.}\end{array}\right\} \qquad (21\text{b})$$

The above are prerequisites for producing a constant value Φ for the system substrate-liquids, which results in the curvilinear shape of the relation $\cos\theta$ *v.* γ_L as in Figure 8.

In practice, it is almost impossible to produce conditions in which the value of the interaction factor Φ can be maintained as a constant. This arises for the following reasons:

(a) It is difficult to select *a priori* a series of the test liquid having simultaneously:
—different total surface energy
—equal dispersive and polar fractions of total surface energy.

(b) The total surface energy of the solid, and its dispersive-polar structure, alter significantly with changes in the ambient humidity (see Table II, where appropriate data relevant to polished steel are listed).

Therefore, it is obvious that in most practical cases each point in the relationship $\cos\theta = f(\Phi, \gamma_L)$ involves a different value of the interaction factor Φ (see Section 5 for further explanation).

From an engineering point of view the region where $\cos\theta \cong 0.6$ to 1.0 plays the most important role and the slope of the plot $\cos\theta = f(\gamma_L)$ needs to be determined for this particular region. Ulti-

TABLE II

Dispersive and polar fractions of surface energy of polished steel, depending upon ambient humidity, and their influence on value of the interaction factor Φ in systems with water (Φ_{S/H_2O}) and non-polar liquids ($\Phi_{S/N.P.}$)

RH[%]	10	20	30	40	60	90
γ_S^d	29.5	28.5	27.5	26.0	24.0	21.0
γ_S^p	14.0	14.0	14.0	14.0	14.0	14.0
$\gamma_S = \gamma_S^d + \gamma_S^p$	43.5	42.5	41.5	40.0	38.0	35.0
$d_S = \gamma_S^d/\gamma_S$	0.678	0.670	0.663	0.650	0.631	0.600
Φ_{S/H_2O}	0.927	0.9308	0.933	0.9383	0.945	0.9549
$\Phi_{S/N.P.}$	0.823	0.818	0.814	0.806	0.794	0.774

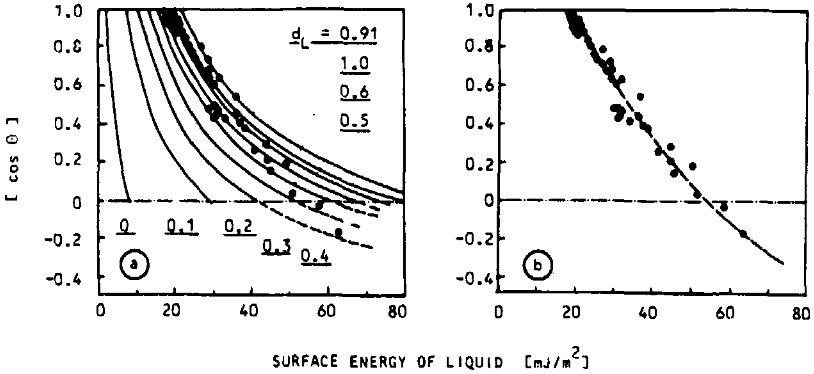

FIGURE 10 Wettability characteristic of polytetrafluoroethylene (Kaelble and Uy[14]), ($\gamma_S = 21.6$ mJ/m^2, $d_S = 0.907$). (a) wettability characteristics depending on polar-dispersive structure of test liquids; (b) approximation of all results despite polar-dispersive structure of the test liquids.

mately the test liquids for determining the wettability characteristic of a given solid [in co-ordinates $\cos\theta = f(\gamma_L)$] must be based on those which can satisfy that condition where $\cos\theta \geq 0.6$.

It is obvious from equations (9) and (17) that the critical surface tension for wetting (γ_C) is not a constant (see also references[14,20]),

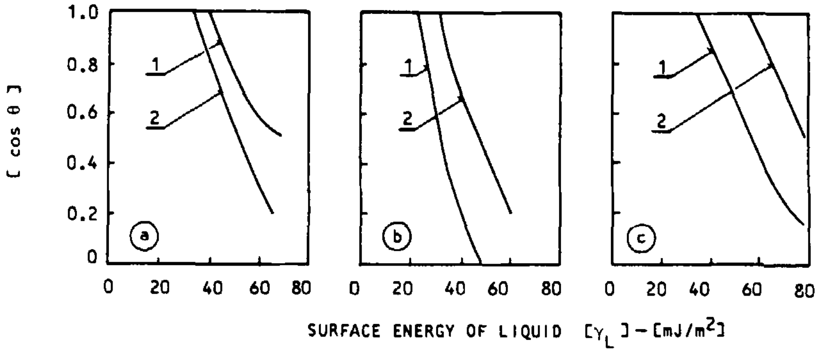

FIGURE 11 Evidence of the relationship $\cos\theta = f(\gamma_L)$ for variety of substrates.
(a) 1 – glass + $C_6H_5Si(OCH_3)$ silane (Lee[19]);
(a) 2 – glass + $CH_3C_0H_4SiCl$ silane (Lee[19]);
(b) 1 – poly (tetrafluoroethylene) (Zisman[17]);
(b) 2 – poly (ethylene) (Zisman[17]);
(c) 1 – silica sand + A1102 silane (Gutowski[18]);
(c) 2 – silica sand (Gutowski[18]).

but depends upon the value of Φ which, in accordance to equation (7), is identical here (for $\cos\theta = 1.0$) to Φ_0. It is also worthwhile to emphasize that values of Φ and ultimately γ_C are relevant to the polar/dispersive structure of the solid and liquid, as equation (17) explains.

5. EXPERIMENTAL EVIDENCE OF THE RELATIONSHIP BETWEEN COS θ AND γ_L

It has been explained that the shape of the graph relating $\cos\theta$ and γ_L depends strictly on the selection of test liquids used for the experimental determination of γ_C. When different test liquids with known values of γ_L have the same dispersivity (d_L), the shape of the relation $\cos\theta$ *v.* γ_L will be curvilinear, as equation (9) explains.

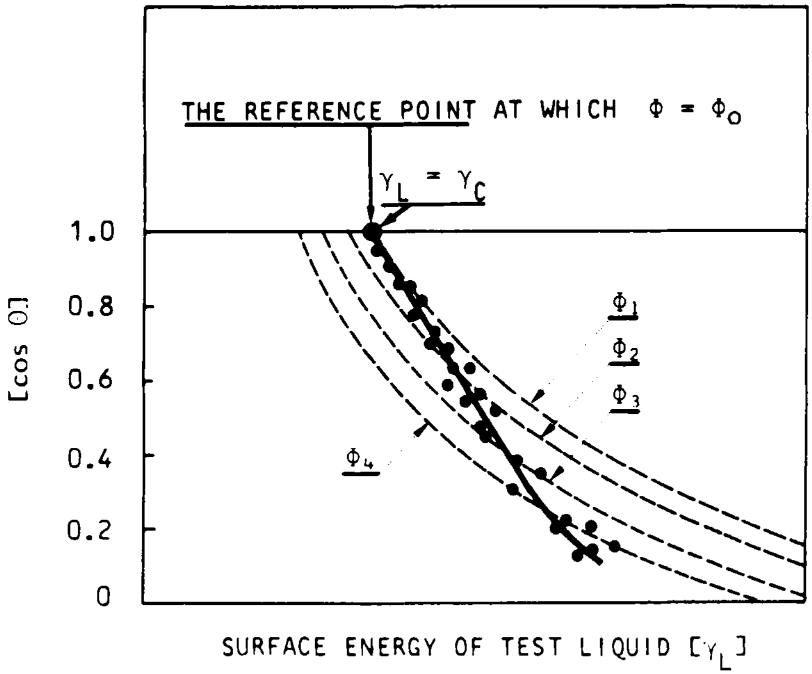

FIGURE 12 Illustration of the variability of the interaction parameter Φ in the rectilinearly approximated relationship $\cos\theta = f(\gamma_L)$, and explanation of the physical sense of the specific bonding efficiency factor Φ_0.

Kaelble and Uy[14] in their research on wettability of polytetrafluoroethylene (see Figure 10a) confirmed the agreement of the theoretical approach with experiments regarding the influence of dispersivity on the relationship cos θ *v.* γ_L. They also concluded that these curvilinear graphs can be approximated in a rectilinear fashion in the range where $0.8 \leqq \cos\theta \leqq 1.0$ with reasonably good results.

The experimental points can be approximated by a straight line for the region $0.6 \leqq \cos\theta \leqq 1.0$ as indicated in Figure 10b for all results without reference to d_L.

It should also be emphasized that the slope $[b_0]$ obtained in Figure 10b is the same as that obtained from Figure 10a for non-polar test liquids (*n*-alkanes that exhibit $d = 1.0$).

Published results [17,18,19], indicate that in many other cases using the latter procedure, the relationship cos θv, γ_L remains rectilinear over a wide range of cos θ (see Figure 11) and only below $\cos\theta \simeq 0.6$ does it become slightly curvilinear.

6. WETTABILITY CHARACTERISTIC OF THE SOLID WHEN Φ IS VARIABLE

There are restricted circumstances under which the interaction factor Φ is constant, as explained in Section 4. When those conditions (21) are achieved, the wettability characteristic of a solid is represented by quasi-hyperbolic curves, *e.g.*

$$(1+\cos\theta).\gamma_L^{1/2} = \text{const} \qquad \text{for } \Phi = \text{const}, \tag{22}$$

as illustrated in Figures 8 and 10.

When Φ becomes variable, the scatter of results in co-ordinates $\cos\theta = f(\gamma_L)$ allows their local approximation by a straight line in the vicinity of $\cos\theta = 1.0$. Each point on this rectilinear wettability characteristic has a different value of the interaction factor Φ. This is clear from Figure 12 which illustrates the rectilinear approximation of scattered experimental results together with semi-hyperbolic curves (9) relevant to the constant value of Φ.

Variability of Φ for the most general case can be determined from equation (5) if cos Θ is replaced by expression (8), *i.e.*

$$\Phi = 0.5(\gamma_L/\gamma_S)^{1/2}[2 - b_0(\gamma_L - \gamma_C)]. \tag{23}$$

Slope "b_0" in equation (23) can be determined experimentally or derived analytically using equations (11) or (12), for a given pattern of variability of Φ in respect to γ_L.

It is assumed for further analytical purposes that two cases have an engineering significance when the wettability characteristic of the solid is locally approximated by a straight line, *viz.*

(a) $\cos\theta = f(\gamma_L)$ expressed by a tangent to a curve expressed by equation (9) at the point where conditions (6) apply, *i.e.* $\cos\theta = 1$.

In this case the following expressions apply:

$$\left.\begin{aligned} b_0 &= -1/\gamma_C, \text{ and} \\ \Phi &= 0.5(\gamma_L/\gamma_S)^{1/2}[3-(\gamma_L/\gamma_C)]. \end{aligned}\right\} \qquad (24)$$

(b) $\cos\theta = f(\gamma_L)$ expressed by a line passing through two points located on the curve expressed by equation (9), which have coordinates related to $\cos\theta = 1.0$ [conditions (6)] and $\cos\theta \cong 0.6$ ($\cos\theta = 0.6$ constitutes a lower limit in view of engineering utility).

In this case the relevant equations retain the same mathematical structure as (14) and (24) but the numerical factors change as follows:

$$\left.\begin{aligned} b &= -0.714/\gamma_C, \text{ and} \\ \varphi &= 0.5(\gamma_L/\gamma_S)^{1/2}[2.714-0.714(\gamma_L/\gamma_C)]. \end{aligned}\right\} \qquad (25)$$

This matter is developed further on Part II.

7. CONCLUSIONS

1) Consideration of the strength of adhesive joint enables joint performance to be defined in terms of interfacial energy and/or thermodynamic work of adhesion.

2) Optimum adhesion (measured by strength of the joint) occurs when the minimum (not necessarily zero) interfacial energy in the system has been acquired.

3) The interaction parameter Φ acquires its particular value defined as $\Phi_0 = (\gamma_S/\gamma_C)^{1/2}$ which is constant *only* at the point where conditions for self-spreading of liquid occur [see conditions (6)]. Physically, it represents the maximum obtainable value of Φ for a given solid.

4) There are two forms of the relationship between $\cos\theta$ and γ_L:

(a) *Curvilinear relationship* $\cos\theta = f(\gamma_L)$.

This case, described by equation (9), is of limited practical value applicable only for the constant value of the interaction factor Φ. This constitutes a very peculiar case obtained when conditions (21) are all simultaneously satisfied.

(b) *Rectilinear relationship cos* $\theta = f(\gamma_L)$.
This case, described by equations (15a) and (15b), is obtained as a result of approximation of the scattered experimental results under random test conditions [when (21) are not applicable], *i.e.* without respect to variation in γ_L, γ_L^d, γ_L^p and Φ.

5) The region in which cos $\theta \cong 0.6 = 1.0$ has engineering importance, so that the test liquids utilized for experimental determination of the relationship cos $\theta = f(\gamma_L)$ must be selected to fit the above specified interval.

6) The equations relevant to the rectilinear case cos $\theta = f(\gamma_L)$ contain parameter Φ_0, which is a constant by the definition.

7) If the test liquids utilized to determine the relationship cos $\theta = f(\gamma_L)$ are selected from groups exhibiting known different dispersivities (*e.g.* Group I: $d = 0.95$; group II: $d = 0.8$, etc), thus values of the critical surface tension for wetting $[\gamma_C]$ and the characteristic slope $[b_0]$ are different for each dispersivity group. If the test liquids with randomized (unknown) dispersive/polar structure are used (provided it is a sufficiently large population of the test liquid), thus values of $[\gamma_C]$ and $[b]$ obtained are the same as those achieved for non-polar test liquids (*e.g.* *n*-alkanes).

8) Variability of the interaction parameter Φ within the rectilinearly approximated, wettability characteristic of the solid is expressed by equation (23) and further, by equations (24) and (26).

For any other approximation than rectilinear, equation (5) applies for determination of the variability pattern of Φ.

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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) component of total 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	particular case of the interaction factor Φ for those conditions where $\cos\theta = 1.0$
d, p	dispersion and polar fraction of surface energy
δ	solubility parameter
θ	equilibrium contact angle