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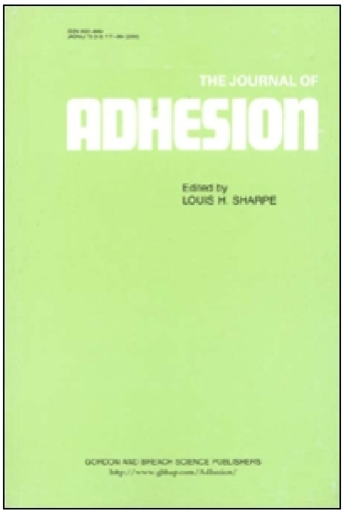

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Influence of Dwell Time on the Adherence of Elastomers

M. Barquins[a]
[a] Laboratoire Central des Ponts et Chaussées, Cellule Mécanique des Surfaces du C. N. R. S., Paris, France

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Influence of Dwell Time on the Adherence of Elastomers

M. BARQUINS

Cellule Mécanique des Surfaces du C.N.R.S., Laboratoire Central des Ponts et Chaussées, Paris, France

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We have studied the influence of the time of application of a given force, pressing a rigid spherical punch against a viscoelastic solid, on the kinetics of detachment when a known tensile force is applied suddenly. The edge of the contact surface is treated as a crack tip propagating in mode I at the interface between the two solids. It is shown that the general kinetics equation proposed earlier, $G-w = w\phi(a_T v)$, relating strain energy release rate G, Dupré's work of adhesion w, and the dissipation function ϕ characteristic of the material tested, is confirmed provided that w is given higher values than those usually deduced from measurement of the contact area by the theory of adherence of elastic solids of Johnson *et al.*[21] It is found both that the time required for fracture varies with contact time t in direct proportion with $t^{0.2}$ and that the work of adhesion varies directly with $t^{0.1}$; this latter point means that the increase in adherence cannot be attributed to the diffusion of the free ends of the elastomeric chains, which would vary directly with $t^{0.5}$. It is shown by a simple calculation that the improvement in adherence with time very probably results from relaxation of the stresses stored in the roughnesses of the surfaces making the contact between the two solids.

INTRODUCTION

Most elastomers have the peculiarity of adhering instantaneously to solid surfaces with which they are placed in contact. This phenomenon, known as tackiness, results basically from the intervention of the molecular attraction forces acting in and around the areas of contact. Commonly, tackiness is evaluated either qualitatively, by touch (finger test), or quantitatively, using a tensile machine that measures the force of separation of a rigid punch with a flat or spherical end in contact with the surface of the elastomer when a fixed

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cross-head velocity is imposed.[1] The maximum value of the force recorded during separation then serves to characterize the tackiness of the material under the experimental conditions chosen: the force of adherence so determined depends not only on the intrinsic properties (surface and viscoelastic) of the tested solid, but also on such experimental parameters as the speed of separation, the temperature, the relative humidity, the initial applied load, and the duration of contact under this initial load. It is the influence of this last factor that we have studied.

The increase in the adherence of elastomers with the contact duration (dwell time effect), quite frequently found and invariably highly visible for the shortest contact times, is most often attributed to the action of two main mechanisms, with the predominance of one or the other depending essentially on the nature and properties of the materials in contact. These two mechanisms, for which it is in general not known how to quantify the effects, are the macroscopic creep of the elastomer, which both undergoes deformation and "wets" the surface of the indenter[2-5] and the microscopic diffusion of the free ends of the polymeric chains across the interface,[6-8] a phenomenon that may in some cases result in the disappearance of the interface. The involvement of this process of diffusion, which occurs when the materials in contact are both elastomeric, can be recognized by the linear variation of the force of adherence with the square root of the dwell time under the initial load. As for the first mechanism mentioned, which results from the wetting power of elastomers and from the variation with time of their compliances, it is found in particular when the materials have a rough surface condition.[2,9] A third process, less frequent, must also be mentioned: the exudation of vulcanizing ingredients. These substances, trapped in the elastomers, gradually migrate to the surface to produce a surface bloom, increasing the surface energy of the materials and subsequently their adherence.[10]

In the study described below, which deals only with the adherence between a rigid spherical punch and the flat surface of a viscoelastic material, it is shown that the introduction of concepts from fracture mechanics, such as strain energy release rate G or stress intensity factor K_I, makes it possible to predict, in addition to the influences on adherence, already mentioned, of the velocity of separation and of the temperature,[11,12] the increase in adherence with the time of application of the initial load.

KINETICS OF ADHERENCE OF VISCOELASTIC SOLIDS

Let us recall that the contact of two solids can be treated as a thermodynamic problem. If U_E, U_P and U_S are the elastic, potential, and interface energies of the system constituted by two bodies in contact, it can be shown that energies

$U = U_E + U_S$ and $U_T = U_E + U_P + U_S$ are thermodynamic potentials for transformations under fixed load and fixed grips conditions, respectively.[13] Similarly, the equations giving the displacement δ of the solids and the strain energy release rate G as a function of contact area A and load P are the equations of state of the system. The contact area under load P is thus the area that minimizes the energy of the system. This contact area may be regarded as an adhesive joint of which the fracture, which is not brutal but progressive, may be seen as the propagation in mode I of a crack at the interface. This is the reason for introducing fracture mechanics concepts to solve the problem of the adherence of viscoelastic solids.

Two solids in contact over area A are in equilibrium if $G = w$, where w is Dupré's work of adhesion (defined in terms of the surface and interface energies of the materials: $w = \gamma_1 + \gamma_2 - \gamma_{12}$). When $G > w$, the separation of the two solids begins, the contact area decreases, and the crack advances; conversely, if $G < w$, the contact area increases and the crack recedes. The difference $(G - w)$ is the force applied per unit length of crack; it is the "motive force" of the crack, which takes a limiting speed v that is a function of temperature. If one supposes that the viscoelastic energy losses are localized on the crack tip, and that they are proportional to w,[14,15] one can write:[13,16]

$$G - w = w\phi(a_T v) \tag{1}$$

where the second member is the drag due to viscoelastic losses at the crack tip (a_T is the shift factor in the Williams–Landel–Ferry transformation). ϕ is a dimensionless function of the speed of propagation and the temperature, and is independent of the loading system, of the geometry and of the nature of the rigid substrate in contact[12,13,16]. Function ϕ is characteristic of the test viscoelastic solid, quite probably directly linked to the frequency dependence of the imaginary component of the Young's modulus. Knowledge of the function $\phi = (G - w)/w$ makes it possible to predict the evolution of the contact in all circumstances.[11,12] Equation (1) assumes only that the rupture is adhesive, *i.e.*, that the crack propagates at the interface, and that viscoelastic losses are limited to the crack tip, meaning that gross displacements must be purely elastic so that G can be calculated in the kinetic phenomena.[12,13,16]

Data from the literature concerning peeling tests at an angle of $\pi/2$[14,15,17,18,20] show that function ϕ varies, over a large range of speeds of propagation, as:

$$\phi(a_T V) = \alpha(T) v^n \tag{2}$$

with $\alpha \sim a_T^n$. Our experimental results, obtained using a glass-polyurethane couple with three different geometries—peeling, adherence of flat punches and adherence of spherical punches—give $n = 0.6$, a value often found in the peeling of elastomeric materials. Our results as whole confirm all aspects of the proposed theory to within about 1%.[13,16] Moreover, the multiplicative effect of w on viscoelastic losses (Eq. (1)) has been confirmed by a test equivalent to peeling at an angle of $\pi/2$, namely measurement of the rolling resistance of a glass cylinder in contact with the polyurethane surface, at various levels of relative humidity.[12,20] Function ϕ is in fact independent of the geometry and of the loading system, and up to a value of 10^3 it varies with $(a_T v)^{0.6}$.

In case of contact between a rigid sphere of radius R and a semi-infinite elastic solid, the geometry chosen for the study of the influence of dwell time on adherence, strain energy release rate G may be derived from the expression of the elastic displacement of two solids in adhesive contact ($w \neq 0$).[21]

$$\delta = \frac{a^2}{3R} + \frac{2P}{3aK} \tag{3}$$

$$G = \frac{3a^2K}{8\pi R^2}\left(1 - \frac{R\delta}{a^2}\right)^2 = \frac{\left(\frac{a^3K}{R} - P\right)^2}{6\pi a^3 K} \tag{4}$$

In these expressions, P is the applied load, a the radius of the contact area, and K a constant of elasticity given by $1/K = 3(1-\nu^2)/4E$, ν and E being the Poisson's ratio and the Young's modulus of the test material respectively. At equilibrium ($G = w$) under load P_0, the radius of the contact area is given by :[21]

$$a_0 = \left\{\frac{P_0 R}{K}\left(1 + \frac{3\pi w R}{P_0} + \left[\frac{6\pi w R}{P_0} + \left(\frac{3\pi w R}{P_0}\right)^2\right]^{1/2}\right)\right\}^{1/3} \tag{5}$$

which is greater than the value $a_H = (P_0 R/K)^{1/3}$ given by Hertz's theory which does not take into account the attractive molecular forces between the two bodies.[22]

The equilibrium relation, $G = w$, may be represented in a diagram (δ, a), giving the variation of the displacement of the centres of gravity of the two solids as a function of the radius of the contact area, using the equation of state (Eq. (4)) of the system. Figure 1 gives the family of equilibrium curves, $\delta(a)$, for various values of w in a concrete case ;[16] the Hertzian theory is illustrated by the curve $\delta(a)_{w=0}$. The relations between δ and a at fixed load P (Eq. (3)) are shown in the same diagram by the curves $(\delta)_P$, which are independent of Dupré's work of adhesion w, and of which the minima, when they exist (for $P > 0$), are all located on the Hertz curve. The dashed curve corresponds to the force of elastic adherence, for experiments at fixed load $P_c = -\frac{3}{2}\pi w R$, for the particular case $w = 100$ mJ·m^{-2}, with point C indicating the limit of stability of the system.

When the equilibrium is broken, for example by suddenly decreasing the

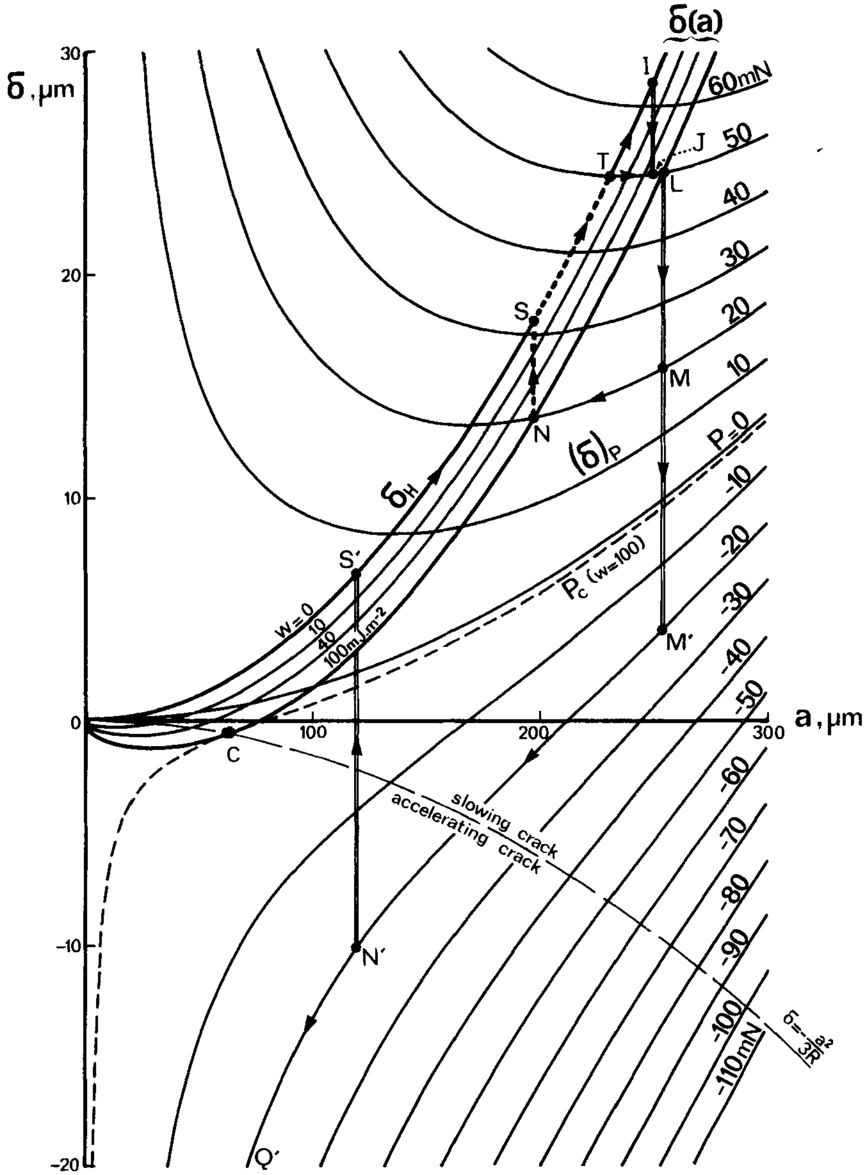

FIGURE 1 Relations between the elastic displacement δ and the contact radius a of a rigid spherical punch ($R = 2.19$ mm) with an elastic solid ($E = 5$ MPa, $\nu = 0.5$). The equilibrium curves for various values of w are curves $\delta(a)$; curves $(\delta)_P$ show variations of δ with a at fixed load P. Curve δ_H is given by Hertz's theory ($w = 0$).

load from P_0 (point L in Figure 1) to $P' < P_0$, strain energy release rate G increases (Eq. 4) and the contact area is decreased by the advance of the crack. It is shown in Figure 1 that one must firstly observe an instantaneous modification of displacement δ at constant contact radius (branch LM or LM') corresponding to the elastic response of the system, followed by a simultaneous variation of δ and a at fixed load P'.† It is also shown in Figure 1 that the evolution along curve $(\delta)_{P'}$ may lead to a new equilibrium state (branch MN), if load P' is greater than P_c, or to rupture of contact (branch $M'Q'$), if not, with the crack propagation speed increasing or decreasing according to whether the sign of $(\partial G/\partial A)_{P'}$ is negative or positive. The locus of propagation speed minima is represented by curve $\delta = -a^2/3R$.[16]

At an equilibrium point, as along a fixed load propagation curve $(\delta)_{P'}$, the elastic solid and the indenter are joined vertically (geometry of fracture mechanics), as always when molecular attractions are involved. Moreover, it can be shown that regardless of the value of P, one always has $P/3\pi GR \geqslant -1/2$.[23]

All of the theoretical predictions have been experimentally confirmed,[12,16] using for the initial dwell time the value of 10 minutes, long compared to the fracture time and such that the contact areas have reached dimensions that are constant with time. In all cases, the kinetics of propagation was studied using Eq. (1) and each time, the dissipation function ϕ, calculated by $(G-w)/w$ from P', w, and the measured contact radius, was represented by the same master curve $\phi(v)$ as in Figure 6.

INFLUENCE OF DWELL TIME ON ADHERENCE—RESULTS

The experiments were carried out using apparatus, described elsewhere[12,16] and shown in Figure 2, consisting essentially of a precision balance supporting, at the end of the arm, a hemispherical glass lens of radius $R = 2.19$ mm. This indenter is applied, for a given duration t_A, under compressive load P, against the flat surface of a polyurethane plate (Vishay PSM4; $E = 5.4$ MPa; $\nu \simeq 0.5$). At the end of time t_A, a tensile force P' is imposed to break the contact. The contact area, illuminated by reflection of monochromatic light, is observed through the lens with a microscope. For a quantitative evaluation of the evolution of the contact area during rupture, a 16 mm camera records the contact areas at 25 frames per second with approximatively ten-fold magnification. The experimental results presented required the examination

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† The instantaneous displacement at constant a is that of a flat punch under a load $P_0 - P'$, and it is $\Delta\delta = 2(P_0 - P')/3aK$.[16]

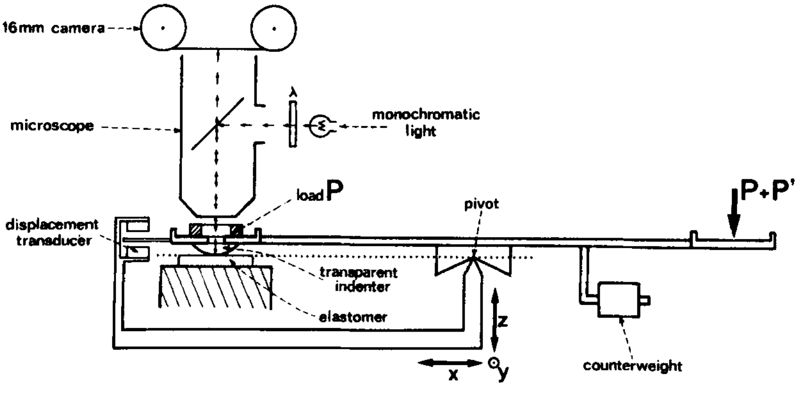

FIGURE 2 Schematic diagram of the apparatus used to study the adherence of a glass spherical cap to viscoelastic materials.

and measurement of 2000 frames. The apparatus also includes an inductive displacement transducer, used to record the displacement δ of the indenter in the test viscoelastic material.

Figure 3 shows the contact radius versus time for instantaneous unloadings from the same initial load $P = 50$ mN to the same final load $P' = -30$ mN for different durations of application of P ranging from 1 minute to 15 hours. Because of the choice of compressive load P and tensile load P', each curve has a point of inflexion, indicating the existence of a propagation speed minimum.[16] The contact area at the inflexion point $a_I = (-P'R/K)^{1/3}$ corresponds to minimised G, the strain energy release rate, whose value at this point is $G_{\min} = -2P'/3\pi R$. It will be noted that $G_{\min}$ is independent of the material, while knowledge of a_I is a means of determining the constant of elasticity K. The curves of Figure 3, obtained for the same load P', thus have points of inflexion at the same radius $a_I = 190\ \mu$m.

In agreement with earlier findings,[16] the initial contact area radii, all greater than the value $a_H = 225\ \mu$m derived from Hertz's theory, increase with dwell time under load P up to the limiting value $a_0 = 244.5\ \mu$m, obtained after a time t_{crit} equal to 10 minutes. The new and surprising result is the increase in the time required for rupture with dwell time beyond t_{crit}, a phenomenon apparently incompatible with the equilibrium state thought to have been reached at t_{crit}, because of the absence of subsequent variation of the contact area. The curves of Figure 3 show that, for a given contact area radius, the longer the dwell time the lower propagation speed $\dot{a} = \mathrm{d}a/\mathrm{d}t$, which has the effect of increasing the time required for complete rupture of the contact between the two solids. On first analysis, this phenomenon may be interpreted by an increase in w with dwell time, resulting in a decrease in the crack

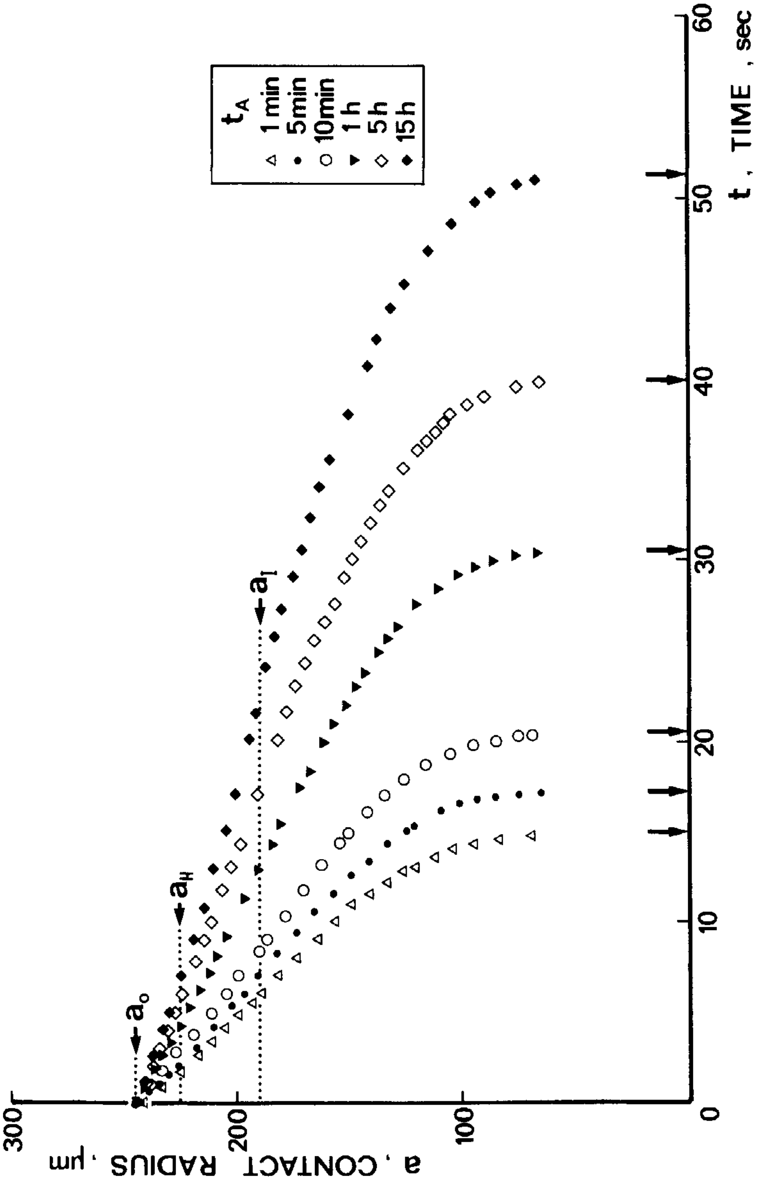

FIGURE 3 Variations, as a function of time, of contact radius for various initial dwell times. (P = 50 mN, P' = −30 mN, R = 2.19 mm, E = 5.4 MPa, ν = 0.5).

"motive", defined by Eq. (1), and consequently a reduction in the propagation speed.

The variation of contact rupture time t_R under load P' as a function of the time of application t_A of load P is shown by Figure 4. These values, deduced from Figure 3, indicate a variation with $t_A^{0.2}$ in the range of durations studied. The deviation from the curve observed at $t_A = 1$ minute (not very large compared to $t_R = 15$ seconds) may be reduced by including the rupture time in the dwell time. Figure 4 also shows the time t_I of crack propagation from the initial contact area to contact radius a_I corresponding to the propagation speed minimum. The joint variation of t_I and t_R with power 0.2 of the time of application of compressive force P suggest that the curves of Figure 3 can be superimposed on a single curve by normalizing the time axis by $(t_R)^{0.2}$, as is confirmed by the plot. There is some dispersion at the time origin because of the non-similarity of the initial contact radii.

The results of Figure 3 may be analyzed using Eq. (1), with the strain energy release rate G calculated by equation 4. Figure 5 gives, for each time of application of force P, the relation between G and propagation speed v, deduced from the slope at each of the points of a curve $a(t)$. For a given time t_A, it

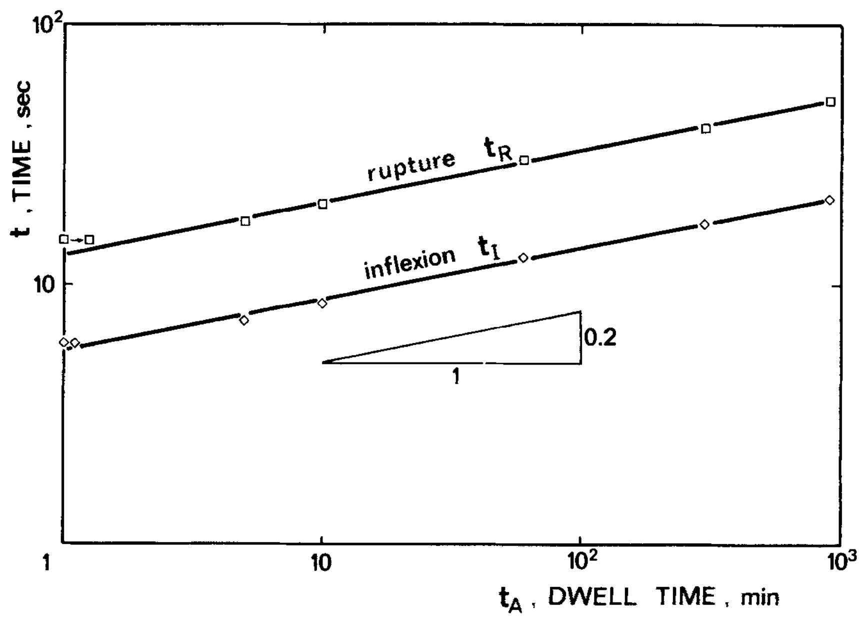

FIGURE 4 Variations, as a function of dwell time, of rupture time t_R and of crack propagation time t_I from the initial contact area to the area of radius a_I corresponding to the minimum of the propagation speed (values deduced from Figure 3).

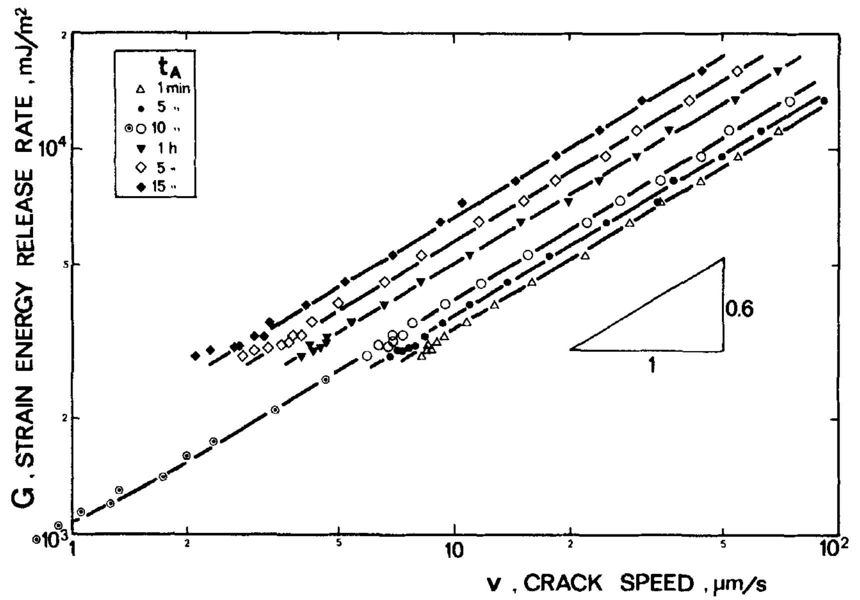

FIGURE 5 Relations between the strain energy release rate and the crack propagation speed, for various dwell times (calculated values derived from Figure 3).

is confirmed that the points corresponding to a slowing down $((\partial G/\partial A)_{P'} > 0)$ and those corresponding to an acceleration of propagation $((\partial G/\partial A)_{P'} < 0)$ lie on a single curve,[16] which confirms the one-to-one correspondence of the relation between G and v, since the minimum speed is invariably observed at the same $G = G_{\min} = -2P'/3\pi R = 2900$ mJ/m^2. The six curves $G(v)$ obtained for the various dwell times studied are, in log–log coordinates, straight and parallel, with $n = 0.6$ as common slope. These results corroborate the earlier findings and are in perfect agreement with equations 1 and 2, bearing in mind that at a high propagation speed ($v > 5\mu$m/s), the values assumed by G are very high with respect to those usually atrributed to w and $G \simeq \alpha(T)wv^{0.6}$. The curve for time $t_A = 10$ minutes is completed by unloading from $P = 50$ mN to $P' = -10$ mN carried out under the same experimental conditions: at small velocities of propagation, the incurvation of the line of points shows that the foregoing approximation is not valid, since w is no longer negligible with respect to G in Eq. (1).

The distribution of the curves of Figure 5 is similar to that obtained in peeling experiments[19] and cylinder rolling experiments[12,20] in an atmosphere of variable humidity, in which the vertical offset results from the variation in Dupré's work of adhesion w with the water vapor content, thereby confirming the multiplicative effect of w on viscoelastic losses at the crack tip.[14] Assigning a value of w to each water vapor content makes it possible to present the results on a single curve in accordance with Eq. (1). In the same way, it is possible to assign to each dwell time t_A a particular value of work of adhesion w so as to obtain the master curve giving the variation of dissipation function ϕ as a function of propagation speed. The necessary determination of a reference couple (dwell time $(t_A)_0$ – work of adhesion w_0) was made as follows: for reference time $(t_A)_0 = t_{\text{crit}} = 10$ min, after which the contact radius remains constant at $a_0 = 244.5$ μm, is assigned the reference value $w_0 = 75$ mJ/m^2 deduced from the $a_0(w_0)$ equilibrium equation (Eq. (5)). It then suffices to assign to the other dwell times: 1 and 5 minutes, 1, 5, and 15 hours, the respective work of adhesion values 63, 70, 92, 106 and 121 mJ/m^2 to obtain the master curve for $\phi = (G-w)/w$ as a function of v, presented in Figure 6. Equation (2) giving function ϕ with $n = 0.6$ is thus confirmed for $\alpha = 5.4 \cdot 10^4$ in SI units, a value that agrees with the results obtained earlier.[12] Knowledge of α and of an apparent work of adhesion w for each dwell time clearly make it possible, from Eqs (1), (2) and (4), by computerized numerical integration,[12] to obtain the various curves of Figure 3. The plot shows a very good superimposition of the computed and experimental curves, except during the first few instants of propagation with long dwell times ($t_A > 10$ minutes). In these cases, as could be expected, the computed contact radii are slightly larger than the radii actually measured. For example, according to Eq. (5), the equilibrium contact radius corresponding to $w = 121$ mJ/m^2 is $a = 250$ μm, rather than the observed $a_0 = 244.5$ μm (which corresponds to $w_0 = 75$ mJ/m^2). These values show, moreover, that a 2% variation in radius a is accompanied by a large concomitant variation of work of adhesion w, close to 50%.

The apparent work of adhesion values, computed to plot the curve of Figure 5, are shown in Figure 7 as a function of their associated dwell times (solid curve); the variation of w with the 1/10th power of this time was observed. Up to $t_{\text{crit}} = 10$ minutes, a good match is found between these apparent values of w and those deduced from Eq. (5), which are shown by the dashed curve; the error bars indicate a variation in radius of ± 1 μm. Beyond $t_{\text{crit}} = 10$ minutes, it must be stressed that, because the contact radius does not vary, Eq. (5)[21] can no longer account for the increase in work of adhesion with dwell time.

Since the work of adhesion cannot increase indefinitely with time, it is to be expected that, for dwell times over 15 hours, a smaller increase rate will be observed, leading to a limiting value that may be estimated to lie between 150 and 300 mJ/m^2, in view of the nature of the links involved in the glass-polyurethane contact. It will also be noted that, because of the very modest variation of w with time, the choice of the reference couple $(t_A)_0 - w_0$ at 8 minutes rather than at 10 minutes would not alter the representation of the

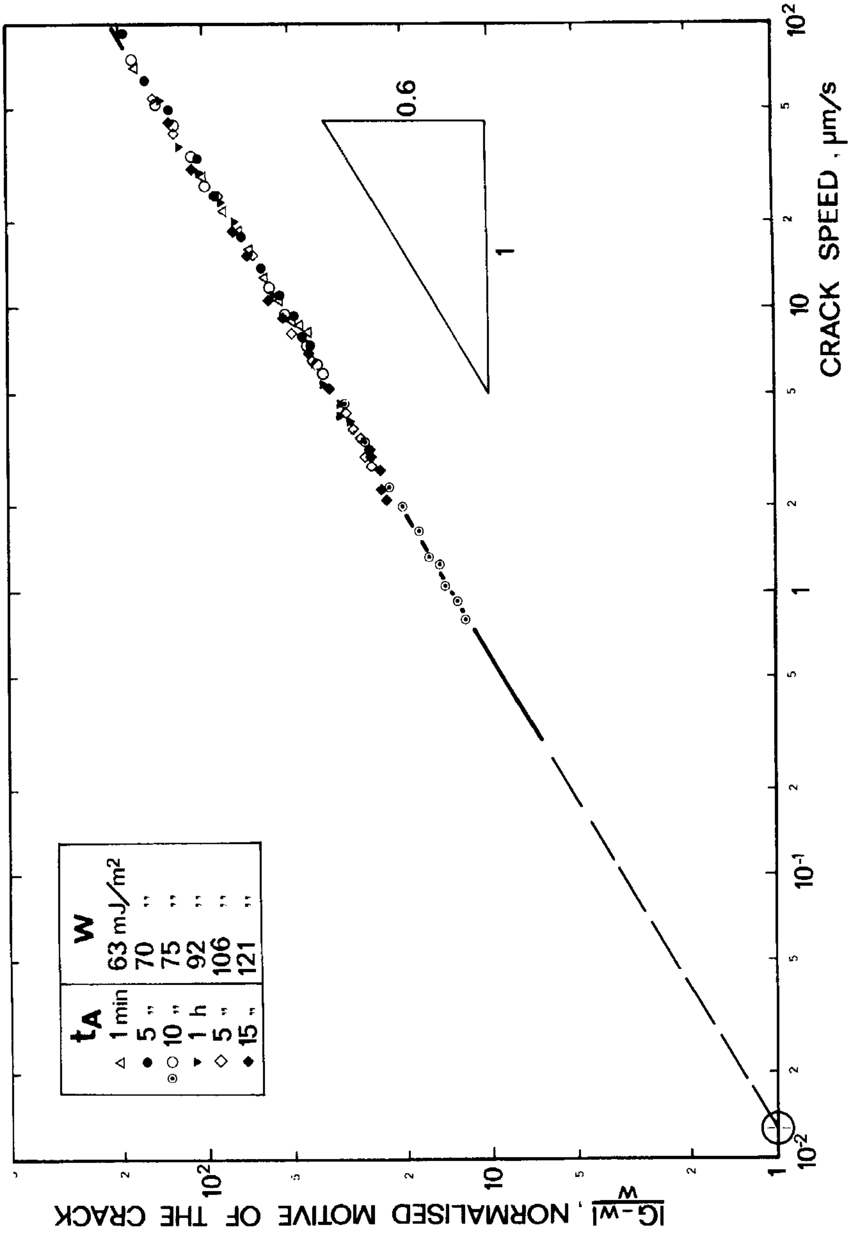

FIGURE 6 "Normalized crack motive" as a function of propagation speed. Master curve derived from Figure 5.

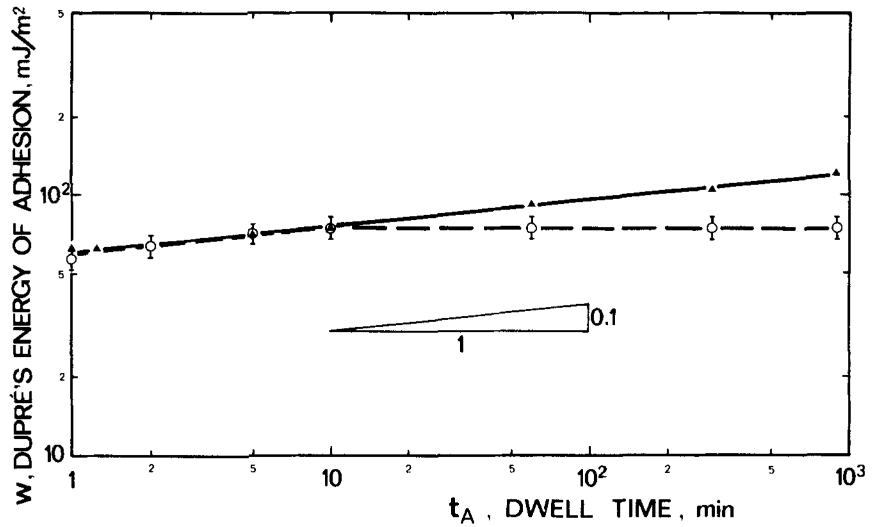

FIGURE 7 Apparent Dupré's work of adhesion as a function of dwell time. (—▲— values derived from Figures 3 and 5, —Φ— values derived from the theory of adherence of elastic solids, Eq. (5).)

phenomenon studied. The association of the results given in Figures 4 and 7 shows that the work of adhesion w varies with the square root of the rupture time for given loading and unloading conditions, a law of variation that has been confirmed for unloadings from $P = 30$ mN to $P' = -20$ mN. Measuring the rupture time is therefore a simple way of determining the work of adhesion by $w^2 \sim t_R$.

DISCUSSION

The increase in the rupture time with the dwell time (Figures 3 and 4), which reflects an increase in adherence, may be interpreted as an increase in work of adhesion w. This is how we have already attempted to explain the increase in the tackiness of elastomers with dwell time.[11,22] The involvement of diffusion of the free ends of the polymeric chains across the interface, often suggested in the case of contact between materials having similar chemical natures to deal with the increase in adherence as an increase in the number of links in the contact area, cannot be maintained here. Figure 7 shows that w varies with power 0.1 of time, rather than the square root to be expected in the case of diffusion. Consequently, the increase in adherence with time must be attributed to a mechanism having a slower kinetics than that of diffusion, such as the relaxation of stresses in the roughnesses of the contacting surfaces. These asperities are highly compressed during the initial loading stage, and the variation of w with $t^{0.1}$ is in good agreement with the kinetics of viscoelastic relaxation of rubber-like materials.[24]

Resticking by added load. Impact

The loading from O to P of a rigid sphere in contact with an elastomeric solid, together with its resticking from P' to $P > P'$, have already been examined.[12,25] A study of adherence assumes, in effect, understanding of the two consecutive processes of loading and unloading. It will be recalled that the application of an added load P (compressive) cause an increase in the contact area through the retreat of the crack. In this solicitation, it is known that the discontinuity of vertical displacement $[u_z]$ at the crack tip begins by vanishing, resulting in the simultaneous cancellation of stress intensity factor K_I and of strain energy release rate G; the stress singularities also disappear. During propagation to $G = 0$, the work of the stresses at the crack tip and the viscoelastic losses are negligible, so that resticking always appears as a very rapid phenomenon.[16,26] It is shown, in Figure 1, that the change by sudden loading ΔP from an equilibrium point N (under load P') to an equilibrium point L (under load $P = P' + \Delta P$) takes place continuously in two successive stages. The first, NT, which is instantaneous, starts with a displacement NS at constant contact area, corresponding to the transition from $G = w$ to $G = 0$ followed by the Hertzian branch ST, corresponding to propagation at $G = 0$. The second, TL, represents the propagation of the crack at constant load, along curve $(\delta)_{P'}$ a slow stage during which the speed decreases and vanishes. Simultaneous measurements of δ and a during loading have confirmed the proposed path NSTL. Furthermore, the Hertzian evolution of the contact (branch ST) has been confirmed by study of the profile of the surface by examination and measurement of Newton's rings.[25]

Thus, the apparent speed of resticking, by comparison with unsticking at the same ΔP, results simply from the elastic response of the system a zero work of adhesion (branch NT in Figure 1), which leads almost instantly to the Hertzian contact radius a_H, which, for $P = 50$ mN, is already 92% of the observed limiting radius a_0 (Figure 3). Moreover, radius a_H may be exceeded and a_0 reached more rapidly by a possible shock at the moment of making contact, or of reloading. As it happens, a slight shock, which is a transient added load, results in a transition from equilibrium point N to equilibrium point L (Figure 1) *via* path NISJL, which includes, as above, an instantaneous stage NSIJ and a slow stage JL of increasing contact area at constant load P. Since the overshoot of curve $(\delta)_P$ on the Hertzian path δ_H (branch TI) leads to a continuous variation in contact radius, as in the absence of a shock (branch

TJ), detectable only by analysis of the evolution of δ, it may be a source of error in the study of the dwell time effect, which concerns only branch TL along curve $(\delta)_P$.

Throughout the stage of resticking from P' to P or of loading from O to P (paths NSTL and OTL of Figure 1, respectively), $G < w$, so that the normalized "motive" of the crack $|G-w|/w$ is equal at most to unity,[12] which means, according to Figure 6, that the maximum speed of growth of the contact radius (corresponding to $G = 0$) is as low as 10^{-2} μm/s. It will be noted that $(G-w)/w$ also assumes the value of unity during unloading, for $G = 2w$. The reference to Figure 6 assumes that the dissipation function ϕ varies, during resticking as during detachment, with power 0.6 of the speed, which is in all likelihood the case, since ϕ is characteristic of the material. It is the existence of a crack "motive" of very low "power" (equal at most to w) that serves to justify the observation of a limiting contact radius a_0 and to explain the hysteresis already encountered in the attainment of equilibrium either by unloading at P or loading under P.[26] Indeed, the smallest obstacle, dust or roughness, or a slight variation in the relative humidity of the ambient air,[19] may arrest the propagation of the crack. This is why the authors of the theory of elastic adherence[21] applied a slight tapping to their experimental apparatus in order to shorten the time required to attain equilibrium; this procedure also had the effect of improving the reproducibility of the measurements.

The very low maximum speed of propagation during resticking, deduced from Figure 6, is not however capable of explaining the observed kinetics. Indeed, a simple calculation shows that if this speed of propagation were held constant, it would take more than 33 minutes for the contact radius to go from the Hertzian value a_H to value a_0, whereas the roughly twenty microns separating these two values are covered in time $t_{\text{crit}} = 10$ minutes. It is therefore probable that in the absence of special precautions, any loading or resticking is accompanied by a shock, so that, in Figure 1, equilibrium point L is always reached from equilibrium point N *via* path NSIJL, rather than the ideal no-shock path NSTL. This hypothesis is, moreover, confirmed by recording with a storage oscilloscope the very brief stage of non-monotonic variation of δ corresponding to path TIJ. It is starting from point J that the low propagation velocities corresponding to motive $G-w$, mentioned above, become observable. It is easy to show that a shock accompanies each loading, by pointing out that the Hertzian load that gives instantaneously, without shock, the limiting contact radius $a_0 = 244.5$ μm is approximately 64 mN, which corresponds to dropping the applied weight $P = 50$ mN from a height of as little as 11 microns above the surface of the sample (a result in which the inertia of the load application apparatus is neglected). Under these conditions, the calculated loading velocity is close to 15 mm/s, a value perfectly compatible with the experimental technique used. Conversely, damped application of the load, to forestall any shock, has the drawback of allowing molecular attractions to act during the entire loading period, so that the Hertzian stage ST (Figure 1) is no longer rigorously followed.[12,25]

Relaxation of stresses in roughness

During loading to P, with or without a shock, the always present roughnesses on the surface are compressed, and so an additional elastic energy is stored locally. For short application times of P, the presence of unrelaxed stresses has the effect, during unloading under P', to increase the crack propagation speed, in agreement with the earlier findings,[18] and consequently to cause the observed decrease in the rupture times (Figures 3 and 4).

Since the crushing of the roughnesses occurs at fixed grips,[27] the relaxation of the corresponding strains occurs "en bloc", independently of the mean distribution of stresses in the contact area. It is known that the contact area, at non-zero work of adhesion, includes two distinct regions:[23,28] a circular center zone of radius $a^* = a[R(P+2a^3K/R)/3a^3K]^{0.5} < a$, in which the vertical normal stress σ_z is compressive, and an annular zone of width $a-a^*$, supported at the edge of the contact area, in which σ_z is tensile. For example, if we take for a the equilibrium value $a_0 = 244.5$ μm (Eq. (5)) and for w the value 75 mJ/m^2, corresponding to $t_{\text{crit}} = 10$ minutes (Figure 5), the radius a^* of the circle along which $\sigma_z = 0$ is then $a^* = 235$ μm. Examination of the curves of Figure 3 shows that, even for the longest dwell times, the kinetics of crack propagation during unloading is not affected by the particular stress distribution in the contact area. Even though the crack tip passes rapidly from a zone subjected to a tensile force to a zone subjected for the same time to a compressive force, no singularity can be seen in the curves of Figure 3, in all likelihood because stress relaxation is independent of the mean pressure distribution, as mentioned above.

Earlier, we attributed the increase in motive $G-w$ of the crack to a decrease in work of adhesion w, with the highest work values corresponding to the longest times of application of P (Figure 5). The increase in this motive may also result from an increase in the strain energy release rate G, with w constant, due to the additional elastic energy stored in the roughnesses, not taken into account in the computation of G. This point of view has the advantage of assuming that the work of adhesion, a function of the physico-chemical state of the surfaces of the solids in contact, is independent of the geometrical state of the surfaces. It should be pointed out, indeed, that if the relaxation of stresses, which takes place either by creep or by the turning over of segments of chains, had the effect of increasing the surface energy of the material, and thus work of adhesion w, we should find the growth of the contact area continuing after t_{crit}.

The increase in G may be estimated by a highly simplified calculation, by treating the roughnesses as spherical caps having the same radius r and the same thickness h, *i.e.*, having a uniform height distribution. Under these conditions, the elastic energy stored in each roughness, for a total crushing $\delta = h$ that results in an individual contact area equal to $2\pi r\delta$, is given after Hertz's theory by $U_E = 2P\delta/5 = 2Kr^{1/2}\delta^{1/2}/5$. Assuming that the roughnesses are contiguous and independent, the additional elastic energy stored in all of the roughnesses making contact is thus $U_E = \Sigma U_E = 2Ka^2(\delta^3/r)^{1/2}/5$. The corresponding variation in the strain energy release rate may then be written:

$$G = \left(\frac{\partial U_E}{\partial A}\right)_P = \frac{2}{5}\frac{K}{\pi}\left(\frac{\delta^3}{r}\right)^{1/2} \tag{6}$$

and is independent of the contact radius in question.

Figure 8 shows the surface condition of the polyurethane sample tested, photographed with the optical microscope equipped with the Nomarski interferential contrast device, which make it possible to discern unevenness of a few tens of Angströms. Figure 8 may also be regarded as a replica of the geometrical state of the surface of the mould used to prepare the sample.

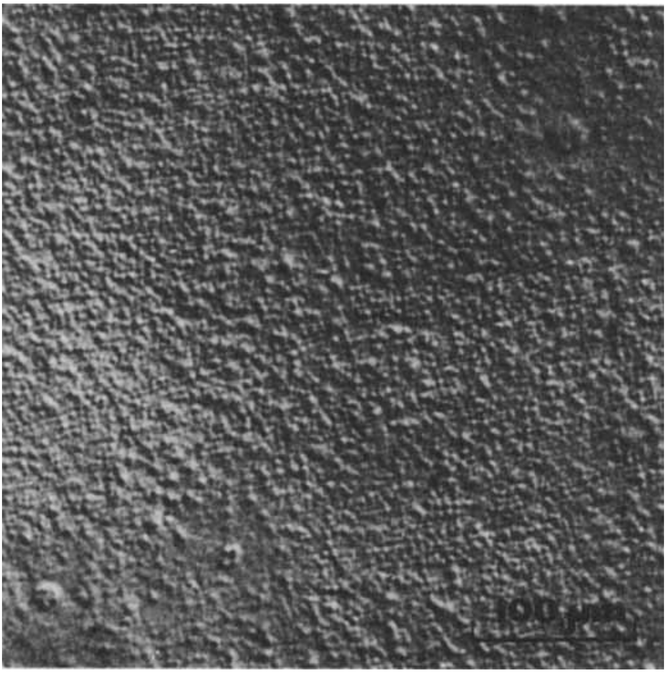

FIGURE 8 Surface condition of the polyurethane sample tested. (Nomarski interferential contrast.)

Evaluating $r = 10$ μm and $h = 0.5$ μm by microscopic examination (values which moreover are in good agreement with those of a sanded metal surface), we calculate by Eq. (6) a maximum variation of strain energy release rate equal to $G = 140$ mJ/m^2. This value perfectly explains the variation in the motive of the crack, wrongly but conveniently ascribed to work of adhesion w (Figure 5). Indeed, assuming that after dwell time $t_A = 1$ minute, corresponding to $w = 63$ mJ/m^2, stress relaxation is still negligible, the reference work of adhesion equivalent to the maximum variation of G then assumes a value close to 200 mJ/m^2, which in fact falls within the range proposed above. It is thus possible to explain the influence of the dwell time on the kinetics of the adherence of elastomers by the variation of strain energy release rate G (Eq. (1)) resulting from the relaxation of the additional elastic energy stored in the roughnesses compressed during contact.

It should, however, be pointed out that adopting the foregoing point of view entails a decrease in function ϕ with respect to previous results (Ref. 16 and Figure 6). In effect, since only the quantity $w\phi$(Eq. (1)), which represents the viscoelastic braking resulting from losses at the crack tip, is experimentally accessible, the choice of a reference value w_0 on the order of 200 mJ/m^2, higher than that usually considered (75 mJ/m^2), imposes a proportional decrease in function ϕ; this amounts to a downward translation by about a quarter of a decade of the master curve of Figure 6, without affecting the variation of ϕ with $v^{0.6}$.

Although incorrect, the hypothesis of an increase in work of adhesion with dwell time nevertheless has the advantage of being able to provide a simplified representation of the principle of a fatigue experiment. For example, subjecting the adhesive joint to alternating cyclic loads creates experimental conditions of work between two apparent works of adhesion values, w_1 (corresponding to equilibrium or prolonged contact) and $w_2 < w_1$ (contact of short duration), perfectly comparable to those used in classic fatigue analyses, for which $w_1 = 2\gamma$ (progression of the crack) and $w_2 = 0$ (reopening of the lips of the crack). We should also note the striking similarity of our results (Figure 6) with the fatigue crack propagation curves well described by Paris' simple empirical law: $da/dN \sim (K_I)^m$.[29] The power 1/0.6 of the variation in strain energy release rate G (which is proportional to K_I^2) with propagation speed corresponds to coefficient $m = 3.2$ of Paris' law, a value well within the range $2 < m < 5$ routinely adopted. A further experiment, now still being developed, subjects the glass lens in contact with the polyurethane plate to alternating loadings from $P > 0$ to $P' < 0$ following an initial cycle of the LM'N'S'T type (Figure 1), with in all likelihood the step TIJ resulting from the shock that is inevitable when P is applied rapidly. In the course of time, the evolution of the cycle up to failure of the adhesive joint is observed, with displacement of point N' towards point Q' along curve $(\delta)_{P'}$ (Figure 1). We hope, through this study, to reach a fine understanding of Paris' law, by demonstrating that the similarity between Eq. (1) and this law in fact shows that crack growth by fatigue of a fragile material is governed by the same basic process as the failure of an adhesive joint by propagation of the interface crack.

CONCLUSIONS

We have shown that, when a rigid spherical punch is applied by a given compressive force against an elastomeric solid, increasing the dwell time has the effect of increasing the time of separation of the solids when a known tensile force is applied to break that contact. The apparent improvement in adherence that results, very often found, is moreover used to advantage in the manufacture of certain rubber products consisting of a number of superimposed plies, such as tires and belts. It can also have undesirable consequences, as when plates of elastomers are stored; and it can also result in the surface deterioration of the component parts of sliding and rolling units, such as seals, drive pulleys, and valve bodies, when they are put back into operation after a prolonged idle time.

After recalling that the edge of the contact area may be regarded as a crack propagating in mode I in the interface, advancing or receding depending on whether strain energy release rate G is greater than or less than Dupré's work of adhesion w, we have explained the rapid evolution of the contact dimensions during loading by the existence of a mechanical shock accompanying the elastic response of the system. In addition, the observation of a limiting value of the contact radius, reached after about ten minutes, has been ascribed to the very slow crack propagation speed during resticking at fixed load, a speed which may vanish at the slightest obstacle.

It has been shown that the general equation of the kinetics of adherence proposed earlier,[16] $G-w=w\phi(a_Tv)$, where ϕ is a dissipation function characteristic of the material, is confirmed provided that we ascribe to w values higher than the one usually deduced from measurement of the contact area using the theory of the adherence of elastic solids of Johnson *et al.*[21] The variation of the work of adhesion with the 1/10th power of the dwell time, which is deduced from the results, rules out the involvement of the diffusion of the free ends of the elastomeric chains, which varies with the 1/2 power, as an explanation of the increase in adherence with dwell time.

In support of the data from the literature concerning, first, the decrease in force of adherence with an accentuation of the roughness of the solids in contact, and second, the acceleration of a crack tip entering a prestressed region, we have put forward the hypothesis, after examination of the surface of the sample tested, that the relaxation of stresses localized in the roughnesses is sufficient by itself to explain the increase in adherence with dwell time. The maximum variation in crack motive $G-w$, estimated at 140 mJ/m^2, perfectly accounts both for the decrease in G resulting from the relaxation of the additional elastic energy stored in the roughnesses, with w retaining a constant reference value, and for the apparent increase or w, with G constant. It remains to understand the fictitious variation of Dupré's work of adhesion with the 1/10th power of the dwell time. This notion of the variation of w with time, while incorrect, should nevertheless enable us to describe the principle of a fatigue experiment in very simple form and to arrive at a fine understanding of Paris's law.

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