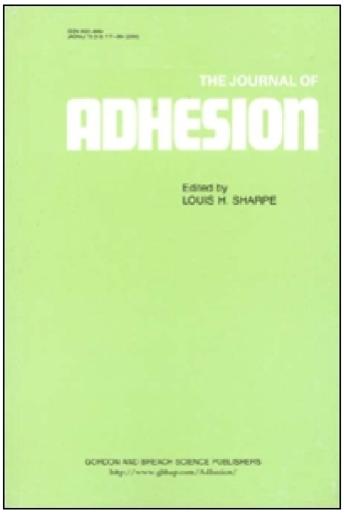


The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Theory of "Cohesive" vs "Adhesive" Separation in an Adhering System

Robert J. Good[a]
[a] Department of Chemical Engineering, State University of N.Y., Buffalo, N.Y., U.S.A.

To cite this Article Good, Robert J.(1972) 'Theory of "Cohesive" vs "Adhesive" Separation in an Adhering System', The Journal of Adhesion, 4: 2, 133 — 154

To link to this Article: DOI: 10.1080/00218467208072218

URL: http://dx.doi.org/10.1080/00218467208072218

J. Adhesion, 1972, Vol. 4, pp. 133–154

Printed in Northern Ireland

Theory of "Cohesive" vs "Adhesive" Separation in an Adhering System†

ROBERT J. GOOD

Department of Chemical Engineering,
State University of N.Y. at Buffalo, N.Y. 14214, U.S.A.

(*Received November* 11, 1971)

It is shown that there is limited validitity to the doctrine that true interfacial separation, in an adhering system, is highly improbable. An analysis employing the Griffith-Irwin crack theory yields these results: The important parameters are, difference in elastic moduli, ΔE; differences in $\mathcal{G}$, the energy dissipation per unit crack extension; thickness, δ_1 or δ_2, of the region where dissipation occurs; and the presence or absence of strong interfacial bonds. If the forces across the interface are appreciably weaker than the cohesive forces in either phase, there is a strong minimum in $\mathcal{G}$ at the interface. For flaws of equal size, an interfacial flaw will be the site of initiation of failure. If strong interfacial bonds are present, then if $\Delta\mathcal{G}$ and ΔE have the same sign, failure is most probable, deep within one phase. If $\Delta\mathcal{G}$ and ΔE have opposite signs, failure may be initiated, and may propagate, at a distance δ from the interface, in the phase with lower $\mathcal{G}$. This may be mistaken for weak-boundary layer failure.

INTRODUCTION

An essential feature, in the mechanical strength of an adhering system, is the location of the site where failure is most likely to be initiated. If a system does not attain the desired level of strength, it is an important question whether a remedy is to be sought in modification of the interface, or in the bulk properties of either phase, or in a "weak boundary layer" (WBL).

The conjecture was set forth in 1947,[1,2] that in a "proper joint", true interfacial failure practically never occurs; and that what is taken for interfacial failure is actually separation in a weak boundary layer, i.e. a layer, of thickness greater than typical atomic dimensions, with mechanical strength

---

†This paper was presented at the *Symposium on Recent Advances in Adhesion* during the 162nd National American Chemical Society Meeting, September, 1971.

considerably less than that of either phase. In the absence of a WBL, failure always occurred (it was said) within the weaker phase.

There is considerable practical usefulness to the WBL principle. Thus it is well known that contamination of a surface can lead to overall weakness. Examples such as a metal with a weakly-coherent oxide, or with a greasy surface, are obvious. A solid polymer may have, at its surface, low molecular weight material such as plasticizer or antioxidant molecules; or if it is crystalline, the surface layer may be amorphous. However, *experimental* proof has never been given for the *universality* of this principle, e.g. proof that it applies, say 99.999% of the time, vs perhaps only 90% of the time. And experimental examples have been accumulating, to indicate that the principle is not universally valid.[3,4] Moreover, certain of the experimental data purporting to prove the principle are open to an alternative explanation. See below. So claims of universality of the principle must rest on its *theoretical* validity. We will now examine this question, and then propose a more general principle which includes the WBL principle, and points out where exceptions to the WBL rule are to be expected.

CRITIQUE OF THE WBL THEORY

First we note an inherent, logical weakness in the WBL principle: the danger of circular reasoning. It is sometimes argued[2] that failure which has the appearance of being at the interface is in itself proof that a WBL was actually present. This "proof" saves the investigator the trouble of an experimental search for evidence for the WBL.

Four theoretical arguments were offered,[1,2] to tie the WBL doctrine to accepted principles of physics. The first is that the probability of advance of an interfacial crack, between one pair of atoms of unlike type at the interface, vs turning into one phase or the other and advancing between like atoms of either species, is $\frac{1}{3}$. For advance past n atoms the probability of continuing at the interface is $(\frac{1}{3})^n$, a vanishingly small number if n is large.

There are three defects in this argument. First, within the hypotheses of the argument, the probability of advance at the interface should be given an exponential weighting in proportion to the bond strengths between unlike molecules, U_{AB}, vs like molecules, U_{AA} and U_{BB}. Neglecting the resolution of stress relative to the bond directions, the relative probability for advance past a single pair of atoms will be of the order of

$$P(AB) = \exp\left(\frac{-U_{AB}}{kT}\right)\bigg/\left[\exp\left(\frac{-U_{AB}}{kT}\right) + \exp\left(\frac{-U_{AA}}{kT}\right) + \exp\left(\frac{-U_{BB}}{kT}\right)\right] \tag{1}$$

$$= 1/\{1 + \exp [U_{AB} - U_{AA})/kT] + \exp [(U_{AB} - U_{BB})/kT]\} \qquad (2)$$

If there are only dispersion forces across the interface, and covalent, ionic or metallic forces within both phases, then the exponentials in Eq. (2) will be very near zero. For advance past n atoms, the probability of continuing all the way at the interface is $[P(AB)]^n$. If U_{AA} and U_{BB} are 80 kcal/mole and U_{AB} is 2 kcal/mole, then $P(AB)$ is equal to $1/[1 + 2\exp(-78/0.6)]$, at 300°K. We can use the binomial theorem to calculate the magnitude of n, such that $1/[(1 + 2\exp(-130)]^n = 0.99$, i.e. such that there is even a 1% probability of departure from the interface. The result is, $n \sim 1 \times 10^{54}$, or a distance larger than 10^{46} cm.

Hence the probablistic argument, when proper weighting is employed, predicts that if the forces across the interface are even one order of magnitude weaker than those in the bulk, an interfacial crack will be *utterly* unable to depart from the surface.

The second defect is, that the probablistic argument ignores the actual structure of an interface and the real mechanism of deformation. It implicitly assumes that there is no dissipative work done, i.e. no plastic deformation, in the failure process. It is, of course, well known that the absence of plastic deformation, in a failure process, is exceedingly rare. An exact mathematical analysis[5,6], of a two-phase *elastic* system, with an interfacial crack which propagates under load, shows that the analysis is "inadmissible"[5] because it leads to a description of the separated, facing surfaces as oscillating (spatially) and doubling back and overlapping each other. England[5] concluded that the model was at fault, particularly the assumption that all deformations are elastic. In experimental studies of fracture, it is only with so anisotropic a material as mica that a purely elastic description of the system is even approximately correct. Thus the neglect of plastic deformation is the second argument against the probablistic proof of the WBL principle.

The third point that must be raised here is the fact, which Andrews[7] has pointed out, that the initiation and the propagation of fracture in a solid are two different problems. The same is true in a two-phase, adhering system. Indeed, the question of the locus of *propagation* is not in general directly relevant to the problem of how to remedy mechanical weakness in an adhering system.

Bikerman's second proof of his WBL principle is, that intermolecular energies and forces follow the relation,

$$U_{AA} > U_{AB} > U_{BB} \qquad (3)$$

which is based on the London theory[8] of the dispersion force:

$$w_{AB} \cong \sqrt{w_{AA}w_{BB}} \qquad (4)$$

where w is the energy at the minimum of the bimolecular potential, for molecules A and B.

However, the inequality, (3) does not apply *in general* to the forces that are responsible for the mechanical cohesive strength of useful solids, and their adhesion. The exceptions to the generalization, (3), occur when the forces are of unlike type. If, for example, one phase is ionic, or a metal oxide, or a metal, and the other a strong covalent polymer, and if there is no chemisorption at the interface, then the energies of interaction across the interface will be of the order of 1 or 2 kcal/mole, vs 50 to 100 kcal for the cohesive forces in each phase. Then Eq. (3) is replaced by

$$U_{AA} > U_{BB} \gg U_{AB} \tag{5}$$

This relationship very commonly describes systems that are of importance with respect to adhesion.

The third proof[2] of the WBL theory is, that the tensile strength of a body increases with decreasing size. This is attributed to random flaws; the probability of a flaw of critical size, for a particular stress, decreases with decreasing volume and surface area. So if we consider successively thinner laminae of either phase, the probability of a flaw existing in the lamina decreases with thickness. For example, if the thickness of the interface is 1 Å, and the two adhering phases are 1 cm thick, the probability of a critical flaw existing at the interface is only $1/(2 \times 10^8)$ of that of finding a flaw the same size in either bulk. Therefore the interface is vastly stronger than either bulk phase.

The trouble with this argument is, that extrapolation of *bulk* properties to *molecular* dimensions is inadmissible; it proves nothing. Moreover, the proof is independent of mechanism of crack propagation; but differences in the dissipative mechanism are responsible for vast differences in the energy requirement for failure. Further, this argument neglects the effect of the shear stresses and strains at the boundaries of the adhesive layer; Gent has recently shown[9,10] that such stress concentrations can account for the dependence of strength on thickness, when the adhesive is viscoelastic.

Finally, there is the proof based on the roughness of real surfaces. It seems highly improbable for a crack to be able to follow the exact contour of a typical, real surface, or even a highly polished surface (which is, in fact, microscopically very rough).

But when we look at the exact analysis of the probablistic argument, above, we see that the former argument would predict that the locus of failure between two strong solids, which have weak interactions between each other, should indeed follow even the most tortuous interface, quite faithfully! Only if there are important plastic processes at the interface, during failure, could the locus of ultimate separation do other than follow the true interface. So we must look very carefully at plastic, dissipative processes if we are to analyse this situation properly; the original development[1,2] of the WBL theory did not do this.

There is another objection to this roughness argument: that of Andrews, noted above. Even if the propagation of fracture follows a locus that jumps off from an asperity of one phase, that does not necessarily tell us anything about where the failure *started*. And it is at the place where failure starts, that preventive measures must be applied, to improve adhesion in real systems.

GRIFFITH-IRWIN THEORY FOR A TWO-PHASE SYSTEM

The Griffith-Irwin crack theory[11,12,13] of fracture shows that, for a solid whose elastic modulus is E, which contains a crack of length l, the stress σ_f at which fracture will occur is given by

$$\sigma_f = k\sqrt{E\mathscr{G}/l} \tag{6}$$

This is the plane-stress formulation, i.e. for a sample that is thin in comparison to its extension in the direction of stress. k is a constant of the order of 1, and

$$\mathscr{G} = 2\gamma_s + \psi \tag{7}$$

$\mathscr{G}$ is the total work, per unit of crack extension, that is either stored as surface free energy (γ_s) or required in other processes (ψ). The principal component of ψ is the irreversible work dissipated in plastic deformation; work is also dissipated as light and as electrical energy, and some work is stored in the defect structure (dislocations, etc.) of a layer that extends some distance below the surface. With rare exceptions, ψ is several orders of magnitude larger than γ_s; so

$$\mathscr{G} \simeq \psi \tag{8}$$

$\mathscr{G}$ and E are mathematically independent variables, in the Griffith-Irwin formulation. Both $\mathscr{G}$ and E are, in general, time dependent;[7,14,15] but for a given geometry and rate of loading and crack propagation, they may be treated as constants, as an approximation for the purposes of this theory. In the original development of the Griffith-Irwin theory, the condition (7) was simply a mechanical instability criterion; for $\sigma < \sigma_f$, the system was deemed mechanically stable, and for $\sigma \geqq \sigma_f$, failure occurred. No account was given of the process in which the crack accelerated, from its original, constant length l (under zero load) to the condition, dl/dt = constant. Recently, consideration has been given to the rate of propagation of a running crack[16-19], to the very slow, creep-like process by which a crack may extend itself (isothermally) until it reaches a critical length[20-24], and to the acceleration of the crack, in the period before it reaches its terminal velocity.[16] With a running crack, the region of the crack tip may be regarded as locally adiabatic;[26,27] and indeed, a serious local temperature rise is observed during fracture[28].

The Griffith-Irwin theory does not exclude the possibility of two different values for $\mathcal{G}$, one corresponding to a slowly-growing crack and the other to a running crack; the latter could be the smaller value. It would be very reasonable that the transition between values of $\mathcal{G}$ would occur as a continuous change. If, on the other hand, the initial crack velocity is zero, it is still very possible that the value of $\mathcal{G}$ is not constant during the period of acceleration. Greensmith and Thomas[29] have shown that, if the Griffith-Irwin criterion is applied to propagating cracks, the fracture energy is an increasing function of the forced rate of propagation. Muller and Knauss[24,25] have shown that this dependence can be predicted from the creep compliance of the material. See also the recent paper of Irwin and Paris[18].

Consider, now, a two-phase, adhering system, with a smooth, sharp interface at the plane, $z = 0$. See Figure 1. The tension is in the z direction.

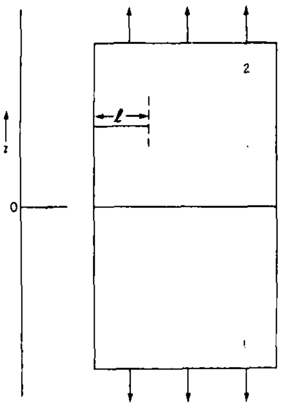


FIGURE 1 Model for this analysis: a two-phase system under tension normal to the interface, with cracks of equal length l (small compared to sample width) at various locations, z, relative to the interface.

We assume that the stress concentrations at the edge of the specimen (or at interfacial flaws) due to shear resulting from differences in Poisson contractions as between phases, are less than the stress concentrations at crack tips due to opening-mode deformations. Let us now assume that cracks exist in the system, of length l, at different elevations relative to the interface.

As the stress is increased, failure will start by extension of that crack for which σ_f, Eq. (6), is least.

If it is permissible to differentiate Eq. (6) with respect to z, we can equate $d\sigma_f/dz$ to zero to locate the extremals of σ_f, and hence $\sigma_{f_{\min}}$. Or we can plot $(E\mathscr{G}/l)$ *vs* z, and inspect for the minimum. To carry out these steps, we must examine the variation of E, $\mathscr{G}$ and l with z. Now, $l(z)$ is a distribution function, which depends on the detailed history of the two phases and the interface, often more than on their intrinsic physical properties. The interfacial flaw density depends on the mode of formation of the interface, e.g. the viscosity of the more fluid phase and the rate of application, as well as the intrinsic contact angle, and the roughness and heterogeneity of the more solid phase. So it is not generally easy to make predictions about $l(z)$.

Yet it is very instructive to make the analysis with l held constant, even though recognizing that a variation in l, say, a large interfacial flaw, could override effects due to E and $\mathscr{G}$.

The dissipative work $\mathscr{G}$ can be considered to be done in a layer of thickness 2δ. Cf. the "catastrophic, thermoplastic shear zone" of Gruntfest[26]. δ may be of the order of 10^{-5} cm; Irwin[11] has given a method for estimating its value; and δ must, in fact, be a quantity that increases with increasing $\mathscr{G}$. The boundaries of this dissipation zone are, of course, not sharp; but it is a fair approximation to think of the zone as a distinct region in space. In the interior of either phase, $\mathscr{G}$ has the values $\mathscr{G}_1$ or $\mathscr{G}_2$. If the center of the dissipation zone is in phase 1 and at a distance less than δ_1 from the interface (or similarly with regard to phase 2 and distance δ_2) then the plastic disturbance in phase 1 will be transmitted across the interface. Continuity of stresses across the interface requires this. Suppose that $\mathscr{G}_2 > \mathscr{G}_1$, and that the intermolecular forces across the interface are of intermediate strength between those in the two bulk phases. (This describes a system such as one polymer surface-grafted on another, or a polymer chemisorbed onto an inorganic solid.) Then the value of $\mathscr{G}$ will vary with z, qualitatively as shown in Figure 2. The drag of molecules of one phase, efficiently transmitted across the interface, causes the plastic deformation to be shared between the phases, provided the separation surface lies between $-\delta_1$ and $+\delta_2$.

Consider next the case in which the forces across the interface are weak, as would be the case for two immiscible polymers, or a polymer that is in molecular contact with an inorganic solid, without chemisorption occurring; i.e., only dispersion forces act across the interface. (The incompatibility of high molecular weight polymers is so extreme that, unless there is a perfect match of solubility parameters, there is generally negligible inter-digitation of even the chain ends, across the interface[30]). In this case, there is inefficient transfer of plastic shear across the interface, because of interfacial molecular slip (even though there should be good transfer of pure tensile force).

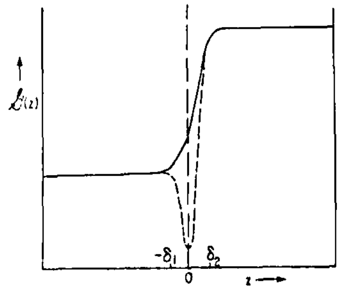


FIGURE 2 Schematic diagram of dependence of $\mathscr{G}$ on z in a two-phase system. Solid line: Intermolecular forces across interface are of comparable strength and density (bonds per unit area) across interface as within the two bulk phases. Transfer of shear stress, and of plastic shear disturbance, across interface is efficient. Dashed line: Forces across interface are weak, and interfacial molecular slip is important.

A disturbance in phase 1, centered at a distance less than δ_1 from the interface, will be strongly damped by the interfacial slip; and there will be relatively little plastic disturbance in phase 2. Consequently there is a strong minimum in $\mathscr{G}(z)$ at the interface. The lowest possible value of the minimum in $\mathscr{G}(z)$ is given by the thermodynamic free energy of adhesion

$$\mathscr{G}_{\min} \geq \gamma_{s1} + \gamma_{s2} - \gamma_{12} \tag{9}$$

where γ_s is the thermodynamic value,

$$\gamma_s = \Delta G^c/2 \tag{10}$$

i.e. the specific surface free energy for change in area by a reversible, "cohesive" separation. γ_s has been shown[31,32,33] to be given approximately by γ_c, the critical surface tension for wetting[34]. Such a low value as that given by Eq. (9) is, however, probably quite uncommon.

For completeness, we should include the possibility of a maximum in $\mathscr{G}$ in the interfacial region. This could arise from some interaction across the interface, e.g. the nucleation of crystallinity in a polymer. Such cases probably do occur occasionally.

The term E, in Eq. (6), arises from the storage of elastic energy in the system. Thus if phases 1 and 2 are of equal volume and cross section, and if W_1 and W_2 are the amounts of stored energy in the two phases, and E_1 and E_2 the respective moduli, then

$$W_1/W_2 = E_2/E_1 \tag{11}$$

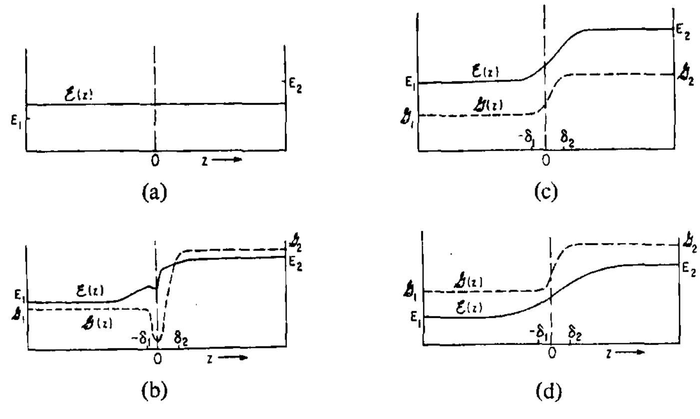
For simplicity in this qualitative matter, we have assumed a homogeneous stress state, i.e. that there is only dilation in the stress direction, and no distortion.

If the crack elongates, at constant displacement of the ends of the system, elastic energy is released from the strain field and converted into the energy which we have called $\mathcal{G}$. This energy is drawn from the strain field at a finite rate; and to reach the crack tip, it must be transmitted through the solid. The rate of transmission is limited by the velocity of sound; for longitudinal waves, the velocity is given by $\sqrt{E/\rho}$, where ρ is density, and for shear waves, the velocity is given by $\sqrt{G/P}$, where G is the shear modulus. This discussion is essentially the same as that of Berry[16] and others (see, e.g., Yokobori[19], who speaks of stress-relief waves). We are looking at the system from the viewpoint of transmission of energy to the crack tip, where previous workers had considered the kinetic energy of the material that separates when the crack lengthens. If the velocity of sound were infinite, then strain energy would be supplied to the crack from every element of volume in each phase, in proportion to the local energy density. The same would be true with finite v_s, if the system were very small, and approximately true if it were extremely thin. But in a real system, the crack cannot outrun its energy supply. This is part of the reason why the limiting crack velocity in fracture is of the order of $\frac{1}{3}$ the velocity of sound[16,17,19]. If $\mathcal{G}$ is large, energy must be drawn from more distant parts of the system than if $\mathcal{G}$ is small.

The relationships, which obtain during the time when a static (or very slowly growing) crack is converted into a running crack, have not as yet been established. The transition from an isothermal system to a locally adiabatic system with "thermoplastic shear" is, no doubt, involved[26]. The time dependence of these processes is not an easy question. We can make a very rough estimate of the size of the energy-release zone, as follows: The velocity of sound in polymers and inorganic solids is of the order of 10^6 cm/sec. The critical step is probably the advance of the crack tip by a distance comparable to δ, so that the rate of energy dissipation, per unit time, increases and approaches a quasi-steady state value. At the end of the advance by $\Delta l \simeq \delta$, the crack velocity is no doubt approaching its terminal velocity, or, say, 10^5 cm/sec. Not knowing the law governing acceleration of a crack, we must be satisfied with an estimate: Let us say $\Delta l = 10^{-5}$ cm in 10^{-9} sec., or 10^4 cm/sec., equivalent to less than 1/10 of the terminal velocity. In 10^{-9} sec., energy can be drawn from a region about 10^{-9} times the mean velocity of sound, $\bar{v}_s$, or about 10^{-3} cm, in diameter.

This estimate is crude, and it indicates that the detailed mechanism of crack initiation is of great importance to our analysis. But it also shows that the assumption, $v_s = \infty$, cannot be made with impunity. Nor can we make, with any great generality, the equivalent assumption that the acceleration of the crack is so slow that, during the critical time interval, energy can be drawn from the furthermost parts of the system. And it is quite obvious that we cannot make the other extreme assumption regarding acceleration (which, we have noted, was implicit in the original Griffith-Irwin formulation) that there is any interval where $d^2l/dt^2 \to \infty$.

This consideration of the involvement of the velocity of sound indicates that the energy-release zone must be considerably thicker than the dissipative zone. This is true for the even stronger reason, that if the thickness were not considerably larger than 2δ, the elastic energy density in a region of thickness 2δ would be so large that the local mechanical strength could not support it. Thus we can assume, as a useful approximation, that the effective modulus is a semi-local property of the materials near the crack tip. If the crack is very deep in phase 1, the appropriate modulus is E_1; and if deep in phase 2, E_2. But if the crack is in phase 1 but near enough to the interface that, during the time Δt in which the crack extends by Δl, some elastic energy can reach it from some volume elements of phase 2, then E_1 must be replaced with some sort of weighted average or "effective" modulus. This we will designate $\varepsilon(z)$; it will be a continuous function of z. See Figure 3, where it will be noted that there is no discontinuity at the interface. We can also remark that, since $\mathscr{G}$ is strongly dependent on the rate of crack extension, and on geometry, so will be the effective modulus, $\varepsilon(z)$, and the thickness of the energy-release zone.



(a) (c)

(b) (d)

FIGURE 3 Variation of $\varepsilon(z)$ and $\mathscr{G}(z)$ with crack location, for various properties of the system. Solid line, $\varepsilon(z)$; dotted line, $\mathscr{G}(z)$.

a) Velocity of sound infinite relative to dimensions of system, or crack acceleration slow. $\varepsilon(z)$ is independent of $\mathscr{G}(z)$ and of z; its value is a weighted mean between E_1 and E_2.

b) Strong forces across interface, $\mathscr{G}_1$ and $\mathscr{G}_2$ large. Region of variation of ε with z is relatively wide, on account of large values of $\mathscr{G}$.

c) Strong forces across interface; $\mathscr{G}_1$ and $\mathscr{G}_2$ small. Region of variation of ε with z is narrower than in (b), because of smaller values of $\mathscr{G}$.

d) Weak forces across interface; cf. dotted curve in Figure (2). Minimum in $\mathscr{G}(z)$ near interface causes crack velocity, for cracks very near the interface, to be larger than for cracks further away. This has the effect on $\varepsilon(z)$ of narrowing the energy-release zone, and making the value of $\varepsilon(z)$ closer to the E of the bulk phase.

In Figure 3, some possible ways are shown in which $\varepsilon(z)$ can depend on the properties of the system. Figure 3a is the case of effectively infinite velocity of sound; 3b and 3c show that the width of the energy-release zone can be a function of the local and bulk values of $\mathscr{G}$, on account of the interaction through the velocity of sound. Figure 3d shows qualitatively that, when there is a strong minimum in $\mathscr{G}$ at the interface, there may be a small dip or inflection in $\varepsilon(z)$ in the same region. This arises because, when $\mathscr{G}$ decreases, the crack velocity adjusts itself so that no more elastic energy is drawn from the strain field than is needed; and sufficient energy is available relatively close to the crack. For a near-interface crack in phase 1, this could mean that $\varepsilon(z)$ would be nearer the value of E in phase 1; and for a similar crack in phase 2, $\varepsilon(z)$ would be nearer E_2.

To be general, we should note a consequence of the fact that $\mathscr{G}(z)$ has a gradient near the interface: The direction in which the crack will advance may be at some angle φ, not necessarily 90°, to the stress direction. When interfacial forces are weak, there will be a region near the interface where the downward gradient is toward the interface, from either phase. At the interface, the gradient of $\mathscr{G}$ will be zero, and so Eq. (6) will apply, as before. Near the interface, the gradient of $\mathscr{G}$ will tend to turn the crack towards the interface. If interfacial forces are strong, the gradient in the direction of the phase with lower $\mathscr{G}$ will lead to propagation at an angle, toward that phase. The micro-mechanical analysis of this dependence of σ_f on angle has not as yet been made. Until it is available, we will employ the approximation of ignoring angular effects, in the derivation, though we will still be able to give some qualitative comment on angle, below.

We now rewrite Eq. (6), in order to differentiate it:

$$\sigma_f = k\sqrt{\varepsilon(z)\mathscr{G}(z)/l} \tag{12}$$

$$\left(\frac{\partial\sigma_f}{\mathrm{d}z}\right)_l = \frac{kl^{-1/2}}{2}\left[\left(\frac{\mathscr{G}}{\varepsilon}\right)^{1/2}\frac{\mathrm{d}\varepsilon}{\mathrm{d}z} + \left(\frac{\varepsilon}{\mathscr{G}}\right)^{1/2}\frac{\mathrm{d}\mathscr{G}}{\mathrm{d}z}\right] \tag{13}$$

σ_f is an extremal when

$$\mathrm{d}\ln\varepsilon/\mathrm{d}z = -\,\mathrm{d}\ln\mathscr{G}/\mathrm{d}z \tag{14}$$

Whether σ_f is a maximum or minimum can be determined by further differentiation of Eq. (13), or, more easily, by inspection. The form,

$$kl[\sigma_f(z)]^2 = \varepsilon(z)\mathscr{G}(z) \tag{15}$$

is convenient for this purpose. While we do not as yet know the detailed dependence of ε and of $\mathscr{G}$ on z, we can use the schematic forms of $\mathscr{G}(z)$ and $\varepsilon(z)$ sketched in Figures 2 and 3.

Let us now examine, systematically, the different combinations of dependence of ε and $\mathscr{G}$ on z.

Case 1

First the simple case, Figure 3a, when the velocity of sound v_s, is infinite, or (which is equivalent) when the time during which the crack accelerates and reaches its limiting speed is long, compared to the time required for energy to reach the crack tip from any part of, the system. The dependence of σ_f on z is, simply, as $[\mathscr{G}(z)]^{1/2}$.

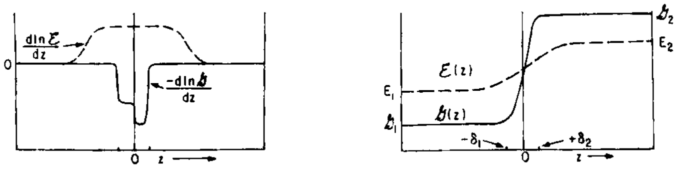
A. If interfacial bonds are strong enough that there is no minimum in $\mathscr{G}$ near $z = 0$, then (for equal crack lengths) the Griffith-Irwin criterion will be satisfied with lowest σ_f for a crack within one bulk phase.

B. If interfacial bonds are weak, and there is a minimum in $\mathscr{G}(z)$ at $z = 0$, then the interfacial crack will be the critical crack.

As already noted, it is unreal to assume $v_s = \infty$; but when the system is small, or the adhering layers are thin, the conclusion from this model may be applicable. Or if the mechanism of acceleration of a crack is actually such that the acceleration time is much longer than our estimate, above, then the velocity of sound may be treated as effectively infinite. This would be a scientifically desirable situation, as it would vastly simplify the analysis, reducing the discussion of cases 2 to 6, below, to only two cases, as above.

Case 2

Next consider the important case where interfacial forces are strong, and ΔE and $\Delta\mathscr{G}$ have the same sign. ($\Delta E \equiv E_2 - E_1$, and $\Delta\mathscr{G} \equiv \mathscr{G}_2 - \mathscr{G}_1$.) Figure 4 shows that there are solutions to Eq. (14) only for large positive or negative values of z. Hence the most probable location of failure initiation, for cracks of equal length, is in the interior of phase 1, i.e. within the "weaker" phase.



(a) (b)

FIGURE 4 (a) $\varepsilon(z)$ and $\mathscr{G}(z)$ plotted together, illustrating case 2; ΔE and $\Delta\mathscr{G}$ have same sign, and interfacial forces strong; (b) $d\ln\varepsilon/dz$ and $-d\ln\mathscr{G}/dz$ for case 2.

Case 3

Figure 5a shows the case where ΔE and $\Delta\mathscr{G}$ have opposite sign, and $|\Delta \log E| < |\Delta \log \mathscr{G}|$. Figure 5b shows the derivatives of $\ln \mathscr{G}$ and $\ln \varepsilon$; and Figure 5c shows the product $\varepsilon(z)\mathscr{G}(z)$. There are four solutions to Eq. 14:

$$z_1 \ll -\delta_1; \qquad z_3 \simeq -\delta_1;$$
$$z_2 \gg \delta_2; \qquad z_4 \simeq \delta_2.$$

It is evident, by inspection of Figure 5c, that the failure stress $\sigma_f(z)$ is lowest at z_4. This means that a flaw at a distance δ_2 from the interface, in the phase with lower $\mathscr{G}$, can act as the critical flaw.

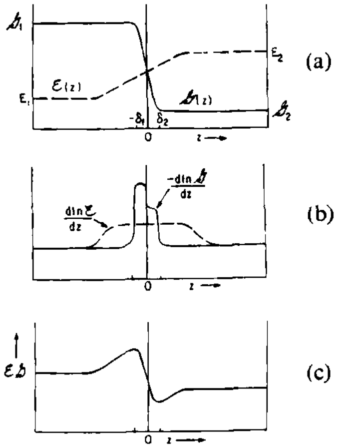


FIGURE 5 Case 3. ΔE and $\Delta\mathscr{G}$ have opposite sign, and $|\Delta\ln E| < |\Delta\ln\mathscr{G}|$; interfacial forces weak. (a) $\varepsilon(z)$ and $\mathscr{G}(z)$. (b) $d\ln\varepsilon/dz$ and $-d\ln\mathscr{G}/dz$. (c) $\varepsilon(z)\mathscr{G}(z)$ vs. z. Note minimum near $z = \delta_2$.

The failure-process zone may, for certain solids, be of appreciable thickness. Then failure at $z_4 = \delta_2$ could leave an easily-detectable layer of substance 2 on the surface of phase. This observation would, under the WBL principle, be interpreted as proof of a weak boundary layer. But the model specifically hypothesized that there is *no* WBL, and that phase 2 is homogeneous right up to the interface. So we have an example, which is subject to experimental confirmation, where the WBL principle would lead inevitably to an incorrect result.

If the dissipation zone is very thin, and substance 2 is colorless, then failure at z_4 could easily be mistaken for true interfacial failure, if a proper microscopic inspection was not made. Suppose, now, that an experimenter were to say to himself, "The interfacial forces *should* have been strong, on account of the way the system was made. Perhaps we should look more carefully for WBL material." He would find traces of substance 2 on the surface of phase 1, and he could easily jump to the conclusion that this result substantiated the universality of the WBL principle. But he would find himself unable to improve his system by removing material from the surface of phase 2, because that phase was in fact homogeneous.

This argument shows how spurious experimental proof of the WBL principle could easily have arisen. It is proof of this kind which we referred to in the introduction; and it is specifically from the finding by many experimenters, of transferred material at a failure surface, that the widespread conviction of validity of the WBL principle has come. Such transfer is, as we have just shown, not proof of the WBL principle, just as the failure to *find* material is not disproof.

There is, of course, another kind of experimental observation of weak boundary layers, *in specific systems*, which is perfectly valid: The identification of the chemical species which form the weak layers. If the transferred material differs in chemical type from either bulk phase, in ways that could not be the consequence of chemical activation and reaction during fracture, *then* it may logically be concluded that a weak chemical layer was present.

Case 4

Figure 6a shows a variant on case 3, in which $\Delta\mathcal{G}$ is less than ΔE, phase 2 having the lower $\mathcal{G}$. The existence of a minimum in $\varepsilon\mathcal{G}$ depends on the relative slopes of $\varepsilon(z)$ and $\mathcal{G}(z)$ in the neighborhood of $z = 0$. In addition to the case sketched in 5a, it is possible that there may be no minimum at all, near $z = \delta_2$; or there may be a minimum below the level of $\varepsilon\mathcal{G}$ within phase 1.

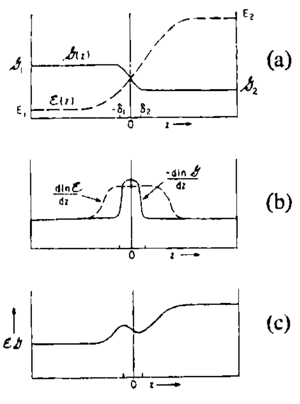


FIGURE 6. Case 4. Same as case 3 (Figure 5) but $|\Delta\ln E| > |\Delta\ln\mathcal{G}|$. Note depth of minimum near $z = \delta_2$.

So the critical crack (for flaws of equal size) may be either well within phase 1, or within phase 2 but near the interface, depending on the values of ΔE and $\Delta\mathscr{G}$ and on the slopes of $\varepsilon(z)$ and $\mathscr{G}(z)$ near $z = 0$.

Case 5

Figure 7a shows the case where $\Delta\mathscr{G}$ and ΔE have opposite sign, and the interfacial forces are weak. Figure 7b shows the derivatives of $\ln \mathscr{G}(z)$ and $\ln \varepsilon(z)$. The curve of $-\mathrm{d}\ln \mathscr{G}/\mathrm{d}z$ has a high enough peak that it can generally be expected to intersect the curve of $\mathrm{d}\ln \varepsilon/\mathrm{d}z$. And if there is an appreciable dip in $\varepsilon(z)$ near the interface, as discussed with respect to Figure 3d, then the two derivatives will most certainly intersect. So a minimum will generally exist, in σ_f, at the interface; see Figure 7c. If we compare Figure 7a with Figure 5a, we can see directly how the fracture will be affected by decreasing the depth of the minimum in the curve of $\mathscr{G}(z)$: As the interfacial slip is decreased, the curve in 7c approaches that in 5c. So the minimum at $z \simeq 0$ shifts to a minimum at $z \simeq \delta_2$.

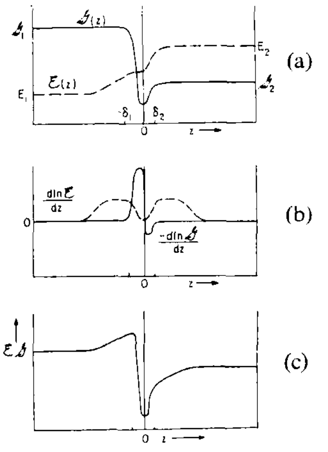


FIGURE 7. Case 5. Interfacial forces weak; ΔE and $\Delta\mathscr{G}$ have opposite sign. Note strong minimum at $z = 0$, in (c).

Case 5 is important because it is the case of true interfacial weakness, i.e. weakness that can be remedied by *chemical* modification. Provision of chemical species (molecules or molecular segments) that will chemisorb, or the formation of the interface by graft polymerization (which is nearly the same thing) will cause case 5 to shift into case 3. Now if that occurs, the most probable location of failure (for constant crack length) moves to

$+\delta_2$. Such a failure would still look like interfacial failure, on hasty inspection, or WBL failure on closer examination. But it would occur at a considerably higher value of σ. In other words, the system would have been strengthened. To attain any improvement beyond that level would require chemical operation on phase 2: not attempts to remove a non-existent WBL, but modifications to increase the local value of $\mathscr{G}$ near the interface. (See below, the discussion of CASING.)

Case 6

Figure 8a shows the case where ΔE and $\Delta\mathscr{G}$ have the same sign, and $\mathscr{G}(z)$ has a strong minimum on account of weak interfacial forces and interfacial slip. It is clear from Figures 8b and c that the existence, and depth, of the minimum in $\varepsilon\mathscr{G}$ at or very near the interface depends on the slopes of $\mathrm{dln}\,\mathscr{G}/\mathrm{d}z$ and $\mathrm{dln}\,\varepsilon/\mathrm{d}z$ in the interfacial region. There may be a minimum below the level of $E_1\mathscr{G}_1$ (as shown with the dashed line in 8c), or it may be above $E_1\mathscr{G}_1$. In the latter case, the most probable site of failure initiation is within phase 1, despite the fact that interfacial forces are weak. Only if the interfacial forces are weak enough that there is a sharp minimum in $\mathscr{G}$, (and possibly, a minimum in ε may also be needed), will the interface be the preferred location.

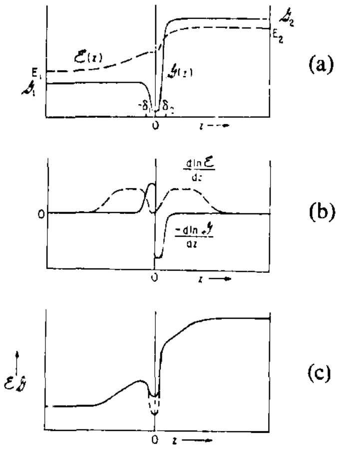


FIGURE 8 Case 6. Interfacial forces weak; ΔE and $\Delta\mathscr{G}$ have same sign. Note that minimum at $z = 0$, in (c), may be below level of $\varepsilon\mathscr{G}$ in bulk phase 1, or possibly may be above it.

DISCUSSION

We have stressed the fact that this analysis is made for equal-length cracks in phases 1 and 2 and at the interface. If an explicit flaw-density function can be constructed for a system, i.e. $l = l(z)$, then the complete derivative, $d\sigma_f/dz$, can easily be written; and the function, $\varepsilon(z)\mathscr{G}(z)/l(z)$ can be plotted against z. Such a function will be nothing more than a modified version of $\varepsilon(z)\mathscr{G}(z)$, which we have already discussed. The novel results in the analysis, above, arose from the physically reasonable *forms* of the functions, $\varepsilon(z)$ and $\mathscr{G}(z)$.

For brevity in this paper, and since as already noted, $l(z)$ is likely to depend on details of the system which we may know little about, we will omit further discussion of $l(z)$, "without prejudice"; i.e., this matter is suitable for taking up in future analyses of the problem.

We have omitted analysis of the effects of time dependence of E and l, and the influence of rate on $\mathscr{G}$; and also the differences in Poisson's ratio, between the phases. These must also be considered explicitly; but we must postpone them, together with the effects of environment, for subsequent treatment. We have neglected the possible variation of E_1 and E_2 near the interface;[35] such variations are of course, quite distinct from the dependence of $\varepsilon(z)$ on distance from the interface. We have also, as mentioned above, neglected the angular dependence of ε and $\mathscr{G}$.

We have already noted that the crucial step in the failure process is the acceleration of the crack, from a static or quasistatic condition to a propagating state. Accordingly, there is an uncertainty in $\mathscr{G}$: If $\mathscr{G}$ is measured, it should be measured for the *transition* between static cracks and running cracks; it should not be measured for cracks in steady-state propagation. And we note that, in measurement, the experimental tendency is likely to be toward the values characteristic of running cracks, even when the experiment is designed with initially static cracks.

It is an important fact that the alternative to our main thesis, which is based on dependence of ε on z as shown in Figures 3b, c and d, is Case 1, (above), where the energy-release zone is, effectively, the entire system. The existence of a minimum in $\varepsilon\mathscr{G}$ at δ_2, in Figures 5c and 6c, is totally dependent on the existence of a region where $d\varepsilon/dz \neq 0$. But this fact does not in the least vitiate the conclusion that, *when forces are weak*, there will be a strong minimum at $z = 0$ regardless of $d\varepsilon/dz$. Thus the prediction, case 1B, can be made with great confidence.

Moreover, the qualitative considerations of angular dependence of σ_f, already noted, lead to a direct refutation of Bikerman's conjecture that even when interfacial forces are weak, a failure locus that starts at the interface will, with overwhelming probability, depart from it, even though initiation took place there. Weak interfacial forces will be accompanied by a steep gradient of $\mathscr{G}$, increasing away from the surface. So the least-energy path for the crack will be the path that does *not* carry it away from the interface. And if the crack should turn away from the interface, toward a region of greater fracture-toughness, a branch would develop in the direction of lower fracture-toughness.

APPLICATIONS

Bombardment of the surface of a polymer with energetic particles[36] (ionized or not) or ultraviolet light (which has very recently been shown to accompany such particles[37] will have at least three effects. It will increase the potentiality for strong interfacial bonds due to free radical or other reactions, or by strong dipoles or hydrogen-bond interactions. It will cause crosslinking, and so (up to moderate dosages) increase toughness, and hence $\mathscr{G}$. Since elastic modulus is well known to increase with crosslink density, this treatment may also increase the modulus. This last effect is subject to a separate analysis; such an analysis has been started in the work of Williams[35], reported in this Symposium. If the crosslinked layer should turn out to be homogeneous and of thickness greater than the energy-release zone (which now seems unlikely) the higher modulus would be used, directly, in our analysis.

Which of the three effects (changes in interfacial reactivity, in local $\mathscr{G}$ and in local E) will dominate, will be a function of the nature and thickness of the affected layer. If the layer is very thin, only the interfacial bonding will be affected. If the layer is comparable to δ, the increase in $\mathscr{G}$ will also be important. If it is appreciably thicker than δ, then the increase in E may be important too. For any particular two-phase system, there will be an optimum in the degree of modification of these three factors. These generalizations are in agreement with the observations of Schonhorn and Hansen[36] in their discussion of CASING.

Interdiffusion of molecules of the two phases deserves comment in view of the fact that Voyutskii[38] considers it to be the one key property with regard to adhesion. In low molecular weight systems with infinite miscibility, interdiffusion can of course produce a transition region with no sharp gradient in $\mathscr{G}$, E or Poisson's ratio; such a system may also be free from interfacial flaws, and the forces across the interface will be comparable to the cohesive forces of the two phases. But if $\Delta\mathscr{G}$ and ΔE have opposite sign, and if the interdiffused layer is not thick, then the mechanical considerations discussed above will still apply; and the most probable region of failure may still be, at distance δ from the interface, in the phase with lower $\mathscr{G}$.

If the two materials are partially miscible, then the layer in which a concentration gradient exists will be of extremely limited thickness, e.g. 2 to 4 molecular diameters (except very close to a critical mixing temperature). The thickness, δ, is generally large compared to a molecular diameter, so all of the conclusions from the model with a molecularly-sharp interface, above, are still valid.

In the important case of two linear, amorphous polymers, the structure of the interface is not as yet very well understood. It is well established that complete miscibility is very rare, even with close matching of solubility parameters, if molecular weights are high. Specific interaction, e.g. hydrogen bonding as in the case of poly(vinyl chloride) with nitrile groups in an acrylonitrile copolymer, seems to be a necessary requirement for miscibility. But no general solution is as yet available, to predict the interpenetration of chain-ends or loops, for two amorphous polymers with cohesive energy densities that are not very different[30]. If appreciable interpenetration exists, and particularly if there are trans-interfacial loops, this could have a major effect on the interfacial slip. It is possible that studies of interfacial separation, in systems of immiscible polymers, may prove to be a tool for investigating interpenetration, and thus for testing the Voyutskii hypothesis.

Finally, we can discuss *true* weak boundary layers. A WBL will, in general, have an extremely low energy-dissipation function, $\mathscr{G}$. It may also have a low elastic modulus. Having a low $\mathscr{G}$, it is irrelevant whether it is strongly bonded to either phase. The Griffith-Irwin criterion immediately predicts that failure will be most likely to occur within the WBL. Thus our model includes a prediction of WBL failure, in addition to predicting the failure locus in the absence of a WBL.

We can now summarize the results of the theory, and draw some conclusions as to the relation of composition and structure to adhesive behavior.

1) If $\Delta\mathscr{G}$ and ΔE have the same sign, and if the forces across the interface are strong, then the most probable site for initiation of failure, for flaws of equal size, is within one phase.

2) If $\Delta\mathscr{G}$ and ΔE have opposite sign and $\Delta \log \mathscr{G} > \Delta \log E$, and the interfacial forces are strong, then the most probable initiation site is near the interface, within the phase with lower $\mathscr{G}$. If $\Delta \log \mathscr{G} < \Delta \log E$, then the most probable point of failure initiation may be near the interface, within the phase with lower $\mathscr{G}$; or it may be farther from the interface, within the phase with lower E. Which of these predictions is applicable will depend on the rates of variation of $\mathscr{G}$ and ε near the interface.

This case amounts to a proffered explanation for experimental results which have in the past been taken as evidence for weak boundary layers. This explanation is one that can be tested experimentally, since it leads to an explicit prediction.

3) *If interfacial forces are weak, true interfacial separation is possible* or even probable.

a) If $\Delta\mathscr{G}$ and ΔE have opposite sign, then failure initiation at the interface is the most probable occurrence. Weak interfacial forces also are likely to cause relatively high contact angles and poor wetting[31,32,39,40], and hence interfacial flaws[3,41], so the probability is high that if interfacial flaws exist, they will be at least as large as the largest flaws in either bulk phase. So conclusion 3a can be drawn with some confidence.

b) If $\Delta\mathscr{G}$ and ΔE have the same sign, then it is only if the intermolecular forces across the interface are very weak that we can confidently predict true interfacial failure. If the forces are of intermediate strength (even though appreciably weaker than the cohesive forces in the bulk phases) then the most probable locus of initiation *may* still be within the phase with lower E and $\mathscr{G}$. A more precise prediction than this can probably be made, but only with a much more detailed analysis of the variation of $\mathscr{G}$ and ε in the interfacial region.

4) The most speculative part of this theory concerns the dependence of ε on z. If we use the less bold hypothesis, shown in Figure 3a, that $\mathrm{d}\varepsilon/\mathrm{d}z = 0$, then the result of the theory is very simple:

A. If interfacial forces are strong, the most probable site of failure initiation is within the phase with lower $\mathscr{G}$ (for flaws of equal size.)

B. If interfacial forces are weak, the most probable site is at the interface. Moreover, the probability of propagation away from the interface depends on the gradient of $\mathscr{G}$ near the interface; a steep gradient (arising from very weak interfacial forces) will militate against propagation away from the interface. Hence the refutation of this aspect of Bikerman's conjecture, which concerns failure propagation, does not rest on the speculative part of the present derivation.

5) To design a system in which the interfacial region is not the most important source of weakness, one should:

a) Provide perfect wetting, to eliminate interfacial flaws.

b) Provide strong interfacial forces, by covalent bonding or chemisorption. (If this latter measure is not possible, components having high group dipole moment, or hydrogen bonding groups, should be incorporated.)

c) Choose materials such that $\Delta\mathscr{G}$ and ΔE have the same sign.

d) Choose materials such that there is the least possible difference in $\mathscr{G}$, E and ν across the phase boundary.

e) Surface treatment such as etching of a polymer, particle-bombardment, etc. may be employed to improve the characteristics indicated in a), b), c) and d) when there is not the freedom to adjust these properties by design of the bulk phases.

b) We recommend that the experimental evidence for the *universality* of the WBL principle be re-examined in the light of our analysis. It is felt that a large part of the perplexity which adhesion chemists, physicists and engineers have felt, during the past two decades, over their lack of success in remedying troubles diagnosed as due to weak boundary layers, may be solved by recognizing that there is no need to blame WBL's for all adhesion troubles.

Acknowledgements

Thanks are expressed to Prof. M. L. Williams, Prof. E. H. Andrews, and Prof. H. Reisman, for discussion of this subject, and to the City University, London, for support of this work while the author was Visiting Professor in the Department of Chemistry in 1971.

References

1. J. J. Bikerman, *J. Coll. Sci.* **2**, 163 (1947).
2. J. J. Bikerman, *The Science of Adhesive Joints*, 2nd ed. (Academic Press, N.Y., 1968).
3. J. R. Huntsberger, in *Treatise on Adhesion*, R. L. Patrick, Ed. (Marcel Dekker, N.Y., 1967),
4. D. H. Kaelble, *Physical Chemistry of Adhesion* (John Wiley, N.Y., 1971).
5. A. H. England, *ASME Trans., J. Appl. Mech.* **32**, 400 (1965).
6. B. M. Malyshev and R. L. Salganik, *Int. J. Fract. Mech.* **1**, 114 (1965).
7. E. H. Andrews, *Fracture in Polymers* (Oliver and Boyd, London, 1968).
8. F. London, *Trans. Faraday Soc.* **33**, 8 (1937).
9. A. N. Gent, *J. Polymer Sci. part A-2*, **9**, 283 (1971).
10. A. N. Gent and E. A. Meinecke, *Polymer Eng. Sci.* **10**, 48 (1970).
11. A. A. Griffith, *Phil. Trans. Roy. Soc. London* **221**, 163 (1920).
12. G. R. Irwin, in *Fracturing of Metals* (Am. Soc. for Metals, 1947), p. 147; *Trans. Am. Soc. Metals* **40**, 147 (1948).
13. G. R. Irwin, in *Treatise on Adhesion*, R. L. Patrick, Ed. (Marcel Dekker, N.Y., 1967).
14. A. T. Di Benedetto, *The Structure and Properties of Materials* (McGraw-Hill, Inc., N.Y., 1967).
15. L. E. Nielsen, *Mechanical Properties of Polymers* (Reinhold, N.Y., 1962).
16. J. P. Berry, *J. Mech. Phys. Solids* **8**, 194, 207 (1960).
17. F. Erdogan, in *Fracture, Advanced Treatise*, H. Liebowitz, ed. (Academic Press, N.Y.), vol. **2**, pp. 498–591.
18. G. R. Irwin and P. C. Paris, *ibid.*, vol. 3, pp. 1–47.
19. T. Yokobori, *An Interdisciplinary Approach to Fracture and Strength of Solids* (Walters-Noordhof, Ltd., Groningen, The Netherlands 1968).
20. R. Kambour, *J. Polymer Sci. A*, **3**, 1713 (1965); *A-2*, **4**, 17, 349, 359 (1966).
21. W. G. Knauss, *Trans. Soc. Rheology* **13**, 291 (1969).
22. W. G. Knauss, *Int. J. Fract. Mech.* **6**, 7 (1970).
23. W. G. Knauss, *J. Composite Mats.* **5**, 176 (1971).
24. K. H. Muller and W. G. Knauss, *Trans. Soc. Rheology* **15**, 217 (1971).
25. K. H. Muller and W. G. Knauss, *J. Appl. Mech.*, paper 71-APM-B, June, 1971, p. 483.
26. I. J. Gruntfest, in *Fracture of Solids*, D. C. Drucker and J. J. Gilman, Eds. (Interscience, N.Y., 1963), pp. 189–93.

27. J. R. Rice and N. Levy, in *Physics of Strength and Plasticity*, A. S. Argon, Ed. (MIT Press, 1969).
28. A. A. Wells, *Trans. Inst. Welding* **15–16**, 34r, (1952–3).
29. H. W. Greensmith and A. G. Thomas, *J. Polymer Sci.* **18**, 189 (1955).
30. P. J. Flory, B. E. Eichinger and R. A. Orwoll, *Macromolecules* **1**, 287 (1968).
31. R. J. Good and L. A. Girifalco, *J. Phys. Chem.* **64**, 561 (1960).
32. R. G. Good, *Advan. Chem. Series* **43**, 74 (1964).
33. R. J. Good, "Wetting", *Soc. Chem. Ind.* Monograph No. 25, 328 (1967).
34. H. W. Fox and W. A. Zisman, *J. Coll. Sci.* **7**, 428 (1952).
35. M. L. Williams, *this journal.*
36. H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.* **11**, 1461 (1967).
37. R. R. Sowell, N. J. de Lollis, H. J. Gregory and O. Montoya, *this journal.*
38. S. S. Voyutskii, *Autohesion and Adhesion of High Polymers* (John Wiley, N.Y., 1963).
39. R. J. Good and E. Elbing, *Ind. Eng. Chem.* **62**, 54–78 March, (1970).
40. R. J. Good, *Aspects of Adhesion*, No. 8, D. J. Alner, Ed. (University of London Press, London). In press.
41. J. R. Huntsberger, *Chem. and Eng. News* **42**, 82 Nov. 2, (1964).