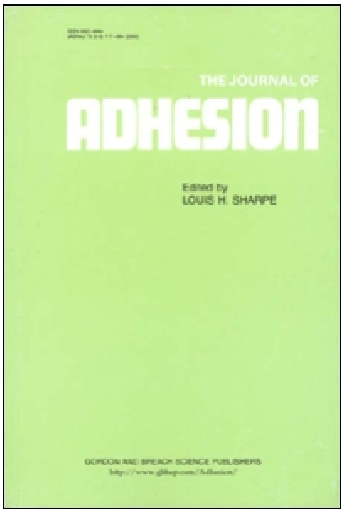

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Adherence of Elastomers: Fracture Mechanics Aspects†

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The adhesion forces which link two solids together are of the same nature as those which insure cohesion of solids (Van der Waals, ionic, covalent or metallic), and their thermodynamic transcription is the Dupré energy of adhesion $w = \gamma_1 + \gamma_2 - \gamma_{12}$, where γ_2 is the surface energy and γ_{12} are interfacial energy. Its maximum value is about $2\,\mathrm{J/m^2}$ for strong binding. However, the force to separate two solids in contact (pull out force or adherence force) depends on a number of parameters including the shape of the solids in contact, their rheological properties, the withdrawal velocity, and the stiffness of the measuring apparatus (soft or hard machines). Adherence is thus characterized by a coupling between mechanics and surface effects and can be studied by fracture mechanics, a field where such a coupling appeared for the first time (Griffith, 1920).

KEY WORDS Adherence; adhesion; cracking; elastic solids; viscoelastic solids; fracture mechanics.

ADHERENCE OF ELASTIC SOLIDS

For two solids in contact over an area A, the edge of the contact can be seen as a crack tip, advancing when the area decreases and receding when the area increases. The energies involved are simply elastic energy U_E, potential energy U_P and total surface energy $U_S = -wA$. Thermodynamics tells us that the crack is in equilibrium when the thermodynamic potential (Gibbs free energy at fixed load

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P, Helmholtz free energy at fixed grips) is extremum, i.e. $G = w$ (Griffith criterion) where G is the strain energy release rate. The equilibrium is stable, unstable or neutral according to the sign of the second derivative of the thermodynamic potential, *i.e.* $(\partial G/\partial A)_P$ at fixed load, or $(\partial G/\partial A)_\delta$ at fixed grips, and thus depends on the shape of the solids and on the stiffness of the loading system. For peeling or double cantilever beam (DCB) with applied momentum, equilibrium is neutral, for a flat punch on a plane or DCB with dead load equilibrium is unstable, DCB with a wedge inserted in it is stable, for a sphere or a cone on a plane it is stable over a range of loads or displacements and becomes unstable at a critical load or displacement. The adherence force is the load corresponding to neutral or unstable equilibrium (at which the crack propagates until complete separation). For a sphere on a plane, for which

$$G = \left(\frac{a^3K}{R} - P\right)^2 / 6\pi a^3 K$$

where a is the radius of contact, and K, an elastic constant, the adherence force is $P = -(3/2)\pi wR$ at fixed load and $-(5/6)\pi wR$ at fixed grips (JKR theory, Ref. 1). The adherence force is not always proportional to w, but can vary as $w^{1/2}$ for flat punch or DCB, or as w^2 for cones.

In the Griffith description, the crack tip has an elliptical shape which leads to singularities at the crack tip, the intensity of which is described by the stress intensity factor K_I. In fact, as pointed out by Barenblatt,[2] such infinite stresses are physically unrealistic. Instead of appearing abruptly at the crack tip, the adhesion or cohesion forces increases progressively, reaching the theoretical strength σ_{th} at the crack tip. They deform the crack as would do any stress system applied to the crack lips, and the crack has a short acute tip (the Barenblatt tip) with no singular stress (stress intensity factors due to external load and to cohesion forces cancel one another). It is this theoretical stress σ_{th} which moves with the crack and breaks the bonds one by one as a tip fastener does. It is also these adhesion or cohesion forces that provoke crack healing when external loading is insufficient ($G < w$). In fact the adherence force between two solids, in contact over an area A, is essentially due to the adhesion forces acting in the Barenblatt tip. For example, in $\pi/2$ peeling adherence is independent of the contact area and a hung load P is sustained only by the forces in the Barenblatt tip. For a sphere on a plane, the pull-out force is almost totally dependent on the value of w at the edge of the contact. This shows that the characterization of an adhesive joint by the mean stress at rupture is nonsense; fracture mechanics concepts must be used.

Since w is the integral of adhesion forces in the Barenblatt tip, the Griffith theory ($G = w$) gives a correct result as long as the Barenblatt tip is small compared to the crack length or to the contact radius. For adherence of soft tiny spheres, the JKR theory ($G = w$) leads to mean stress well above σ_{th}, and it not valid. The profile of the deformed sphere becomes smooth and the adherence is $P = -2\pi wR$ (DMT theory, Ref. 3). A simplified version of the Barenblatt model is the Dugdale model where the adhesion or cohesion force is assumed to have a constant value σ_0 over a length d at the crack tip. In this case, G, or more precisely the integral J, becomes simply $\sigma_0\delta_t$ where δ_t is the crack opening displacement at the limit of the cohesion zone. (A good example is liquid bridges where σ_0 is the Laplace pressure γ/r (r is the radius of the meniscus), and $\delta_t = 2r \cos \theta$ the crack opening displacement, hence $J = G = 2\gamma \cos \theta$. Evaluating G from the variation of potential energy at constant volume of the liquid bridge gives the force of adherence.[4]

ADHERENCE OF VISCOELASTIC SOLIDS

Elements of volume near the trajectory of a moving crack undergo a cycle of stress when the crack tip comes on and then comes off, whose characteristic time is of the order of d/v (where d is the length of the cohesion zone and v the crack velocity) and whose magnitude is proportional to σ_{th} and hence to w. In a dissipative material energy is lost during such a cycle, and the crack instead of continuously accelerating until the Rayleigh velocity, takes a limit velocity v, which is a function of the generalized force $G - w$ that moves the crack. In a viscoelastic solid the drag force on the crack will be proportional to w and a function of the loss modulus E'', a frequency dependent quantity, so that in the absence of inertial effects, one can write (Andrews and Kinloch,[5] Maugis and

Barquins[6])

$$G - w = w\varphi(a_T v)$$

or (1a)

$$G = w\phi(v)$$

(the factor a_T holds for temperature-velocity equivalence) which generalizes, for any geometry, the equation given by Gent and Schultz[7] for peeling. Inertial effects can be accounted for by writing

$$G = w\phi(a_T v) - \frac{dU_K}{dA} \tag{2}$$

where U_K is the kinetic energy of the system. Eq. (1) holds only for viscous drag which cancels with the crack velocity. A static friction term has certainly to be added for materials such as metals, where a finite stress must be applied to dislocations before they move and dissipate energy. Eq. (1) was quite well verified in all its consequences for adherence of glass on elastomers when only Van der Waals forces act, with crack propagation for $G > w$, and crack healing for $G < w$.[6,8] For polyurethane the variation of $\varphi(v)$ as $v^{0.6}$ at low velocity was correlated with the variation of E'' as $\omega^{0.6}$ at low frequency.

At high frequencies the loss modulus generally decreases, and the loss function $\varphi(v)$ decreases above a critical velocity v_c corresponding to a critical value G_c. As a negative resistance branch cannot be observed, the crack velocity jumps, sometimes over several decades, on a second positive branch, giving catastrophic failure. In the presence of an active medium reducing w, *i.e.* the forces in the Barenblatt tip, the $G(v)$ curve is shifted as long as the active medium can follow the crack velocity. If it can follow it until the velocity v_c, a loading that would have given subcritical crack growth, gives a catastrophic failure. This is the essence of Rehbinder embrittlement effects.[9] If, for specimen with stable geometry factor, *i.e.* $(\partial G/\partial A) > 0$, as peeling or double torsion, one tries to impose a mean velocity V in the negative resistance branch $d\varphi/dv < 0$, stick-slip motion is observed. The classical picture of a relaxation oscillation cycle between G_c, the second positive branch, $G_{\min}$, and the first positive branch, is valid only in absence of inertial effects. For peeling of an adhesive tape, Eq. (2), when variation of peel angle is neglected, leads to a Lienard differential equation which gives limit cycles in the phase place $G(v)$, quite distinct from the $\varphi(v)$ curve, with Hopf bifurcation at G_c and $G_{\min}$.[10,11] Three first order differential equations appear with peel angle variation, that can explain chaotic motion in some ranges of the parameters.

OTHER LOSSES

Besides the viscoelastic losses $w\varphi(a_T)$ due to the stresses moving with the crack, other losses can act and drag the crack. For instance, the presence of a liquid can reduce the surface energy and shift the $G(v)$ curve, but also gives rise to viscous drag larger than viscoelastic ones above a critical velocity, until cavitation occurs, as observed by Carré and Schultz[12] for peeling, and Michalske and Frechette[13] for rupture of glasses in water.

When weak binding (*e.g.* Van der Waals) occurs between a solid and a polymer, the threshold value G_0 for vanishing crack speed is the thermodynamic work of adhesion w. However, for strong interfacial bonds, values up to 100 J/m^2 for G_0 are easily reached, which are of the same order of magnitude as the value G_0^* obtained for bulk polymers (*e.g.*, by tearing). In this case, it is probable that molecular chains strongly held at the interface are drawn from the polymer as in crazing, and one can tentatively add to $w\varphi(a_T v)$ a friction term νfL where ν is the density of strong chemical bonds at the interface, L the length of polymer chains and f their friction coefficient, as proposed by de Gennes[14] for refracture of polymers after healing. Such an equation could account for the results of Ahagon and Gent[15] and Chang and Gent[16] on the proportionality of G_0 to the concentration of interfacial bonds and on the influence of crosslinking. The maximum value of ν is of the same order of magnitude as the number of chains broken by a crack in a bulk polymer and varies as $M^{-1/2}$. As L varies with the molecular weight M, the maximum value of G_0 is the G_0^* of the bulk polymer and varies as $M^{1/2}$ as observed by Gent and Tobias.[17] The problem of adherence in the presence of strong bonds is thus quite similar to that of fracture of bulk polymers where chains or fibrils are extracted and broken if too long. In the latter case G becomes independent of the molecular weight as discussed recently by

Prentice.[18] As the stress in the craze zone is nearly constant, this zone is a perfect example of a Dugdale zone at a crack tip[19].

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