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 development was achieved 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):

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

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

where \(E\) and \(v\) are respectively the Young modulus and

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Figure 1. Schematic representation of the JKR experiment.

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, \(W = 2y\) where \(y\) is the elastomer-air surface tension).3

Another theory by Derjaguin, Muller, and Toporov (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 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

(2) Hertz, H. In Miscellaneous papers; McMillan & Co.: London, 1896.
(4) Derjaguin, B. V.; Muller, V. M.; Toporov, V. J. Colloid Interface Sci. 1975, 62, 314.
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 $P_{\text{PO}}$) is also a measurement of the work of adhesion since one can easily see that

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

(2)

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

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

(3)

where $a_{\text{min}}$ 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. 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, $a^2(P)$) 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. Numerical simulations seem to show that a long-range potential can, by itself, induce such a hysteresis. 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. 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. 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. 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. Furthermore, the surface of mica can be modified by deposition of organic layers enabling one to tailor their adhesion properties. $K$ 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 $W_{\text{PO}}$ and $W_l$ occurred. Recent experiments, which have used the atomic force microscope (AFM) to probe the local adhesion properties of surfaces measure similar effects. In these experiments, only $P_{\text{PO}}$ 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 $a^2(P)$, 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, but usually $K$ is measured independently or calculated. Some authors have used the JKR geometry to measure $K$ during the loading phase 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, Silgard 170) prepared by cross-linking of end-functionalized poly(dimethylsiloxane) (PDMS). A slight excess of cross-linker was used to prevent blooming on the surface.

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 micro manipulator. 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) 500 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. 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 gives 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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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.

**Discussion**

Several reasons can be invoked to explain the difference between $W_l$ and $W_u$. 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. Several 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; 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...
of relatively short PDMS dangling chains are small compared to the effects seen here.\textsuperscript{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 \(-\text{Si(CH}_3\text{)}_3\)-H) is necessary for a hysteresis of the magnitude observed here to occur.\textsuperscript{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.\textsuperscript{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 groups being oxidized to Si-OH, which can then form hydrogen bonds across the interface. In the case of 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 $K_1 = K_{\text{ul}}$. Although the absolute values were observed to vary slightly from one experiment to another, the trend was always $K_{\text{ul}} > K_1$. The difference is always much greater in the case of extracted materials: for the sample shown in Figure 3, for instance, $K_{\text{ul}} > 2 K_1$. 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.\textsuperscript{22}

A possible explanation for this effect can be ascribed to pressure-induced surface reactivity by analogy to the stress-induced surface reconstruction.\textsuperscript{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 $a^2(P)$ that could be described by the same $K$ value as the loading one and a distribution of works of adhesion along the interface.\textsuperscript{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 $K = K_1$) in order to determine $W$ for each contact area during the unloading regime. The calculation gives

$$W(a) = \frac{1}{6\pi a^2 K_1} \left( a^3 K_1 - P(a) \right)^2 \quad (4)$$

Figure 5 shows the variations of $W_{\text{ul}}$ along the interface for the sample the data for which are shown in Figure 3. The large variations of $W_{\text{ul}}$ 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\textsuperscript{6}

$$\frac{\partial G}{\partial a} = 0 \quad (5)$$

where $G$ is the energy release rate

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

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

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

Plugging the expression for $G$ in eq 6, one gets

$$P_{\text{FO}} = -\left[ a_{\text{min}} \frac{6 K^2}{R^2} - 2 \pi K a_{\text{min}} \frac{\partial W}{\partial a} \right]^{1/2} = -\left[ a_{\text{min}} \frac{6 K^2}{R^2} - 2 \pi K a_{\text{min}} \right]^{1/2} \quad (7)$$

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 $a_{\text{min}} = 85 \pm 2$ \textmu m. Equation 4 gives $W_{\text{PO}} = 485 \pm 20$ mJ m\textsuperscript{-2}, which is consistent with the other points of Figure 5. Using eq 3 with $K = K_1$ would give $P_{\text{PO}} = -0.32 \pm 0.02$ mN, while eq 7 yields $P_{\text{PO}} = -1.3 \pm 0.15$ mN (for this last part of the calculation, $(\partial W/\partial a)_p (a = a_{\text{min}})$ was estimated from Figure 5).
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 $K_t$ and $K_w$ 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 $P_{KQ}$. 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 obtained24 (if $\delta W/\delta \alpha$ 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 $W_{al}$ 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. $r < a_{max}$) is given by

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

(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 $K_I = [W/\varepsilon/(1 - v^2)]^{1/2}$) 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 $W_{al}$ increases monotonically with decreasing $a$.

Upon unloading to a contact radius $a < a_{max}$, 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 $W_{al}$ vs $\sigma$ as shown in Figure 6 for the data of Figure 5. Note that while $\sigma$ is tensile, $W_{al}$ remains close to the value determined for the loading portion $W_l$. However, as $\sigma$ becomes more and more compressive, $W_{al}$ increases dramatically, just the qualitative behavior expected if the variations of $W_{al}$ with $a$ were due to a pressure-induced chemical reaction.

We would have then expected a dependency of $W_{al}$ with the maximum load at which the system was subjected (keeping a unique $W_{al}$ vs $\sigma$ relationship). We have mentioned above that small variations in the maximum load did not seem to have much effect on $W_{al}$. 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 $W_{al}$ vs $\sigma$ 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.

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