Surface free energies of alkylsiloxane monolayers supported on elastomeric polydimethylsiloxanes

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Abstract—Self-assembled monolayers (SAMs) of alkylsiloxanes on elastomeric polydimethylsiloxane (PDMS) are excellent model systems with which to study interactions between surfaces. The surface free energies of several monolayer-coated PDMS surfaces were determined by measuring the deformations produced from the contact between semispherical lenses and flat sheets of the elastomer under controlled loads. The contact deformations were analyzed using the theory of Johnson, Kendall, and Roberts (JKR) to estimate the surface free energies of the monolayer films, which were compared with the values obtained from contact angles. It is shown that the surface free energies of not only the apolar, but also the polar non-associative surfaces can be adequately described by considering only the dispersion forces. Polarity as obtained from the contact angles of water has no general significance in estimating the interfacial interactions across the polar non-associative surfaces.

Keywords: Surface free energy; adhesion; contact angle; surface modification; monolayer; contact deformation.

1. INTRODUCTION

Surface energies of low-energy solid materials are usually determined from contact angles. The measured contact angles are related to the surface and interfacial energies according to the well-known Young's equation [1]:

$$\gamma_{sv} = \gamma_{lv} \cos \theta + \gamma_{sl}. \tag{1}$$

Here the system is assumed to be at thermodynamic equilibrium, and γ_{lv}, γ_{sv}, and γ_{sl} stand for the interfacial free energies of the liquid–vapor, solid–vapor, and solid–liquid interfaces. An estimation of γ_{sv} from Young's equation cannot, however, be done in a straightforward manner since γ_{sl} is, in general, not known. Thus, there have been significant efforts to generalize Young's equation so that γ_{sl} can be expressed in terms of γ_{sv} and γ_{lv}. Before we discuss these different generalizations of Young's equation, it will be instructive to point out another important equation of interfacial interactions, which was given by Dupré [2]. The Dupré equation,

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - W_{sl}, \tag{2}$$

amounts to a conservation of energy in a reversible process of adhesion and separation of two phases. Combination of equations (1) and (2) yields

$$W_{sl} = \gamma_{lv}(1 + \cos \theta), \tag{3}$$

which is known as the Young–Dupré equation. Equation (3), which suggests that the work of adhesion between a solid and a liquid is equivalent to the change in

the free energy of the liquid drop due to deformation, is the most fundamental equation for analyzing the energetics of solid surfaces. After Dupré, the next major impetus in the research on contact angles was due to Zisman [3], who introduced the well-known parameter 'γ_c'—the critical surface tension of wetting. However, it was realized that γ_c is a measure of the surface energy of the solid but not equal to it, because the interfacial tension need not be zero even if θ were zero. Subsequent to Zisman, several authors developed theories of adhesion and contact angles that attempted to express W_{sl} in terms of the surface free energies of solids and liquids. All these treatments assumed 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 [4] of the Dupré equation is

$$W_{sl} = 2(\gamma_{lv}\,\gamma_{sv})^{0.5}. \tag{4}$$

Combination of equations (3) and (4) yields the equation

$$\gamma_{lv}(1 + \cos\theta) = 2(\gamma_{lv}\,\gamma_{sv})^{0.5}. \tag{5}$$

According to equation (5), γ_{sv} of a solid can be determined from the surface tension of a single test liquid and its contact angle.

For systems that are polar, the surface free energies were assumed to be composed of two parts: dispersion (γ^d) and polar (γ^p), i.e. $\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p$. The commonly used generalization [5] of the Dupré equation is

$$W_{sl} = 2(\gamma_{lv}^d\,\gamma_{sv}^d)^{0.5} + 2(\gamma_{lv}^p\,\gamma_{sv}^p)^{0.5}. \tag{6}$$

In view of equation (6), equation (3) becomes

$$\gamma_{lv}(1 + \cos\theta) = 2(\gamma_{lv}^d\,\gamma_{sv}^d)^{0.5} + 2(\gamma_{lv}^p\,\gamma_{sv}^p)^{0.5}. \tag{7}$$

In addition to the geometric mean combining rule, another widely used generalization [equation (8)] of equation (3) uses the harmonic mean combining rule of the surface free energy components [6]

$$\gamma_{lv}(1 + \cos\theta) = 4\gamma_{lv}^d\,\gamma_{sv}^d/(\gamma_{lv}^d + \gamma_{sv}^d) + 4\gamma_{lv}^p\,\gamma_{sv}^p/(\gamma_{lv}^p + \gamma_{sv}^p). \tag{8}$$

While equations (7) and (8) are widely used to estimate the γ_{sv} values of solids, very few rigorous comparisons between predicted and experimental values have yet been made [7, 8]. In earlier papers [7, 8], we presented an experimental system based on a methodology developed by Johnson, Kendall, and Roberts [9] that allowed a direct estimation of the surface free energies of several model low-energy surfaces. Most of the discussions in refs 7 and 8 were, however, centered around the dispersion forces. In this paper, we extend the discussion to the 'so-called' polar interactions across condensed phases in order to test the validity of equations (7) and (8).

2. MEASUREMENT OF SURFACE FREE ENERGY FROM CONTACT DEFORMATION

The measurements of the surface free energies were made from the deformations resulting from the contact between a semispherical lens and flat sheets of elastomeric PDMS under controlled loads. The work of adhesion between the elastomer surfaces were determined according to the theory of Johnson, Kendall, and Roberts (JKR).

The basic experimental system [7, 8] consisted of a semispherical lens and a flat sheet of elastomeric PDMS (Dow Corning Syl-170). The surfaces of both the lens and the sheet were modified chemically using self-assembled alkylsiloxane monolayers [7, 8, 10]. In a typical experiment, the lens was slowly brought into contact with the flat sheet and an external load was then applied (Fig. 1). The deformations produced at the contact of the two surfaces were measured as a function of both compressive and decompressive loads. These load-deformation data were analyzed [9] using the equation

$$a^3 = (R/K)\{P + 3\pi R W + [6\pi R P W + (3\pi R W)^2]^{0.5}\}, \tag{9}$$

to estimate the work of adhesion (W) between the polymer surfaces. In this equation, a (in cm) is the radius of the contact deformation, R (in cm) is the radius of curvature of the lens, P (in dynes) is the external load, and K (in dynes/cm^2) is the composite modulus. In these studies, the value of K was typically 5×10^6 dynes/cm^2. The surface free energy was taken to be one half of the work of adhesion (W).
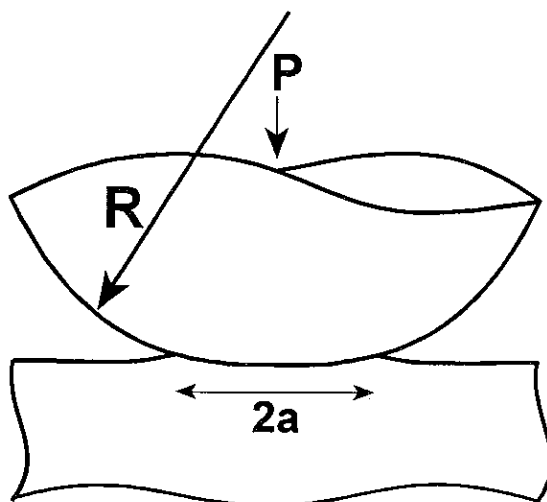

Figure 1. Contact between a semispherical lens and a flat sheet of PDMS results in the formation of a circular region of radius a. For clarity, the area of contact is exaggerated. The surfaces of both the lens and the flat sheets were modified by using self-assembled alkylsiloxane monolayers (SAMs).

3. CHEMICAL MODIFICATION OF PDMS

The chemical composition of the PDMS surface was modified using a procedure described previously [7, 8]. Exposure of PDMS to an oxygen plasma generated a thin (<50 Å by X-ray photoelectron spectroscopy) silica-like layer* [11] on its surface, which was modified by reacting with alkyltrichlorosilanes ($Cl_3Si(CH_2)_nR$) to form the monolayers. Silanes used to modify PDMS^{ox} were $Cl_3Si(CH_2)_{10}CH_3$, $Cl_3Si(CH_2)_2(CF_2)_7CF_3$, $Cl_3Si(CH_2)_{11}OCH_3$, $Cl_3Si(CH_2)_{11}OCOCH_3$, and $Cl_3Si(CH_2)_{11}Br$. We denote the material produced by

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*The plasma-oxidized surface of PDMS is like that of silica as evidenced from infrared and X-ray photoelectron spectroscopy.

reaction of PDMS^{ox} and a chlorosilane as PDMS^{ox}—O$_3$Si(CH$_2$)$_n$R, where R is CH$_3$, CF$_3$, OCH$_3$, etc. X-ray photoelectron spectroscopy verified the presence of the relevant functional groups on the monolayer-coated PDMS surfaces (see Fig. 2). Infrared spectroscopy indicated that these monolayers were in the liquid-like state. The contact angles of water, perfluorodecalin, hexadecane, and di-iodomethane on these surfaces are tabulated in Table 1. Note that the monolayer surfaces containing ether and ester groups have water contact angles less than 90° and are therefore more polar than the surfaces containing methyl, perfluoro-methyl, and bromide groups, for which the contact angles were greater than 90°.
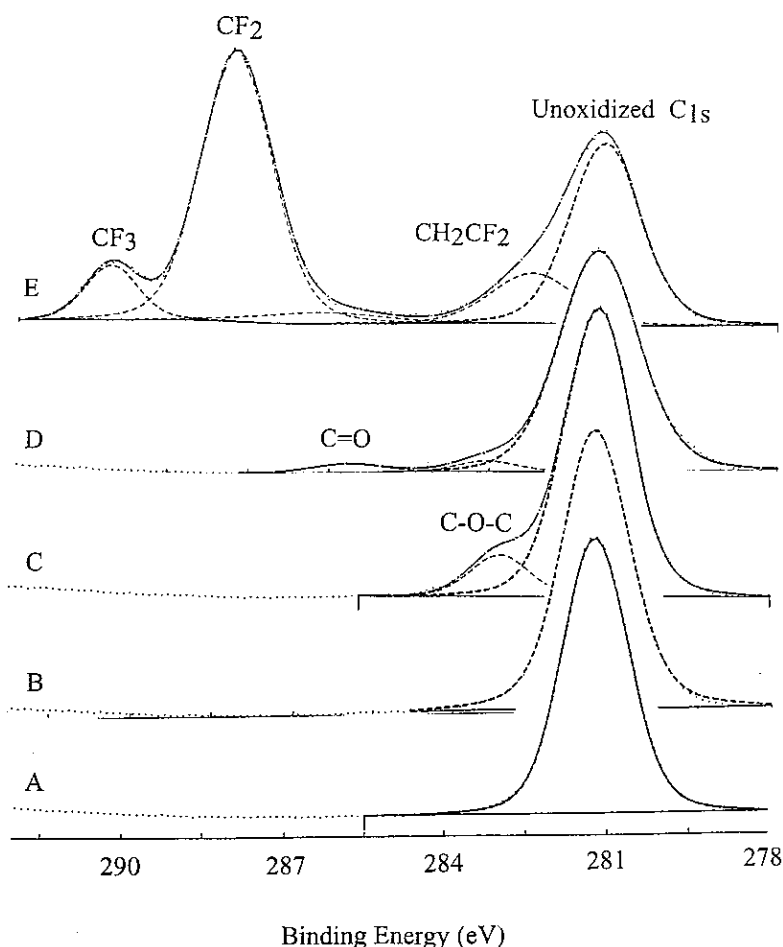
Figure 2. High resolution XPS scans of the C$_{1s}$ region of the unmodified and functionalized PDMS surfaces. (A) Unoxidized PDMS; (B) PDMS^{ox}—O$_3$Si(CH$_2$)$_{10}$CH$_3$; (C) PDMS^{ox}—O$_3$Si(CH$_2$)$_{11}$OCH$_3$; (D) PDMS^{ox}—O$_3$Si(CH$_2$)$_{11}$OCOCH$_3$; (E) PDMS^{ox}—O$_3$Si(CH$_2$)$_2$(CF$_2$)$_7$CF$_3$.

Table 1.
Contact angles of several liquids on functionalized PDMS

System	θ_a^W	θ_r^W	θ_a^{HD}	θ_r^{HD}	θ_a^{PFD}	θ_r^{PFD}	θ_a^{DM}	θ_r^{DM}
—CF$_3$	113	105	71	68	35	35	98	67
—CH$_3$	112	110	41	40	37	37	73	73
—OCH$_3$	80	76	24	20	—	—	55	54
—CO$_2$CH$_3$	76	73	0	0	—	—	45	45
—Br	90	85	0	0	—	—	42	40

Under the heading 'system', only the terminal functionalities are given. The generic formula of the functionalized PDMS is PDMS^{ox}—O$_3$Si(CH$_2$)$_{11}$R, where R is CH$_3$, OCH$_3$, etc. The complete formula for the fluorocarbon monolayer-treated PDMS is PDMS^{ox}—O$_3$Si(CH$_2$)$_2$(CF$_2$)$_7$CF$_3$ (see text for details). θ_a and θ_r represent the advancing and receding contact angles, respectively. W, HD, PFD, and DM stand for water, hexadecane, perfluorodecalin, and diiodomethane, respectively. The surface tensions of these liquids are 72.8 mN/m (water), 27.7 mN/m (hexadecane), 18.2 mN/m (perfluorodecalin) and 49.3 mN/m (diiodomethane).

4. COMPARISON BETWEEN THE SURFACE FREE ENERGIES OBTAINED FROM CONTACT ANGLES AND CONTACT DEFORMATIONS

In a typical load-deformation cycle, the measured hysteresis of adhesion was small for these surfaces and thus the averages of the values obtained from the compressive and decompressive loads are reported. In Tables 2 and 3, we present the averages of these values and compare them with the values obtained from the contact angles of diiodomethane and water [see equations (5)–(8)]. For the fluorocarbon surface, we estimated the surface free energy using the contact angle of a fluorocarbon liquid—perfluorodecalin. As the hysteresis of the contact angles was also low, we used the averages of the advancing and receding angles to calculate the surface free energies.

Tables 2 and 3 summarize the γ_{sv}^d, γ_{sv}^p, and γ_{sv}^{tot} ($\gamma_{sv}^d + \gamma_{sv}^p$) values of these materials as obtained from the geometric and harmonic mean combining rules. For the methyl and perfluoromethyl surfaces, the γ_{sv}^p values are small and thus do not contribute significantly to the total surface free energy. For the other surfaces, the γ_{sv}^p values are significant. For the ether- and ester-containing surfaces, the surface free energies as obtained from contact deformations did not correlate with the total surface free energies obtained from contact angles using either the geometric or the harmonic mean combining rule. However, the agreement between the directly measured γ_{sv} values and the values (γ_{sv}^d) obtained from the contact angles of dispersive liquids is generally good for all the surfaces examined.

The surfaces used in these investigations were either dispersive or polar non-associative. The dispersive surfaces interact only via London interactions. The polar non-associative surfaces, while they can form hydrogen bonds with water, interact with a surface of similar chemical properties only via London and electrostatic forces. These surfaces fall in the category of monopolar surfaces described in ref. 12. An electrostatic interaction between these surfaces may be

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*The surface free energy values obtained using hexadecane are usually similar to those obtained using diiodomethane (see ref. 8). Since diiodomethane exhibits a large hysteresis on the fluorocarbon surface, these contact angles could not be used.

Table 2.

Surface free energies (in mJ/m^2) of PDMS as a function of the surface chemical compositions (geometric mean)

System	γ_{sv}^{JKR}	γ_{sv}^{d}	$\gamma_{sv.W}^{p}$	γ_{sv}^{tot}
—CF$_3$	16.0	15.0	0.8	15.8
—CH$_3$	20.8	20.6	0.09	20.7
—OCH$_3$	26.8	30.8	6.4	37.2
—CO$_2$CH$_3$	33.0	36.0	6.4	42.4
—Br	36.8	37.9	1.7	39.6

γ_{sv}^{JKR} values indicate that the surface free energy values were obtained from the JKR experiments. γ_{sv}^{d} and γ_{sv}^{p} values were determined using equations (5) and (7). γ_{sv}^{d} values were determined using the contact angle of diiodomethane for all surfaces except the perfluoromethyl surface, for which the contact angle of perfluorodecalin was used. γ_{sv}^{tot} is the total surface free energy, which is the sum of dispersion and polar components.

Table 3.

Surface free energies (in mJ/m^2) of PDMS as a function of the surface chemical compositions (harmonic mean)

System	γ_{sv}^{JKR}	γ_{sv}^{d}	$\gamma_{sv.W}^{p}$	γ_{sv}^{tot}
—CF$_3$	16.0	15.2	3.6	18.8
—CH$_3$	20.8	23.5	0.4	23.9
—OCH$_3$	26.8	32.2	10.9	43.1
—CO$_2$CH$_3$	33.0	36.7	11.5	48.2
—Br	36.8	38.4	5.6	44.1

Surface free energy values from contact angles were estimated by using equations (5) and (8). For other notations, see Table 2.

envisaged if the polar groups are oriented. The adhesion results, however, suggest that the electrostatic interactions are not significant—if they were significant, the total surface free energies would have been different from the prediction based on dispersion forces. The fact that electrostatic interactions are not significant suggests that the head group regions of the monolayers are sufficiently disordered, thus allowing random dipoles to cancel each other's field. This picture is consistent with the liquid-like state of the monolayers evidenced by infrared spectroscopy. (Details of the infrared spectroscopy will be published separately.)

The low contact angle (i.e. <90°) of water on the polar functional monolayers is a result of forming hydrogen bonds with water. However, the polar components of the surface free energies of these surfaces as obtained from the water contact angles are fictitious and have very little in common with the forces that constitute cohesive interaction between these surfaces. Since these surfaces are polar non-associative, they cannot form hydrogen bonds with each other, and

thus the energy of cohesion for these surfaces is given by the dispersion forces only.

5. CONCLUSION

The method described here, which is based on measuring contact deformations in compliant polymeric systems, is sensitive to small variations in the chemical compositions of the surfaces and thus it can be used to conduct systematic studies into the relations btween energetics and surface constitution. The method is complementary to measuring the contact angle, because it provides directly an estimate of the surface free energy of the solid, which is estimated only indirectly from the contact angle. The major finding of this study, that the cohesive interaction between polar non-associative surfaces originates entirely from the dispersion forces, is consistent with the views expressed by Fowkes as well as Good and co-workers [12, 13].

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