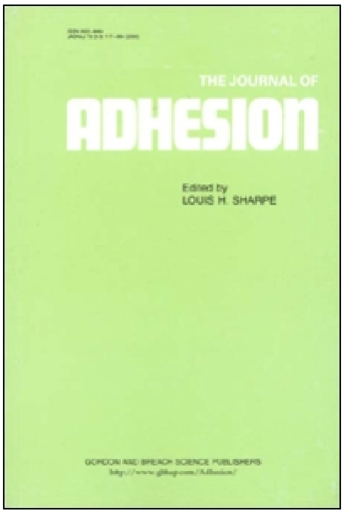

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Peel Adhesion of Solid Films-The Surface and Bulk Effects

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Peel Adhesion of Solid Films—The Surface and Bulk Effects

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The peel strength of rubber and paint films has been measured over a range of peeling velocities using a dead weight method. At low peel rates the peel force is fairly constant but rises rapidly at higher peeling speeds.

Experiments show that the peel strength is a function both of the energy of interfacial bonds which must be broken as peeling proceeds and of bulk energy losses in a viscoelastic peeling material.

The interfacial effect has two components: an equilibrium surface force which accounts for the peel strength at low velocities, and a viscous peeling force which depends on the peeling rate. This viscous interfacial force explains the increase in peel strength of purely elastic films at higher peeling velocities.

The energy loss in the bulk of the peeling film introduces two additional effects: a magnification of the peel strength in steady peeling over a certain velocity range, and a slowing down or stopping of peeling as transient relaxation occurs shortly after the application of the peel force.

I INTRODUCTION

Adhesion tests, which have much in common with fracture experiments on homogeneous materials, are usually interpreted theoretically using the energy balance criterion of Griffith.[1] In this theory, the strength of an adhesive joint is expressed in terms of a surface energy which depends on the materials forming the joint. Extensions of Griffith's theory have been successful in demonstrating how adhesion depends on the geometry and elastic properties of an adhesive system.[2,3]

The basic difficulty of this theory is the physical explanation of the surface energy term. Griffith interpreted the surface energy as the solid analogue of liquid surface tension and indeed estimated the surface energy of solid glass by extrapolating from surface tension measurements on molten glass. Unhappily, values of surface energy obtained in this way are usually much too low to account for the strength of homogeneous solids or of adhesive bonds. Also the apparent rise in surface energy with increasing fracture rate poses a fundamental problem. Even more difficult to explain on this basis is the occasional slowing and stopping of a crack shortly after the initiation of fracture.

In the literature, three approaches to these problems may be found, reflecting the views of engineers, physical chemists and rheologists respectively. The pragmatic contribution made by Orowan[4] and Irwin[5] was to replace the surface energy by an empirically determined quantity $R/2$ where R was termed the fracture energy. Subsequent developements of this approach, a branch of fracture mechanics, have concentrated on expressing R as a function of variables such as temperature, crack length and so on. A more fundamental view, which originated with Griffith, maintains that fracture depends mainly on surface forces acting between two bodies in close contact. Both reversible and irreversible surface forces have been proposed involving adsorption,[6] electrical charge separation[7] and diffusion.[8] Unfortunately for the surface chemists, it is impossible to separate two adhering bodies without deforming them and consequently the rheological properties of the materials must also be considered. In certain instances the bulk deformation is thought to dominate the fracture process.[9,10,11]

Clearly, a combination of these separate views is required to produce a more complete picture of adhesion and fracture phenomena. The global quantity, fracture energy, is a function of the surface and bulk processes which in turn may be expressed in molecular terms. It is the purpose of this paper to distinguish and measure the surface and bulk effects. In the first part an energy balance is constructed for the peeling system and the influence of lossy processes is predicted. Secondly, experiments designed to distinguish between surface and bulk effects are described and finally the results are analysed in detail.

II PEELING TEST—GENERAL THEORY

The peeling test, shown in Figure 1, has many theoretical advantages when used in the study of fracture: the peeling shape is simple and has been measured,[12] the geometry is weak allowing low stress experiments avoiding material non-linearity, and the geometry remains nominally constant as fracture proceeds so that under constant load steady fracture would be expected.

A theory of peel strength may be derived from an energy balance approach. The total energy U_T in the system is the sum of several energy terms, the principal components being the surface energy U_S, the strain energy U_E, the potential of the load U_P and the thermal energy U_L.

$$U_T = U_S + U_E + U_P + U_L \tag{1}$$

From the principle of energy conservation, this sum does not change when a small additional length ds of film is removed so that

$$\frac{\mathrm{d}U_T}{\mathrm{d}s} = 0 \tag{2}$$

The evaluation of the energy terms will now be considered for three simple cases, here termed *elastic peeling*, *steady peeling* and *transient peeling*.

Elastic peeling

For an elastic material peeling without energy conversion into heat and without significant film extension after separation from the substrate, U_E and U_L are constant so that

$$U_P = -FX = -F[s - (L - s)\cos\phi] \tag{3}$$

$$U_S = Wbs \tag{4}$$

where W may be identified with the work of adhesion.[13] Applying condition 2 we get

$$F = \frac{Wb}{(1 - \cos\phi)} \tag{5}$$

an attractively simple relationship.[14,15]

Steady peeling

In steady peeling the peel velocity and the peel bend shape are constant but heat is generated in the film so that U_L increases. Equation 5 must therefore be modified to give

$$F = \frac{1}{(1 - \cos\phi)}\left(Wb + \frac{\mathrm{d}U_L}{\mathrm{d}s}\right) \tag{6}$$

Two basic loss mechanisms may contribute to the heating of the film: an interfacial heating $\mathrm{d}U_{LS}$ associated with the irreversible separation of film and substrate, and a bulk heating $\mathrm{d}U_{LB}$ due to hysteresis losses in the visco-elastic peeling material. Treating these as independent we may write

$$F = \frac{1}{(1 - \cos\phi)}\left(Wb + \frac{\mathrm{d}U_{LS}}{\mathrm{d}s} + \frac{\mathrm{d}U_{LB}}{\mathrm{d}s}\right) \tag{7}$$

This is the equation to be analysed experimentally in sections 3 and 4 and theoretically in Sections 5, 6 and 7.

Transient peeling

In order to explain some curious transient phenomena exhibited by peeling films, it is necessary to study the case where the shape of the peel bend changes with time. This is a very difficult rheological problem since the elastic energy term no longer remains constant but is a function of bend shape which varies with time and peeling rate. However, after making some judicious simplifying assumptions an approximate theory may be derived. This is considered in Section 8.

III EXPERIMENTAL

The experimental objective was to distinguish and measure the surface and bulk effects in a peeling test. This is not an easy task since the bulk and surface properties of a material are closely related. Moreover, fracture tends to be a function of the product of surface and bulk properties so that both must contribute to fracture strength—this is shown most clearly in the Griffith theory where strength depends on the product of elastic modulus and adhesive energy.

Here we define the surface effect as that localised within about 10^{-2} μm of the interface so that for an ordinary peeling film, the surface contribution would not be expected to change with film thickness. However, it might be expected to vary strongly with surface treatment. The bulk effect on the other hand results from energy changes in the bulk of the material at distances greater than about 10^{-2} μm from the crack tip. This bulk effect would therefore be a function of film thickness yet would not be expected to vary with surface treatment. Certainly the bulk effect should be much influenced by changes in rheological properties of the materials used. However, care must be exercised here since such rheological changes may also have a bearing on the surface region, particularly where high stresses arise locally around the crack tip.

Having considered these arguments, four types of experiment were performed, two to isolate the surface effect and two more to study the bulk influence.

In the first experiment the thin film material was chosen to have a small bulk relaxation. It was envisaged that this would reduce the bulk losses to a small value and allow the surface effect to be studied in relative isolation. In order to localize the effect even further a very low strength interface was chosen, that between silicone rubber and poly(methylmethacrylate) (I.C.I. Perspex). Such low loads were necessary to peel these materials, less than 1 gm for a 1 cm width film of rubber, that it was hoped that non-linear effects could be avoided. The maximum strain in the peel bend was 4 percent, well within the linear region for this rubber. Of course, the strain near the crack tip must have risen to very high values, but it was thought that, for this system, gross energy losses due to this effect would be small. The fracture appeared to be reversible in this instance; the peeled film could be brought into contact with the Perspex and a strong bond formed after a short time. This suggested that local surface damage was slight.

Another experiment, also designed to indicate the magnitude of the surface contribution involved the measurement of peeling from a substrate before and after the application of a monolayer of surface active material. Any change in peel strength in this instance can only be attributed to a change in the surface properties.

Two further experiments were carried out to highlight the bulk effect. First a material with a large bulk relaxation was selected. Uroalkyd paint coated on clean glass was used. Although the glass was initially a high energy surface, readily wetted by water, after peeling the paint from its surface, the contact angle with water became appreciable and it was suspected that a thin layer of material from the paint remained on the glass after removal of the paint film. The adhesive energy in this case was therefore not expected to be very different from the rubber-Perspex system.

The second experiment designed to show the bulk effect involved the peeling of different thicknesses of rubber film from Perspex.

The experimental arrangement is shown in Figure 1. A film of liquid polymer was spread to a given thickness onto a sheet of optically smooth glass or Perspex and allowed to cure. New Perspex samples were used, the surface being washed gently in warm water and detergent and rinsed for a time in tap water until the water contact angle reached about 70 degrees. The glass was vapour degreased in isopropanol until the surface was readily wetted by water. The solidified polymer film was then partially peeled from the substrate and a weight attached. Peeling of the material was observed through the transparent substrate, the line of separation of the surfaces being clearly defined by white light interference fringes, and the peel velocity was measured. By varying the peel force a range of peeling velocities was studied from 10^{-3} μm sec^{-1} to 10^{4} μm sec^{-1}. All the measurements were made at 18°C.

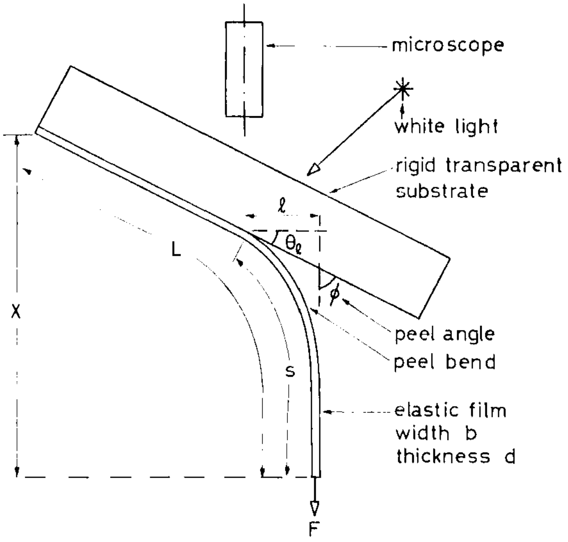

FIGURE 1 Elastic film peeling from a rigid substrate.

IV RESULTS

The dependence of peel force on peel angle was first investigated for a silicone rubber peeling from a Perspex plate. This rubber sample was 0.012 cm thick, 1 cm wide and was cured at 80°C for a week. Peeling was carried out at a number of different angles and the peeling force corresponding to very low peeling speeds (10^{-2} μm sec^{-1}) was measured. This force could be determined with some precision since the peeling force was not very dependent on peel rate at such low speeds of separation. The results, given in Figure 2 show reasonable agreement with the theory of Eq. (7) down to peel angles of about 12 degrees. In subsequent experiments the peel angle was maintained at $\phi = (\pi/2)$.

In order to investigate the surface contribution to peel strength, peeling measurements were carried out on films of room temperature cured silicone rubber cast on Perspex plates. This rubber was chosen for its low losses under the conditions of these tests. In order to define the rheological properties of the rubber in the peculiar geometry of the peeling test, the following method was adopted. A length of film was peeled off, the remainder of the film was clamped to prevent further peeling and a load was suspended from the free end of the hanging rubber strip. The parameter l, the distance between the

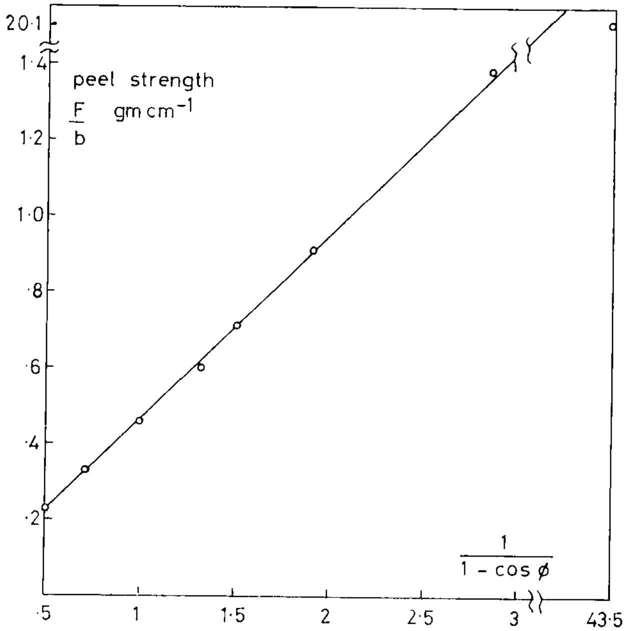

FIGURE 2 Dependence of peel strength on peel angle for a silicone rubber film on a Perspex substrate.

point of separation of Perspex and rubber and the line of application of the load, could then easily be measured as a function of time using a low power microscope. Figure 3 curve a) shows how *l* varied with time for a rubber strip 0.020 cm thick under a load of 1.02 gm. The Young's modulus is proportional[12] to the square root of *l* and may be seen to be relatively constant for this rubber, decreasing by about 5 percent in one hour.

When a film of this rubber was peeled from Perspex, the results shown in Figure 4 (points a) were obtained. At low velocities, less than about 10^{-1} μm sec^{-1}, the peel force became independent of peel rate but at higher velocities the peel force was seen to increase rapidly.

An important observation made during these experiments was that immediately after the load was applied to the film, the peeling velocity was highest. After a short time, another measurement of peel rate showed that the peeling had slowed down. The peel velocity changed typically by a factor of two during the period of the experiment as indicated by the spread of the points (a) in Figure 4 along the velocity axis. This slowing of the peel rate with time at constant load could not be explained in terms of a surface effect, since the phenomenon was quite reproducible at various points on the

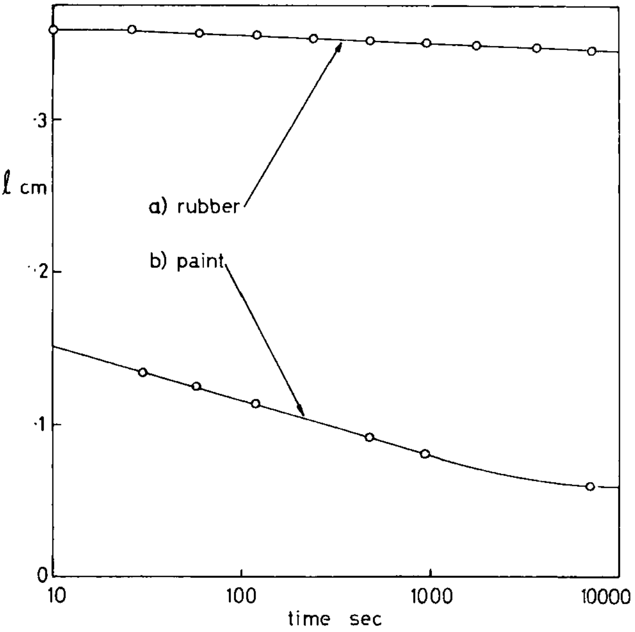

FIGURE 3 Relaxation of bend shape with time for the rubber and paint films.

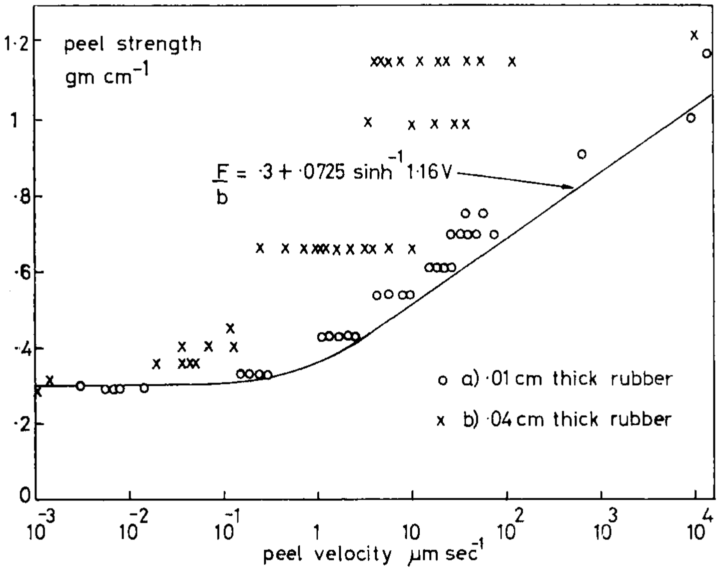

FIGURE 4 Peel strength of rubber from Perspex.

surface of the Perspex. The phenomenon is reminiscent of the crack slowing which sometimes occurs in the fracture of homogeneous materials and is probably of similar origin. It appeared that the gradual deceleration of the peeling paralleled the change in shape of the film with time. The suggestion was that the slowing was due to relaxations in the bulk of the rubber film. This conclusion was reinforced by the measurements of peeling force made on thicker rubber films peeling from Perspex (Figure 4 points b). When the film thickness was increased to 0.020 cm the peel velocity slowed by a factor of about four when the film thickness was 0.040 cm by a factor of about 40. A typical peel velocity versus time curve is shown in Figure 10 for a rubber film 0.040 cm thick peeling under a load of 0.66 gm.

When the peeling force was increased so that the peel velocity rose to about 1 cm $\sec^{-1}$ the slowing of the film could not be detected. It appeared that, at such high peeling speeds, the bulk losses had insufficient time to occur before the material had traversed the peel bend.

The bulk effect was further accentuated by using a polymer film with a large room temperature relaxation. In this case the polymer was a uroalkyd paint film 0.004 cm thick peeling from glass. The relaxation was measured in the same way as before and Figure 3 curve b shows that here the Young's

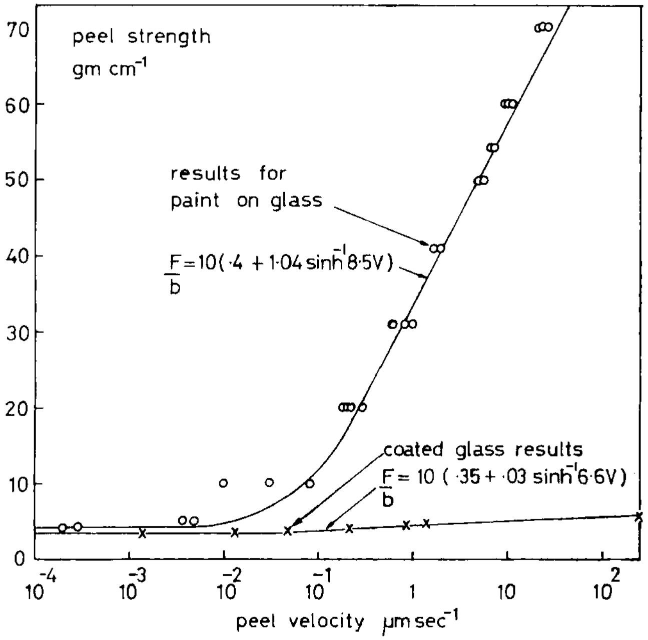

FIGURE 5 Peeling of a paint film from glass with and without a surface coating of dimethyl-dichloro silane.

modulus fell by a factor of about ten in one hour. Peeling results for this system are shown in Figure 5. The same basic shape of peel strength–peel velocity curve was obtained although the strength was much higher than for rubber on perspex. Once again some slowing of peeling was observed. When the glass was coated with a layer of dimethyl dichloro silane by retraction from solvent prior to painting, the peel adhesion was markedly different as Figure 5 illustrates. Athough the low velocity peeling force was reduced only slightly, at higher speeds the peel strength was reduced enormously by the surface treatment. In addition the slowing of peeling became very noticeable in this case, the peeling actually stopping after a short time.

V DISCUSSION OF EXPERIMENTAL RESULTS

Some qualitative conclusions may be drawn immediately from the experimental results. The most striking observation is that the peel force— velocity curves, Figures 4 and 5 and others not presented here, exhibit a characteristic shape. At low velocities (less than 10^{-2} μm sec^{-1}) the peel force tends to a value which is independent of peel rate. At higher peel rates the peel force rises rapidly and continuously. Figure 4 gives a clue to the cause of this behaviour since these results were obtained using a material whose bulk losses were small. The characteristic shape of the curve must therefore be a result largely of surface effects. Equation 7 for this case becomes

$$F = bW + \frac{\mathrm{d}U_{LS}}{\mathrm{d}s} \tag{8}$$

It is reasonable to suppose that at low peeling rates the irreversible component of Eq. 10 tends to zero so that the low speed peel equation is

$$F = bW \tag{9}$$

The equilibrium adhesive energy on this basis is 300 mJ m^{-2} which corresponds to a bond energy of about 4 kcal mole^{-1}, not an unreasonable value for the rubber Perspex interface.

The increase in adhesive force at higher peel speeds appears to be due to an interfacial dissipative process related to the rate at which the film and substrate are separated. This tentative theory is supported by the results of Figure 5 where the effect of a monolayer on the glass surface is shown. In the high speed peeling regime the peel force is dramatically reduced by coating the glass although the low speed force is not much affected. These results suggest that the surface forces between the solid bodies comprise a viscous component in addition to the reversible attractive component. A model for this behaviour is discussed in Section 6.

The influence of bulk losses on the peel strength is evident from two effects. First the very obvious slowing down of peeling as a function of time after the application of the peel load appears to depend on the bulk properties of the peeling film. This is shown by the results of Figure 4, points (b), where the slowing effect was increased by increasing the film thickness. Also in the experiments of Figure 5 the slowing effect became more obvious when the surface influence was reduced by the surface active monolayer. The mechanism of crack slowing is considered in Section 8.

The second consequence of bulk losses may be seen in the high value of peel force for the slow peeling regime of Figure 5. A load of 4 gm was required to initiate peeling of a 1 cm wide paint strip at very low speed. This high peel force is very difficult to explain in terms of adhesive energy alone. For example Eq. (11) would suggest an adhesive energy of 4000 mJ m^{-2} which is equivalent to a bond energy of around 50 kcal $mole^{-1}$, an incredibly high value for this system. It would appear that hysteresis losses in the peeling film must be invoked to explain such high adhesion. The magnitude of these hysteresis losses is estimated in Section 7.

VI THE SURFACE EFFECT

The experimental results suggest that the interfacial forces make two contributions to the peel strength of solid films, a reversible contribution due to the equilibrium separation of interfacial bonds of energy W, and a dissipative contribution determined by the rate of fracture of the bonds. These observations may be explained in terms of the following theory.

It is often assumed that two solid surfaces may be separated merely by overcoming the equilibrium interfacial forces of energy W associated with the surface bonds[16]. Figure 6 curve (a) shows a potential energy curve representing the adhesive energy between one solid surface and another as the surfaces are separated. As Tomlinson[17] and others have pointed out, this model cannot account for the irreversible component of the adhesive force. However, if an energy barrier is introduced, as in Figure 6, curve (b), a mechanism for the viscous component arises and the peel force may be calculated. In this case the potential curve is considered to consist of at least two equilibrium states of energy W and W' respectively separated by the energy barrier which causes energy loss as the surfaces are separated or joined. If the system is in the W state and a force is applied to separate the surfaces then using the theory of absolute reaction rates[18] the energy loss would be given by

$$\frac{dU_{LS}}{ds} = bA \sinh^{-1} BV \quad (10)$$

where b is the width of the peeling film
V is the peel velocity
and A and B are temperature dependent constants.

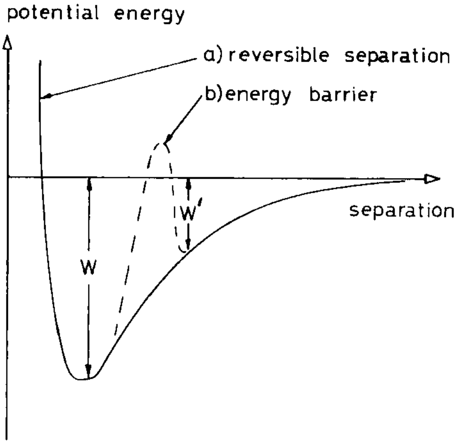

FIGURE 6 Variation of potential energy as one surface approaches another.

The peel strength is therefore

$$\frac{F}{b} = W + A \sinh^{-1} BV \quad (11)$$

Equation 11 which is applicable to the 90 degree peeling of elastic materials has been plotted in Figure 4 to fit the results for the silicone rubber. The line was plotted to fit the short time measurements of velocity since it was felt that these velocities represented a reasonable approximation to the steady state condition. The spread of points along the velocity axis merely reflects the magnitude of the bulk slowing effect. The equation describes the results tolerably well.

It is worth considering some mechanisms which may account for this energy barrier. The possibilities may be divided into two major groups, non-local, where the energy loss occurs in the material surrounding the crack-tip and local, where the energy loss occurs at the interface.

There is much evidence to support the non-local mechanism of energy loss. When fracture surfaces are closely inspected, there are often signs of damage in a more of less thin layer close to the crack path. The damage may be a result of plastic flow[5] or orientation[19] due to the high strains around the crack tip. These flow mechanisms are almost certainly a major factor in the fracture of tough, ductile and non-linear materials. However it is difficult to explain the fracture of elastic, brittle, low strength substances on this basis.[20]

A local mechanism, however, can provide an explanation in the latter case. In its simplest form an interfacial energy loss may be understood in geometrical terms[9] where, because the interface is not plane, a shear component arises at the interface and frictional work is done. On an atomic scale, the same geometrical considerations apply to the diffusion theory of Voyutskii.[8] Where cleavage produced atomically smooth surfaces, as in the fracture of mica, these geometrical ideas are inapplicable and a molecular, interfacial mechanism must be sought. Early interfacial energy barriers were discussed by Deryagin[21] to explain the stability of colloids and by Glasstone *et al*[18] in connection with the adsorption of gases on metals. More recently Deryagin and Krotova[14] and Blake and Haynes[22] have proposed interfacial energy barrier theories.

It is profitable to pursue the connection between the results of Blake and Haynes and the present work. They studied the hysteresis of contact angle at the interface between a solid, a liquid and its vapour and measured the deviation of contact angle from its equilibrium value at low velocities. If the liquid surface is treated as a skin which gradually rolls into contact with the solid surface as the liquid advances, the parallel between this geometry and that of Figure 1 is apparent. Their results may be expressed in terms of an interfacial viscous force F_v where

$$\frac{F_v}{b} = A \sinh^{-1} BV \qquad (12)$$

Where b is the length of the three phase boundary, A and B are temperature dependent constants and V is the velocity of the boundary. For methylene iodide on smooth nylon, Eq. (12) becomes[23]

$$\frac{F_v}{b} = 0.0017 \sinh^{-1} 0.045\ V \qquad (13)$$

where F_v is in gm, b in cm and V in μm sec^{-1}. It is evident that these constants are not grossly different from those found in the adhesion experiments reported here.

VII BULK LOSSES IN STEADY PEELING

Bulk losses have been shown experimentally to produce two effects: an increase in peel force in steady peeling and a slowing of peeling immediately after the application of the peeling force. Here we will restrict ourselves to the case of steady peeling, where the film travels at constant speed. In this example therefore, the shape of the peel bend remains constant as time progresses and, for viscoelastic films this shape will be given by a simple bending theory.[12] If 90 degree peeling is considered, then Eq. (7) reduces to

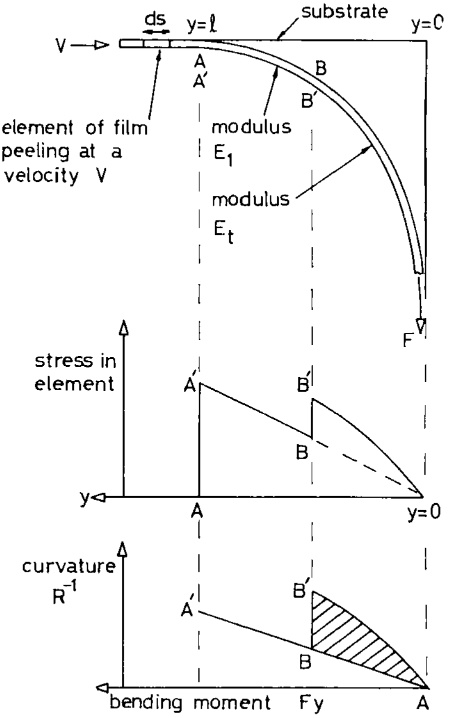

FIGURE 7 An element of film traversing the peel bend.

$$F = Wb + \frac{\mathrm{d}U_{LS}}{\mathrm{d}s} + \frac{\mathrm{d}U_{LB}}{\mathrm{d}s} \tag{14}$$

and we see that it is necessary to calculate $\mathrm{d}U_{LB}/\mathrm{d}s$, that is, the irreversible bulk energy loss as a small element $\mathrm{d}s$ of film is peeled (Figure 7). This approach gives a physical picture of the process—however, the same result arises directly from the energy balance method used in Section 8.

Imagine the element of viscoelastic material approaching the point A where separation of film from substrate just occurs. At this point the element is suddenly stressed in a rather short time and the film acquires a curvature $1/R$. The plot of curvature versus bending moment can be used to calculate the elastic energy in the element since this energy is $\frac{1}{2}Fy(1/R)\,\mathrm{d}s$.[24] The elastic modulus of the material at the point A is relatively high (E_1) because the stress was applied in a short time. However, after a certain time has elapsed, the material relaxes and the elastic modulus falls to E_t. By this time the element has moved to B and the stress and curvature of the element suddenly increase as a result of the relaxation. The bending stress in the element then gradually decreases to zero as the element progresses out of the bend zone. The energy lost in this process is related to the area of the hysteresis loop shaded in Figure 7 so that

$$\frac{\mathrm{d}U_{LB}}{\mathrm{d}s} = (\text{shaded area } ABB') \tag{15}$$

It is evident from this discussion that the energy loss in this example is due to hysteresis in the film material as it traverses the peculiar stress-strain cycle of the peel bend. For a hysteresis loss to arise, the relaxation of the material must occur within the stress strain cycle. The loss is therefore a function of the relaxation time and the peel velocity.

Clearly the maximum hysteresis loss occurs when the relaxation arises shortly after the stress is imposed at the point A, that is, when $y = l$. In this case the simple bending theory applies and the area of the hysteresis loop may be calculated to give

$$\frac{\mathrm{d}U_{LB}}{\mathrm{d}s} = F\left(1 - \frac{E_t}{E_1}\right) \tag{16}$$

Eq. (16) is important because it shows that the hysteresis contribution depends not only on material properties but also on the applied force. When combined with Eqs. (14) and (10) this formula leads to an expression for the maximum peel strength of viscoelastic materials in steady peeling.

$$\frac{F}{b} = \frac{E_1}{E_t}\,(W + A \sinh^{-1} BV) \tag{17}$$

Using the value of $(E_1/E_t) = 10$ derived from bending experiments on paint films, Eq. (17) is plotted to fit the results of Figure 5. The adhesive energy on this basis was found to be about 400 mJ m^{-2}, not an unreasonable value for this system.

Obviously, Eq. (17) applies only over a certain range of peeling velocities for at very low peel rates the hysteresis losses will fall to zero. This behaviour is illustrated in Figure 8 where the resultant steady peeling force is seen to be the product of an interfacial force and a hysteresis component. The span of the hysteresis 'plateau' is governed by the rates of stress rise and stress fall in a given peeling geometry. The peculiar nature of the peel test, with its fast stress rise and slow stress decrease, tends to give a broad hysteresis plateau covering several decades of log (velocity), so that the sharp rise and fall of peel strength at extreme speeds may be outside the experimental range of velocities.

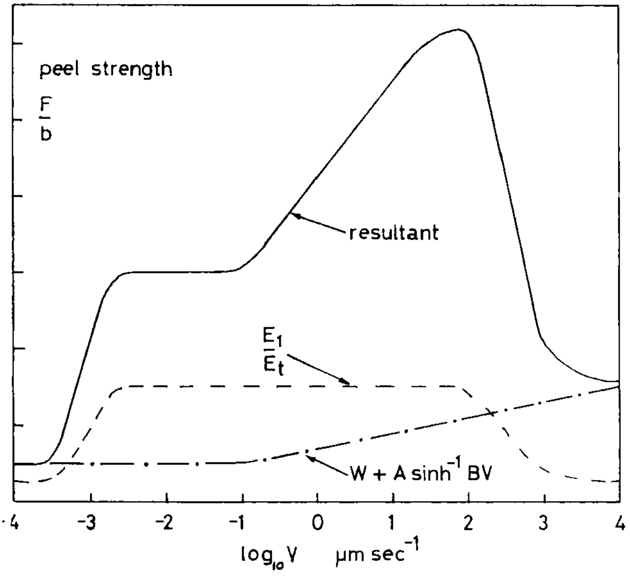

FIGURE 8 Peel strength as a function of velocity in steady peeling-the bulk hysteresis factor (E_1/E_t) and the surface factor ($W + A \sinh^{-1} BV$) are multiplied to give the resultant peel strength.

Experiment

According to the preceding argument, peel strength depends on the elastic properties of the materials. A simple experiment was designed to test this idea. Instead of depending on a change in elastic modulus of the peeling film, a change which cannot be produced suddenly, a sharp change in thickness of the peeling film was employed. A decrease in film thickness is equivalent to a relaxation of modulus of the peeled material, so that an increased peel strength should result when the film thickness changes. Other things being equal, a sharp increase in thickness from d_t to d_1 should raise the peel force from F_t to F_1, where

$$\frac{F_1}{F_t} = \left(\frac{d_1}{d_t}\right)^3 \tag{18}$$

In order to test this equation, a rubber film was peeled at a low speed (1 μm sec^{-1}) and the force F_t measured. At the point where the thickness of the film was sharply increased, by glueing another piece of rubber to the outer surface of the film, it was necessary to increase the load to F_1 to resume peeling. The results are shown in Table I and demonstrate that Eq. (18) although not perfect, gives fair agreement with experiment.

TABLE I

$\frac{d_1}{d_t}$	$\left(\frac{d_1}{d_t}\right)^3$	$\frac{F_1}{F_t}$
1.17	1.60	1.67
1.92	7.1	6.2
1.93	7.2	7.3
2.3	12.2	9.0
2.33	12.6	10.9
2.42	14.1	11.5

VIII BULK LOSSES IN TRANSIENT PEELING

In Section 7 bulk hysteresis losses were shown to increase the peel strength of a viscoelastic film in steady peeling. However, these hysteresis losses cannot fully account for the slowing of peel rate observed experimentally shortly after the application of the peeling force. To explain this phenomenon it is necessary to study the case of transient peeling where the shape of the peel bend changes with time. In general the bend shape changes in a most complex way depending on time and peel rate. Here we consider only the simplest example where it is assumed that the peeling is so slow that the bend shape is given by the elementary bending theory.

Consider the situation illustrated in Figure 9. When the peel force F was applied, the point P was coincident with the point 0 of separation of film and substrate. After some time the point P has travelled a short distance Δy and the film OP has an elastic modulus E_1 which is considered to remain constant at short times. The remainder of the peeling film PF is viscoelastic and has relaxed in the interval since the application of the force, so that its elastic modulus is E_t, and the shape parameter is l_t, which is gradually decreasing with time owing to the relaxation. In effect the peeling film is a composite of two elastic systems, one of effectively constant modulus and the other of decreasing modulus.

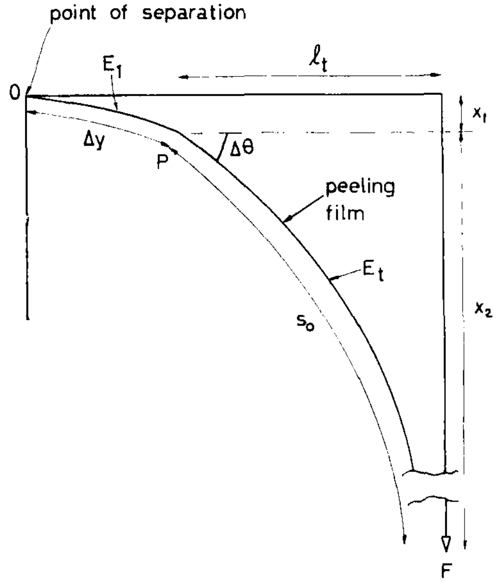

FIGURE 9 Transient peeling of a thin film viewed when the film has peeled a short distance Δy after the initial application of the force F.

Physically, it is easy to see why slowing of peeling should occur in this composite system. Imagine that further relaxation takes place in the modulus E_t. The parameter l will decrease and so the bending moment applied to the short elastic element OP will be reduced. This element will therefore spring back, tending to do work on the force F. In consequence, therefore, the relaxation of E_t leads to an increase in free energy of the system, an increase which can be supplied only if the peeling rate drops. The analysis (Appendix 2) leads to the equation for peel strength

$$\frac{F}{b} = \frac{E_1}{E_t} \frac{(W + \mathrm{A} \sinh^{-1} BV)}{\left(1 + \frac{K 2 \Delta y}{V} \frac{1}{l_t} \frac{\mathrm{d} l_t}{\mathrm{d} t}\right)} \tag{19}$$

Experiment

In order to test Eq. (19) a film of silicone rubber 0.040 cm thick was peeled from a Perspex substrate under a load of 0.66 gm and the peel velocity measured as a function of time. In this experiment the parameter l_t was about 1.25 cm and the total distance travelled by the film in the experiment was 0.214 cm so that the condition of slow peeling was approximately observed. In addition the elastic modulus of the film was approximately constant over the test period so that $E_1 \approx E_t$. The experimental results are given in Figure 10 where it is seen that the peel rate dropped considerably during the test from more than 6 μm sec^{-1} to less than 0.3 μm sec^{-1}.

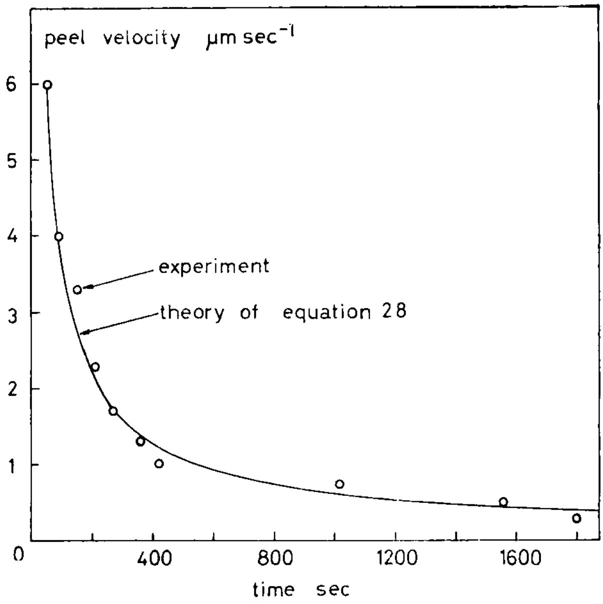

FIGURE 10 The slowing of peeling with time after the application of the force to a rubber film on Perspex.

Equation (19) was fitted to these results in the following manner. The surface constants W, A and B were obtained from the thin film rubber peeling results (Figure 4).

$$W = 0.3 \text{ gm cm}^{-1}$$

$$A = 0.0725 \text{ gm cm}^{-1}$$

$$B = 1.16 \text{ sec } \mu\text{m}^{-1}$$

The term $(1/l_t)(\mathrm{d}l_t/\mathrm{d}t)$ was taken as

$$\frac{1}{l_t}\frac{\mathrm{d}l_t}{\mathrm{d}t} = \frac{-0.0323}{t}$$

Starting values of V, t and y were inserted from the results of Figure 10 and other values of V and t were then generated numerically to fulfil Eq. (19) the constant K being adjusted until a reasonable fit was obtained. Figure 10 shows a theoretical plot closely fitting the experimental results where the value of K was 2.48.

IX CONCLUSIONS

Experiments have shown that both interfacial and bulk mechanisms make a contribution to the peel strength of thin solid films.

The interfacial effect, invoked to explain the peel strength of elastic materials, has two components: an equilibrium contribution required to break the interfacial bonds reversibly and a dissipative component required to overcome an energy barrier at the surface. At low speeds the reversible effect dominates but as the peeling velocity is increased above 1 μm sec^{-1} the dissipative process becomes more significant.

The bulk contribution to peel strength introduces two further effects: a magnification of peel force over a certain velocity range and a slowing down or stopping of peeling shortly after the peel load is applied. The magnification of peel force arises in steady peeling, where separation of the materials occurs at constant speed and constant bend shape, and is due to hysteresis in the material undergoing a stress-strain cycle as it traverses the bend. Slowing or stopping of peeling occurs in transient peel conditions where the shape of the peel bend changes with time. Under these circumstances, relaxation of the peel bend, as a result of energy losses in a part of the viscoelastic material, leads to an increase in free energy of the system. Consequently, in a system where peel velocity increases with peel force, relaxation produces a slowing of crack propagation. This mechanism of crack arrest is thought to be a general one and may prove important in studies of fatigue and related phenomena.

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NOMENCLATURE

A Temperature dependent constant
b Width of peeling strip
B Temperature dependent constant
d, d_1, d_t Thickness of peeling film
E, E_1, E_t Young's modulus of film
F Force hanging on a peeling film
F_v Force causing contact angle hysteresis
I_A Second moment of area of film about neutral axis
K Constant in transient peel theory
l, l_1, l_t Distance between crack tip and line of force application
L Total length of peeling film
r Variable in bending theory $r = \frac{y}{l}\sqrt{1 - \sin\theta}$
R Fracture energy and radius of curvature of bent film
s, s_0 Length measured along peeled film
t Time
U_T, U_S, U_E, U_P, U_L Energies
$\mathrm{d}U_{LS}$, $\mathrm{d}U_{LB}$ Energy loss components due to surface and bulk processes
V Velocity of peeling
W, W' Adhesive energies
X, x, x_1, x_2 Distance measured along direction of force application
y, Δy Distance measured perpendicular to direction of peel force
ϕ Peel angle
θ, θ_l, $\Delta\theta$ Angle between film and y axis

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APPENDIX I Excess length in the peel bend

Owing to the bend in the peeling film, the length of the film is greater than the length of the x axis (Figure A1). This excess may be calculated.

$$\text{Excess length} = \int (\mathrm{d}s - \mathrm{d}s \sin \theta)$$

$$= \int_0^l \frac{(1 - \sin \theta)}{\cos \theta} \,\mathrm{d}y$$

$$= \int_0^{\sqrt{1 - \sin \theta_l}} \frac{1 - (1 - r^2)}{\sqrt{1 - (1 - r^2)^2}} \frac{l \,\mathrm{d}r}{\sqrt{1 + \sin \theta_l}}$$

$$= \frac{l}{\sqrt{1 - \sin \theta_l}} (\sqrt{2} - \sqrt{1 + \sin \theta_l})$$

$$= 2EI_A F(\sqrt{2} - \sqrt{1 + \sin \theta_l})$$

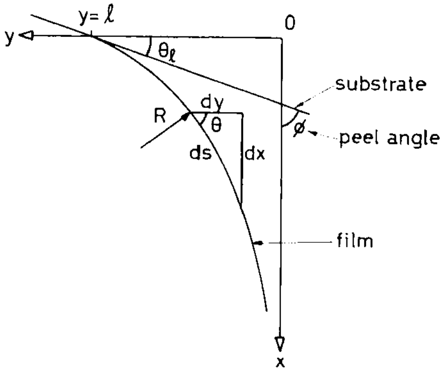

FIGURE A1 Elastic energy and excess length for a hanging elastic film.

APPENDIX II Peel strength under transient peeling conditions

When transient peeling occurs, the peel force may be calculated by applying Eqs. (1) and (2) to the system of Figure 9.

Surface energy

The surface energy U_S is given by

$$U_S = b(s_0 + \Delta y)W$$

Elastic energy

The elastic energy is composed of two terms, the energy in the first part of the film *OP*, and that in the second part *PF*

$$U_E = \frac{(Fl_t)^2}{2E_1 I_A}\Delta y + \sqrt{2E_t I_A F}\,(\sqrt{2} - \sqrt{1 + \sin\Delta\theta})$$

Here, the elastic energy in the stress distribution close to the point 0 has been neglected. If the force F is small this omission is probably justifiable.

Potential energy

The potential energy U_P in the applied load F is given by

$$\begin{aligned} U_P &= -F(x_1 + x_2) \\ &= -Fx_2 \qquad \text{since } x_1 \text{ is very small} \\ &= -F\left(s_0 - \sqrt{\frac{2E_t I_A}{F}}(\sqrt{2} - \sqrt{1 + \sin\Delta\theta})\right) \end{aligned}$$

from Appendix 1.

Energy loss

As the modulus E_t relaxes, heat energy is liberated in the film *PF* due to irreversible processes in the viscoelastic material. The rate of energy loss may be calculated by imagining that the film is clamped at P so that no peeling can occur. In this case all energy changes in the relaxing film are completely converted into heat.

$$U_L + 2Fl_t(\sqrt{2} - 1) = 0$$

$$\frac{dU_L}{dt} = -2F\frac{dl_t}{dt}(\sqrt{2} - 1)$$

Total energy

The total energy U_T in the system is then given by

$$U_T = b(s_0 + \Delta y)W + \frac{F^2 l_t^2 \Delta y}{2E_1 I_A} + 2\sqrt{2E_t I_A F}\,(\sqrt{2} - \sqrt{1 + \sin \Delta\theta})$$

$$-Fs_0 - \int 2F\frac{\mathrm{d}l_t}{\mathrm{d}t}(\sqrt{2} - 1)\,\mathrm{d}t$$

If $\Delta\theta$ is small the third term in this expression reduces to

$$2Fl_t(\sqrt{2} - 1) - \frac{2F^2 l_t^2}{2E_1 I_A}\Delta y$$

so that

$$U_T = b(s_0 + \Delta y)W - \frac{F^2 l_t^2}{2E_1 I_A}\Delta y + 2Fl_t(\sqrt{2} - 1) - Fs_0 - \int 2F\frac{\mathrm{d}l_t}{\mathrm{d}t}(\sqrt{2} - 1)\,\mathrm{d}t$$

$$\frac{\mathrm{d}U_T}{\mathrm{d}s} = bw - \frac{F^2 l_t^2}{2E_1 I_A} - \frac{F^2 \Delta y}{2E_1 I_A}2l_t\frac{\mathrm{d}l_t}{\mathrm{d}s} + 2F\frac{\mathrm{d}l_t}{\mathrm{d}s}(\sqrt{2} - 1) - 2F\frac{\mathrm{d}l_t}{\mathrm{d}s}(\sqrt{2} - 1)$$

$$= bW - \frac{E_t F}{E_1} - \frac{E_t}{E_1}\frac{2F\Delta y}{V}\frac{1}{l_t}\frac{\mathrm{d}l_t}{\mathrm{d}t}$$

Apply the condition of Eq. (2) and including the interfacial loss leads to a general expression for the peel strength of a relaxing film.

$$\frac{F}{b} = \frac{E_1}{E_t}\frac{(W + A\sinh^{-1}BV)}{\left(1 + \dfrac{K2\Delta y}{V}\dfrac{1}{l_t}\dfrac{\mathrm{d}l_t}{\mathrm{d}t}\right)}$$

In this expression, which is effectively the fracture energy for this system, a constant K has been inserted to compensate for the numerous assumptions made in the transient peel derivation.

The equation applies not only to the transient condition but also to steady peeling and to peeling of elastic films. When the shape does not change with time (in steady peeling), this reduces to Eq. (17) and when, in addition, $E_t = E_1$ it reduces to Eq. (11).