

Isotope Effect in Adhesion

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We report the first observation of an isotope effect in adhesion. A significant increase in adhesion hysteresis was observed when the OH groups at the $-\text{Si}-\text{OH}$ and $-\text{P}(\text{O})(\text{OH})_2$ surfaces were replaced by OD groups. Our observations support the mechanism of H-bonding with PDMS chains, and also confirm that dissipative processes dominate adhesion and adhesion hysteresis behavior.

Adhesion is one of the most ubiquitous phenomena in nature that governs many practical processes. It is a complex, multifaceted phenomenon that involves factors such as surface chemistry and thermodynamics, polymer chemistry and physics, hydrodynamics and mechanics. Hydrogen bonding (H-bonding) at an interface between two materials enhances their adhesion¹ and results in a significant increase in adhesion hysteresis.²

We investigated adhesion using the contact deformation mechanics method (JKR) developed by Johnson, Kendall, and Roberts.³ This experimental method is based on an equilibrium contact mechanics analysis of the stresses between elastic curved bodies under load, accounting for the thermodynamic work of adhesion. It has been widely used for the direct estimation of the work of adhesion using different elastic surfaces.⁴ The radius of contact, a , between an elastic sphere and a flat rigid surface at equilibrium is described by

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

where R is the radius of the sphere, P is the applied load at the contact interface, K is the effective elastic constant at the interface, and W is the thermodynamic work of adhesion between two surfaces.

The JKR apparatus used in these studies is based on a Nikon microscope equipped with vertical illumination that allows the use of opaque substrates without the loss of image sharpness. The instrument is placed on a vibration isolation table and is housed in a polycarbonate enclosure. The sample and PDMS lens are enclosed in a plastic box, which is equipped with humidity and temperature sensors that allows continuous control of relative humidity and temperature. The PDMS hemisphere is placed at the end of the cantilever using a tape-spring, which acts to further reduce vibration instability. The lens can be pressed on or released from the sample surfaces by the controlled movement of a micromanipulator that holds the lens, and is connected to a speed-controlled stepper-motor. The load at the interface is measured by an electrobalance, and a charge-coupled device (CCD) camera connected to the computer captures the

contact image. The image of the contact area is analyzed using NIH software, with uncertainty of <5%.

Cross-linked PDMS networks were prepared from low polydispersity PDMS polymers with vinyl end-groups synthesized from hexamethyl cyclotrisiloxane.⁵ The narrow molecular weight distribution resulting from this particular polymerization method allows us to create model networks containing almost no defects and only a tiny amount of unreacted chain ends, and thus nearly ideal elastic behavior, as in the process developed by Patel et al.⁶ PDMS hemispheres were prepared by allowing the cross-linker-mixed polymer droplets on perfluoroalkylsilane-treated glass slide to cure in a heated (60 °C) vacuum desiccator for 3 days, similar to procedures used in previous investigations.^{2,4a,7}

Silicon wafers were cleaned in hot $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution at 80 °C for 20 min, rinsed with distilled water, dried under N_2 , and kept immersed in clean water until used. Phosphonic acid surfaces were prepared by self-assembly of 11-mercaptoundecane phosphonic acid [$\text{HS}(\text{CH}_2)_{11}\text{PO}(\text{OH})_2$], on gold substrates. Gold substrates were prepared by the evaporation of gold onto preheated (300 °C) glass slides under high vacuum (10^{-7} Torr). Prior to adsorption, the gold substrates were cleaned in an Ar plasma reactor (~ 1 Torr) for 30 s. The substrates were immersed in 0.1 mM thiol solution in ethanol for several hours, then washed with fresh ethanol and distilled H_2O , and dried with N_2 . The thickness estimated by ellipsometry was 15 ± 1 Å, and the contact angle for distilled H_2O was $\leq 20^\circ$.

We created a D_2O atmosphere during the JKR experiment by bubbling N_2 through D_2O (Aldrich) and introducing it into the box housing the OH surface and PDMS hemisphere. By changing the volume of the nitrogen bubbled, we could control the relative humidity (RH). Typically, purging with D_2O -saturated N_2 continued for 90 min before the loading started, and was continued throughout the experiment. Experiments under H_2O and D_2O atmospheres were carried out at the same RH, with identical preparation procedures and with PDMS lenses with as identical an R as possible.

Deuterated silanol surfaces were prepared in two ways. In the first, the clean silicon wafer was immersed in D_2O for 16 h. In the second, the wafer was immersed in 37% DCl in D_2O (Aldrich) for 30 s to catalyze H/D exchange and then was

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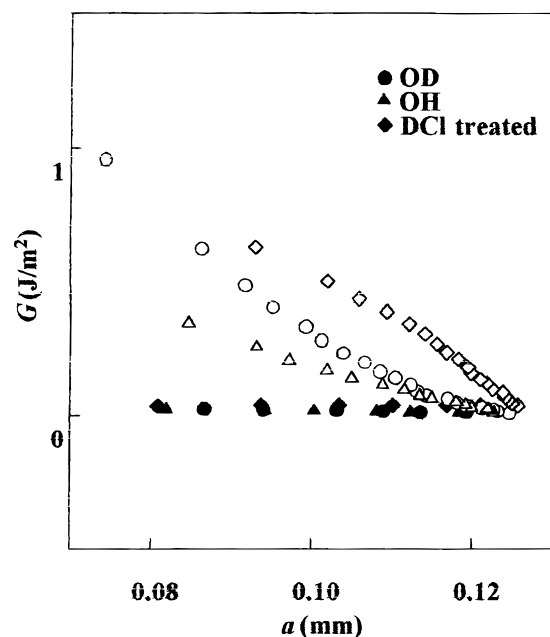


Figure 1. Energy release for loading (closed symbols) and unloading (open symbols) processes for 68 K PDMS hemispheres on Si-OD and Si-OH surfaces, with 0 min waiting at maximum loading.

washed thoroughly with D₂O and left immersed in D₂O for 16 h. We believe that this process ensures that the electrostatic state of the two Si-OD surfaces are comparable and that a difference in adhesion will not result from, for example, charge on either surfaces due to protonation or deprotonation. Deuterated phosphonic acid surfaces were prepared by leaving the monolayer immersed in D₂O for 16 h. In both cases, the substrate was briefly dried with nitrogen, and immediately introduced into the high-humidity box in the JKR apparatus.

We have argued before⁷ that adhesion between PDMS cross-linked networks and SiO₂ surfaces is strongly affected by the formation of H-bonds between surface Si-OH groups and PDMS Si-O-Si moieties. To date, there has been no *direct* observation of such H-bonds using, for example, infrared spectroscopy. However, if substitution of the surface OH groups with OD groups significantly affects adhesion energy, it will provide support for the H-bonding mechanism.

Because adhesion processes are hysteretic and dissipative in nature, no matter how slowly the crack propagates, the chains in the vicinity of the crack tip must stretch before they detach. The detachment of an individual chain should be rapid and irreversible, and a substantial portion of the energy stored in the stretched chain (prior to detachment) will be lost in the process. Therefore, the work done on separating two surfaces from adhesive contact is larger than that released when these surfaces come into contact; that is, $\Delta W = (W_U - W_L) > 0$, where W_U and W_L are the adhesion energies for unloading and loading two solid surfaces, respectively.

Another source of adhesion hysteresis are the irreversible transformations that take place on contact and result in structural reorganization of the interface. In the present case, these are H-bonds formed between surface Si-OH groups and PDMS Si-O-Si moieties.⁷ There have been many studies of adhesion hysteresis;^{2,4a,8} however, there is still no clear understanding of the complex bulk and surface phenomena that determine adhesion hysteresis, as well as of their relative importance. An especially intriguing question is whether the difference between H- and D-bonds is large enough to result in observable differences in adhesion hysteresis.

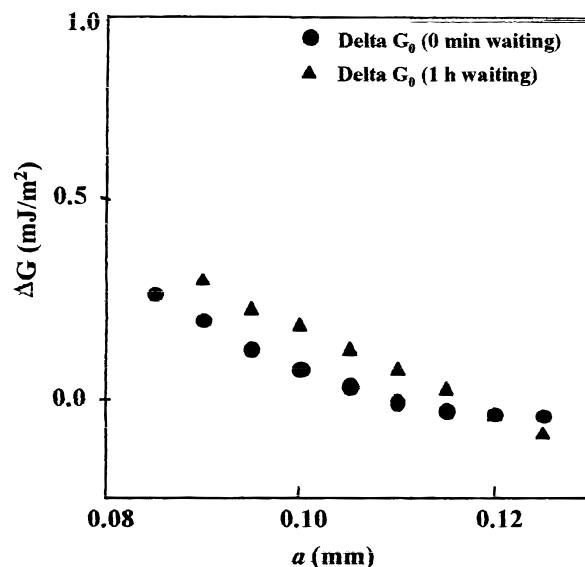


Figure 2. Difference in energy release in the experiments with and without a 1-h waiting period.

We were intrigued by the observation that adhesion of cross-linked PDMS networks to silanol surfaces exhibits a time-dependent hysteresis.⁷ When experiments were carried out with different dwell time at the same maximum load, adhesion hysteresis increased significantly with the increasing contact time. We attributed the hysteresis to H-bonding between the naturally present surface Si-OH groups on the silicon wafer and the Si-O-Si groups of the PDMS. The number of interfacial H-bonds increases with time, due to pressure-induced reorganization of the PDMS network near the interface, which brings the Si-OH and Si-O-Si groups into a capture range. We also observed that during the waiting period, the load measured by the balance decreased continuously with no apparent change in the contact area. This result is a signature of the increasing adhesion due to increased number of H-bonds. Thus, as the adhesion energy increases, a smaller applied load is required to balance the elastic stresses for a given contact area.

Figure 1 shows plots of the energy release, G , as a function of the contact radius a . The elastic constants determined from the loading process were used to calculate the energy release for the unloading process according to eq 2.

$$G = \frac{(a^3 K/R - P)^2}{6\pi K a^3} \quad (2)$$

Figure 1 shows that Si-OD surfaces exhibit a significantly larger adhesion hysteresis compared with their Si-OH counterparts in experiments carried out in 70–80% RH. Moreover, the Si-OD surfaces formed by the DCl treatment show an even larger hysteresis than those treated with HCl, suggesting that the procedure results in a more efficient H/D exchange and/or hydrolysis of siloxane bonds at the surface. We repeated the experiment but kept the system under maximum load for 60 min before the start of unloading. Figure 2 presents the difference in energy release ($\Delta G = G_{OD} - G_{OH}$) in the experiments with and without a 1-h waiting period. This result is in agreement with the suggested time-dependent, pressure-induced reorganization of the PDMS network at the interface.

The previous experiments were carried out using the stepwise protocol, with 5-min dwell time between each loading and unloading step. This protocol does not allow plotting energy

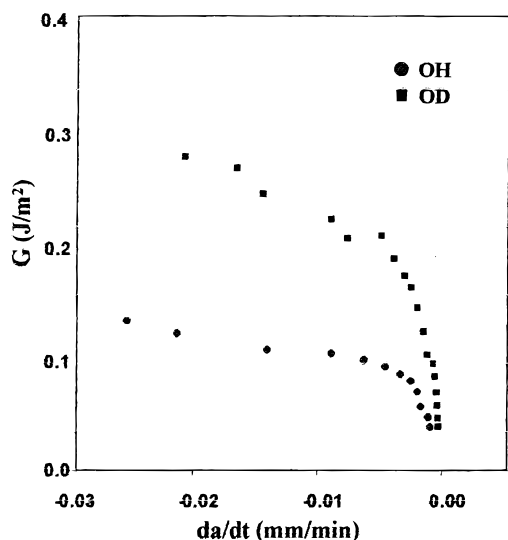


Figure 3. Energy release for unloading processes for 68 K PDMS hemispheres on Si-OD and Si-OH surfaces at 40% RH. Loading and unloading rate was 4.5 $\mu\text{N/s}$.

release as a function of the crack propagation rate da/dt . We have repeated the experiments using the continuous mode (with loading and unloading rate of 4.5 $\mu\text{N/s}$). The results are presented in Figure 3. Clearly, the isotope effect is very significant, substantiating the proposed H-bonding interactions between the PDMS and Si-OH(D) surfaces. Yet, there is a possibility that the observed isotope effect is the result of a difference between surface Si-OH and Si-OD concentrations, resulting from differences in SiO_2 reaction rates with H_2O and D_2O . Thus, experiments must be carried out where surface concentration of OH and OD groups is the same.

It was shown before, that the adhesion energy between a self-assembled monolayer (SAM) surface and a PDMS cross-linked network is a function of both surface acidity and the number of H-bonding donor and acceptor moieties.⁹ Because SiO_2/Si surfaces do not provide systematic control of the number of surface acidic groups, we turned to phosphonic acid surfaces formed by the self-assembly of 11-mercaptoundecyl phosphonic acid on Au(111).¹⁰ The experiment was carried out at 90% RH, using a 48 K PDMS cross-linked hemisphere. Figure 4 shows that the difference between adhesion to -OD and -OH surfaces is significant.

The magnitude of the isotope effect in the two systems reported here is quite remarkable considering the strength of the H-bonding interactions. Chaudhury and co-workers¹¹ have measured the interaction between a single PDMS chain and a Si-OH group using atomic force microscopy (AFM). Their results suggest that the strength of a single H-bond between silanol and siloxane groups is 1.5 kT or 3×10^{-3} Kcal mol^{-1} . They also used calorimetry to measure the heat of adsorption of PDMS on silica gel and found energies in the range 130–150 millicalories g^{-1} or 16 mJ m^{-2} . Yet, the strength of adhesion measured and the isotope effect observed in our studies are orders of magnitude larger. We believe that this difference is because adhesion between PDMS and an OH surface cannot be understood based on the energy of individual interactions, because of the collective nature of the interfacial interactions associated with the PDMS chains. Moreover, the energy release, G , represents predominantly dissipative processes, such as the elastic energy associated with the stretching of polymer chains at the crack tip during crack propagation, and the energy associated with the deformation of the PDMS network as a result

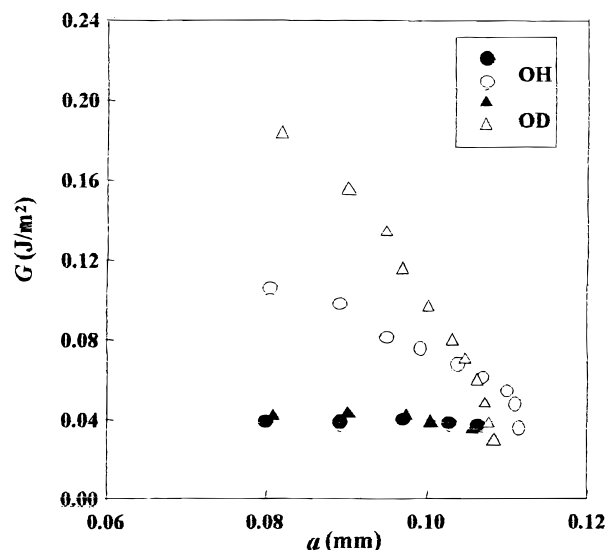


Figure 4. Energy release rate for loading (closed symbols) and unloading (open symbols) processes for 48 K PDMS hemispheres on deuterated and on protonated phosphonic acid surfaces, using the stepwise loading and unloading mode.

of interfacial interactions. It can be expected that these energies scale with interfacial interactions.

In the stepwise loading and unloading protocol used in some of the experiments,⁷ a change in an external force—both on loading and on unloading—imposes a new equilibrium state for the system that is characterized by a global minimum in its free energy. This global minimum is a function of molecular interactions and configurations and of temperature, on an atomistic level, or of elastic deformations, surface contact energies, and separations at the crack tip, in a continuum mechanics theory such as JKR. The system then strives to relax toward the new equilibrium state, dissipating energy in the process. The relaxation time to attain this new equilibrium state depends on the difference between the initial and new states of the system and on its interactions and coupling to external reservoirs. In the next step, the force is adjusted again, defining still another equilibrium state, and so on.

Upon loading, the external forces and the surface attractive forces are synergetic at the crack tip, leading to relatively small relaxation times. For slow enough loading steps, the system will thus trace a succession of states that 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 strong short-range surface attractive forces resulting from H-bonding are antagonistic. This antagonism leads to a higher barrier in the equilibrium free energy as a function of deformation, which also depends on the system interactions and temperature. Upon unloading, this higher barrier leads to relaxation times significantly longer than the time steps, and hence the system may not attain an equilibrium state at the end of each time step. Then a sequence of nonequilibrium states at nonminimal values of the free-energy function at each time step results, giving rise to the irreversible force-separation unloading curve and adhesion hysteresis. This situation also explains why adhesion hysteresis increases with a faster variation of the force or with longer relaxation times.

Eyring's theory of rate processes suggests that the relaxation time is inversely proportional to the transition rate for escaping over the free-energy barrier, which is a product of an atomic or molecular vibrational frequency and an Arrhenius-type thermal activation rate.¹² This type of vibrational frequency depends on

molecular interactions and configuration. Hydrogen-bonding interactions may amplify the free-energy barriers for adhesion by strongly affecting the conformational entropy of the PDMS chains at the interface. Vibrational frequencies of OH and OD bonds exhibit a strong isotope effect and are also strongly sensitive to the presence of H-bond networks at higher surface concentrations of OH and OD groups. These phenomena are also evident in the Smoluchowsky and Fokker–Planck versions of the mean-field molecular dynamics equations, where the atomic relaxation times are proportional to their mass and sensitive to their environment.¹³ Upon further unloading, the breaking of the H-bonds is followed by an even slower relaxation of the polymer network to a new equilibrium state, which explains the large curvature of the unloading curves in such systems and tends to magnify their adhesion hysteresis even further.

In conclusion, we report here the first observation of an isotope effect in adhesion. A significant increase in adhesion hysteresis was observed when the OH groups at the $-\text{SiOH}$ and $-\text{P}(\text{O})(\text{OH})_2$ surfaces were replaced by OD groups. Our observations clearly support the mechanism of H-bonding with PDMS chains, and also confirm that dissipative processes dominate adhesion and adhesion hysteresis behavior. Experiments carried out using the stepwise and continuous loading and unloading protocols lead to similar conclusions.

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