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Study of the Self-Adhesion Hysteresis of a Siloxane Elastomer Using the JKR Method

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The JKR method measures the adhesion between two spheres or a sphere and a plane surface, all materials being elastomers. We have used this technique to study the self-adhesion of a siloxane elastomer. Our results demonstrate that there is a large difference of behavior (hysteresis) between the loading and unloading regimes when the soluble fraction of the networks has been extracted. The unloading regime is then not described by the classical application of the JKR model. We believe that the work of adhesion measured during the unloading regime is not constant along the contact area but rather decreases from its center toward its edges. This behavior may be the signature of the JKR pressure profile (compressive in the center of the contact area and tensile near its edges) the sign and magnitude of which influence the formation of hydrogen bonds across the interface. A generalization of the JKR model that includes this feature is proposed and gives a good description of the experimental data.

Introduction

For obvious reasons, the search for a reliable test of adhesion is of long-standing interest. Many tests have been developed; for example, the peel test or the blister test have been widely used for measuring adhesion between polymer thin films and various substrates. However, in the case of elastomeric materials, the study of adhesion in a sphere–sphere or sphere–plane geometry has become increasingly popular since its theoretical analysis by Johnson, Kendall, and Roberts.[1] In particular, the volume under deformation is small and viscoelastic effects are minimized.

Hertz was the first to describe the mechanical behavior of two elastic spheres (or a sphere and a plane surface) pressed together in the absence of surface tensions.[2] A major improvement of this theory was achieved by Johnson et al.[1] by the introduction of surface tensions (JKR theory). In the following, we will consider only the case when the two materials pressed together are made of the same elastomer. Furthermore, only the sphere–plane geometry will be discussed.

In that case, the radius of the contact area is given by (Figure 1):

$$a^3 = \frac{R}{K}(P + 3\pi WR + (6\pi WRP + (3\pi WR)^2)^{1/2}) \qquad (1)$$

$$K = \frac{2E}{3(1 - \nu^2)}$$

where E and ν are respectively the Young modulus and the Poisson ratio of the elastomer, R is the radius of the undeformed sphere, P is the applied load, and W is the thermodynamic work of adhesion (in our case, $W = 2\gamma$ where γ is the elastomer–air surface tension[3]).

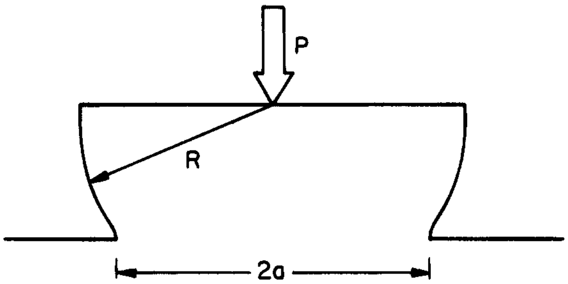

Figure 1. Schematic representation of the JKR experiment.

Another theory by Derjaguin, Muller, and Toporov[4] (DMT theory) has challenged this result by convincingly arguing that long range forces were to be considered also *outside* the contact area. However, as it has been recognized even in the early papers of the Russian school, the effect of these forces is very small for materials of high radius of curvature and low elastic modulus[5] as it is the case here. They thus will not be considered any further. A complete description of the transition between the two laws, which are shown to be the two extreme cases of a more complete theory, can be found in ref 6.

It has to be noted that a *mechanical* hysteresis always takes place when using this technique. When the two surfaces are brought together, a jump occurs at some point establishing a finite contact area even at zero load. This jump is the manifestation of the free energies of the surfaces. As the load is increased, the contact area increases. When the load decreases, the contact area also

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decreases following an identical path as during the loading regime. The difference is that, in this unloading regime, negative loads can now be attained.

Eventually, of course, the sphere and the plane separate. The measurement of the force at which this separation occurs (the "pull-off" load P_{PO}) is also a measurement of the work of adhesion since one can easily see that[1]

$$P_{PO} = -\frac{3}{2}\pi R W \tag{2}$$

P_{PO} is thus dependent of the elastic constants of the material. Equation 2 can also be rewritten as

$$P_{PO} = -\frac{{a_{min}}^3 K}{R} \tag{3}$$

where a_{min} is the minimal contact area just before pull-off.

The JKR theory has proved to describe a number of experimental results for a variety of systems quite satisfactorily.[1,7-10] However, several authors have reported an *adhesion* hysteresis different in its nature from the mechanical hysteresis described before. Namely, the curves $a(P)$ (or, as they are more commonly represented, $a^3(P)$) recorded during the loading and unloading phases do not superimpose as would be required by the JKR theory. This effect has sometimes been attributed to the bulk viscoelasticity of the elastomers. This explanation, however, can be ruled out for several experiments in which the interfacial phenomena are clearly dominant.[9,10] Numerical simulations seem to show that a long-range potential can, by itself, induce such a hysteresis.[11] Whether this hysteresis is a thermodynamic effect or a kinetic one (which would vanish at infinitely low rates of separation) is however still an open question for contradictory results are reported in the literature.[12] In the following, the subscripts "l" and "ul" will refer respectively to loading and unloading experiments.

Despite this effect, several authors have used this technique to study the adhesion behavior of several types of systems. For instance, the effect of the molecular weight between cross-links on the adhesion of several elastomers on various solid surfaces has been extensively studied.[13] This parameter has been shown to have basically no effect on W_l whereas it had a strong effect on W_{ul}. Using only unloading experiments, Brown has studied the extraction of polyisoprene chains from a polyisoprene gel at various rates.[14] Experiments using a siloxane network are described in ref 10. Chemical modifications of the surfaces were tested as well as the role of the surrounding medium, demonstrating a particularly good agreement with the JKR theory.

Another series of experiments has been conducted using the surface force apparatus (SFA) in which molecularly smooth mica is glued on glass. The mica–mica adhesion can then be studied in various media.[8] Furthermore, the surface of mica can be modified by deposition of organic layers enabling one to tailor their adhesion properties.[9] K is then an effective elastic constant that takes into account the compliances of the mica, the glue, and the glass. A good agreement with the JKR theory has been reported for these experiments. When mica was replaced by a polymer, however, some discrepancies between W_{PO} and W_{ul} occurred.[9b] Recent experiments, which have used the atomic force microscope (AFM) to probe the local adhesion properties of surfaces[15] measure similar effects. In these experiments, only P_{PO} is measured and the JKR model (or derived theories) are used for the interpretation.

An analysis of eq 1 shows that, by recording a full curve $a^3(P)$, one can independently determine the work of adhesion W and the elastic constant K by a two-parameter fit (the radius of the sphere, R, can be accurately measured independently). This procedure has been occasionally used,[9,10] but usually K is measured independently[13b] or calculated.[14] Some authors have used the JKR geometry to measure K during the loading phase[13] and used this measured value to determine works of adhesion during the loading and unloading regimes. We will discuss the validity of these different procedures below.

Experimental Section

The siloxane elastomer used in this study is a commercial material (Dow Corning, Sylgard 170) prepared by cross-linking of end-functionalized poly(dimethylsiloxane) (PDMS).[10] A slight excess of cross-linker was used to prevent blooming on the surfaces.[16b]

The experimental device is similar to the one already described in refs 10 and 17. Briefly, a lens of the siloxane elastomer is brought to contact with a film made of the same elastomer by using a micromanipulator. The contact area is followed with an optical microscope (Nikon, Diaphot) and the force is measured with an analytical balance (Mettler).

Lenses were prepared by cross-linking droplets of the uncured material on fluorinated glass slides. The plane films were prepared in a flat bottom polystyrene Petri dish.

We have performed experiments on the neat elastomers (as they were obtained after curing) and on extracted gels. In the latter case, the lens and the film were soaked in chloroform (a good solvent of PDMS) for 24 h. During the soaking, the solvent was changed 3 times. After this procedure, the fraction of extracted material was 7–9% by weight (a longer exposure to solvent did not increase this sol fraction). After extraction, the solvent was removed from the network by drying in vacuum at 60 °C.

During the experiment the lens is supported by a "spring" made of transparent tape which itself is connected to the micromanipulator.[10] The spring constant was measured to be 4 ± 1 N/m, which is low enough so that the experiments were performed in a manner such that the load rather than the displacement is controlled (the compliance of the elastomer being much lower than that of the spring).

The micromanipulator was driven by a servo-controlled motor which gave a range of attainable rates of variation of the load from 10 nN/s to 500 μN/s. Unless otherwise stated, our rate of loading or unloading was 5 ± 1 μN/s.

The pull-off force was measured as the last balance reading before separation during the unloading portion of the experiment.

Results

Figure 2 depicts a typical loading–unloading curve for unextracted material. Clearly, the loading and unloading parts are different. The fits of the experimental points by

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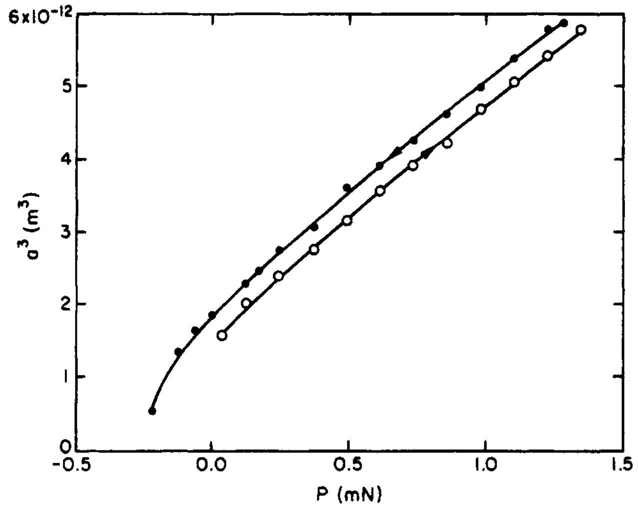

Figure 2. Loading (○) and unloading (●) curves for an unextracted network. The solid lines are the best fits by the JKR model (eq 1).

eq 1 lead to the following results:

$$W_l = 37 \pm 3 \text{ mJ/m}^2 \qquad K_l = 0.40 \pm 0.01 \text{ MPa}$$

$$W_{ul} = 56 \pm 3 \text{ mJ/m}^2 \qquad K_{ul} = 0.43 \pm 0.01 \text{ MPa}$$

There is a jump on the loading curve (not shown) that corresponds to a slightly negative load which is consistent with numerical simulation results.[11] The expected value for W is $W = 2\gamma$, where γ is the surface tension of PDMS ≈ 20 mJ/m^2. W_l is thus consistent with this value as well as with previous experiments;[10] W_{ul}, however, is larger.[18]

This hysteresis effect is much more remarkable when using the extracted material as depicted in Figure 3. In this case, the parameters are similar to those obtained with the unextracted material in the loading part of the curve ($W_l = 39 \pm 2$ mJ/m^2; $K_l = 0.40 \pm 0.02$ MPa). The unloading part, in contrast, can only be described by high values for W and K

$$W_{ul} = 328 \pm 3 \text{ mJ/m}^2 \qquad K_{ul} = 1.10 \pm 0.05 \text{ MPa}.$$

No satisfactory fit could be obtained by using the same value of K for the analysis of the loading and unloading regimes.

The measured pull-off force leads to $W_{PO} = 40 \pm 5$ mJ/m^2 in the unextracted case and $W_{PO} = 328 \pm 5$ mJ/m^2 in the extracted case. Both values are compatible with W_{ul}. However, in the case of the extracted network, using eq 3 with $K = K_{ul}$ would give $a_{min} \approx 93$ μm, which is significantly larger than the measured value ($\approx$85 μm). This 9% discrepancy is far above the experimental uncertainties. We shall come back to this point in the Discussion.

Rate dependence experiments showed no effect (from 0.5 to 50 μN/s) on any of the parameters and neither did the time during which the maximum load was applied (from a few seconds to several hours). These results are partially illustrated by Figure 4 where several hysteresis loops are depicted for different experimental conditions. The effect of the maximum load itself was not systematically explored in this study, but small variations seem to have little effect on the hysteresis.

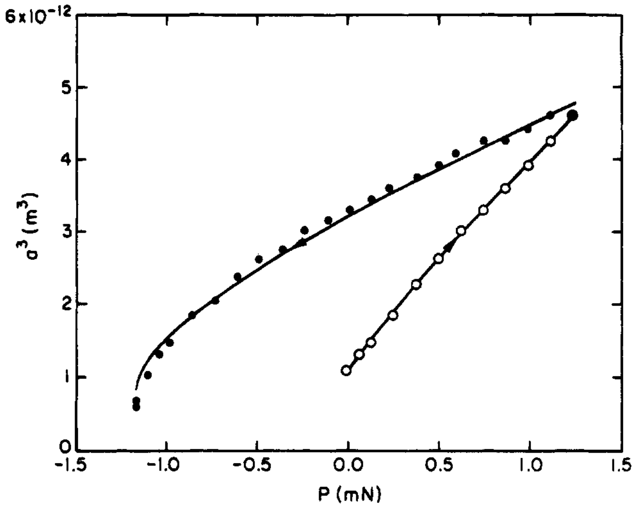

Figure 3. Loading (○) and unloading (●) curves for an extracted network. The solid lines are the best fits by the JKR model (eq 1).

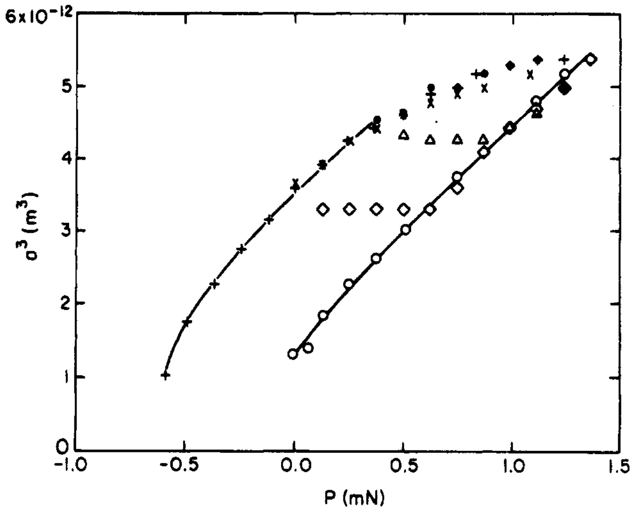

Figure 4. Hysteresis loops for an extracted network: ○, first loading (2 μN/s); ●, first unloading (8 μN/s) after a wait period of 2 min at 1.4 mN; △, second loading (2 μN/s); ×, second unloading (8 μN/s) after a wait period of 10 s at 1.4 mN; ◇, third loading (2 μN/s); +, third unloading (2 μN/s) after a wait period of 10 s at 1.4 mN. The lines are the best fits by eq 1: $W_l = 40 \pm 3$ mJ/m^2, $K_l = 0.41 \pm 0.01$ MPa; $W_{ul} = 150 \pm 5$ mJ/m^2, $K_{ul} = 0.56 \pm 0.02$ MPa.

Discussion

Several reasons can be invoked to explain the difference between W_l and W_{ul}. The presence of a shear component, which has to be considered because of the asymmetric geometry of the experiment (sphere/plane), can be ruled out for these incompressible materials[19] (subsequent experiments in the sphere/sphere geometry showed similar effects).

Another possible cause for hysteresis for the imperfect networks of the type considered here is the interpenetration of dangling chains of the opposite network;[14] the lack of dependence of the results on the rate of loading or unloading makes such an explanation for the hysteresis seen here unlikely as do our unpublished results on model imperfect networks, which seem to show that the effects

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(18) The hysteresis of adhesion for these unextracted samples is higher than those reported in ref 10. However, the formulations of the PDMS networks used in ref 10 and in the present study are slightly different. The current composition has more Si$-$H groups, which can indirectly affect the adhesion properties of the gels as discussed below.

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of relatively short PDMS dangling chains are small compared to the effects seen here.[20]

We believe that the hysteresis results from a chemical reaction, namely the formation of an hydrogen bond, across the interface. Specifically, separate experiments on model networks have shown that an excess of cross-linker (with unreacted $-Si(CH_3)_2-H$) is necessary for a hysteresis of the magnitude observed here to occur.[20] In addition, if the extracted PDMS network is dried in a very good vacuum at room temperature, little hysteresis is observed. In contrast, if the surfaces of the same networks are treated with HCl, the hysteresis becomes very large.[21]

All these results are consistent with the excess Si–H groups being oxidized to Si–OH, which can then form hydrogen bonds across the interface. In the case of the samples dried in vacuum at 60 °C, we suspect that the excess Si–H groups become thermally oxidized by the residual oxygen in the relatively modest vacuum used for the drying. This hypothesis of a hydrogen bonding across the interface is further supported by the fact that the surfaces giving rise to high hysteresis show an aging process. This decay could be the consequence of a decreased reactivity of the surfaces due to their contamination (no decay was observed when the surfaces were held under nitrogen in a sealed container). This mechanism can also explain the quasi-absence of hysteresis when using the unextracted networks: Before extraction, the PDMS chains making up the sol fraction can bloom to the surface and either prevent the oxidation of the Si–H groups or separate the potential hydrogen bonding groups in the two networks on either side of the interface.

Whatever the exact cause of this hysteresis, we would like to point out the important result that $K_l \neq K_{ul}$. Although the absolute values were observed to vary slightly from one experiment to another, the trend was always $K_{ul} > K_l$. The difference is always much greater in the case of extracted materials: for the sample shown in Figure 3, for instance, $K_{ul} > 2K_l$. Since, in the JKR model, K is an elastic constant describing the *bulk* properties of the elastomer (eq 1), it cannot be different in the loading and unloading regimes and the only possible conclusion is that the JKR model as we have used it is invalid in our particular experiment. Let us note that this situation is more general since such an effect can be found also in adhesion experiments involving modified mica surfaces.[8,22]

A possible explanation for this effect can be ascribed to pressure-induced surface reactivity by analogy to the stress-induced surface reconstruction.[16] The particular pressure profile across the interface [1] (compressive at the center and tensile close to the edges) can induce a work of adhesion that would vary *along* the interface. For instance, if one thinks of a reactive interface, the process bonding the two surfaces together (such as the hydrogen bonding described above) can be very pressure sensitive. In that case, we would expect an unloading curve $a^3(P)$ that could be described by the same K value as the loading one and a distribution of works of adhesion along the interface.[23] By forcing the fit of our data by a single set of W and K parameters, we would then get an artificially different value of K than the one measured during loading, as we, in fact, observe.

To avoid imposing such artificial (and incorrect) values of K, one can invert eq 1 (keeping $K = K_l$) in order to determine W for each contact area during the unloading regime. The calculation gives

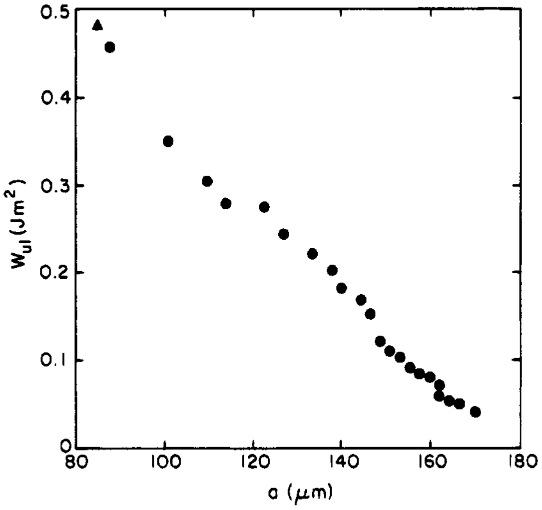

Figure 5. Variations of W_{ul} along the interface. The dots are the transcription of Figure 3 using eq 4 and $K = K_l$. The triangle is the calculated value of W_{PO} using $a = a_{min}$ in eq 4.

$$W(a) = \frac{1}{6\pi a^3 K_l}\left(\frac{a^3 K_l}{R} - P(a)\right)^2 \qquad (4)$$

Figure 5 shows the variations of W_{ul} along the interface for the sample the data for which are shown in Figure 3.

The large variations of W_{ul} with a make a new analysis of the results near pull-off necessary.

When W is independent of a, the pull-off conditions (the conditions for instability) are given by[6]

$$\left(\frac{\partial G}{\partial a}\right)_P = 0 \qquad (5)$$

where G is the energy release rate

$$G = \frac{(a^3K - RP)^2}{6\pi a^3 R^2 K}$$

However, this simplification is no longer valid when W_{ul} is a function of a and a generalization of this equation must be made. The conditions for which instability appears are then given by

$$\left(\frac{\partial(G - W)}{\partial a}\right)_P = 0 \qquad (6)$$

Plugging the expression for G in eq 6, one gets

$$P_{PO} = -\left(\frac{{a_{min}}^6 K^2}{R^2} - 2\pi K {a_{min}}^4 \left(\frac{\partial W}{\partial a}\right)_P (a = a_{min})\right)^{1/2} \qquad (7)$$

If W is independent of a, one recovers eq 3. However, the corrective term may become significant when the variations of W with a are important.

In order to test these equations, we compared their predictions with the results depicted on Figures 3 and 5. The measured pull-off force was −1.172 mN and a_{min} = 85 ± 2 μm. Equation 4 gives W_{PO} = 485 ± 20 mJ·m^{-2}, which is consistent with the other points of Figure 5. Using eq 3 with $K = K_l$ would give P_{PO} = −0.32 ± 0.02 mN while eq 7 yields P_{PO} = −1.3 ± 0.15 mN (for this last part of the calculation, $(\partial W/\partial a)_P\,(a = a_{min})$ was estimated from Figure 5).

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[23] Experiments on model networks show that K_l is indeed the "true" elastic constant of the gel.[20]

Hence, there is excellent agreement between the experimental value and the result of the computation using eq 7. In contrast, the result obtained by a straightforward application of the classical form of the JKR theory (eq 3) is off by a factor of 4.

In view of these results, the results obtained in some previous studies where the variations of W with a were ignored or where K_l and K_ul were artificially allowed to take on different values may have to be reconsidered.

This new analysis of the pull-off may also be useful for our understanding of AFM images. In that case, the working load is often close to P_PO. Using eq 3 to determine a_min can strongly overestimate this parameter (and consequently, overestimate the penetration of the tip in the sample). This might be the reason why better lateral resolutions than what is usually predicted are commonly obtained[24] (if $\partial W/\partial a$ is large, a large force does not necessarily mean a large area of contact (i.e. a poor lateral resolution)).

Finally, we can check the plausibility of our hypothesis that a pressure-induced surface reaction is responsible for the variations of W_ul with a. Let us assume that the yield of the reaction is maximum at the maximum positive load (or maximum contact area a_max), which corresponds to the maximum pressure (or minimum tensile stress) at each point in the area of contact (of course, the extent of reaction at any point will increase as the pressure is increased; we simply assume it is monotonic and irreversible). The stress $\sigma(r)$ at radius r within the maximum area of contact (i.e. $r < a_\mathrm{max}$) is given by

$$\sigma(r) = \left(\frac{3KW_\mathrm{l}}{2\pi a_\mathrm{max}}\right)^{1/2} \frac{1}{\left(1 - \dfrac{r^2}{a_\mathrm{max}{}^2}\right)^{1/2}} - \frac{3Ka_\mathrm{max}}{2\pi R}\left(1 - \frac{r^2}{a_\mathrm{max}{}^2}\right)^{1/2} \tag{8}$$

The first term on the right-hand side of eq 8 is tensile and results from the singular stress field (characterized by the stress intensity factor $K_\mathrm{l} = [W_\mathrm{l}E/(1-\nu^2)]^{1/2}$) of the "crack" being healed by the area of contact. The second term is the classical Hertzian solution for the pressure distribution under the contact. At any area of contact of radius a, the expression for $\sigma(r)$ is similar except for a replacing a_max. It is straightforward to show that eq 8 corresponds to the largest compressive stress (pressure) at any r upon either loading to or unloading from the area of maximum contact as long as W_l is constant or W_ul increases monotonically with decreasing a.

Upon unloading to a contact radius $a < a_\mathrm{max}$, the circumferential "crack" surrounding the contact area encounters an annular area of interface which has experienced the stress $\sigma(a)$ given by eq 8. $W(a)$ can be calculated using eq 4. Since from our hypothesis, $W(a)$ is determined by $\sigma(a)$, we can cross plot W_ul vs σ as shown in Figure 6 for the data of Figure 5. Note that while σ is tensile, W_ul remains close to the value determined for the loading portion W_l. However, as σ becomes more and more compressive, W_ul increases dramatically, just the qualitative behavior expected if the variations of W_ul with a were due to a pressure-induced chemical reaction.

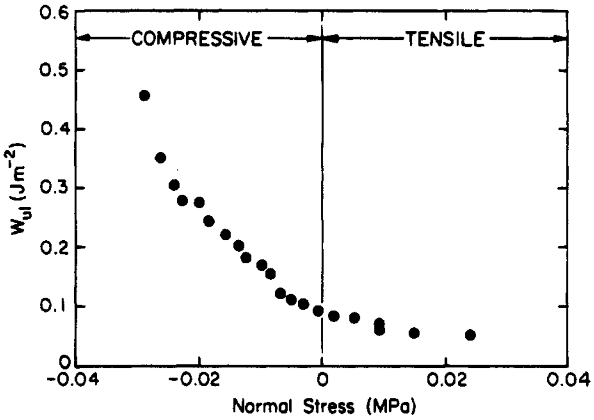

Figure 6. Influence of the normal stress on W_ul. W_ul increases drastically for compressive values of the stress.

We would have then expected a dependency of W_ul with the maximum load at which the system was subjected (keeping a unique W_ul vs σ relationship). We have mentioned above that small variations in the maximum load did not seem to have much effect on W_ul. However, experiments with model networks which offer more reproducible surfaces than the extracted commercial PDMS elastomers are under way and preliminary results are consistent with the assumption of single W_ul vs σ relationship.

Conclusion

In conclusion, we have demonstrated that the classical way of using the JKR model is not always applicable even in the case of incompressible elastomers.

The pressure profile across the interface can produce a work of adhesion that varies from the center to the edge of the area of contact and a new way of interpreting the results that includes this feature must be used. This new analysis provides a better description of the experimental data and may also provide new insight into the interpretation of related experiments such as scanning force microscopy.

Some aspects of the exact physicochemical origin of the observed hysteresis are still unclear, but complementary experiments on model elastomer systems currently under way should aid in our understanding of these origins.

Acknowledgment. We thank H. Brown, C. Cohen, and J. Israelachvili for fruitful discussion and the Office of Naval Research for financial support. P.S. thanks the French ministry of foreign affairs for a Lavoisier Grant.

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