General Concepts of Adhesion

A. T. DiBENEDETTO, Department of Chemical Engineering,
Washington University, St. Louis

This paper presents a general review of concepts explaining the nature
of adhesion at an interface between 2 condensed phases. The relation-
ship between the surface energy of a solid and its theoretical tensile
strength is explored. A molecular concept of surface energy is pre-
sented in which the relationships among intermolecular forces, sur-
face tension, and work are discussed. A general description of inter-
faces and triple junctions and their relationship to contact angle
wettability and adhesive bonding are then presented. Two examples
of the effects of adhesion on the mechanical properties of composite
materials are used to illustrate the importance of adhesion in multi-
phase systems.

•TO UNDERSTAND material behavior, one must examine structures at various levels.
At a microstructural level, for example, the presence of voids, notches, grain bound-
aries, and other gross imperfections have effects on a number of important physical
properties such as tensile strength, fracture toughness, and corrosion resistance.
Many other properties are not dependent primarily on macroscopic flaws but rather
depend on molecular structure and morphology. To understand properties such as yield
strength, ductility, and diffusivity, one must examine the material at a crystallographic
level (with tools such as X-ray diffraction and electron microscopy) where unit cell
structures, dislocations, and other molecular defects can be observed. Still other prop-
erties such as electrical and thermal conductivity, magnetic susceptibility, and dielec-
tric strength depend on the behavior of electrons, photons, phonons, and other subatomic
particles.

This paper deals with properties that are, to one degree or another, dependent on
the structural details of surfaces. As we will see, however, there are natural rela-
tionships between the so-called "surface" properties and the "bulk" properties of ma-
terials. If one considers physical properties from a molecular point of view, this is
not at all surprising because the molecular properties of a surface must obviously be
related to the molecules that make up the whole material.

As an illustration of this last point, let us consider the tensile strength of a brittle,
elastic solid, where the theoretical limit of strength depends on the energy required to
produce a fractured surface; i.e., it depends on the surface tension of the material.

Consider a unit thickness sheet in plane stress with a small crack, as shown in Fig-
ure 1. According to Griffith ($\underline{9}$), the tensile strength of the sheet with a small micro-
crack is determined by the conditions that permit the crack to propagate through the
cross section. The Griffith criterion for crack instability is that the crack will become
unstable and the material will fail catastrophically when the free energy, G, of the ma-
terial decreases with the crack size, i.e., $dG/d\ell \leq 0$. As the crack grows, strain
energy, G_e, is released, $G_e = (\pi \ell^2 \sigma^2)/E$, and surface energy, G_s, is required to form
the new surfaces, $G_s = 4\ell\gamma$, where σ is the external stress, E is the Young's modulus,
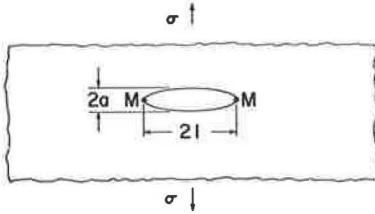
Figure 1. Elliptical microcrack causing maximum stress at M.

and γ is the surface energy per unit area. Hence, the Griffith criterion for fracture in plane stress is

$$\frac{\partial}{\partial \ell} (G_e + G_s) = -\frac{2\pi\ell\sigma^2}{E} + 4\gamma \leq 0 \qquad (1)$$

The theoretical breaking stress σ_b is, thus,

$$\sigma_b = \left(\frac{2E\gamma}{\pi\ell}\right)^{1/2} \qquad (2)$$

Equation 2 shows that the tensile strength of the sheet is determined by the surface energy of the solid, γ, the stiffness (or Young's modulus), E, and the size of the microflaw at which the break occurs.

In composite materials the importance of surfaces is magnified because of the fact that the behavior of composites also depends on the nature of the interfaces between filler and matrix. Tensile strength, fracture toughness, chemical resistance, and elastic moduli, for example, all depend on the degree of adhesion between phases. The degree of adhesion is, in turn, controlled by a number of physical and chemical factors. Among the former are surface area, surface roughness, degree of wetting, difference in moduli and Poisson's ratios, and differences in thermal expansion coefficients. Among the latter are differences in cohesive energies, polarities, surface energies, relative solubilities and susceptibilities to heat, oxidation, and hydrolysis. The strength of an interface will depend in a very complicated fashion on a combination of these factors.

In general, one may say that there is some theoretical maximum bond strength that can be developed under ideal conditions of perfect molecular contact, as shown schematically in Figure 2. The primary loss of strength is due to failure of the molecules
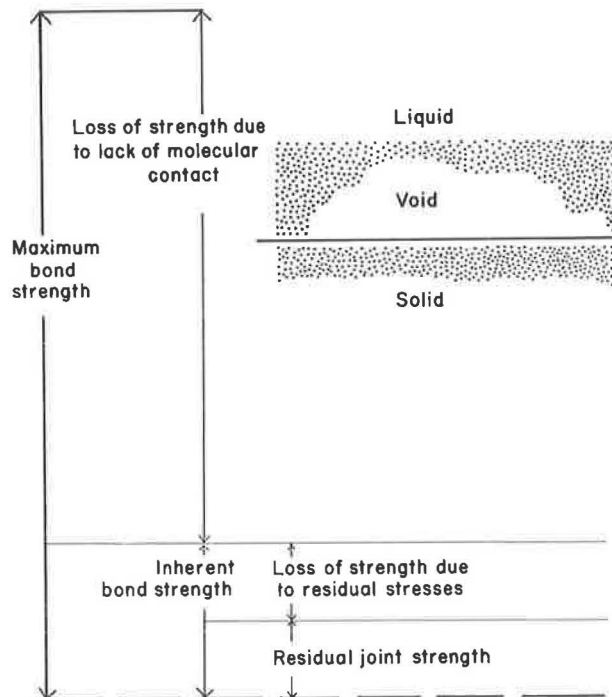

Figure 2. Factors affecting adhesive bond strength.

to approach their proper bonding distances of a few angstrom units. One may visualize this as a microvoid at the interface that is then capable of concentrating stress and causing premature failure. A second major loss in bond strength comes about from the development of residual stresses at the interface. Normally, a matrix or adhesive is applied in the fluid state and then solidified by cooling or chemical reaction or both. This invariably causes a differential shrinkage at phase boundaries that leads to undesirable stress concentrations. The net residual joint strength may be only a very small fraction (i.e., less than 1 percent) of the theoretical limit.

A MOLECULAR CONCEPT OF SURFACE ENERGY

When an atom or a molecule is in the bulk of a solid material, it is surrounded by a fixed number of nearest neighbors. In a crystalline solid with a closely packed cubic lattice, for example, each atom is surrounded by 12 nearest neighbors. Each molecule is thus constrained to vibrate in a "cage" of nearest neighbors. The thermal, or Brownian, motion of the atom will tend to keep it moving within the cage in a random fashion, while the intermolecular forces will tend to keep the atom constrained to its average lattice position at the center of the cage. This latter energy, called the potential energy of interaction, is approximately equal to the sum of the bond energies with nearest neighbors. Thus, the total potential energy of a given atom in a closely packed crystal lattice is roughly 12 times the bond strength between a single pair of atoms.

An atom in the free surface of a material has fewer nearest neighbors because it has essentially no near neighbors in the vapor phase. The missing interatomic bonds cause such an atom to have a smaller potential energy (i.e., less negative) than atoms within the bulk of the material. This "extra" energy relative to the bulk state is the surface energy of the material.

Surface energy is related to the work required to increase the area of a surface. Consider a unit area of soap film on a movable wire frame as shown in Figure 3. In order to hold the movable wire in place, a force of $2\gamma_{SV}$ dynes/cm of wire must be applied. In order to move the wire an infinitesimal amount, dx, to the left, an energy of $(2\gamma_{SV})(1)(dx)$ ergs must be expended. The total interfacial area increases in the process by an amount of $(2)(1)(dx)$ cm^2. The energy expended per unit area of new surface formed is thus $2\gamma_{SV}dx/2\,dx = \gamma_{SV}$ ergs/cm$^2 = \gamma_{SV}$ dynes/cm. Because more molecules are now at the surfaces, this process is equivalent to bringing some of the molecules from the bulk of the solid into the free surfaces, thus breaking a certain number of chemical bonds.

In this latter example, the surface energy has been equated to the mechanical work required to form a unit area of surface at constant temperature and pressure. This is numerically equivalent to the "Gibbs free energy" G_{SV} of the system

$$\gamma_{SV} = \Delta G_{SV} = \Delta H_{SV} - T\Delta S_{SV} = \Delta H_{SV} + T\left(\frac{\partial \gamma_{SV}}{\partial T}\right)_r \tag{3}$$

For an isotropic fluid, there is a numerical equivalence between surface energy and surface tension. Because the most stable state of a material is one of minimum free energy (at constant temperature and pressure), isotropic fluids will tend toward a shape of minimum area per unit volume (i.e., a spherical shape). For anisotropic solids, the constraint of specific lattice geometry causes γ_{SV} to be orientation dependent because the surface energy will depend on the planar orientation of the crystal surface. This means that a spherical shape is not necessarily the most stable for a mass of anisotropic solids.
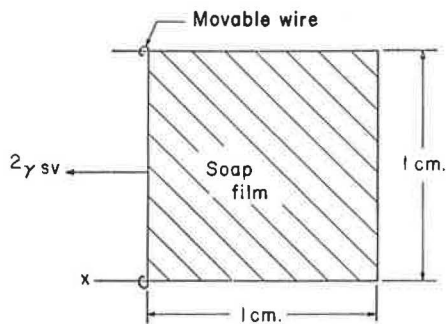

Figure 3. Illustration of surface tension.

INTERFACES

In the preceding section, the properties of free surfaces were discussed. These can also be considered as solid-vapor or liquid-vapor interfaces. Adhesive layers, inclusions in solids, grain boundaries in polycrystalline materials, or other similar situations are liquid-liquid, liquid-solid, and solid-solid interfaces. The properties of such interfaces can normally be described as triple junctions. A few illustrations are shown in Figure 4. Type a represents an inclusion of B in the grain boundary between 2 regions of material A. In the absence of a grain boundary in A, this would represent an inclusion B in a homogeneous matrix of A. Because surface energy and surface tension are synonymous in isotropic materials, the equilibrium state for the junction can be described by making a force balance about the point of intersection for the 3 regions.

$$\gamma_{AA} = 2\gamma_{AB} \cos\frac{\theta}{2} \qquad (4)$$

where γ_{AA} is the tension in the A-A interface, and γ_{AB} is the tension in the A-B interface. For the case where A is homogeneous with no boundaries, $\gamma_{AA} = 0$ and $\theta = 180$ deg. Thus, if B is an isotropic fluid capable of attaining an "equilibrium" shape, it would take on a spherical shape in a homogeneous fluid matrix.

Figure 4b shows a triple junction, or meniscus, for liquid B in a capillary tube A. The case with a small contact angle, θ, represents good wetting of the capillary wall, while the case with a large contact angle represents poor wetting of the capillary wall.

Figure 4c shows a fluid drop, L, on a flat solid surface, S. Region V is either vapor or another liquid. The small contact angle represents good wetting, while the large contact angle represents poor wetting. At equilibrium,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

or

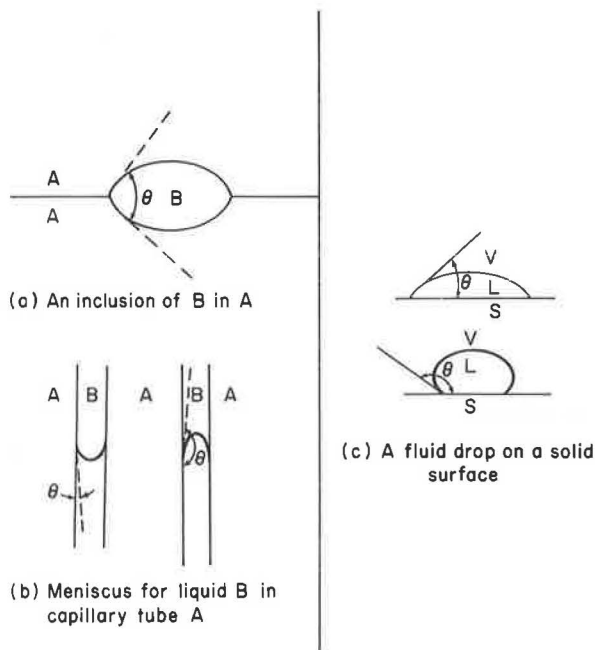$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad (5)$$

Equation 5 fixes the limits for absolutely no wetting and also for spontaneous wetting. If $\gamma_{SV} \geq \gamma_{LV} + \gamma_{SL}$, θ must be zero, and spontaneous wetting can occur. If $\gamma_{SL} \geq \gamma_{SV} + \gamma_{LV}$, θ must be 180 deg, which means that L cannot wet S to any extent.

Wetting is favored when the substrate is free of contamination (γ_{SV} is maximum), when the adhesive has an affinity for the substrate (γ_{SL} is low) resulting in a low interfacial tension, or when the surface tension of the adhesive is low (γ_{LV} is low). Surface roughness modifies the wetting characteristics because the fluid must move up and over asperities. For spreading on the rising side of an asperity, wetting is probably hindered, whereas on the falling side it is probably aided. Most important is the possibility of air being trapped under a spreading fluid, thereby changing the equilibrium contact angle. There is no accurate

(a) An inclusion of B in A

(b) Meniscus for liquid B in capillary tube A

(c) A fluid drop on a solid surface

Figure 4. Triple junctions.

way of predicting the net effects of roughness, but Wenzel has suggested that the equilibrium contact angle on a rough surface is given as

$$\cos \theta = r \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{6}$$

where r is the ratio of the true surface area to the mean plane surface area. Equation 6 suggests that, if θ is less than 90 deg, wettability is enhanced by roughness and, if θ is greater than 90 deg, wettability is hindered by roughness.

When a liquid spreads over a porous surface, it must wet the capillary passages in order to displace the air in the pores. In a cylindrical open pore of diameter d, the depth of penetration is equal to

$$\sqrt{\frac{\cos \theta \; \gamma_{LV} \; dt}{4\eta}}$$

where t is time and η is viscosity. Thus, as $\theta \to 90$, $r \to 0$, and $\eta \to \infty$, it takes a very long time to fill a pore. If the pore is closed at one end, the gas is merely compressed, trapping a void at the interface. Pore shape also affects the wettability. Filling a diverging cone, for example, requires an increasing surface energy as one moves to a wider section; thus, filling a diverging pore is not thermodynamically favored.

ADHESIVE BONDING ACROSS INTERFACES

There are several ways that 2 materials can interact across a phase boundary. The 2 most important types of bonding action can be classified as mechanical interaction and chemical interaction.

A mechanical interaction can be a geometrical effect where there is an interlocking of the 2 components across an interface. This type of action can be important when one of the substances is porous and the other can penetrate the pores and solidify. Adhesives for paper and wood may at least partially depend on this kind of bonding. A second type of mechanical interaction depends on a frictional resistance due to squeezing one component around an inclusion of the other. The shrink fitting of a wheel on a rim is a good analog for this type of action. In a composite material, differential thermal expansion can cause a "shrink fitting" around a rigid inclusion that can result in a significant compressive force on the inclusion and, thus, high "frictional adhesion." It can be shown that the compressive loading on an isolated filament in a glass fiber-epoxy composite can result in a frictional bond of 200 to 1,000 psi. In a heavily loaded composite, in which there are many fiber-fiber interactions, the stress fields around any one filament become extremely difficult to calculate accurately, and it is hard to say what the mechanical adhesion is. It is reasonably well accepted, however, that, if one wishes to have interfaces that are at least as strong as the constituent materials in shear, it is necessary to develop some kind of chemical bonding.

Chemical bonding at an interface is developed by wetting the solid surface with a fluid. Once molecular contact has been attained, the 2 phases can interact through intermolecular forces. The magnitude of the interaction depends on the type of chemical bonds formed.

Chemical bonding can be classified into primary and secondary bonding. Primary bonds, schematically shown in Figure 5, generally have bond energies of the order of 30 to 100 k-cal/g-mole and involve interatomic distances of 1 to 3 Å. This leads to theoretical strengths of the order of 10^6 to 10^7 psi. Primary bonding can be either ionic, covalent, or metallic. An ionic bond is an electrostatic interaction between highly electronegative (e.g., F) and highly electropositive (e.g., Na) atoms. When 2 such elements interact, the electronegative element draws an outer shell electron away from the electropositive element, thereby forming an anion and a cation. These will then coulombically interact to form an electrostatic bond, as shown in Figure 5a. A covalent bond is a true sharing of the electron orbitals of the interacting atoms as shown in Figure 5b. The outer shell electrons of such atoms lose their identity and

form molecular orbitals that bind the nuclei of the interacting atoms. This manifests itself as a high electron density along the internuclear axis. Metallic bonds are similar to covalent bonds in that outer shell electrons are shared by the nuclei of many atoms.

The effects of primary bonding are of importance to composites technology. The mixing of a metal matrix with a metal or oxide reinforcement often results in intermetallic compound formation at interfaces. Such reactions have a marked effect on the composite properties. Likewise, organic matrices can be chemisorbed onto surfaces, resulting in the formation of organic compounds at the interfaces. It is very likely, for example, that the glass-silane coupler-organic matrix interfaces involve some type of condensation reactions that in some cases result in cohesive interfaces, as shown in Figure 6.

Secondary, or Van der Waal's, bonds, shown schematically in Figure 7, generally have bond energies of the order of 0.5 to 10 k-cal/g-mole and involve interatomic distances of 3 to 5 Å. This leads to theoretical strengths of the order of 10^5 to 10^6 psi. These bonds are thus an order of magnitude weaker than primary bonds. Secondary bonding arises from electrostatic and inductive interactions among charges, dipoles, and multipoles in adjacent molecules or from London dispersion interactions (Van der Waal's forces) between molecules.

(a) Ionic bonding
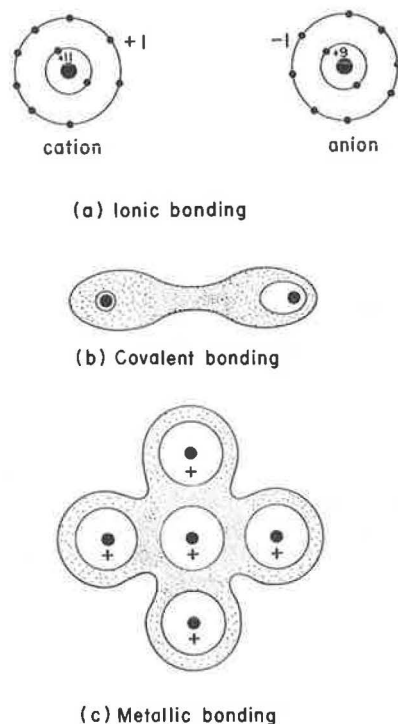

(b) Covalent bonding

(c) Metallic bonding
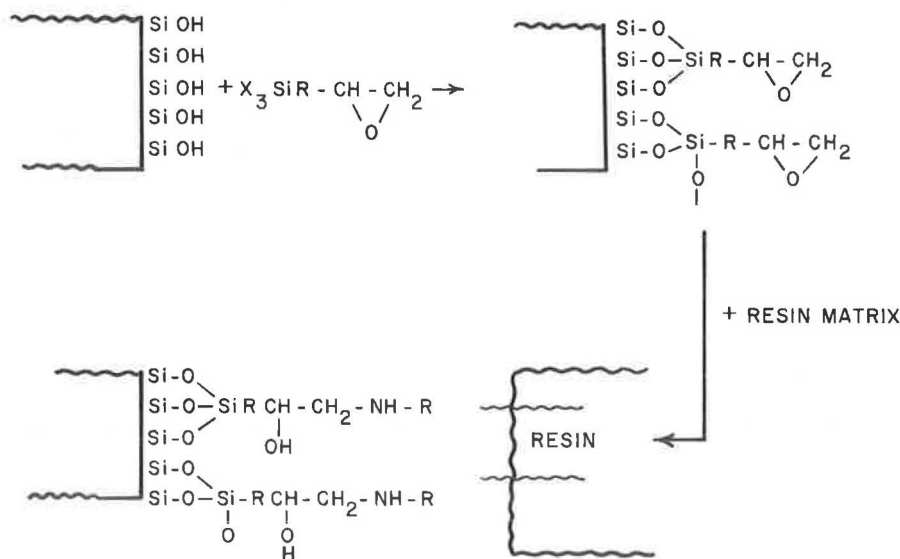
Figure 5.   Types of primary chemical bonding.

Figure 6. Coupling reaction at a glass-silane-epoxy interface.

Qualitatively, when 2 relatively simple molecules, separated by a distance r, interact in this manner, the potential energy of interaction can be represented by a function of the form

$$\phi_{12} = \frac{B}{r^m} - \frac{A}{r^n} = (-\phi_{12}^*)\left[\left(\frac{r^*}{r}\right)^m - 2\left(\frac{r^*}{r}\right)^n\right] \qquad (7)$$

where the first term is a net repulsion and the second term is a net attraction. The quantities A and B are constants, m is constant at about 10 to 30, and n is constant at about 1 to 7, depending on the type of secondary bond. Equation 7 generally looks like the curve shown in Figure 8. The minimum represents the maximum interaction potential, and the distance at the minimum r* represents the most stable distance between particles.

The interaction energy between 2 materials across an interface and the tensile strength of the resulting adhesive bond can be related to intermolecular forces by considering the energy of adsorption of a single molecule A at a distance, d, from a solid surface, as shown in Figure 9.

The interaction between the molecule and an annular ring below the solid is $N_A 2\pi r$ dr dz ϕ_{12} where N_A is the molecular density. One may integrate a potential function such as Eq. 7 over the whole solid to obtain the total energy of interaction of molecule A with the solid. If one then multiplies by the density of the adsorbed material, N_L, the total interaction energy can be estimated. To a zero order of approximation one can show that the maximum energy of adsorption for Van der Waal's bonding is given by

$$(\phi_{adsorption})_{max} \rightarrow 2.5\ N_A\ N_L^{2/3}\ (\phi_{12}^*)(r^*)^3 \qquad (8)$$

If one assumes that r* → 3 to 4 Å, $N_A \rightarrow N_B \rightarrow 4 \times 10^{22}$ particles/cc, and $\phi_{12}^* \rightarrow 0.3$ to 7.0 k-cal/g-mole, the energy of adsorption becomes $(\phi_{adsorption})_{max} \rightarrow 60$ to 2,000 ergs/cm². Experimental data for the energy of adhesion of liquids to high-energy solids show that dispersion bonding results in energies of 100 to 200 ergs/cm².

Thus, we see that even with the very crude molecular model chosen here one may easily predict the proper order or

(a) Interacting dipoles

(b) Dipole can induce moments in other molecules

(c) London dispersion interactions occur even between neutral molecules

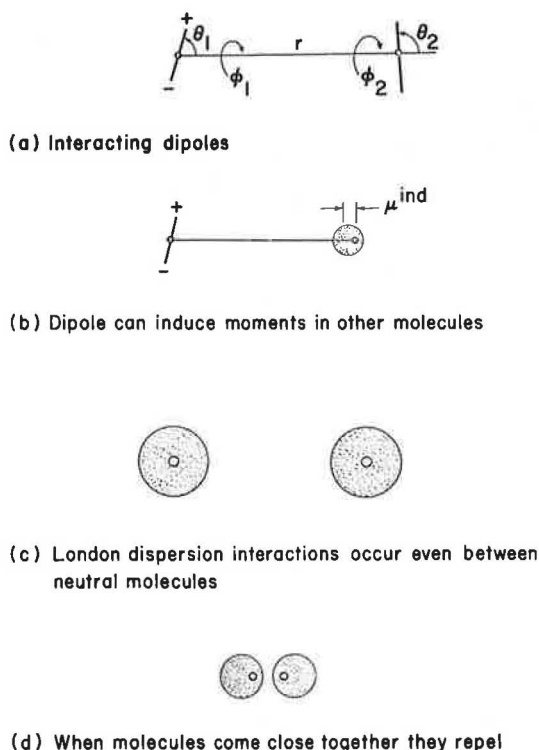(d) When molecules come close together they repel
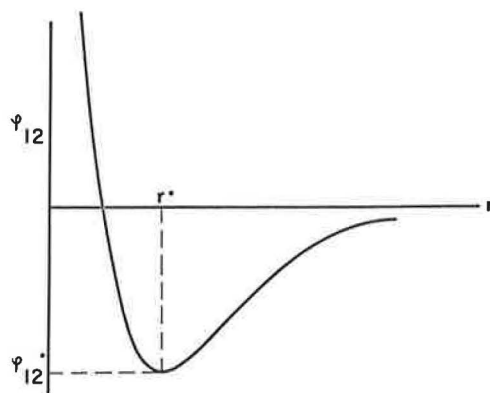
Figure 7. Secondary interactions.

Figure 8. Schematic representation of the net interaction potential between 2 molecules.
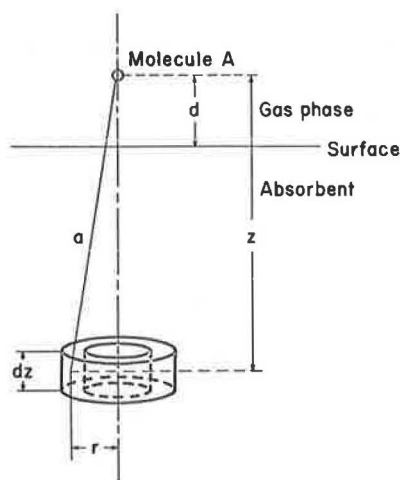
Figure 9.   Interaction of a molecule with a plane surface.

magnitude for the energy of interaction for 2 materials in molecular contact across an interface.

Because the intermolecular force is related to the intermolecular energy by $f = -d\phi/dr$, one may also estimate a theoretical maximum tensile strength for the interface by differentiating Eq. 7 to obtain an equation relating force and interplanar separation and then by evaluating the force at the maximum where $df/dr = 0$. To a zero order of approximation it can be shown that

$$f_{max} \rightarrow 4.5 \ r^{*2} \ N_A \ N_L^{2/3} \ \phi_{12}^* \tag{9}$$

Using the same numbers as before for the molecular constants, one obtains a theoretical maximum tensile strength of $f_{max} \rightarrow$ 60,000 to 1,500,000 psi. Experimental data show that the actual tensile strength of an interfacial bond rarely exceeds 200 to 2,000 psi. Thus, we see that the actual tensile strength of an interfacial bond is only a small fraction of the theoretical bond strength.

Because the energy calculations were reasonable, one can assume that, if wetting and molecular contact are attained at an interface, even relatively weak Van der Waal's forces should give a strong, cohesive interface. The low mechanical strength is thus controlled by factors other than molecular cohesion. In real composite materials, the phases are not always compatible, and wetting and molecular contact are not necessarily attained. The low mechanical strength of an interface is most certainly caused by microscopic and submicroscopic defects. Probable causes of such defects will include imperfect wetting, shrinkage on solidification, thermal stresses, dirty surfaces, and cracks and voids in the interfacial layer. One of the challenges of composites technology is to overcome these defects through improved fabrication techniques.

Because of a lack of knowledge of intermolecular forces combined with an uncertainty of the true nature of any given interface, one cannot readily predict the properties of an interface a priori. A practical method of analysis can be developed, however, by combining the concept of intermolecular forces with a knowledge of the thermodynamic properties of surfaces.

The total intermolecular potential energy of interaction between an adhesive and an adherent is merely a measure of the work of adhesion between the 2 bodies and is, therefore, related to the surface tension at the interface. Figure 10 shows the relationship between the surface free energies and the work of adhesion.

$$-\phi_{ads} = W_A^\circ = \Delta G_{T,p} = \gamma_A + \gamma_B - \gamma_{AB} \tag{10}$$

In this case the work of adhesion is related to the surface free energies of the 2 solids in a vacuum. Likewise, the specific cohesion of a solid can be represented by

$$W_C^\circ = \Delta G_{T,p} = 2\gamma_A \tag{11}$$

This equation, schematically shown in Figure 10, shows that the work required to break a solid along a specific crystallographic plane is equal to the free energy required to form the 2 free surfaces in a vacuum. When solid-solid interfaces are broken in the presence of air, the free energies of the surfaces in the presence of an absorbed film of air are used rather than the surface energies in vacuum. More importantly, one is often interested in the work required to pull a liquid away from a solid surface, leaving the equilibrium adsorbed vapor film on the surface. Then, Eq. 10 is written as

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{12}$$
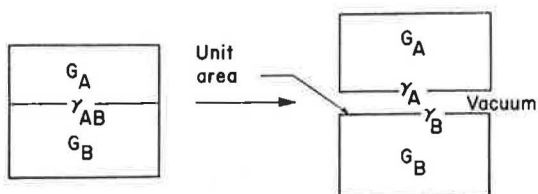
$$\Delta G_{T,p} = \gamma_A + \gamma_B - \gamma_{AB} = W_A^\circ$$

= Work of adhesion
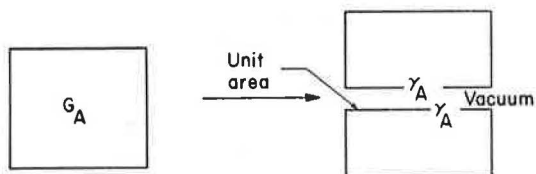
$$\Delta G_{T,p} = 2\gamma_A = W_C^\circ$$

= Work of cohesion

Figure 10. Schematic representation of relation between surface free energies and work.

where the subscripts S and L replace A and B and γ_{SV} and γ_{LV} are the surface free energies of the solid and liquid respectively for surfaces in equilibrium with the saturated vapor. The use of Eqs. 5, 10, and 12 gives

$$W_A^\circ = W_A + (\gamma_S - \gamma_{SV}) = \gamma_{LV}(1 + \cos\theta) + \pi_e \tag{13}$$

In Eq. 13, the work of adhesion W_A° is the work required to break a unit area of solid-liquid interface in vacuum, producing solid-vacuum and liquid-saturated vapor interfaces. The quantity π_e is the change in free energy accompanying the immersion of a film-free solid in a saturated vapor. It is often referred to as the equilibrium film pressure of the adsorbed vapor film.

The heat of immersion, H_i°, can be measured calorimetically by placing a powdered solid in an evacuated container, immersing the container in a fluid within a calorimeter, breaking the container, and monitoring the accompanying energy change. The free energy change may be expressed as

$$\Delta G_i = \gamma_{SL} - \gamma_S = \gamma_{LV} - W_A^\circ = \Delta H_i^\circ + T\left(\frac{\partial \Delta G_i}{\partial T}\right)_p \tag{14}$$

The enthalpy of immersion is, thus,

$$\Delta H_i^\circ = \gamma_{LV} - W_A^\circ - T\left(\frac{\partial \gamma_{SL}}{\partial T}\right)_p + T\left(\frac{\partial \gamma_S}{\partial T}\right)_p \tag{15}$$

The enthalpy of adhesion, ΔH_A°, may be similarly defined as $W_A^\circ - T\left(\frac{\partial W_A^\circ}{\partial T}\right)$, so that the heats of immersion and adhesion are related by

$$\Delta H_i^\circ = \gamma_{LV} - T\left(\frac{\partial \gamma_{LV}}{\partial T}\right)_p - \Delta H_A^\circ = \Delta H_{LV} - \Delta H_A^\circ \tag{16}$$

Thus, one may obtain the enthalpy of adhesion by subtracting the measured enthalpy of immersion from the total surface enthalpy of the liquid (because heats of immersion are generally negative, the enthalpy of adhesion is generally larger than the surface enthalpy of the liquid).

Experimental measurements of contact angles, equilibrium film pressures, heats of immersion, and interfacial tensions can be used as quantitative measures of the molecular interaction at an interface. Conversely, it should be possible to estimate these properties from knowledge of the intermolecular forces. Although we do not have enough analytic information to make accurate predictions, it is possible to make reasonable estimates of these properties on a number of simple systems by combining elementary dispersion force theory with experimental data on the surface tensions of the pure components.

EFFECTS OF ADHESION ON THE MECHANICAL PROPERTIES
OF COMPOSITES

Let us consider 2 examples of the effects of interfacial bonding in order to illustrate the importance of adhesion and surface properties to the mechanical behavior of composites.

Consider first the yield strength of glass-reinforced polyphenylene oxide (PPO) composites. An untreated glass surface has little adhesion to PPO. Treatment of the glass surface with γ-amino propyltriethoxysilane (A-1100) makes it capable of some bonding to the plastic. Figures 11 and 12 show the improvement in strength directly attributable to the improved bonding with glass bead and with E-glass fiber reinforcement respectively. Figures 13 and 14 show electron scanning microscope pictures of a small portion of the fracture surfaces of the PPO-glass bead composites. Figure 13 shows a typical situation for untreated beads, where the plastic has easily pulled away from the glass surfaces, leaving the beads sitting in large craters on the surface. Figure 14 shows the improvement in adhesion, where the plastic stays in contact with the surface until voids form away from the interface and propagate inward. Figure 15 shows a transmission electron photograph of the interface between an A-1100 treated glass bead and the adhering matrix. It is clear that the response of the matrix to the propagating crack front is considerably different in the vicinity of the interface. There exists a layer of about 7,000 Å in thickness that is seemingly oriented relative to the glass surface. This is an indication that viscous flow has not occurred in this region.
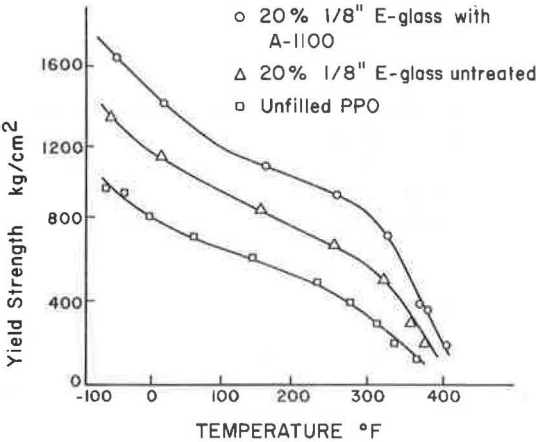

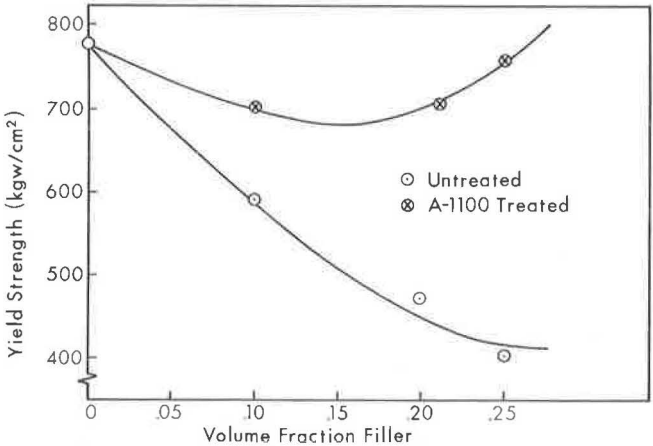Figure 11. Yield strength for glass fiber random reinforced PPO.

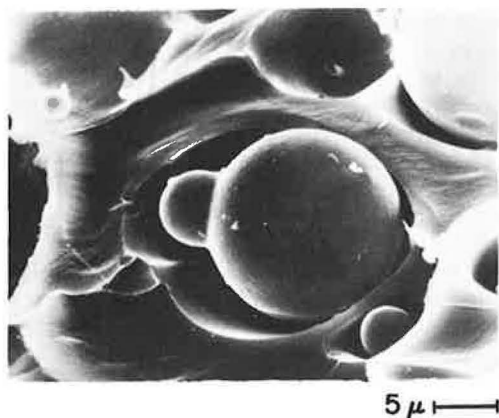Figure 12. Effect of surface treatment on strength of glass bead-PPO composites.

Figure 13. Fracture surface of a 10 percent by volume untreated glass bead-PPO composite.
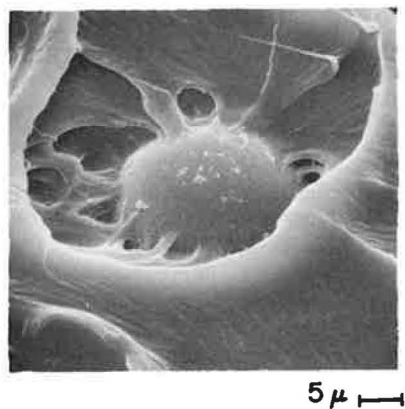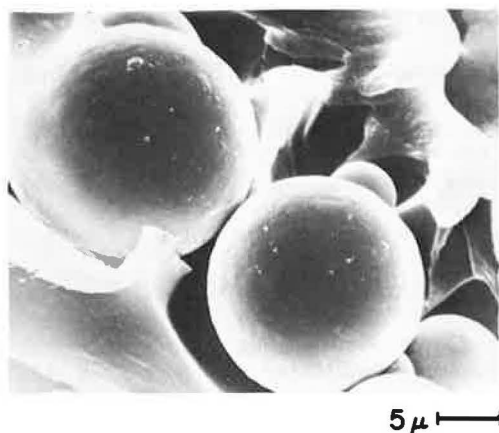
Figure 14. Fracture surface of a 10 percent by volume A-1100 treated glass bead-PPO composite.
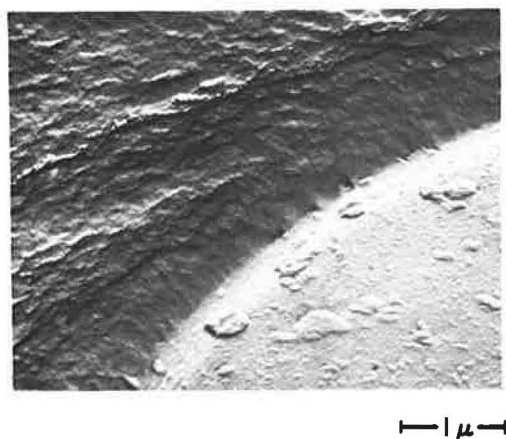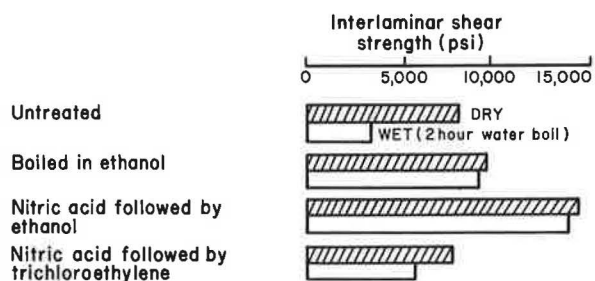
Figure 15. Transmission electron photograph of the PPO-glass bead interface of an A-1100 treated composite (fracture surface replica).

Interlaminar shear strength (psi)

	0	5,000	10,000	15,000

Untreated — DRY / WET (2 hour water boil)

Boiled in ethanol

Nitric acid followed by ethanol

Nitric acid followed by trichloroethylene

CONTACT ANGLE OF EPON 828 ON BORON FILAMENTS
(JONES & PORTER ref.)

Untreated	27-30°
After hot ethanol	7
After trichloroethylene	14

Figure 16. Effects of surface treatments on boron-epoxy composites.

A most important nonmechanical function of an adhesive interface in a composite is the protection of the surfaces of the high strength fibers from chemical attack and physical damage. If the matrix does not wet the fiber, it can accomplish neither of these. As an illustration, consider the effects of surface treatment on boron fibers (Fig. 16). The finite contact angles indicate a lack of spontaneous wetting. A treatment with hot ethanol, however, promotes the best wetting conditions. Because boron and boron oxide surfaces have high energy, 25 times higher than the epoxy resin, the lack of spontaneous wetting probably indicates the presence of dirt and other impurities. An untreated surface thus gives a weak bond and poor resistance to boiling water. The poor resistance to boiling water is probably indicative of the solubility of boron oxide in water. Boiling in ethanol probably removes the boron oxide and partially cleans the surface, leading to better strength and strength retention. Etching in nitric acid followed by boiling in ethanol gives the most complete surface cleaning and thereby gives the best strength and strength retention.

REFERENCES

1. Chemistry and Physics of Interfaces. American Chemical Soc., Washington, D.C., 1965.
2. Zisman, W. A. Industrial and Engineering Chemistry, Vol. 55, No. 10, 1963, pp. 19-38.
3. Clark, F., Rutzler, J. E., and Savage, R. L., eds. Adhesion and Adhesives: Fundamentals and Practice. John Wiley and Sons, New York, 1954.
4. Davies, J. T., and Rideal, E. K. Interfacial Phenomena. Academic Press, New York, 1961.
5. Gomer, R., and Smith, C. S., eds. Structure and Properties of Solid Surfaces. Univ. of Chicago Press, 1953.
6. Adams, N. K. The Physics and Chemistry of Surfaces. Oxford Univ. Press, London, 1941.
7. Mykura, H. Solid Surfaces and Interfaces. Dover Publications, New York, 1966.
8. Weiss, P., ed. Adhesion and Cohesion. Elsevier Publishing Co., New York, 1962.
9. Griffith, A. A. Philos. Trans., Royal Soc., London, Series A, Vol. 221, 1920-21, p. 163.