

# Adhesion Hysteresis and Friction

Manoj K. Chaudhury\* and Michael J. Owen

Dow Corning Corporation, Midland, Michigan 48686

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The kinetic friction forces between semispherical lenses of elastomeric poly(dimethylsiloxanes) (PDMS) and chemically modified mica surfaces were measured at a low sliding speed (0.02 mm/s). The surface of mica was modified using self-assembled monolayers of alkyl- and fluoroalkylsilanes. Even though the surface free energy of the fluorocarbon monolayer is lower than that of the hydrocarbon monolayer, its friction against PDMS was found to be greater than that of the hydrocarbon monolayer. The values of the friction forces do, however, follow the same general trend as the hysteresis of adhesion between PDMS and the monolayer-coated mica surfaces. This study provides evidence that the hysteresis of adhesion is an important consideration for understanding friction between surfaces.

In the tribological studies of both polymer on polymer<sup>1</sup> and metal on polymer<sup>2</sup> there is a general trend for a solid of higher surface free energy to have a higher friction than one of lower surface free energy. There are, however, exceptions to this generalization. Briscoe and Evans<sup>3</sup> as well as DePalma and Tillman<sup>4</sup> observed that the friction forces of the fluorocarbon monolayers are higher than those of the hydrocarbon monolayers despite fluorocarbons having lower surface free energies<sup>5</sup> than hydrocarbons. The objective of this study is to point out the parallelism that exists between the anomalous tribological properties of fluorocarbon monolayers with another interfacial phenomenon—adhesion hysteresis.

The adhesion hysteresis<sup>6</sup> between solid elastic materials has some features that are common to the hysteresis of contact angles. If a semispherical solid is brought into contact with another flat surface, the interfacial forces operating across the interface tend to deform the solids and thus increase their area of contact.<sup>7</sup> If the elastic forces of the materials are known, the adhesion energies between the two surfaces can be determined using the theory of Johnson, Kendall, and Roberts.<sup>7</sup> In a typical experiment of adhesion hysteresis,<sup>6</sup> the adhesion energies are first determined from the compressive loads followed by the decompressive loads. Compressive load-deformation experiments are analogous to the advancement of a liquid drop on a solid surface, because in both cases the interfacial areas continue to increase. By comparison, the decompressive load-deformation experiments are analogous to the retraction of a liquid drop from a solid surface. Like the hysteresis in wetting, the adhesion energies obtained from the compressive loads are not always the same as those obtained from the decompressive loads—there is generally a finite hysteresis in adhesion energies. Plastic deformations,<sup>8</sup> disentanglement and orientation of the polymer chains,<sup>9</sup> and partial interdigitation<sup>6,10</sup> of the surface functional groups are thought to be the possible causes of adhesion hysteresis for elastic materials.

Studies<sup>6</sup> of adhesion between thin monolayer films of fluorocarbon and hydrocarbon, supported on elastomeric poly(dimethylsiloxane) (PDMS), showed that the adhesion hysteresis for the fluorocarbon monolayers was significantly higher than that of the hydrocarbon monolayers. Since friction between surfaces arises from the same types of dissipative processes as those that cause adhesion to be hysteretic, the two phenomena should be formally related. Unfortunately, no simultaneous measurements of adhesion hysteresis and friction have so far been made to validate the above hypothesis. In what follows, we describe an experimental protocol, using deformable lenses of PDMS and flat films of mica, that allowed simultaneous measurements of friction and adhesion hysteresis using the same systems, thus providing a basis to test the interrelationship between the two interfacial phenomena.

The experimental system consisted of semispherical lenses of elastomeric poly(dimethylsiloxane) (PDMS)<sup>11</sup> and surface-modified muscovite mica. The friction forces were measured under sliding modes using a modified version (Figure 1) of an apparatus reported in ref 6. The surface of mica was modified<sup>12</sup> by chemisorption of  $\text{Cl}_3\text{Si}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{Cl}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$ . X-ray photoelectron spectroscopy verified the presence of the relevant functional groups on the monolayer-coated mica surfaces. The advancing contact angles of hexadecane on the fluorocarbon and hydrocarbon monolayers were 80° and 48°, respectively. The friction forces were measured by bringing small semispherical lenses of PDMS ( $R \approx 1.4$  mm) with a flat mica film (thickness  $\approx 0.05$  mm) under zero normal load and then sliding the lens against mica at a speed of about 0.02 mm/s. The friction force was registered in the electrobalance that was connected to the mica in a cantilever beam configuration. The area of contact was viewed through a microscope using transmission optics and recorded in a video monitor. The fine positioning of the PDMS lens was controlled with an electrically driven micromanipulator.

In the sliding experiments, the contact area between the PDMS lens and the fluorocarbon monolayer was slightly less circular than that of the hydrocarbon monolayer. Although, the deviation of the area of contact from

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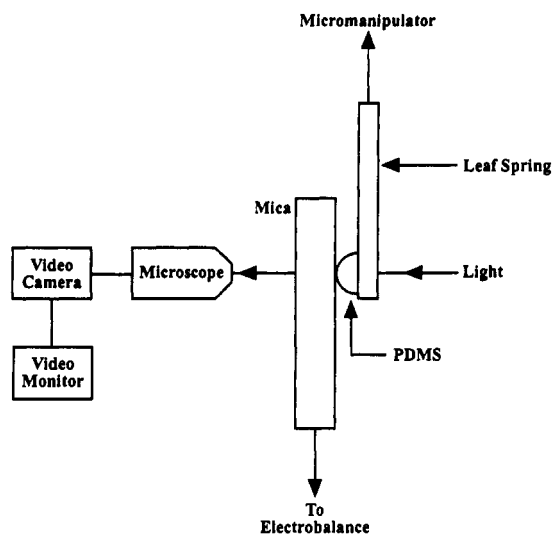
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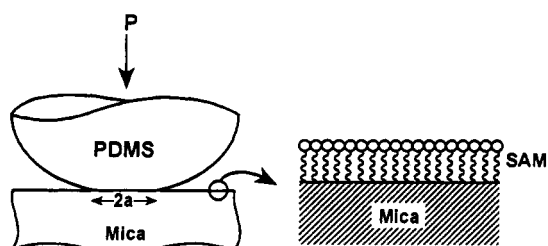
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(11) PDMS used in the friction and adhesion experiments was synthesized with a commercially available kit (Dow Corning Sylgard 184, Midland, MI). The cross-linking density of this rubber is about  $10^{-4}$  mol/cm<sup>3</sup>.

(12) The conditions used to modify the surface of mica were the same as those reported in Chaudhury, M. K.; Whitesides, G. M. *Science* 1992, 255, 1230. Although the alkylsiloxane monolayers on mica were not hydrolytically as stable as those prepared by Kessel and Granick (Kessel, C. R.; Granick, S. *Langmuir* 1991, 7, 532), they were quite stable in the nonpolar environments and suitable for the mechanical tests reported in this paper.



**Figure 1.** Schematic diagram of the apparatus used to measure friction force between PDMS and mica.



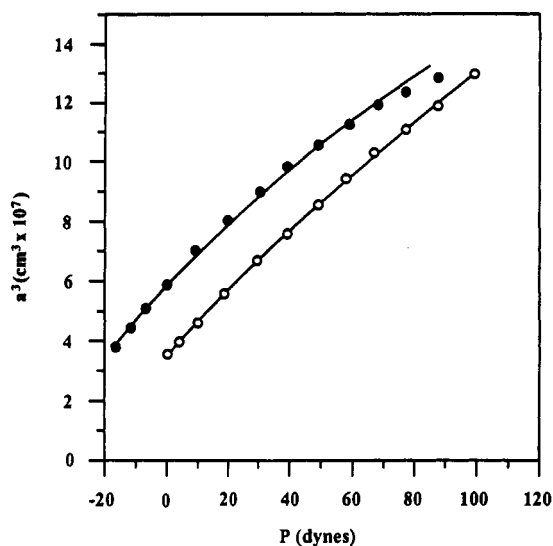
**Figure 2.** Schematic diagram of the apparatus used to measure adhesion hysteresis. For clarity the area of contact is exaggerated.

circularity is itself a measure of adhesion hysteresis, its magnitude was determined separately according to the method described in ref 6. In a typical experiment of adhesion hysteresis, the PDMS lens ( $R = 0.9$  mm) was brought slowly into contact with the monolayer-coated mica, and an external load was then applied (Figure 2). The contact deformation resulting from the contact between the PDMS lens and mica increased in response to the external loads. Deformations were measured soon (10–15 s) after the loads were varied. At the end of the compressive cycle, the load was decreased stepwise and contact deformations were measured again until the lens completely separated from the mica. All of these measurements were made under ambient conditions with the temperature of the laboratory at 23 °C and the relative humidity at 50%. The data obtained from these load-deformation studies were analyzed according to the theory of Johnson, Kendall, and Roberts<sup>7</sup> to estimate the adhesion energies ( $W$ )

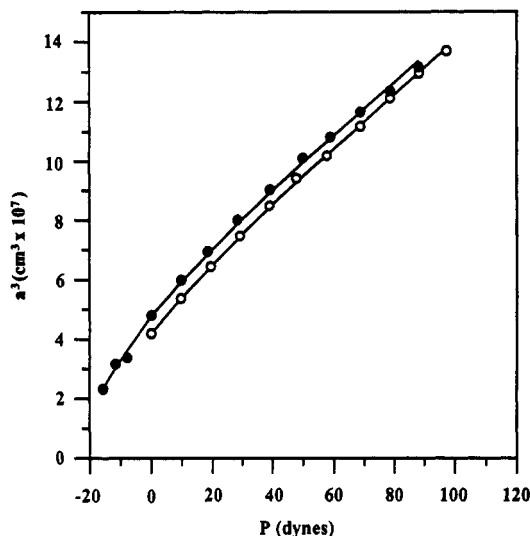
$$a^3 = (R/K) \{P + 3\pi RW + [6\pi RPW + (3\pi RW)^2]^{0.5}\} \quad (1)$$

In this equation,  $a$  (cm) is the radius of the contact deformation,  $R$  (cm) is the radius of curvature of the lens,  $P$  (dyn) is the external load, and  $K$  (dyn/cm<sup>2</sup>) is the composite modulus. In our studies, the values of  $K$  clustered around  $1.5 \times 10^7$  dyn/cm<sup>2</sup>, the magnitude of which ensured that all the deformation occurred in the polymer during the contact of the PDMS lenses with mica.

The normalized friction force (interfacial shear strength) for the PDMS–fluorocarbon monolayer was found to be  $21.4 (\pm 0.7) \times 10^5$  dyn/cm<sup>2</sup>, which is significantly higher than the value  $(4.6 (\pm 0.2) \times 10^5$  dyn/cm<sup>2</sup>) obtained for the PDMS–hydrocarbon monolayer. These values of the friction forces do not follow the trend of surface free



**Figure 3.** Adhesion hysteresis between PDMS and fluoroalkylsiloxane monolayer. The open circles represent the data obtained from compressive loads and the closed circles represent the data obtained from decompressive loads. The solid lines in both plots are predicted from eq 1. The adhesion energies obtained from the compressive and decompressive loads are  $32.2 (\pm 1.4)$  and  $62.7 (\pm 6.1)$  ergs/cm<sup>2</sup>, respectively.



**Figure 4.** Adhesion hysteresis between PDMS and alkylsiloxane monolayer. The open and closed circles represent the data obtained from the compressive and decompressive loads, respectively. The solid line is as predicted from eq 1. The adhesion energies obtained from the compressive and decompressive loads are  $38.4 (\pm 1.3)$  and  $45.6 (\pm 3.7)$  ergs/cm<sup>2</sup>, respectively.

energies<sup>13</sup>—the surface free energy of a fluorocarbon–air interface (9.5 ergs/cm<sup>2</sup>) as obtained from the contact angle is significantly lower than that of the hydrocarbon–air interface (19.3 ergs/cm<sup>2</sup>). Lower surface free energy of the fluorocarbon surface would imply lower adhesion with PDMS than that of the hydrocarbon surface—this supposition is based upon the geometric mean combining rule<sup>13</sup> of adhesion energies for dispersive systems. However the load deformation experiments (Figures 3 and 4) show a mixed story. While the adhesion energy (32.2 ergs/cm<sup>2</sup>) between PDMS and the fluorocarbon monolayer as obtained from the compressive part of the loading-

(13) The surface free energies of the monolayer-coated mica were determined from the contact angles of hexadecane and using the equation of Good, Girifalco, and Fowkes. Girifalco, L. A.; Good, R. J. *J. Phys. Chem.* 1957, 61, 904; Good, R. J.; Girifalco, L. A. *J. Phys. Chem.* 1960, 64, 561; Fowkes, F. M. *Ind. Eng. Chem.* 1964, 56, 40.

unloading cycle is actually slightly lower than that (38.4 ergs/cm<sup>2</sup>) of the PDMS-hydrocarbon monolayer, the decompressive adhesion energies follow the opposite trend.<sup>14</sup> The decompressive adhesion energies of the fluorocarbon and hydrocarbon monolayers follow the similar trend observed in friction. Because of the higher decompressive adhesion energy (62.7 ergs/cm<sup>2</sup>) the fluorocarbon monolayer is expected to have higher friction than the hydrocarbon monolayer, for which the decompressive adhesion energy is found to be 45.6 ergs/cm<sup>2</sup>. However, the ratio of these two adhesion energies is only about 1.37, which is much smaller than the ratio (4) of the friction forces for these two surfaces. While it is premature to make any quantitative comparison between friction forces and adhesion energies, we believe that the adhesion energies alone are insufficient to explain large differences in the frictional properties of the two monolayer surfaces. The magnitude of the adhesion hysteresis relates directly to the dissipation of interfacial energy during a contact and separation process, which should be relevant to frictional dissipation. Adhesion hysteresis may also be relevant to friction in the following way. The contact line produced at the intersection of PDMS, monolayer, and air can be pinned if hysteresis of adhesion persists. We observed that the contact line deforms for hysteretic surfaces much like the deformation of the triple phase contact line of a liquid drop on a hysteretic surface. This kind of line pinning and line deformation will cause an additional resistance to motion and thus higher friction. This resistance, in analogy to the hysteresis of wetting, will be a direct function of adhesion hysteresis. This extra resistance will be absent for systems that show no adhesion hysteresis, in which case, friction should primarily be a function of adhesion energy.

Adhesion hysteresis implies that the interface is in a nonequilibrium state, the origin of which may be due to partial interdigitation of the surface functional groups or other types of reconstructions of the surface structure. Early studies of Timmons and Zisman<sup>15</sup> indicated that the fluoroalkyl chains do not pack well into a condensed

film. It was shown that the hysteresis of the contact angles of liquids on fluorocarbon monolayers is a simple function of their molecular volumes. For example, the hysteresis (23°) of diiodomethane, whose molecular volume is 80.5 cm<sup>3</sup>/mol and which can penetrate more easily into the fluorocarbon film, is significantly higher than that (1°) of hexadecane, whose molecular volume is 292.6 cm<sup>3</sup>/mol. We found, in our studies with surface modified mica, that the hysteresis of contact angle of diiodomethane (35°) on the fluorocarbon monolayer is significantly higher than that (1°) on the hydrocarbon monolayer. These results concur with those of Timmons and Zisman.<sup>15</sup> We also found that the hysteresis (12°) of a liquid poly(dimethylsiloxane) (MW 5000) on the fluorocarbon monolayer was significantly higher than on the hydrocarbon monolayer (1°). These results of wetting hysteresis as well as the results of adhesion hysteresis indicate that the PDMS molecules penetrate into the fluorocarbon monolayer but not into the hydrocarbon monolayer, which might explain the abnormal tribological properties of the fluorocarbon monolayers against PDMS.

While a model of hysteresis based on the interdigitation of surface functional groups seems feasible for smooth and compliant materials, there may be cases where hardness and roughness of the materials might exclude such a possibility. For the contact of hard solids, it is not clear to what extent the adhesion hysteresis persists and how it is manifested. Examples of adhesion hysteresis for hard solids have, however, been provided by Burnham et al.<sup>16</sup> These authors reported significant hysteresis in the adhesion of a tungsten AFM tip with surface-modified alumina. We believe that a comprehensive study of adhesion and friction using AFM and the macroscopic measurements, of the type discussed here, will be valuable in understanding the molecular origin of adhesion hysteresis as well as friction.

The systems chosen in these studies were such that the sliding occurred smoothly. We have other observations, where sliding took place in a stick-slip fashion. Significant distortions of the contact circle—indicative of strong line pinning—could also be found when stick-slip occurred. The correlation between adhesion hysteresis and stick-slip behavior is currently being investigated.

(14) These adhesion hysteresis experiments were performed under quasi-static conditions. The friction experiments were however performed under dynamic conditions for which the contact time was about 5 s. The adhesion hysteresis observed at such time scales was about 34 and 5 ergs/cm<sup>2</sup> for the fluorocarbon and hydrocarbon surfaces, respectively. These values are similar to the values obtained from quasi-static measurements.

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