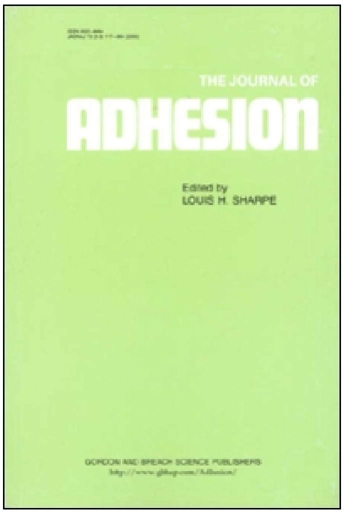

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Kinetics of Contact between Smooth Solids

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Kinetics of Contact between Smooth Solids

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The diameter of the circular contact region formed between a smooth rubber sphere and a glass plate has been studied as a function of time under a variety of loading conditions.

Theoretically, the system is viewed as a circular crack which can move through the glass-rubber interface in two directions: one to form the contact and the other to break it. Discussion centres principally on the speed at which the crack propagates, and on a sudden stopping of the crack which leads to adhesive hysteresis.

INTRODUCTION

The equilibrium between smooth elastic spheres in close proximity has been discussed by Johnson, Kendall and Roberts.[1] Contact in such circumstances was shown to be dictated by the conflict between attractive surface forces which draw the surfaces together on the one hand and elastic forces tending to push the bodies apart on the other.

In the course of this equilibrium study, it became apparent that a certain time had to be allowed for the contact to attain its final size. Obviously some other forces, in addition to the surface attractions and elastic repulsions, were producing this kinetic phenomenon. Another interesting feature of these observations was that the contact size depended slightly on the direction of motion of the contacting bodies. If the bodies were separating at a given load, the final contact diameter was often bigger than when the bodies were approaching under the same load. This adhesive hysteresis in the contact size had been noted previously by Drutowski.[2]

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The aim of this paper is to investigate more fully the kinetics of contact between a rubber sphere and a glass plate. In particular, attention is paid to two factors: the one governing the rate of approach or separation of the surfaces and the other dictating the hysteresis in the final contact size.

The work is of direct relevance to a method devised by Wetzel[3] for testing the tackiness of adhesives. In this test, a sophisticated version of the "thumb" method, a hemispherical probe is rested on the adhesive surface for a short time under a certain load and the force required to detach the probe is a measure of the tack. Tackiness, determined in this way, is dominated by kinetic effects, depending strongly on probe withdrawal speed, temperature and time of contact.[4]

Much prior study of adhesives has concentrated on the fracture rather than the formation of adhesive bonds, high breaking strength being the desirable property. Non-equilibrium effects are prominent in such studies. Not only is the strength of adhesive joints rate and temperature dependent[5, 6] —the force required to propagate a crack through the adhesive interface is usually several orders of magnitude higher than the equilibrium bond strengths would suggest.

There is an obvious parallel here between adhesive and cohesive strength. An equilibrium theory of cohesive strength[7] leads to the idea that cracked structures should be very weak. The fact that such structures are very much stronger than predicted suggests that kinetic effects are dominant in the fracture process. Such effects have been known for many years; at least since the observations of Mariotte[34] in the seventeenth century. Grenet[8] and Preston[9] mentioned the variation in strength of glass with time, and more recently Zhurkov[10] has measured the time to failure of many different materials at various temperatures.

Generally speaking, high modulus solids do not exhibit tackiness; it is usually impossible to produce noticeable adhesion between glass or metal bodies because of their surface roughness.[11] An exceptional material in this respect is mica, studied by Obreimoff[12] Orowan[13] and Bailey and Courtney-Pratt.[14] Cleaved mica, in common with smooth rubber, exhibits appreciable tackiness and shows the usual kinetic adhesion effects. Time is required for mica contacts to reach their final size and hysteresis in the contacts is often noticeable.

In contrast with solids, liquids always show a measurable tackiness since liquid–liquid or liquid–solid contact is not much impeded by undeformable surface asperities. However, it is interesting to note that kinetic phenomena, analogous to the solid contact effects described here, are observed when liquid contacts are formed or broken. Again the change in contact size is time dependent and hysteresis may often be observed.[15, 16, 17]

It is clear from these considerations that kinetic phenomena are quite generally found in contacting systems. In the first part of this paper a theory is proposed to describe the two major effects: the time required for contacts to change in size and the contact size hysteresis. Application of this theory to the rubber-glass adhesive system is then experimentally justified.

THEORY

The aim of a kinetic theory of contact is to describe the approach to equilibrium of two bodies being joined or separated. It is convenient therefore to start with the equation of equilibrium for the system and to see how this must be altered to account for kinetic effects.

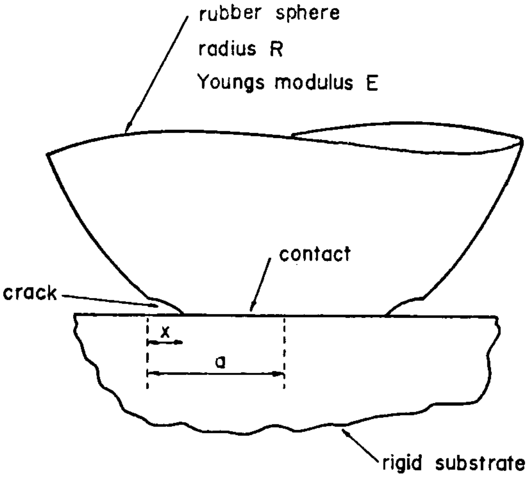

FIGURE 1 Geometry of the crack for the coming-off experiment.

Here we will consider the case of an elastic sphere in contact with a rigid plane under zero load (Figure 1). This system may be viewed as a circular crack capable of propagating into or out of the contact region as the bodies are separated or joined. The equilibrium state for this geometry was shown by Johnson, Kendall and Roberts[1] to result from a balance between elastic energy in the sphere and surface energy in sphere and plate. The elastic energy is given by $16Ea^5/135R^2$ and the surface energy is given by $-\pi a^2\gamma$, where γ is the equilibrium adhesive energy per unit contact area, so that applying the criterion due to Griffith,[7] equilibrium ensues when

$$\frac{d}{da}\left[-\pi a^2\gamma + \frac{16}{135}\frac{E}{R^2}a^5\right] = 0 \tag{1}$$

i.e.

$$\gamma - \frac{8}{27\pi}\frac{E}{R^2}a^3 = 0 \tag{2}$$

It is now necessary to see how this equation may be modified to describe both change of contact diameter with time and contact size hysteresis. Two modifications are shown to be needed: firstly the use of the well-known rate dependent adhesive energy and secondly the introduction of a term to account for the effect of bulk viscoelastic relaxations on the crack propagation. This second, viscoelastic term is what concerns us principally.

RATE DEPENDENT ADHESIVE ENERGY

A large number of workers have studied the slow growth of cracks. Cohesive failure has been investigated by, for example, Greensmith and Thomas[18] and Knauss,[19] and adhesive failure by Kaelble,[6] Gent and Petrich[5] and Kendall.[20] Adhesive and cohesive failure of rubber has been compared by Andrews and Kinloch.[21]

The important result, reported by Greensmith[22] for cohesive fracture and by Gent and Kinloch[23] for adhesive failure, is that the equilibrium equation, for example Eq. 2, may be generalized to include non-equilibrium conditions by making the adhesive energy a function $\Gamma(V)$ of crack velocity. This function is then a material property independent of geometry and loading mode. In our sphere on plate geometry, the modified form of Eq. (2)

$$\Gamma(V) - \frac{8}{27\pi}\frac{E}{R^2}a^3 = 0 \tag{3}$$

shows clearly why a certain time is necessary to approach the equilibrium condition. It should be emphasized at this stage that, although equations of this sort have been experimentally verified, the interpretation of the rate dependent adhesive energy is difficult. The conventional interpretation for viscoelastic material is to invoke viscoelastic dissipation near the crack front,[23] this dissipation mirroring the loss properties of the bulk material. Other workers have used a combination of bulk and interfacial properties to account for the rate dependent adhesive energy; the viscoelastic losses give the rate and temperature dependence but are themselves proportional to the equilibrium adhesive energy.[21] Yet another theory suggests that $\Gamma(V)$ is largely due to interfacial forces, an energy barrier resisting separation at the adhesive junction.[20] All theories, however, have a common feature: they relate to energy dissipation near the crack tip.

VISCOELASTIC TERM

Having modified the equilibrium equation to account for these crack tip energy losses, it is now important to show how the crack propagation is affected by a viscoelastic relaxation in the bulk of the material. A large body of complicated mathematics has been presented elsewhere to show the effect of viscoelasticity on the fracture criterion.[19, 24, 25, 26] Here, with the aid of a simple model, one particular effect of viscoelasticity is outlined and incorporated in the equilibrium equation to illustrate how hysteresis could arise.

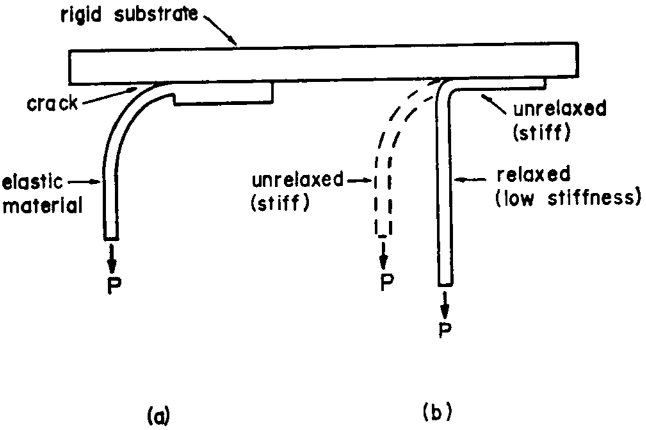

FIGURE 2 a) A crack travelling through an elastic medium is arrested when it meets a region of high stiffness.

b) For a viscoelastic material, the stressed region relaxes and therefore has a lower modulus than the unstressed material, leading to a situation analogous to (a).

The model is shown in Figure 2(a) and consists of an elastic rubber strip peeling from a glass surface under constant load P. Again, this is viewed as a crack propagating at constant speed along the rubber-glass interface. When the crack meets a region of increased stiffness the crack velocity is suddenly very much reduced; even to zero if the change in stiffness is sufficiently marked.[27] The stiffness change has been depicted as an increase in thickness but could equally well be an increase in elastic modulus. The reason for the crack arrest is, of course, the resistance to deformation of the stiffer material, preventing the force P from doing so much work as previously. Now consider the peeling of a viscoelastic material (Figure 2b). Here, before relaxation occurred, the material was of constant modulus. After the viscoelastic relaxation, however, the material may be separated into two components, the relaxed material of low modulus and the yet unstressed material of high modulus. This situation is now entirely analogous to Figure 2a and the crack is arrested in the same way.

ANALYSIS OF MODEL

This model for the effect of viscoelasticity on crack propagation has been quantified for the peel geometry[28] and may be expressed mathematically for the sphere and plate geometry as follows.

We realize that in the bulk of the viscoelastic sphere (Figure 1) the modulus E is decreasing and causing elastic energy to be converted into heat. This production of heat is removed from the energy balance by focusing attention on a small region of length x just traversed by the crack. The elastic energy due to this short crack increment is written

$$\frac{16}{135}\frac{E}{R^2}[(a-x)^5 - a^5] \simeq -\frac{16}{27}\frac{Ea^4}{R^2}x \tag{4}$$

and the new fracture criterion becomes

$$\frac{d}{dx}\left\{-\pi(a-x)^2\Gamma(V) - \frac{16}{27}\frac{Ea^4}{R^2}x\right\} = 0 \tag{5}$$

which for $a \gg x$ reduces to

$$\Gamma(V) - \frac{8}{27\pi}\frac{Ea^3}{R^2}\left[1 + \frac{x}{E}\frac{dE}{dx}\right] = 0 \tag{6}$$

This equation is simplified by writing

$$\frac{dE}{dx} = \frac{1}{V}\frac{dE}{dt} \tag{7}$$

and using the experimental knowledge that for rubber

$$\frac{1}{E}\frac{dE}{dt} = -\frac{C}{t} \tag{8}$$

for a reasonable range of time, where C may be called the relaxation constant. The final theoretical equation for short cracks becomes

$$\Gamma(V) - \frac{8}{27\pi}\frac{Ea^3}{R^2}\left[1 - \frac{Cx}{Vt}\right] = 0 \tag{9}$$

Inspection of Eq. (9) shows that, at high crack speeds and short crack lengths, the viscoelastic term is negligible. The kinetics of contact under these conditions are therefore dictated by the rate dependent adhesive energy. Numerical solution of Eq. (9) verifies this conclusion. However, when the crack slows down on approach to equilibrium, a remarkable thing happens. The viscoelastic term suddenly becomes significant, the crack velocity decreases and this causes a further catastrophic increase in the viscoelastic effect. The crack therefore suddenly stops. This crack-stopping catastrophe is the suggested cause of contact hysteresis, here defined as the difference in contact diameter (or adhesive energy) for coming-off and coming-on tests. This definition is analogous to that of contact angle hysteresis.

EXPERIMENTAL

The experimental objectives were of three main kinds: first to define the equilibrium state of the contact between two bodies, secondly to show that the cracks propagating through the contact did stop in accordance with the theory, and thirdly to distinguish clearly between the rate dependent adhesive energy effect and the bulk viscoelastic effect.

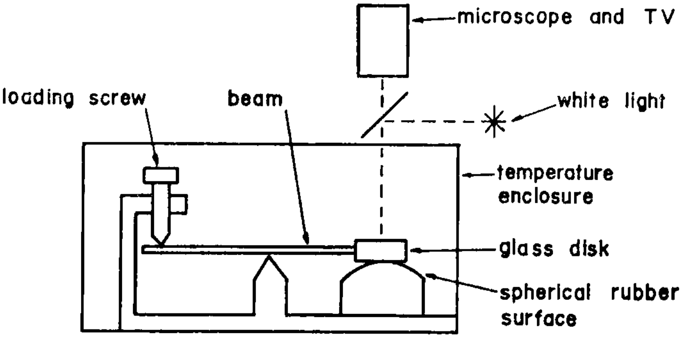

FIGURE 3 The experimental arrangement.

Figure 3 shows the experimental arrangement. A glass disc was counterbalanced using the beam to give a near zero load. This optically smooth plane glass could then be brought carefully into contact with the smooth rubber spherical surface by means of the loading screw. Meanwhile, the approaching contact was viewed through the microscope in reflected white light, Newton's rings eventually appearing as the surfaces came into close proximity. Suddenly, the surfaces were observed to jump together very dramatically in a manner reminiscent of the mica surfaces of Tabor and Winterton.[29] The contact circle, then grew rapidly towards its equilibrium diameter. This was a "coming-on" experiment. In order to define the equilibrium value of the contact diameter more closely it was necessary to approach equilibrium from the other direction by doing a "coming-off" experiment. In this case the surfaces were pressed together for a short time to form a large contact circle. The applied load was then reduced to zero and a crack was seen to propagate through the contact, the crack gradually decreasing in speed as the equilibrium diameter neared. Previous work on the study of crack propagation has largely dealt with the separation of surfaces. The important contribution here is the measurement of cracks propagating backwards, that is, to produce contact of the surfaces. Clearly, the equilibrium state of the system lies somewhere between the ultimate states of approach and separation.

The problem of crack stopping was experimentally difficult. Obviously a crack velocity of zero cannot be measured; it is only possible to put upper limits on the crack speed by observing the crack for longer and longer periods. In the present work the maximum period of crack observation was one week so that the lowest crack speed measurable was around 10^{-4} μms^{-1}. When the crack had not noticeably moved over a period of one week, crack arrest was said to have occurred and this was represented on the experimental graphs by a point at 10^{-4} μms^{-1}. A video recorder was used to follow the change in size of the contact. The time resolution was 0.02 s but the spatial resolution was about 30 μm. A velocity range of eight decades was covered.

Distinguishing between the rate dependent adhesive energy term and the viscoelastic effect was achieved in two ways. The obvious technique was to adjust the relaxation constant C of the rubber in order to influence the viscoelastic term in Eq. (9). It was possible to vary the relaxation constant by a factor of ten by changing the curing time of the rubber, at the same time keeping the composition constant in the hope that the interfacial properties would be relatively unaffected. The second method for distinguishing the viscoelastic effect depended on changing the temperature. Previous work[5, 21] has shown that cracks propagate faster at higher temperatures, the shift along the log (velocity) axis corresponding to the W.L.F. shift for mechanical properties. The viscoelastic term would not be expected to shift with temperature in exactly the same way and should therefore be recognizable. Electrical heating was used to raise the temperature to 100°C and carbon dioxide to reduce the temperature to -40°C, the temperature being maintained constant to ± 1°C during any one test.

MATERIALS

Natural rubber was used, batches being formulated according to the recipe of Table I. The rubber was cured against concave glass lenses of 3 cm radius of curvature in the manner described by Roberts.[30] By varying the cure time at a temperature of 145°C, samples with different relaxation properties but essentially similar surface conditions were produced, and their adhesion could then be tested.

TABLE I

	gm
Natural rubber	200
Zinc oxide	10
Stearic acid	6
Sulphur	5
MBTS	1.2

From the point of view of verifying Eq. (9) it was important to compare both the surface and bulk properties of the rubber samples. For this purpose, flat sheet specimens produced in a similar manner by curing against a smooth glass plate were used. Surface properties were compared by placing a small water drop on the rubber surfaces and measuring the advancing contact angle after 10 minutes. Nominally similar samples of 40-minute cured rubber all gave the same contact angle of 79 degrees within experimental error. Samples which had only been cured for 10 minutes and even uncured samples also gave this result despite the obvious differences in mechanical properties of the rubbers. This suggested that the moulding process was producing similar surfaces on all the samples so that hysteresis in this case could not be accounted for by surface roughness or heterogeneity.[31]

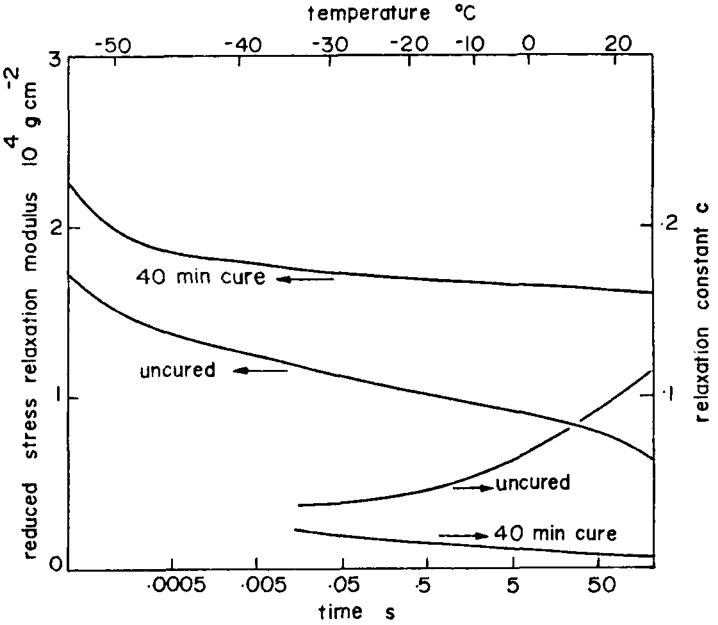

FIGURE 4 Relaxation modulus and relaxation constant for cured and uncured rubber.

The bulk properties of the rubber specimens were compared by stress relaxation testing at different temperatures on an Instron testing machine. Figure 4 shows the results of these tests for an uncured and 40-minute cured samples, measurements having been superposed using the W.L.F. shift.[32] The uncured rubber has a slightly lower modulus than the cured sample but a much higher relaxation constant over much of the time temperature range. There was some variability in the values of E and C between samples; for example, in five nominally identical specimens of 40-minute cured rubber at

20°C the modulus varied from 1.4×10^6 Nm^{-2} to 2.0×10^6 Nm^{-2} with a mean of $(1.7 \pm 1) \times 10^6$ Nm^{-2}, and the relaxation constant C varied from 0.0055 to 0.008 with a mean of $(7.3 \pm 0.3) \times 10^{-3}$. When the modulus was measured by the Hertz method using the spherical samples immersed in Teepol solution to remove the surface attractive effects[1] good agreement with the tensile tests was obtained. The rubber properties were not particularly strain dependent up to strains of around 20%. In fact, the relaxation constant remained fairly steady at much higher strains.

RESULTS

Typical results for a 40-minute cured sample are given in Figure 5 where the contact diameter is plotted as a function of time, both on logarithmic scales, for the coming-off and coming-on experiments. In the coming-off case the contact diameter change by a factor of more than 2 and the measurements were obtained very reliably. The coming-on results were less reliable since the early stages of the contact were established in a very short time and measurements were restricted to less than a 20% change in contact diameter. Also, air bubbles were often trapped inside the contact region during the coming-on tests.

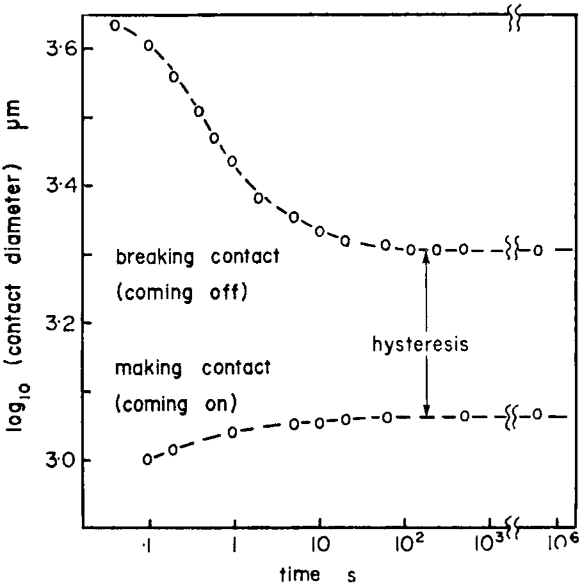

FIGURE 5 Change of contact diameter with time for cured rubber at zero applied load and 20°C.

From these results it was possible to draw some preliminary conclusions. Both coming-on and coming-off curves showed similarities. Crack speed was a maximum at the shortest times and the cracks then gradually slowed until, after about 600 seconds, no further movement could be detected even after a week's time. There was no evidence that equilibrium was reached in either coming-on or coming-off experiment though it was clear that the equilibrium contact diameter rested somewhere between the two extremes of final contact size. The same question of identifying equilibrium arises in the measurement of contact angles where advancing and receding angles represent the limits of equilibrium in this case.

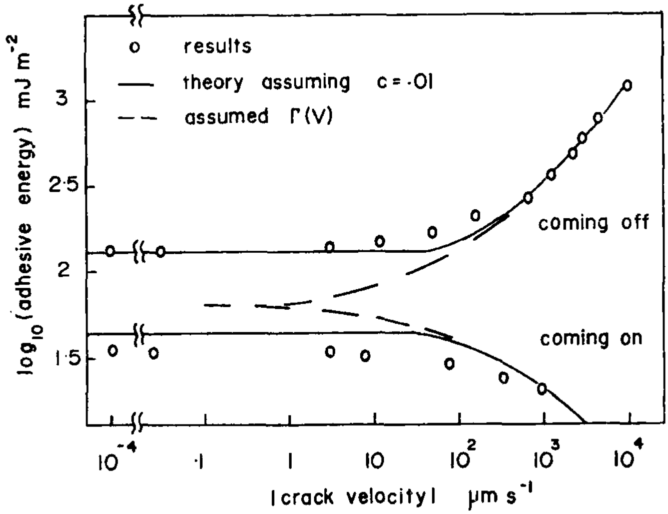

FIGURE 6 Adhesive energy for cured rubber at zero load.

A second observation was that, within the resolution of the experiments, the cracks did stop. The tentative conclusion was that, although equilibrium was not attained, no additional approach to equilibrium would be observed despite further extension of the experiment.

The results, therefore, show two distinct regimes of behaviour in accord with the theoretical model. At short times the cracks propagate, slowing down as equilibrium nears. At long times the cracks are arrested in spite of the fact that equilibrium has not been reached.

For the purposes of comparison with Eq. (9) it is convenient to plot the results of Figure 6 in terms of the adhesive energy $\Gamma(V)$ calculated from Eq. (3). According to Gent and Kinloch[23] the adhesive energy versus crack velocity curve is characteristic of the material combination and independent of geometry and loading mode. Figure 6 gives the experimental points, taking the crack velocity as positive for both coming-on and coming-off cracks. The theoretical curve derived from Eq. (9) is also shown and gives a reasonable description of the results.

This theoretical curve was derived in the following manner. A function $\Gamma(V)$ was first chosen arbitrarily to fit the data at high crack speeds. Solution of Eq. (9) shows that the viscoelastic term $-(Cx/Vt)$ is negligible at these crack speeds. The form of the function $\Gamma(V)$ does not really matter, since no adequate theory at present exists to explain it, but the power law below gave a reasonable fit

$$\log\frac{\Gamma}{\Gamma_0} = A\left(\log\frac{V}{V_0}\right)^B, \qquad \Gamma > \Gamma_0 \tag{10}$$

the constants A and B and the equilibrium state Γ_0, V_0 being arbitrarily chosen. The arbitrary curves used in this study are shown as broken lines in Figure 5. Then taking experimental values of a, t, x, E and R and assuming a value of $C = 0.01$, Eq. (9) was solved numerically to give the theoretical line. The assumed value of C was thought to give reasonable agreement with the values measured in the stress relaxation tests on the strip samples, considering the variation in those results and the differences in geometry. For the coming-on theory both x and V were taken to be negative.

At this point it is important to comment on the nature of the contact in these observations. The sharp boundary of the contact circle observed in the optical microscope defines a sudden change in separation of the glass and rubber. Outside the contact circle the surfaces are some micrometres apart and do not contribute to the adhesion. However, inside the contact, the surfaces are less than 60 nm apart, the contact appearing quite black as though the rubber were a liquid flowing onto the glass. Although strong adhesion is observed immediately after establishing optical contact, the adhesion continues to increase afterwards. Measurements showed an increase in adhesion of about 40% per decade of contact time after optical contact was achieved. This increase roughly agrees with the results of other workers.[33] In order to reduce this dwell-time effect which has not been included in the theory of Eq. (9), the time of optical contact before carrying out a coming-off experiment was maintained constant at 60 seconds.

Some comment on repeatability of the results is called for at this juncture. Two very noticeable effects may be mentioned. Firstly, for any given sample of rubber, the first few contact tests gave results differing significantly from subsequent tests.

The reason for this is not clear. However, after a number of contact make and break cycles, the results became very reproducible for a period of some days, after which surface deterioration became noticeable. Secondly there was some variation in results among the nominally similar rubber samples.

Again, differences appeared in both hysteresis and the dynamic parts of the results. The hysteresis, expressed in terms of $\log_{10}$ (adhesive energy) ranged from 0.8 to 0.3, the sort of variation to be expected theoretically from the observed differences in relaxation properties between samples. Changes in the crack speed versus adhesive energy curves were less easy to explain. Although the shape of this curve appeared to remain constant for the different specimens, the experimental curves could be displaced along the velocity axis by anything up to a factor of ten. Clearly the surface properties of the rubber did change significantly between samples.

EFFECT OF TEMPERATURE

The principal reason for changing the temperature was the identification of the two effects proposed in the theory, the rate dependent adhesive energy and the bulk viscoelastic effect. Kaelble[6] and Gent and Petrich,[5] working with adhesive tape systems, showed that when the temperature was changed, the rate dependent adhesive energy curve shifted without change in shape along the log (crack velocity) axis by a characteristic amount. The hysteresis component would not be expected to shift in this way and should therefore be identifiable.

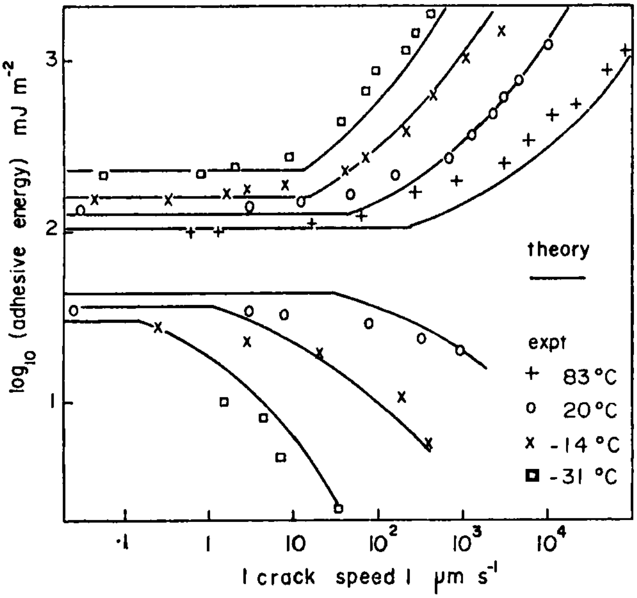

FIGURE 7 Effect of temperature on adhesive energy of cured rubber.

Figure 7 shows the experimental results for both coming-on and coming-off. The coming-on results are particularly interesting since, in the past, only the breaking of contacts has been considered. A number of features stand out. Firstly, it is apparent that the high crack speed regions do run parallel at the different temperatures and may be superposed by a shift along the log (velocity) axis. The low speed regions, however, obviously cannot be shifted in the same way and this fact lends credence to the idea that a different mechanism of cracking is operating at these low speeds. A reassuring observation was that the observed differences in contact hysteresis at different temperatures could be accounted for by substituting in Eq. (9) the appropriate value of *C*, the relaxation constant, at the different temperatures.

A second feature was that the velocity shifts required to superpose the rate-dependent adhesive energy results were different for coming-on and coming-off. The coming-on cracks were much more strongly affected by temperature than those coming-off. This is a surprising observation which may possibly be explained in terms of the gas which had to be displaced when forming a contact. Gas bubbles were invariably trapped in the contact region as the surfaces were brought together and could be observed gradually leaking away, presumably through a small interfacial gap.[35]

It is interesting to note that the shifts for the coming-off curves did not correspond to the W.L.F. shifts found for other viscoelastic materials.[23] In Figure 7 the theoretical curves have been plotted according to an Arrhenius-type temperature dependence. Although this did not give a perfect description of the results, the fit was better than that given by the W.L.F. equation.

EFFECT OF MATERIAL RELAXATION

The results reported so far correspond to fully cured rubber whose relaxations are relatively slight at room temperature. Uncured rubber, by comparison, relaxes about ten times more quickly and should give greater hysteresis according to Eq. (9), allowing a further distinction to be drawn between the rate dependent adhesive energy and the viscoelastic effect. Adhesion measurements shown in Figure 8 do indeed demonstrate a larger hysteresis, a factor of 3.2 in contact diameter in this case compared with 1.7 for the cured material. The theory again gave fair agreement with experiment when the relaxation constant was taken as 0.1. This value compares with the value of 0.084 ± 0.01 measured in stress relaxation tests.

Agreement with theory was also obtained on two other fronts. First it was evident that, for uncured material the crack stopped very quickly, in about 10 seconds compared to about 10 minutes for the cured rubber. Secondly the coming-off final contact size was rather dependent on the distance travelled by the crack. This observation lends support to the crack length dependence of the crack arrest term of Eq. (9). Experiments on one sample again gave good repeatability: two such runs are shown in Figure 8. However, different samples gave widely different hysteresis values ranging from 1.4 to 2.0 when expressed as $\log_{10}$ (adhesive energy).

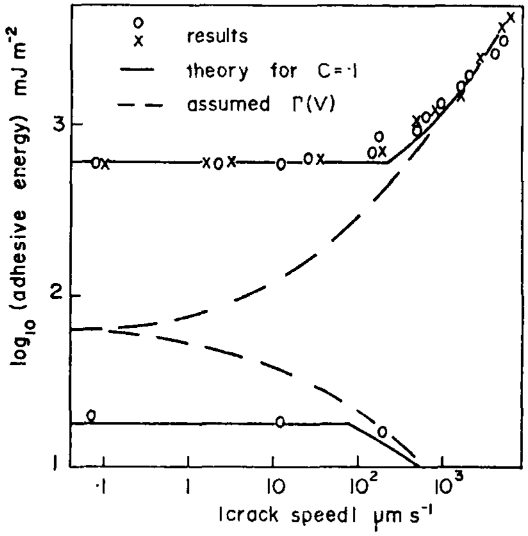

FIGURE 8 Adhesive energy for uncured rubber at zero load.

EFFECT OF LOADING

From the point of view of adhesive joint strength it is important to consider the separation of bodies under an applied stress. The equilibrium behaviour of the sphere-flat joint under a tensile force $-P$ has been mentioned by Johnson *et al.*[1] who showed that Eq. (2) must be modified to give

$$\gamma - \frac{8}{27\pi}\frac{E}{R^2}a^3\left[1 - \frac{9RP}{16Ea^3}\right]^2 = 0 \tag{11}$$

As the tensile force is increased, the equilibrium contact size diminishes to a critical point where equilibrium is no longer possible and separation of the surface occurs. The critical load in this case is

$$-P = \tfrac{3}{2}\gamma\pi R \tag{12}$$

Dynamic experiments on the rubber sphere and glass plate contact were carried out by loading the system to a certain contact size, then suddenly applying a negative load and watching the change in contact diameter with time. The results of Figure 9, expressed in terms of adhesive energy calculated from Eq. (11), demonstrate dramatically that resistance to crack growth

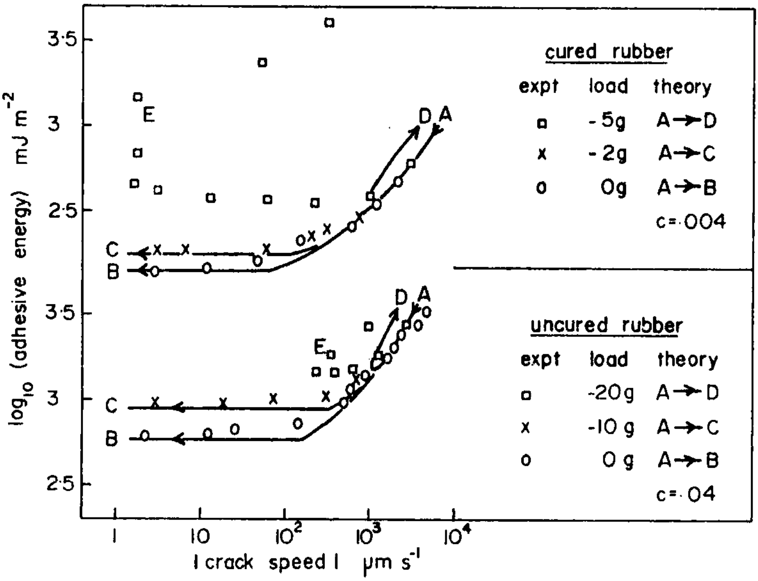

FIGURE 9 Effect of pull-off load on crack propagation.

increases with crack length. For short cracks slowing down near A, the results all lie on the zero load curve AB and the adhesive energy is a function of velocity only. However, as the cracks grow, the results deviate more and more from this curve until at the point E, where the crack begins to accelerate to fracture the joint, the deviations are very marked.

In order to arrive at a theoretical description of these results, a modified form of Eq. (9) was used

$$\Gamma(V) - \frac{8}{27\pi}\frac{E}{R^2}a^3\left[1 - \frac{9RP}{16Ea^3}\right]^2\left[1 - \frac{C}{Vt}\left(\frac{a_1^5 - a^5}{5a^4}\right)\right] = 0 \qquad (13)$$

In this equation the applied load $-P$ has been taken into account and the viscoelastic term has been changed. This change was necessary because under negative loads the cracks travelled further and the short crack approximation (Eq. 4) was less valid than in the zero load experiments. a_1 is the original contact radius and a the current contact radius in this case. As Figure 9 shows, this equation gives a measure of agreement with experiment. The major problem with the theory was that the theoretical cracks were much more unstable than the experimental ones and were arrested more readily.

The pull-off results are conveniently presented in the form of a time to failure plot (Figure 10) of the type used by Zhurkov.[10] Such a plot shows clearly how the joint strength is dominated by the dynamics of crack growth. At high loads the failure is controlled by the rate dependent adhesive energy term. Below a certain load, however, the viscoelastic term becomes significant and prevents further crack propagation even though equilibrium has not been reached. Observations of the cracks over a period of a week demonstrated that crack arrest had indeed occurred. In this case, the cured rubber gave a long time joint strength four times the equilibrium strength, calculated from Eq. (12), and the uncured rubber gave a joint twenty times stronger than an equilibrium calculation predicted.

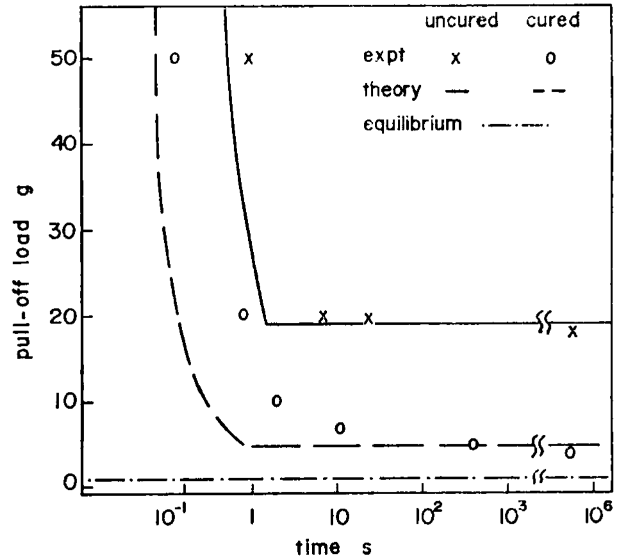

FIGURE 10 Time to failure of cured and uncured rubber joints.

CONCLUSION

The adhesive contact between smooth natural rubber and glass has been shown to exhibit marked kinetic properties analogous to those observed in tack, fracture and wetting studies. These kinetic influences which retard the approach to equilibrium of surface and elastic forces, are of two kinds:

a) a dependence of adhesive energy on crack speed arising from a dissipation of energy near the crack tip and

b) an adhesive hysteresis which is shown to arise from bulk viscoelastic relaxations in the material.

Although the surface kinetic forces merely slow down the onset of equilibrium, the hysteresis forces prevent its attainment even after very long times. Joint strength under static conditions can therefore be many times higher than an equilibrium theory would predict.

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