Tackiness of Elastomers

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Probe tack testing procedure can be analysed by the fracture mechanics theory previously proposed by the authors for adherence of spheres or punches at fixed load or fixed grips conditions. Tack curves obtained by computer integration closely coincide with experimental ones. So, the influence of various parameters such as cross-head velocity, stiffness of the testing machine or temperature, on tackiness can be predicted.

INTRODUCTION

The tackiness refers to the ability of an elastomer to adhere instantaneously to a solid surface, or to itself, after only a brief time of contact under low application pressures. This ability can be assessed by the finger test or with a tensile testing machine by recording the force to separate the elastomer from a rigid ball or a rigid flat punch (Kamagata *et al.*[1]). The maximum force during separation (tack force) or the dissipated energy (tack energy) is used to characterize the tackiness.

However, the physical significance of the measurement and the comparison between different tests[1] are not evident because the intrinsic properties of materials (surface energy and viscoelastic properties) as well as the experimental parameters (cross-head velocity, initial load, temperature) are involved in this complex phenomenon.

As shown below, the introduction of fracture mechanics concepts, such as the strain energy release rate G, or the stress intensity factor K_I, enables one to take into account all the experimental conditions and to predict any feature,

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Presented at the International Conference on Adhesion and Adhesives of the Plastics and Rubber Institute held at Durham University, England, September 3–5, 1980.

such as increase of tackiness with increasing cross-head velocity or decreasing temperature (as experimentally observed by Bates[2] or Counsell and Whitehouse[3]).

KINETICS OF ADHERENCE OF VISCOELASTIC BODIES

Let us consider two elastic bodies in contact over an area A under a tensile load. The separation of the two bodies can be seen as the propagation of a crack toward the centre of the contact, the crack extension being in mode I (opening mode, with crack faces moving perpendicularly apart).

Equilibrium of the system under a force P can be tested by making a virtual variation dA of the contact area, at constant temperature, and writing that the free energy $\mathfrak{F}$ cannot be increased by a subsequent evolution of the isolated system. For a reversible and isothermal change the variation of the free energy is equal to the variation of total energy U_T, and we can write:

$$d\mathfrak{F} = dU_T = dU_E + dU_P + dU_S \leqslant 0$$

where U_E, U_P, U_S are respectively the stored elastic energy, the potential energy of the load P and the stored energy at the interface, defined by:

$$dU_S = (\gamma_1 + \gamma_2 - \gamma_{12})dA = -wdA$$

(γ_1 and γ_2 are the surface and γ_{12} the interfacial energies of the two bodies, and w the Dupré's energy of adhesion or thermodynamic work of adhesion).

The strain-energy release rate is here written as:

$$G = \partial U_E/\partial A + \partial U_P/\partial A$$

so that the variation of the free energy in a spontaneous change is:

$$d\mathfrak{F} = dU_T = (G - w)dA \leqslant 0$$

The equilibrium is thus given by:

$$G = w$$

and this equilibrium relation is called Griffith's criterion. It links P to A for equilibrium at fixed load.

The strain energy release rate, G, is related to the stress intensity factor by $G = K_I^2/E$ for plane stress and $G = K_I^2(1 - v^2)/E$ for plane strain (E is the Young's modulus and v the Poisson ratio). When $G > w$, the separation of the two bodies starts. GdA is the mechanical energy released when the crack extends by dA. The breaking of interface bonds requires the energy wdA and the excess $(G - w)dA$ is changed into kinetic energy if there is no dissipative factor. Thus, there is a "crack extension force" $G - w$ applied to unit length of crack. Under this force, the crack takes a limiting speed v, which is a function of

the temperature (through the Williams–Landel–Ferry (WLF) shift factor a_T), and one can write[4–5]:

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

where ϕ is a dimensionless function of crack speed, v, and temperature, T, independent of the geometry of the system and the loading conditions.

The right-hand side of Eq. (1) is the drag due to viscoelastic losses at the crack tip and is proportional to w as proposed by Gent and Schultz[6] and Andrews and Kinloch.[7] In this equation surface properties (w) and viscoelastic properties (ϕ) are clearly expressed separately from elastic properties, loading conditions and geometry of system that solely appear in G. When the function ϕ, a characteristic of the viscoelastic material, is known, then Eq. (1) enables us to predict the kinetics of detachment, provided that the failure is an adhesive failure and the viscoelastic losses are limited to the crack tip. The last condition means that gross displacements must be elastic for G to be valid in kinetic phenomena.

Literature data of 90°-peeling tests[6–11] show the dissipative function ϕ varies, over a large range of crack speed, as:

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

with $\alpha \sim a_T^n$. Our experimental results[4–5] on polyurethane material, for three geometries: peeling, adherence of rigid flat punch and adherence of rigid ball (Figure 1), leads to $n = 0.6$, a result often found for peeling of rubber-like materials.[8–9,11] The multiplicative effect of w on viscoelastic losses (Eq. (1)), proposed by Andrews and Kinloch,[7] was verified by measuring the rolling resistance of a glass cylinder in contact with a polyurethane surface, for various relative humidity ratios.[11,12]

For a rigid sphere of radius R in contact on an elastic half-space, the strain energy release rate G can be deduced,[4–5] from the elastic displacement δ given by Johnson et al.[13] theory of the contact of elastic solids with non-zero surface energy

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

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

In these equations P is the applied load, a the radius of contact area, and K an elastic constant given by $1/K = 3(1 - v^2)/4E$. At equilibrium under a load P_0, the contact radius is given[13] by:

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

which is larger than the Hertzian value $a_H = P_0 R/K$ that does not take into account the molecular attraction between the two bodies in contact (Figure 2).
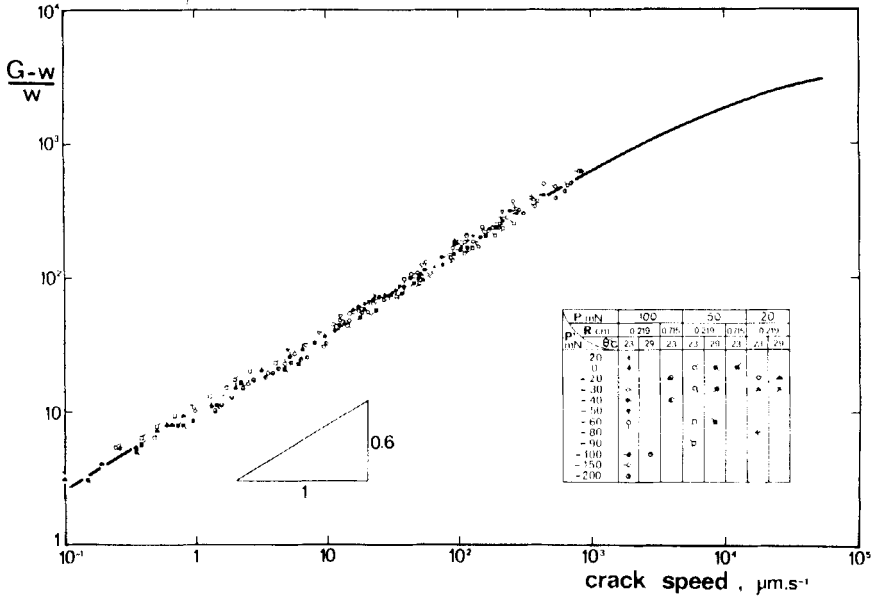
FIGURE 1   Dissipative function $\phi [= (G-w)/w]$ versus crack velocity for polyurethane at 23°C. Data points are for various unloadings of a glass ball, from P to P', and two radii and two temperatures; the results for $\theta = 29$°C were shifted on those corresponding to $\theta = 23$°C by the WLF transform, with $T_g = -50$°C. The same master curve (heavy line) was obtained from separate peeling experiments.

When the equilibrium is broken, by unloading from P_0 to $P' < P_0$ for instance, G increases, the area of contact $A = \pi a^2$ decreases, and the crack speed increases or decreases according to the sign of the derivative $(\partial G/\partial A)_{P'}$.[4-5] In all the cases, the dissipative function ϕ, (equal to $(G-w)/w$ and computed from the value of P', w and the measured a), can be represented by the master curve shown in Figure 1.

TACKINESS

Most adherence tests of rubber-like materials are conducted with a rigid ball as indenter,[1-3] attached to a tensile machine imposing a constant withdrawal speed $\dot{\Delta}$. If the stiffness of this testing machine is infinite, the same speed $\dot{\delta} = \dot{\Delta}$ is applied to the indenter, and there is a competition between increasing δ at constant a, and decreasing a at constant δ for increasing G:

$$\frac{dG}{dt} = \left(\frac{\partial G}{\partial \delta}\right)_a \dot{\delta} + \left(\frac{\partial G}{\partial a}\right)_\delta \dot{a}.$$
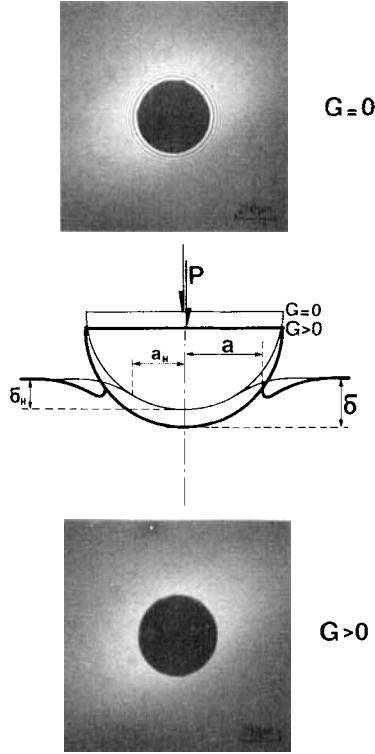
FIGURE 2 Views of Newton's rings and corresponding diagram profiles of the surface for the hertzian contact ($G = 0$) and the adhesive contact ($G = w = 64 \, \text{mJ/m}^2$) of a glass ball ($R = 0.2 \, \text{cm}$) on a polyurethane surface ($E = 5 \text{MPa}, v \simeq 0.5$) for the same acting load $P = 50 \, \text{mN}$. (The upper view is obtained just as the load is applied, and the lower 3 min later.)

The recorded force first increases, then decreases. Starting from an equilibrium point (δ_0, P_0, a_0) defined by $G = w$, one can impose to the ball a fixed cross-head velocity $\dot{\delta} = d\delta/dt$ and compute[5,14] the crack propagation v and the variation $P(t)$ from Eqs (1), (2), (3) and (4).

The crack velocity is given by:

$$v = \frac{da}{dt} = \left(\frac{3a^3 K}{8\pi R^2 \alpha w} \left[1 - \frac{R\delta}{a^2} \right]^2 - \frac{1}{\alpha} \right)^{1/n} \tag{5}$$

and its variation by

$$\frac{d^2 a}{dt^2} = \frac{1}{n} \left(\frac{da}{dt} \right)^{1-n} \cdot \left(\frac{3a^2 K}{8\pi R^2 \alpha w} \right) \cdot \left(1 - \frac{R\delta}{a^2} \right) \left[\left(\frac{R\delta}{a^2} + 3 \right) \frac{da}{dt} - \frac{2R}{a} \frac{d\delta}{dt} \right] \tag{6}$$

(this acceleration is taken into account to improve the precision of the calculation). The equations were solved by the following method. From equilibrium values a_0 and δ_0, one increments δ to δ_1 by $\delta_1 = \delta_0 + \dot{\delta}\Delta t$; then

$$\left|\frac{da}{dt}\right|_1 \quad \text{and} \quad \left|\frac{d^2a}{dt^2}\right|_1$$

are computed by above equations with a_0 and δ_1. An approximate value a_1^* is thus obtained by:

$$a_1^* = a_0 - \left|\frac{da}{dt}\right|_1 \Delta t - \left|\frac{d^2a}{dt^2}\right|_1 \frac{\Delta t^2}{2} \tag{7}$$

from which the correct values

$$\frac{da_1}{dt} \quad \text{and} \quad \frac{d^2a_1}{dt^2}$$

are calculated, by Eqs (5) and (6) with a_1^* and δ_1 instead of a_0 and δ_1; hence the true a_1 by Eq. (7). By such incrementations of δ one can compute $a(t)$ and the corresponding force $P(t)$, from Eq. (3). So force-displacement curves are obtained that can be compared with experimental results.

When the stiffness $k_m = dP/d\delta_m$ of the testing machine cannot be considered infinite with respect to the stiffness of the initial contact $k_s = (\partial P/\partial \delta)_{A_0} = 3a_0K/2$, the system can be represented by a sphere attached to the machine with a spring of stiffness k_m. So, the crosshead displacement Δ is divided into elastic displacement δ_m of the spring and displacement δ of the sphere, such that:

$$\Delta = \delta + \delta_m = \delta + \frac{P}{k_m} \tag{8}$$

The velocity of displacement $\dot{\delta}$ of the sphere is linked to the cross-head velocity $\dot{\Delta}$ by:

$$\dot{\delta} = \frac{d\delta}{dt} = \frac{1}{1 + \dfrac{3}{2}\dfrac{aK}{k_m}} \cdot \left[\dot{\Delta} - \frac{3K}{2k_m}\left(\delta - \frac{a^2}{R}\right)\frac{da}{dt}\right] \tag{9}$$

obtained from Eqs (3) and (8). In these conditions, using Eq. (9) and its derivative

$$\frac{d^2\delta}{dt^2} = \frac{\dfrac{3}{2}\dfrac{K}{k_m}}{1 + \dfrac{3Ka}{2k_m}}\left[\left(\delta - \frac{a^2}{R}\right)^2\frac{d^2a}{dt^2} + \frac{2d\delta}{dt}\frac{da}{dt} - \frac{2a}{R}\left(\frac{da}{dt}\right)^2\right]$$

the displacement δ_i is given by

$$\delta_i = \delta_{i-1} - \left|\frac{d\delta_i}{dt}\right| \Delta t - \left|\frac{d^2\delta_i}{dt}\right| \frac{\Delta t^2}{2}.$$

Then the corresponding a_i and P_i are obtained as above, by Eqs (5), (6), (7) and (3).

Figure 3 compares the computed curve to the experimental one directly obtained from the tensile machine. The apparatus used was similar to the ball tack tester described by Kamagata et al.[1] A glass ball (radius $R = 2.19$ mm) was contacted with a polyurethane surface (specimen usually used for photoelasticity studies, $E = 365$ N/cm^2, $v \simeq 0.5$, $T_g = 223$ K, and $n = 0.6$) under an initial load $P_0 = 96$ mN. After a fixed contact time (5 min), at the temperature $T = 295$ K, a cross-head velocity $\dot{\Delta} = 0.5$ mm/mn was imposed to the glass ball with a stiffness $k_m = 394$ N/cm $= 12$ k_s. To obtain the best superposition of computed and experimental curves, the two parameters w and α have been adjusted ($w = 57$ mJ/m^2, $\alpha = 4.75$ 10^4 SI units) into the range of experimental values previously observed. In these conditions the agreement with experiments is very satisfying, the variations being smaller than 3%.

Figure 4 is a force-displacement plot showing the predicted influence of the cross-head velocity $\dot{\delta}$ (here $k_m = \infty$ and $\dot{\delta} = \dot{\Delta}$). The maximum value of the
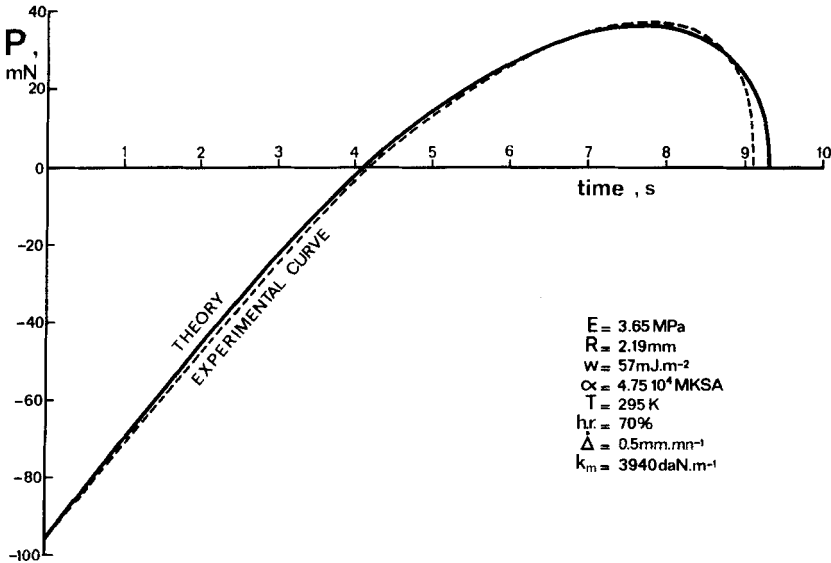

FIGURE 3 Adherence force versus time of a glass ball on a polyurethane surface. Comparison between computed and experimental curves.
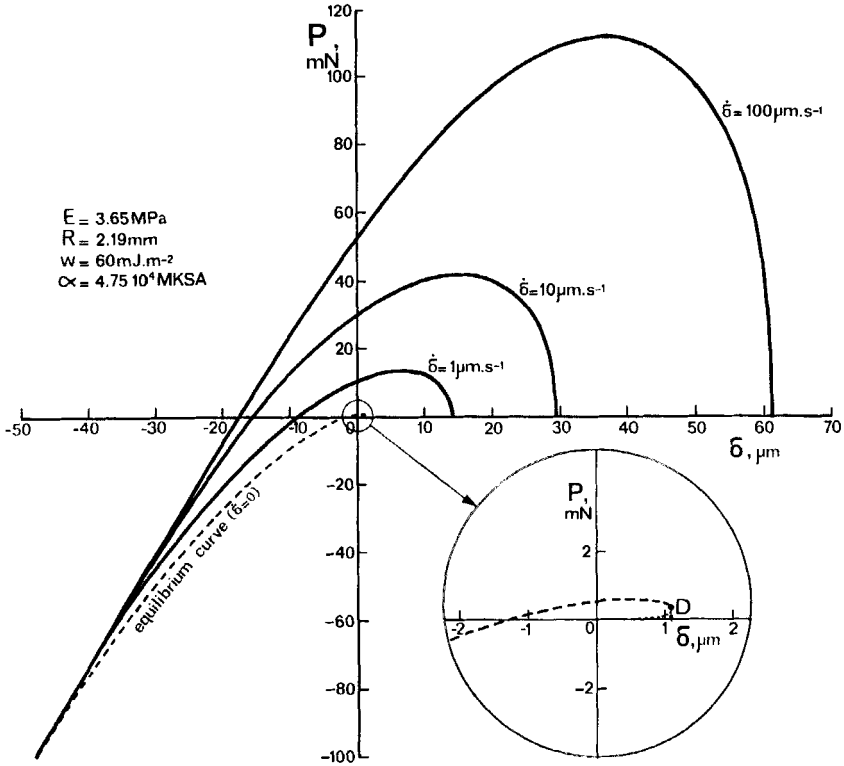
FIGURE 4   Influence of withdrawal speed on the tack force (computed curves).

tensile force (the tack force or the adherence force in the chosen experimental conditions), increases with δ, just as the dissipated energy (which is equal to the work $\int_{A_0}^{0} G\,dA$ of the singular stresses at the crack tip[12]). As a good approximation, this dissipated energy or tack energy is the area under the curve $P(\delta)$ restricted to the tensile region. The curve $\dot\delta = 0$ (dotted line) is the equilibrium curve $G = w$. It must be pointed out that a cross-head velocity as low as $\dot\delta = 1$ μm/s is high enough to have an adherence force more than 30 times the quasistatic value at fixed displacement, $P_c = 5\pi wR/6$ (point D).

Figure 5 shows the predicted influence of surface properties, and more especially the influence of Dupré's work of adhesion. As expected, large w values lead to large values for rupture time, for P_{max} and for the tack energy. The dashed curve, for $w = 0$, corresponds to the force-displacement relation in the Hertz theory. It is well known that tack force increases with dwell time,[1,2,15,16] probably due to diffusion through the interface and/or relax-

ation of stresses stored in asperities making the contact between two bodies (roughness effect). This fact can be interpreted as an increase of w from zero to its equilibrium value, and the result can be seen in Figure 5.

Equation 1 together with Eq. 2 enables one to predict the influence of temperature. Once the value $\alpha = \alpha_0$ is experimentally determined for a given temperature T_0, one can calculate α for any temperature by the *WLF* transform by $\alpha = \alpha_0(a_T)^n$, with $n = 0.6$ for our specimen. For instance, with $\alpha_0 = 4.75 \cdot 10^4$ SI units calculated from Figure 1, ($T_0 = 295$ K), one has:

<div align="center">

TABLE I

Parameter α versus temperature

</div>

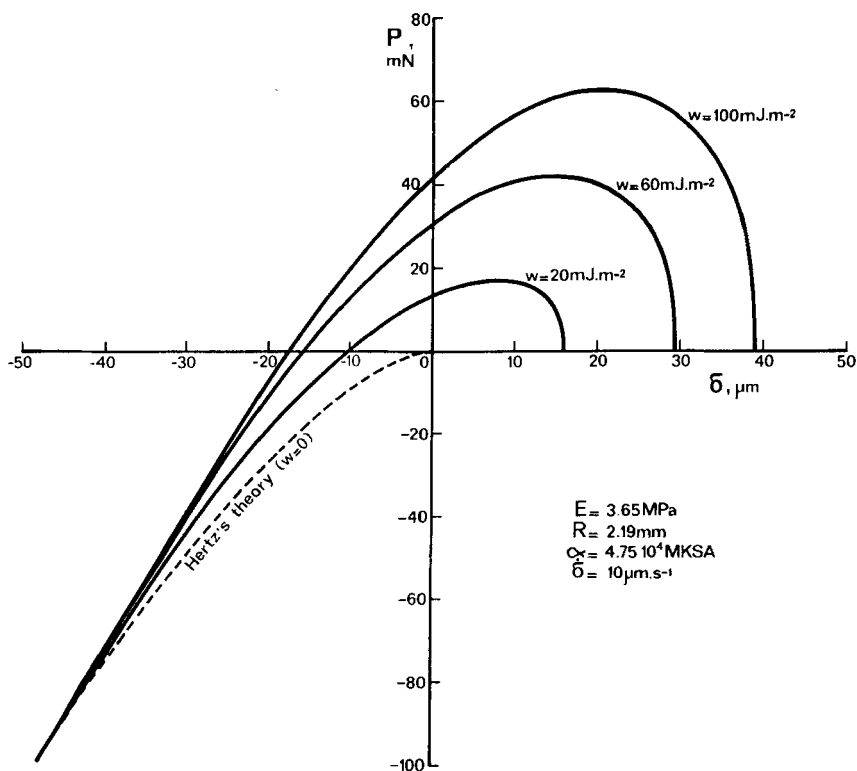| T (K)	293	303	313	323	333
α (SI units $\times 10^{-4}$)	6.48	2.58	1.32	0.74	0.45

FIGURE 5   Influence of surface energies on the tack force (computed curves).
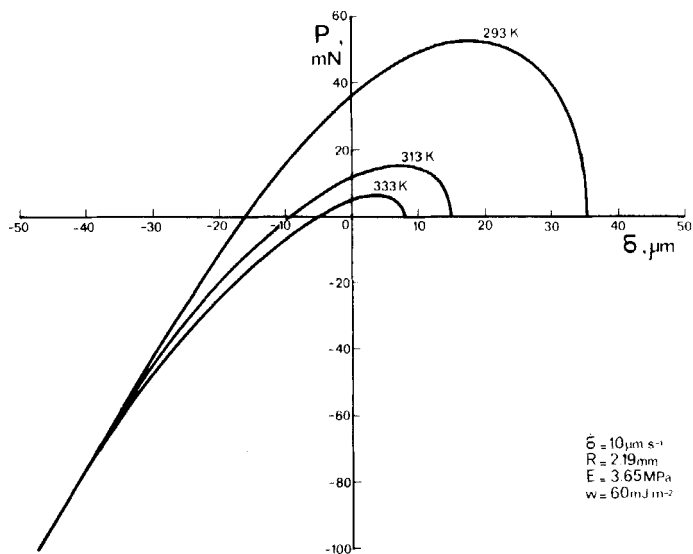
FIGURE 6 Influence of temperature on the tack force (computed curves).

These data have been used to plot the theoretical curves shown in Figures 6, 7 and 8. Increasing temperature decreases viscoelastic losses at the crack tip, and leads to shorter rupture time and lower tack force and tack energy. The general behaviour displayed by these calculated variations with δ for various
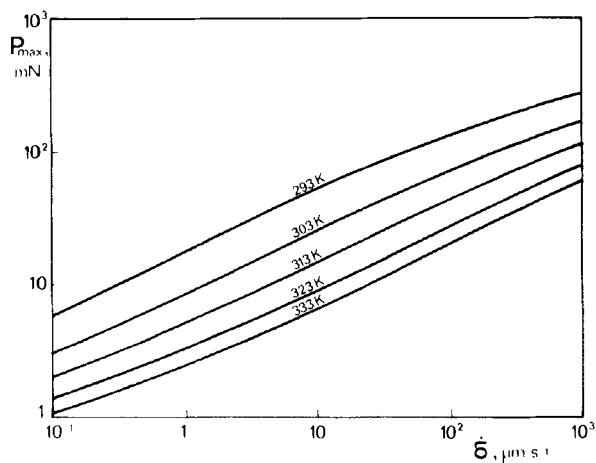

FIGURE 7 Tack force (P_{max}) as a function of withdrawal speed and temperature (computed curves).
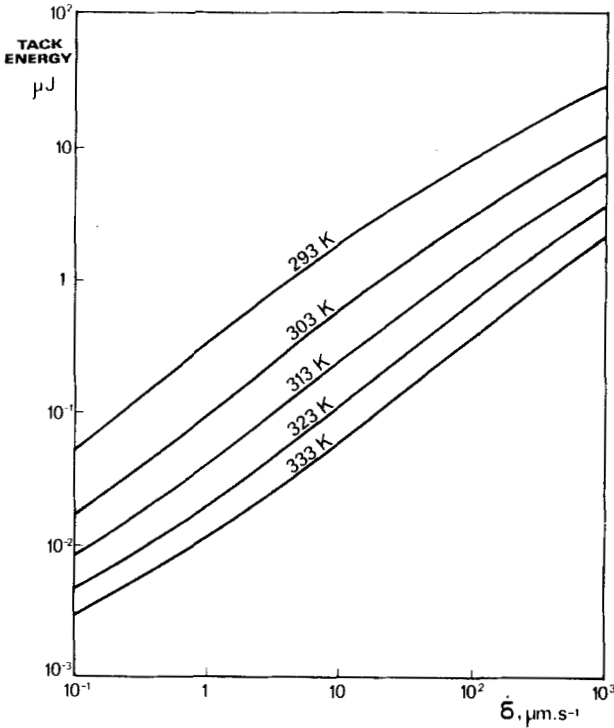
FIGURE 8   Tack energy as a function of withdrawal speed and temperature (computed curves).

temperatures (Figures 7 and 8) is in complete agreement with recent experimental data given in the literature.[2-3]

It can also be shown,[12] that above a loading or displacement threshold, the adherence force P_{max} becomes independent of the initial equilibrium conditions. This fact can justify using P_{max} for evaluation of the tackiness of elastomers.

The necessity of taking into account the stiffness k_m of the testing machine to draw the force-displacement curve $P(\delta)$, when this stiffness cannot be considered as infinite with regard to the stiffness k_s of the initial contact area, is displayed in Figure 9. This figure shows, from Eq. 9, the variation of $\dot{\delta}$ with time for a given cross-head velocity $\dot{\Delta}$, and a stiffness ratio $k_m/k_s = 12$ corresponding to the data of Figure 3. If k_m/k_s is non-infinite, the true $\dot{\delta}$ remains lower than the withdrawal speed $\dot{\Delta}$ during most of the rupture time, then $\dot{\delta}$ rapidly increases up to rupture. The smaller ratio k_m/k_s the larger the difference between $\dot{\delta}$ and $\dot{\Delta}$, and this point must be taken into account for comparison of different samples.
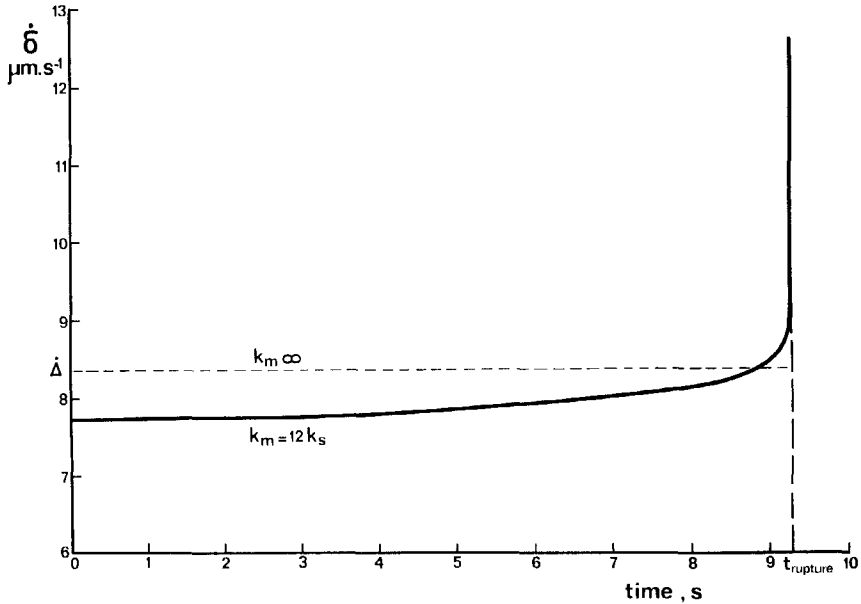
FIGURE 9   Probe speed versus time for a given stiffness (corresponding to the data of Figure 3).

CONCLUSION

Probe tack testing procedure can be analysed by the fracture mechanics theory previously proposed by the authors for adherence of spheres or punches at fixed load or fixed grips conditions. Tack curves obtained by computer integration closely coincide with experimental ones. So, the influence of intrinsic properties of materials (viscoelastic properties and superficial energy) and experimental conditions (cross-head velocity, stiffness of the testing machine, radius of sphere, initial load, temperature) on tackiness, can be predicted.

Acknowledgements

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