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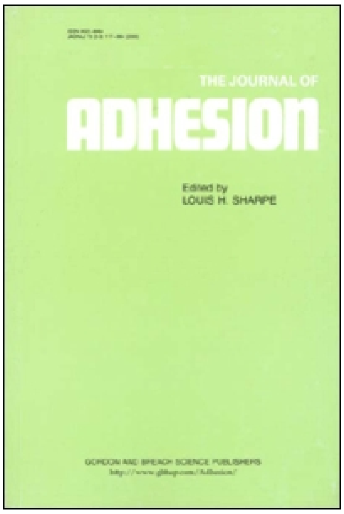

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The Relation of Continuum Mechanics to Adhesive Fracture

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The Relation of Continuum Mechanics to Adhesive Fracture

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From the standpoint of continuum mechanics, there is an essential similarity between cohesive and adhesive failure. Continuum mechanics can, therefore, be used to analyze adhesive fracture including certain cases of interfacial debonding, by applying an extension of the Griffith energy balance concept. Present researches permit a consideration of the influence of material behavior such as viscoelasticity and geometric parameters such as interlayer bond thickness. These advances and quantitative predictions of failure are reviewed with special reference to the characteristic adhesive fracture energy, new or applicable test methods, and its connection with the association between macro- and micro-constitution of the media. Various testing methods for determination of the adhesive fracture energy are discussed. A pressurized bubble or blister at the interface is shown to have certain advantages. Experimental results from various materials using this test will be presented as confirmation of the model.

INTRODUCTION

There appears to be a growing appreciation of the interdependence of mechanics and physical chemistry in the analysis and design of adhesive joints. The point of view of the present paper is from that of mechanics, with the objective of indicating how a wide variety of the characteristic features appearing in adhering systems can be analyzed with particular attention to predicting the debonding threshold. Further, it is intended to focus attention upon those material properties, namely deformation modulus and specific fracture energy, which are most directly associated with the

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chemistry and molecular structure of the material in order to encourage polymer and physical chemists to provide the analysts and materials engineers with the fundamental data required.

Since the early experimental work of de Bruyne[1] and the adhesive joint stress analysis proposed by Reissner and Goland[2], there have been many contributions providing a more scientific background to assist the technological development. The review by Patrick[3] is typical of the state of the art, and in particular includes a discussion of the use of fracture mechanics ideas developed by Griffith for cohesive fracture of brittle materials. The adhesively bonded test specimen used by Ripling *et al.*[4] was one of the first to incorporate an energy criterion of failure as compared to the earlier ones using an allowable maximum stress or strain criterion.

Generally speaking, adhesively bonded joints involve sharp corners and voids between adjacent different media which act as stress concentrators, particularly after a crack or imperfection arises at such a location. In a typical case consisting of two adherends and a third interlayer material as the bonding adhesive, there are several potential loci of failure, a cohesive failure in any of the three materials, or an adhesive failure at either of the two interfaces. The engineering problem is to determine the location of the weakest link and the magnitude of stress which is required to cause failure. The assessment proceeds from either of two points of view, depending upon whether or not inherent flaws or sharp corners are considered to be present.

In the first case, the material is thought of as continuous, as in the normal tensile specimen, and a maximum tensile stress is obtained from the materials laboratory. Actually there is, of course, always some reasonably uniform distribution of small voids present, whose size is related to the method of material fabrication. A simple example is a polymer which is mixed rapidly and contains finely dispersed air bubbles. Even with de-gassing some distribution of flaws will exist on some dimensional scale. The average tensile strength therefore reflects their presence, and the dispersion of strength data about the norm describes the uniformity of the flaw distribution. Because most standard materials are made under reasonably controlled conditions, it is not surprising to find that some sort of consistent (average) stress or stress-functional criterion can be used to predict failure.

Under more complicated conditions, such as the multi-axial stressing of a turbine disk, it is customary to assume that the failure criterion is based on the octahedral shear stress (τ_{oct}) containing all three principal stresses, (σ_i) and defined as

$$\tau_{\text{oct}} = K\sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2} \tag{1}$$

in which $i = 1, 2, 3$. Assuming the criterion applies, one predicts failure whenever this combination of principal stresses at any point in the past exceeds τ_{oct}. And how is τ_{oct} determined? If (1) is a *universal* failure criterion, it must also apply to the failure of a simple uniaxial tensile specimen having stresses $\sigma_1 = \sigma_{\text{tens}}$, and $\sigma_2 = \sigma_3 = 0$. Thus substituting into (1) one finds that

$$\tau_{\text{oct}} = K\sqrt{2\sigma_{\text{tens}}^2} \tag{2}$$

so that upon solving for the desired constant K and resubstituting into (1), one finds that failure is expected under a multi-axial principal stress combination whenever at some point in the body

$$\sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2} > \sqrt{2}\sigma_{\text{tens}} \tag{3}$$

or in the more general case, denoted by Region I, whenever (see Figure 1)

$$F(\sigma_1, \sigma_2, \sigma_3) > \sigma_{\text{tens}} \tag{4}$$

where F is some function of the principal stress at a point.

The difficulty with many adhesive joints however is that they can possess very high stress concentrations at corners or along bond lines, and usually contain substantially larger than average internal flaws, frequently as the result of absorbing water or poor wetting of the interfaces. In any event, the flaw distribution becomes denser and/or of larger size than the average size for which an average tensile strength would be appropriate. Thus the maximum permissible allowable stress is decreased. Griffith[5] provided the first estimate of degradation as a function of the flaw size by considering the problem of a small, through, line crack in a thin sheet of brittle material. While theoretically the stress at the crack tips is (mathematically) infinite for an elastic body,[6] thus giving rise to an infinite local stress at even small applied loadings—a degree of concentration for which (4) is useless—Griffith avoided this problem by considering the strain energy in the sheet, which, as an integration of the stress, remained finite. He proposed that cohesive fracture would commence at a critical applied stress σ_{cr}, when the incremental loss of strain energy of deformation with increasing fracture area just exceeded the work required to create new fracture surface. Hence, in his case, with the strain energy of deformation due to the presence of the crack of length $2a$ being $U = \pi a^2 \sigma_{\text{cr}}{}^2/E$

$$\frac{\partial}{\partial a}\left[\pi a^2 \sigma_{\text{cr}}{}^2/E\right] > \frac{\partial}{\partial a}\left[4a\gamma_c\right]$$

from which the finite critical applied stress was determined, in Region II, as

$$\sigma_{\text{cr}} > \sqrt{\frac{2}{\pi}\frac{E\gamma_c}{a}} \tag{5}$$

in which E is Young's modulus, a the half-crack length, and γ_c the cohesive fracture energy density (in-lbs/in^2, or erg/cm^2).

The combination of these two criteria, one flaw insensitive (Region I) and the other dependent upon flaw size (Region II) thus permits the designer to select a maximum allowable design stress providing he knows,† or determines by tests in the laboratory on pre-cracked thin sheet tensile specimens with known crack size, a, the critical crack size, a^* (Figure 1). This critical crack size is deduced by the intersection of normal, nominally unflawed, tensile data (σF_{cr}) and initially pre-cracked sheet which follows the Griffith curve data (σG_{cr}). Once it is recognized that (4) and (5) are not competing failure criteria, but instead are complementary, it is possible to approach the design against failure in a more direct manner.

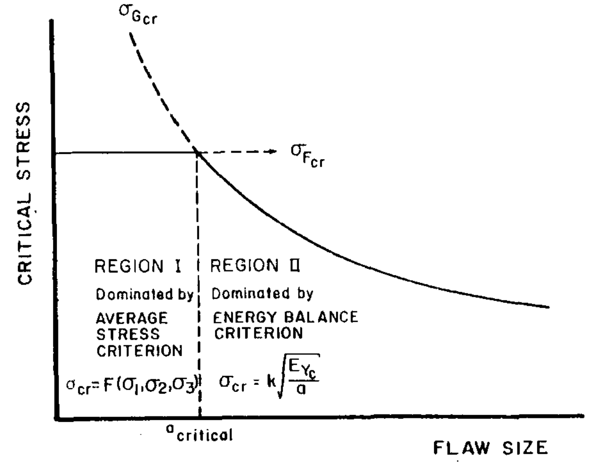

FIGURE 1 Dominant fracture regions depending upon inherent flaw size.

Turning now from cohesive to adhesive failure, it is merely necessary to establish that in principle and from the standpoint of a continuum mechanics analysis, cohesive and adhesive fracture are similar. Cohesive failure in any of the three materials of our earlier three-layered bond example can thus be treated by (4) or (5). The new feature is how to treat an adhesive debonding at an interface. If there is no flaw at the interface, e.g. no surface roughness or air bubble, and no end to the joint, an unlikely situation, then in principle (4) can be applied on the basis of normal tensile testing of layered specimens—providing they do fail essentially at the bond line.

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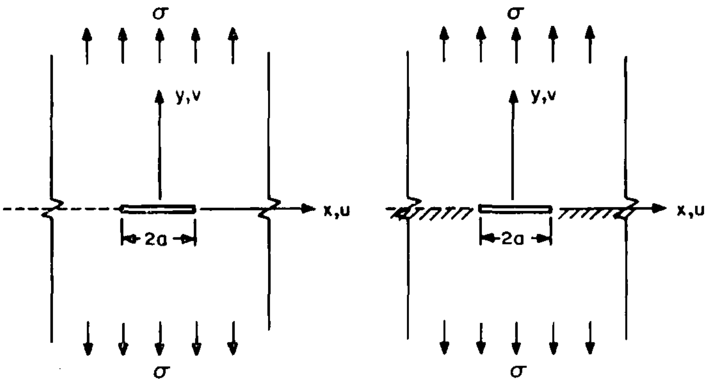
† The technically important problem of measuring the inherent flaw size in a part, preferably by some non-destructive test (NDT) method as ultrasonic wave reflection, X-ray, etc., will not be covered in this paper. Obviously, if the inherent flaw size is unknown, *a priori*, the analyst does not know whether to choose Region I or Region II criteria.



Boundary Conditions: $|x| > a$

(1) $v(x,o) = o$

(2) $\tau(x,o) = G[\partial u(x,o)/\partial y + \partial v(x,o)/\partial x] = o$

or because of (1), equivalently,

(2a) $\dfrac{\partial u(x,o)}{\partial y} = o$

Figure 2a. Cohesive fracture

$$\sigma_{cr} = \sqrt{\frac{2}{\pi}\,\frac{E\gamma_c}{a}} \qquad (5)$$

Boundary Conditions: $|x| > a$

(1) $v(x,o) = o$

(2) $u(x,o) = o$

Figure 2b. Adhesive Fracture

$$\sigma_{cr} = \sqrt{\frac{2}{\pi}\,\frac{E\gamma_a}{a}} \qquad (6)$$

FIGURE 2 Comparison of essential boundary conditions for cohesive and adhesive fracture. The difference is slight and concerns only whether the lateral displacement, $u(x, 0)$, or its normal derivative, $\partial u(x, 0)/\partial y$, is prescribed. Both sets of boundary conditions lead to singular stresses (Refs. 9, 12).

The character of elastic stress singularities to be expected for various geometric discontinuities was investigated by Williams[7,8] and later extended to the first analysis of the character of the stress singularities along the interface between dissimilar media[9]. In this case when a crack existed along the line of demarcation of the two materials, the stress singularity was likewise singular, although not necessarily solely of the $r^{-1/2}$ type† as is found for a crack in a single material. It subsequently became attractive to inquire whether the same approach as Griffith used could be applied to predict the stress required to further separate or fracture the (adhesively bonded) interface between two different media, again notwithstanding the predicted existence of an infinite stress at the crack point for even small applied loads.

† Actually in most cases a new characteristic oscillatory stress singularity arises although for a rigid-elastic incompressible interface it becomes identical to that for cohesive failure, i.e. $\sigma \sim r^{-1/2}$ (ref. [9]).

The phenomenological similarity in the two cases becomes clear. In the Griffith problem the finite length of the central crack $2a$, lies, say, along the x axis, with the upper and lower half planes occupied by the same material; in the second problem, the materials above and below the x axis are different. For the purposes of discussion, we shall assume the material in the lower half plane to be infinitely rigid (e.g. glass) with respect to that in the upper half plane (e.g. rubber), and assume perfect adhesion over $|x| > a$. The stresses at the crack ends, $|x| = a$, are both singular. In the first case the Griffith critical stress is the classic example of cohesive fracture and well-known; in the second, the analogous example of perfect adhesive failure is the subject of this paper.

Before looking into the second problem in more detail, it is pertinent to comment upon the distinction between the mechanics and chemistry viewpoints. As structured above, the mechanics approach is straightforward and consists of two parts: (1) conduct the stress analysis for an edge-bonded specimen having a central finite crack at the interface with a rigid boundary, and (2) express the incremental new surface energy generated as the crack extends. This latter part, however, requires interpretation.† In the cohesive fracture problem, with the same material on both sides of the extending crack, Griffith used $\Delta\Gamma = 4\gamma_c \Delta a$ as the incremental energy per unit thickness. The factor four arises because both ends of the crack are assumed to extend equally, and each end creates two new surfaces, one above and one below the crack. The specific energy γ_c has been subscripted to denote the value associated with cohesive failure. For adhesive failure, it would be appropriate, although not necessarily unique to write $\Delta\Gamma = 2\gamma_a \Delta a$ to denote that only two new free surfaces are formed in the elastic material. While this leaves open to surface chemists the question of any quantitative relation between γ_a and γ_c, as long as γ_a is a fundamental material constant, it can be used subsequently for predicting adhesive failure in a different geometric or loading configuration. The analogy between cohesive and adhesive fracture is complete and results similar to (5) can be obtained, except that the *adhesive* fracture energy must be used in the criticality condition

$$\sigma_{cr} = \sqrt{\frac{2}{\pi}\frac{E\gamma_a}{a}} \tag{6}$$

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† It should be clear that a continuum mechanics analysis does not, of itself, differentiate between a cohesive or adhesive mechanism of failure. The distinction lies in the behavior implied by using a particular one of the respective energies in the formulas, namely γ_c (cohesive) or γ_a (adhesive). Furthermore there appears to be no direct association between the critical surface tension and the continuum mechanics analysis of the unstable infinitesimal deformation of a solid, although for special cases the critical surface stress to cause a spherical flaw to become unstable has been deduced by Williams and Schapery.[10,11]

to predict adhesive fracture between a rigid-incompressible material combination. Hence with this connection formally established, the entire body of analytical knowledge in cohesive fracture mechanics can be transferred to analyze adhesive debonding.

A few examples will serve to illustrate the point on both an approximate and exact basis.

ANALYTICAL DETERMINATION OF ADHESIVE FRACTURE ENERGY-ELASTIC

The simplest illustration of the concept involved borrows from the Obreimoff[12] proposition for determining cohesive fracture energy by using a split cantilever beam (Figure 3). The strain energy stored in the top linear elastic beam, assumed clamped at the end of the split, is one-half of the work done by the applied force (F) acting through the equilibrium displacement

$$U = 1/2 \cdot F \cdot FL^3/3EI \tag{7}$$

in which $I = b(2t)^3/12$ is the moment of inertia. Also the incremental increase in the new area, counting only that associated with the top beam in order to be consistent with (7), is $\partial\Gamma = \gamma_c^\delta(L \,.\, b)$. Thus, equating the two, one finds

$$\gamma_c = \frac{\partial\Gamma}{\partial(L\cdot b)} = \frac{\partial U}{\partial(L\cdot b)} = \frac{F^2L^2}{2bEI} = \frac{6F^2L^2}{Eb^2(2t)^3} \tag{8}$$

or in terms of the maximum outer fiber stress σ_0 developed at the bonded end

$$\sigma_o = \sqrt{3\gamma_c E/t} \tag{8a}$$

from which γ_c can be deduced from the measurable quantities in (8) at the instant of fracture.

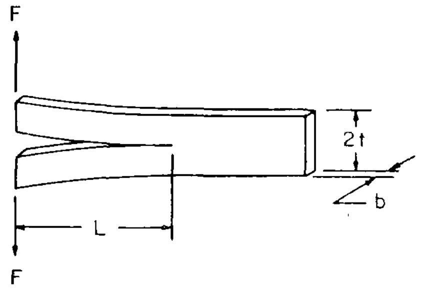

FIGURE 3 Double cantilever cleavage specimen.

If now the geometry is changed such that the top beam is bonded to a rigid substrate instead of to its mirror image, a little reflection indicates that within the approximation of elementary beam theory the analysis is identical to (8) except that the quantity which will be deduced is γ_a, the *adhesive* fracture energy required to separate the beam from its attachment.

Centrally unbonded thick plate of finite thickness (Figure 4a)

Another fairly simple example, and one which permits a reasonable degree of generality for illustrating several other characteristics is an elastic strip plate of debond width $2a$, infinite length, and thickness, h. Depending upon the thickness of the plate, it may be analyzed as one containing predominantly bending energy ("thick plate"), stretching energy with little bending energy ("membrane"), or a combination of the two ("thin plate"). The elementary calculation[13] paralleling (8) above would be for a thick plate in which case analysis with classical elasticity results in

$$\gamma_a = \frac{\partial U}{\partial(2a)} = \frac{p^2 a^4}{18D} = \left[\frac{2(1-\nu^2)}{3}\left(\frac{a}{h}\right)^3\right]\frac{p_{cr}^2 a}{E} \tag{9}$$

where p is the uniform pressure loading, a is the distance from the center of the plate to the clamped ends and h is the plate thickness.

The above simple illustrations incorporate several approximations which do not exactly reflect the actual plate behavior, namely (a) plane sections do not remain plane especially near the end of the crack, (b) there will be some stress and some strain energy stored in that part of the beam past the assumed fixed end at L, (c) there will be (mathematically) infinite stresses at the point of the crack, (d) plastic flow probably occurs at the crack tip, and (e) the fracture criticality condition is only a necessary one. Nevertheless, information useful in design is obtained, mainly because the values of γ_c and γ_a so obtained are used in analyzing applications incorporating the same approximations.

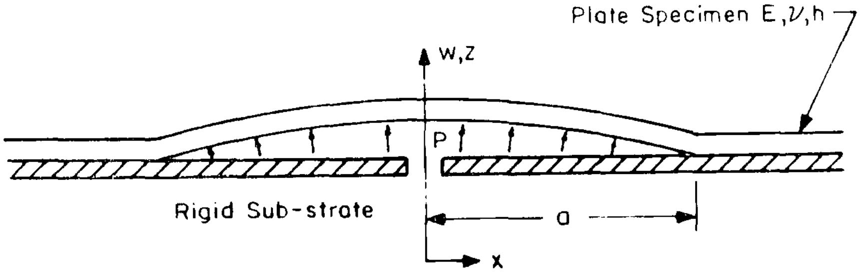

FIGURE 4a Pressurized blister specimen.

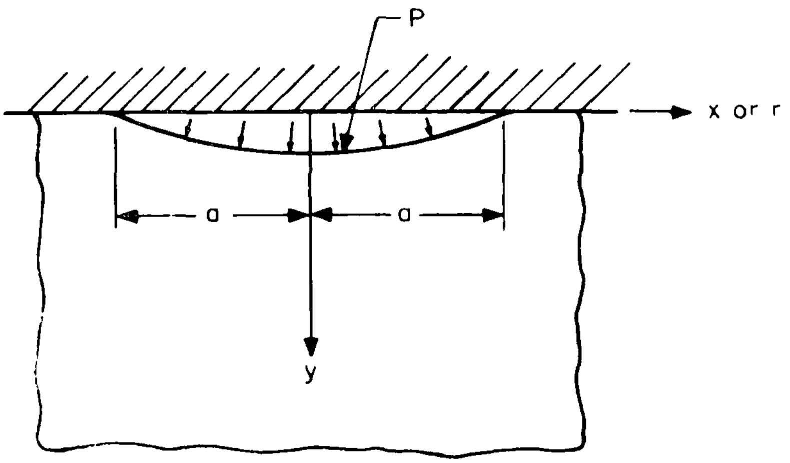

FIGURE 4b Pressurized block specimen with penny-shaped circular flaw or infinite strip central unbond.

Centrally unbonded block of infinite extent (Figure 4b)

It is not necessary however, so far as continuum mechanics stress analysis is concerned and the problem demands, to accept all of these confining assumptions. If the thickness of the plate of the previous example increases, it finally becomes so thick that simple theory is no longer applicable. In the limit therefore, one considers a semi-infinite half space which is unbonded over a width $2a$ and infinite length. After integrating strain energy of deformation over the volume, and equating its change with respect to increased debond area to the adhesive fracture energy one finds that[14]

$$\gamma_a = \frac{3\pi}{8}\frac{p_{cr}^2 a}{E} \; : \quad \nu = \frac{1}{2} \tag{10}$$

which can be compared with (9).

Centrally unbonded thin plate of finite thickness

Another related geometry can also be easily dealt with. When the plate thickness becomes rather small the stretching energy due to in-plane stresses increases compared to the bending energy. Indeed in the limit case of a very thin plate or membrane, the bending energy is vanishingly small compared to the energy of stretching. A rubber balloon falls into this category and its non-linear increase in size with internal pressure is a matter of common experience. In this case one finds it necessary to consider both the stretching displacement $u(x)$ as well as the normal bending deflection, $w(x)$. Two differential equations are involved, but the solution for an infinite length strip unbonded over a length $2a$, and clamped at both ends is available[15,16] actually for both a pressure and temperature loading. The latter solution may be expected to be of some value in conjunction with estimating debonding due to the curing stresses after polymerization.

Williams[15,16] has given the general solution for this problem, actually including varying pressure, temperature, and material properties, as well as for both clamped and simply supported plate boundary conditions. From these more general solutions and graphs of the results it is a sufficient illustration for our present purpose to extract only one of the simpler results, i.e. the membrane strip, to show the extent of more sophisticated analysis which is available if desired or necessary. The pertinent equations are

$$\frac{3(1-\nu^2)}{4}\frac{pa^4}{Eh^4} = \left[\left(\frac{w_o}{h}\right)^2 - \frac{3}{2}(1+\nu)\alpha\Delta T\left(\frac{a}{h}\right)^2\right]\frac{w_o}{h} \tag{11a}$$

$$\gamma_a = \frac{4Eh}{3(1-\nu^2)}\left(\frac{h}{a}\right)^4\left[\frac{7}{6}\left(\frac{w_o}{h}\right)^2 - \frac{3}{2}(1+\nu)\alpha\Delta T\left(\frac{a}{h}\right)^2\right]\left(\frac{w_o}{h}\right)^2 \tag{11b}$$

$$\sigma_s = \frac{pa^2}{2w_oh} = \frac{2E}{3(1-\nu^2)}\left(\frac{h}{a}\right)^2\left[\left(\frac{w_o}{h}\right)^2 - \frac{3}{2}(1+\nu)\alpha\Delta T\left(\frac{a}{h}\right)^2\right] \tag{11c}$$

where E, ν, h, and a, etc. are as previously defined, w_o is the center deflection of the strip, α is the temperature coefficient of expansion and ΔT the temperature change. In the simple case, for example, of no heating $\Delta T = 0$, and

$$\left.\frac{\gamma_a/a}{E}\right|_{\Delta T=0} = \frac{7}{6}\sqrt[3]{\frac{3(1-\nu^2)}{4}}\left(\frac{a}{h}\right)\left(\frac{P_{cr}}{E}\right)^4 \tag{12}$$

or in terms of the critical pressure for a known adhesive fracture

$$\frac{p_{cr}}{E} = \sqrt[4]{\frac{288}{344(1-\nu^2)}}\left(\frac{h}{a}\right)^{1/4}\left(\frac{\gamma_a/a}{E}\right)^{3/4}; \quad \text{membrane} \tag{13}$$

which values are of interest to compare to the previously derived ones

$$\frac{P_{cr}}{E} = \sqrt[2]{\frac{3}{2(1-\nu^2)}}\left(\frac{h}{a}\right)^{3/2}\left(\frac{\gamma_a/a}{E}\right)^{1/2}; \quad \text{thick plate} \tag{14}$$

$$\frac{P_{cr}}{E} = \sqrt{\frac{8}{3\pi}}\left(\frac{\gamma_a/a}{E}\right)^{1/2}; \quad \text{infinite block} \tag{15}$$

As all the numerical constants are of order unity, it is interesting to note that for the same materials, the critical stress predicted for thinner membranes is substantially above that predicted using plate theory. The specific transition from the thick plate through the thin plate regions to the membrane can be deduced if desired using the appropriate thin plate expressions from Ref. 15. Just recently Bennett[17] has completed the similar analysis for the circular or blister configuration with arbitrary thickness, and using numerical analysis has filled in the precise calibration curve between the two limits given earlier for the elementary case (Ref. 18).

Thermal debonding of a membrane

Another simple calculation can also be made as an outgrowth of the foregoing plate strip analysis, illustrating the type of estimates which can be made for blisters which debond from surfaces, as in paint, when subjected to too much heat. While the basic solution for an arbitrarily variable temperature distribution through a thin plate is given in Ref. 16, it is particularly easy to see the nature of the result from the criticality condition (11b), in which the value of w_o/h to be inserted is taken from the possible equilibrium conditions of the strip in (11a). For example, if there is no imposed pressure, and the temperature is uniformly distributed through a membrane, (11c) gives the buckling or bulge deformation with temperature as

$$w_o/a\,|_T = [(3/2)(1 + \nu)\alpha\Delta T]^{1/2} \tag{16}$$

thus in (11b) $\Delta T_{\rm cr}$ to cause unbonding is

$$\gamma_a = \frac{4}{3}\frac{Eh}{1 - \nu^2}\left[\frac{7}{6}\left(\frac{w_o}{a}\right)_T^2 - \frac{3}{2}(1 + \nu)\alpha\Delta T\right]\left(\frac{w_o}{a}\right)_T^2 = \frac{Eh}{2}\frac{1 + \nu}{1 - \nu}(\alpha\Delta T)^2$$

or

$$\alpha\Delta T_{\rm cr} = \sqrt{\frac{2(1 - \nu)}{1 + \nu}\frac{\gamma_a/h}{E}} \tag{17}$$

which should give a reasonably good estimate for very thin polymer films.† For thicker or metallic films, the more complete analysis[13] must be used.

In any event, the point of this section is to show that continuum mechanics can in principle be developed to treat the rather complicated problem of adhesive debonding of a heated or, what is the same thing, cure shrunk bond. The only real question is the practical one of required accuracy for time invested within the economical necessity.

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† If the blister is not subjected to pressurization, and if the temperature difference is negative, i.e. relative cooling of the thin film, then the only solution of (11a) would be zero deflection. Under such a condition, uniform tensile stress of $\sigma_s = E|\alpha\Delta T|/(1 - \nu)$, would develop in the film (see (11c)).

Localized modulus variation near the interface

It frequently happens that there are localized changes in the material properties of two different materials when they are placed in contact. On the one hand they can be due to chemical interaction, or frequently more mechanical as when a liquid polymer is cast and cured against a fixed surface. In this latter case, the random growth of the polymer chains is inhibited as they approach the fixed boundary and tend to bend and lie parallel to its surface. The net result is a localized boundary layer or "skin effect", which is expected to produce a different result than if the, say, material modulus was uniform directly up to the interface.

Again, we find there are two ways of approaching this problem from the point of view of continuum mechanics. First of all, it makes little difference in principle to a stress analysis as to whether the material properties are isotropic, or inhomogeneous. In practice, however, it is usually more desirable to obtain a qualitatively correct answer and improve it to the degree required. This philosophy is pertinent here, and the problem could be formulated as one of two dissimilar orthotropic materials bonded along the abscissae $x > 0$ and free along $x < 0$. Actually this was done several years ago in one case in conjunction with analyzing the characteristic stresses which might arise in the vicinity of a geophysical fault between two strata[9]. In that case however, the material properties above and below the fault were assumed individually and separately isotropic and homogeneous. An analytical extension of this problem based upon our earlier work, and now being completed, assumes that there are orthotropic properties in the media, essentially such that the Young's modulus $E = E(y)$, to account for a harder or softer material near the interface than in the interior.

A more direct way of exhibiting the general effect however is to use the simpler case of a split beam, in order to show again that this variation can be treated—and improved upon in accuracy as the circumstances warrant. Consider, therefore, the plate strip shown in Figure 5 where the origin of the axis of y is at the bottom of the thickness, h. After assuming plane sections remain plane under bending, only two conditions are required. First, by assumption, the sum of the x-forces integrated with respect to y, N_x, are zero, and the moment of the internal stresses must equal the externally applied moment. Upon selecting a representative modulus variation which can approximate either an increased or decreased localized interfacial stiffness,

$$E = E_o + E_1 \exp(-\lambda y/h) \tag{18}$$

depending upon the sign chosen for E_1 (see Figure 5a), one can apply the force and moment conditions to find what amounts to a multiplicative

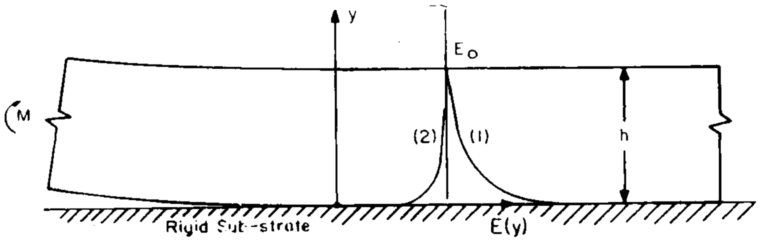

FIGURE 5a Skin effect modulus variation $E(y) = E_0 + E_1 \exp(-\lambda y/h)$. Curve (1) shows $E_0 > 0$, curve (2) shows $E_1 < 0$.

correction factor $g(\lambda, E_1/E_o)$ to the modulus E_o due to the change in interfacial stiffness.

In most cases of adhesive joints, the chemical or mechanical effect dies away very rapidly such that the decay constant, λ, in (18) is quite large, typically of the order of 10 to 20; furthermore, generally $|E_1/E_0| < 1$. Under these conditions the general results[19] given in the symposium proceedings can be simplified to give

$$E = E_o g(\lambda, E_1/E_0) = E_0[1 + (3/\lambda)(E_1/E_0) + \ldots]; \quad \lambda \gg 1 \tag{19}$$

If, therefore, we consider the centrally unbonded pressurized strip (compare Eq. 9) the associated approximation accounting for the interfacial stiffness effect would be

$$\gamma_a = \frac{p^2a^4}{18D} = \frac{p^2a^4}{18D_o}\left[1 - \frac{3}{\lambda}\frac{E_1}{E_o} + \cdots\right] \tag{20}$$

There are two questions to be answered here however. First, whether the formula is being used to measure γ_a from (20), or second, whether γ_a is known from, say, an independent measurement and the effect of a change in the surface modulus at $y = 0$, i.e. $E_s = E_o + E_1$, upon bond strength is being examined. In the latter form, with γ_a fixed by the interface conditions, the inversion of (9) gives

$$P_{cr} = \sqrt{\frac{3}{2}\frac{(E_0 + E_1)\gamma_a/a}{(1 - \nu^2)}\left(\frac{h}{a}\right)^3}\left(\frac{1 + \dfrac{3}{2\lambda}\dfrac{E_1}{E_o} + \cdots}{1 + \dfrac{E_1}{E_o}}\right)^{1/2} \tag{21}$$

The correction factor in brackets is plotted in Figure 5b and shows for example, that if the stiffness in the interior is substantially less than the interface stiffness, measured by the decay constant λ, the bond strength will drop off according to (21). Contrarily, if any softening lies at the interface, with complete (harder) cure in the interior, the bond strength will increase.

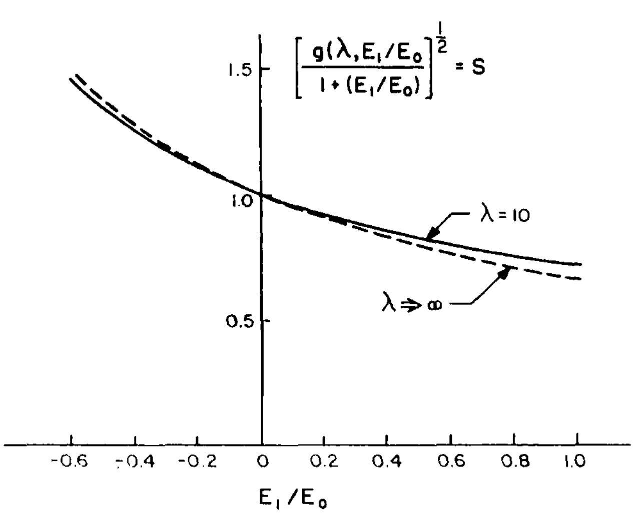

FIGURE 5b Effect on increasing critical stress S times due to skin effect modulus.

To reiterate however, the first point, if the test is being used to deduce γ_a, the bulk property away from the interface, i.e. E_0, is being used in the formulas, then only an apparent value of γ_a will be calculated, within the factor $g(\lambda, E_1/E_0)$.

The effect of an intermediate adhesive interlayer

While in some cases it is sufficient to consider only a bimaterial system, such as a plate or block cast onto a substrate, it more frequently happens that two pre-formed materials are bonded together with a third, adhesive, material. There has been frequent discussion on the relative merits of this interlayer material, such as should it have a high modulus, or be very thin. It is possible to analyze a model of such a multilayer bonded joint, and the one chosen for illustrative purposes consists of a centrally unbonded elastic strip plate bonded to a rigid substrate by an elastic adhesive of different material properties (E^1, ν^1) and thickness (h^1). The same elementary plate theory approach can be used in which it is assumed the adhesive interlayer behaves as a common Winkler foundation of modulus, k. It proves possible to estimate rather easily the effect of the interlayer, for a long, centrally debonded, sheet[20] or for a circular[21] blister specimen. (The cross sections would be the same in either case, although in practice the centrally unbonded strip geometry is of course more difficult to test because it is not easy to seal the ends when the specimen is pressurized.)

For illustrative purposes, however, because the formulas are simpler, consider the centrally bonded strip as a clamped beam. The solution of the

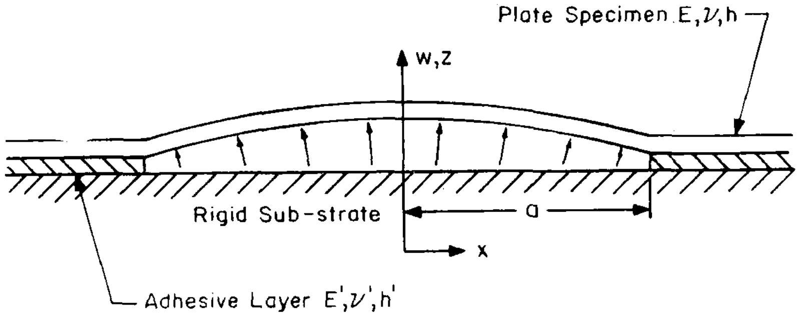

FIGURE 6 Blister specimen with finite thickness adhesive interlayer (Ref. 21).

field equation results in a critical pressure for the case of a thin elastic plate in which the primed quantities refer to the interlayer. For this situation, it will be noted that the critical pressure to cause failure increases with either a stiffer interlayer modulus or a reduced interlayer thickness. Specializing the general results[19,20] to the usual case of a relatively stiff sub-stratum, $k \to \infty$, one has

$$P_{cr} = \sqrt{\frac{3}{2}\frac{(h/a)^3}{(1-\nu^2)}\frac{E\gamma_a}{a}}\left[1 - 2\frac{h}{a}\sqrt[4]{\frac{(1+\nu^1)(1-2\nu^1)}{3(1-\nu^1)(1-\nu^2)}\frac{E/h}{E^1/h^1}}\right]$$

$$\cong p_{cr}^{(o)}\left[1 - C\left(\frac{h^1}{E^1}\right)^{1/4} + \cdots\right] \tag{22}$$

It should also be noted that it is the *ratio* of h^1/E^1 that is the major controlling parameter, not the modulus or thickness separately. This point probably has more general practical implications.

It is also possible to obtain an initial estimate for the locus of failure in the case the substratum is not rigid. In this case, providing the lower adherend is platelike, the elastic analysis leading to (22) can be extended to the "double-blister" situation in which adhesive fracture can take place between the interlayer and either of the two adherends, or alternatively, depending upon the adhesive strength ($\sim E\gamma_a/a$), within any of the three materials as a cohesive failure. A summary of the principal results is given in the proceedings[19] based upon the separate more complete analysis.[22] Inasmuch as these results have not yet been confirmed by experiment, further discussion will be omitted.

THE PRESSURIZED BLISTER EXPERIMENTAL CONFIGURATION

So far there has been considerable emphasis upon a centrally unbonded infinite plate strip pressurized blister configuration. The reason is mainly because of the relative ease with which the various changes in geometry and materials could be dealt with analytically and thus exhibit the major phenomenological features. From the experimental point of view however, this configuration is rather poor because of the difficulty in pressure sealing the open ends of the strip. Several other practical matters also impede a simple evaluation of the adhesive fracture energy. First, we have found that it is difficult to construct a specimen for which the adhesive bonding or glue does not accumulate at the crack ends or along the sides of the specimen thus leaving a lump at precisely the point where the debond is to initiate. Also, it is often not easy to control the atmospheric environment surrounding the progressing debond and while these and other practical objections can be overcome, our search for an alternate simple test specimen led to consideration of the pressurized blister test originally proposed by Dannenburg[23] for the adhesion of paint. A Griffith-type energy balance of this geometry, but with a central point loading, was next contributed by Malyshev and Salganik[24]. Our work consisted of combining these two features, i.e. a self centering uniform pressurization specimen and a continuum mechanics energy balance, into the pressurized blister or circular pancake specimen (Figure 7).

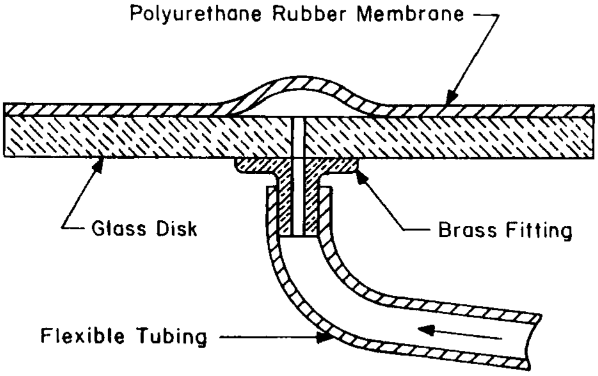

FIGURE 7 Sketch of pressurized blister specimen (Ref. 17).

The pressurized blister test

Paralleling the development of Eqs. (9–10) consider therefore a thin elastic disk bonded to a rigid substrate for which one may write from the principle of energy conservation, that the work done by the applied pressure moving through the virtual displacement must be balanced by the change in internal strain energy plus the change in the energy to create any new surface. One finds for the case of an aleastic "blister" on a rigid substrate

$$\gamma_a = \frac{3(1-\nu^2)}{32}\frac{p_{\mathrm{cr}}^2}{E/a}\cdot\left(\frac{a}{h}\right)^3 \tag{23}$$

It proved experimentally convenient to observe the critical pressure, P_{cr}, at the same instant as the radius increased, thus expressing (23) in the form

$$p_{\mathrm{cr}} = \frac{\{512\,Eh^3\gamma a/[3(1-\nu^2)]\}^{1/2}}{(2a)^2} = \frac{k\gamma_a}{(2a)^2} \tag{24}$$

which thus leads one to expect a hyperbolic-type variation of the experimental data of p_{cr} versus blister diameter squared, as confirmed in Ref. 18.

APPLICATIONS

In the previous discussion, the major emphasis has been upon the analytical and experimental ease with which a technically useful potentially time-temperature dependent quantity, the adhesive fracture energy, $\gamma_a(t/a_T)$, can be measured. It should be recognized however that the end result is not property measurement alone, but to use these data subsequently to analyze other engineering configurations and to be able to predict, *a priori*, when adhesive debonding will occur. Providing then only that the interface conditions in the new design are identical to the laboratory specimen for which γ_a was measured, e.g. surface roughness, cleanliness, environment, and that numerical complexities of the stress analysis are not insurmountable, which is unlikely in these days of high speed computers, there is no reason why this engineering fracture assessment cannot be made. It should be emphasized that this point is independent of whether or not the physical chemist understands the connection, if any, between the specific fracture energy γ_a, and the interfacial molecular structure.

From an engineering standpoint, this measured γ_a value is more useful than the commonly obtained "peel strength" because within some qualifications expressed in the conclusions, as the fracture energy is a fundamental material property, independent of being measured in tension shear, or torsion it can be determined once, and then used in the subsequent stress and fracture calculations much like the other material property data, e.g. Young's modulus, Poisson's ratio, or tensile strength.

The following examples include some of those with which we have had personal experience and a reasonable amount of quantitative success.[19]

Thermal debonding of a rubber cylinder from its container[25]

In this case, a glass cylinder was filled with a polyurethane rubber having a lower coefficient of thermal expansion than the glass. After curing, the temperature was to be dropped, tending to pull the rubber inward from the container walls and debonding it at the ends. While more detail will be reported in a subsequent paper, note here that the design curve showing safe and unsafe operation was confirmed by a measurement of adhesive debonding, recorded by X-ray analysis, at the end of the rubber at the glass interface.

Material shear-out in a cylinder under axial acceleration[26]

In a somewhat similar geometry except for the tube being steel and the filling being a solid rocket fuel, it was desired to predict the maximum axial acceleration which could be withstood without the fuel debonding from the sides of the cylinder. Using a separate measurement of γ_a between propellant and steel and the simple analysis given in reference, bounds upon the limiting acceleration could be estimated.

Explosively bonded blister steel specimens

Through the courtesy of a colleague, Dr. A. A. Ezra, University of Denver, we obtained several explosively welded steel specimens. They were essentially thick cubes approximately one inch on a side to which had been explosively bonded on one side, a thin steel sheet of one-tenth inch in thickness. After carefully tapping through the block perpendicular to the thin plate, pressurized oil was applied through the hole in an attempt to lift off the sheet in a blister experiment. After several tries, a successful technique was developed and an adhesive fracture energy approaching 90 percent of the cohesive fracture energy ("fracture toughness") of the steel was attained. In a sense the ratio of γ_a/γ_c could be viewed as a weld efficiency, although it is too early our exploratory investigations to be definite. A recent report on this subject in has just been presented by DeVries *et al.*[27]

Evaluation of dental adhesives

The analysis of the pressurized blister test was conducted assuming that plate and/or membrane theory was adequate to handle the stress analysis, even acknowledging other shortcomings in the analysis. Fortunately, the block specimen does not contain many of these approximations, and furthermore is very appropriate for a series of tests in conjunction with our dental research. For a very thick (infinite) block of elastic material, an exact analysis can be made based upon the work of Mossakovskii and Rybka.[14] In this case the adhesive fracture energy between the two materials can be evaluated as

$$\gamma_a = p_{cr}^2[2(1 - v^2)/\pi](a/E) \tag{19}$$

including the effect of the stress singularities. Preliminary work in our laboratory using the pressurized block, primarily in conjunction with our dental adhesive evaluation, has indicated such an experimental configuration is feasible.[28]

Adhesive debonding of an elasto-plastic plate from a rigid substrate

Another paper,[19,29] presents some early results and experimental data for the debonding of a metal plate strip or beam from a rigid substrate. A bimaterial combination is considered, with no interlayer, and deformations of the substrate are neglected. The problem is a direct analog to the first one considered in this paper based upon the classical Obreimoff calculation. Whereas this previous case, and most others encountered in the literature assume elastic deformations and classical beam-bending theory—even when the assumptions are patently violated as in a 90° bend in a bend! These calculations consider a material whose stress-strain curve is assumed to be elastic-purely plastic with the limiting plastic stress being σ_0. While many materials do not completely follow such an ideal non-strainhardening material behavior, the results are important because it exhibits the qualitative effects to be expected due to plasticity, and moreover, has some direct application to a double pressurized blister test in which for example, two explosively welded beams or plate strips having an initially small area of central unbonding can be separated. (In principle, if the materials were identical and chemically clean, then the measured adhesive fracture energy between them should approach the cohesive fracture energy in either of the two separately. In some of our tests to date, we have achieved values of γ_a of the order of 90 percent of the γ_c values in steel.)

The elasto-plastic analysis proceeds in essentially the same manner as before, with the basic assumption that plane sections remain plane after straining even though the stress distribution changes from linear up to the elastic limit to a truncated triangle as the outer beam fiber, and subsequently the inner fibers, reach the (maximum) yield stress. It should be mentioned, incidentally, that it is not necessary for the beam to debond from the substrate; it could be so "soft" that a fully-developed plastic hinge develops at the clamped end before the adhesive strength of the bond is reached.

Our preliminary experiments on bonded aluminum beams have been encouraging, although structural bonding adhesives (3M Company 2216B/A) were used rather than explosive welding. Values of $\gamma_a = 9 \times 10^5$ ergs/cm^2 $= 5$ in-lbs/in^2 were obtained in the experiments reported more fully in Refs 19, 29. As emphasized earlier however, the important point to make in this paper is that another engineering material parameter, this time plasticity, can be incorporated quantitatively into a continuum mechanics analysis.

Adhesive debonding of a single lap shear joint

Building upon the classical Goland-Reissner elastic analysis[2], which was one of the first analytical attempts at predicting adhesive debonding, Chang *et al.*[30] have with minor modifications incorporated the Goland-Reissner calculations of stresses in the adherend and adhesive interlayer into an energy balance calculation of the same type used in all the Region II type fractures discussed herein. The main purpose of the calculation was to see if the results predicted from the energy balance would be more consistent in predicting fracture than the maximum stress (Region I) type criterion which was initially adopted (1944). In short, the answer is affirmative and was confirmed by experiment.

On the other hand the test results also showed that in the time-temperature regime wherein the mechanical properties would normally be expected to be constant, there was a noticeable ($\sim 20\%$) variation in the adhesive fracture energy which could not be explained except by assuming the mode of fracture, and the associated new surface being generated, was being influenced by the relative amounts of shear and normal stress being imposed on the interfaces. This result of course is not unexpected, but, as discussed further in the conclusions, has led us to make a more detailed examination of the problem with specific reference to various adhesive configurations used in engineering design.

Time dependent (viscoelastic) adhesive fracture

In none of the examples described to date has the time and/or temperature dependence of the material properties been introduced explicitly. In many polymers, however, and certain metals at elevated temperatures, these effects can have a profound effect upon cohesive or adhesive fracture. Our present understanding permits some quantitative deductions providing the material behavior is linearly viscoelastic. By utilizing a spherical flaw model of a flaw in an incompressible but linearly viscoelastic medium subjected to uniform external tension, Williams[11] was able to deduce an exact extension of Griffith brittle fracture theory for this special case. It verified the intuitive feeling that the time-dependent critical stress, σ_{cr}, to initiate fracture was of the qualitative form

$$\sigma_{cr}(t_f) = k\sqrt{\frac{E^*(t_f) - \gamma_c}{a}} \tag{25}$$

where a was the flaw size. $E^*(t_f)$ is a time-dependent modulus which may be different for each loading history. However, for qualitative purposes it may be thought of as a relaxation modulus which decreases from a high short time, glassy value (E_g) to a low, long time, rubbery modulus (E_e) over several decades of time. For a constant value of γ_c, the time to fracture (t_f) would be given implicitly by (25). Since that paper[11], Bennett *et al.*[31] have shown that γ_c is also time-temperature dependent, varying, in a polybutadiene by a factor of 50 over 6 decades of log time. This behavior leads one to suspect that similar variation could be anticipated for γ_a. This latter suspicion has recently been verified on a polyurethane-quartz material combination[32]. Hence the expected adhesive behavior would be of the qualitative form

$$\sigma_{cr}(t_f) = k\sqrt{\frac{E^*(t_f)\gamma_a(t_f)}{a}} \tag{26}$$

As a simple example, consider the response of a centrally debonded pressurized strip of linear viscoelastic material[33]. The time-dependent deflection (w) of the strip of length $2a(t)$ can be deduced to be

$$24Iw[x, t; a(t)] = L^{-1}[\bar{q}(p)p\bar{D}_{crp}(p)][a^2(t) - x^2]^2 \tag{27}$$

in which L^{-1} indicates an inverse Laplace transform, and $\bar{q}(p)$ and $\bar{D}_{crp}(p)$ indicate Laplace transforms of the time-dependent loading per unit width $q(t)$, and creep compliance, $D_{crp}(t)$ respectively. The center of the strip is at $x = 0$ and the strip is assumed rigidly clamped at $|x| = a(t)$†. The length of the beam, $2a(t)$ can change with time if debonding occurs at these bonded ends. For this long strip the moment of inertia per unit length, including the plane strain factor of $(1 - \nu^2)$ in the modulus can be expressed as $I = h^3/[12(1-\upsilon^2)]$ ends. For this long strip the moment of inertia per unit length,

---

† R. J. Nuismer has pointed out that for adhesive debonding the solution (27) does not satisfy the strict boundary conditions of the elementary beam theory, i.e. $w[a(t), t] = \partial w[a(t), t]/\partial x = 0$, which require that the material be undisturbed for $|x| > a(t)$. For this region, as far as the material response is concerned, it recognizes zero time as beginning only after the debond passes the debond point and not from the time of initial load application which could be substantially prior to any debond. From the physical standpoint, because the beam theory only imposes approximate boundary conditions at the clamped end, actually stress and deformation does extend past the assumed clamped end position. Thus, the material for $|x| > a(t)$ would actually sense time measured from the time of initial load application. A more complete calculation is underway. Meanwhile, the results of (27) seem to lead to reasonable answers.

including the plane strain factor of $(1 - \nu^2)$ in the modulus can be expressed as $I = h^3/[12(1 - \nu^2)]$.

The integro-differential equation for the determination of the time-dependent crack position, $a(t)$, after applying the time-dependent form of the energy balance[11] becomes

$$\int_0^t [a^2(\tau) - 3a^2(t)]L^{-1}\bar{q}p\bar{D}_{\text{crp}} \frac{\partial}{\partial t} \{q(\tau)[a^2(\tau) - 3a^2(t)]\}d\tau = 36I\gamma_a(t) \tag{28}$$

But up to the time of fracture initiation, $t = t_f$, the length of the beam has still not changed from its initial length $a(0) \equiv a_o$, so that one can write

$$\int_0^{t_f} - 2a_o{}^2 2L^{-1}[\bar{q}p\bar{D}_{\text{crp}}] \frac{\partial}{\partial t} [-2a_o{}^2 q(\tau)]\, d\tau = 36I\gamma_a(t_f) \tag{29}$$

from which the time to fracture, t_f, is to be deduced. It is apparent that the time to initiation of the unbond will depend upon the history of the pressurization $g(t)$ and the viscoelastic material properties reflected in the creep compliance.

As a simple illustration, assume the pressurization linearly increases with time,

$$q(t) = mt \tag{30}$$

Inserting this loading into (29) and computing the inverse Laplace transform from its convolution integral as

$$L^{-1}[\bar{q}(p) \cdot p \cdot \bar{D}_{\text{crp}}(p)] = mD^{(1)}(t)$$

in which it is convenient to define

$$D^{(i+1)}(t) = \int_o^t D^{(i)}(\xi)d\xi; \quad D^{(o)}(t) \equiv D_{\text{crp}}(t)$$

one finds

$$(mt_f)^2 = q^2(t)\Big|_{\text{ramp}} = \frac{[18E_q I\gamma_a(t_f)]/a_o{}^4}{\left[\dfrac{D^{(2)}(t_f)}{D_g t_f/2}\right]} \tag{31}$$

In the case of a very fast rise in pressurization, the debonding will take place in vanishingly small times for which $D^2(t_f \to 0) \to D_g t_f/2$ so that

$$q^2 \underset{\substack{\text{sharp}\\ \text{ramp}}}{\to} \frac{18E_g I\gamma_a{}^{(g)}}{a_o{}^4} = \frac{3}{2(1 - \nu^2)}\left(\frac{h}{a_o}\right)^3 \frac{E_q\gamma_a{}^{(g)}}{a_o} \tag{32}$$

which approaches the elastic result (9). For other, slower loadings, the character of (31) is as expected from the qualitative considerations because the creep compliance is approximately the inverse of the relaxation modulus, and the double integration of the compliance characterization happens to be that which corresponds to a ramp-loading input, i.e. other loading histories give a different number or combinations of integrals of the compliance.

It is also possible to deduce from the general integro-differential equation (28), the velocity of the crack after fracture initiation, although for montonic increasing loading in thin sheets, for example, it appears that plasticity will have to be incorporated in order to predict finite crack propagation velocities. It appears that for decreasing loads after initiation, finite crack velocities may be calculated without invoking plastic dissipation. Further effort in this area is required because there are certain experimental advantages in deducing the critical fracture energy from photographic measurements of a moving crack as compared to somewhat subjectively deducing the "first" motion of a small pre-cut flaw.

CONCLUSION

Because of the growing technological need for a more cooperative effort between continuum mechanics and physical chemistry in order to improve the quality and understanding of adhesive bonds, this paper has attempted to describe how adhesive failure would be treated from the standpoint of a stress analyst. Two complementary fracture criteria are involved depending upon the size and distribution of inherent flaws in the vicinity of the interface. In the more probable case of Region II or flaw controlled failure, there are essentially two deformational mechanical property descriptors required, e.g. shear modulus and bulk modulus, which for rubbery (incompressible) polymers can be reduced to a relaxation modulus. In addition, there are the specific fracture energies of cohesion of the individual component materials and of the adhesive interfaces.

With some minor reservations regarding the geometry of the assembly because it affects the accuracy of predicting the stress and strain fields in a practical computational sense, there are only two major impediments to a technologically satisfactory solution to adhesive bonding problems. First, it is necessary to know the size and location of any above average size initial or inherent flaws in the part in order that an appropriate mechanics analysis can be made. Massive, opaque, or inert parts give problems because present non-destructive testing (NDT) techniques are not wholly satisfactory Second, in the absence of further help from the chemist, a mechanics analyst presently relies upon the similarity of conditions in his test specimen and engineering prototypes as far as surface preparation and bonding conditions are concerned. Then the fracture energies measured in the laboratory can be used to predict fracture in other configurations of the same material combinations—without any knowledge of the chemistry involved!

Nevertheless, in all cases of bonded, different materials, there is upon separation, a combination of shear and extensional stress present. If therefore the test configuration, e.g. the blister test, does not exactly duplicate the proportionate amount of shear and extension present in the desired engineering design configuration, then one can not be completely sure that the measured value of γ_a will be the correct one to use in the prediction of fracture, notwithstanding the fact that the total work required to initiate debonding may be known. Using cohesive fracture terminology, material separation by extensional stress (only) is denoted Mode I, and by shear stress (only) Mode II or III depending upon its direction along the fracture surface. Now it develops that if the stresses are all known in the configuration either analytically or by numerical analysis, then the total work to create new adhesive surface can be deduced, at least as far as the mechanics is concerned. A problem arises however, because it is customary to define the total work (Γ) is the product of the specific fracture energy (γ_a) multiplied by the *projected* area of the fracture. If then an extensional mode of loading produces a different *actual* (roughened) area of fracture than does a shear mode of loading to the same critical absorbed energy at fracture, Γ_{cr}, then one would deduce an apparently different specific fracture energy γ_a^{I} *vs* γ_a^{II}, because of the assumed equal and constant value of the projected area incorporated in the definition of Γ_{cr}. While as a practical matter, the differences between a test and actual configuration may be minimized, particularly by appropriate choice of the test specimen so as to be generally representative of the conditions in the design, one should recognize the existence of this implicit assumption and proceed to establish the magnitude of its effect. At the present time we are conducting a series of tests in conjunction with fractographic measurements to this end. The ultimate objective is to be able to use the technical knowledge of adhesive failure in one interface situation to extrapolate to a somewhat different one with a minimum amount of testing. It is believed that here increased cooperation between mechanics and chemistry is essential, and for discussion purposes, the idea of an Interaction Matrix proposed by Kelley and Williams[34-37] is suggested as a possible point of departure in this joint venture.

There is one additional complexity that requires comment, and its brevity should not detract from its importance. Somewhere between the levels of continuum mechanics and quantum mechanics, it seems reasonable to anticipate a working hypothesis associating the cohesive fracture energies $\gamma_c{}^1$ and $\gamma_c{}^2$ of two *solid* materials and their combined adhesive fracture $\gamma_a^{(1,2)}$, e.g. $\gamma_a^{(1,2)} = (\gamma_c^{(1)} \cdot \gamma_c^{(2)})^{1/2}$ for certain cases of dispersion-controlled interactions. Indeed, Fowkes, Good, and others are intimately involved in this subject, and Fowkes has published a fairly recent paper whose title "Calculation of the Work of Adhesion by Pair Potential Summation"[38] neatly emphasizes the missing link as far as the continuum mechanics interest is concerned.

Thus while temporarily the mechanics analyst can circumvent a physiochemical understanding of adhesion by similarity testing, such as using the pressurized blister, block specimen, or even a shear test, additional contributions from the chemists on even an *ad hoc* basis showing reasonably quantitative associations between cohesive and adhesive fracture energy, albeit with "interfacial environmental" qualifications, would be most welcome.

Acknowledgement

This paper draws heavily upon previous work including a recent contribution to the Ninth Annual Conference on Adhesion and Adhesives[39] at City University, London, and a series of lectures at the University of Utah. Portions of this research were supported by the National Aeronautics and Space Administration and the National Institute of Dental Research. In addition, the author wishes to acknowledge expressly the educational, stimulating, and frequently spirited discussions with his colleagues and co-authors, especially K. L. DeVries, F. R. Eirich, and F. N. Kelley.

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