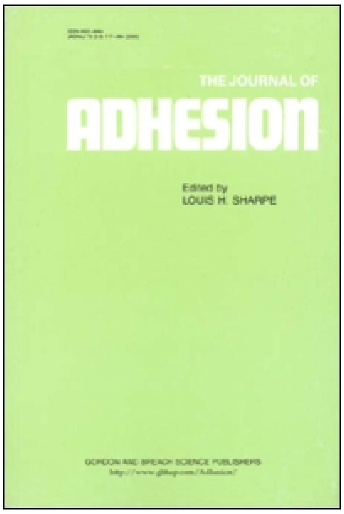

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Surface Energy, Wetting and Adhesion

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Surface Energy, Wetting and Adhesion

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Surface energies of solids can be estimated using contact angles of liquids of known surface tension and susceptibilities for polar or acid-base interactions. Interfacial tensions and work of adhesion can be calculated using these estimated energies. There are three circumstances in which performance or bond strengths are related directly to surface energies: when separation occurs interfacially, when interfaces are not completely wetted, and when third phases are present at the interface.

INTRODUCTION

Workers in the field of adhesion continue to hold conflicting views of the relative importance, if any, of surface or interfacial energies to bond strength.

The purpose of this paper is to show that adhesive performance is often determined by surface energies, to point out explicitly the assumptions involved in estimating surface energies using contact angles, and to suggest that polar interactions are not negligible.

WORK OF ADHESION AND SURFACE ENERGY

The work of adhesion, W_a, is the negative value of the interaction potential at equilibrium separation of adhering phases. This can be expressed as:

$$W_a = A_{\text{eff}}/12\pi r_{012}^2 \tag{1}$$

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where A_{eff} is the effective interaction constant and r_{012} is the effective separation of phases.

A_{eff} is determined by the nature of the materials and, in view of recent improvement in understanding, is best considered as the sum of long range Van der Waals and short range interactions. When the intervening space or phase is other than a vacuum Van der Waals interactions must be described by the continuum theory (Lifshitz,[1] Dzyaloshinskii *et al.*[2], Israelachvili and Tabor,[3] and Parsegian and Ninham.[4] This theory and also pair-wise summation methods for dispersion forces have been extended into the short-range distance regime showing good agreement between interaction potentials and the change in surface energies.

There is no generally useful theory, however, for short-range forces which depend strongly on the nature and distribution of atoms or sub-molecular groups at the interface.

When interactions consist entirely of Van der Waals forces, A_{eff} can be calculated with good accuracy. Values for r_{012}, however, are not readily calculated and enter into W_a as estimates or adjustable parameters.

The work of adhesion is directly related to surface free energies (γ_i) of adhering materials:

$$W_a = 2\phi(\gamma_1\gamma_2)^{1/2} \quad (2)$$

Assuming that Good's[5] interaction parameter ϕ makes Eq. (2) exact, its utility depends on how well ϕ and γ_i can be measured or estimated.

It is convenient to separate ϕ into two factors: ϕ_a accounting for discrepancies between estimated and actual values of A_{eff}, and ϕ_r accounting for deviation of r_{012} from estimates based on the geometric mean of r_{011} and r_{022}.

Gardon[6] showed that induction forces could be neglected and Van der Waals force contributions to the interaction potential are essentially the sum of dispersion and dipolar interactions:

$$A_{12} = A^d_{12} + A^p_{12} \quad (3)$$

and similarly, for surface free energy:

$$\gamma_i = \gamma^d_i + \gamma^p_i. \quad (4)$$

Define the fractional contributions of dispersion and polar forces as:

$$d = \gamma^d_i/\gamma_i \quad \text{and} \quad p = \gamma^p_i/\gamma_i. \quad (5)$$

Neglecting induction forces $d+p = 1$, and:

$$\phi_a = (d_1 d_2)^{1/2} + (p_1 p_2)^{1/2}. \quad (6)$$

Let phase 1 be a solid exhibiting surface free energy γ_{so} when in equilibrium with its own vapor only, and phase 2 a liquid with surface free energy γ_{lv} when in equilibrium with its own vapor.

The interfacial tension between a solid and liquid is:

$$\gamma_{sl} = \gamma_{so} + \gamma_{lv} - W_a \tag{7}$$

The relationship among the three interfacial energies is also defined thermodynamically by:

$$\gamma_{so} - \pi_e - \gamma_{sl} = \gamma_{lv} \cos\theta \tag{8}$$

where π_e is the spreading pressure of the liquid's vapor on the solid surface and θ is the equilibrium contact angle.

Replacing ϕ_a in Eq. (2) by its value from Eq. (6) gives:

$$W_a = 2\phi_r[(\gamma^d_{so}\gamma^d_{lv})^{1/2} + (\gamma^p_{so}\gamma^p_{lv})^{1/2}]. \tag{9}$$

It has been shown that π_e is usually negligible when $\theta \geqslant \sim 5°$. Neglecting π_e and introducing $\gamma_{lv}\cos\theta$ for $\gamma_{so} - \gamma_{sl}$ into Eq. (7), using the right hand side of Eq. (9) for W_a and rearranging gives:

$$1 + \cos\theta = (2\phi_r/\gamma_{lv})[(\gamma^d_{so}\gamma^d_{lv})^{1/2} + (\gamma^p_{so}\gamma^p_{lv})^{1/2}]. \tag{10}$$

If low molecular weight liquids exhibit nearly identical values for ϕ_r with a given solid, and ϕ_r is close to unity or can be estimated, Eq. (10) can be used [7] to evaluate surface energies of solids by measuring contact angles of two liquids differing appreciably in their fractional polarities. Introducing values for θ in Eq. (10) along with γ^d_{lv} and γ^p_{lv} of the liquids yields two equations which can be solved simultaneously for γ^d_{so} and γ^p_{so}.

When γ^d_i and γ^p_i are known for two materials, since γ, d and p are obtained directly from γ^d_i and γ^p_i, values for ϕ_a can be calculated using Eq. (6) and W_a using Eq. (2). This has been used with good results (Kaelble,[8] Kaelble *et al.*[9, 10].

This approach is obviously questionable when short-range forces may contribute significantly. Fowkes[11] proposes that W_a is better evaluated using:

$$W_a = 2(\gamma^d_1\gamma^d_2)^{1/2} + nf(C_aC_b + E_aE_b) + W^p_a \tag{11}$$

TABLE I

Comparison of GGOW and Fowkes methods for calculating W_a.

Polymer	Method	γ_{so}	γ^d_{so}	γ^p_{so}	W_a	W^d_a
Data for TCP-Phenol (28/72) $\gamma_{lv} = 39.9$ $d = 0.88$ $p = 0.12$						
EVA	Fowkes		36.9		78.7	72.2
	GGOW	42.0	36.1	5.9	81.8	71.2
Polyimide	Fowkes		45.2		79.4	79.9
	GGOW	52.3	43.4	8.9	91.4	77.9
Data for water $\gamma_{lv} = 72.8$ $d = 0.3$ $p = 0·7$						
Polyimide	Fowkes		45.2		101.4†	63.1
	GGOW	52.3	43.4	8.9	104.1	61.5

† Average of 99.7 for 0.1N HCl and 103.1 for 0.1N NaOH.

where $(C_aC_b+E_aE_b) = -\Delta H$, the enthalpy of acid-base interactions as given by Drago[12]; n is the moles of a–b interactions per unit area, and f converts enthalpy to free energy.

Fowkes considers polar contributions to W_a negligible. This interesting concept treats short-range forces solely on the basis of Lewis acid-base interactions and to date is supported by only limited data.

Since use of disperson and polar contributions has been and still seems useful (Gledhill *et al.*[13], Schultz *et al.*[14]), it was of interest to compare directly what might be called the Good, Gardon, Owens and Wendt (GGOW) method with that of Fowkes. Data obtained for two polymers similar to those used by Fowkes[15] permitted the comparisons of Table 1.

Agreement is good for ethylene–vinyl acetate copolymers with tricresyl phosphate–phenol. The basic polyimide showed significant polar interaction with both TCP–phenol and water calculated using GGOW. Surprisingly, despite the fact that for phenol $C_a = 0.44$, $E_a = 4.33$ and for water $C_a = 0.33$, $E_a = 2.45$, Fowkes' data shows no donor-acceptor interaction with phenol but appreciable with water—especially the basic 0.1 N NaOH. These data suggest that polar interactions are not negligible.

Choosing between the GGOW and Fowkes' approaches is currently difficult. Polar contributions are undoubtedly included in Drago's E_a and E_b values, and on the other hand donor-acceptor interactions are probably included in polar interactions calculated using the GGOW method.

If dipolar and acid-base interactions are both included explicitly, ϕ can be defined as:

$$\phi = \phi_r[(d_1d_2)^{1/2}+(p_1p_2)^{1/2}+\Delta] \tag{12}$$

and, further, if Δ is defined as:

$$\Delta = -nf\Delta H/\phi_r(\gamma_1\gamma_2)^{1/2}, \tag{13}$$

the Good–Gardon and Fowkes concepts are combined in a form consistent with Eq. (2) but requiring modified ways of evaluating ΔH and p_i.

As indicated earlier, the ability to estimate ϕ is limited also by difficulty in assigning realistic values for ϕ . The atomic density at the interface is probably the most important single factor determining interfacial energies. This is seen, for example, in the Parachor which relates surface energy to the 4th power of density, and Hoernshemeyer[16] showed that the low surface energy of fluoropolymers is due to low atomic density rather than the nature of the intermolecular interactions.

SURFACE ENERGY AND ADHESIVE PERFORMANCE

Despite theoretical uncertainties and experimental difficulties, let us assume that W_a can be estimated with reasonable accuracy. How then do these values relate to adhesive performance or bond strength?

Intuitively best performance is expected for completely wetted systems exhibiting maximum interfacial contact between materials interacting to give high values of W_a.

Wetting

It has been stated often[17,18] that complete wetting requires that liquid adhesives exhibit zero contact angles with the solid adherends. The curves of Figure 1 show the relationship between W_a and γ_{lv} for various values of the interaction parameter ϕ. These are plotted in a convenient dimensionless form as ratios with respect to the solid surface free energy. If zero contact angles were required, only those adhesives with surface energies giving values of W_a/γ_{so} lying above the dashed line would wet the adherend completely, and consequently reliable performance would require limiting the choice of adhesives to those satisfying this criterion. It is evident that this

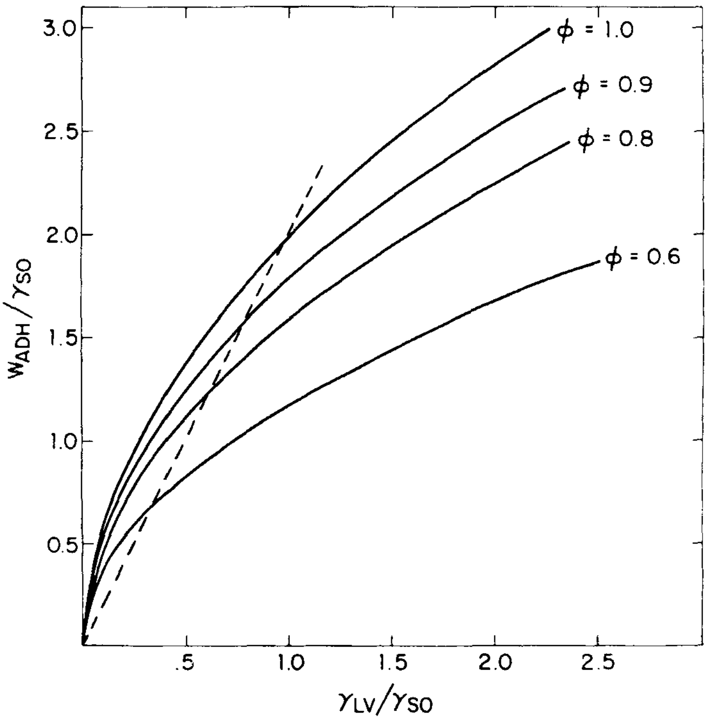


FIGURE 1 W_a/γ_{so} *vs.* γ_{lv}/γ_{so} for various ϕ.

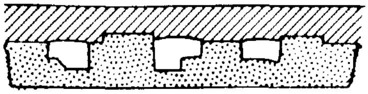
would be very restrictive and many adhesives not meeting the zero contact criterion interact more strongly with the solid giving higher W_a.

Let us test the validity of this criterion by calculating the change in free energy associated with wetting. The appropriate model to examine is that of Figure 2 in which an adhesive layer has not completely wetted the solid (2a). The change in free energy on wetting (2b) is given by:

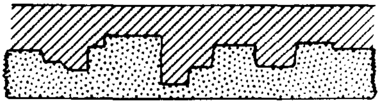
$$\Delta F = -\gamma_{lv}(1+(\Omega/A)\cos\theta) \qquad (14)$$

where Ω is the actual surface area and A is the projected surface area. This shows that the free energy decreases on wetting in all cases except the rare possibility that $\cos\theta$ is negative and the absolute value of $(\Omega/A)\cos > 1$.

Most practical adhesives exhibit acute contact angles with their adherends and would be completely wetted at equilibrium. The zero contact angle criterion is not valid, and choice of potentially useful adhesives need not be arbitrarily restricted.



a- SUBSTRATE INCOMPLETELY WETTED



b-SUBSTRATE COMPLETELY WETTED

WETTING OF A SOLID SUBSTRATE BY A FLUID ADHESIVE

FIGURE 2 Schematic representation of wetting. (Reprinted from *Treatise on Adhesion and Adhesives*, vol. 1, p. 128, courtesy of *Marcel Dekker*.)

Locus of failure

If Bikerman's[19] arguments were correct, that is, properly made (equilibrium) bonds could not fail at the interface, and if completely wetted interfaces were obtained invariably, there would be no relationships between surface energies and bond strength.

It is easy to show[20, 21], however, that interfacial separation is consistent with thermodynamic criteria. Interfacial separation may occur (is thermodynamically favored) when $\phi(\gamma_{so}/\gamma_{lv})^{1/2}$ and $\phi(\gamma_{lv}/\gamma_{so})^{1/2}$ are both less than unity (Figure 3).

Do these criteria have practical significance? Bonds cannot be tested reversibly and performance is undoubtedly limited by a critical stress at some point in the bonded structure. Critical stresses in bulk phases are related directly to surface free energies:

$$\sigma_c \sim 2\gamma_1 r_{011}^{-1} \tag{15}$$

and critical interfacial stresses are related to W_a:

$$\sigma_c \sim 2\phi(\gamma_1\gamma_2)^{1/2} r_{012}^{-1}. \tag{16}$$

Note that critical interfacial stresses are a function of r_{012}^{-2} since ϕ_r also is proportional to r_{012}^{-1}. If the effective interfacial separations were 20% larger than values estimated using $r_{012} = (r_{011}r_{022})^{1/2}$ critical interfacial stresses would be diminished by ~35% and the likelihood of interfacial separation greatly increased.

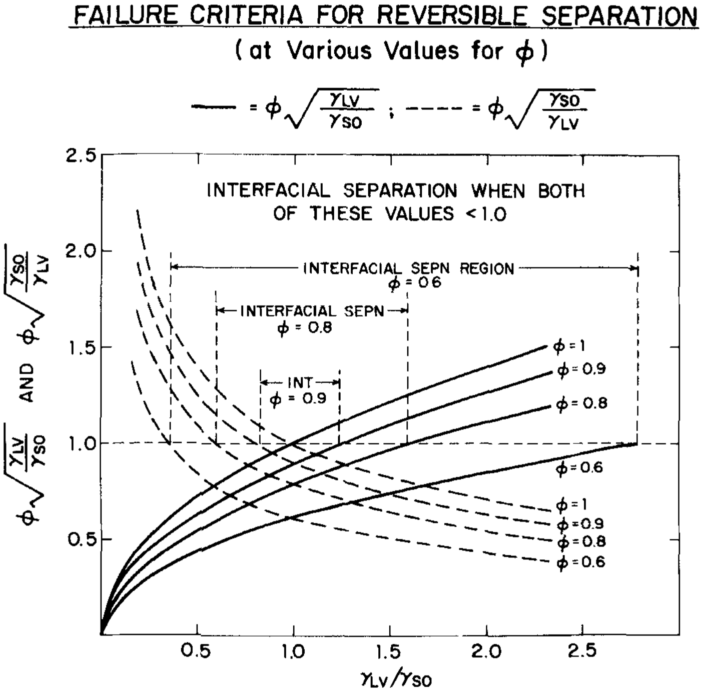


FIGURE 3 Thermodynamic failure locus criteria.

The actual failure locus, of course, depends on a multitude of factors whose interactions determine the distribution of stress. Among these are sample geometry, direction and rate of loading, temperature-rate responses of all visco-elastic phases, and the size, shape and distribution of flaws or included phases.

The thermodynamic criteria for interfacial separation are often met and the mode of loading is frequently such that failures do occur at interfaces. Under these circumstances the interfacial critical stress is limiting and performance is directly related to surface energies.

Interfaces not at equilibrium

Despite the conclusion that most practical adhesive systems are completely wetted at equilibrium, practical bonds are often not at equilibrium. Sometimes arbitrarily selected bonding conditions are simply not suitable. Higher temperatures and/or longer times are required. Often restrictions are imposed by production requirements or the thermal stability of materials. A large fraction of practical problems would be solved if bonding conditions could be changed significantly. The relatively long times required for wetting of adherends by constrained viscous adhesives is illustrated by the bonding of poly(*n*-butyl methacrylate) to steel (Figure 4). The poor bond strength of the sample bonded at 100°C is best explained in terms of stress concentration at unwetted areas of the interface.

When equilibrium is not attained and bonding conditions are limiting, performance is directly related to surface energies. Rates of wetting are determined by the spreading pressure of the adhesive on the solid and the adhesive viscosity at bonding temperatures. The maximum spreading pressure π_{ls} is given by:

$$\pi_{ls} = \gamma_{so} - \gamma_{sl}. \tag{17}$$

When two thermoplastic materials are bonded, the time-temperature requirements are set by the larger of the two values π_{12}/η_1 or π_{21}/η_2 which determines the maximum rate of approach to equilibrium, and consequently the size and distribution of interfacial voids when wetting is incomplete.

Solution applied adhesives are often not at equilibrium. When free energy is diminished through selective adsorption of solvent which remains at the interface until evaporation has concentrated the polymer solution to the point where its viscosity is excessive—or worse the solution is below the glass transition temperature, the immobilized polymer solution cannot rewet the substrate after the adsorbed layer of solvent evaporates. Such interfaces can be far from equilibrium and show poor performance unless the structure is heated well above T_g for an extended time. Here, too, performance is determined in part by interfacial energies.

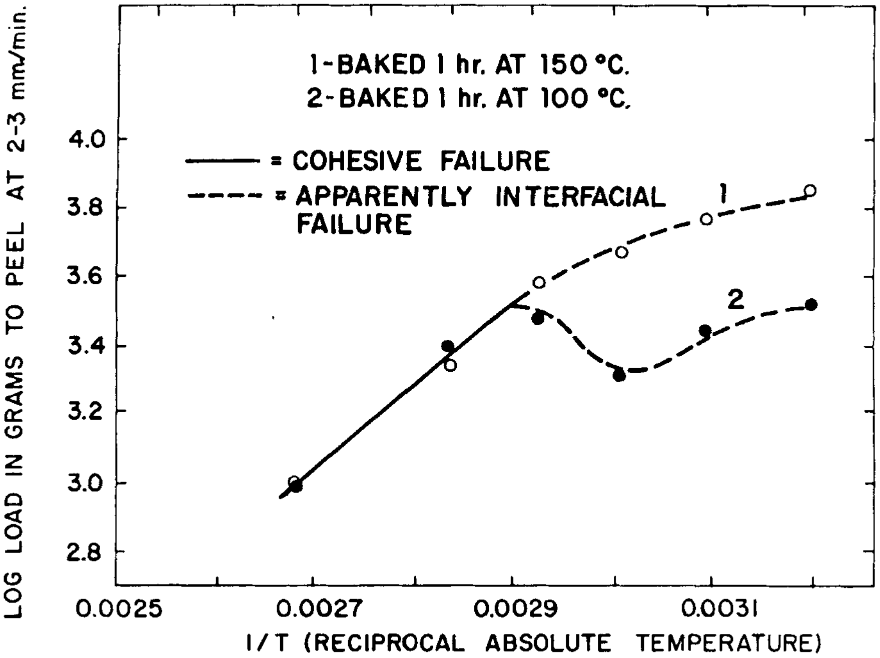


FIGURE 4 Influence of bonding on performance. [Reprinted from *J. Polym. Sci. A* 1, 2247 (1963), courtesy John Wiley and Sons.]

Multi-phase systems

Another circumstance in which performance is directly related to interfacial energies arises when additional liquid phases are present. At equilibrium wetting will be complete but interfaces may be heterogeneous.

When insoluble fluid contaminants exhibit interfacial tensions with other phases such that

$$(\gamma_{cs}-\gamma_{ls})/\gamma_{cl} < 1 \tag{18}$$

(where c = contaminant, l = liquid and s = solid), any contaminant reaching the interface will remain there exhibiting finite contact angles with the solid:

$$\theta = 180 - \cos^{-1}[(\gamma_{cs}-\gamma_{ls})/\gamma_{cl}]. \tag{19}$$

Such trapped droplets act as flaws or cracks causing stress concentration at their boundaries related to droplet size and contact angles.

If $(\gamma_{cs}-\gamma_{ls})/\gamma_{cl}$ should reach (-1), the contaminating liquid would collect as a stable separate interphase and bond strength would be set by the thickness and viscosity of the layer if it remained fluid at use temperature. If such layers solidify on cooling, they may influence performance by changing distribution of stress, or by fracturing at a low applied load if the layer's critical stress is low. The existence of these limiting conditions, however, is established by the relative interfacial energies.

CONCLUSIONS

Performance is often determined directly or indirectly by interfacial energies. Useful estimates of surface energies of solids can be obtained experimentally but more work is needed to improve their quality. Work aimed at accomplishing this may be most fruitful if attention is focused on measuring short range forces. Characterising surfaces by their interactions with a broader spectrum of test liquids should allow weighing effective dipolar and donor-acceptor contributions.

References

1. E. M. Lifshitz, *J. Exp. Theor. Phys. USSR* **29,** 94 (1955).
2. I. E. Dzyaloshinskii, E. M. Lifshitz and L. P. Pitaevskii, *Adv. Phys.* **10,** 165 (1961).
3. J. N. Israelachvili and D. Tabor, *Prog. in Surf. and Mebr. Sci.* **7,** 1 (1973).
4. V. A. Parseghian and B. W. Ninham, *Biophys. J.* **10,** 664 (1970).
5. L. A. Girifalco and R. J. Good, *J. Phys. Chem.* **61,** 904 (1957).
6. J. L. Gardon, *Enc. of Polym. Sci. & Tech.* Mark, Gaylord, Bikales, eds. Interscience, W.Y. (1965).
7. D. K. Owens and R. C. Wendt, *J. App. Polym. Sci.* **13,** 1741 (1969).
8. D. H. Kaelble, *J. Adhesion* **2,** 66 (1970).
9. D. H. Kaelble, J. P. Dynes and E. H. Cirlin, *J. Adhesion* **6,** 23 (1974).
10. D. H. Kaelble, P. J. Dynes and L. Maus, *J. Adhesion* **8,** 121 (1976).
11. F. M. Fowkes, *J. Adhesion* **4,** 155 (1972).
12. R. S. Drago, G. C. Vogel and T. E. Needham, *JACS* **93,** 6014 (1971).
13. R. A. Gledhill, A. J. Kinloch and S. J. Shaw, *J. Adhesion* **9,** 81 (1977).
14. J. Schultz, K. Tsutsumi and J-B., Donnet, *J. Coll. & Interface Sci.* **59,** 277 (1977).
15. F. M. Fowkes, *Coat. & Plas. Preprints* **37,** 605 (1977), (173rd ACS Mtg.).
16. D. Hoernshemeyer, *J. Phys. Chem.* **70,** 2628 (1966).
17. W. A. Zisman, *Ind. Eng. Chem.* **55,** 19 (1963).
18. L. H. Sharpe and H. Schonhorn, *Adv. in Chem.* **43,** 189 (1964).
19. J. J. Bikerman, *Science of Adhesive Joints* (Acad. Press, N.Y. 1961).
20. J. R. Huntsberger, *J. Polym. Sci. A-1* **46,** 1339 (1963).
21. J. R. Huntsberger, *J. Adhesion* **7,** 289 (1976).