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Adhesion Between Hydrolyzed Surfaces of Poly(dimethylsiloxane) Networks[†]

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ABSTRACT: The JKR technique was used to study the adhesion hysteresis between hydrolyzed poly(dimethylsiloxane), PDMS, networks. PDMS model networks were synthesized and then hydrolyzed for various lengths of time in a 0.1 M HCl aqueous solution. It was found that as the exposure time of the networks to the HCl solution increased, the adhesion hysteresis increased. This hysteresis could be reduced by up to 80% by exposing the hydrolyzed networks to hexamethyldisilazane, which replaces the silanol end-functionality with a trimethylsilyl group. This dramatic reduction of the hysteresis suggests that the bulk of the adhesion hysteresis arises from a surface reconstruction reaction between silanol groups. We have also analyzed the unloading rate dependence of the adhesion hysteresis and found that it is probably due to the rate of bond dissociation.

1. Introduction

It is of great interest to many scientific fields to learn how one can tailor the microstructure of a surface to produce either high or low adhesion to a similar (or dissimilar) substrate. To do so, it is necessary to understand the source of adhesion and of adhesion hysteresis in the materials being used. Adhesion hysteresis is a term used to describe the situation where upon contact of two surfaces there is a surface reconstruction that results in a much higher energy per unit contact area measured during separation than was measured during loading. Adhesion hysteresis may be a result of bulk viscoelasticity, entanglement at the interface (mechanical adhesion hysteresis), chemical bond formation (chemical adhesion hysteresis), or several other surface interactions.[1,2] The so-called JKR test[3] has recently become widely accepted as an accurate and reproducible means for determining the adhesive qualities of elastomers (or an elastomer in contact with a rigid surface). We have utilized the JKR test to further investigate the role surface hydrolysis plays in the adhesion hysteresis observed in poly(dimethylsiloxane), PDMS, networks.

The JKR test is a simple test based on contact mechanics that has been more fully described elsewhere.[3−6] In brief, the JKR test determines the strain energy release rate, G, necessary to maintain a certain radius of contact a between two elastic hemispheres of radius R_1 and R_2 under a contact force, P. P is related to G by

$$G = \frac{(P_H - P)^2}{6\pi K a^3} \qquad (1)$$

where $K = 2E/(3(1 - \nu^2))$, is an elastic stiffness, E is Young's modulus, and ν is Poisson's ratio, assuming that the hemispheres are identical. $P_H = Ka^3/R$ is the Hertz contact pressure, the pressure that would be required to produce the measured a if there were no adhesive forces, i.e. $G = 0$; and $R^{-1} = R_1{}^{-1} + R_2{}^{-1}$. E and ν are determined from the a vs P data during loading. If equilibrium loading and unloading conditions are achieved, and if there is an absence of interface reconstruction, G should equal W, the equilibrium work of adhesion. In the case of two identical surfaces in contact, W is defined as twice the surface energy, γ, of that material. In the case of model PDMS networks, W is approximately equal to 44 mJ/m^2. While such "ideal" results can be obtained from the JKR test,[6] it is more frequently observed that the G during loading is approximately W, but G during unloading may be much larger[7] and may vary with both the rate of unloading[8,9] and a.[4,10] It is therefore of interest to investigate such adhesion hysteresis because it appears to be related in some instances to penetration of chains into the networks and in others to interface reconstruction giving rise to chemical bonding across the interface.

The existence of adhesion hysteresis in commercial PDMS (nonmodel) networks[11] that have been sol extracted has been reported by Silberzan et al. and others.[4,5] To accurately define the source of this adhesion hysteresis, we have synthesized model PDMS networks and then modified them to simulate the commercial material by adding a controlled amount of cross-linker[12] in excess of that needed to form a perfectly cross-linked network. In commercial PDMS networks, an excess of the silane functional cross-linker is added to prevent the surface from "blooming". We have found that these excess silane groups play a major role in the chemical adhesion hysteresis in their own right; however, they cannot account for the total hysteresis observed. It is well known that at ambient conditions, in the presence of water vapor in the air, silane groups may hydrolyze to form silanol groups:

$$\equiv\text{SiH} + \text{H}_2\text{O} \rightarrow \equiv\text{SiOH} + \text{H}_2$$

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These silanol groups may also cause a chemical adhesion hysteresis, as described below.

Silanol end groups have a higher surface energy than that of the PDMS network, so they prefer to remain below the surface. When two such surfaces are brought into contact, a surface reconstruction may occur and the (≡SiOH) groups on opposite sides of the interface can combine to form hydrogen bonds or condense to form (≡Si—O—Si≡) bonds, with water as the condensate. The energies needed to break such bonds are much higher than the energy required to separate neat PDMS surfaces (bound by van der Waals forces). Hence, the adhesion between such surfaces is greater than that between typical PDMS surfaces.

In the PDMS networks with excess cross-linker added ("imperfect networks") it was found that as the rate of separation of the interface decreased, the amount of energy needed for this separation decreased; i.e., the adhesion hysteresis decreased.[12] We have also used the hydrolyzed networks to further investigate the rate dependence of chemical adhesion hysteresis.

2. Experimental Section

Model PDMS networks were prepared following the procedure of Patel et al.[13] PDMS chains were synthesized via a ring-opening polymerization and end-capped with vinyl groups. The molecular weight of the PDMS was controlled to be in the range from 30 000 to 50 000 with a polydispersity index of <1.18. The end-capping reaction reached ≈90% of completion, as determined by thin layer gel chromatography. The networks were formed by hydrosilation using a tetrafunctional cross-linker, tetrakis(dimethylsiloxy)silane, and a *cis*-dichlorobis(ethyl sulfide)platinum(II) catalyst. Drops of the PDMS/cross-linker/catalyst solution were placed on fluorinated glass slides[14] and then annealed at a temperature of 35 °C under vacuum for 3 days to form hemispheres. In the experiments reported here the cross-linker/PDMS ratio was adjusted so as to produce "ideal" networks with minimum sol fraction (<1%) being extracted by swelling in toluene; nevertheless, any residual sol fraction was extracted from each hemisphere.

Each surface of these ideal networks was then hydrolyzed in 0.1 M HCl aqueous solution for various times to produce silanol groups near the surface of the network. To assure that the changes in adhesion hysteresis we observe after hydrolysis are due to the silanol groups, we attempted to react these with hexamethyldisilazane. Hydrolyzed networks were exposed to hexamethyldisilazane as a liquid and as a vapor. Those treated with the liquid were immersed in hexamethyldisilazane for 12 h. The vapor exposure was carried out in a desiccator with aluminum sulfate present as a getter, also for 12 h.

The JKR apparatus and technique have been described previously.[4,5] A hemisphere of the PDMS network is brought into contact with a hemisphere that has the exact same surface treatment history. Unless otherwise noted, the load is applied at the constant rate of approximately 2.4 μN/s until a maximum load of about 1 mN is reached. The contact is maintained at this load for ~12 h and then unloaded at the same rate until the elastomeric hemispheres separate. The radius of the area of contact a is measured at fixed intervals of applied load throughout the experiment. For the rate dependent tests, the rate of unloading was decreased from 2.4 μN/s to 0.6 and 0.1 μN/s by adding a 643:1 gear box in series to the JKR system.

3. Results and Discussion

3.1. Source of Adhesion Hysteresis. The results from the JKR experiment on the model PDMS networks, before hydrolysis, are shown in Figure 1. The G measured during loading and unloading was independent of a and was equal to the work of adhesion of PDMS ($W = 2\gamma \approx 44$ mJ/m^2). The concurrence of the loading and unloading data shows this to be a nonhysteretic system. The G curves of the model networks were independent of the rate of unloading.

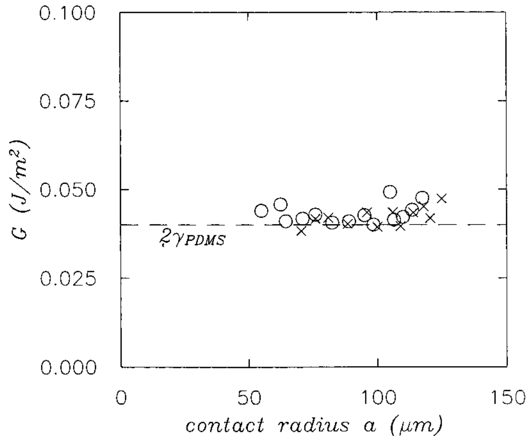

Figure 1. Model PDMS network self-adhesion measurement. The loading (crosses) and unloading (open circles) curves coincide, indicating that this system is nonhysteretic. This is confirmed by the constant value of G that is approximately twice the surface energy of PDMS ($2\gamma_{\text{PDMS}} \approx 44$ mJ/m^2), as shown by the dashed line.

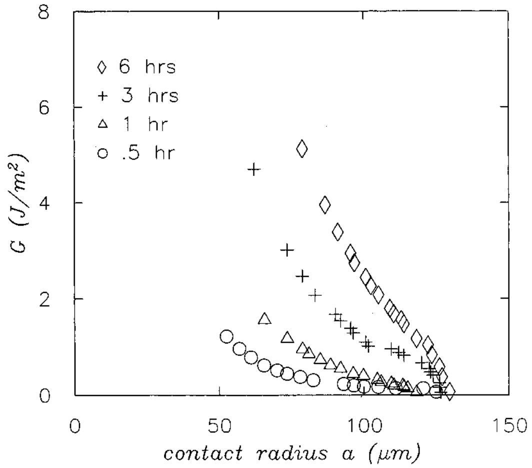

Figure 2. Unloading G curves for PDMS networks exposed to 0.1 M HCl aqueous solution for various lengths of time. As the exposure time increases, the G during unloading increases. The exposure times are marked by different symbols in this figure.

After these model networks were hydrolyzed, there was a dramatic increase (2 orders of magnitude) in the unloading G (Figure 2). While the loading G vs a curve remains constant at ≈44 mJ/m^2, the unloading G vs a curves increase as a shrinks from the maximum contact radius to the center of contact. This adhesion hysteresis increases as the length of exposure time to the HCl solution increases. Treatment times longer than 6 h produce even larger values of G (see results from the 12 h exposure in Figure 5). Extraction of the hydrolyzed PDMS networks in toluene did not have any effect on the results. Diluting the HCl solution to 0.05 M also did not alter the observed hysteresis (see Figure 3).

It should be noted that the measured values of the elastic constant K for the hydrolyzed networks were the same (within experimental error) as those measured before the hydrolysis. This suggests that the hydrolysis treatment is affecting only surface regions (not the bulk) of the networks.

We have also used contact angle measurements to study the hydrolyzed PDMS surface. Deionized water

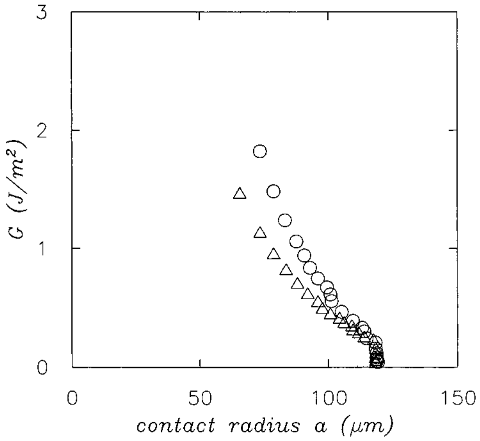

Figure 3. Unloading *G* curve for PDMS networks exposed to 0.05 M HCl aqueous solution (triangles), which is within experimental error of the results from those networks exposed to the 0.1 M solution (circles).

contact angle measurements on PDMS films that were hydrolyzed for 12 h yielded 121° (±2°) advancing and 71° (±2°) receding. Typical values for our untreated PDMS network surface are 118° (±2°) for advancing and 90° (±2°) for receding. A glass or quartz surface covered with silanol groups has a contact angle of close to 0° with water.

These results suggest that in air, the hydrolyzed PDMS surface reconstructs to expose the (—CH_3) groups of the PDMS chain and to bury the (≡SiOH) end groups. Both the loading JKR tests and the advancing contact angle measurements show results typical for a methyl-covered surface. When the PDMS surface comes into contact with water or with another PDMS surface, the buried (≡SiOH) groups diffuse to the interface and the unloading JKR, and receding contact angle tests reflect this changed interface. The fact that the receding contact angle is higher than that of a surface covered with (≡SiOH) groups shows that the hydrolysis of PDMS does not produce a close-packed layer of silanol groups on the surface.

To demonstrate that the adhesion hysteresis is due to the presence of silanol groups at the surface of the networks, we have exposed the networks to hexamethyldisilazane. Hexamethyldisilazane reacts with the silanol groups to replace the (—OH) functionality with a trimethylsilyl group, thereby masking the contribution of the (—OH) group to the adhesion hysteresis (see scheme 1 in Figure 4. Our results are shown in Figure 5 where the hysteresis could be reduced by an order of magnitude by this treatment, but *G* still remained an order of magnitude higher than the nonhysteretic value for PDMS. Figure 6 shows that samples that had not been exposed to the acid treatment were seen to have higher *G* values after exposure to the hexamethyldisilazane. These results may be due to the fact that the reaction of hexamethyldisilazane with silanol groups releases ammonia (NH_3) as a by-product. Ammonia can act as a hydrolysis agent in the presence of water, thereby recreating (≡SiOH) groups. This hypothesis is illustrated by scheme 2 in Figure 4.

To avoid this reaction, we exposed the networks to a vapor of the hexamethyldisilazane in the presence of aluminum sulfate, used as a getter for the ammonia. This procedure was used on networks exposed to the acid solution for 3 and 6 h with no noticeable effect on the hysteresis. Thus, either the ammonia is not removable by this method or the remaining adhesion hysteresis arises from another source.

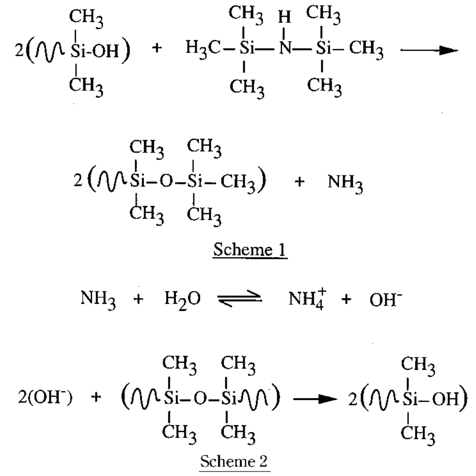

Figure 4. Reaction schemes of (1) hexamethyldisilazane reacting with silanol groups, and (2) ammonia undergoing a proton exchange with water, which may then act as a hydrolysis agent to create (≡SiOH) groups on a PDMS surface.

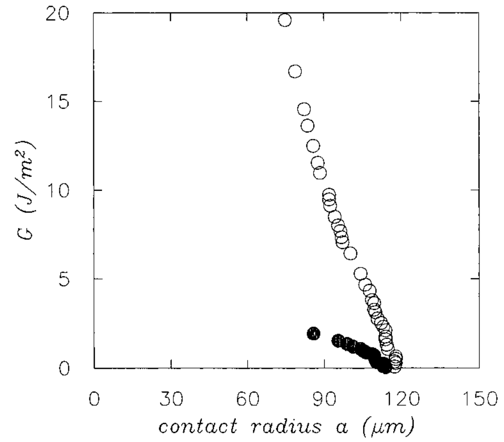

Figure 5. Unloading *G* values of PDMS networks exposed to 0.1 M HCl aqueous solution for 12 h (open circles) and then immersed in liquid hexamethyldisilazane to mask the ≡SiOH end groups (closed circles). The treatment with hexamethyldisilazane reduces the adhesion hysteresis by an order of magnitude, but it still remains an order of magnitude higher than the nonhysteretic value for PDMS.

3.2. Unloading Rate Dependence of Adhesion Hysteresis. The dependence of *G* on the rate of unloading was determined by decreasing the unloading speed from 2.4 μN/s to 0.6 and 0.1 μN/s. The results from these experiments on networks exposed to the acid solution for 1 h are shown in Figure 7. As the rate of unloading decreases, the values of *G* asymptotically approach a value of approximately 0.25 J/m², which is well above the nonhysteretic value for PDMS. The initial increase in *G* observed in these samples occurs when the very small changes in *a* cannot be distinguished from the experimental error present in this apparatus. This regime is not well understood and may be due to transient effects. It is of interest to determine whether *G* is a function of the rate of unloading, $\partial P/\partial t$ (where *t* is time), or of the crack growth rate $r \equiv -\partial a/\partial t$, where $\partial a/\partial t$ is the change of the contact radius with time. We have experimentally determined *r* for the unloading rate experiments by measuring the change in *a* between fixed time intervals. The dependence of *G* on log(*r*) for the data in Figure 7 is plotted in Figure 8. The data from the three unloading rates used lie on a simple master curve. For this curve, *G* remains relatively constant at approximately 0.25 J/m²

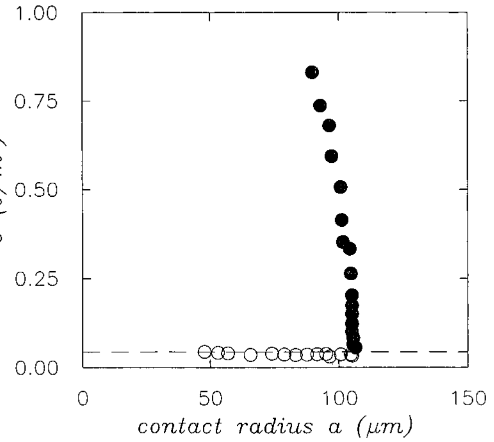

Figure 6. Unloading G curve from an unhydrolyzed model network (open circles) compared to that of a model network exposed to hexamethyldisilzane in liquid form (closed circles). A large increase from the original nonhysteretic results is observed. The dashed line indicates the value for twice the surface energy of neat PDMS.

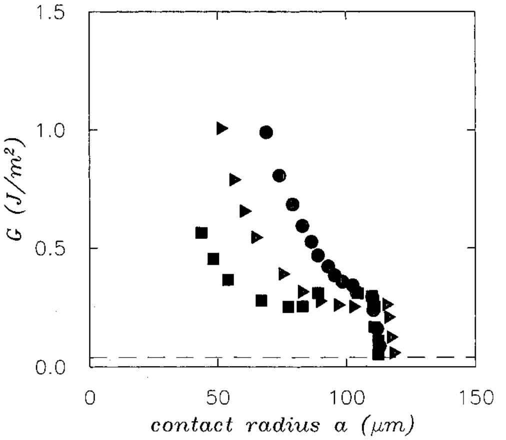

Figure 7. Rate dependence of G in hydrolyzed samples. The samples were unloaded at rates of 2.4 μN/s (circles), 0.6 μN/s (triangles), and 0.1 μN/s (squares). As the unloading rate decreases the G also decreases to an asymptotic value above the nonhysteretic value for PDMS (shown by a dashed line).

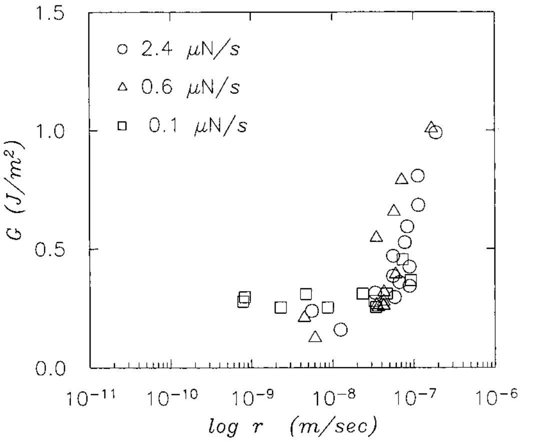

Figure 8. Values for G from figure 7 plotted as a function of the logarithm of the rate of crack growth. The data from all three unloading rates overlap on a master curve that shows a region that is rate dependent ($r > 1 \times 10^{-7}$ m/s) and a region where the G seems to have reached a rate independent value at rates slower than 1×10^{-7} m/s.

until r reaches $\approx 1 \times 10^{-7}$ m/s. At faster rates, the value for G increases rapidly to approximately 1.0 J/m^2.

Usually, rate-dependent hysteresis is attributed to a mechanical entanglement at the interface or to a bulk viscoelasticity of the materials. However, because a significant amount (~80%) of the adhesion hysteresis in this system could be removed by the hexamethyldisilazane treatment, the main source of adhesion hysteresis must be of a chemical nature. The only entanglement that could occur at the interface would be from dangling, unreacted PDMS chain ends across the interface. The extraction of these chain ends would contribute a negligible amount of disentanglement at the interface during unloading. This is similar to the results found in imperfect networks where the catalyst was poisoned. Although the dangling chains must still exist, they can no longer form secondary bonds and they are easily pulled out, as evidenced by the large reduction in adhesion hysteresis in the poisoned systems. Also, the fact that the T_g of PDMS is ≈ -120 °C makes PDMS a nearly perfectly elastic material at room temperature, and it is therefore very unlikely that any bulk viscoelasticity is contributing to the adhesion hysteresis in this system. This is also substantiated by the fact that K is constant in all of our tests. Therefore we believe the crack growth rate dependence in these systems is due to the rate dependent dissociation of bonds formed between (≡SiOH) groups.

Next we attempt to use a simple kinetics model to study our rate dependent results. If the two separating hemispheres of the JKR test are considered as the opening surfaces of a propagating crack, the kinetic theory of fracture may be used to study the rate dependent results. This theory is based on the fact that an applied tensile stress on a bond can increase the rate of bond dissociation.[15−21] In a previous study,[12] we have shown that the kinetic theory of bond fracture can model the rate dependence of the chemical adhesion hysteresis in the imperfect PDMS networks with reasonable results. We use the same approach here.

The details of the application of the kinetic rate theory to the JKR unloading experiment may be found in ref 12. Briefly, we assume that (1) the crack will propagate only when bonds at the crack tip are broken, (2) the time it takes to break a bond is independent of the number of bonds present, and (3) the bond will break when the applied stress is the critical stress. With these assumptions, the relation between a, r, and G is given by

$$\ln(2\pi a r) = \ln\left(\frac{A}{\rho}\right) + \ln\left(\sinh\left[\frac{\left(\frac{\beta\sqrt{K}}{\sqrt{\pi x_c}}\right)\sqrt{G(r)} - \Delta G^\circ}{k_b T}\right]\right) \qquad (2)$$

$$A = \frac{\lambda k_b T}{h}\exp\left(\frac{-\Delta G^*}{k_b T}\right)$$

where ρ is the number of bonds per unit area, λ is the bond displacement between the bonded and unbonded states, k_b is Boltzmann's constant, T is temperature, h is Planck's constant, β is the activation volume of one bond, K is the elastic stiffness from eq 1, x_c is the distance from the crack tip, ΔG^* is an activation barrier between the bonded and unbonded states, and ΔG° is half the free energy difference between a bond in the broken and unbroken states.

The 2.4 and 0.6 μN/s unloading rate experiments were fitted using eq 2. The results from the fitting are shown in Figure 9, and the corresponding values for the fitting parameters are shown in Table 1. It should be noted that the G from the 0.1 μN/s experiment showed very little rate dependence, and it was difficult to obtain a

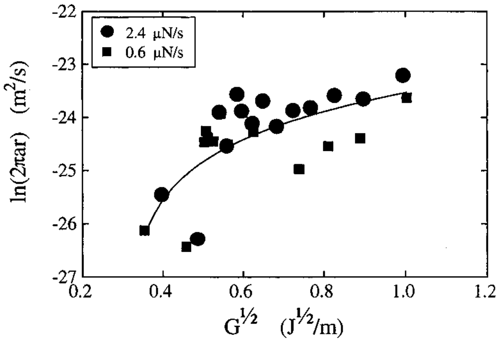

Figure 9. Unloading data from hydrolyzed PDMS networks from the 2.4 and 0.6 μN/s unloading rates plotted as $\ln(2\pi ar)$ as a function of $\sqrt{G}$. The solid line represents the best fit of the data with eq 2.

Table 1. Results from Fitting of Rate-Dependent Data with the Kinetic Rate Theory of Bond Dissociation

A/ρ (m^2/s)	$\beta(K/\pi x_c)^{1/2}$ (m^5 Pa)$^{1/2}$	$\Delta G°/k_bT$
1.36×10^{-10}	0.62	0.2

good fit for these data with this model. Therefore, the results from this experiment were not included in Figure 9. Below we discuss the values obtained from this model for the fitting parameter values.

This model assumes that ρ is constant over a. It may be argued that ρ could change with position in the contact zone because it may depend on the local pressure profile defined by the JKR theory. According to the JKR pressure profile the tensile stresses are highest at the edge of contact, and then they drop off rapidly so that the majority of the area of contact is under compressive stress. Thus more bonds could form toward the center of contact. This effect should only be dependent on the magnitude of the applied load and not on the rate of unloading. However, we find that for the same maximum applied load, G decreases as the unloading rate decreases. Hence the spatial distribution of ρ before the initiation of unloading does not significantly affect the interpretation of the unloading data. Therefore estimating ρ to be constant seems to be justified.

The values for A/ρ found for our samples are three orders of magnitude larger than those found by Sha et al. ($\approx 10^{-14}$),[21] who successfully used this model to describe the rate of breaking of fibrils in a craze[22] for poly(methyl methacrylate) (PMMA) materials. While the value for ρ is not known for the hydrolyzed surfaces, contact angle measurements show that the surface coverage of (≡SiOH) groups is much less than that of a close packed surface. Also, Gent et al.[23] have calculated the low speed fracture energy of a fully formed PDMS network as $G_c \sim 75$ J/m^2. This value corresponds to the maximum areal density of network chains crossing a polymer interface. From this we conclude that the areal density of bonded (≡SiOH) groups necessary to achieve $G_c \sim 5$ J/m^2 (as measured in Figure 2) is far less than the maximum density.

The value for A should be larger in our system as well. The bonds being broken have a lower ΔG^* than the carbon–carbon bonds in the PMMA fibrils, and λ should be much larger for PDMS than for PMMA. It is thus reasonable that our value for A/ρ is ~3 orders of magnitude larger than that of PMMA.

The factor β is the product of the activation area of one bond, A, and the length a bond or polymer chain stretches before breaking, λ. From the contact angle and JKR experiments we know that the surface coverage of (≡SiOH) groups is much less than that of a close-packed surface. Assuming A to be on the order of 1 nm^2, λ is approximately 100 Å, K is that measured by the JKR experiment ($\approx 10^5$ Pa), and $x_c \approx 1$ nm, we arrive at a value for the second fitting parameter

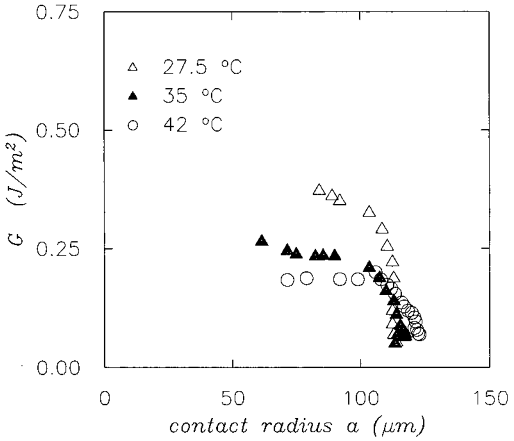

Figure 10. Unloading data from PDMS networks hydrolyzed for 1 h and unloaded at 0.6 μN/s at various temperatures. As the temperature increases, the adhesion hysteresis decreases.

$$\frac{\beta\sqrt{K}}{\sqrt{\pi x_c}}$$

on the order of 1, which is in reasonable agreement with the value found by fitting.

The value for $\Delta G/k_bT$ of a (≡Si–O–) bond is ≈300. The value of $\Delta G/k_bT$ for a hydrogen bond between polymer chains is somewhat less than $\Delta H/k_bT$, the enthalpy of a hydrogen bond (≈9, for a hydrogen bond between poly(vinylphenol) and poly(n-butyl methacrylate) as given by Painter et al.[24]). The change in free energy has a contribution from the entropy increase caused by the increase in disorder when such a bond is broken. We estimate that the $\Delta G/k_bT$ will be reduced by about 50% from its enthalpic value. The value obtained from the fitting of the data is 0.2, however, which is an order of magnitude less than our estimate. It may be that the silanol hydrogen bonds are weaker than those used for the estimate above. In general, the fit of the experimental data by this model is reasonable, and we conclude that the rate dependence of G is due to the effect of the rate of bond dissociation on the force required to cause this dissociation.

A series of experiments were performed at different temperatures to study the nature of the rate dependence. The temperature was increased using a heat lamp and stabilized for one hour before the samples were unloaded at 0.6 and 0.1 μN/s. The temperature was kept constant at 35 and 42 °C (depending on the experiment) during the entire unloading cycle. The results from the 0.6 μN/s test may be seen in Figure 10. As the temperature increased, the adhesion hysteresis decreased. However, because the hysteresis was so low in these samples, it was difficult to analyze the data to prove or disprove the bond dissociation model. Also, by increasing the temperature, the stability of the JKR apparatus was compromised;[25] therefore these experiments were not pursued further.

4. Conclusions

The origin and nature of the adhesion hysteresis found in hydrolyzed PDMS surfaces was investigated using the JKR technique. Model PDMS networks were hydrolyzed to various degrees by immersion in a weak HCl acid solution for specific lengths of time. The adhesion hysteresis was found to increase strongly with hydrolysis time. By reaction of the hydrolyzed networks with hexamethyldisilazane, the silanol functionality was chemically masked, and the adhesion hysteresis was seen to decrease significantly. These results suggest that the main source of adhesion in this system is an interface reconstruction that leads to chemical bonding by the silanol groups across the interface. Contact angle measurements confirm the presence of surface reconstruction in these hydrolyzed networks. The dependence of the adhesion hysteresis on the rate of unloading was shown to be due to the dependence of G on the crack growth rate. A simple model that accounts for the rate of bond dissociation was proposed to describe the rate-dependent experimental data.

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