

Adhesion Hysteresis Studies of Extracted Poly(dimethylsiloxane) Using Contact Mechanics

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We present results of adhesion studies of poly(dimethylsiloxane) (PDMS) crosslinked hemispheres, before and after extraction, carried out using contact mechanics (the JKR apparatus.) Three types of PDMS networks were prepared with increasing crosslinker-to-PDMS ratio ($r = 1.7, 2.2, 2.7$). Adhesion hysteresis was observed only after the PDMS hemispheres were extracted (toluene, Soxhlet, 20–24 h.) The size of hysteresis increased systematically with the decreasing ratio (increasing percentage of extracted weight.) Brief extraction yielded smaller hysteresis, which disappeared after 12 days. It is concluded that the entanglement of tethered chains and their interdigitation with cross-linked PDMS network at the interface may be the dominating mechanisms for the observed adhesion hysteresis.

Introduction

Most real processes involving adhesion and wetting are hysteretic or energy dissipating. In adhesion processes, the work done on separating two surfaces from adhesive contact is larger than that released when these surfaces come into contact, i.e., $\Delta W = (W_U - W_L) > 0$, where W_U and W_L are the adhesion energies for unloading (receding) and loading (advancing) two solid surfaces, respectively. In the JKR experiment, adhesion hysteresis means that some irreversible transformation has taken place, which may result from surface and bulk effects.

Examples of bulk effects are relaxation processes in the cross-linked PDMS network. Surface effects are due to energy barriers.¹ Possible mechanisms that may cause energy barriers are the formation of hydrogen bonds, the interdigitation of tethered chains with cross-linked PDMS networks, and the contortion of a contact line due to surface imperfections. While there have been many studies of adhesion hysteresis,^{2–6} there is still no clear understanding of the complex bulk and surface phenomena, and their relative importance, in determining adhesion hysteresis. In this paper we report the results of experiments aimed at elucidating contributions of the PDMS elastomer structure and dynamics to adhesion hysteresis.

The development of contact mechanics methods and the introduction of the JKR apparatus by Chaudhury^{3–5} have made possible systematic studies of adhesion using hemisphere elastomers. The preferred elastomer has been poly(dimethylsiloxane) (PDMS) rubber, due to the straightforward synthesis of the polymer and the simple cross-linking process. Using the JKR technique, it is possible to investigate the contribution of different surface and material properties to adhesion. Gaining extensive knowledge of detailed correlations between the chemistry and dynamics of surfaces and their properties will make possible the design and reproducible preparation of polymer surfaces. Such capabilities may have significant technological applications.

The JKR theory is a continuum contact mechanical model developed by Johnson, Kendall, and Roberts.⁷ It is an extension of the Hertz theory,⁸ developed for cases where adhesive forces operate at the interface between two elastomers. The JKR technique has been widely used by Chaudhury,^{2,4,5,8–10} Kramer,² Brown,^{10–13} Tirrell,^{14–17} and Shull,^{18,19} and it allows direct estimate of the free energy and work of adhesion of many inorganic and organic surfaces. The radius of contact, a , between an elastic semispherical surface and a flat nonelastic surface at equilibrium is described by the equation

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

where R is the radius of curvature of the spherical elastomer, P is the applied load at the contact interface, K is the elastic constant of the elastomer, and W is the thermodynamic work of adhesion between two surfaces (Figure 1). The JKR experimental method has been increasingly used because (a) the volume under deformation is small and viscoelastic effects are minimized³ and (b) it can be applied to tailored organic self-assembled monolayers (SAMs). However, the JKR equation is only an approximation, and thus agreement with experiments is not always possible. Because K and W are obtained from parameter fitting of experimental P and a data to the equation, and because of the nonequilibrium nature of the experiment, K is not a idealized parameter, and often deviates from known values of the bulk elastic constant. Furthermore, because it is also a fitted pa-

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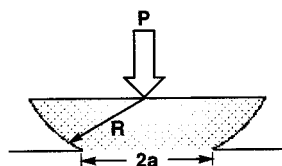


Figure 1. Schematic diagram of the JKR experiment.

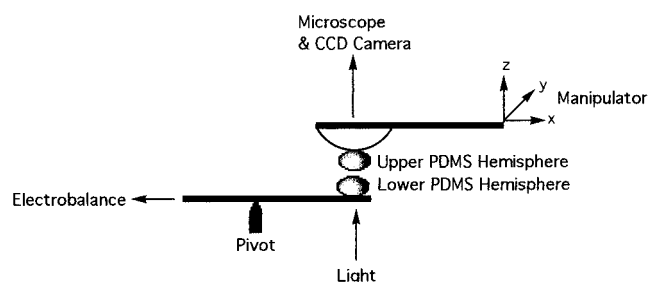


Figure 2. Schematic diagram of the experimental apparatus.

rometer, W may not be the true work of adhesion, especially when strong interactions exist at the interface. The equation is continued to be used, however, since there is no alternative theory.

Experimental Section

Vinyl-terminated PDMS with 11 000 average molecular weight and polydispersity of 2.76 was a gift from Genesee Polymer Corp. (GP-511). The cross-linker was tetrakis(dimethylsiloxy)silane, (Gelest Inc.) and the catalyst was *cis*-dichlorobis(diethyl sulfide)platinum(II) (Strem Chemicals). Transparent PDMS network hemispheres for JKR experiments were prepared by placing small droplets (0.5–1.5 mm radius) of PDMS with cross-linker and catalyst on microscope slides that were previously treated with $\text{Cl}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$. Curing (hydrosilation cross-linking)^{20,21} was carried out in the desiccator, at 60 °C for 3 days, under vacuum. This process removed the tiny amount of toluene used to dissolve the catalyst. Three types of PDMS hemispheres were prepared by changing the cross-linker ratio ($r = 1.7, 2.2$, and 2.7). r is the stoichiometric ratio of silane hydrogens to vinyl groups. Notice that there is no optimum quantity of cross-linker, because of the broad molecular weight distribution. Extraction to remove the soluble sol fraction was carried out with toluene using Soxhlet for 20–24 h. The solvent was removed from the network by drying in a vacuum desiccator at 60 °C for 3 days. After this procedure, the measured fraction of extracted material was 7 to 3% by weight from the stoichiometric ratio 1.7:2.7 respectively.

The experimental apparatus is illustrated schematically in Figure 2. The upper lens is adjusted in the x, y, z directions by using the micromanipulator. The lower lens is placed on one end of a lever arm, which is connected to an electrobalance. Using the microscope and a video camera, the contact area is measured. The entire JKR apparatus is located on an optical table that is vibration isolated. All data points are gathered every 5 min to allow for viscoelastic relaxation in the cross-linked network. R is measured by placing the CCD camera on the microscope stage and imaging the hemisphere. The uncertainty in this measurement is $\pm 5\%$. The uncertainty in W and K is ± 5 –10%. Atomic force microscopy (AFM) was carried out on a Digital Instrument Nanoscope III.

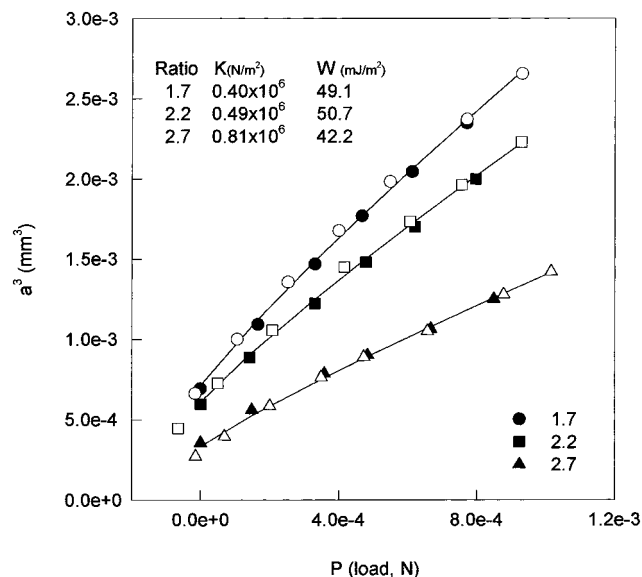


Figure 3. Loading (closed symbols) and unloading (open symbols) curves for as prepared PDMS hemispheres with different stoichiometric ratios of crosslinker.

Results and Discussion

Before extraction (as prepared hemispheres) self-adhesion experiments show no hysteresis (Figure 3). Also, while for $r = 2.7$, $W = 42 \text{ mJ m}^{-2}$, in agreement with $W = 2\gamma$, where γ is the PDMS surface free energy (20 mJ m^{-2}), for $r = 2.2$ and 1.7 , W is 50.5 and 49.1 mJ m^{-2} , respectively. Furthermore, for $r = 2.7$, $K = 0.81 \times 10^6$ much larger than 0.49×10^6 and $0.40 \times 10^6 \text{ N m}^{-2}$ for $r = 2.2$ and 1.7 , respectively. The trend in K , as well as the high value $r = 2.7$, agrees with the expectation that as cross-linking density increases, the resulting network is less elastic. The fact that the trend is not monotonic is probably due to the polydispersity of the PDMS.

We have observed before nonhysteretic behavior in experiments made with hemispheres of homemade 68K PDMS networks, with polydispersity of ≤ 1.2 and extractable material of only $\sim 1\%$, when loading and unloading were carried out in a stepwise manner, i.e., with a 5 min waiting period after each data point,²² thus assuming enough relaxation time. Systematic experiments in our laboratory (not shown here) show that all relaxation processes take place within ≤ 3 min. However, we have consistently used 5 min to make sure that the observed contact area is stable. Using the stepwise protocol allows the system to get rid of fast relaxation processes that involve network reorganization under changing loads. Therefore, the observed hysteresis reflects long relaxation times, which are associated with strong surface interactions. Interestingly, adhesion promotion was observed for $r = 1.7$ and 2.2 ($W = 49.1$ and 50.5 mJ m^{-2} , respectively), while hysteresis was not.

When adhesion experiments were carried out between two hemispheres with different r values, no hysteresis was observed. Figure 4 presents such an experiment, where the two unextracted hemispheres have r values of 1.7 and 2.7 . Interestingly, K obtained from fitting to the JKR equation ($0.50 \times 10^6 \text{ N m}^{-2}$) is similar to the K obtained from self-adhesion experiments of hemispheres with $r = 2.2$ values, suggesting that the expected relationship between cross-linking density and K is detected by the contact mechanics technique even when

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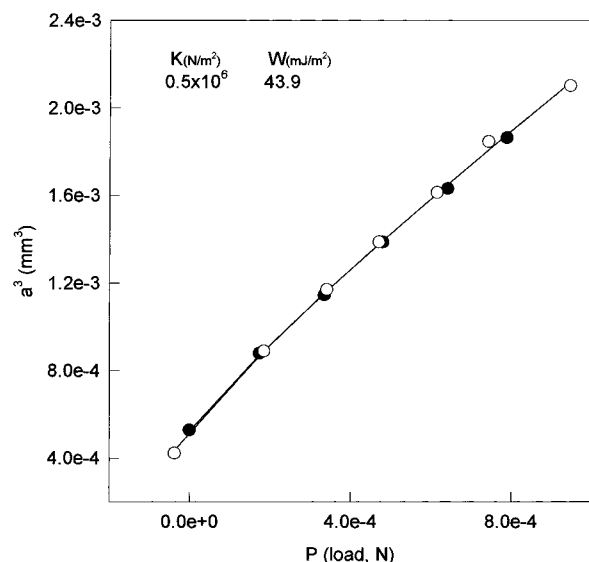


Figure 4. Loading (closed symbols) and unloading (open symbols) curves for two different, as prepared, PDMS hemispheres (upper hemisphere $r = 1.7$; lower hemisphere $r = 2.7$).

the interface between the two elastomer surfaces is unsymmetrical. On the other hand, the work of adhesion (43.9 mJ m^{-2}) is closer to that obtained from self-adhesion experiments of $r = 2.7$ hemispheres.

To reconcile these observations we propose that tethered and free chains at the interface serve as adhesion promoters via the entanglement mechanism. In the present studies, one expects for $r = 1.7$ and 2.2 more free chains at the interface, and hence adhesion promotion. We suggest that adhesion hysteresis is absent, since free chains at the interface can easily transfer from one hemisphere to the other during crack propagation, and disentanglement is fast enough to be completed during the 5 min waiting period. In other words, the system is still in the fast relaxation domain, since polymer chains have not been exposed to strong interactions. Since entanglement across the interface requires at least pairs of chains, adhesion promotion ($\Delta W = W - 2\gamma$) should be determined by the surface with the *small* number of tethered chains. Therefore, in the experiment presented in Figure 4, it is the hemisphere with $r = 2.7$ that determines the value of ΔW .

As noted above, the effective elastic constant K , obtained from parameter fitting, in the adhesion studies between two different hemispheres is $0.50 \times 10^6 \text{ N m}^{-2}$. Calculations carried out using K values obtained from self-adhesion of $r = 1.7$ and $r = 2.7$ hemispheres estimated a K value $0.67 \times 10^6 \text{ N m}^{-2}$. This inconsistency may be another manifestation of the fact that one cannot use equations developed for the bulk elastic constant in this case. The JKR theory assumes that the elastic properties are the same throughout the body under load. This is not the case, since interactions at the interface between hemispheres (which result in a work of adhesion) change the dynamics of polymer chains and hence the *effective* elastic constant near the interface.

After Soxhlet extraction in toluene, all loading-unloading curves show significant hysteresis (Figure 5). Furthermore, there is a significant trend in W_U , and its value increases from 57.7 to 70.8 to 119.4 mJ m^{-2} for $r = 1.7, 2.2$, and 2.7 , respectively. The trend in K is as before extraction, where ΔK in each case— ΔK being $K_{\text{extracted}} - K_{\text{unextracted}}$ —is within experimental error. In addition, there

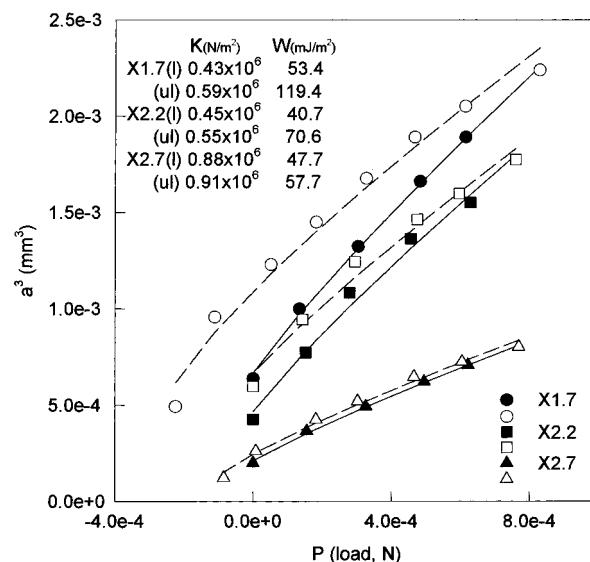


Figure 5. Loading (closed symbols) and unloading (open symbols) curves for as prepared PDMS hemispheres with different stoichiometric ratios of cross-linker.

is a clear trend in adhesion hysteresis, with the latter increasing as r decreases.

Six mechanisms can be proposed to explain the observed trend in W_U and adhesion hysteresis: the increase of surface roughness due to extraction, the formation of H-bonds at the interface, the cross-linking of chain-ends due to existence of cross-linker and catalyst at the interface, the entanglement of tethered chains, the interdigitation of tethered chain and cross-linked networks, and the plastic deformations due to free volume resulting from the extraction.

AFM studies of hemisphere surfaces before and after extraction are presented in Figures 6 and 7. Before extraction, surface roughness is small, with an rms value of 28 \AA . After extraction, roughness increases, and the rms value is 110 \AA . While surface roughness increases after extraction, it increases for all r values. Hence, increased adhesion due to the interlocking of the two surfaces cannot explain by itself the trends in W_L and W_U presented in this paper, and other factors must play an important role.

Silberzan *et al.* have studied the adhesion of extracted PDMS and suggested the possibility of H-bonding of Si-OH groups, proposing that the latter result from thermal oxidation of unreacted cross-linking agents ($\text{Si-H} \rightarrow \text{Si-OH}$). However, if this mechanism was the dominated one in the present studies, the observed trend in adhesion hysteresis should have been the opposite; i.e., the hysteresis should increase as the quantity of cross-linker is increased, with the highest observed hysteresis for $r = 2.7$, which is not the case.

That the cross-linking reaction will continue after 20–24 h of Soxhlet extraction is not reasonable since the catalyst is highly soluble in toluene. Furthermore, if this mechanism was important, a finite hysteresis should be observed for the unextracted hemispheres, which is not the case. Nevertheless, we have exposed $r = 1.7$ hemispheres to 1 mM solution of octanethiol in toluene to poison the platinum catalyst. Self-adhesion experiments were identical to those presented in Figure 5, confirming that cross-linking reaction across the interface cannot be a viable mechanism.

We have suggested that entanglement of *tethered* chains may be an important mechanism in adhesion promotion. The question is what is the contribution of this mechanism to adhesion hysteresis. In this case, chains are connected

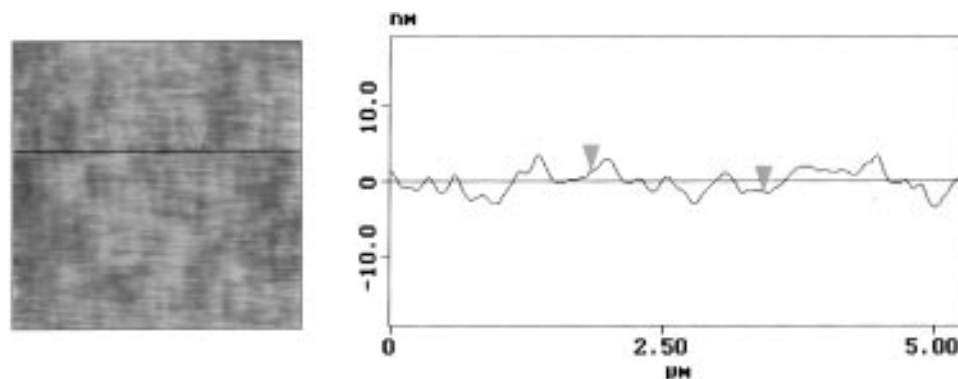


Figure 6. AFM image (contact mode) of an as prepared $r = 1.7$ hemisphere.

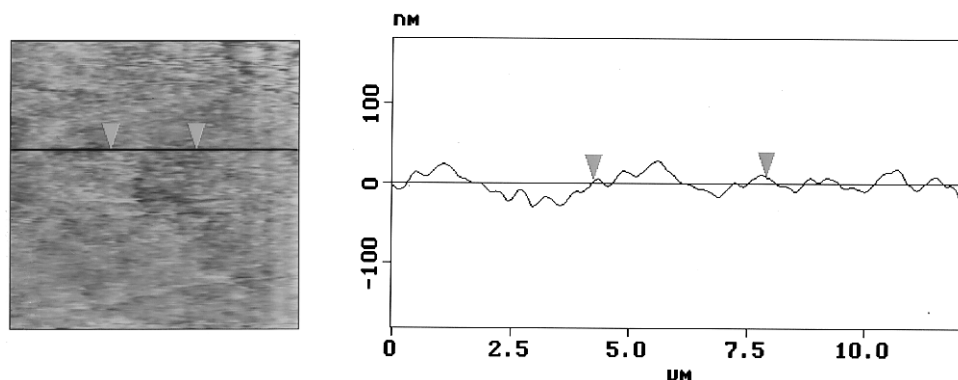


Figure 7. AFM image (contact mode) of extracted (24 h, Soxhlet, toluene) $r = 1.7$ hemisphere.

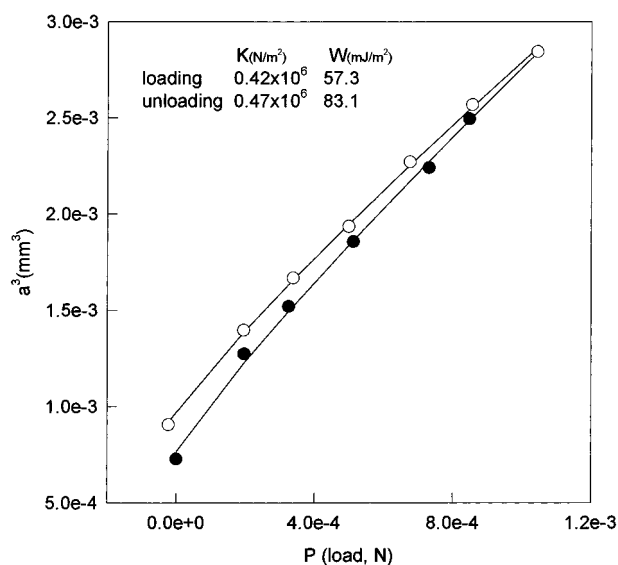


Figure 8. Loading (closed symbols) and unloading (open symbols) curves for as prepared and extracted $r = 1.7$ PDMS hemispheres (upper hemisphere extracted; lower hemisphere as prepared).

in one end to the cross-linked network and cannot transfer from one side of the interface to the other without breaking chemical bonds, and therefore their entanglement may contribute to adhesion hysteresis. Indeed, the observed trends in adhesion and adhesion hysteresis are the expected ones, since the number of tethered chains increases with decreasing r .

To further examine the difference between extracted and unextracted hemispheres, experiments were carried out where the upper hemisphere was extracted and the lower unextracted. Figure 8 presents typical results for $r = 1.7$ hemispheres. Notice that W_U (83.1 mJ m⁻²) is about average between 49.1 mJ m⁻² (W_U for the unex-

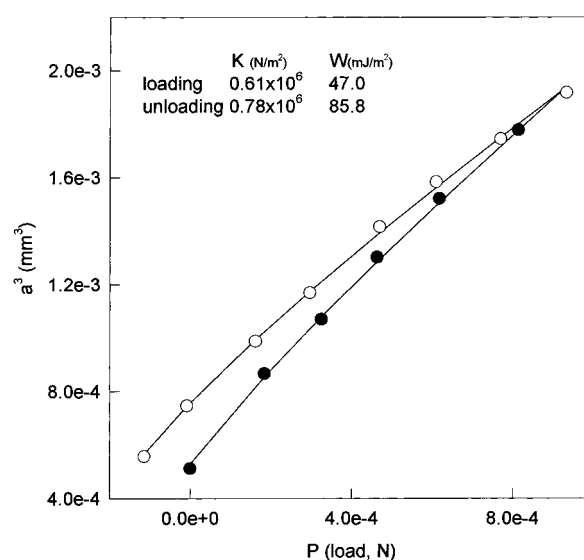


Figure 9. Loading (closed symbols) and unloading (open symbols) curves for different ratios of extracted (24 h, Soxhlet, toluene) PDMS hemispheres (upper hemisphere $r = 1.7$; lower hemisphere $r = 2.7$).

tracted hemisphere) and 119.4 mJ m⁻² (W_U for the extracted hemisphere). We shall come back to this result after discussing the issue of extracted zone.

The interdigitation of tethered chains with cross-linked PDMS network at the interface should scale with N , where N is the total number of tethered chains at the interface. To examine this postulate, we carried out experiments between extracted $r = 1.7$ and 2.7 hemispheres. Figure 9 presents the results. One can argue that if only chain entanglement was the mechanism, one could expect, again, that the surface with the smaller number of tethered chains ($r = 2.7$) will determine the resulting hysteresis. This is not the case, and the value of W_U , 85.8 mJ m⁻²,

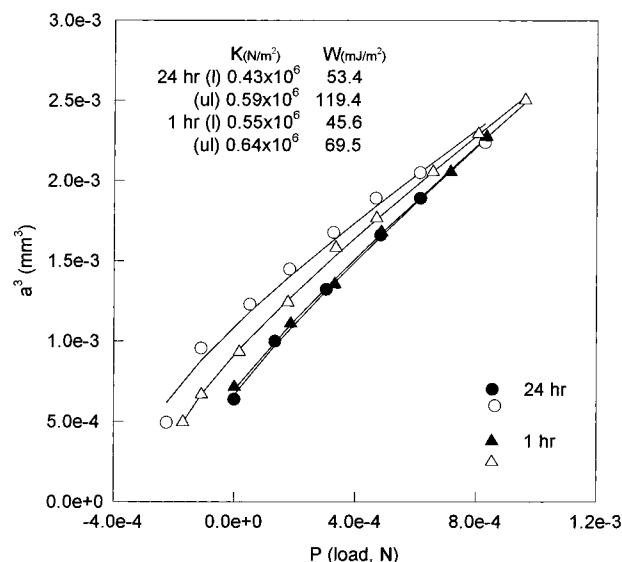


Figure 10. Loading (closed symbols) and unloading (open symbols) curves for differently extracted $r=1.7$ PDMS hemispheres. The circles are for 24 h toluene Soxhlet extraction, and the triangles are for 1 h toluene extraction

is an average between the values of W_U for the self-adhesion experiments of extracted hemispheres (119.4 and 57.5 mJ m^{-2} , for $r = 1.7$ and 2.7, respectively). This suggests that interdigitation of tethered chains and cross-linked network at the interface must be an important mechanism.

By now we have presented experimental evidence to support an adhesion hysteresis mechanism where tethered chains at the interface entangle and interdigitate with the cross-linked network. Since the extracted hemispheres were heated to 60 °C and kept in vacuum for 3 days, the question of temperature effects should be addressed. Therefore, we have carried out extraction experiments, where hemispheres were consequently kept under vacuum at room temperature (25 °C) for three days. Self-adhesion experiments of these extracted hemispheres showed a significantly smaller hysteresis, suggesting that the number of tethered chains at the interface is smaller. This is not surprising because the migration of tethered chains that are trapped in the cross-linked network to the surface is a slow process, which should be strongly temperature dependent.

Free volume cannot exist in cross-linked networks of liquidlike chains, and after extraction of the sol fraction the network reorganizes, which results in extracted zones. We propose that tethered chains and cross-linked networks across the interface is driven partially by the release of stress energy in the penetration zone. To further investigate this issue we carried out an experiment in which $r = 1.7$ PDMS hemispheres were treated briefly with toluene.

We cleaned the surface of $r = 1.7$ hemispheres with toluene for 1 h, at room temperature, to remove the sol fraction on the surface and to eliminate the possibility of significant extracted zone effects. The hemispheres were kept in vacuum at 60 °C for 24 h. After this procedure, the same self-adhesion experiment was performed. Interestingly, the unloading curve lies between that of the corresponding curve in the extracted system and the loading curve (Figure 10), suggesting a smaller number of tethered chains at the surface.

The data presented above are intriguing. Notice that we have prepared hemispheres by curing at 60 °C under vacuum. If more tethered chains migrate to the surface

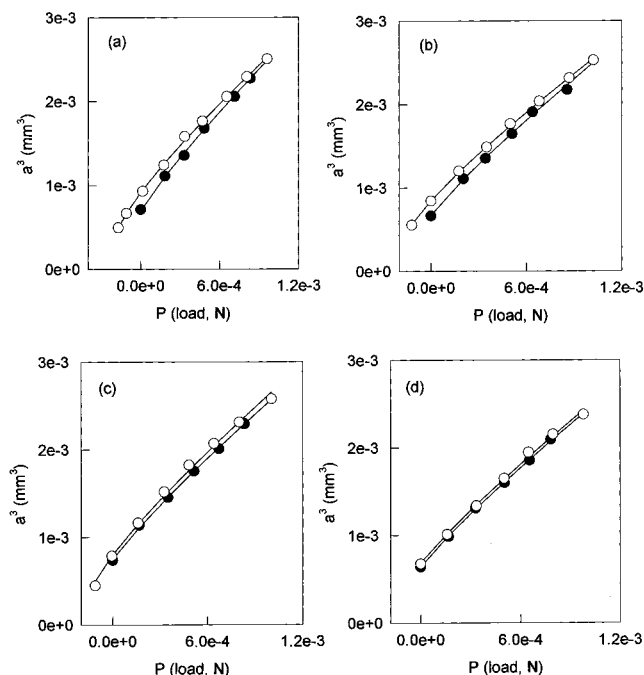


Figure 11. Time-dependent self-adhesion experiments of extracted (1 h toluene) $r = 1.7$ PDMS hemispheres: (a) 0 h; (b) 24 h; (c) 120 h; (d) 288 h.

because of higher temperature, why do we observe the hysteresis only after extraction? The answer we propose is that the migration of tethered chains to the surface is significantly enhanced by the formation of extracted zone.

We have no direct measurement of the thickness of the extracted region, but suggest that the data presented so far implies that viscoelastic processes cannot be the dominating mechanism (Although reptation and interdigitation of chains are critical in determining viscoelastic behavior of polymers in the bulk, polymers in confined environments such as thin films exhibit different behavior.) This is because the trends in both adhesion and adhesion hysteresis can be related directly to the number of tethered chains at the interface and to the extracted zone. We suggest that there is coupling between the extracted zone and the tethered chains in the interdigitation process. Thus, once two extracted hemisphere surfaces are brought into contact, the tethered chains from one hemisphere interdigitate the other utilizing the extracted zone and *vice versa*. This should explain the experiment described above, where one of the hemispheres was extracted and the other was not. The extracted zone was available only in one hemisphere, resulting in half of the W_U value observed for the self-adhesion of extracted $r = 1.7$ hemispheres.

Further support for the importance of the extracted zone in determining adhesion hysteresis comes from time-dependent studies of the briefly-washed hemispheres. We repeated self-adhesion experiments for the 1 h-washed hemispheres after 24, 120, and 288 h. Figure 11 shows that after 288 h there is no hysteresis, but while $K = 0.57 \times 10^6 \text{ N m}^{-2}$, significantly larger than K for unextracted hemispheres ($0.40 \times 10^6 \text{ N m}^{-2}$), W is smaller (43.7 vs. 49.1 mJ m^{-2}) and closer to the traditional value of 2γ . The smaller value of W suggest that the mechanism proposed above for adhesion promotion in unextracted hemispheres is not operational here, because all free chains were removed from the surface by the toluene washing process. The lack of adhesion hysteresis is due to the lack of extracted zone, and its time-dependent nature suggests that this results from the migration of free and tethered

chains into the extracted zone. These results provide further support to the suggestion that the coupling of tethered chains and the extracted zone contributes significantly to adhesion hysteresis.

That the value of K is larger indicates that the changes induced by extraction may not be completely reversible, at least in the time frame of this experiment. What comes out from the experiments described in this paper, as well as from other experiments carried out in our laboratory, is that K , which results from fitting of a and P data to the JKR equation, does not represent the bulk elastic constant, but an effective constant of the experiment,¹⁹ depending both on the bulk elastic constant and on the properties of the extracted zone. This extracted zone is not small, because deformations extend to large distances in cross-linked networks and are not confined to a thin layer near the contact area.²³ This explains why K increases significantly when surface interactions increase.

Conclusions

We presented results of adhesion studies of PDMS cross-linked hemispheres, before and after extraction, carried out using contact mechanics. Three types of PDMS networks were prepared with increasing cross-linker-to-PDMS ratio ($r = 1.7, 2.2, 2.7$). Adhesion hysteresis was observed only after the PDMS hemispheres were extracted. The size of hysteresis increased systematically with decreasing r (increasing percentage of extracted weight). Brief extraction yielded smaller hysteresis which disappeared after 12 days.

The results presented in this paper are another indication of the complexity of contact mechanics experiments

and especially of the PDMS cross-linked systems. Because of this complexity, it is hard to completely understand the different sources of hysteresis, the coupling among them, and their relative importance. We presented a number of possible mechanisms and, by using an elimination process, could conclude that H-bonding and cross-linking at the interface are not the controlling mechanisms. Entanglement of tethered chains and their interdigitation with the extracted cross-linked PDMS network at the interface are probably the dominating mechanisms.

We emphasize that the JKR theory used to analyze the results in the experiments presented here is imperfect. This is because (a) it is an *equilibrium* theory and thus incapable of accounting for adhesion hysteresis that originate from irreversible, dissipative effects and (b) it assumes an idealized linear elastic response (i.e., stress distribution at contact) under small perturbation from equilibrium of *homogeneous*, Newtonian, elastic bodies under load and with short-range attractive interactions at contact, as characterized by bulk elastic constants. The existence of extensive inhomogeneous extraction zones at the interface (which by their very nature may be out of equilibrium) is inconsistent with such assumptions.

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