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## Correlation Between Surface Free Energy and Surface Constitution

MANOJ K. CHAUDHURY AND GEORGE M. WHITESIDES

Self-assembled monolayers (SAMs) of alkylsiloxanes on elastomeric PDMS (polydimethylsiloxane) were used as model systems to study interactions between surfaces. Surface free energies ( $\gamma_{SV}$ ) of these chemically modified surfaces were estimated by measuring the deformations that resulted from the contact between small semispherical lenses and flat sheets of the elastomer under controlled loads. The measured surface free energies correlated with the surface chemical compositions of the SAMs and were commensurate with the values estimated from the measurements of contact angles. This study provides direct experimental evidence for the validity of estimates of the surface free energies of low-energy solids obtained from contact angles.

MEASUREMENT OF CONTACT ANGLES is a technique that is highly sensitive to the composition and properties of surfaces (1). The measured quantities are related to the surface and interfacial free energies through Young's equation (2) (Eq. 1).

$$\gamma_{SV} = \gamma_{LV} \cos\theta + \gamma_{SL} \quad (1)$$

Here the system is assumed to be at thermodynamic equilibrium, and  $\gamma_{LV}$ ,  $\gamma_{SV}$ , and  $\gamma_{SL}$  stand for the surface and interfacial free energies of the liquid-vapor, solid-vapor, and solid-liquid interfaces, respectively. One use of Eq. 1 is to estimate  $\gamma_{SV}$ —a fundamental thermodynamic state parameter characterizing the surface of materials. Although  $\gamma_{LV}$  can be determined directly,  $\gamma_{SL}$  cannot, in general. Thus there have been several efforts to express  $\gamma_{SL}$  in terms of  $\gamma_{SV}$  and  $\gamma_{LV}$  in order to reduce the number of unknowns in Young's equation.

This objective has been best achieved (3) by treatments that assume specific forms for the intermolecular forces that operate across condensed phase boundaries. For systems where the London dispersion interactions are prominent, the most commonly used generalization of Young's equation is (3):

$$\gamma_{SV} = \gamma_{LV} (1 + \cos\theta)^2/4 \quad (2)$$

Equation 2 occupies a central position in estimating the surface free energies of low-energy solids. Because the values of  $\gamma_{SV}$  of solids cannot, in general, be measured directly (4), no rigorous comparison between

predicted and experimental values validates this equation. In this report, we present an experimental system based on a methodology developed by Johnson, Kendall, and Roberts (JKR) (5) that allowed direct estimation of the surface free energies of several model low-energy surfaces. This system provides a suitable experimental basis for systematic evaluation of Eq. 2.

The basic protocol of these measurements is to study spreading occurring at the interface between two elastomeric solids. Solids, like liquids, have a tendency to spread on other solids. The driving force for this spreading, like that on solid-liquid interfaces, is the minimization of the interfacial free energies. Thus when a curved solid is brought into contact with a flat substrate, a deformation occurs at the zone of contact. The magnitude of this deformation is determined by the balance of the interfacial and elastic energies. If the elastic constants of the materials are known, the interfacial energies can be estimated directly from contact de-

mations (5–12). The materials used in these experiments must be compliant and have very smooth surfaces. We have shown that elastomeric PDMS meets these requirements well (12, 13), and we chose this polymer for our contact deformation experiments.

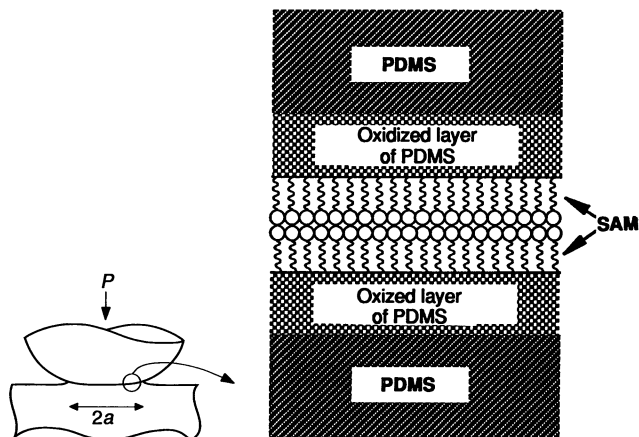
The basic experimental system (12) comprises a semispherical lens and a flat sheet of elastomeric PDMS (Dow Corning Sylgard 170). The surfaces of both lens and sheet were modified chemically using the technology of self-assembled organic monolayers (12–14). In a typical experiment (Fig. 1), the lens was slowly brought into contact with the flat sheet, and an external load was then applied. A spontaneous deformation occurred at the contact zone as soon as the lens touched the flat sheet (Fig. 2). This deformation increased in response to the external loads. Deformation was measured as a function of applied load. 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 flat sheet. All of the measurements were made under ambient conditions with the temperature of the laboratory  $\sim 23^\circ\text{C}$  and the relative humidity  $\sim 50\%$ . The data obtained from these load-deformation studies were analyzed (15) by using Eq. 3 to estimate  $\gamma_{SV}$  for the surface of the elastomer.

$$a^3 = (R/K)\{P + 6\pi R\gamma_{SV} + [12\pi RP\gamma_{SV} + (6\pi R\gamma_{SV})^2]^{0.5}\} \quad (3)$$

In Eq. 3,  $a$  (cm) is the radius of the contact deformation,  $R$  (cm) is the radius of curvature of the lens,  $P$  (dynes) is the external load, and  $K$  (dynes/cm<sup>2</sup>) is the composite modulus. In our studies, values of  $K$  clustered around  $5 \times 10^6$  dynes/cm<sup>2</sup>.

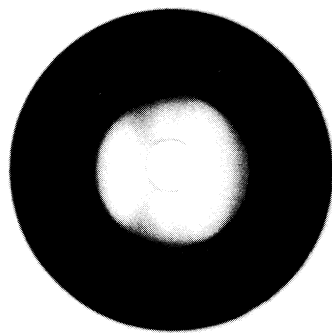
We controlled the chemical composition of the surface of PDMS using a procedure described previously (12, 16). Exposure of PDMS to an oxygen plasma generated a thin [ $<50 \text{ \AA}$  by x-ray photoelectron spectroscopy

**Fig. 1.** Contact between a semispherical lens and flat sheet of PDMS results in the formation of a circular region of radius  $a$ . For clarity, the area of contact is exaggerated. The surfaces of both the lens and flat sheets were modified by using alkylsiloxane self-assembled monolayers (SAMs). In a typical load-deformation experiment, the radius of the lens was  $\sim 1$  mm and the thickness of the flat sheet was  $\sim 1.5$  mm.



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**Fig. 2.** Photomicrograph showing the contact area (innermost circle) resulting from the contact between a lens ( $R = 0.72$  mm) and a flat sheet of  $\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_{10}\text{CH}_3$  under zero load. The radius of contact deformation was  $\sim 92$   $\mu\text{m}$ .

(XPS) silica-like layer (17) on its surface. We denote this surface as  $\text{PDMS}^{\text{ox}}$ . Chemisorption of alkyltrichlorosilanes [ $\text{Cl}_3\text{Si}(\text{CH}_2)_n\text{R}$ ] onto  $\text{PDMS}^{\text{ox}}$  produced monolayers of the corresponding alkylsiloxanes. By varying the head-group functionalities (R) of these silanes, the chemical compositions of the surface of the PDMS lens and sheet could be controlled. Silanes used to modify  $\text{PDMS}^{\text{ox}}$  were  $\text{Cl}_3\text{Si}(\text{CH}_2)_{10}\text{CH}_3$ ,  $\text{Cl}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$ ,  $\text{Cl}_3\text{Si}(\text{CH}_2)_{11}\text{OCH}_3$ ,  $\text{Cl}_3\text{Si}(\text{CH}_2)_{11}\text{Br}$ , and  $\text{Cl}_3\text{Si}(\text{CH}_2)_{11}\text{OCOCH}_3$ . We denote the material produced by reaction of  $\text{PDMS}^{\text{ox}}$  and a chlorosilane as  $\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_n\text{R}$ . We used XPS to verify the presence of the relevant functional groups on the monolayer-coated PDMS surfaces. One remarkable feature of these surfaces was that they all exhibited negligible hysteresis (18) in contact angles, except for the fluorocarbon surface, which exhibited large hysteresis with diiodomethane (Table 1). The observation of low hysteresis was particularly important in our studies because it suggested that the measured contact angles are close to equilibrium values and that Young's equation should be valid.

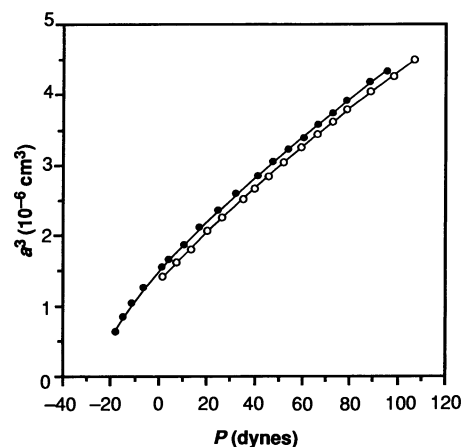
The result of a typical load-deformation study (19) is shown in Fig. 3. There was generally finite but small hysteresis in con-

tact deformations as obtained from the compression and decompression cycles. This hysteresis resulted in two different values of  $\gamma_{\text{SV}}$  for a specific surface. In Table 1, we present these values and compare them with the values obtained from the contact angles of hexadecane and diiodomethane. For the methyl and perfluoromethyl surfaces, we also report the surface free energies obtained from the contact angles of perfluorodecalin. In all cases, we used the average of the advancing and receding contact angles to estimate  $\gamma_{\text{SV}}$ .

The data tabulated in Table 1 show that small variations in the chemical compositions of the alkylsiloxane monolayers have a profound effect on adhesion of these surfaces and that the values of  $\gamma_{\text{SV}}$  measured by using Eq. 3 agree remarkably well with those estimated using contact angles (3). There are, however, several details about these data that deserve comment. First, we note that the surface free energies of the methyl surface as estimated from the contact angles of hexadecane and diiodomethane are higher than those obtained with the contact angle of perfluorodecalin. Conversely, the surface free energy (20) of the fluorocarbon surface as obtained from the contact angles of hexadecane is lower than that obtained by using perfluorodecalin (21). The values of  $\gamma_{\text{SV}}$  measured directly off the methyl surface certainly agree well with those obtained from the contact angle of hexadecane and diiodomethane but not with that obtained using a fluorocarbon liquid. The situation becomes reversed for the fluorocarbon surface (see Table 1).

For  $\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_{11}\text{OCH}_3$ , the surface free energy as obtained from the contact angle of hexadecane is somewhat lower than that obtained from the contact angle of diiodomethane. Although the reason for this discrepancy is not clear, it is plausible that diiodomethane has a greater ability to interact with underlying functional groups (that is, ether groups) than does hexadecane (22). This observation is similar to that reported for the SAMs of  $\omega$ -mercap-

(PFD); and 49.3 dynes/cm (DM).  $\gamma_{\text{SV}}^{\text{com}}$  and  $\gamma_{\text{SV}}^{\text{decom}}$  indicate the surface energy values obtained from compression and decompression experiments, respectively.  $\gamma_{\text{SV}}^i$  indicates the surface energy value as obtained from contact angle measurements using liquid *i*. The errors in estimating  $\gamma_{\text{SV}}$  values were less than 1  $\text{erg}/\text{cm}^2$ .



**Fig. 3.** Plots of  $a^3$  against  $P$  showing weak hysteresis for the surface  $\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_{10}\text{CH}_3$ . The radius of the lens was 0.97 mm. 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. 3.

toethers [ $\text{HS}(\text{CH}_2)_{16}\text{O}(\text{CH}_2)_n\text{CH}_3$ ;  $n = 0$  to 5] on gold, where hexadecane was inferred to be a more surface-sensitive probe liquid than water and glycerol (23). The agreement between the values of  $\gamma_{\text{SV}}$  for the methyl ether surface ( $\text{R} = \text{OCH}_3$ ) obtained from the contact angle of hexadecane and direct measurement indicates that adhesion between solids is very surface sensitive (24). The methyl ester surface ( $\text{R} = \text{CO}_2\text{CH}_3$ ) was wettable by hexadecane, indicating the head group region of this surface is significantly disordered and populated with the carbonyl groups. The measured surface free energy of this surface is consequently higher than that of the methyl ether surface and is in reasonable agreement with the estimate based on the contact angle of diiodomethane. A similar high wettability (and thus high surface energy) is also observed for the surface containing bromide groups ( $\text{R} = \text{Br}$ ).

These studies demonstrate that self-assembled alkylsiloxane monolayers on PDMS are excellent model systems for studying

**Table 1.** Contact angles of several liquids on functionalized PDMS and surface free energies of these systems.  $\theta_a$  and  $\theta_r$  represent advancing and receding contact angles, respectively; HD, PFD, and DM stand for hexadecane, perfluorodecalin, and diiodomethane, respectively. The surface tensions of these three liquids are: 27.7 dynes/cm (HD); 18.2 dynes/cm

Surface	Contact angles (degrees)						Surface free energies ( $\text{ergs}/\text{cm}^2$ )				
	$\theta_a^{\text{HD}}$	$\theta_r^{\text{HD}}$	$\theta_a^{\text{PFD}}$	$\theta_r^{\text{PFD}}$	$\theta_a^{\text{DM}}$	$\theta_r^{\text{DM}}$	$\gamma_{\text{SV}}^{\text{com}}$	$\gamma_{\text{SV}}^{\text{decom}}$	$\gamma_{\text{SV}}^{\text{HD}}$	$\gamma_{\text{SV}}^{\text{PFD}}$	$\gamma_{\text{SV}}^{\text{DM}}$
$\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$	71	68	35	35	98	67	15.5	16.5	12.7	15.0	
$\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_{10}\text{CH}_3$	41	40	37	37	73	73	19.5	22.0	21.5	14.7	20.6
$\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_{11}\text{OCH}_3$	24	20			55	54	26.5	27.0	25.7		30.8
$\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_{11}\text{OCOCH}_3$	0	0			45	45	32.5	33.5			36.0
$\text{PDMS}^{\text{ox}}\text{-O}_3\text{Si}(\text{CH}_2)_{11}\text{Br}$	0	0			42	40	36.0	37.5			37.9

adhesion between surfaces. The method described here, which is based on deformations in a compliant polymeric lens and sheet, is sensitive to small variations in the compositions of the surface. In terms of analyzing surface energetics, it is complementary to measuring contact angles. Although we have so far studied systems that interact primarily through London-van der Waals forces, the method can also be used to investigate more complex interfacial interactions (for example, hydrogen bonding) by incorporating relevant functional groups on the surface of the PDMS (25).

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- In his classic paper (1), Zisman wrote: "Unfortunately, the effect of constitution on either  $\gamma_{SV}^0$  or  $\gamma_{SL}$  is still unknown, and neither quantity can be studied until a satisfactory experimental method for measuring it has been found..." (Note that the symbol  $\gamma_{SV}^0$  in this statement has, basically, the same physical meaning as that of  $\gamma_{SV}$ ; the superscript "0" implied that the measurements are made under saturated vapor pressure.) One major experimental difficulty in analyzing the energetics of solid surfaces arises because most real systems exhibit hysteresis of some sort, indicating that they are not at thermodynamic equilibrium. Young's equation strictly applies only at equilibrium.
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- The original JKR equation was expressed in terms of  $W$ , the work of adhesion. For two similar surfaces,  $W$  is equal to  $2\gamma_{SV}$ , and thus we have expressed the

JKR equation in terms of  $\gamma_{SV}$ .

- The conditions used for silanization of PDMS<sup>ox</sup> were slightly different from those reported in (12). Under new conditions, desiccators containing paraffin oil solutions of silanes were evacuated to about 0.001 torr for 30 min. Oxidized PDMS samples were usually placed at about 1.5 cm from the oil level. The concentrations of silanes were 60  $\mu$ l of silane per 3 g of paraffin oil, except for the fluoroalkylsilane for which the concentration was 5  $\mu$ l silane per 3 g of paraffin oil. We could consistently obtain surfaces exhibiting low hysteresis using these conditions.
- The exact nature of the plasma-oxidized surface of PDMS is unclear. Most reports, however, agree that it contains silanol groups. For examples, see: D. W. Fakes, M. C. Davies, A. Brown, J. M. Newton, *Surf. Interface Anal.* **13**, 233 (1988); D. W. Fakes, J. M. Newton, J. M. Watts, M. J. Edgell, *ibid.* **10**, 416 (1987); M. Morra *et al.*, *J. Colloid Interface Sci.* **137**, 11 (1990). The findings of Fakes *et al.* indicated that the structure of the surface resembles that of inorganic silica. Morra *et al.* believe that the structure is more complex. The formation of surface silanols is, however, widely accepted. The surface properties of the silane-treated PDMS<sup>ox</sup> are, however, determined by the composition and structure of the silane, not by the underlying oxide layer (12, 13). The wettability properties of the silane-treated PDMS<sup>ox</sup> surfaces are similar to those of the corresponding monolayers formed on silicon wafer.
- The methyl ether surface, when freshly formed, exhibited significant hysteresis in both contact angles and contact deformations (not reported here). It was necessary to rinse this surface in decalin, ethanol, and water in order to minimize hysteresis.
- The load-deformation and contact-angle measurements were performed on different samples taken from the same batch.
- The origin of the large hysteresis of diiodomethane on the fluorocarbon surface is not clear. Because of the high hysteresis, we did not use this liquid to calculate  $\gamma_{SV}$  of the fluorocarbon surface.
- Similar anomalies in the values of  $\gamma_{SV}$  for the fluorocarbon and hydrocarbon surfaces (as estimated using contact angles) have also been observed by Fowkes [F. M. Fowkes, *Adv. Chem. Ser.* **43**, 99 (1964)]. Non-ideal interaction between fluorocarbons and hydrocarbons is also well known in their solubility properties [see J. H. Hilderbrand and R. L. Scott, *Solubility of Non-Electrolytes* (Reinhold, New York, ed. 3, 1950)].
- These differences cannot be explained on the basis of the surface swelling because neither hexadecane nor diiodomethane swells monolayer-coated PDMS.
- C. D. Bain and G. M. Whitesides, *J. Am. Chem. Soc.* **110**, 334 (1988). The term "high surface sensitivity" is used here loosely. Whether the liquids (water, glycerol, or diiodomethane) sense the underlying functional groups by long-range forces or by perturbing the structure of the surface is not clear.
- High surface sensitivity of adhesion has also been demonstrated recently by Burnham *et al.* [N. A. Burnham, D. D. Dominguez, R. L. Mowery, R. J. Colton, *Phys. Rev. Lett.* **64**, 1931 (1990)], who used an atomic force microscope to measure the force between tungsten and different surfaces, including Langmuir-Blodgett films of stearic acid and  $\omega,\omega,\omega$ -trifluorostearic acid deposited on Al/Al<sub>2</sub>O<sub>3</sub>. In these studies the adhesion force between tungsten and monolayer-coated alumina changed remarkably when the surface composition varied from -CH<sub>3</sub> to -CF<sub>3</sub>.
- M. K. Chaudhury, unpublished results.
- M.K.C. acknowledges support from Dow Corning. The initial stages of this work at Harvard University were supported in part by the Office of Naval Research and the Defense Advanced Research Projects Agency. We thank M. J. Owen (Dow Corning) for many valuable discussions.

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## Dissociation of Individual Molecules with Electrons from the Tip of a Scanning Tunneling Microscope

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The scanning tunneling microscope (STM) can be used to select a particular adsorbed molecule, probe its electronic structure, dissociate the molecule by using electrons from the STM tip, and then examine the dissociation products. These capabilities are demonstrated for decaborane(14) (B<sub>10</sub>H<sub>14</sub>) molecules adsorbed on a silicon(111)-(7 × 7) surface. In addition to basic studies, such selective dissociation processes can be used in a variety of applications to control surface chemistry on the molecular scale.

THE SCANNING TUNNELING MICROSCOPE (STM) can be used to control the structure and properties of materials on surfaces at the atomic or molecular level. The STM has been previously used to transfer clusters of atoms from the STM tip to the sample (1), to write molecular-scale marks on graphite (2), to reposition adsorbed atoms and molecules on metal surfaces (3, 4), and to reversibly transfer individual atoms between a surface and a tip by

the application of voltage pulses (4-6). At a somewhat more macroscopic level, the STM has been used for a variety of nanometer-scale surface modifications (7, 8), including the deposition and etching of materials on surfaces, the electron-stimulated desorption of adsorbates (9), and the exposure of lithographic films using the STM tip as a field-emission electron source (10). In this report, we discuss the dissociation of individual adsorbed molecules using low-energy electrons from the tip. With the STM, one can select a particular adsorbed molecule, probe its electronic structure, dissociate the molecule, and then examine the dissociation products.

We investigated decaborane (14)

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