Direct Measurement of Interfacial Interactions between Semispherical Lenses and Flat Sheets of Poly(dimethylsiloxane) and Their Chemical Derivatives

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The deformations resulting on contacting small (1-2 mm) semispherical lenses of elastomeric poly-(dimethylsiloxane) (PDMS) with the flat sheets of this material were measured in air and in mixtures of water and methanol. The measurements in air were carried out in two ways: as a function of external loads, and under zero load but with variations in the sizes of the lenses. The measurements in liquids were carried out under zero load and varied the composition of the liquid mixtures. These experimental data were analyzed by using a theory of Johnson, Kendall and Roberts to obtain the works of adhesion between PDMS surfaces in the air and liquid media. The strength of interaction between PDMS surfaces decreased in mixtures of water and methanol as the concentration of methanol increased. A small interaction persisted even in pure methanol. The interfacial free energies (γ_{sl}) of the PDMS–liquid interfaces obtained from these measurements, together with the contact angles of these liquids on PDMS, were analyzed by using Young's equation. This analysis provided an estimate of the surface free energy of the polymer (γ_{sv}) that was consistent both with the value obtained from measurements made in air and with the value estimated from the analysis of the contact angles of nonpolar liquids on PDMS using the Good–Girifalco–Fowkes equation. This research also developed ways to modify the surface of PDMS chemically and thus to control its properties. The chemically derivatized poly(dimethylsiloxanes), in the form of lenses and flat sheets, were subjected to load-deformation measurements similar to those used for unmodified PDMS. These functionalized PDMS surfaces exhibited hysteresis in contact deformations, whereas no hysteresis was detected for unmodified PDMS. The origin of this hysteresis is not clear at present. The observation of hysteresis at solid–solid interfaces is relevant to understanding adhesion to these surfaces.

Introduction

A fundamental issue in surface science is to correlate macroscopic processes—wetting, adhesion, friction—occurring at surfaces with their molecular-level fine structures. Although the basic concepts of surface energetics were worked out by the physicists[1,2] of the 19th century, attempts to correlate energetics with the constitutive properties of surfaces gained major impetus only after Fox and Zisman.[3] Their attempts to correlate wetting with surface constitution stimulated Good and Girifalco[4] and Fowkes[5] to develop general semiempirical models for interfacial structure and energy. These models have been conceptually important in understanding liquid–liquid, liquid–solid, and solid–solid interfaces, but their quantitative aspects have gone largely unverified, mainly because thermodynamic parameters needed to test the models were not always accessible experimentally.

Liquid–liquid interfaces are the simplest to analyze thermodynamically, because the surface free energies of the pure components and their interfacial free energies can all be measured independently. The interfacial models proposed by Good, Girifalco, and Fowkes were thus tested with such systems. Solid–solid and solid–liquid interfaces are more difficult to characterize, because neither their interfacial free energies nor the surface free energies of the solids are readily measurable. Studies of wetting of solids by liquids provide estimates of the works of adhesion between the solids and liquids, from which predictions about the surface free energies of the solids can, at times, be made.[4,5] For direct estimation of the surface free energies of solids, one would, however, hope to examine solid–solid interfaces directly. If a convenient experimental protocol to examine solid–solid interfaces could be developed, systematic studies into relations between energetics and surface constitution could be carried out at the level employed by Zisman et al.[3,6] in their studies of liquid–solid interfaces. We show here how this goal can be achieved for elastomeric solids and demonstrate how these studies can complement the results obtained from conventional contact angle measurements. An experimental system applicable to studies of interactions between two elastomeric solids is not presently applicable to the broader problem of studying nonelastomeric materials. Nonetheless, these techniques provide a significant extension of classical surface chemistry to solids and should, with modifications, be applicable to many problems involving one elastomeric and one nonelastomeric component.

When a convex elastic solid comes into contact with another solid substrate, the adhesion forces, acting across the interface, tend to deform the solids and thus to increase the area of their contact. Since this deformation is opposed by the elastic restoring forces, its magnitude is small for solids of high moduli but measurable for solids of low elastic moduli, such as organic elastomers. Hertz first proposed the theory of contact between two elastic solids.[7] He calculated both the profile of the region of deformation and the distribution of stresses around the contact zone when an external load was applied. In this treatment, no

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(1) Young, T. *Miscellaneous Works*; Peacock, G., Ed.; Murray: London, 1855; 1.

(2) Gibbs, J. W. *Collected Works*; Longmans, Green: New York, 1906; Dover: New York, 1961; Vol. 1.

(3) Fox, H. W.; Zisman, W. A. *J. Colloid Sci.* 1950, 5, 514.

(4) Girifalco, L. A.; Good, R. J. *J. Phys. Chem.* 1957, 61, 904. Good, R. J.; Girifalco, L. A. *J. Phys. Chem.* 1960, 64, 561.

(5) Fowkes, F. M. *Ind. Eng. Chem.* 1964, 56, 40.

(6) Zisman, W. A. *Adv. Chem. Ser.* 1964, No. 43, 1.

(7) Hertz, H. *Gesammelte Werke*, Leipzig, 1895.

consideration was given to the effects of surface forces operating across the interfaces. Solid–solid deformation induced by the action of surface forces was successfully modeled first by Johnson, Kendall, and Roberts (JKR).[8] These authors assumed that the attractive forces were confined within the area of contact and used the principle of detailed energy balance to develop a general expression for the contact deformation as a function of the surface and elastic properties of the solid materials.

An alternate model was proposed by Derjaguin, Muller, and Toporov (DMT)[9] as an improvement of an earlier model proposed by Derjaguin,[10] where the assumption was made that all the attractive forces lay outside the area of contact and that the contact region was under compression described by the Hertzian strain profile. A full analysis of the problem of contact deformation was carried out more recently by Muller, Yushchenko, and Derjaguin,[11] who showed that both the JKR and DMT models are limiting cases of a more general situation. Horn et al. have discussed the differences between the various theories of deformation.[12] The analysis of Muller et al. showed that the DMT model applies to solids of high elastic moduli, whereas the JKR model applies to solids of low elastic moduli. Since our current studies are of a solid of low elastic modulus, the JKR model is more relevant for our purpose.

For the contact between two spherical solids, the JKR model predicts the radius (a) of contact deformation resulting from the joint influences of surface and external forces to be given by eqs 1–3

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

where

$$1/K = (3/4)\{(1 - \nu_1^2)/E_1 + (1 - \nu_2^2)/E_2\} \quad (2)$$

$$1/R = (1/R_1) + (1/R_2) \quad (3)$$

P is an external load; W is the work of adhesion; R_1 and R_2 are the radii of curvature of the two spheres. ν_1, ν_2 and E_1, E_2 are the Poisson ratios and elastic moduli of the two bodies. [Note: In this paper we use cgs units: P is expressed in dynes; a and R in cm; E and K in dyn/cm^2, and W in ergs/cm^2.] For contact between a sphere and a flat plate, the radius of curvature of the latter is infinity and R becomes the radius of curvature of the sphere. If the elastic modulus of one of the components is much larger than the modulus of the other component, the deformation will only be within the softer component. Thus, depending upon the values of R_1, R_2, E_1, and E_2, combination of a wide variety of materials can be described by eq 1.

In order to test eq 1, Johnson et al.[8] pressed together two optically smooth, rubber hemispheres and measured the area of contact as a function of applied load. These experiments were carried out in air, under water, and under a dilute detergent solution. The data obtained from these studies obeyed eq 1, from which the work of adhesion between the spheres could be determined. This study created an active interest among physicists,[12-17] who applied the concept to study the mechanistic aspects of such phenomena as adhesion, friction, and fracture and, in turn, provided further evidence in favor of eq 1. This technqiue has not, however, been properly exploited for surface chemical investigations, despite its potential for yielding surface thermodynamic parameters—surface free energies of solids (γ_{sv}), works of adhesion (W) at solid–solid interfaces, and interfacial free energies (γ_{sl}) at solid–liquid interfaces—complementary to those obtained from other conventional studies such as contact angle. Our current major aim is to correlate the surface thermodynamic parameters obtained from these types of measurements with the constitutive properties of the interfaces in order to develop an understanding of the chemistry of solid surfaces in general and of adhesion in particular.

A meaningful and systematic execution of such a study requires fulfilling the following stringent conditions. First, the surfaces of the deformable test materials must be very smooth and homogeneous. It must be possible to cast them into spherical or semispherical shapes, and—in order to vary their constitutive properties—it should be possible to modify their surfaces chemically without affecting their other physical properties. Fortunately, carefully prepared elastomeric poly(dimethylsiloxane) (PDMS) meets these specifications. The surface of this elastomer is very smooth; no features could be found by electron microscopic examination even at a resolution of 200–300 Å. The contact angles of nonswelling liquids (e.g. water and methanol) on PDMS exhibit negligible hysteresis (2°–3°), implying that the surface of PDMS is homogeneous. Stress-free polymers (qualitatively judged by examining them with a cross-polarized microscope) can be prepared in the form of convex lenses and flat sheets suitable for the load-deformation studies. We also developed convenient methods to modify the surfaces of these lenses and sheets chemically using the technology of self-assembled organic monolayers[18,19] as a means to vary and control their constitutive properties.

The basic experiment was to bring a semispherical lens and a flat sheet of PDMS into contact (Figure 1) and then to measure the resulting contact deformation under controlled loads. In what follows next, we first present results obtained for unmodified PDMS. The surface free energy of the unmodified PDMS, as obtained from the deformation studies, will be compared with that obtained from detailed contact angle measurements. We will then describe a method of modifying the surface of PDMS using the technology of self-assembled organic monolayers and report results obtained by application of similar load-deformation experiments to these surfaces.

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(9) Derjaguin, B. V.; Muller, V. M.; Toporov, Yu. P. *J. Colloid Interface Sci.* 1975, *53*, 314.

(10) Derjaguin, B. V. *Kolliod Z.* 1934, *69*, 155.

(11) Muller, V. M.; Yushchenko, V. S.; Derjaguin, B. V. *J. Colloid Interface Sci.* 1980, *77*, 91. (See also Pashley, M. D. *Colloids Surf.* 1984, *12*, 69.) Muller et al. distinguished the behavior of contact based on a dimensionless parameter $\mu = (32/3\pi)[(9RW^2)/(8\pi K^2 Z^3)]^{1/3}$, Z being the intermolecular separation. It was shown that the DMT method applies when μ is small (<1), and the JKR method applies when μ is large. For PDMS, the value of μ was found to be on the order of 10^4, so the JKR model was the clear choice for PDMS.

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(13) Kendall, K. *J. Phys., D: Appl. Phys.* 1973, *5*, 1782; 1975, *8*, 1449, 1722, 512; *Proc. R. Soc. London, A* 1975, *A341*, 409; 1975, *A344*, 287; *J. Adhesion* 1975, *7*, 137; *J. Mater. Sci.* 1976, *11*, 638, 1263, 1267; 1975, *10*, 1011.

(14) Maugis, D.; Barquins, M. *Adhesion and Adsorption of Polymers*; Polymer Science and Technology; Lee, L. H., Ed.; Plenum Press: New York, 1980; 12A, 203; Barquins, M.; Courtel, R. *Wear* 1975, *32*, 133.

(15) Roberts, A. D.; Othman, A. B. *Wear* 1977, *42*, 119.

(16) Tabor, D. *J. Colloid Interface Sci.* 1977, *58*, 2.

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(19) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* 1989, *5*, 1074. Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B.; Pershan, P. S.; Axe, J. D. *J. Am. Chem. Soc.* 1989, *111*, 5852.
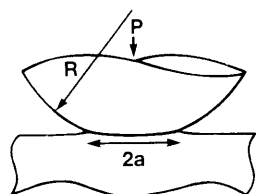
Figure 1. Contact between a deformable semispherical solid with radius of curvature R and a deformable flat plate results in the formation of a circular region of radius a. The external medium might be either air or a liquid. The deformation at the zone of contact results from the simultaneous effects of the surface and external (P) forces. For clarity, the area of contact is exaggerated. In our experiments involving elastomeric poly(dimethylsiloxane), P ranged from 0 to 200 dyn; the radius of the semisphere ranged from about 1 to 2 mm; the radius of the contact deformation ranged from about 100 to 250 μm. The thickness of the flat sheet was about 1.5 mm.
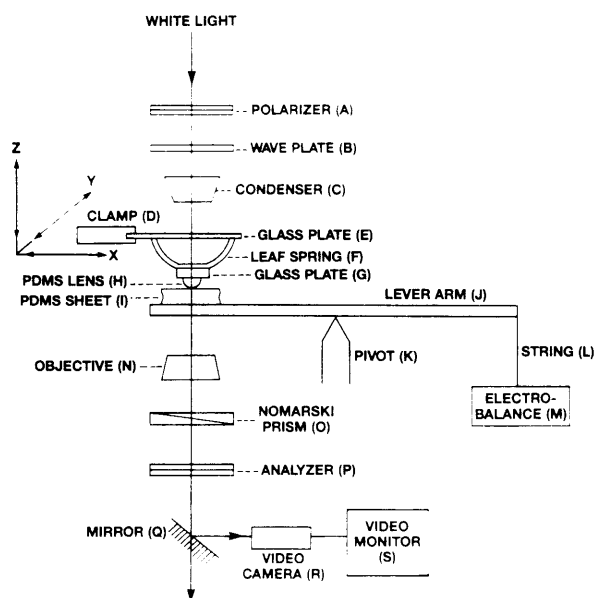

Figure 2. Apparatus used to measure contact deformation between a PDMS lens and a PDMS sheet in air is shown schematically. The flat sheet (I) was placed on one end of the lever arm (J) whose other end was connected to an electrobalance (M). The leaf-spring (F) was a semicircular strip of transparent adhesive tape. The glass plate (G) was mounted with the leaf-spring simply by pressing it against the adhesive layer. The lens (H) adhered sufficiently with the glass plate without any adhesive. The lens (H) could be translated up, down, or sideways. When the lens came into contact with the flat sheet (I), any extra load was registered on the electrobalance. The corresponding contact deformation was recorded in the video monitor (S).

Results and Discussion

Interaction between Semispherical Lenses and Flat Sheets of PDMS in Air. Interactions between two PDMS surfaces in air were studied by using the apparatus shown in Figure 2. The flat sheet rested on one end of a lever arm; the other end of the lever arm was connected to an electrobalance. The lens was brought into contact with the sheet. Any positive or negative load applied on the lens, while it was in contact with the sheet, was determined by using the electrobalance and the corresponding contact deformation was recorded in the video monitor. This apparatus was also equipped for still photography (not shown in the diagram). Figure 3 shows a typical photomicrograph of the contact zone resulting from the contact of a lens and a flat sheet of PDMS in air.

Two types of experiments were carried out in air. In the first experiment, the radius of the lens was kept fixed
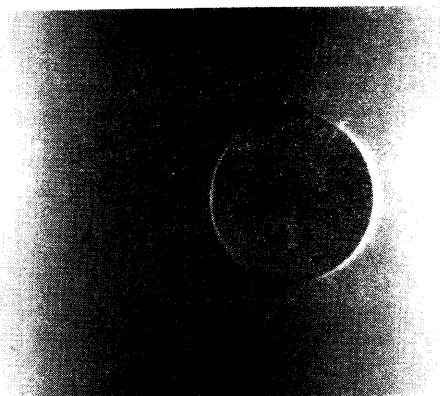

Figure 3. Photomicrograph showing the contact area (radius = 154 μm) resulting from the contact (in air) between a lens (R = 1.44 mm) and a flat sheet of PDMS. The edge of the lens is outside the field of view. There was no external load on the lens and hence the deformation was solely due to the effect of surface forces.

and the deformation was measured as a function of external load. The load was first increased from zero to about 200 dyn and then decreased back to zero. In the second experiment, the deformations resulting from the contact of lenses of various sizes with a flat sheet of PDMS were measured by using the same apparatus, but at zero load.

Figure 4 summarizes the results obtained from the first experiment, where a^3 is plotted as a function of P for a lens of radius 1.44 mm. The data obtained from both the loading and unloading experiments fall on the same curve, indicating no hysteresis in these contact deformations: that is, the deformations are reversible. These experimental data (loading and unloading data taken together) were analyzed with eq 1 using a numerical regression method with W and K as input variables. The best fit between the experimental data and eq 1 yielded values of W and K as 44.1 ($\pm$1.0) ergs/cm^2 and 4.83 ($\pm$0.06) $\times$ 10^6 dyn/cm^2, respectively.[20]

The contact deformations obtained for the lenses of various sizes under zero load were analyzed as follows. If there is no external load ($P = 0$), eq 1 reduces to

$$a^3 = 6\pi WR^2/K \qquad (4)$$

According to eq 4, a plot of a^3 versus R^2 should be a straight line passing through the origin. Figure 5 shows such a plot. The linear relation between a^3 and R^2 is as predicted by eq 4. From the slope of this straight line, and using the above value of K (4.83 ($\pm$0.06) $\times$ 10^6 dyn/cm^2), the value of W is 42.5 ($\pm$0.5) ergs/cm^2. The close agreement of the values of W obtained from the above two experiments demonstrates the self-consistency of these two procedures. The surface free energy (γ_{sv}) of the polymer is given as half of the work of adhesion.[4] The average value of γ_{sv} estimated from the data in Figures 4 and 5 is thus 21.8 ($\pm$0.8) ergs/cm^2.

Surface Energy of PDMS from Contact Angles. This section briefly reviews the theory of contact angles needed to estimate the γ_{sv} of PDMS and for later discussion.
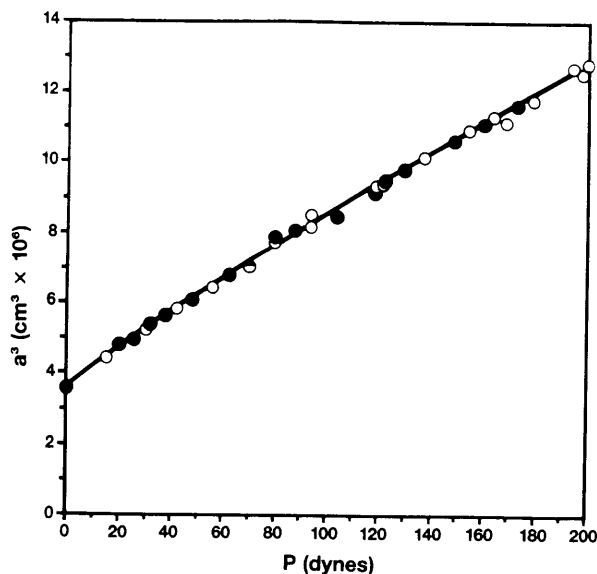
Figure 4. Plot of a^3 against P following the form expected from eq 1. The data were obtained from the load-deformation experiments using unmodified PDMS. The radius of the lens used in these measurements was 1.44 mm. The open circles (O) represent the data obtained from increasing loads and the closed circles (●) represent the data obtained from decreasing loads: there is no hysteresis. The solid line was obtained from the analysis of these data by using eq 1.

There are several methods[3-6] to estimate the surface free energy of a solid from the contact angles (θ) of non-wetting liquids, all involving Young's equation[1]

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (5)$$

Here, γ_{ij} (ij stands for lv, sv, and sl) represents the surface tension (or surface free energy) values of the i–j interface.[21] Since γ_{sl} cannot in general be determined a priori, eq 5 by itself is not useful for estimating γ_{sv}, and hence approximate methods are needed. The earliest method is due to Fox and Zisman.[3] According to this method, the cosines of the contact angles of a number of liquids on a solid surface are plotted against the surface tensions of the test liquids. The line obtained from such a plot is extrapolated to $\cos \theta = 1$; the corresponding surface tension of the liquid, which demarcates those liquids that would spread on the solid as a thin continuous film from those that would not, is termed the critical surface tension of the solid (γ_c). The definition of γ_c and a simple application of Young's equation yields[3]

$$\gamma_c = \gamma_{sv} - \gamma_{sl} \quad (6)$$

Equation 6 shows that γ_c is a measure of the surface free energy of the solid but is not necessarily equal to it, because γ_{sl} need not be zero even when θ is zero. Fox and Zisman's appoach was later revised by Good and Girifalco[4] and Fowkes,[5] who recognized the importance of separating the various forces that constitute the surface and interfacial free energies. If the forces operating across an interface are purely dispersive in nature and if the γ_{sv} and γ_{lv} values represent the true surface free energies of the solid and liquid (i.e. when the adsorptions of vapor are negligible),

Figure 5. Plot of a^3 against R^2 following eq 4. The data were obtained from the contact deformations of lenses of various sizes and a flat sheet of PDMS in air. There was no external load on these lenses, and thus the deformations were purely due to surface forces.

the work of adhesion at the solid–liquid interface can be expressed as a geometric mean of the two surface free energies as

$$W = 2(\gamma_{sv}\gamma_{lv})^{0.5} \quad (7)$$

According to Dupré,[22] the work of adhesion W can be expressed in terms of γ_{sv}, γ_{lv}, and γ_{sl} as

$$W = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (8)$$

Combination of eqs 7 and 8 yields

$$\gamma_{sl} = \{(\gamma_{sv})^{0.5} - (\gamma_{lv})^{0.5}\}^2 \quad (9)$$

This revision[23] shows that γ_{sl} becomes zero as γ_{lv} approaches γ_{sv}. Consequently, γ_c is equal to γ_{sv} only when the predominant forces across an interface are purely dispersive. Equation 9, in conjunction with eq 5, becomes eq 10, known as the Good–Girifalco–Fowkes equation

$$\cos \theta = -1 + 2(\gamma_{sv}/\gamma_{lv})^{0.5} \quad (10)$$

According to eq 10, surface free energy of a nonpolar solid would be found more accurately by plotting $\cos \theta$ against $(\gamma_{lv})^{-0.5}$ rather than γ_{lv}. Equation 10 also allows the estimation of γ_{sv} of a nonpolar solid from the contact angle of a single nonpolar liquid.

For PDMS, γ_{sv} is expected to result mainly from dispersion forces. Hence γ_c for PDMS should, as a first approximation, be equal to its γ_{sv}. The values of γ_c of PDMS reported in the literature[24,25] are in the range of 22–24 ergs/cm^2. We also made an independent estimate of its γ_{sv} from contact angle measurements. An experimental difficulty was encountered in measuring the contact angles of organic liquids on PDMS, since most organic

(21) The term "surface excess free energy" is more appropriate for a solid surface than surface tension (appropriate for liquids). The identity between the surface free energy and surface tension is strictly valid for liquid surfaces. For liquids it is possible to change the surface area quasistatically without doing work against the elastic forces. For solids, however, the presence of the elastic forces complicates the definition of surface tension. The definition of surface tension when applied to solids can be justified only if the composition of the surface remains constant during an experiment.
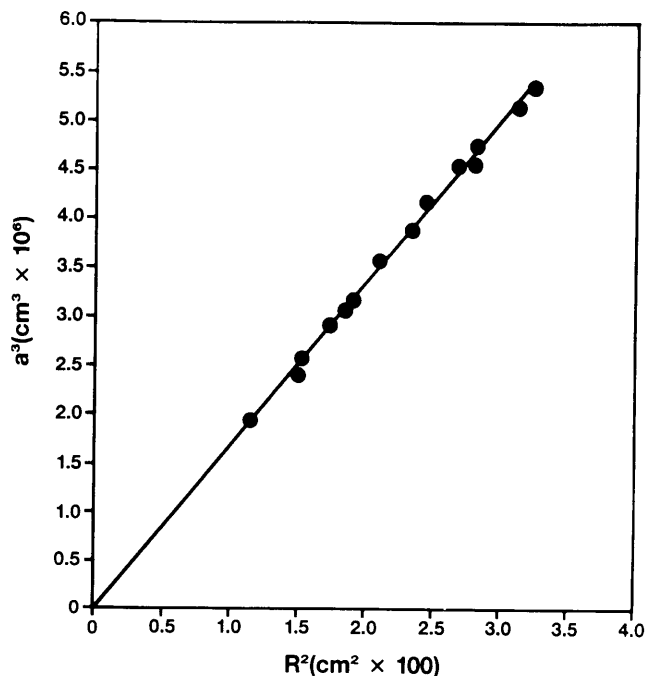
(22) Dupré, A. *Théorie Mécanique de la Chaleur.* Paris, 1869.
(23) Raleigh [Raleigh, *Philos. Mag.* 1883, *16*, 309] was the first to use a geometric mean approach to problems of interfacial tensions. He arrived at eq 9, tested it for water–oil interface and rejected it. He did, however, explain the discrepancy by remarking that "the action of one fluid upon another might follow an altogether different law from its action upon itself."
(24) Zisman, W. A. In *Symposium on Adhesion and Cohesion*; Weiss, P., Ed.; Elsevier: New York, 1962; p 176.
(25) Owen, M. J. *J. Coatings Technol.* 1981, *53*, 49.

liquids swell PDMS to a greater or lesser degree. Methylene iodide was one organic liquid that did not swell PDMS. The contact angle of methylene iodide on PDMS was 70° with no visible hysteresis. With this value, γ_{sv} of PDMS was found to be 22.1 ergs/cm^2 from eq 10. Contact angles of two other probe liquids, namely, hexadecane and paraffin oil, were also measured. Both of these liquids swelled PDMS. In order to minimize the effects due to swelling, we measured the contact angles within a few seconds after the application of the drops on the surface. The advancing and receding contact angles of hexadecane of PDMS were 40° and 26°, respectively. With these values, γ_{sv} of PDMS was calculated to be 21.6 and 24.9 ergs/cm^2, respectively. By use of the advancing (51°) and receding (40°) contact angles of paraffin oil on PDMS, γ_{sv} of PDMS was found to be 21.5 and 25.3 ergs/cm^2, respectively. Note that both the liquids yield similar values of γ_{sv} for PDMS. Because of swelling, however, we believe the values of γ_{sv} from receding contact angles to be less accurate than those from advancing contact angles. Values of γ_{sv} of PDMS obtained from the advancing contact angles are similar to that (22.1 ergs/cm^2) obtained from the contact angle of methylene iodide and are also close to the values (21–22.5 ergs/cm^2) obtained from contact deformation experiments.

Surface tension of liquid PDMS,[26] in the limit of infinite molecular weight, is about 21 ergs/cm^2, well within the limit predicted for solid PDMS. The agreement between the surface free energies of solid and liquid PDMS indicates a similar orientation of the surface groups (i.e. methyl groups) in both the liquid and cross-linked solid state. Owen[25] first suggested this possibility on the basis of the high flexibility of PDMS backbone.

Interaction between a PDMS Lens and Flat Sheet in Water–Methanol Mixtures. The interactions between PDMS surfaces were measured by bringing a lens of radius 1.52 mm into contact with a flat sheet in water–methanol mixtures of different compositions[27] using the apparatus shown in Figure 6. Figure 7 summarizes the data obtained by calculating the work of adhesion between the PDMS surfaces in these liquid mixtures using eq 4. The adhesion between PDMS surfaces was strongest in pure water and decreased as the hydrophobicity of the liquid increased; a weak but measurable adhesion persisted between PDMS surfaces even in pure methanol. This experiment shows the influence of the medium on the work of adhesion between two hydrophobic surfaces of constant chemical composition. Since the interfacial free energy γ_{sl} at a solid–liquid interface is given by half of the value of W_{sls}, its magnitude is easily calculated from the data shown in Figure 7. Figure 8 compares these values of γ_{sl} with the surface tensions (γ_{lv}) of water–methanol mixtures measured at air–liquid interfaces. The two curves are almost parallel (except at very low concentration of methanol), indicating that the surface activity of methanol at air–solution interfaces is roughly the same as that at PDMS–solution interfaces.

Direct Estimation of the γ_{sv} of PDMS Using Young's Equation. We discussed above a method to estimate γ_{sv} of PDMS from the contact angle of hexade-

(26) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.

(27) We estimated the influence of buoyancy as follows: The density of PDMS is about 0.99 g/cm^3—a value roughly the same as water (1 g/cm^3). Hence there should not be any buoyancy effect in water. In methanol, the weight of the lens, after correcting for buoyancy, was 0.54 mg. This weight corresponds to a value of P of 0.5 dyn, which is much lower than the effective weight [$6\pi WR$ = 21 dyn] of the surface forces (see ref 8). Hence, the effect of buoyancy could be safely neglected in methanol as well.
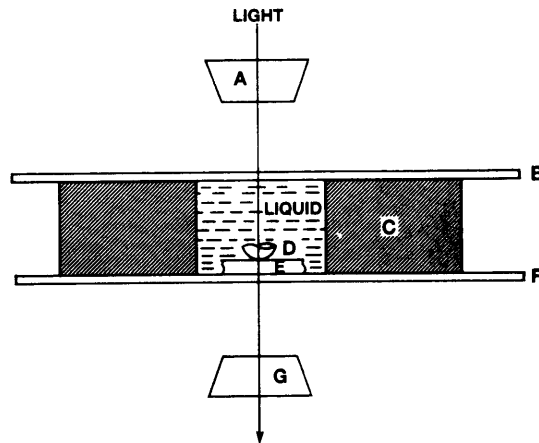

Figure 6. Contact deformations under liquids measured by placing a lens (D) in contact with a flat sheet (E) of PDMS in a liquid medium. The experimental cell is made of Sylgard 170 (C), which has a rectangular hole at the center. The cell is sandwiched between two glass slides (B and F). This assembly is placed in between the condenser (A) and objective (G) of an optical microscope.
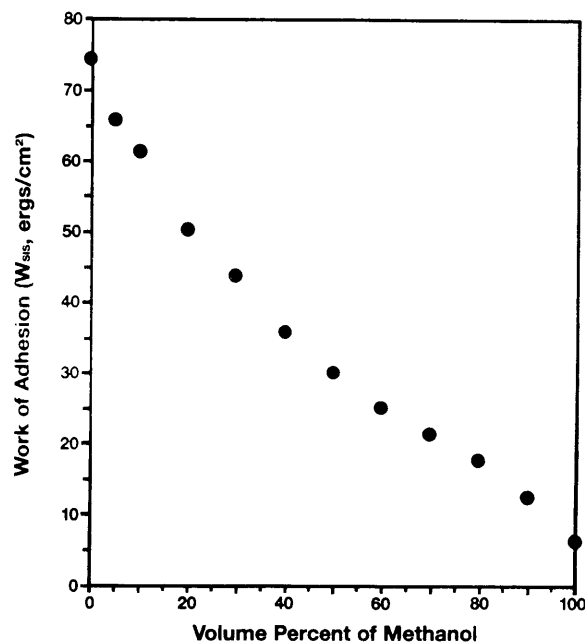

Figure 7. Works of adhesion (W_{sls}) between two PDMS surfaces in mixtures of water and methanol plotted against the volume percent of methanol in the mixtures. To generate this plot, the data obtained from the deformation experiments under the mixtures of water and methanol were analyzed according to eq 4. The radius of the lens used in these experiments was 1.52 mm.

cane and paraffin oil using the Good–Girifalco–Fowkes (GGF) equation (eq 10). This equation assumes that the interaction is entirely due to dispersion forces and that a geometric mean combining rule for the interfacial interaction could be employed.

Here, we describe an alternate method to determine γ_{sv} of PDMS from Young's original equation. This method is neutral with respect to the nature of forces constituting γ_{sv} or γ_{lv}. Since γ_{lv}, γ_{sl}, and θ were all measured for water–methanol mixtures on PDMS, we could construct a plot of $\gamma_{lv} \cos \theta$ vs γ_{sl}. This plot, according to Young's equation, should be a straight line, whose intercept in the $\gamma_{lv} \cos \theta$ axis is the surface free energy of the polymer. Figure 9 summarizes the results and indicates that the expected linear relation is observed. To generate such a plot, both the advancing and receding contact angles of water–methanol mixtures were used. The average value of γ_{sv}
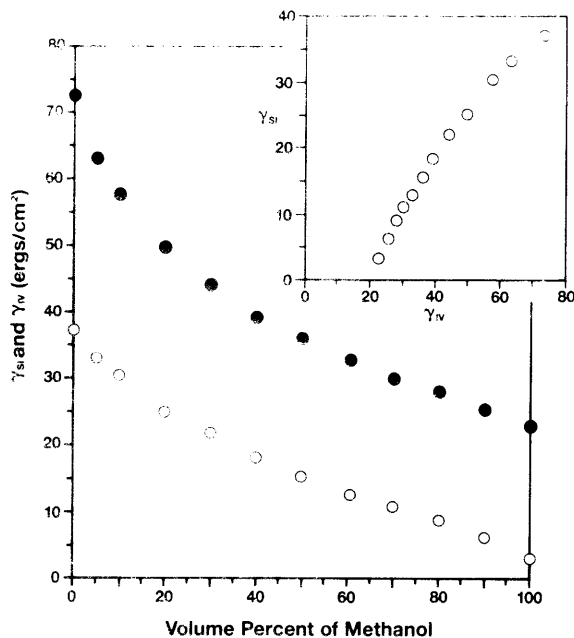
Figure 8. Surface tensions (γ_{lv}) of water–methanol mixtures at the air–solution interfaces compared with the interfacial free energies (γ_{sl}) of water–methanol mixtures at PDMS–liquid interfaces. The closed symbols (●) represent γ_{lv} and the open symbols (○) represent γ_{sl}. In the inset, γ_{sl} is plotted against γ_{sv}.
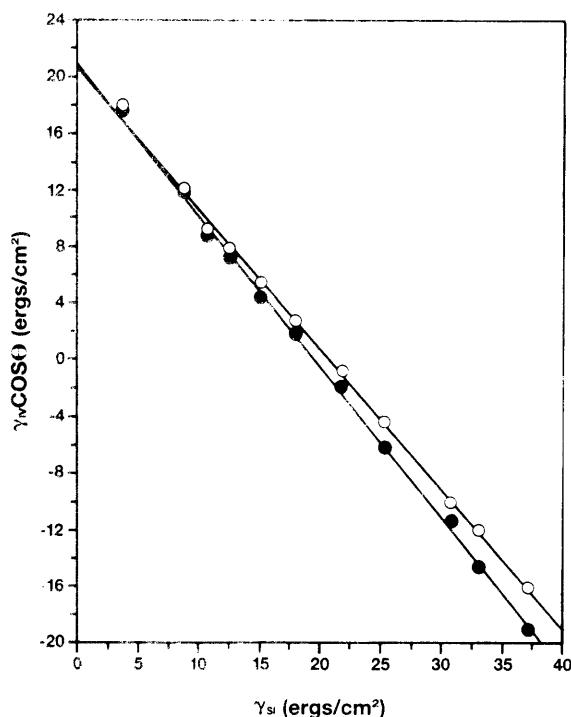

Figure 9. Plot of $\gamma_{lv} \cos \theta$ against γ_{sl} for the mixtures of water and methanol on PDMS obeying Young's equation (eq 5). Closed (●) and open (○) circles correspond to the data obtained from the advancing and receding contact angles, respectively. The values of γ_{sl} were obtained from Figure 8. The linear correlations between $\gamma_{lv} \cos \theta$ and γ_{sl} are in accordance with Young's equation. The intercepts in the $\gamma_{lv} \cos \theta$ axis yield the value of γ_{sv} of PDMS as 20.9 ergs/cm² (from θ_r) and 21.2 ergs/cm² (from θ_a), respectively.

for PDMS was estimated as 21.1 (±0.2) ergs/cm², in agreement with the value (21–22.5 ergs/cm²) obtained from the measurements made in air. Since the hysteresis in contact angles is small over the entire range of compositions, the slopes of the two lines shown in Figure 9 are also very close (1.08 from θ_a and 0.99 from θ_r).

We conclude this section with a special note on Young's equation. We mentioned before that γ_{sv} or γ_{sl} at the solid–

vapor or solid–liquid interface cannot in general be measured independently. There are, however, two reported cases where all four parameters of Young's equation could be estimated independently. Johnson et al.[8] studied the interaction of two smooth rubber spheres in air and in water. They estimated the values of γ_{sv} and γ_{sl} as 35 and 3.4 ergs/cm², respectively. With these values, the predicted contact angle (64°) of water on rubber agreed well with the experimental value of 66°. This demonstration of Johnson et al. was the first experimental proof of Young's equation. The other report was by Pashley and Israelachvili,[28,29] who estimated the γ_{sv} (27 ± 2 ergs/cm²) of mica coated with an organic monolayer and the γ_{sl} (11 ± 2 ergs/cm²) at the interface between this surface and a dilute surfactant solution (γ_{lv} = 40 ergs/cm²) using force balance experiments. The experimental contact angle (64°) of the surfactant solution on the monolayer coated mica agreed with the prediction (66°) based on Young's equation. Neither of these two reports discussed the possible influence of nonidealities of their surfaces of the type expected to give rise to contact angle hysteresis. Our experiments with PDMS provide a third example where all the parameters of Young's equation were independently measured for 12 different conditions, using both the advancing and receding contact angles. We take the agreement between the γ_{sv} values obtained from Figure 9 (using both advancing and receding contact angles) and the values estimated from the measurements in air as another direct proof of Young's equation.

There is, however, a detail about these data that deserves comment. Even though PDMS exhibits a low hysteresis in contact angles (2°–3°), in terms of energy, the hysteresis is significant for water–methanol mixtures, especially in the range of higher water concentrations (Figure 9). Since analysis of advancing and receding angles gives different values of γ_{sl}, one may ask which value is the more accurate (or, perhaps, the more appropriate for a given type of experiment). For this discussion, let us consider the case of pure water where the hysteresis is most pronounced. The term $\gamma_{lv} \cos \theta$ for water for PDMS obtained from advancing and receding contact angles is –18.8 and –15.9 ergs/cm², respectively. Using the value of γ_{sv} as 21.8 ergs/cm² (an average value obtained from the measurements in air), we estimate the interfacial free energy (γ_{sl}) at the water–PDMS interface to be 40.6 ergs/cm² from θ_a and 37.7 ergs/cm² from θ_r, respectively.[30] The latter value agrees with the γ_{sl} (37.2 ergs/cm²) obtained from contact deformations. This agreement is consistent with the picture that the lens, while coming to contact with the flat sheet, expels the liquid from between the two solids. Since the liquid being expelled is in the receding mode, the work of adhesion between the two PDMS surfaces is related to the γ_{sl} value obtained from the receding contact angle of this liquid in an air–liquid–solid system.

Effect of Surface Pressure. The surface free energy of a solid (γ_s) is half of the reversible work needed to separate two semiinfinite slabs of the solid under vacuum (or in an atmosphere of a gas that does not interact with

(28) Pashley, R. M.; Israelachvili, J. N. *Colloids Surf.* **1981**, *2*, 169. Pashley et al. (Pashley, R. M.; McGuiggan, P. M.; Horn, R. G.; Ninham, B. W. *J. Colloid Interface Sci.* **1988**, *126*, 569) later improved the quality of monolayers adsorbed on mica by using higher purity surfactant. The value of γ_{sl} obtained with this improved system was higher (28–36 ergs/cm²) than the value reported in their earlier work.

(29) Israelachvili, J. N. *Adv. Colloid Interface Sci.* **1982**, *16*, 31.

(30) The interfacial tension at the liquid PDMS–water interface was found to be 42–44 ergs/cm² [Kanellopoulos, A. G.; Owen, M. J. *Trans. Faraday Soc.* **1971**, *67*, 3127]. These values were closer to the value obtained from advancing contact angles of water of PDMS than the value obtained from receding contact angles.

the surface). Adsorption of vapor onto the surface reduces the magnitude of γ_s by a term $(\pi = \gamma_s - \gamma_{sv})$, known as the surface pressure.[31,32] There is substantial discussion in the literature concerning the importance of surface pressure (π) to contact angles. Adamson[33] suggested that the surface pressure resulting from the adsorption of vapor on solid surface can be significant, even for low-energy surfaces. Zisman,[6] Good,[34] and Fowkes[35] suggested that π may be significant for high energy surfaces and when θ is close to zero, but its effect can be safely neglected for low energy surfaces and when θ is much greater than zero.

For phenomenological treatments of contact angles, the importance and interpretaton of π are irrelevant; for proper interpretation of the value of γ_{sv} (as is the case with the measurements with PDMS described in this paper), the magnitude of π is important.

The best method to estimate the value of π is gas adsorption.[33] Since we have no data on gas adsorption, our arguments are only qualitative. Had the term π been significant, we feel that the γ_{sv} obtained from analysis of the data in Figure 9 would have differed from the value obtained from the measurements made in air. In addition, since π depends on the composition of the solvents, it should have caused the plots of $\gamma_{lv} \cos \theta$ vs γ_{sl} (Figure 9) to deviate from linearity. Since this plot is linear, we believe that the value of π is small. This inference suggests that γ_{sv} obtained from these measurements is the true surface free energy (γ_s) of the polymer.

Effect of Surface Roughness. Up to this point, our analysis of contact deformations has assumed that the PDMS lens and PDMS sheet make molecular contact and that any liquid between the two is completely excluded when the two are brought into contact. The assumption that the polymer surfaces make uniform van der Waals contact has no direct experimental support. The values for the surface free energy obtained by the JKR analysis and from the contact angle measurements are, however, in satisfactory agreement is indirect support for the validity of the assumption of contact. If intimate molecular contact is established between two surfaces, it must be because the surfaces are smooth or that the elastomeric polymer conforms to the other surface by depressing or extending its surface asperities. Verification of this assumption through direct measurements is important and is the subject of future investigations. Roughness can complicate the analysis of contact deformations and contact angles in other ways. Contact angle is influenced roughness. The contact angle on a rough surface is not strictly described by Young's equation, and the effect of hysteresis must be considered. Rough surfaces and those showing other nonidealities may exhibit metastable states.[36] Poly(dimethylsiloxane) surfaces prepared from Sylgard 170 (Dow Corning) however, exhibit negligible hysteresis in contact angles for water–methanol mixtures (Figure 9). The close agreement of γ_{sv} of PDMS (i.e. 21.2 and 20.9 ergs/cm²) obtained by using the advancing and receding contact angles of water–methanol mixtures on PDMS suggests that the hysteresis in contact angles has no profound effect. We also believe, based on the following arguments, that when the two surfaces are brought into contact in liquids, the liquids are displaced from between them.
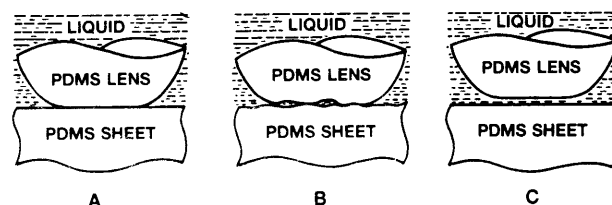
(31) Bangham, D. H.; Razouk, R. I. *Trans. Faraday Soc.* **1937**, *33*, 1459.

(32) Harkins, W. D.; Livingston, H. K. *J. Chem. Phys.* **1942**, *10*, 342.

(33) Adamson, A. W. *Physical Chemistry of Surfaces*, 3rd ed.; John Wiley and Sons: New York, 1976.

(34) Good, R. J. *J. Colloid Sci.* **1975**, *52*, 308.

(35) Fowkes, F. M.; McCarthy, D. C.; Mostafa, M. A. *J. Colloid Interface Sci.* **1980**, *78*, 200.

(36) Dettre, R. H.; Johnson, R. E. *Adv. Chem. Ser.* **1964**, *No. 43*, 112.

Figure 10. Three possible ways a lens might come into contact with a flat sheet under a liquid: (A) lens and flat sheet make true molecular contact with each other with no liquid between them; (B) what might happen if the surfaces were rough; (C) a film of liquid present between the two surfaces.

Figure 10 shows the various possibilities for a lens opposing a flat sheet through a liquid. The liquid may be completely excluded from between the two surfaces and intimate contact may be made between them (Figure 10A); the lens may make partial contact with the sheet and pools of liquid may remain between them (Figure 10B); surfaces may repel one another (Figure 10C). This last possibility is unlikely for our system. We wish to determine whether the situation shown in Figure 10A or Figure 10B is most representative of our case. A detailed analysis of the effect of roughness on adhesion is complex; here we present a simplified but plausible description of the problem. Assume that Figure 10B is correct; the apparent interfacial work of adhesion (W'_{sls}) is then proportional to the fraction of the total area in molecular contact, i.e.

$$W'_{sls} = rW_{sls} \qquad (11)$$

Here, W_{sls} $(=2\gamma_{sl})$ is the true work of adhesion and r is the fraction of the total area that is in intimate molecular contact.[37] Using eq 11, Young's equation becomes

$$\gamma_{lv} \cos \theta = \gamma_{sv} - (1/r)(\gamma'_{sl}) \qquad (12)$$

Here, γ'_{sl} $(= W'_{sls}/2)$ is the apparent interfacial free energy obtained from contact deformations using rough surfaces. According to eq 12, a plot of $\gamma_{lv} \cos \theta$ vs γ'_{sl} will be a straight line, whose slope is $1/r$. Note that this plot should still yield the correct value of γ_{sv}, although the slope of this line would differ from unity. The values of the slopes obtained from the two plots, shown in Figure 9, are 1.08 from θ_a and 0.99 from θ_r; both of these values are close to unity. For this reason, we feel that γ'_{sl} and γ_{sl} are experimentally indistinguishable, that is, the liquids are, in fact, displaced and contact is made between PDMS surfaces (Figure 10A).

Forces Required to Pull a PDMS Lens from a Flat Sheet of PDMS. Equation 1 indicates that the contact area will be reduced to zero only if P is negative. If P is negative, a real solution of eq 1 exists when $6\pi WRP \le (3\pi WR)^2$, where the equality sign represents the limiting case of the two solids just touching each other. By use of this equality, the force necessary to separate the two solids is given by

$$P = 1.5\pi RW \qquad (13)$$

We tested this result of Johnson et al.[8] by measuring the force necessary to pull PDMS lenses of various sizes off a flat sheet using the apparatus shown in Figure 2. The results are summarized in Figure 11. The linear dependence of the adhesion force on R is in accordance with eq 13. From the slope of this line $(1.5\pi W = 213$ ergs/cm²), we calculated the value of W as 45.2 ergs/cm². This value of W yields a value for γ_{sv} of 22.6 ergs/cm², in agreement with the values obtained from the equilibrium contact deformations. This result is another indication that the

(37) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.
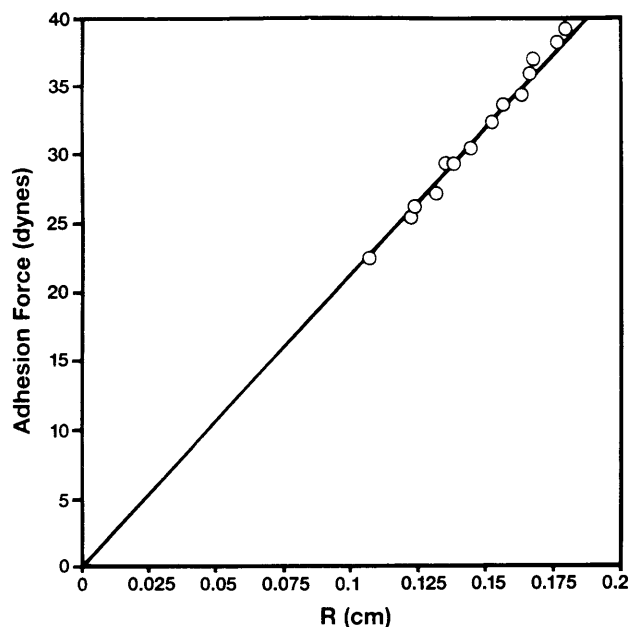
Figure 11. Adhesion (pull-off) forces between semispherical lenses and a flat sheet of PDMS varing linearly with the radius (R) of curvature of the lenses. These data are in accordance with eq 13. The surface free energy of PDMS obtained from this plot is 22.6 ergs/cm².

deformations on contact between the lenses and flat sheets of PDMS are mostly elastic in nature: had viscous dissipative effects in the PDMS been important, the experimental pull-off force would have been higher than that predicted by eq 13.

Experiments with Synthetic Model Surfaces. The contact deformation experiments carried out with unmodified PDMS established four important properties of this system: (i) the surface of PDMS was smooth and homogeneous; (ii) the contact between PDMS surfaces was purely elastic; (iii) contact deformations were reversible; (iv) intimate contact was established spontaneously between two PDMS surfaces both in air and in liquids. This pattern of characteristics was ideal for experiments of the type described here and stimulated us to investigate whether similar contact deformation experiments could be conducted with surface-modified PDMS. Experiments with modified surfaces could be useful for studying the relationship between adhesion and surface constitution. In this section, we first describe methods to modify the surface of PDMS. We then discuss the results obtained from the load-deformation studies using these modified surfaces. We conclude by comparing the surface free energies of these modified surfaces with values obtained from contact angles.

The surface of PDMS is converted to silica on exposure to an oxygen plasma.[38] These oxidized surfaces can be further functionalized by reaction with alkyltrichlorosilanes (Scheme I). Reaction with silanes is a method commonly used to modify glass, silica, or other oxide surfaces.[39] Recent studies[18,19] have indicated that long-chain alkyl trichlorosilanes on reaction with silica form well-ordered monolayer films. We hoped that long-chain alkyltrichlorosilanes would also form well-ordered monolayers on reaction with oxidized PDMS (PDMS^ox).

We carried out these reactions by exposing PDMS^ox to the vapors of these silanes under reduced pressure rather

Scheme I. PDMS Functionalized by Oxidation in an Oxygen Plasma To Generate a Silica Surface[a]
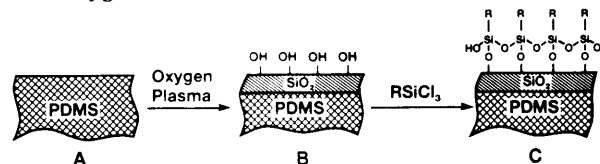
[a] This superficial silica layer is further functionalized by reaction with functional alkyltrichlorosilanes.

Table I. Surface Free Energies of Silane-Modified PDMS Surfaces[a]

system	θ_a, (deg)	θ_r, (deg)	γ_{sv}, ergs/cm², from	
			θ_a	θ_r
PDMS	40 (s)	26 (s)	21.6	24.9
PDMS^ox	0	0	–	–
PDMS^ox–O₃Si(CH₂)₉CH₃	42	40	21.0	21.6
PDMS^ox–O₃Si(CH₂)₂(CF₂)₇CF₃	83	69	8.7	12.8

[a] θ_a and θ_r are the advancing and receding contact angles of hexadecane in degrees. Surface free energies (γ_{sv}) are calculated for each sample by using both the advancing (θ_a) and receding (θ_r) contact angles and using the Good–Girifalco–Fowkes equation (eq 10, see text). (s) indicates that PDMS swells in hexadecane; the swelling of PDMS was, however, prevented on the monolayer-coated PDMS surfaces. (–) indicates that the value of γ_{sv} was not estimated because of inadequate contact angle values.

than to solution of silanes, because PDMS swells in most organic liquids. Studies of the reaction of PDMS^ox with a number of organofunctional silanes will be reported separately. Here we present the results concerning surface thermodynamics obtained by using $Cl_3Si(CH_2)_9CH_3$ and $Cl_3Si(CH_2)_2(CF_2)_7CF_3$.

The surface free energies (γ_{sv}) of PDMS^ox–O₃Si(CH₂)₉-CH₃ (the product of reaction of PDMS^ox and $Cl_3Si(CH_2)_9$-CH₃) and PDMS^ox–O₃Si(CH₂)₂(CF₂)₇CF₃ (the analogous material from reaction of PDMS and $Cl_3Si(CH_2)_2(CF_2)_7$-CF₃) were obtained from the contact angles of hexadecane and by using eq 10; these energies are summarized in Table I. Although we have no direct estimate of the structural order exhibited in these modified surfaces, we believe, by analogy with the previous work, that the outermost layer of PDMS^ox–O₃Si(CH₂)₉CH₃ is populated with CH₃ groups and has order similar to that of other self-assembled monolayers comprising n-alkyl units. The order in the fluorocarbon containing surface is less certain.

Zisman and his collaborators[3,6] first suggested values of γ_c for solid surfaces that were characteristic of certain functional groups: –CH₃, 22 ergs/cm²; –CH₂–, 31 ergs/cm²; –CF₂–, 18 ergs/cm²; –CF₃, 6 ergs/cm². These γ_c values were obtained by plotting the cos θ of several liquids as a function of their surface tensions and extrapolating to cos $\theta = 1$. As mentioned before, a better way to obtain γ_c (and thus γ_{sv} of a nonpolar solid) is to plot cos θ against $(1/(\gamma_{lv})^{0.5})$. This procedure reduces the errors of long extrapolations inherent in Fox and Zisman's procedure. Fowkes,[5,40] using the latter method, found values of γ_{sv} of these surfaces that followed the same sequence as Fox and Zisman's γ_c values: γ_{sv} values of surfaces composed of –CH₃, –CH₂–, –CF₂–, and –CF₃ groups were 21, 35, 19.5, and 10.4 ergs/cm², respectively.

The comparison between γ_{sv} of PDMS^ox–O₃Si(CH₂)₉-CH₃ with Fowkes' values indicates that its surface is composed mainly of –CH₃ groups. This value also agrees with two other values of γ_{sv} reported for surfaces composed

(38) Fakes, D. W.; Davies, M. C.; Browns, A.; Newton, J. M. *Surf. Interface Anal.* **1988**, *13*, 233.

(39) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1982.

(40) Fowkes, F. M. *Adv. Chem. Ser.* **1964**, *No. 43*, 99. Fowkes, F. M. In *Surfaces and Interfaces*; Burke, Reed, Weiss, Eds.; Syracuse University Press: Syracuse, NY, 1967; p 197.

of close-packed $-CH_3$ groups: one (γ_{sv} = 19.3 ergs/cm^2) was prepared by adsorbing long-chain alkanethiols ($HS(CH_2)_{21}CH_3$) onto gold[41] and the other (γ_{sv} = 20 ergs/cm^2) by reacting long-chain alkyltrichlorosilanes ($Cl_3Si-(CH_2)_{17}CH_3$) on silica.[42] These values of surface free energy, coupled with the fact that PDMS^{ox}–$O_3Si(CH_2)_9$-CH_3 exhibits low hysteresis in contact angle, strongly suggest that its outer surface is ordered and composed mainly of $-CH_3$ groups.

We cannot reach a clear conclusion concerning the order of PDMS^{ox}–$O_3Si(CH_2)_2(CF_2)_7CF_3$, other than to note that the low value of γ_{sv} clearly indicates that the surface is composed mainly of fluorinated groups. Values of γ_{sv} for this surface estimated from the advancing and receding contact angles of hexadecane range from 8.7 to 12.8 ergs/cm^2, values close (10.4 ergs/cm^2) to that expected of a surface populated mainly with $-CF_3$ groups. The high hysteresis in these contact angles suggests significant (but difficult to quantify) disorder for this surface.[43]

Interaction between Oxidized PDMS Surfaces. The surface free energy of oxidized PDMS is much higher than that of unoxidized PDMS. This assertion is based on two major observations: zero contact angle of water, and high adhesion between two oxidized surfaces of PDMS. We found that two oxidized surfaces of PDMS, when brought into contact, adhered so strongly that they could not be separated without causing cohesive failure in the polymer samples. Strong adhesion between these surfaces was also reflected in the load-deformation experiments as discussed below.

The deformation resulting on contacting a lens (R = 1.21 mm) of PDMS^{ox} with a flat sheet of this material was measured as a function of external load. Because the contact area did not decrease during the unloading experiments and the joint fractured only cohesively, no useful information could be obtained from the unloading experiments other than to note that the force required to fracture such a joint was nearly 2 orders of magnitude higher than that required for unmodified PDMS. The data obtained from the loading experiments are summarized in Figure 12. The analysis of these data in light of eq 1 yielded values of W and K as 117 (±2) ergs/cm^2 and 5.11 (±0.06) × 10^6 dyn/cm^2, respectively. Note that the value of K obtained from this measurement is similar to the value of K (4.8 × 10^6 dyn/cm^2) for unmodified PDMS. The value of γ_{sv} of PDMS^{ox} was found to be 58.5 ergs/cm^2, which is nearly 3 times the value of γ_{sv} for unmodified PDMS.

Interactions between Surface-Functionalized PDMS Surfaces: Cohesive Interactions. This section describes the results of the load-deformation experiments involving surface-functionalized PDMS lenses and PDMS sheets. Both the lens and sheet had the same chemical groups. PDMS sheets and PDMS lenses, which had been functionalized according to Scheme I, were subjected to the load-deformation studies (the lens and flat sheet had the same chemical groups) using the apparatus shown in Figure 2. The results of these experiments are shown in Figures 13 and 14. In contrast to the unmodified PDMS (Figure 4), hysteresis was observed in these experiments. Horn, Israelachvili, and Pribac[12] also noted a hysteresis
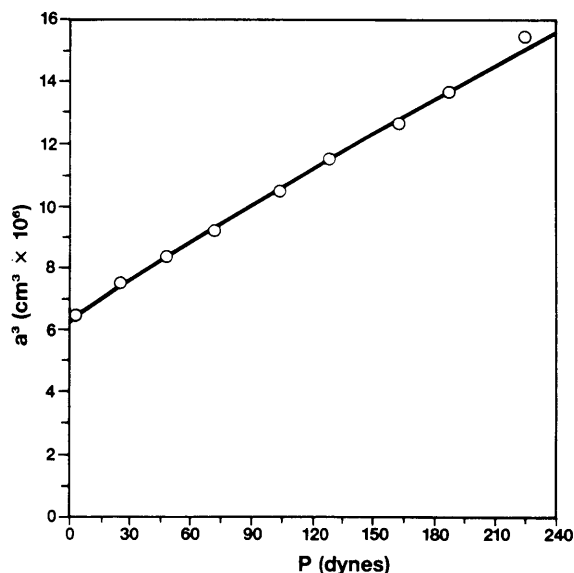
(41) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J. E.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

(42) Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 6136.

(43) H. Biebuyck (Harvard University, unpublished observations) found that a monolayer surface composed of $-CF_3$ groups prepared by adsorbing $HS(CH)_2(CF_2)_7CF_3$ onto gold exhibited higher hysteresis in contact angles than the surface prepared by adsorbing $HS(CH_2)_9CH_3$ onto gold.

Figure 12. Plot of a^3 against P for PDMS^{ox} following the form expected from eq 1. The data were obtained from the loading experiments only. The radius of the lens was 1.21 mm.
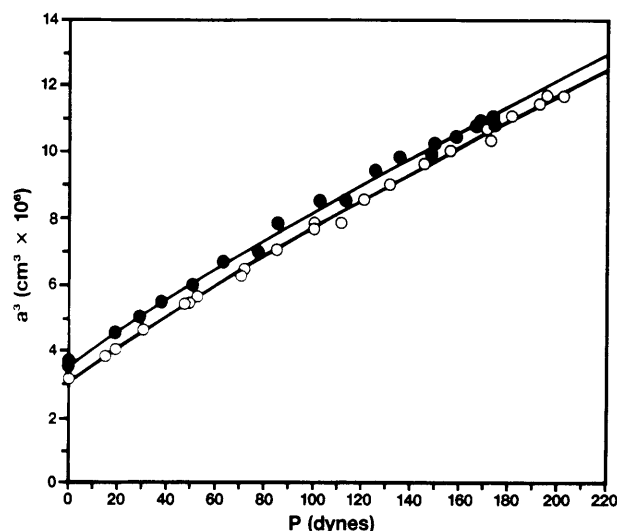

Figure 13. Plots of a^3 against P showing weak hysteresis for the surfaces of PDMS^{ox}–$O_3Si(CH_2)_9CH_3$. The radius of the lens was 1.4 mm. The open circles (O) represent the data obtained from the increasing loads and the closed circles (●) represent the data obtained from the decreasing loads. The solid lines in both plots are predicted from eq 1.

in the deformation resulting from the contact between two curved mica surfaces. The authors suggested plastic deformation in the glue supporting the mica surface to be a possible cause of this hysteresis. In our case, the lack of hysteresis in contact deformation for unmodified PDMS implies that its occurrence in experiments using functionalized PDMS must originate from surface effects and not from any bulk viscoelastic effects. The hysteresis was much smaller on the surface of PDMS^{ox}–$O_3Si(CH_2)_9CH_3$ than on that of PDMS^{ox}–$O_3Si(CH_2)_2(CF_2)_7CF_3$ surfaces. These results follow the same general trend observed in the hysteresis of contact angles. The loading and unloading data obtained for each surface were analyzed separately by using eq 1. For PDMS^{ox}–$O_3Si(CH_2)_9CH_3$, the values of K obtained from the loading and unloading experiments are 4.91 (±0.07) × 10^6 and 5.02 (±0.14) × 10^6 dyn/cm^2, respectively. For PDMS^{ox}–$O_3Si(CH_2)_2(CF_2)_7$-CF_3, these values are 5.08 (±0.38) × 10^6 and 4.89 (±0.28) × 10^6 dyn/cm^2, respectively. All of these values are very close to the value of K (4.83 (±0.06) × 10^6 dyn/cm^2)
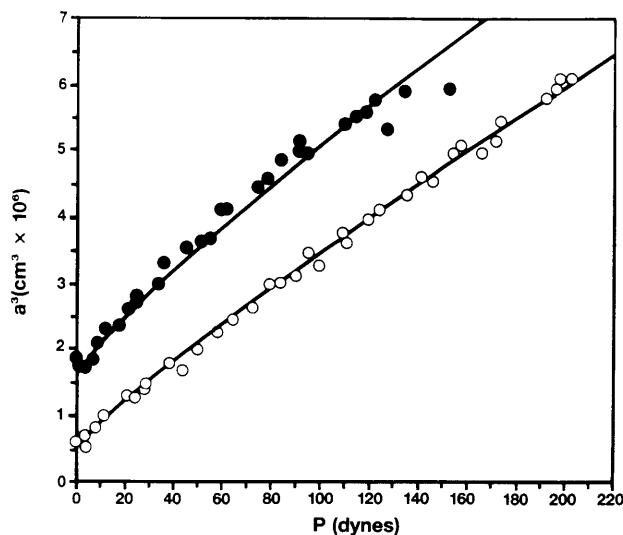
Figure 14. Plots of a^3 against P for the surfaces of $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7CF_3$ exhibiting large hysteresis. The radius of the lens was 1 mm. The open circles (O) represent the data obtained from the increasing loads and the closed circles (●) represent the data obtained from the decreasing loads. The solid lines are obtained from the analysis of these data using eq 1.

Figure 15. Results of the load-deformation experiments using a lens of $PDMS^{ox}$–$O_3Si(CH_2)_9CH_3$ and a flat sheet of $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7CF_3$. The open (O) symbols indicate the data obtained from increasing loads and the closed symbols (●) represent the data obtained from decreasing loads.

obtained for unmodified PDMS. This similarity suggests that the elastic modulus of PDMS is not affected by the steps used in surface modifications.

The values of W for $PDMS^{ox}$–$O_3Si(CH_2)_9CH_3$ obtained from the increasing loads ($W = 41.1$ (± 1.0) ergs/cm²) are similar to those obtained from decreasing loads ($W = 48.1$ ($+2.1$) ergs/cm²). The corresponding values of W for $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7CF_3$ (14.2 (± 2.8) and 42.0 (± 4.1) ergs/cm² from loading and unloading experiments, respectively) differ to a much greater extent. The surface free energies of $PDMS^{ox}$–$O_3Si(CH_2)_9CH_3$ and $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7CF_3$ obtained from the advancing contact angles of hexadecane are 21.0 and 8.7 ergs/cm², respectively (Table I), predicting values of W for these surfaces of 42.0 and 17.4 ergs/cm². These values are comparable to those obtained from the loading experiments but are lower than the values obtained from unloading experiments (see above). Using receding contact angles of hexadecane, these values of W are predicted as 43.2 and 25.6 ergs/cm² for these $-CH_3$ and $-CF_3$ surfaces, respectively. Although the agreement between this value of W and that obtained from unloading experiments is satisfactory for $PDMS^{ox}$–$O_3Si-(CH_2)_9CH_3$, the prediction is poor for $PDMS^{ox}$–$O_3Si-(CH_2)_2(CF_2)_7CF_3$.

In summary, the works of adhesion between these surfaces obtained from increasing load deformations are comparable to the predictions based on advancing contact angles. The work of adhesion obtained from the decreasing load deformations has little or no correlation with the values predicted from either advancing or receding contact angles. $PDMS^{ox}$–$O_3Si(CH_2)_9CH_3$ is better behaved than $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7CF_3$. The origin of the hysteresis at the solid–solid interfaces is unclear.

We also measured the pull-off forces between these functionalized surfaces using the apparatus shown in Figure 2. For $PDMS^{ox}$–$O_3Si(CH_2)_9CH_3$, the force needed to pull off a lens of $R = 1.4$ mm from a flat sheet was 32 (± 1) dyn. For $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7CF_3$, the force needed to pull off a lens of $R = 1$ mm from a flat sheet was 19 (± 1) dyn. These pull-off forces, in view of eq 13, predict values for W of 48.5 and 40.3 ergs/cm² for $PDMS^{ox}$–$O_3Si(CH_2)_9$-CH_3 and $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7CF_3$, respectively. These values are in excellent agreement with the values
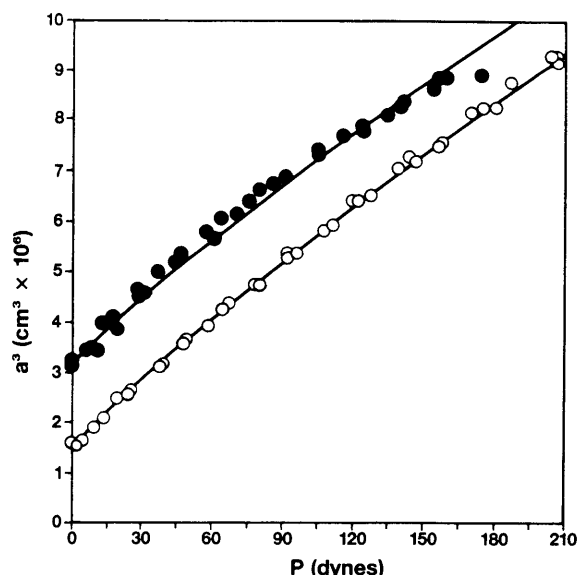
of W obtained from the decreasing load-deformation experiments.

Adhesive Interaction between Alkylsiloxane and Fluoroalkylsiloxane Monolayers. This section discusses the interaction between $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7$-CF_3 and $PDMS^{ox}$–$O_3Si(CH_2)_9CH_3$. Deformations resulting from the contact between a lens ($R = 1.28$ mm) of $PDMS^{ox}$–$O_3Si(CH_2)_9CH_3$ and a sheet of $PDMS^{ox}$–$O_3Si-(CH_2)_2(CF_2)_7CF_3$ were measured as a function of increasing and decreasing loads. Significant hysteresis in contact deformations was observed in these experiments (Figure 15). Although this hysteresis is qualitatively similar to that observed for surfaces containing similar functional groups (Figures 13 and 14), there is an important difference between them in terms of kinetics. While the areas of contact between the surfaces composed of identical functional groups did not change with time during either the loading and unloading experiments, the area of contact between the fluorocarbon and hydrocarbon surfaces changed with time during unloading experiments. No noticeable time-dependent response was observed during the loading experiments, however. Figure 16 exemplifies the relaxation kinetics of the area of contact between fluorocarbon and hydrocarbon surfaces. In this experiment a load of 200 dyn was applied to a lens of $PDMS^{ox}$–$O_3Si(CH_2)_9CH_3$ while it was in contact with a sheet of $PDMS^{ox}$–$O_3Si(CH_2)_2(CF_2)_7CF_3$; the load was subsequently reduced to zero. The contact area continued to decrease with time and reached a plateau value after about 800 s (Figure 16). This relaxation process is qualitatively similar to what is known as "creep" in the fracture of polymers.[26]

The data corresponding to the unloading experiments (Figure 15) were taken within 15–20 s of varying the loads; hence these values were highly nonequilibrium. The effective work of adhesion calculated from the unloading data is 58.0 (± 3.0) ergs/cm², which is higher than the values obtained for the surfaces containing similar functional groups (see above). The value of K obtained from this experiment is 5.58 (± 0.18) × 10⁶ dyn/cm², which is also slightly higher than the value of K (4.8 × 10⁶ dyn/cm²) for unmodified PDMS.

The data obtained from the loading experiments were better behaved and did not exhibit dissipative charac-
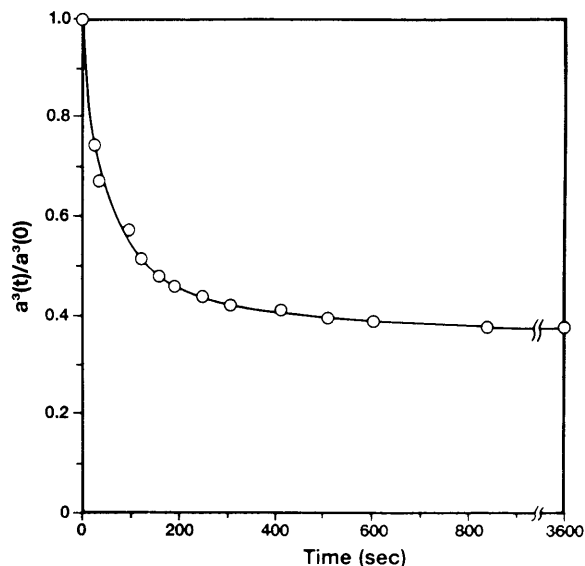
Figure 16. Area of contact between a lens of $PDMS^{ox}-O_3Si-(CH_2)_9CH_3$ and a flat sheet of $PDMS^{ox}-O_3Si(CH_2)_2(CF_2)_7CF_3$ as a function of time when a load is applied on the lens and then removed. The data are presented in the dimensionless form, $a^3(t)/a^3(0)$, where $a(t)$ is the contact radius at time t and $a(0)$ is the initial contact radius.

teristics; consequently, the value of K $(4.80\ (\pm0.09) \times 10^6$ $dyn/cm^2)$ obtained from this experiment is close to that $(4.83 \times 10^6\ dyn/cm^2)$ of unmodified PDMS. The work of adhesion $(23.3\ (\pm0.1)\ ergs/cm^2)$ between the fluorocarbon and hydrocarbon surfaces as obtained from these loading experiments is intermediate to the values obtained for surfaces[44] containing similar functional groups $(41.1\ ergs/cm^2$ for $PDMS^{ox}-O_3Si(CH_2)_9CH_3$ and $14.2\ ergs/cm^2$ for $PDMS^{ox}-O_3Si(CH_2)_2(CF_2)_7CF_3$.

Summary and Conclusions

The objective of our research was to explore determination of contact deformation at solid–solid interfaces as a technique for determining surface thermodynamic properties. Poly(dimethylsiloxane), with its excellent surface and bulk properties, is a good model system for these studies. The deformations resulting on contacting semispherical lenses and flat sheets of PDMS are spontaneous and reversible (i.e. free of hysteresis). These contact deformations conform well with the JKR model and yield values of γ_{sv} in agreement with the predictions based on contact angles. The agreement between the γ_{sv} values obtained from these measurements and the adhesion (pull-off) forces indicates that the deformation at the contact between a lens and flat sheet of PDMS is purely elastic in nature; i.e. there are no concomitant dissipative processes. Comparisons of the experiments carried out in air and under mixtures of water and methanol establish that intimate contact between PDMS surfaces takes place in both cases.

An important part of these studies was to develop ways to modify the surface of PDMS and to subject these modified surfaces to the deformation experiments similar to those used for unmodified PDMS. The experimental procedure based on alkylsilylation of the SiO_2 layer on the surface of plasma oxidized PDMS seems to yield surface monolayers having order similar to that achieved on

silicon/SiO_2 wafers. Experiments with these functionalized PDMS surfaces exhibit hysteresis in contact deformations, an observation that is qualitatively consistent with the trend observed in contact angle hysteresis. Values of γ_{sv} for these modified surfaces obtained from increasing load deformations are similar to the predictions from contact angles; values obtained from decreasing load deformation are higher than the predictions based on contact angles. The important conclusions from these studies are as follows:

(1) Studies of contact deformations can provide surface thermodynamic parameters for solid–solid and solid–liquid interfaces that are not available from conventional studies of contact angles. Contact deformations in conjunction with contact angles provide a more complete analysis of solid–solid and solid–liquid interfaces than either technique alone.

(2) This method is limited by the constraints that both solids must be smooth and at least one must be elastomeric and deformable. The breadth of applicability can be increased by modifying the surfaces of the components.

(3) A special reason for studying the chemistry of solid surfaces is to elucidate the joint roles of surface chemistry and rheology in adhesive fracture processes. Our current studies are limited to pure elastic responses of the two components. The adhesion forces are thus primarily determined by the surface properties and by the geometry of the interacting components. The adhesion forces observed for unmodified PDMS are consistent with the surface free energies obtained from contact angles, because unmodified PDMS exhibits negligible hysteresis in contact deformations. For functionalized PDMS, which exhibited hysteresis both in contact angles and in contact deformations, the measured adhesion forces have little correlation with the predictions based on contact angles. The observation of hysteresis complies with the existence of metastable surface states,[36] which might even give rise to time-dependent responses. The origin of these metastable states needs to be examined in detail to understand their influence on adhesion and fracture. It should be possible to extend these measurements to viscoelastic systems. By carefully controlling the viscoelastic and surface properties, we hope to develop a more complete picture of solid–solid adhesion.

Experimental Section

General Information. Poly(dimethylsiloxane) (Sylgard 170) was supplied by Dow Corning Corp., Midland, MI. The liquids used for the various measurements were water, methanol, methylene iodide, paraffin oil, and hexadecane. Water was purified with a Nanopure water purifier (Barnstead) and had a surface tension of about $72.8\ ergs/cm^2$. When the surface of this water was compressed in a Langmuir trough to one-tenth of its original area, the surface tension of the water decreased by only $0.3\ ergs/cm^2$, indicating that the surface of the water was not contaminated. Methanol (Fisher) was high-purity HPLC grade and had a surface tension of $22.8\ ergs/cm^2$. Methylene iodide (Aldrich) was used without further purification; the surface tension of methylene iodide was found to be $49.4\ ergs/cm^2$. Paraffin oil (Fisher) was purified by equilibriating it with neutral grade alumina (Fisher) and had a surface tension of $32.4\ ergs/cm^2$. Hexadecane was purified by passing it through a column of neutral grade alumina. The measured surface tension of hexadecane was $27.6\ ergs/cm^2$. The trichlorosilanes $Cl_3Si(CH_2)_9CH_3$ and $Cl_3Si(CH_2)_2(CF_2)_7CF_3$ were obtained from Petrarch and PCR, respectively, and distilled prior to use. The microsyringes (Gilmont) used to measure contact angles and to prepare PDMS lenses were obtained from VWR. Plasma oxidation was carried out in a Harrick Plasma Cleaner (Model PDC-23G, 100 W). Contact angle measurements were carried out with a Ramé Hart goniometer (Model 100). The microscope used to measure contact deformation was purchased

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(44) Further examination of the energetics at the fluorocarbon-hydrocarbon interface is not possible at present because of the high hysteresis in contact angles and contact deformations. We are currently developing ways to prepare monolayer surfaces of low hysteresis. An account of these studies will be published in due course.

from Nikon (Nikon Diaphot Inverted Microscope), equipped with a video camera, a video monitor, and a still camera.

Preparation of Semispherical Lenses and Flat Sheets of PDMS. The components for preparing the elastomers were supplied in two parts, Sylgard 170A and Sylgard 170B (Dow Corning Co., Midland, MI). These two parts primarily comprised the components of a reaction mixture having vinyl end-capped oligomeric dimethylsiloxane ($H_2C=CH(Si(CH_3)_2O)_nSi(CH_3)_2$-$CH=CH_2$ (average value of n is about 250)), a methyl hydrogen siloxane (($H_3C)_3Si(OSiHCH_3)_5(OSi(CH_3)_2)_3OSi(CH_3)_3$) as cross-linking agent, and a platinum complex as a catalyst for the hydrosilation reaction. As obtained, these components both contained reinforcing fillers. Upon storage the fillers sedimented down. The clear components were poured out of the containers. A 50:50 mixture (w/w) of the two clear components was stirred in a plastic weighing cup using a glass rod. Trapped air bubbles resulting from the agitation of the mixture were removed by applying gentle vacuum (60–70 mmHg for about 30 min). Small drops (1–2 μL) of the transparent mixture were applied with a microsyringe onto the surface of a smooth glass microscope slide, which had previously been treated with $Cl_3Si(CH_2)_2(CF_2)_7CF_3$ to reduce adhesion to it. The hydrosilation polymerization reaction was carried out at 65 °C for 1 h. The fluoroalkylsilane-treated glass slide served two purposes: first, it provided a flat substrate from which the lenses could be removed easily after they had cured completely; second, the silicone drops formed a finite angle (66°) of contact on the surface. By controlling the volume of the drops, lenses of various radii of curvature could be formed. The radii of curvature of the cured drops at the central regions were measured directly from their photographs. The prepared lenses had radii of curvatures less than 2 mm. The cured lens could be easily removed from the glass slides and manipulated by holding it at its edge by a fine-pointed tweezer. The flat sheets of silicone elastomer (thickness 1.5 mm) were prepared from the same materials used in preparing the lens. These sheets were obtained by curing the two-component reaction mixture in a flat-bottomed polystyrene petri dish. The surfaces of the sheets exposed to the air during curing were the ones contacted to the lens during the deformation experiments. Electron microscopy of these PDMS surfaces revealed no surface features even when examined at a resolution of 200–300 Å. Long ripples (about 1 mm) were occasionally visible by eye on portions of these surfaces; these regions were avoided during the deformation measurements.

Apparatus Used To Measure Contact Deformation in Air. Figure 2 is the diagram of the apparatus used to measure contact deformation as a function of external load. It is related to the apparatus used by Barquins and Courtel to study rubber friction.[14] The lens (H) could be brought slowly in contact with, or detached slowly from, the flat sheet (I) of PDMS using a manipulator (not shown in the figure) attached to the clamp (D). The leaf spring (F) indicated in Figure 2 was a semicircular strip of adhesive tape. Since the load transferred to the assembly of the lens and flat sheet was controlled by the vertical displacement of the clamp (D), much of the vertical displacement resulted in deformation of the leaf-spring, and thus the relative displacement of the lens was small. The leaf-spring acted as a displacement buffer and thus provided finer control of the load transmitted to the lens. The flat sheet of PDMS rested on one end of a lever arm (J) whose other end was connected to an electrobalance (M). The center of the arm was freely suspended on a sharp pivot (K). Any excess load applied on the lens during the course of a load-deformation experiment was registered on the electrobalance, which had a sensitivity of 1 dyn. The lens could be brought into contact with the flat sheet at zero load by careful operation of the manipulator. The area of contact was measured by an inverted microscope (Nikon, Diaphot) equipped with a video camera (R) and a video monitor (S). Differential interference contrast (DIC) optics was used to view the contact area, which yielded a sharply defined edge of the contact circle. The DIC was particularly useful when measurements were made in liquids. All the measurements were made directly from the screen of the video monitor.

Apparatus Used To Measure Contact Deformations under Liquids. Measurements in a liquid were carried out in a rectangular cell, prepared from Sylgard 170 (Figure 6). A rectangular hole (3.0 cm × 1.5 cm × 0.7 cm) was created at the

center of a rectangular slab (5.0 cm × 4.8 cm × 0.7 cm) of a cured silicone elastomer. This slab was placed flat on a glass slide (5.0 × 7.5 cm) previously treated with $Cl_3Si(CH_2)_2(CF_2)_7CF_3$, which rendered it hydrophobic. The hydrophobic polymer and the hydrophobic glass slide created a good hydrophobic seal, through which neither methanol nor water leaked. A strip of PDMS sheet (1.0 cm × 2.0 cm) was placed inside this cell and then the cell was filled with the desired liquid. The PDMS lens was held at its edge by a fine-pointed tweezer and brought slowly through the liquid and placed onto the flat sheet. The top of the cell was sealed by covering it with another glass slide also treated with fluoroalkylsilane. All the components of this cell were periodically dismantled for rigorous cleaning. The cleaning was done by ethanol, methanol, and distilled water. (*Note:* This cell could have been designed with all glass components. Silicone elastomer was used primarily because it was readily available, the cells were easy to prepare, and several cells could be designed at once.) The contact area was viewed through a 4× microscope objective that had a working distance of 16.2 mm from the specimen. The working distance from the stage to the condenser was 20.5 mm, which permitted enough room to manipulate the specimens.

Measurements of Contact Deformations Obtained by Using Unfunctionalized PDMS in Air. The lenses and sheets were rinsed in HPLC grade methanol before use and air-dried. Only those lenses were used that projected circular aspects when viewed through the microscope and were free from gross defects (Figure 3). In order to carry out a load-deformation experiment, a lens ($R = 1.44$ mm) was brought into contact with a flat sheet of PDMS in air. Neither the temperature nor the humidity of the room was controlled. The average temperature and relative humidity of the laboratory were 24–25 °C and 45–50%, respectively. After the lens was placed on the flat sheet very carefully, the contact deformation was measured. Additional load was applied by pressing the lens against the flat sheet. After the load reached a steady value, the contact deformation was measured again. The load was increased from a zero value to about 200 dyn and the deformations were measured at random intervals. At the end of this experiment, load was removed from the lens and the deformation was again measured as the load continued to decrease from 200 dyn to zero. This experiment was repeated by placing the lens on different locations of the flat sheet. A second set of experiments was performed by measuring the deformation as a function of the radius of curvatures of the lenses. Lenses of radii ranging from ~1 to 2 mm were placed on a flat sheet of PDMS under the condition of zero load. In all experiments involving unmodified PDMS, the contact deformations were spontaneous and reversible. Although the measurements were generally made within minutes of contact between the lens and sheet, no noticeable change of the contact area could be seen even after an additional hour of contact. This observation implied that measurements were made under equilibrium conditions.

Measurements of Pull-Off Forces. The maximum force needed to pull a lens out of contact with the flat sheet of PDMS was measured by slowly removing the lens from the sheet. We did not have precise control over the speed of detachment; it was done as slowly as possible by manual operation. Precise control over speeds was not necessary in these experiments, because the system behaved purely elastically. The adhesion (pull-off) forces were measured as a function of the radii of curvatures of several lenses, which were previously used for equilibrium deformation experiments.

Measurements of Contact Deformations in Liquids. A set of measurements was carried out under liquids rather than in air. Since the work of adhesion depends on the medium, using a liquid provided a convenient way to alter the surface work term.[45] The interactions between PDMS lens and PDMS sheet were examined under mixtures of water and methanol. To establish the reversibility of these systems, the lens was removed from the surface and replaced at different locations; the observed

(45) Gent and Schultz (Gent, A. N.; Schultz, J. J. *Adhesion* 1972, *3*, 281) used a similar procedure to alter the surface work term in their studies on the correlation between fracture surface energy and thermodynamic work function.

values of the contact areas were reproducible.[46] Cavitation[47] was sometimes a problem when the measurements were made in pure water. When it occurred, a ring of vapor was found to surround the contact circle. Prolonged degassing of water eliminated this problem. In all experiments, degassed water was used even though it was found that the cavitation did not occur in mixtures of water and methanol.

Measurements of Contact Angles. Water, paraffin oil, hexadecane, methylene iodide, methanol, and various mixtures of water and methanol were used for the contact angle measurements. Quasistatic advancing and receding contact angles were measured according to the method of Neumann and Good.[48] Following this technique, a small drop of about 1 μL was formed on the solid surface using a needle attached to a microsyringe. While the drop was still in contact with the needle, additional liquid was added to the drop to advance the drop edge as slowly as possible. After the three-phase contact line had stopped moving, the advancing contact angle was measured.[49] Receding contact angles were measured following the same procedure after withdrawing the liquid from the drop. While most measurements of contact angles were done under quasistatic conditions, the contact angles of paraffin oil and hexadecane on unmodified PDMS were measured quickly (within a few seconds) after advancing or retreating the drops, because these liquids swell PDMS. Contact angles of methylene iodide, paraffin oil, and alkane were measured under ambient conditions. Contact angles of water–methanol mixtures were measured in an environmental chamber by equilibriating the atmosphere of the chamber with solutions having compositions that were the same as those used for the contact angle measurements.

Chemical Functionalization of Poly(dimethylsiloxane). The details of the techniques involved in functionalizing PDMS surfaces will be described in a separate publication. Briefly, PDMS sheets and lenses were oxidized in an oxygen plasma for 45 s at 0.2 Torr O_2 pressure in a Harrick plasma cleaner at the lowest power setting. This procedure yielded a very hydrophilic surface (θ_a of water was zero), which reacted readily with Cl_3-$Si(CH_2)_9CH_3$ and $Cl_3Si(CH_2)_2(CF_2)_7CF_3$. Traditionally, modifications of inorganic oxides by silanes have been done from an organic solvent. Most organic solvents swell PDMS to a greater

and lesser degree. Because of this problem, the reactions between PDMS^{ox} and the silanes were carried out by exposing the PDMS^{ox} to the vapors of various chlorosilanes under reduced pressure. A second advantage of carrying out the adsorption from the vapor phase was that the higher molecular weight silanes could not interfere with the adsorption of the silane monomers because they could not transfer to the vapor phase. A plastic weighing cup containing 3 g of paraffin oil and 200 μL of silane was first placed in a desiccator, which was then evacuated to about 0.15 Torr to remove volatiles (the advantage of dissolving the silane in the paraffin oil was that the solution could be reused several times). The desiccator was back-filled with nitrogen and the oxidized PDMS samples were placed at a distance of about 1.5 cm from the oil level.[50] The desiccator was again evacuated to 0.15 Torr. The desiccator at this point was disconnected from the vacuum pump and allowed to remain in that condition for 2 h. At the end of 2 h, the samples were removed from the desiccator. All the steps starting from the insertion to the removal of samples were performed inside a glovebag, purged with nitrogen (or argon).

Load-Deformation Experiments with Functionalized PDMS. The load-deformation experiments involving functionalized PDMS surfaces were similar to those used for unmodified PDMS surfaces. The measurements were made in air by bringing a functionalized lens into contact with a functionalized flat sheet. The lens and the flat sheet contained either similar or dissimilar functional groups. Measurements were generally made within minutes after the applied loads were varied. For the contact between hydrocarbon and fluorocarbon surface, the contact area exhibited dynamic response during unloading experiments and, hence, the measurements were made within 15–20 s after the loads were varied. The measurements were repeated on several locations of the flat sheet using a single lens except for PDMS^{ox}. For two surfaces of PDMS^{ox} measurements could not be made on several locations, because failure took place within the polymer upon separation. For surfaces containing similar functional groups, the adhesion (pull-off) forces were measured from different locations of the functionalized sheets. For the hydrocarbon–fluorocarbon interface, the pull-off forces depend significantly on the rate of separation and are not reported here. This subject will be discussed in a separate publication.

(46) Although we have not directly established whether there was damage in the lens during these operations, we infer from the reproducibility of the contact deformations on several locations of the flat sheet that the lens was not damaged. If the lens was contaminated by dust or damaged accidentally, the defect could be easily discerned by the deviation of the area of contact from circularity.

(47) Christenson and Claesson (Christenson, H. K.; Claesson, Per M. *Science* 1988, *239*, 390) reported cavitation when two hydrophobic mica surfaces were brought into contact in degassed water. The degree of cavitation was found to be related to the hydrophobicity of the surfaces.

(48) Neumann, A. W.; Good, R. J. *Surface and Colloid Science*; Good, R. J., Stromberg, R. A., Eds.; Plenum Press: New York, 1979; Vol. 11, p 31.

(49) Watching for the three-phase contact line to come to a quasistatic value is very important. For example, the instantaneous advancing contact angle of water on PDMS is about 108°. However, if watched carefully, the three-phase line is found to advance slowly even after the cessation of the addition of any further liquid to the drop—and a quasistatic contact angle of 105–106° is obtained. The contact angle of a nonswelling liquid on PDMS obtained from captive bubble methods[33] should, however, be more reliable than the sessile drop method. Our preliminary measurements of θ_a and θ_r of water on PDMS using the captive bubble methods are, however, in agreement with the values obtained from the sessile drop method.

(50) We later found that monolayers of identical qualities can be formed by placing the same anywhere within the desiccator.