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STUDIES OF ADHESION TO MOLECULARLY ENGINEERED SURFACES USING CONTACT MECHANICS METHODS

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Abstract. We synthesized a number of poly(dimethylsiloxane) (PDMS) polymers with different molecular weights, and prepared model PDMS networks with a systematic change of cross-link density, and therefore elastic constant (K). Self-adhesion studies of PDMS hemispheres using the JKR method—the contact mechanics of solids spreading their interfacial area under load—reveal that hysteresis which results from relaxation processes in the elastomer can be practically eliminated using stepwise loading and unloading protocols. The adhesion of crosslinked PDMS surfaces to self-assembled monolayers with different chemical functionality was investigated. Interfacial H-bonding was shown to be an important chemical interaction causing significant adhesion hysteresis. The number of H-bonds between PDMS and silanol groups on SiO_2/Si surfaces increased with time of the contact under a constant load, indicating pressure-induced reorganization of the PDMS network near the interface. The interaction between PDMS and carboxylic acid groups showed somewhat smaller hysteresis which suggests weaker H-bonding strength. The interaction between PDMS and functionalized biphenyl groups exhibited small 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 non-specific (van der Waals, dipolar) and specific (donor-acceptor, H-bond, acid-base) interactions.

INTRODUCTION

The ability to control surfaces and interfaces is critical for the development of new technologies and the modification of existing ones in materials research and engineering. Yet, there is little understanding of the relationship between surface chemistry and adhesion. With the recent development of the contact mechanics methods—the JKR technique—for the study of adhesion, it has become possible to carry out 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.

The JKR theory is a continuum contact mechanical model developed by Johnson, Kendall, and Roberts [1] that considers the effect of surface energy on the properties of an elastic contact and has been widely used by Chaudhury [2-5], Kramer [6], Brown [5,7], and Tirrell [8], for direct estimation of the surface free energy and the work of adhesion using functionalized PDMS surfaces. The radius of contact, *a*, between an elastic semispherical surface and a flat nonelastic surface at equilibrium is described by the equation

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

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 elastomer, and *W* is the thermodynamic work of adhesion between two surfaces.

EXPERIMENTAL

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, 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

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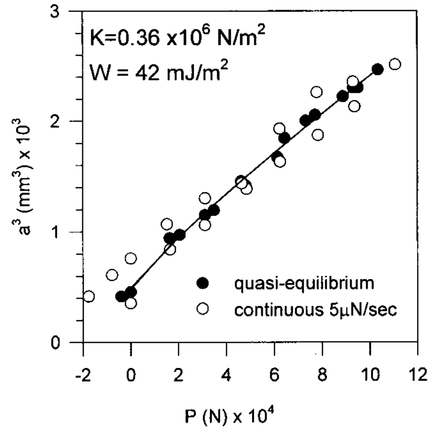

Figure 1. Radius of contact, a^3 vs. load, P in self-adhesion of two PDMS lenses (MW=68K).

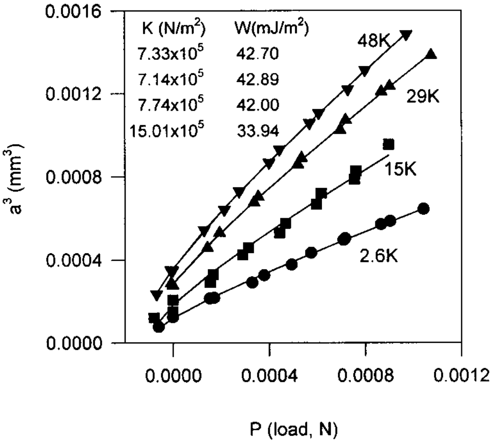

Figure 2. a^3 vs. load, P in PDMS self-adhesion experiments using PDMS lenses of different molecular weights.

hysteresis as a function of molecular weight.

One example for the chemical interaction attributed for adhesion hysteresis is the formation of H-bonds. We investigated time-dependent adhesion hysteresis when H-bonding exists between the PDMS lens and oxidized silicon wafer surface. Silicon wafers were cleaned in H_2SO_4/H_2O_2 solution, rinsed with H_2O and dried under N_2. Three experiments were carried out with different waiting periods between maximum loading and the start of unloading. As shown in Figure 3, the initial hysteresis (0 min waiting) is very significant and much larger than that observed in other experiments with continuous loading (Figure 1). The hysteresis can be attributed to the H-bonding between the naturally-present surface Si-OH groups on silicon wafer and the Si-O-Si groups of PDMS (Figure 4). The fact that the hysteresis increases with the increasing time of contact indicates that there is a time-dependent and pressure-induced reorganization of the PDMS network near the interface that increases the number of H-bonds. Notice that a^3 does not increase with time, indicating that these H-bonds are not strong enough to deform the hemisphere near the contact line. Hence all the observed change in hysteresis results from chain reorganization at the PDMS-Si/SiO_2 interface. Interestingly, when the silicon wafers were cleaned using Ar plasma, 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.

The interaction between PDMS and $HS(CH_2)_{15}COOH$ monolayer (shown in Figure 5) also demonstrates the same effect of the H-bonding between the PDMS Si-O-S groups and the carboxylic acid -OH groups. The effect of H-bonding on adhesion hysteresis shows a marked distinction when compared to another type of chemical interaction such that between PDMS and CH_3- or F- biphenyl SAMs on gold (shown in Figures 6 and 7) which contain no source of H-bonding. The slopes of the H-bonding-related unloading curves (Figures 3 and 5) increase as the separation advances whereas the unloading curves from the interaction between PDMS and the functionalized biphenyl thiol SAMs (Figures 6 and 7) are almost straight lines with constant slopes. We believe that the hysteresis observed in Figures 6 and 7 is caused by dipolar interaction. The interaction between PDMS and nonpolar $HS(CH_2)_2(CF_2)_9CF_3$ surface (shown in Figure 8) exhibits very small hysteresis since there is no irreversible chemical interaction. In addition, the rigidity of the perflurocarbon chains and of the biphenyl groups precludes the possibility of surface reorganization of the monolayers which can be another source of hysteresis. Currently we are in the process of investigating van der Waals and dipolar interactions using a series of biphenyl SAMs with different chemical functionality.

This distinction in the unloading curvature seems to indicate the difference in the nature between non-specific interaction (van der Waals, dipolar) and specific interaction (donor-acceptor, H-bond, acid-base). Furthermore, the strength of H-bond is generally much greater than the other type of interaction, and thus it is likely during the

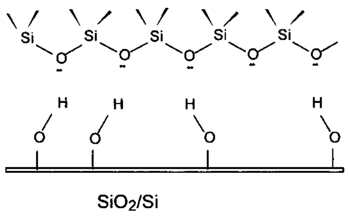

Figure 3. H-bonding between PDMS and silanol groups on SiO_2/Si surfaces.

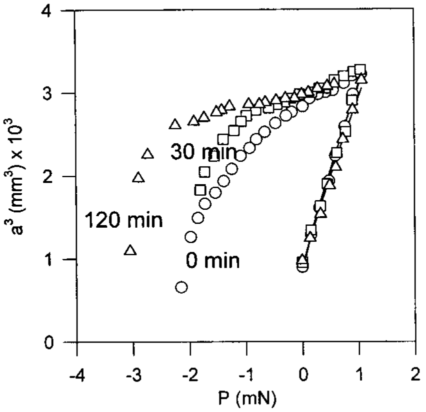

Figure 4. H-bonding interaction between PDMS and SiO_2/Si surface with different waiting time between maximum loading and the start of unloading.

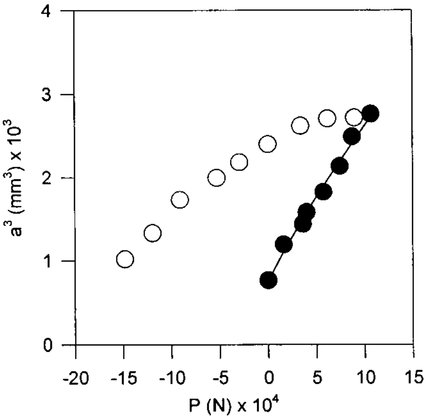

Figure 5. H-bonding interaction between PDMS and SAM of -COOH.

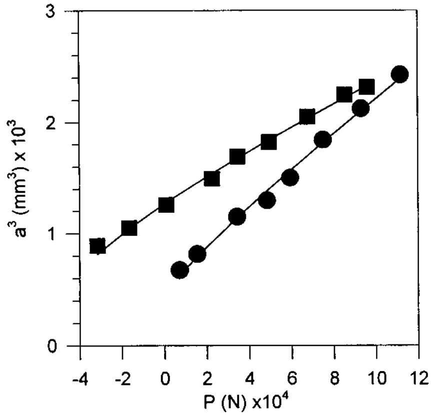

Figure 6. Surface interaction between PDMS and CH_3-biphenyl thiol SAM.

unloading process the PDMS at the crack tip is extensively stretched by the attempts to pull apart strongly interacting surfaces until the bonds break. In such case a good amount of adhesion energy is consumed in plastic dissipation at the crack tip, and the unloading data are 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 as a function of contact radius, a [20]

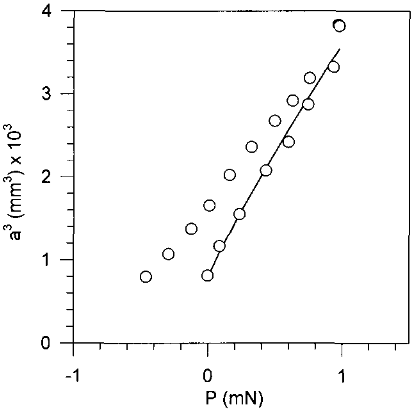

Figure 7. Surface interaction between PDMS and F-biphenyl thiol SAM.

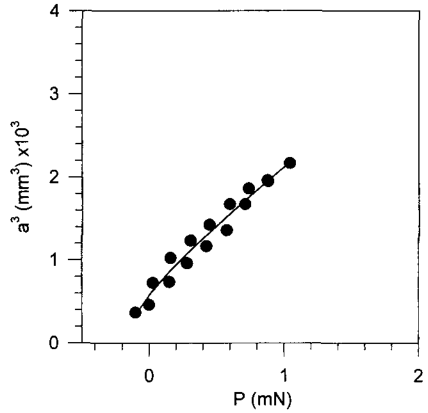

Figure 8. Surface interaction between PDMS and $CF_3(CF_2)_9(CH_2)_2SH$ SAM.

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

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 [20]:

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

where A is the contact area, and U_E and U_P are the stored elastic energy and the potential energy of the load, respectively. Figures 9 and 10 show the calculated values of G plotted with respect to the contact area, πa^2. The elastic constant, K, was estimated for each experiment by fitting the loading data to the JKR equation (1), assuming that the loading part followed the JKR behavior. For the loading data the value of G is mostly constant near the value of W for all the experiments, indicating that the loading proceeded more or less near equilibrium. On the other hand, for the unloading data, G increases continuously as the separation increases for all the experiments except for the case of the perfluorocarbon SAM. This indicates $\partial G/\partial A<0$, which means unstable equilibrium where the separation can spontaneously increase toward a new stable equilibrium. The plots show highest values of G of unloading for the H-bonding interaction between PDMS and silanol groups and somewhat lower for that between PDMS and carboxylic acid groups. The unloading G for the dipolar interaction (PDMS and biphenyl functional groups) is much lower than that for H-bonding interaction. Detailed studies are underway to further elucidate these issues.

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relative humidity and temperature. PDMS hemisphere can be pressed on or released from the SAM surfaces by the controlled movement of micromanipulator that holds the hemisphere, and connected to an accurate speed controller. The load at the interface is measured by sensitive electrobalance with automatics data acquisition to the computer. The contact image in captured by a video camera connected to the computer, and image analysis is carried out using an NIH software.

Model PDMS networks were prepared using low polydispersity PDMS polymers synthesized from hexamethyl cyclotrisiloxane. [9-11] The narrow molecular weight distribution resulting from this particular polymerization method 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 tetrafunctionalized hydrosilylation crosslinker was accurately controlled (somewhat more than stoichiometric ratio) in order to yield more complete crosslinking and thus optimal elastic behavior, as in the process developed by Patel et al. [12] PDMS lenses were prepared by allowing the polymer droplets to crosslink in a heated vacuum desiccator for 3 days as described by Perutz et al. [13]

Self-assembled monolayers (SAMs) prepared on the surface of gold from functionalized thiols were used as molecularly engineered surfaces with different chemical functionality. These thiol monolayers on gold are especially suited for studies of adhesion because of the possibility of fine-control of diverse surface functional group structure and concentration since it is relatively easy to functionalize and purify thiols compared to other precursors such as chlorosilane derivatives. In addition, SAMs of thiols on gold have well-characterized homogeneous and close-packed structure with strong chemical and thermal stability. In this study, we have used SAMs of $HS(CH_2)_2(CF_2)_9CF_3$, $HS(CH_2)_{15}COOH$, $HS(C_6H_4)_2CH_3$, and $HS(C_6H_4)_2$ F on gold following the procedure described elsewhere [14-16].

RESULTS AND DISCUSSION

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. In the JKR experiment, adhesion hysteresis means that some irreversible transformation has taken place on contact. This transformation may be a simple dissipative mechanical—i.e., strain, stress— relaxation in the PDMS elastomer, a chemical interaction at the interface due to existing or migrating functional groups, unreacted PDMS chains that segregate to/from the interface, and interpenetrating unreacted PDMS chains (only when the other material is also a polymer). An example for a chemical interaction across the interface is the formation of H-bonds (see below.) Since studies are focused on understanding of the chemical foundation of adhesion, it is important that adhesion hysteresis is understood.

Many authors have investigated the origin of adhesion hysteresis in the JKR experiments and attributed them to different effects such as irreversible chemical interaction between surface molecular groups [2], reorganization, entanglement, or interdigitation of surface molecular chains [8,17], viscoelastic energy loss due to plastic deformation of the elastomer [18], heat dissipation, and contact history [17]. In our effort aimed at decoupling different sources of hysteresis (whether chemical, mechanical, or kinetic, etc.) we first carried out the JKR experiments of self-adhesion of PDMS using two identical surfaces in order to eliminate the chemical effect on the adhesion so that observed hysteresis can be related to other effects. When continuous loading and unloading were carried out, the system was hysteretic as shown in Figure 1. However, if loading and unloading were carried out in steps, allowing the system to approach "quasi-equilibrium" after each step (for 5 min), the hysteresis apparently disappeared. We believe that the process responsible for the observed hysteresis in the continuous loading experiment was the incomplete (and thus dissipative) mechanical relaxation of the PDMS crosslinked network because it takes a finite length of time for the change of mechanical potential energy (applied by the load) to be balanced against those of elastic energy and surface adhesion energy. This experiment provided a procedure in which we can eliminate any mechanical effect on the observed hysteresis; all our experiments utilized this step-wise loading and unloading protocol. When the JKR equation (1) was used to fit the equilibrium data of PDMS self-adhesion in order to estimate the parameters W and K using the least square method, W came out to be $42 mJ/m^2$ which is approximately twice the surface free energy of PDMS commonly determined from the contact angle measurements and in adequate agreement with previous investigators' works [2, 19].

We have repeated the experiment with PDMS hemispheres of different molecular weights, utilizing step-wise loading and unloading, and did not observe any hysteresis (Figure 2). When the data was fitted to the JKR equation, the work of adhesion for rubbers with MW between 15K and 68K was 42 ± 1 mJ m^{-2}, in agreement with the expected value of 42 mJ m^{-2}. These hemispheres allow the systematic investigations of adhesion and adhesion

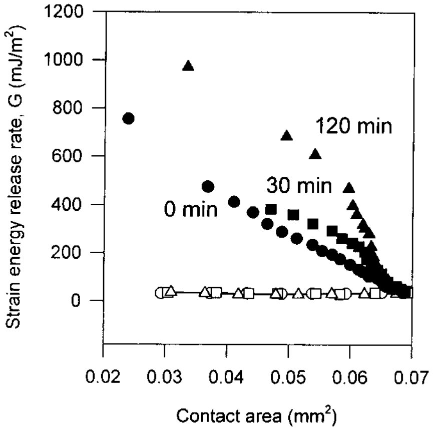

Figure 9. Strain energy release rate vs. contact area for the H-bonding interaction between PDMS and Si-OH on SiO_2/Si. Hollow and filled symbols indicate loading and unloading data, respectively.

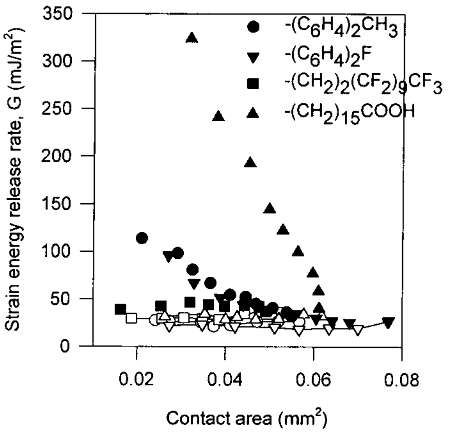

Figure 10. Strain energy release rate vs. contact area for the interaction between PDMS and various SAMs. Hollow and filled symbols indicate loading and unloading data, respectively.

REFERENCES

1. K.L. Johnson, K. Kedall, and A.D. Roberts, Proc. R. Soc. London Ser. A **324**, 301 (1971).
2. M.K. Chaudhury and G.M. Whitesides, Langmuir **7**, 1013 (1991).
3. M.K. Chaudhury and G.M. Whitesides, Science **255**, 1230 (1992).
4. M.K. Chaudhury, J. Adhes. Sci. Technol. **7**, 669 (1993).
5. B. Zhang Newby, M.K. Chaudhury, and H.R. Brown, Science **269**, 1407 (1995).
6. P. Silberzan, S. Perutz, E. Kramer, and M.K. Chaudhury, Langmuir **10**, 2466 (1994).
7. H.R. Brown, Annual Rev. Mater.Sci. **21**, 463 (1991).
8. W.W. Merill, A.V. Pocius, B.V. Thakker, and M. Tirrell, Langmuir **7**, 1975, (1991).
9. C.L. Lee, C.L. Frye, and O.K. Johnson, Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem. **10**, 1361 (1969).
10. C.L. Lee and O.K. Johnson, J. Polym.Sci.: Polym. Chem. Ed. **14**, 729 (1976).
11. C.L. Lee, U.S. Patent No. 3 445 426 (1969).
12. S.K. Patel, C. Malone, J.R. Cohen, J.R. Gilmore, and R.H. Colby, Macromolecules **25**, 2541 (1992).
13. S. Perutz, J. Wang, C.K. Ober, and E.J. Kramer, 1996 ACS Meeting Proceedings, 45 (1996).
14. A. Ulman, S.D. Evans, Y. Shnidman, R. Sharma, J.E. Eilers, and J.C. Chang, J. Am. Chem. Soc. **113**, 1499 (1991).
15. A. Ulman, Ultrathin Organic Films: From Langmuir-Blodgett to Self Assembly (Academic Press, Boston, 1991).
16. A. Ulman, Chem. Rev. **96**, 1533 (1996).
17. Y.L. Chen, C.A. Helm, and J.N. Israelachvili, J. Phys. Chem. **95**, 10736 (1991).
18. R.G. Horn, J.N. Israelachvili, and F. Pribac, J. Colloid Interface Sci. **115**, 480 (1987).
19. M.K. Chaudhury, Materials Science and Engineering **R16**, (19) No. 3, (1996).
20. D. Maugis and M. Barquins, J. Phys. D: Appl. Phys. **11**, 1989 (1978).