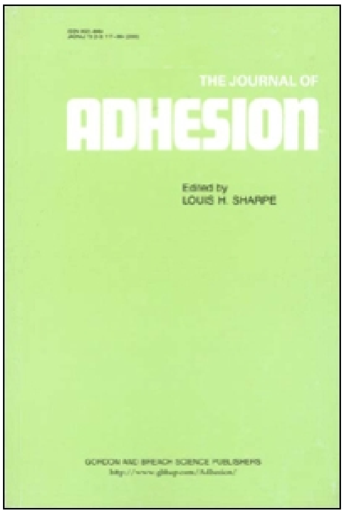

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SELF-ADHESION HYSTERESIS IN POLYDIMETHYLSILOXANE ELASTOMERS

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SELF-ADHESION HYSTERESIS IN POLYDIMETHYLSILOXANE ELASTOMERS

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Self-adhesion hysteresis has been investigated in crosslinked poly(dimethylsiloxane) (PDMS) lenses using the Johnson, Kendall, and Roberts technique. The experimental conditions involved relatively short contact times for which interchain penetration effects across the interface are minimal. Only lenses that had been extracted in toluene displayed self-adhesion hysteresis. The same lenses demonstrated no adhesion hysteresis when pressed against tethered polystyrene substrates, indicating that hysteresis was caused by surface interactions and not bulk viscoelastic effects. Extraction produces hysteresis by removing the free chains, which normally lubricate the interface, inhibiting the adhesion mechanism. Self-adhesion hysteresis was only observed for networks with a high molecular weight between crosslinks. More tightly crosslinked networks did not display self-adhesion hysteresis, even at extended contact times under load. By inhibiting the hydrosilylation reaction between residual vinyl and silane groups in the PDMS lenses, self-adhesion hysteresis was prevented, suggesting that the formation of chemical crosslinks across the interface caused the

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observed hysteresis. The molecular weight dependence of the hysteresis can be interpreted in terms of the Lake-Thomas model [1] for fracture in elastomers.

Keywords: JKR; Self-adhesion hysteresis; PDMS elastomers; Chemical crosslinks; Molecular weight effects

INTRODUCTION

The JKR experiment has become a widely used method for the direct determination of the surface free energy and the work of adhesion between solids. Based on a continuum contact mechanics model developed by Johnson, Kendall, and Roberts [2], the JKR method has been used to investigate several elastomeric systems using the type of surface forces apparatus first introduced by Chaudhury [3–5]. The JKR theory is an extension of Hertzian contact theory and accounts for the adhesive forces between two soft elastomeric spheres, which are responsible for producing a contact area larger than that predicted by the Hertz analysis [6].

Hemispherical elastomers manufactured from functional polydimethylsiloxanes (PDMS) have been among the most studied systems because of the ease of synthesis and ability to vary the elastomer characteristics while maintaining excellent mechanical properties. Several authors, however, have reported the occurrence of self-adhesion hysteresis during experiments, which is not predicted by the JKR theory [7–12]. This hysteresis typically manifests itself as a difference between the loading and unloading curves, whereas JKR theory predicts that the unloading and loading curves should superimpose. In most cases hysteresis is positive, implying that more energy is required to separate the two surfaces than to bring them into contact and that it may be the result of either bulk viscoelasticity or the buildup of adhesion during the period of contact.

If bulk viscoelastic effects can be discounted, any observed hysteresis must be caused by the development of adhesion during contact. While the precise origin of adhesion hysteresis is not clear, it has been attributed to irreversible chemical reactions between surface molecular groups [9], specific interactions between functional groups [7, 10], the formation of entanglements across the interface [8, 13], and the action of capillary forces due to ambient humidity [12]. In addition, hysteresis has been observed to increase with increasing molecular weight between crosslinks [11].

Silberzan *et al.* [7] observed hysteresis on the unloading of two PDMS hemispheres that had been extracted in chloroform and dried under vacuum. It was postulated that excess unreacted Si-H bonds in the elastomer were oxidized at room temperature to Si-OH and promoted hydrogen bonding between the surfaces. Perutz *et al.* [9] observed adhesion hysteresis between PDMS networks that had been deliberately hydrolyzed by exposure to 0.1 M HCl aqueous solutions. Hysteresis was found to increase with exposure time. When the silanol end groups were replaced by reaction with hexamethyldisilazane (which replaces the endgroup with a trimethylsilyl group) the hysteresis was reduced by up to 80%. Hysteresis was attributed to a surface reconstruction reaction between silanol groups.

In contrast, Emerson *et al.* [13] demonstrated that the presence of SiH groups was not required for hysteresis to occur between toluene-extracted hemispheres. Unreacted SiH groups were removed by reaction with ethylene gas, but hysteresis was still observed. In this case it was argued that hysteresis resulted from the entanglement of chains across the interface. Choi *et al.* [8] also observed adhesion hysteresis only between PDMS elastomers after extraction in toluene. Entanglements were also given as the reason for the observed hysteresis. It was shown that the amount of extracted material was a function of the crosslinker to PDMS ratio and was also correlated with the amount of hysteresis.

Kim *et al.* [10] observed the hysteresis between PDMS hemispheres and various self-assembled monolayers on silica surfaces. Hysteresis was observed for PDMS hemispheres in contact with bare silicon wafers. Less hysteresis was observed for a surface consisting of carboxylic acid groups, an even smaller amount of hysteresis was observed for a surface functionalized with biphenyl groups, and virtually no hysteresis was observed for a surface modified with a perfluorocarbon. These differences were explained in terms of specific interactions at the surface with the high degree of hysteresis observed against bare silica substrates resulting from hydrogen bonding. Choi *et al.* [14] examined the effect of increased acidity on the adhesion between PDMS hemispheres and various OH functionalized self-assembled monolayers on gold substrates. Adhesion increased with increasing acidity and density of OH groups, though the relationship was highly nonlinear.

Pickering *et al.* [12] measured the adhesion of PDMS against both glass and mica in air and dry nitrogen. He observed that adhesion hysteresis depended strongly on the initial contact time, ambient humidity, and hydrophilicity of the surface and deduced that capillary forces increased the observed adhesion.

Leger [15] extensively studied the effects of chain interpenetration across the interface on the adhesion between crosslinked PDMS lenses and PDMS brushes tethered to flat substrates. Leger's results illustrate the effects of molecular weight between crosslinks, brush length, and contact time on adhesion enhancement by interfacial chain interpenetration. Under conditions that meticulously avoided the complications of interfacial reactions, they found that contact times as long as a month or more were required to reach equilibrium chain penetration across the interface. Contact times of this magnitude are considerably longer than those employed in most adhesion hysteresis studies, suggesting that chain interpenetration across the interface is not an important mechanism to account for the adhesion hysteresis observed by most researchers.

In the absence of bulk viscoelastic and chain interpenetration effects, an understanding of the causes of adhesion hysteresis can provide valuable information regarding the molecular origins of the adhesion mechanisms occurring at the polymer-polymer interface. Further, knowledge of the mechanisms causing hysteresis is helpful when making practical decisions such as whether or not to extract the sol fraction from the elastomer, which are important experimental issues.

The goal of the research presented in this article is to gain insight into the origins of adhesion hysteresis by studying the self-adhesion of PDMS elastomeric lenses. A custom-built JKR surface forces apparatus has been used to probe self-adhesion hysteresis in these lenses by altering parameters including the molecular weight between crosslinks, the contact time, the maximum load, and allowing for the possibility of interfacial chemical reactions. The effects of sol extraction have also been investigated.

BACKGROUND

The JKR theory describes the equilibrium relationship between the radius of contact, a, and the applied load, P, for an elastic hemispherical lens in contact with either another lens or a flat rigid substrate. An energy balance approach was originally used to derive the JKR equation [2]:

$$a^3 = \frac{R}{K}\left(P + 3W\pi R + \sqrt{(6W\pi RP + (3W\pi R)^2)}\right), \tag{1}$$

where K is the average modulus for the system, W is the thermodynamic work of adhesion, and R is the radius of curvature. Equation

(1) can be compared with the original Hertz equation, which neglects the effects of adhesive forces:

$$a^3 = \frac{RP}{K}. \tag{2}$$

For a lens-on-lens experiment, R is given by

$$R = \frac{R_1 R_2}{(R_1 + R_2)}, \tag{3}$$

where R_1 and R_2 are the individual radii of curvature for both lenses. The average modulus of the system, K, is given by

$$K = \frac{4}{3\pi(k_1 + k_2)}, \tag{4}$$

where k_1 and k_2 are the elastic constants of each hemisphere and are related to the Young's modulus by

$$K_i = \frac{1 - v_i^2}{\pi E_i}, \tag{5}$$

where v is Poisson's ratio. For a hemispherical lens pressed against a rigid substrate all the deformation is confined within the lens and the modulus is given by

$$K = \frac{4}{3\pi(k_1)}. \tag{6}$$

In this case, R is simply the radius of curvature of the single sphere.

The JKR experiment typically consists of pressing a soft hemispherical elastomeric lens into either a flat substrate or another lens. The nature of the experiment requires that the lens is transparent and must also be mounted on a rigid optically clear support. R is independently determined from a side-view image of the lenses, so by monitoring the contact radius as a function of applied load, a two-parameter fit of the data to the JKR equation can be used to obtain K and W.

The JKR theory assumes that the deformations involved are small compared with the dimensions of the samples involved so that the bodies can be treated as semi-infinite elastic media. At larger strains nonlinear elasticity must be taken into account [16]. Secondly, the theory assumes that equilibrium is reached at each step for both loading and unloading. Care must be taken to ensure that kinetic effects do not become an issue, especially when dealing with situations involving the development of significant adhesion during contact. Derjaguin, Muller, and Toporov (DMT) [17] have presented an alternative analysis for the contact between two spheres in which the attractive forces lay outside the area of contact (in JKR theory they are confined within the area of contact). Maugis [18] later demonstrated that both JKR and DMT theory are limiting cases of a more general situation and that DMT theory applies to hard bodies with high elastic moduli, while JKR theory is appropriate for softer solids such as polymeric elastomers.

EXPERIMENTAL PROCEDURE

PDMS Lens Synthesis

PDMS elastomeric lenses were made using an addition cure reaction. Crosslinking was accomplished using the hydrosilylation reaction between a silane group and a vinyl group in the presence of platinum catalyst. Divinyl-terminated PDMS (6000; 28,000 g/mol) were used as the starting materials for the PDMS lenses. A poly(methylhydrosiloxane-dimethylsiloxane) copolymer (1950 g/mol, 25–30% MeHiO) was used as a crosslinker. A platinum-cyclovinylmethyl complex (3–3.5% Pt, low-temperature catalyst) was used as catalyst. 1-dodecanethiol was used to poison the platinum catalyst after the crosslinking reaction. All materials were purchased from Gelest, Inc. (Morrisville, PA, USA) and used as received.

To manufacture lenses, vinyl-terminated PDMS and the crosslinker were weighed out into a plastic beaker and thoroughly mixed using a glass-stirring rod. 10 g batches were made at one time. A 100 μl drop of platinum catalyst solution was then added to the mixture, which was again thoroughly mixed for at least 1 min. Small drops of between 0.5 and 2 mm in diameter were placed onto glass slides pretreated with (tridecafluoro-1,1,2,2-tetrahydrooctyl)1-trichlorosilane using an oiler (medium, DL-32). This low-energy surface was necessary in order for sufficiently hemispherical droplets to be formed. The lenses were transferred to a vacuum oven and heated to 65°C for at least 2 h. This time has been shown to be sufficient to achieve full cure for this system by Hu [19].

After curing, the lenses were allowed to cool to room temperature before removal from the vacuum oven and were then divided into separate batches according to further treatment. One batch was set aside immediately for use without further treatment as unextracted lenses. Other lenses had the sol fraction (unreacted precursor) extracted and were used in this form. Finally, some lenses were extracted and also treated with a thiol solution to poison the residual platinum catalyst and prevent any further reactions. Lenses to be extracted were immersed in toluene in a Petri dish for 1 h after which the solvent was replaced with fresh toluene and the lenses immersed for another hour. The solvent was then discarded and the lenses immersed in a 50/50 mixture of toluene and methanol for 1 h. The methanol was added in order to slow down the next step, which was drying in air. This intermediate step was necessary in order to avoid drying too quickly, which caused cracking of the lenses if drying was carried out directly from toluene. For lenses to be poisoned, 1-dodecanethiol was added to the first toluene wash (1 wt%). The sol fraction of the lenses was estimated by measuring the weight of the lenses before curing and after extraction. Dried lenses were stored in sealed plastic Petri dishes ready for use in the JKR experiments.

PS Substrate Preparation

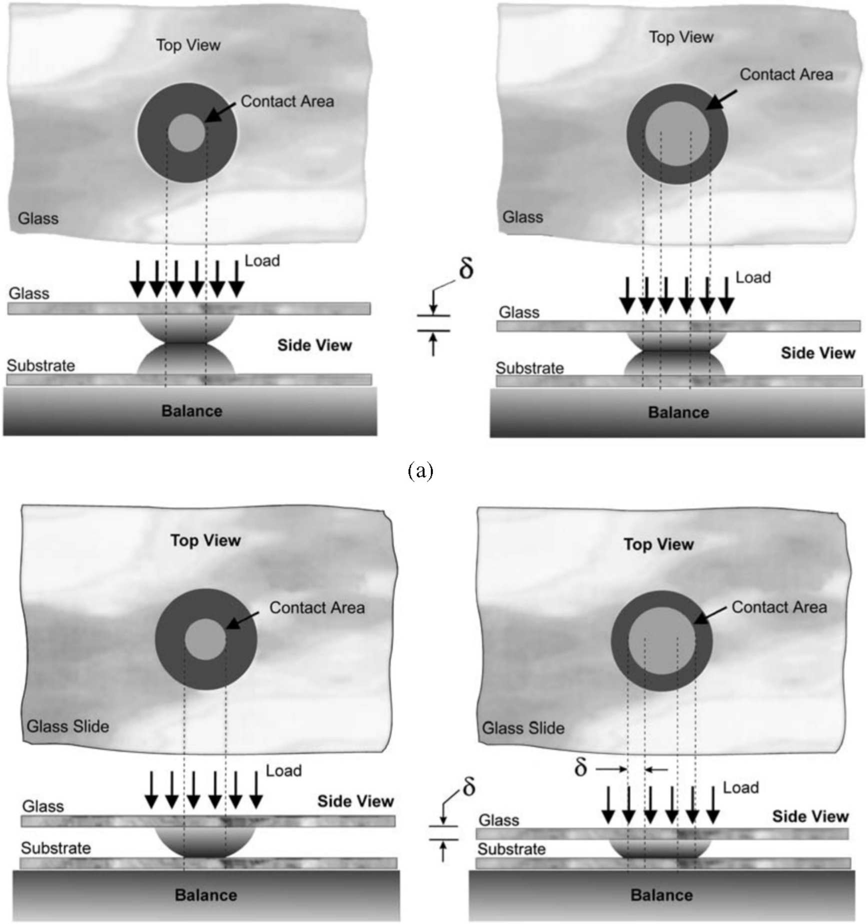
A trimethoxysilane terminated polystyrene (PS-Si(OCH_3)$_3$) ($M_n =$ 209,000 g/mol), synthesized anionically, was purchased from Scientific Polymer Products, Inc. (Ontario, NY, USA) and silicon wafers (100) were purchased from Wafer World, Inc. (West Palm Beach, FL, USA). A Headway Research, Inc. (Garland, TX, USA) photo-resist spinner was used to spin coat the PS-Si(OCH_3)$_3$ from a toluene solution onto clean silicon wafers, which had previously been cut into 2.5 cm × 1.25 cm pieces. After film deposition, the wafers were heated under vacuum to 165°C for 1 h to promote anchoring of the PS to the silicon, *via* coupling of the trimethoxy endgroups to the silicon surface. The wafer with the grafted PS film was then washed several times in toluene until an optically clear surface was obtained. A PS concentration of 5 wt% in toluene at a spin speed of 1000 rpm produced an average PS layer thickness, after washing, of 29 nm.

JKR Measurements

The contact mechanics apparatus used for the JKR measurements was designed and built at Sandia National Laboratories (Albuquerque, New Mexico, USA) and has been fully described elsewhere [13]. The system consists of an environmental chamber that allows the temperature to be controlled and that eliminates air currents that could interfere with measurements. The elastomer lenses and substrates are entirely enclosed in the chamber during experiments. An electronic force balance forms the bottom surface of the chamber and measures the load *via* a connection to the associated PC system. A motion controller and series positioning stage accomplish motion control of the loading arm. The contact area is captured as an image *via* a lens, CCD camera, and software on the PC. The system automates the loading and unloading process, and measurements are performed under constant displacement conditions.

Two kinds of JKR experiments were performed using this apparatus: either between an elastomer lens and a planar substrate or between two elastomer lenses (self-adhesion experiments). The two situations are depicted in Figure 1. In the first case, a suspended hemispherical lens was brought into contact with a planar substrate below it. A vacuum applied through a small hole bored vertically through the load arm enabled a glass cover slip to be suspended from underneath the load arm, with about 3 mm extending out over the substrate. The lens was then attached at its base to the underside of the cover slip, so that it was suspended directly over the substrate. This enabled an unobscured view of the contact area to be obtained by the lens and CCD camera. The substrate was secured to the bottom of the environmental chamber by a small piece of double-sided tape on the underside of the silicon wafer fragment. For the lens-on-lens experiment, the setup was similar except that the second lens was placed upright on a clean silicon wafer secured to the bottom of the environmental chamber.

The force balance was tared before any experiments were started. The suspended lens was lowered from the "home" position until just above the substrate or other lens. The image and lighting were adjusted to obtain a good image. The suspended lens was then translated to the desired position ready for the start of the experiment. For lens-on-lens experiments, a larger lens was used as the bottom lens so that accurate centering of the smaller upper suspended lens could be achieved. The computer, using incremental changes in displacement, controlled loading and unloading automatically. For lens-on-substrate experiments 3 μm steps were used, and for lens-on-lens experiments 6 μm steps were used. The time between each step was programmed to be 5 min in order to allow equilibrium to be reached. At each step, the load, displacement, and a time-tagged image were automatically recorded. Loading continued until the maximum-programmed load, typically 0.5 g, had been reached. At this point unloading would commence using the same step size and time interval as for loading. Data collection automatically stopped when the measured load reached zero. Measurements in the pull-off regime were completed manually until the upper lens completely detached from the lower lens or substrate.

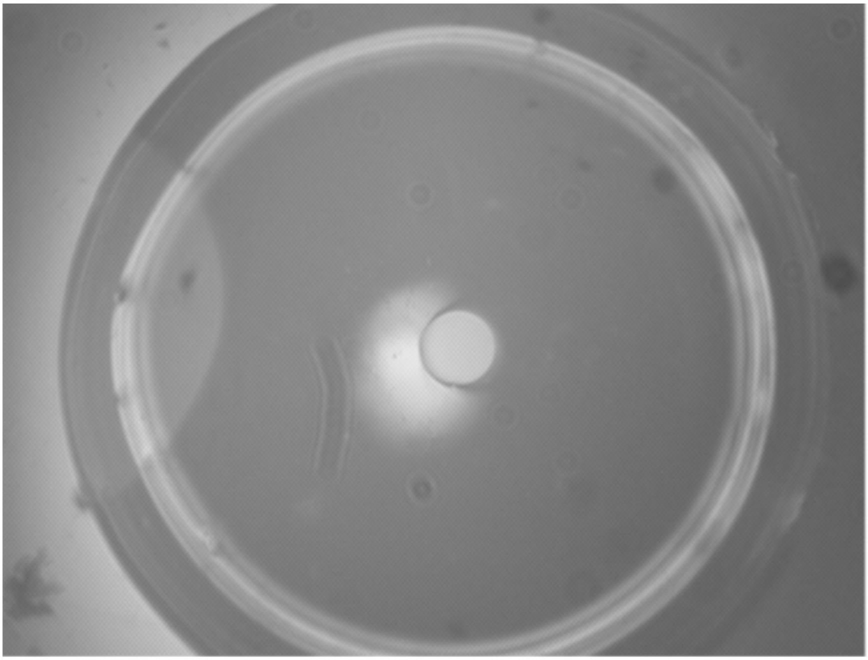


(a)

(b)

FIGURE 1 The two possible arrangements for the JKR modulus and hysteresis experiment: (a) hemisphere-on-hemisphere and (b) hemisphere on a rigid substrate. *Emerson, J. A., Miller, G. V., et al. (1999). "Self-Adhesion Hysteresis of a Model Siloxane Elastomer." Proc. ACS Div. Poly. Mat. Sci. Eng. Vol. 81: 385.*

Image analysis was performed after each experiment to determine the contact radius using Media Cybernetics (Siber Spring, MD, USA) ImagePro Plus (v. 3.0.00.00). An example of the observed change in the contact area with load is shown in Figure 2. Images of optical



(a)

FIGURE 2 The change in contact area with load for an extracted PDMS lens ($M_c = 28{,}000\,\mathrm{g/mol}$) in contact with a tethered PS substrate at (a) zero load and (b) a load of 0.475 g (magnification is approximately 40×). (*Continued.*)

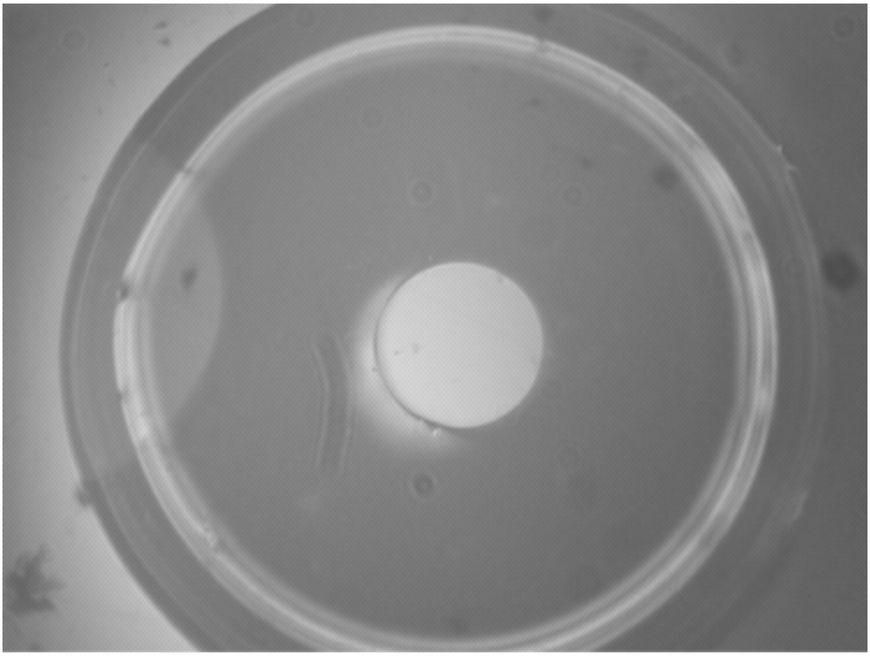
calibration grids were taken in the same position as the lenses to provide a reference for the image analysis software.

After every experiment a side-view photograph of each lens was taken, which allowed the calculation of the radius of curvature, R, from the geometry:

$$R = \frac{d^2}{8h} + \frac{h}{2}, \tag{7}$$

where d and h are the lens base width and height, respectively. An example side view image is shown in Figure 3.

K and W were then determined by a two-parameter fit of the loading curve data to Equation (1). Hysteresis was determined from any difference between the loading and unloading curves. All experiments were carried out at room temperature and approximately 25% relative humidity.



(b)

FIGURE 2 (Continued.)

RESULTS AND DISCUSSION

Four different kinds of PDMS networks, with differing molecular weight between crosslinks, were synthesized. The modulus, K, and thus the average molecular weight between crosslinks, M_c, was varied by changing the molecular weight of the vinyl-terminated PDMS precursor and by altering the quantity of crosslinker. Cure time was not used as a method for controlling the network properties to avoid the possibility of an incomplete reaction continuing at room temperature and resulting in lenses whose properties would change with time. Therefore, all lenses were fully cured as described in the previous section.

The high molecular weight vinyl-terminated PDMS precursor (28,000 g/mol) was used to form looser networks, while a lower molecular weight (6000 g/mol) was used for forming tighter networks. The same crosslinker, a poly(methylhydrosiloxne-dimethylsiloxane) copolymer (2,000 g/mol), with a silane functionality of approximately 8, was used in all cases. Two different ratios of crosslinker to end-functional

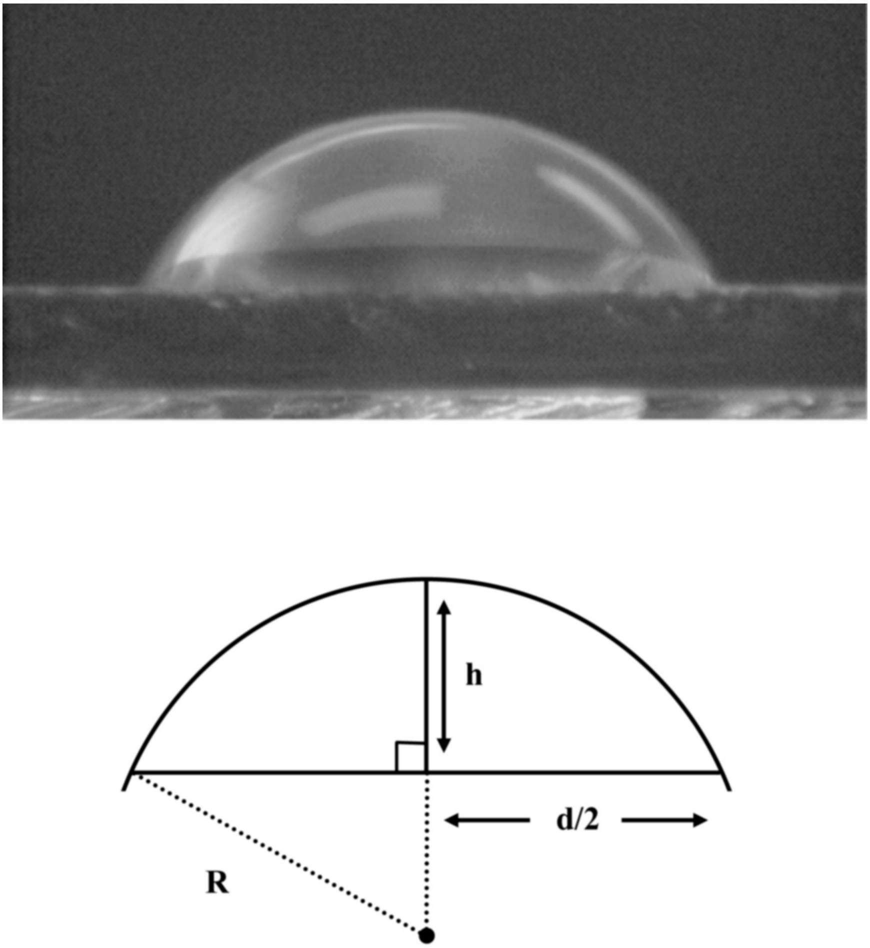


FIGURE 3 Geometry of a lens obtained from an image of its side view (magnification is approximately 40×). The radius of curvature is calculated from Equation 7.

PDMS were used (based on R, the ratio of the number of moles of silane groups to the number of moles of vinyl groups, not to be confused with the radius of curvature in the JKR equation). In one case the crosslinker was in excess of stoichiometry ($R = 1.3$), and in the other less crosslinker was present than vinyl-terminated PDMS ($R = 0.7$).

A typical JKR result for an unextracted PDMS lens *versus* a tethered PS substrate is shown in Figure 4. The tethered PS brush on silicon

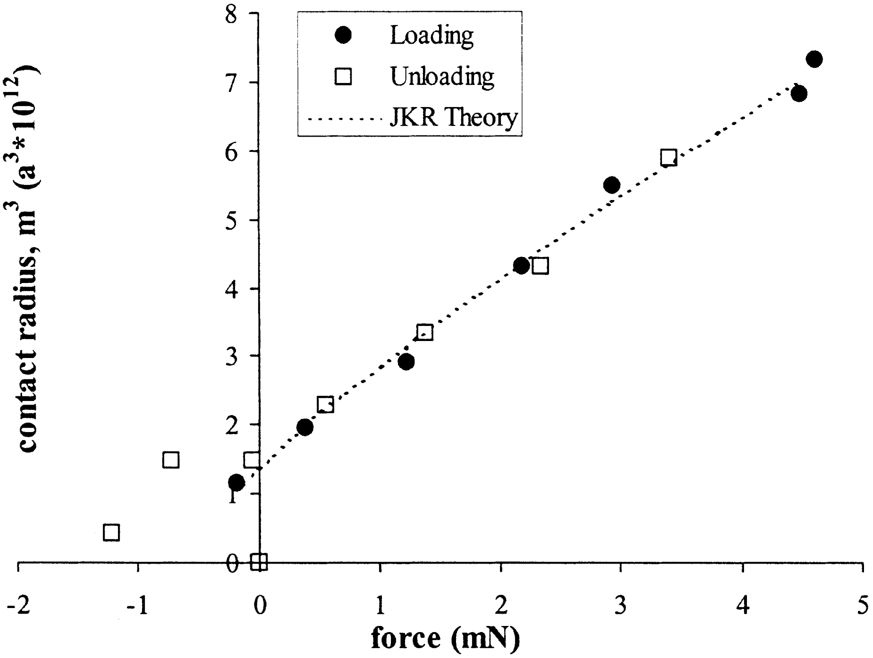


FIGURE 4 JKR loading and unloading curves for an unextracted 6KR13 PDMS lens *versus* a tethered PS substrate ($K = 1.723 \pm 0.157$ MPa; $M_c = 7400$ g/mol).

wafer provided a "neutral" surface for measurements, *i.e.*, a surface that was not capable of any kind of interactions apart from van der Waals interactions with the PDMS lens. No hysteresis is evident and this was true for all unextracted lenses in contact with PS substrates. The characteristics of the unextracted lenses are given in Table 1. For all lenses, the two parameters K and W were determined by performing a nonlinear least-squares fit of the loading curve data to the JKR equation. M_c was estimated from rubber elasticity theory:

$$M_c = \frac{\rho RT}{G}. \tag{8}$$

Assuming a Poisson's ratio of 0.5, a lens in contact with a flat rigid substrate G is related to the effective modulus, K, by

TABLE 1 Mechanical Properties of the Postcure Unextracted PDMS Lenses

	PDMS (g/mol)	R (SiH/vinyl)	wt% crosslinker*	K (MPa)	M_c (g/mol)	sol wt%
6KR07	6000	0.7	5.58	0.419 ± 0.023	30,400	12.9
6KR13	6000	1.3	9.89	1.723 ± 0.157	7400	2.9
28KR07	28,000	0.7	1.25	0.027 ± 0.004	472,300	21.0
28KR13	28,000	1.3	2.30	0.569 ± 0.028	22,400	4.0

*Molecular weight of crosslinker was 2,000 g/mol (functionality = 8).

$$G = \frac{3K}{16}. \tag{9}$$

For two hemispherical lenses in contact with each other, the shear modulus is given by

$$G = \frac{3K}{8}. \tag{10}$$

It is clear from the data in Table 1 that reducing the amount of crosslinker produces looser networks with a correspondingly higher M_c. When the crosslinker is in excess, M_c is primarily determined by the molecular weight of the vinyl-terminated PDMS precursor, and the amount of extracted material is at a minimum. For lenses created with a less than stoichiometric amount of crosslinker, the large amount of extracted material is indicative of a high proportion of unreacted free chains left over after cure. The uncertainties in K and W for individual lenses were taken as twice the standard error of the fitted parameters (95% confidence intervals). Where several measurements on one kind of lens were taken, the reported values for K and W are weighted averages.

To examine the effect of maximum loading, some unextracted lenses were measured with a maximum load of up to 10 g. These measurements, however, invariably produced unrealistic estimates of W. Further investigation showed that the JKR equation is insensitive to changes in W at higher loads, and the value of W can change by a large amount without much impact on K. In fact, at high loads the JKR equation can be approximated by the original Hertz expression (Equation (2)). Another possible contributing factor to unrealistic W values at high loads is that the assumption that deformations are small relative to the sample dimensions is no longer valid. For these reasons, the maximum load in all subsequent experiments was restricted to 0.5 g.

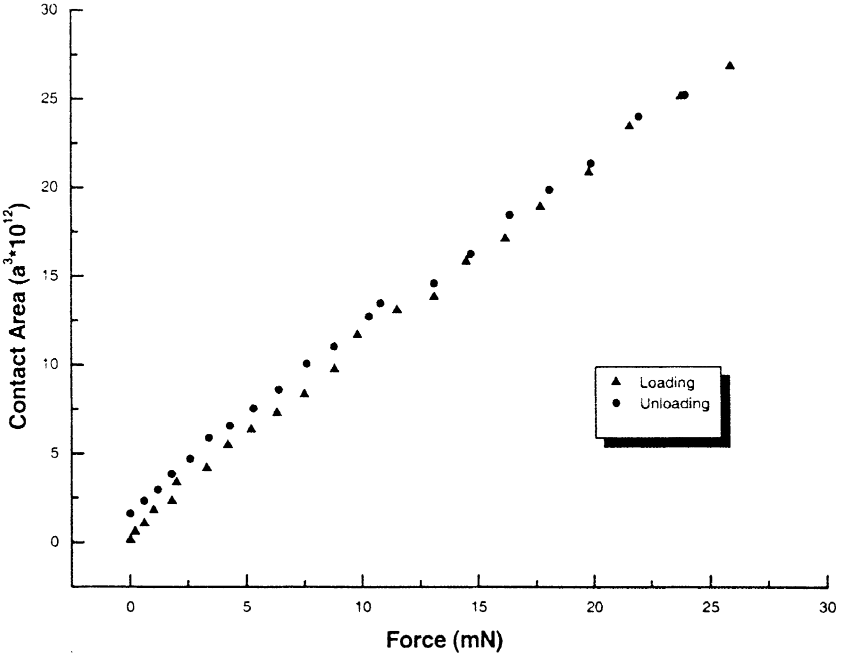
A theoretical value for W can be calculated from

$$W = \gamma_1 + \gamma_2 - \gamma_{12}, \tag{11}$$

where W is the thermodynamic work of adhesion for two surfaces 1 and 2 in intimate contact; γ_1 and γ_1 are the surface energies of 1 and 2, respectively; and γ_{12} is the interfacial tension between 1 and 2. Literature values for the surface energies of PS and PDMS are 40.7 [20] and 21.7 [3] mJ/m^2, respectively. From the work of Hu [19], a value of 5 mJ/m^2 was found for the interfacial tension between PS and PDMS, yielding an overall value of 57.4 mJ/m^2 for the work of adhesion between PS and PDMS. Taking a weighted average of all the values obtained for extracted 6KR13 lenses yielded a value for W of $57.1 \pm$ (5.7) mJ/m^2, which agrees well with the value predicted by theory.

Whether or not to extract lenses is an important question that must be addressed. No crosslinking reaction goes to completion, especially if one reactant is in excess. This inevitably leads to a residual sol fraction in the gel. By choosing the correct conditions this can be minimized but not completely eliminated, as can be seen from Table 1. It is preferable to remove this sol fraction by extracting postcure crosslinked lenses in a suitable solvent because the free chains in the gel can act as diluents, weakening the elastomer. Furthermore, the unreacted precursors can migrate out of the gel and contaminate the interface, interfering with the adhesion measurements. However, various authors have reported the appearance of hysteresis in extracted lenses where there was none before extraction, as shown in Figure 5. Therefore, the effects of extraction on the elastomer properties must be understood in order to make a reasonable assessment of the advantages and disadvantages of extraction.

The JKR results for extracted lenses *versus* the PS substrates are shown in Figure 6. Again, there is no evidence of any hysteresis for any extracted lens in contact with PS. The effects of extraction on the mechanical properties of the lenses can be seen in Table 2. The modulus for the 6KR07 lenses increases after extraction, while the modulus for the 6KR13 lenses stays virtually constant. In contrast, the modulus for the 28KR13 lenses decreases significantly. The most plausible explanation for this is that the vinyl-terminated PDMS precursor used for the first two kinds of lenses is below the entanglement molecular weight, M_e, for PDMS (8,100 g/mol) [21]. The unreacted chains act as diluents, weakening the overall mechanical properties of the lenses. The modulus increases when these free chains are removed by extraction. In the case of the 28KR13 lenses, the precursor

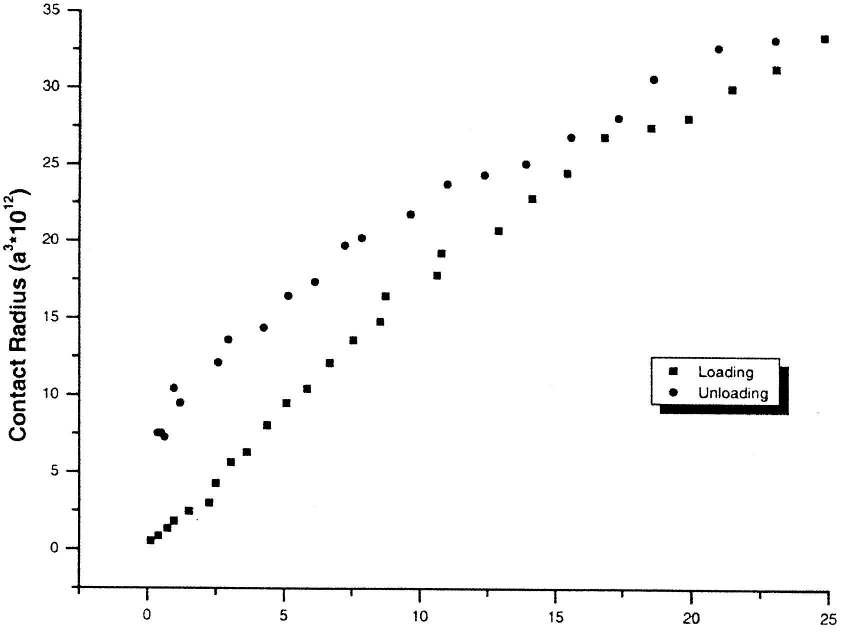


(a)

FIGURE 5 JKR self-adhesion results for two hemispheres in contact with each other (a) before extraction and (b) after extraction. *Emerson, J. A., Miller, G. V., et al. (1999). "Self-Adhesion Hysteresis of a Model Siloxane Elastomer." Proc. ACS Div. Poly. Mat. Sci. Eng. Vol. 81:385.* (*Continued.*)

is above the entanglement molecular weight, and therefore the free chains can contribute to the mechanical strength (because M_c is determined by both chemical and physical crosslinks). When these chains are removed by extraction there is a resultant decrease in the modulus due to the loss of the mechanical strength that the chains had imparted. The 28KR07 lens was so weak after the extraction process that it was easily and irreversibly deformed. For this reason, these lenses were not used further in adhesion studies.

Figure 7 shows the JKR results for the lens *versus* lens (self-adhesion) experiments using the extracted PDMS lenses. Here there is strong evidence of self-adhesion hysteresis for some of the lenses. Because no hysteresis was observed for the same lenses in contact with the neutral PS substrate, it is clear the observed hysteresis is not a bulk phenomenon but arises from the buildup of some kind of adhesive force at or near the surfaces of the two lenses.



(b)

FIGURE 5 (Continued.)

Further, the appearance of hysteresis depends on the molecular weight between crosslinks. The 6KR07 and 28KR13 lenses with $M_c > M_e$, both display self-adhesion hysteresis. On the other hand, the much tighter 6KR13 network, with $M_c < M_e$, does not display any hysteresis. The questions arise as to what effects the extraction process has on the lenses that allow the adhesion hysteresis mechanism to develop, and why this mechanism depends on the molecular weight between crosslinks. Examination of the lenses under a microscope after extraction did not reveal any obvious differences with lenses before extraction. The unextracted sol fraction clearly plays an important role in preventing the hysteresis mechanism from occurring.

In order to probe further into how kinetics might influence the development of adhesion hysteresis, an additional experiment was performed in which two 6KR13 lenses were kept at maximum load for 24 h between loading and unloading to see if any adhesion hysteresis developed. The JKR curve for this experiment is shown in

(a)

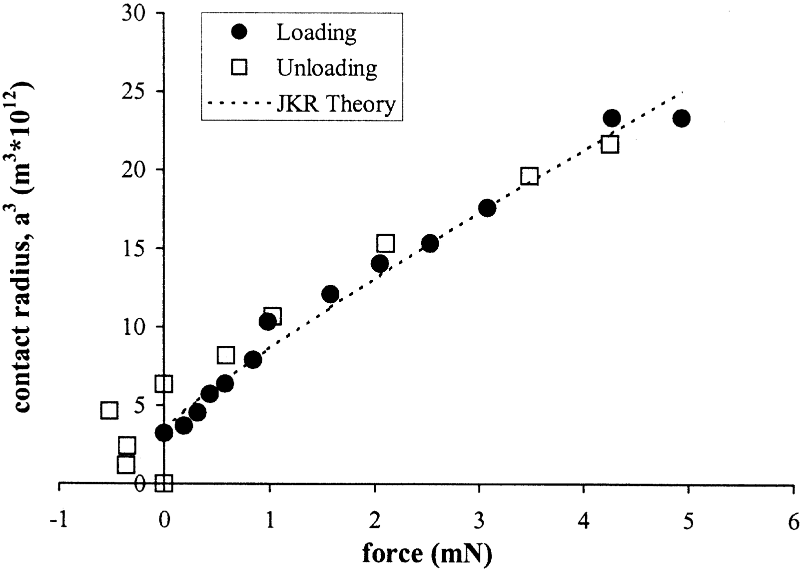


FIGURE 6 JKR loading and unloading for extracted PDMS lenses *versus* tethered PS: (a) 6KR07 ($K = 0.538 \pm 0.016$ MPa; $M_c = 23{,}800$ g/mol), (b) 6KR13 lens ($K = 1.704 \pm 0.065$ MPa; $M_c = 7{,}500$ g/mol), and (c) 28KR13 ($K = 0.496 \pm 0.025$ MPa, $M_c = 25{,}800$ g/mol). (*Continued.*)

Figure 8. From the figure it is clear that very little, if any, adhesion has developed, suggesting that the contact time does not explain the differences observed between the tighter and looser networks (though how long it would take to reach true equilibrium is unknown).

The two most likely mechanisms responsible for the observed adhesion hysteresis include an interfacial chemical reaction between unreacted vinyl and silane functional groups on either side of the interface. An interfacial crosslinking reaction of this nature would form connector chains across the interface that enhance the adhesion. Alternatively, physical entanglements could be formed across the interface by dangling chains interpenetrating between the two networks. In both cases pressure-induced deswellling could cause free chains in unextracted lenses to migrate to the interface. These free chains would essentially act as lubricants inhibiting either mechanism in unextracted lenses. It seems intuitive that the extraction of free chains from the network would create more free volume in looser

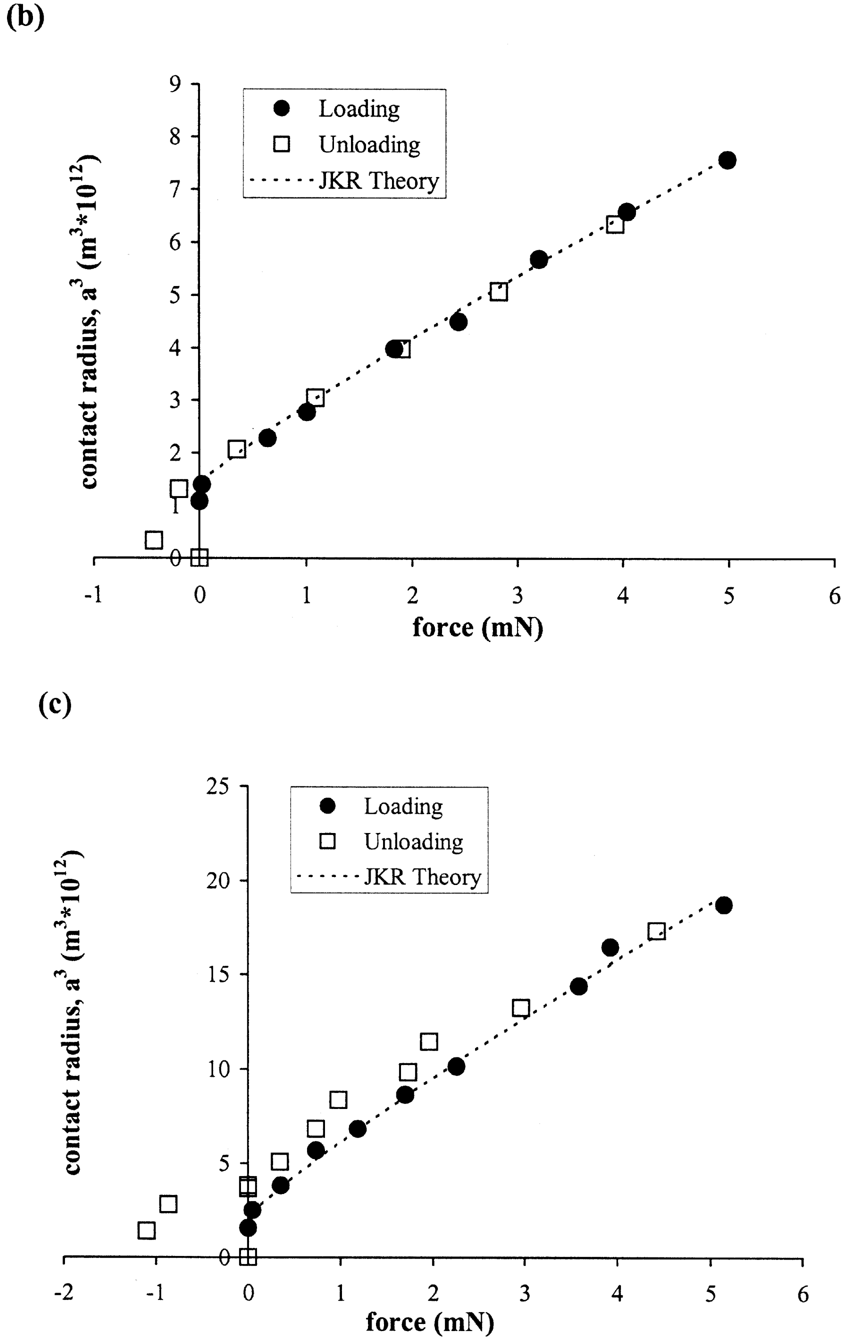


FIGURE 6 (Continued.)

TABLE 2 Effects of Extraction on K and M_c for PDMS Lenses

	Before		After	
	K (MPa)	M_c (g/mol)	K (MPa)	M_c (g/mol)
6KR07	0.419 ± 0.023	30,600	0.538 ± 0.016	23,800
6KR13	1.723 ± 0.157	7400	1.704 ± 0.065	7500
28KR07	0.027 ± 0.004	474,700	—	—
28KR13	0.569 ± 0.028	22,500	0.496 ± 0.025	25,800

networks, which would then be amenable to the swelling required to incorporate diffusing interpenetrating chains. Whether these chains could interpenetrate sufficiently to form effective entanglements across the interface is open to question.

One more experiment was performed in order to attempt to ascertain finally whether chain interpenetration or chemical reactions were responsible for the observed hysteresis. To eliminate the possibility of

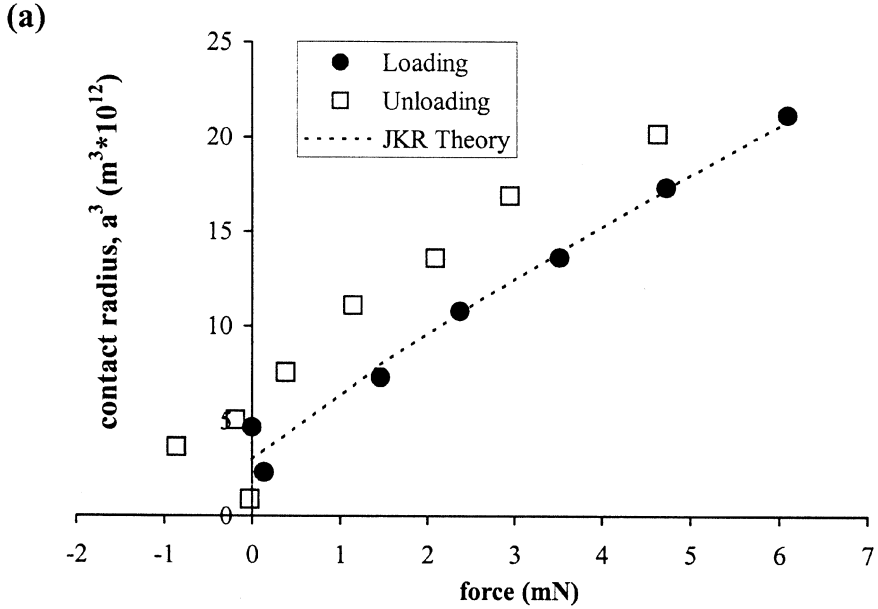
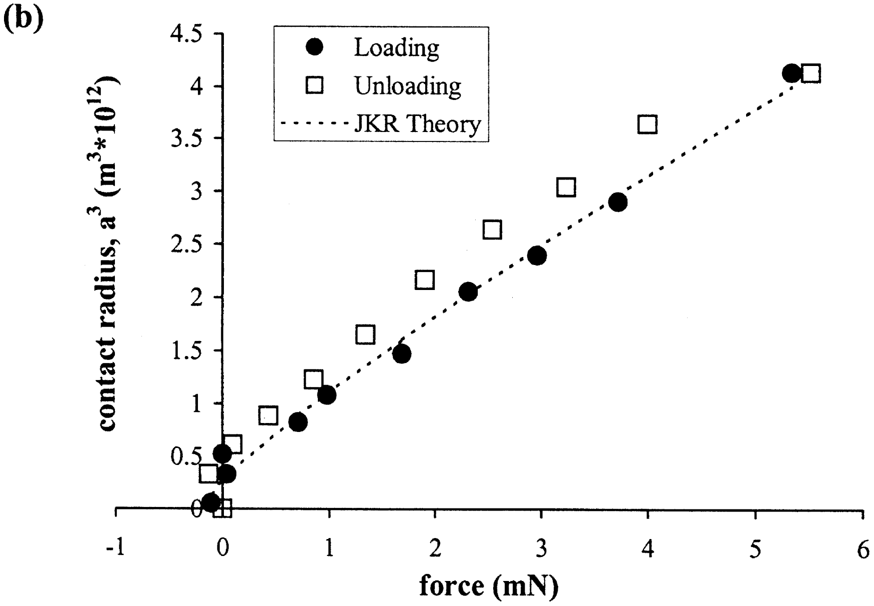


FIGURE 7 JKR self-adhesion loading and unloading for extracted PDMS lenses (a) 6KR07 ($M_c = 23{,}800$ g/mol), (b) 6KR13 ($M_c = 7{,}500$ g/mol), and (c) 28KR13 ($M_c = 25{,}800$ g/mol). (*Continued.*)



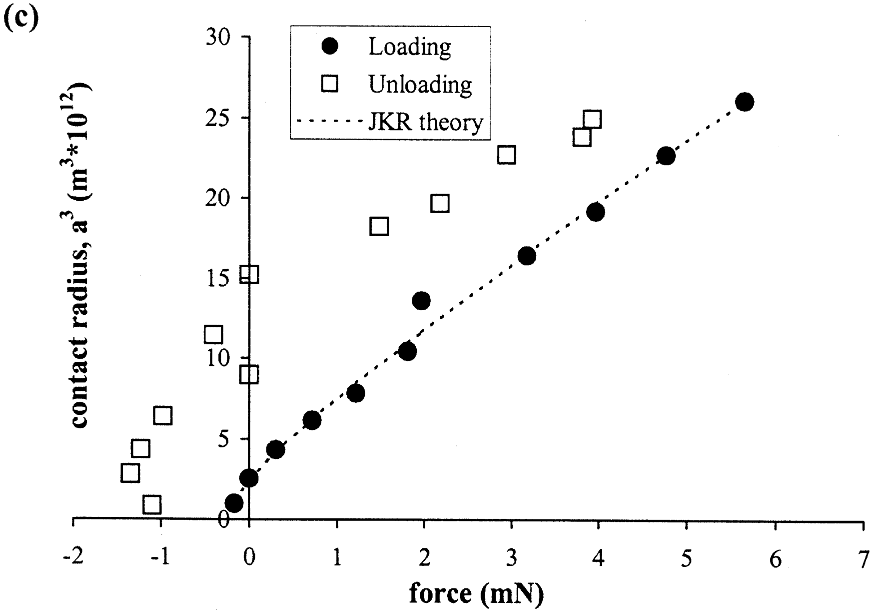


FIGURE 7 (Continued.)

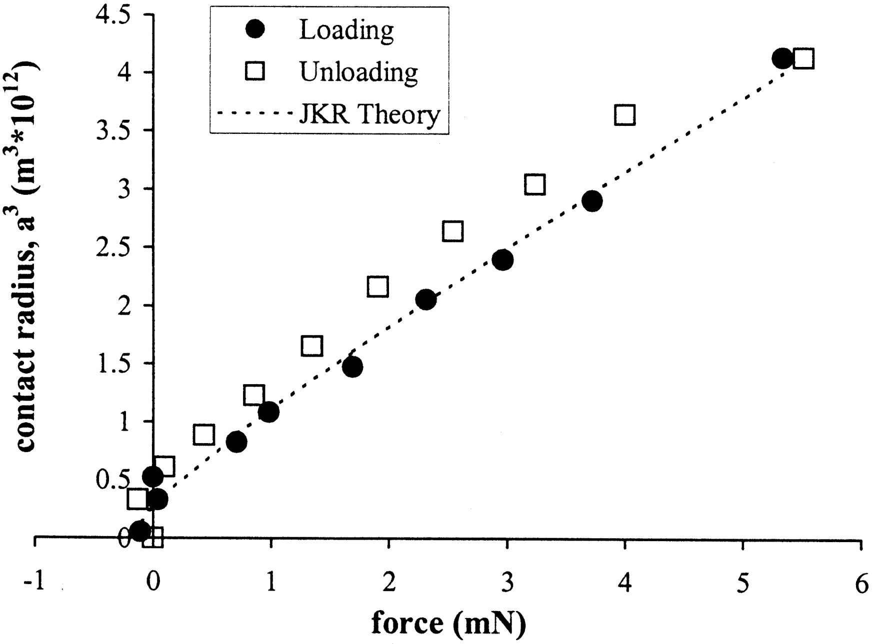


FIGURE 8 JKR self-adhesion loading and unloading for two extracted 6KR13 PDMS lenses ($M_c = 7{,}500\,\mathrm{g/mol}$). Unloading was performed after maintaining contact for 24 h under the maximum load (0.5 g).

a hydrosilylation reaction between unreacted SiH and vinyl groups, several 28KR13 PDMS lenses were taken and poisoned with a thiol solution as described in the experimental section. The same self-adhesion JKR experiment was performed as for the nonpoisoned networks, and the resultant loading and unloading curves are shown in Figure 9. This shows that removing the possibility of a chemical reaction has virtually eliminated the adhesion hysteresis. This suggests that adhesion hysteresis between extracted PDMS elastomers is due predominantly to a hydrosilylation reaction between residual vinyl and silane groups, which form chemical crosslinks across the interface and not physical entanglements caused by chain interpenetration. The absence of interpenetration effects in the present measurements are most likely associated with the slow kinetics of the interpenetration process. Adhesion measurements between crosslinked PDMS lenses and PDMS brushes grafted to planar interfaces clearly document that physical entanglement associated with chain interpenetration across the interface can profoundly increase the adhesion [15]. For brush

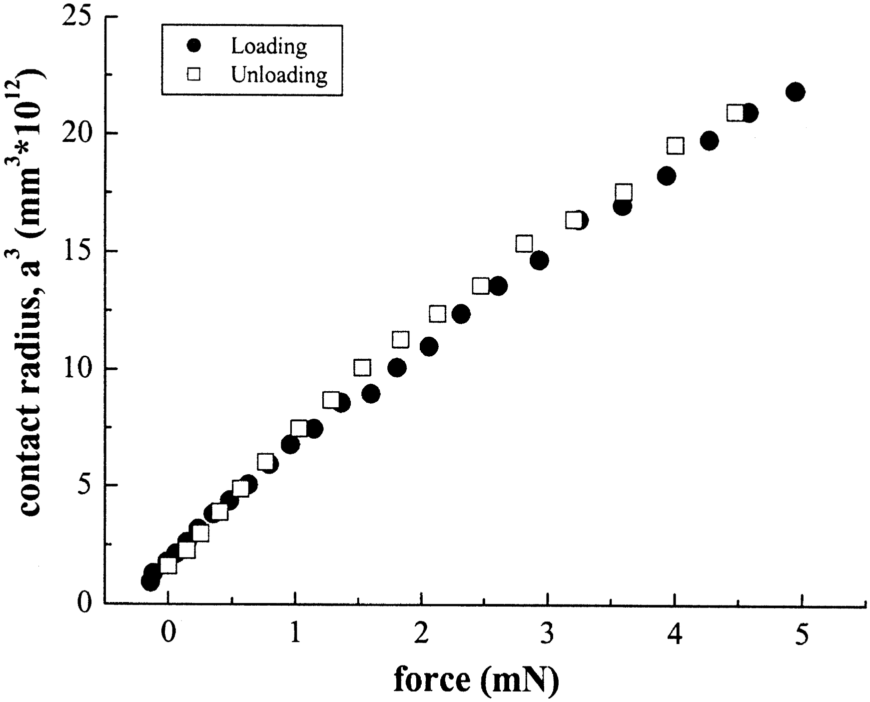


FIGURE 9 JKR self-adhesion loading and unloading for two extracted PDMS lenses ($M_c = 23{,}800$ g/mol) subjected to pretreatment with a thiol solution.

molecular weights similar to the present M_c values, equilibrium penetration required contact times of one month or more. Even the extended contact time of 24 h used herein is apparently insufficient to allow for significant chain interpenetration.

The dependence of hysteresis magnitude on the molecular weight between crosslinks can be explained in terms of the Lake-Thomas model for fracture in elastic polymers. They proposed that for fracture to occur in a crosslinked elastomer the growing crack tip has to cross a number of polymer connector chains, containing n monomer units, whose crosslinks lie on opposite sides of the plane of crack propagation. For crack propagation to occur these chains must be broken. Since the forces are transmitted primarily by the crosslinks, all bonds in the same connector chain must be stretched to nearly breaking force in order to break a particular bond. The total energy required will, therefore, be much greater than that of a single bond. By this reasoning, the fracture toughness was predicted to be:

$$G = \frac{1}{2} L N_b n_b U_b, \tag{12}$$

where L is the average distance between crosslinks (unstrained), N_b is the number of connector chains per unit volume, n_b is the average number of main-chain bonds in a connector chain, and U_b is the bond dissociation energy. If the reasonable assumption is made that the number of bonds in a connector chain is proportional to the molecular weight between crosslinks, M_c, the fracture toughness after interfacial bond formation, and therefore the magnitude of adhesion hysteresis, should increase with M_c, as is borne out by the results presented in Figure 7. The occurrence of interfacial reactions thus provides a reasonable explanation for the self-adhesion hysteresis behavior observed between PDMS lenses.

CONCLUSIONS

Self-adhesion hysteresis has been investigated in crosslinked PDMS lenses using the JKR technique. Extraction was found to alter the lens mechanical properties. The effects depended on whether the molecular weight of PDMS precursor was below the molecular weight for entanglements, M_e. For precursors below M_e, extraction of the sol fraction increased the modulus, K. For precursors above M_e, extraction decreased the modulus. No adhesion hysteresis was observed for any unextracted or extracted lens in contact with a “neutral” tethered PS substrate. Hysteresis was only observed in lens-on-lens experiments after extraction, suggesting that its origins are from surface interactions and not due to bulk viscoelastic losses. Further, self-adhesion hysteresis was only observed for networks with a molecular weight between crosslinks higher than the entanglement molecular weight. More tightly crosslinked networks did not display self-adhesion hysteresis, even at longer loading times. Unextracted networks do not display self-adhesion hysteresis because unreacted free chains encouraged by pressure-induced deswelling can migrate to the interface, causing a lubrication effect that inhibits the adhesion hysteresis mechanism. Extraction removes the lubricating free chains, allowing the adhesion mechanism to become active. Further experiments found that when the platinum catalyst used to synthesize the PDMS lenses was poisoned, the adhesion hysteresis disappeared, even after extraction. Since the contact times employed were insufficient to promote significant interfacial chain interpenetration, this result suggests that the formation of chemical crosslinks across the interface by a hydrosilylation reaction between residual silane and vinyl groups is the predominant mechanism responsible for adhesion hysteresis. The magnitude of self-adhesion hysteresis increases with the molecular weight between crosslinks, consistent with the expectations of the Lake-Thomas model for fracture in elastomers.

REFERENCES

[1] Lake, G. J. and Thomas, A. G., *The Strength of Highly Elastic Materials*, (London, 1967).

[2] Johnson, K. L., Kendall, K., and Roberts, A. D., *Proc. R. Soc. Lond. A.* **324**, 301 (1971).

[3] Chaudhury, M. K. and Whitesides, G. M., *Langmuir* **7**, 1013–1025 (1991).

[4] Chaudhury, M. K. and Whitesides, G. M., *Science* **255**, 1230–1232 (1992).

[5] Chaudhury, M. K., *J. Adhesion Sci. Technol.* **7**, 669–675 (1993).

[6] Hertz, H., *Miscellaneous Papers*, (Macmillan, London, 1896).

[7] Silberzan, P., Perutz, S., Kramer, E. J., and Chaudhury, M. K., *Langmuir* **10**, 2466–2470 (1994).

[8] Choi, G. Y., Kim, S. J., and Ulman, A., *Langmuir* **13**, 6333–6338 (1997).

[9] Perutz, S., Kramer, E. J., Baney, J., and Hui, C. Y., *Macromolecules* **30**, 7964–7969 (1997).

[10] Kim, S., Choi, Y., Nejaz, J., Ulman, A., and Fleischer, C., *Langmuir*, (1997) Vol. 13, pp. 6850–6856.

[11] Choi, G. Y., Zurawsky, W., and Ulman, A., *Langmuir* **15**, 8447–8450 (1999).

[12] Pickering, J. P., Meer, D. W. v. d., and Vancso, G. J., *Proc. ACS Div. Poly. Mat. Sci. Eng.*, **81**, 389 (1999).

[13] Emerson, J. A., Miller, G. V., Sorensen, C. R., and Pearson, R. A., *Proc. ACS Div. Poly. Mat. Sci. Eng.*, **81**, 385 (1999).

[14] Choi, G. Y., Kang, J. F., Ulman, A., Zurawsky, W., and Fleischer, C., *Langmuir* **15**, 8783–8786 (1999).

[15] Leger, L., *Macromol. Symp.* **149**, 197 (2000).

[16] Shull, K. R., Ahn, D., and Mowery, C. L., *Langmuir* **13**, 1799–1804 (1997).

[17] Derjaguin, B. V., Mueller, V. M., and Toporov, Y. P., *J. Colloid Interface Sci.* **53**, 314–326 (1975).

[18] Maugis, D., *J. Colloid Interface Sci.* **150**, 243–269 (1992).

[19] Hu, W., *Interfacial Activities of Block Copolymers in Immiscible Homopolymer Blends*; (University of Connecticut, Storrs, 1993) p. 185.

[20] Wu, S., *Polymer Interface and Adhesion*; 1st ed., (Marcel Dekker, New York, 1982).

[21] Mark, J. E., Eisenberg, A., Graessley, W. W., Mandelkern, L., and Koenig, J. L., *Physical Properties of Polymers*, American Chemical Society, Washington D.C., (1984).