Effect of Chemical Functionality on Adhesion Hysteresis

Soojin Kim,[†] Gun Young Choi,[†] Abraham Ulman,*,[†] and Cathy Fleischer[‡]

*Department of Chemical Engineering, Chemistry, and Materials Science, and
The NSF MRSEC for Polymers at Engineered Interfaces, Polytechnic University,
Brooklyn, New York 11201, and Material Science and Engineering Division,
Eastman Kodak Company, Rochester, New York 14650*

Studies of adhesion and adhesion hysteresis were carried out using cross-linked poly(dimethyl siloxane) (PDMS) semispherical surfaces and self-assembled model surfaces containing different chemical functionalities, using the JKR method, the contact mechanics of solids spreading their interfacial area under load. Hysteresis resulting from fast relaxation processes in the PDMS elastomer network was practically eliminated using stepwise loading and unloading protocols. The interfacial H-bonding between PDMS and both Si−OH and −COOH surfaces was shown to be an important chemical interaction causing significant adhesion hysteresis. The number of H-bonds between PDMS and Si−OH surfaces increased with contact time under compressive load, indicating pressure-induced reorganization of the PDMS network near the interface that increased the number of H-bonds. The interaction between PDMS and functionalized biphenylthiolate monolayers exhibited a smaller hysteresis, which is believed to be caused by dipolar interaction, whereas that between PDMS and nonpolar perfluorocarbon groups showed negligible hysteresis. The distinction in the behavior of the unloading data between H-bonding related interaction and dipolar interaction seems to indicate the difference in the nature between nonspecific (van der Waals, dipolar) and specific (donor−acceptor, H-bond, acid−base) interactions.

Introduction

Surface properties depend on the chemical and physical details of the structure at the molecular level. Fundamental understanding of the relationship between surface chemistry and adhesion requires stable chemically engineered surfaces, and self-assembled monolayers (SAMs) of thiolates on gold surfaces are ideal model surfaces for such studies.[1,2] Recently, we have launched a program to address this issue, whereby we study the adhesion of molecularly engineered model surfaces, using the contact deformation mechanics method (JKR) developed by Johnson, Kendall, and Roberts.[3]

The JKR theory is a continuum contact mechanics model, based on the energy balance of the elastic contact between curved solid surfaces under load, that takes into account the effect of surface energy. The experimental method, developed by Chaudhury,[4,5] has been widely used by several investigators and their co-workers[4−10] for the direct estimation of the work of adhesion, and thus surface free energy, using different elastic surfaces. The radius of contact, *a*, between an elastic semispherical surface and a flat nonelastic surface at equilibrium is described by the equation

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

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 system, and *W* is the work of adhesion between two surfaces. In the JKR experiment,

a and *P* are measured experimantally, while *K* and *W* are obtained from parameter fitting of *a* and *P* data to the JKR equation, eq 1.

In many 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 the unloading and loading processes, respectively. This type of hysteretic behavior is common with most practical interfacial phenomena, such as wetting. Since it is well-known that practical adhesion phenomena are hardly governed by equilibrium thermodynamic properties, but mostly by dynamic processes which arise from the changes of metastable thermodynamic states,[11] understanding hysteretic behavior, which is a representation of such interfacial dynamic processes, will be critical in developing technologies to control adhesion.

In adhesion experiments, hysteresis indicates the occurrence of some transformation on contact. A number of mechanisms considered to be the cause of adhesion hysteresis are reported in the literature.[12] For example, hysteresis may be caused by energy dissipation due to impact upon contact of two surfaces, viscoelastic or plastic bulk deformation of the contacting materials, and the surface roughness or heterogeneity.[13] Hysteresis can also be caused by the rearrangement or reconfiguration of molecular groups at the interfaces due to chemical interaction between two surfaces. Terms such as "interdigitation," "interdiffusion," "interpenetration," and "reptation" have been used by a number of authors describing such processes.[4,10,12]

In practical adhesion systems, hysteresis occurs by the combination of many effects, including those examples listed above, which are usually highly coupled. Therefore,

† Polytechnic University.
‡ Eastman Kodak Company.
⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1997.

(1) Ulman, A. *Ultrathin Organic Films: From Langmuir-Blodgett to Self Assembly*; Academic Press: Boston, MA, 1991.
(2) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
(3) Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London Ser.* **1971**, *A324*, 301.
(4) Chaudhury, M. K.; Whitesides, G. M. *Langmuir* **1991**, *7*, 1013.
(5) Chaudhury, M. K.; Whitesides, G. M. *Science* **1992**, *255*, 1230.
(6) Ahn, D.; Shull, K. R. *Macromolecules* **1996**, *29*, 4381.
(7) Tirrell, M. *Langmuir* **1996**, *12*, 4548.

(8) Silberzan, P.; Perutz, S.; Kramer, E.; Chaudhury, M. K. *Langmuir* **1994**, *10*, 2466.
(9) Brown, H. R. *Annu. Rev. Mater. Sci.* **1991**, *21*, 463.
(10) Merill, W. W.; Pocius, A. V.; Thakker, B. V.; Tirrell, M. *Langmuir* **1991**, *7*, 1975.
(11) Chaudhury, M. K. *Mater. Sci. Eng.* **1996**, *R16*, 97.
(12) Chen, Y. L.; Helm, C. A.; Israelachvili, J. N. *J. Phys. Chem.* **1991**, *95*, 10736.
(13) Horn, R. G.; Israelachvili, J. N.; Pribac, F. *J. Colloid Interface Sci.* **1987**, *115*, 480.

for the fundamental studies of adhesion related to surface chemistry, it is desirable to use model systems that can provide consistency in the mechanics, such as uniform and homogeneous surfaces, but versatility in the chemical control. SAMs can be molecularly engineered for the chemical groups of interest, and since adhesion is generally believed to be controlled by the properties of the outermost 5−10 Å surface groups, SAMs prepared from functionalized thiols on flat Au(111) surfaces[1,2,14] may be utilized as models for polymer surfaces. In addition to having well-characterized homogeneous and close-packed structures with strong chemical and thermal stability, these SAMs enable the fine-control of diverse and wide range of surface functional group structures and concentrations.

Cross-linked poly(dimethyl siloxane) (PDMS) has been a popular elastomer for JKR studies by many investigators,[4,5,8−10,15] due to its optically smooth surfaces and transparency as well as its excellent elastic properties. Recently, method to synthesize "model" PDMS networks has been developed.[16] The elastic properties of these networks are well characterized, and they are known to have only a tiny amount of un-cross-linked chain ends which could otherwise interfere and complicate adhesion measurements. Therefore, these model PDMS networks provide ideal elastomer surfaces for the JKR experiments, free from interpenetrating pendant chains, for instance.

Our efforts are aimed at obtaining fundamental insight into the chemical foundation of adhesion and adhesion hysteresis and ultimately being able to engineer surfaces to control adhesion and hysteretic behavior. We have been trying to delineate different effects on adhesion hysteresis, especially chemical effects, and to study their roles. It is the purpose of this paper to report some of our findings on the adhesion hysteresis affected by chemical functionality, with particular attention to H-bonding, from interactions between solid model surfaces of self-assembled monolayers and a cross-linked PDMS network.

Experimental Section

The JKR apparatus in our laboratory is based on a Nikon microscope equipped with vertical illumination that allows using metallic substrates without loss of image sharpness. The instrument is placed on a vibration isolation table and is housed in a polycarbonate enclosure, and the sample and PDMS hemisphere are enclosed in a plastic box, which is equipped with humidity and temperature sensors. This allows for purging with nitrogen and controlling relative humidity and temperature. A PDMS hemisphere can be pressed on or released from the sample surfaces by the controlled movement of micromanipulator that holds the hemisphere, and connected to a speed-controlled stepper motor. The load at the interface is measured by an electrobalance. The contact image is captured by a CCD camera connected to the computer, and the image analysis is carried out using National Institutes of Health (NIH) software.

SAMs of $HS(C_6H_4)_2F$, $HS(C_6H_4)_2CH_3$, $HS(CH_2)_2(CF_2)_9CF_3$, and $HS(CH_2)_{15}COOH$ (Figure 1) were formed by the spontaneous adsorption onto gold substrates[1,2,14] which were prepared by the evaporation of gold onto glass slides. Prior to adsorption, the gold substrates were cleaned in the argon plasma reactor (~1 Torr) for a few minutes. The substrates were immersed in 0.1 to 1 mM thiol solutions in ethanol for several hours and then washed with fresh ethanol and dried with N_2. The resulting monolayer films were characterized by ellipsometry and contact angle measurements.

Cross-linked PDMS networks were prepared from low polydispersity PDMS polymers with vinyl end-groups synthesized
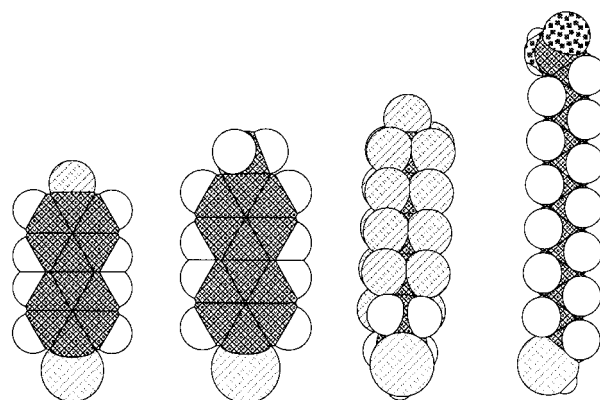

Figure 1. Thiols used in the present study from (left to right): $(HS(C_6H_4)_2F)$, $(HS(C_6H_4)_2CH_3$, $HS(CH_2)_2(CF_2)_9CF_3$, $HS(CH_2)_{15}$-COOH.

from hexamethylcyclotrisiloxane.[17−19] The cross-linker was tetrakis(dimethysiloxy)silane, (Gelest Inc.) and the catalyst was *cis*-dichlorobis(diethyl sulfide)platinum(II) (Strem Chemicals). The narrow molecular weight distribution resulting from this particular polymerization method (≤1.2) allowed us to create a model network containing almost no defects and only a tiny amount of unconnected chain ends; hence, the possibility of viscoelastic processes in the JKR experiment can be minimized. The amount of tetrafunctional hydrosilylation cross-linker was accurately controlled (somewhat more than the stoichiometric ratio) in order to yield more complete cross-linking and thus nearly ideal elastic behavior, as in the process developed by Patel and co-workers.[16] PDMS hemispheres were prepared by allowing the cross-linker-mixed polymer droplets on fluorosilane-treated glass slide to cross-link in a heated vacuum desiccator for 3 days, as in the procedures in the previous investigators' works.[4,8]

Results and Discussion

Most previous studies of adhesion by the JKR method in the literature attributed adhesion hysteresis to the various effects outlined above. Since we wanted to decouple different sources of hysteresis occurring in experiments on our setup, we first carried out the experiments of self-adhesion of model PDMS network using *two identical PDMS hemisphere surfaces*. This could eliminate the chemical effect on the adhesion, so that observed hysteresis can be related to the other effects.

Experiments were conducted using PDMS hemispheres cross-linked from 68K molecular weight polymer. When the loading and unloading procedures were carried out continuously at a constant speed of 15 μN/s, the a^3 vs P plot displayed hysteretic behavior as shown in Figure 2. In an attempt to understand the source of this hysteretic behavior we have carried out experiments using different rates. We have found that even at a slow rate of ~0.4 μN/s there was still a residual hysteresis.

To understand the reltive contributions of the loading and unloading processes to hysteresis, we performed experiments in which identical cross-linked 68K hemispheres were studies, and the contact area (A) was monitored, while the system was allowed to relax at maximum load. Figure 3 presents the results of five experiments, all using the same loading or unloading rate of 10 μN/s, in which 68K hemispheres were used. In the first experiment, the hemispheres were brought to contact (▲), in the second, the system was loaded to a 30 mG

(14) Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E.; Chang, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 1499.

(15) Choi, G.-Y.; Ulman, A. *Langmuir*, in press.

(16) Patel, S. K.; Malone, C.; Cohen, J. R.; Gilmore, J. R.; Colby, R. H. *Macromolecules* **1992**, *25*, 2541.

(17) Lee, C. L.; Frye, C. L.; Johnson, O. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1969**, *10*, 1361.

(18) Lee, C. L.; Johnson, O. K. *J. Polym. Sci.: Polym. Chem. Ed.* **1976**, *14*, 729.
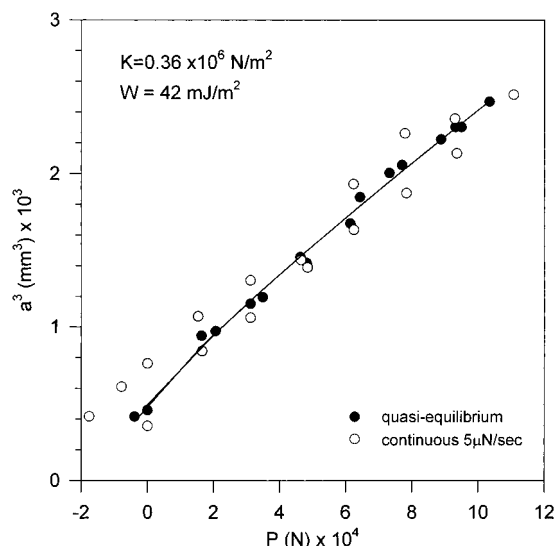
(19) Lee, C. L. U.S. Patent No. 3 445 426, 1969.

Figure 2. Radius of contact, a^3 vs load, P, in self-adhesion of two PDMS lenses (MW = 68K) in the loading and unloading experiments. The solid curve and parameters are the fitted results of the data using the JKR equation.
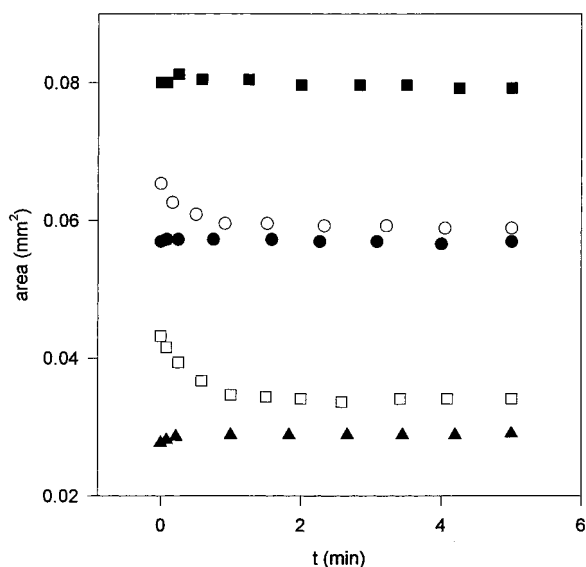

Figure 3. Loading and unloading experiments using two identical 68K cross-linked PDMS hemispheres: (▲) hemispheres brought to contact; (●) a system under 30 mG load; (■) a system under 60 mG load; (○) a system after loading to 60 mG and unloading to 30 mG; and (□) a system after loading to 60 and unloading to 0 mG.

balance reading (●), and in the third, the system was loaded to 60 mG (■). In all cases, *a* increased very slightly, but approached a constant value in less than 0.5 min. The fourth experiment is after loading to 60 mG and unloading to 30 mG (○), and the fifth is after loading to 60 and unloading to 0 mG (□). Clearly the system in unloading requires more time to relax to a constant contact area, and this is probably the source of hysteresis in the continuous loading and unloading experiments. But even in this case it occurs in less than 2 min. Therefore, we decided to wait 5 min between each loading and unloading steps, thus allowing the system to approach a "quasi-equilibrium". The time required for this relaxation, or the relaxation kinetics, is known to be dependent on the molecular weight of the polymer network.[20] However, we have not yet carried out systematic investigation of this
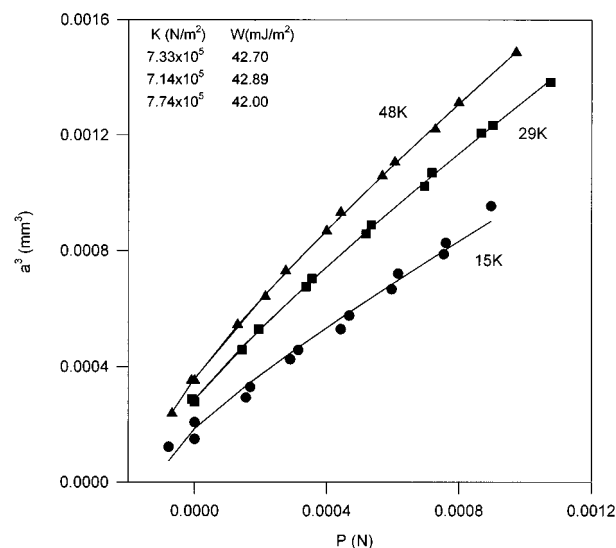
(20) De Gennes, P. G. *Introduction to Polymer Dynamics*; Cambridge Press: Cambridge, England, 1990.

Figure 4. a^3 vs load, P, in PDMS self-adhesion experiments using PDMS lenses cross-linked from polymers of different molecular weights

kinetics. Nevertheless, this experiment provided a procedure in which we can eliminate any cross-linked network effect on the observed hysteresis, as is apparent from the absence of hysteresis using this protocol (Figure 2). Accordingly, all our experiments from this point utilized this stepwise loading and unloading protocol.

Fitting the equilibrium data of PDMS self-adhesion to the JKR equation (eq 1), using the least-squares method, resulted in the estimation of W, 42 mJ/m^2. This value is approximately twice the surface free energy of PDMS commonly determined from the contact angle measurements and is in agreement with results of other investigators.[4,11] Repeated experiments with PDMS hemispheres cross-linked from polymers of different molecular weights (15K to 68K) resulted in no observable hysteresis (Figure 4), and the work of adhesion estimated from the same data fitting procedure came out to be 42 ± 1 mJ/m^2, in agreement with one another. These hemispheres allowed the systematic investigations of adhesion and adhesion hysteresis as a function of cross-linking density. However, we did not find any dependence of the work of adhesion on cross-linking density in self-adhesion experiments.

Since we observed that the kinetics of loading and unloading play a significant role in adhesion hysteresis, we became interested in the effect of contact time on adhesion hysteresis, which may be of importance. We investigated time-dependent adhesion hysteresis when H-bonding exists between the PDMS hemisphere and oxidized silicon wafer surface. Silicon wafers were cleaned in hot H_2SO_4/H_2O_2 solution, rinsed with distilled water, and dried under N_2. Three experiments were carried out with different waiting periods between maximum loading and the start of unloading. In order to be consistent, the maximum loading was kept the same for all three experiments. As shown in Figure 5, the hysteresis on the PDMS−Si wafer interactions was much larger than that observed in the other experiments with continuous loading (Figure 2). The hysteresis can be attributed to H-bonding between the naturally-present surface Si−OH groups on silicon wafer, and the Si−O−Si groups of PDMS, as illustrated in Figure 6. Interestingly, when the silicon wafers were cleaned using argon plasma, no, or very little hysteresis was observed. This is probably because the outermost layers of the native SiO_2 have been removed, thus leaving a surface with no Si−OH groups.
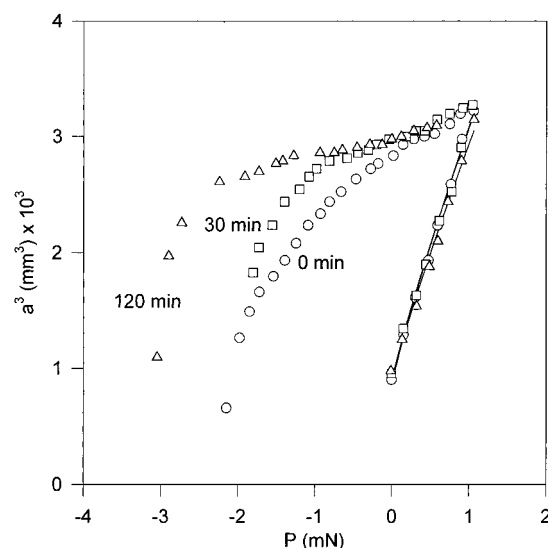
Figure 5. Loading and unloading experiments using PDMS and silicon wafer with different waiting times between maximum loading and the start of unloading. The results show hysteresis due to H-bonding interaction between Si−O−Si and Si−OH surfaces.
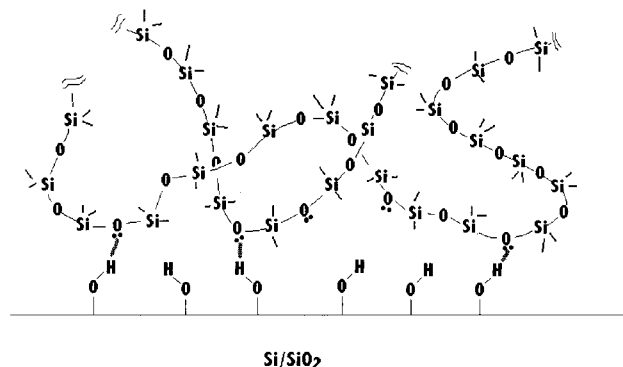

Figure 6. H-bonding between PDMS and sitanol groups on SiO$_2$/Si surfaces.

The magnitude of the H-bonding effect is remarkable, considering the strength of the H-bonding interactions. Chaudhury and co-workers[21] have recently measured the interaction between a single PDMS chain and a Si−OH group using AFM. Preliminary results suggest that a strength of a single H-bond between silanol and siloxane groups is ≤1.5 kT or ≤3 × 10^{-3} kcal mol^{-1}. Yet, the observed hysteresis points to orders of magnitude larger energies. This is because adhesion between PDMS and an OH surface cannot be understood based on the energy of individual interactions, due to of the collective nature of the interfacial interactions associated with the PDMS chains. The unloading is associated predominantly with dissipative processes such as the elastic energy associated with the stretching of polymer chains at the interface during crack propagation, U_E, and the deformation energy associated with the deformation of the PDMS network as a result of interfacial interactions and load, U_D. U_E and U_D scale with interfacial interactions; therefore, as these interactions become stronger, U_E and U_D increase, and adhesion hysteresis increases as well.

Figure 5 shows that the hysteresis increased with the increasing time of contact. This indicates that there was time-dependent pressure-induced reorganization of the PDMS network near the interface that increased the
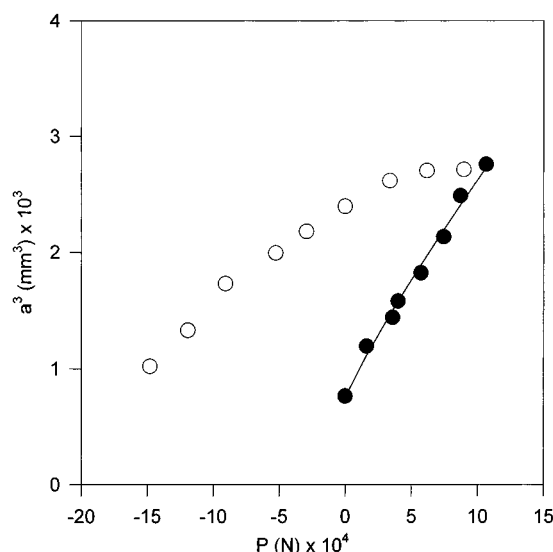

Figure 7. Loading (filled circles) and unloading (hollow circles) data showing the 14-bonding interaction between PDMS and SAM of −COOH.

number of H-bonds. The greater the number of H-bond, the greater is the hysteresis.[11] Since the formation of H-bond is almost instantaneous, most of the transformation occurring during this longer time can only be the chain reorganization of the PDMS network. It was observed that during the waiting time the load measured at the interface continuously decreased—without significant change in the contact area—and contributed to the increased hysteresis with contact time. Because we believe that the overall contact equilibrium—not thermodynamic equilibrium of individual polymer chains—was maintained during this waiting period—i.e., the total energy, U_T, which is expressed as the sum of the mechanical potential energy, U_M, the elastic energy, U_E, and the surface adhesion energy, U_S in the JKR analysis, remained constant—a decrease in the load measured at the interface without apparent change in A indicates decreases in U_M and U_E, accompanied by an increase in U_S. Our hypothesis that the chain reorganization increased the *number* of H-bonds which lead to the increase of adhesion energy supports this reasoning. Such chain reorganization, we claim, is an example of the interfacial dynamic processes that occur due to the metastable thermodynamic states of the polymer chains and eventually bring to some time-dependent progression towards the minimum energy state.[11] Analogous observation of molecular reorientation at interfaces affecting adhesion, where the surfaces were initially hydrophobic on approach but became more hydrophilic on separation ("flip-flop") and which also depended on the contact time, was reported in the literature.[22]

It should be noted that our system did not have the "fixed-load" condition (constant P with a dead weight), in which case the contact area probably might have increased with time as U_S increased with more H-bond formation. This experiment demonstrated that there is a strong dependence of adhesion hysteresis on contact time, particularly in contacts involving strong chemical interaction. Therefore, in all our following experiments, we adopted the consistent procedure in that we wait 0 min after the final loading measurement and before the start of unloading.

The interaction between PDMS and HS(CH$_2$)$_{15}$COOH monolayer (shown in Figure 7) is another demonstration of the effect H-bonding between the PDMS Si−O−Si groups and the carboxylic acid −OH groups has on ad-
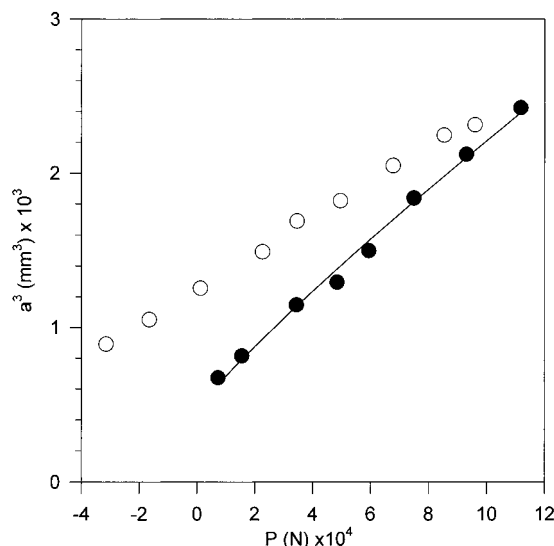
(21) Chaudhury, M. K. Private communication.

Figure 8. Loading (filled circles) and unloading (hollow circles) data showing the surface interaction between PDMS and CH_3- biphenylthiol SAM.
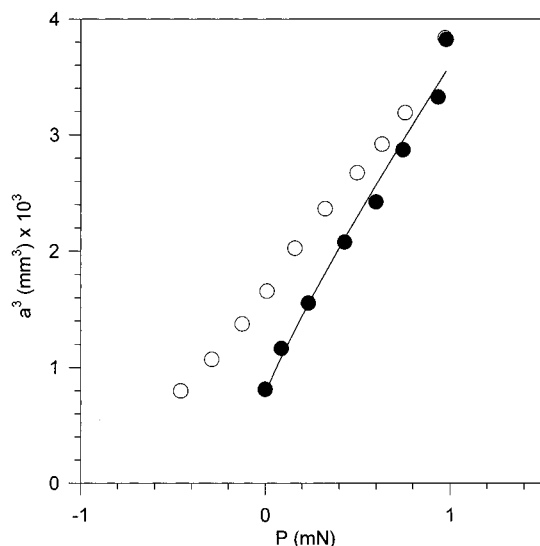

Figure 10. Loading (filled circles) and unloading (hollow circles) data showing the surface interaction between PDMS and $CF_3(CF_2)_9(CH_2)_2SH$ SAM.

Figure 9. Loading (filled circles) and unloading (hollow circles) data showing the surface interaction between PDMS and F—biphenylthiol SAM.

hesion hysteresis. Note, that the shape of the unloading curve is similar to that obtained in experiments using Si—OH surfaces (Figure 4).

Figures 8 and 9 show adhesion hysteresis resulting from another type of chemical interaction, those between PDMS and CH_3- or F—biphenyl SAMs on Au(111). Since there is no source of H-bonding in CH_3- or F—biphenyl SAM surfaces, the hysteresis observed in the plots is believed to be caused by a dipolar interaction between PDMS and the SAMs as a result of the dipole moment created by the polar biphenyl groups. Presently we are in the process of investigating van der Waals and dipolar interactions using a series of biphenyl SAMs with different chemical functionalities.

In order to confirm that all the observed hysteresis was caused by chemical interaction, whether H-bonding or dipolar interaction, we investigated the interaction between PDMS and the nonpolar $HS(CH_2)2(CF_2)_9CF_3$ surface in which no specific chemical interaction or transformation, except van der Waals, is conceivable. Figure 10 exhibits very small or negligible hysteresis, suggesting that the process was virtually reversible and confirming
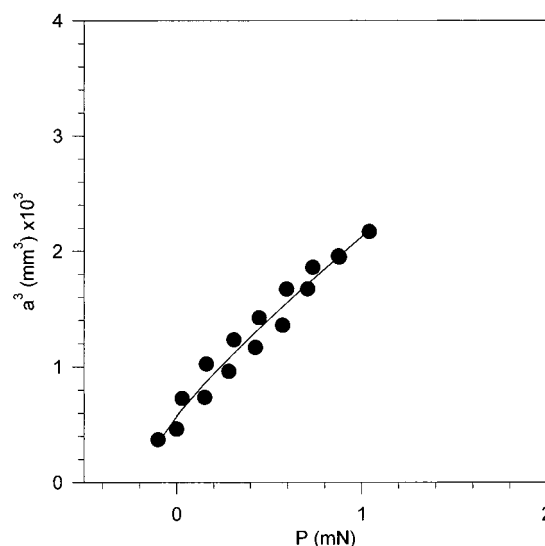
that the hysteresis observed in the other experiments had strong dependence on chemical functionality. In both the perflurocarbon monolayers and the biphenyl monolayers considered in this work, the possibility of surface reorganization of the monolayer molecules—e.g., *trans-gauche* transformation in long alkane chains—which can be another source of hysteresis, could be ruled out on account of the rigidity of the molecular groups.

When we compare the hysteresis caused by H-bonding and the hysteresis from a dipolar interaction between PDMS and CH_3- or F—biphenyl SAMs, we notice a marked distinction between the two. The slopes of the H-bonding-related unloading curves (Figures 5 and 7) increase as the separation advances, whereas the unloading curves from the interaction between PDMS and the functionalized biphenyl thiol SAMs (Figures 8 and 9) are almost straight lines with constant slopes. We conjecture that this distinction in the unloading curvature (variable curvature in H-bonding related unloading vs constant slope in dipolar interaction unloading) may be an indication of the difference in the nature of specific interaction (donor—acceptor, H-bond, acid—base) and nonspecific interaction (van der Waals, dipolar). Since specific interactions involve certain amount of energy for making or breaking bonds—whereas nonspecific interactions have no specific bond formation or bond energy associated with them—their separation processes are likely affected by the kinetics of bond dissociation and/or crack velocities which perhaps increase rapidly as the contact area decreases. Consequently, the separation is very slow near the beginning of the unloading where the contact area is large, and the crack speed increases as the contact area decreases.

In general, the strength of the H-bond is relatively greater than other types of interactions, and thus breaking these bonds during the unloading process probably induces extensive stretching of the PDMS network by the attempts to pull apart strongly interacting surfaces. In such a case a good amount of energy is consumed in viscoelastic energy dissipation (or stretching of the PDMS network) at the crack tip, and the unloading data are observed in a significant departure from the JKR regime. In the viewpoint of fracture mechanics, the contact experimental data can be expressed in terms of the strain energy release rate, G[23]
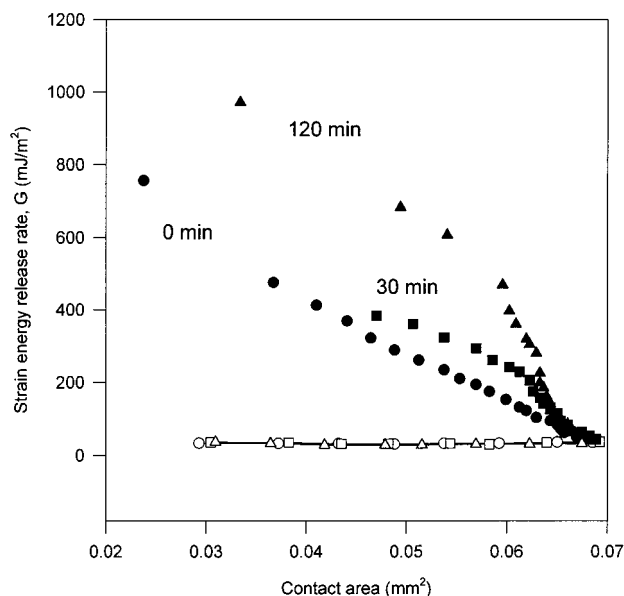
Figure 11. Strain energy release rate vs contact area for the H-bonding interaction between PDMS and Si−OH on SiO₂/Si. Hollow and filled symbols indicate loading and unloading data, respectively.

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

where P_H is the apparent Hertz load ($P_H = a^3 K/R$) which would produce the radius of contact, a, in the absence of surface forces. G is defined as[22]

$$G = \left(\frac{\partial U_E}{\partial A} + \frac{\partial U_M}{\partial A}\right) \tag{3}$$

where A is the contact area, and $G - W$ is characterized as viscoelastic losses at constant crack speed, where W is the thermodynamic work of adhesion.

Figure 11 shows the calculated values of G plotted with respect to A for the H-bonding interaction between PDMS and Si−OH. Notice that because of the stepwise loading and unloading protocol we use, one cannot plot G as a function of crack velocity. The elastic constant, K, was estimated for each experiment by fitting the loading data to the JKR equation (eq 1), assuming that the loading part follows the JKR behavior. For the loading, the values of G are mostly constant near the value of W for all the experiments, indicating that the loading proceeded near contact equilibrium. On the other hand, for the unloading, G values increase continuously as the separation increases (with decreasing A). In the theory of fracture mechanics, $dG/dA < 0$ implies unstable contact equilibrium and spontaneous crack propagation for the case of "brittle" fracture (as opposed to viscoelastic fracture). In the present case, during the course of the 5 min between a typical unloading step and measurement, crack extension reached a very slow steady state. Therefore, the tensile strain energy was presumed to have been expended in stretching the network at the crack tip, instead of spontaneously accelerating the crack propagation. Additionally, the fact that G continuously increases with decreasing A in the plots can be viewed as an evidence that the number of H-bonds per unit area of contact increased progressively toward the center. This is because
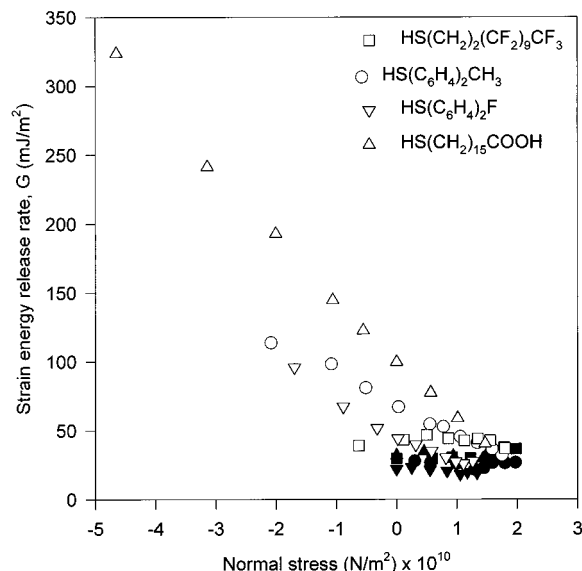
(22) Chen, Y. L. E.; Gee, M. L.; Helm, C. A.; Israelachvili, J. N.; McGuiggan, P. M. *J. Phys. Chem.* **1989**, *93*, 7057.
(23) Maugis, D.; Barquins, M. *J. Phys. D: Appl. Phys.* **1978**, *11*, 1989.

Figure 12. Strain energy release rate vs normal stress for the interaction between PDMS and various SAMS. Filled and hollow symbols indicate loading and unloading data, respectively.
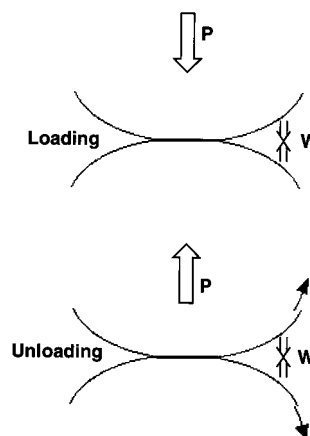

Figure 13. Scheme showing that, on loading, the external forces (P) and the surface attractive forces (W) are synergetic at the crack tip, while upon unloading, the external forces and the surface attractive forces are antagonistic for small separations at the crack tip. The arrows in the unloading experiment represent the force stretching the PDMS network at the crack tip.

the total contact time under compressive stress (including the sum of the 5 min between data points) was the longest in the center.

Figure 12 shows the calculated values of G for the interactions between PDMS and the SAMs (of Figures 7−9) plotted with respect to the normal stress, P/A. Plotting G vs P/A provided the graph easier for comparison of the SAMs, when there was a slight variation (up to 12%) in the PDMS hemisphere sizes. The plots show much lower values of unloading G for all, compared to the plots regarding H-bonding in Figure 11. Notably, for the interaction between PDMS and perfluorocarbon SAM which was practically due to reversible contact and separation processes, there was virtually no viscoelastic loss associated with the separation process. Detailed studies are underway to further elucidate these issues.

Conclusions

Studies of adhesion and adhesion hysteresis were carried out between cross-linked poly(dimethyl siloxane) (PDMS) semispherical surfaces and self-assembled model

surfaces containing different chemical functionalities, using the JKR method, the contact mechanics of solids spreading their interfacial area under load. Self-adhesion experiments using identical cross-linked PDMS networks showed hysteresis even at very slow loading and unloading rates. This is because upon loading, the external forces (P) and the surface attractive forces (W) are synergetic at the crack tip (Figure 13), leading to relatively small relaxation times, so that for slow enough loading steps the system will trace a succession of states which is close to a series of minimal free energy states modeled by an equilibrium model, such as the JKR theory. In contrast, upon unloading, the external forces and the surface attractive forces are antagonistic for small separations at the crack tip (Figure 13), resulting in a barrier in the equilibrium free energy as a function of deformation, which also depends on the system interactions and temperature. For the strong interfacial H-bonding interactions, where relaxation times are long relative to the time steps upon unloading, the system may not attain an equilibrium state at each time step. This leads to a sequence of nonequilibrium states at nonminimal values of the free-energy function at each time step, giving rise to the irreversible force-separation unloading curve and adhesion hysteresis. That relaxation times increase with contact time under maximum compressive load, indicates that pressure-induced reorganization of the PDMS network near the interface occured by increasing the number of H-bonds.

The interaction between PDMS and functionalized biphenylthiolate monolayers exhibited smaller hysteresis, which is believed to be caused by dipolar interaction, whereas that between PDMS and nonpolar perfluorocarbon groups showed negligible hysteresis. The distinction in the behavior of the unloading data between H-bonding related interaction and dipolar interaction seems to indicate the difference in the nature between nonspecific (van der Waals, dipolar) and specific (donor−acceptor, H-bond, acid−base) interactions.