Estimation of Adhesion Hysteresis Using Rolling Contact Mechanics

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The energy needed to separate two surfaces is usually greater than that gained by adjoining the two. The difference of these two adhesion energies, also known as adhesion hysteresis, is of significant importance in polymer surface science because it carries information about the nonequilibrium processes occurring at interfaces. Here we describe a methodology that allows estimation of adhesion hysteresis at polymer−inorganic interfaces using rolling contact mechanics. The method is illustrated with hemicylindrical lenses of poly(dimethylsiloxane)s (PDMS) rolling on silicon wafers.

Introduction

Recently, the methods of contact mechanics, as developed by Johnson, Kendall, and Roberts,[1] have gained significant attention in studying the surface energetics and adhesion of deformable solid materials. A main reason for its popularity stems from the fact that the method is simple yet versatile and provides valuable information about the nonequilibrium processes occurring at interfaces. In its simplest form, the method entails bringing a sphere into contact with another sphere or a flat plate.[2−13] The interfacial forces cause a circular deformation in the zone of contact, which increases with external load. A mechanical calibration of the load-deformation data yields the work of adhesion between the two solids. The experiment is usually conducted as a function of both increasing and decreasing loads. The works of adhesion obtained from these loading and unloading experiments are not necessarily equal to each other—usually an adhesion hysteresis persists. Recently, the method of rolling contact mechanics has been introduced.[14−18] Rolling of a cylinder on a flat surface can be viewed as the propagation of two cracks, one closing at the advancing edge and the other opening at the receding edge. It has been shown in a previous publication[18] that the work of adhesion at the receding edge (W_r) is related to that at the advancing edge (W_a) as follows:

$$W_r = W_a\left\{2\left(\frac{b}{b_0}\right)^{3/2} - 1\right\}^2 \tag{1}$$

where $2b_0$ and $2b$ are the widths of contact for a stationary and rolling cylinder on a flat plate, respectively.

We have previously used eq 1 to estimate W_r in some studies involving hydrogen bonding interactions between solid surfaces.[18] In that treatment, it was imperative that the value of W_a be known a priori in order to estimate W_r. Here we present a method to estimate the values of W_a and W_r independently and simultaneously. The starting point of our analysis is based on eqs 2 and 3, which relate W_a and W_r to the rolling torque and external load acting on the cylinder.[17,18]

$$P + \sqrt{2\pi E^* b W_r} = \frac{\pi E^* b^2}{4R} + \frac{2\tau}{b} + \frac{8\tau PR}{\pi E^* b^3} \tag{2}$$

$$P + \sqrt{2\pi E^* b W_a} = \frac{\pi E^* b^2}{4R} - \frac{2\tau}{b} - \frac{8\tau PR}{\pi E^* b^3} \tag{3}$$

Here P and τ are the external load and torque acting on unit length of the cylinder. E^* is defined as $1/E^* = (1 - \nu_1^2)/E_1 + (1 - \nu_2^2)/E_2$. E_i and ν_i, respectively, are the Young's moduli and Possion ratios of the cylinder and substrate. R is the radius of curvature of the cylinder and b is the half-width of contact deformation (Figure 1).

The Method of Rolling Contact Mechanics. The basic protocol used to carry out the rolling contact experiment is shown schematically in Figures 1 and 2. The method had been discussed previously in ref 18. Briefly, an elastomeric hemicylinder, attached to a thin glass plate, is first brought into contact with a flat substrate resting on an electrobalance. The cylinder is rolled on the flat plate by tilting one end of the thin glass plate with a micromanipulator. As the cylinder rolls, the net normal force applied on the cylinder is recorded in a computer that is connected to the electrobalance. The force at first increases and then reaches a constant value (Figure 3). Video microscopic study shows that the width of contact between the cylinder and flat plate also increases with load and remains constant when the force reaches the

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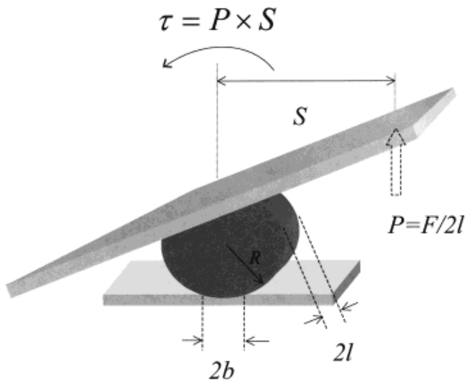

Figure 1. Schematic of a hemicylinder rolling on a flat plate. The hemicylinder was rolled on the flat substrate by applying an external load P to one end of the glass plate. The torque per unit length needed to roll the hemicylinder is the product of P and S.

plateau value. However, as the receding edge traverses past the junction of the old and new contact area, an instability occurs causing the contact width and the force to decrease abruptly to a lower value. The instability, as discussed previously,[18] results from the discontinuity of the time-dependent work of adhesion at the junction of old and new contacts. The force (F) registered on the balance is same as that needed to roll the cylinder, which allows estimation of the rolling torque per unit length of cylinder from the following equation: $\tau = FS/2l$. Once the normal load ($P = F/2l$), the rolling torque ($\tau = PS$), and the contact width ($2b$) are measured in a given experiment, W_a and W_r can be evaluated from the solution of eqs 2 and 3. Next we illustrate this procedure by rolling a hemicylinder of elastomeric poly(dimethylsiloxane) (PDMS) on a silicon wafer, where significant hysteresis of adhesion persists.

The elastomer (Dow Corning Sylgard 184) is produced by a platinum catalyzed hydrosilation reaction between a vinyl ended dimethylsiloxane oligomer and a methyl hydrogen siloxane cross-linker. The resultant polymer is an elastomer having a glass transition temperature of −116 °C, an elastic modulus of 1.3 MPa, and surface energy of 22 mJ/m^2. After contacting these hemicylinders with clean silicon wafers for 10 min, they were rolled using a micromanipulator.[18] Both the normal loads and contact widths were measured as rolling proceeded, the plateau values of which were used to estimate W_a and W_r.

Two criteria were used to examine the validity of the adhesion energy values obtained from these rolling experiments. One was to perform a standard loading−unloading experiment.[18,19] In that, W_a was obtained from the contact width ($2b_0$) of the PDMS cylinder on a silicon wafer at zero load and using:

$$W_a = \frac{\pi E^* {b_0}^3}{32R^2} \tag{4}$$

The validity of eq 4 has been demonstrated in previous publications.[18,20] The hemicylinder was then pressed against the silicon wafer with a load of 20 mN for 10 min. When the load was removed, the contact width, at first, decreased and then reached a quasi-equilibrium value, from which W_r was estimated using eq 4. These W_a and W_r values were compared with those obtained from the rolling contact mechanics.

Table 1. Advancing (W_a) and Receding (W_r) Works of Adhesion of a PDMS Hemicylinder (Sylgard 184) Rolling on a Silicon Wafer

	P (N/m)	S ($\times 10^{-3}$m)	τ (mJ/m)	W_a (mJ/m^2)	W_r (mJ/m^2)
trial 1	0.375	2.30	0.861	47	614
trial 2	0.567	1.69	0.957	40	669
trial 3	0.610	1.44	0.881	41	620
trial 4	0.741	1.13	0.834	39	587
trial 5	0.410	2.14	0.876	38	614
average				41 ± 3	621 ± 27

The other criterion used to check the validity of the adhesion energies obtained from rolling contact mechanics[14,15] is based on the principle of total energy conservation. When a cylinder rolls on a flat plate, new surface areas are created at the trailing (or receding) edge while free surface areas disappear at the advancing edge. The concomitant change of surface energy is provided by the external torque. An energy conservation approach yields

$$W_r - W_a = \tau/R \tag{5}$$

Equation 5 was used as another check for the validity of the adhesion energies obtained from eqs 2 and 3.

Results and Discussion

With a silicone (Dow Corning Sylgard 184) hemicylinder ($R = 1.52$ mm) and a clean silicon wafer, we carried out several rolling experiments by applying the external force at different values of S (Figure 1), all other conditions being constant. Table 1 summarizes the values of P, S, and τ as well as those of W_a and W_r obtained from eqs 2 and 3. Note that the values of W_a and W_r cluster around 41 ± 3 and 621 ± 27 mJ/m^2, respectively, which agree well with the values of W_a (45 mJ/m^2) and W_r (639 mJ/m^2) obtained from the standard loading−unloading experiments. It is noteworthy that the value of τ is nearly constant even though S varies from 0.11 to 0.23 cm, implying that the value of P is adjusted by the system to ensure a constant torque (τ). A constant torque is a requirement for the total energy conservation as reflected in eq 5. Indeed, the adhesion hysteresis (580 ± 30 mJ/m^2) obtained from eqs 2 and 3 is in perfect agreement with that (580 ± 30 mJ/m^2) predicted by eq 5.

Similar experiments were also carried out with another silicone hemicylinder (Dow Corning Sylgard 170), the modulus (0.65 MPa) of which is half that of Sylgard 184. The surface chemical properties of both the elastomers are very similar to each other. The values of W_a and W_r for this elastomer as estimated using eqs 2 and 3 were 45 and 745 mJ/m^2, respectively. From the rolling torque ($\tau = 1.69$ mN) and the radius ($R = 2.43$ mm) of the hemicylinder, the estimated adhesion hysteresis (695 mJ/m^2) is found to be in excellent agreement with that (700 mJ/m^2) obtained using eqs 2 and 3. It also agrees with the value (689 mJ/m^2) of adhesion hysteresis estimated from the standard loading−unloading experiments. These agreements provide strong support to the validity of using rolling contact mechanics in estimating the adhesion hysteresis in polymeric systems. The self-consistency of the adhesion hysteresis values obtained from these different methods also provide further support to the fact that rolling of hemicylinder is primarily controlled by opening (K_I) model fracture process, which forms the basis of eqs 2 and 3.

The results obtained with the hemicylinder rolling on a flat surface prompted us to investigate if similar

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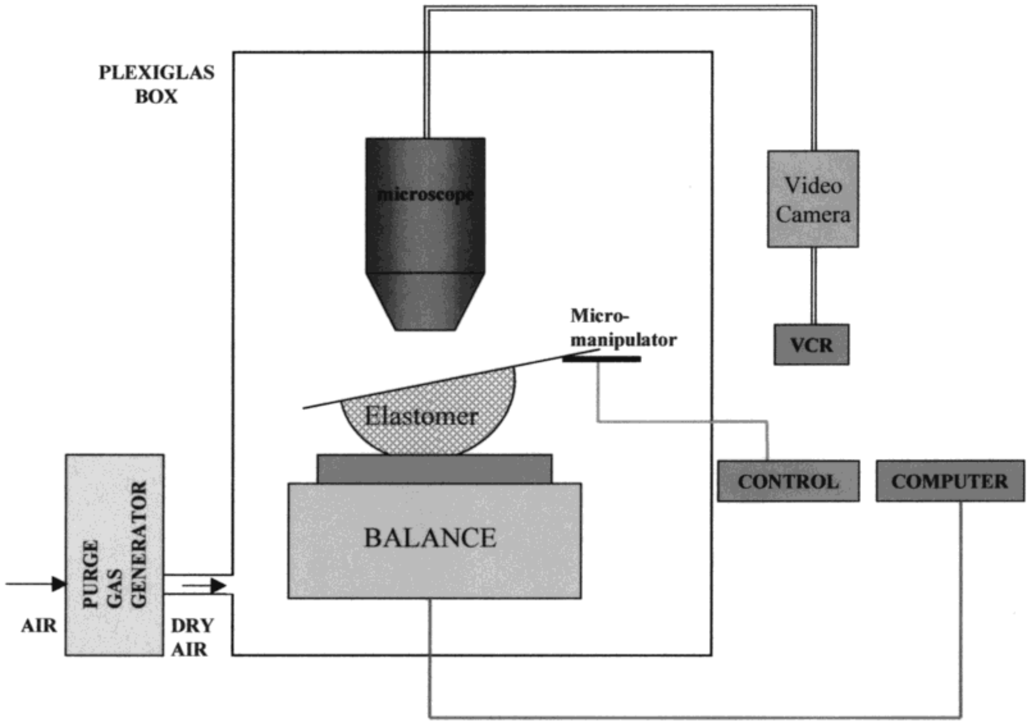

Figure 2. Schematic of the apparatus used in rolling contact experiment. The entire system is encased inside a Plexiglas box, which is constantly purged with dried air. The rolling experiment was performed under a reflection microscope equipped with a video camera. The flat substrate was placed on an electrobalance, which was connected to a desktop computer for data collection and analysis. The hemicylinder was rolled on the test substrate by using a micromanipulator, which tilts one edge of the glass slip attached to the hemicylinder. The speed of rolling was adjusted to 45 μm/s by a control unit.

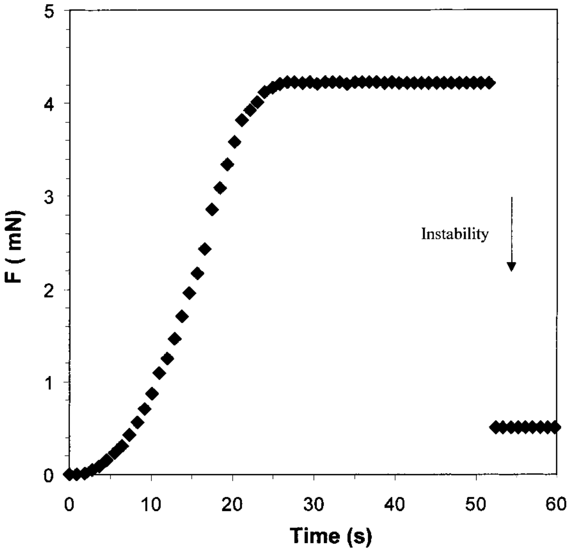

Figure 3. Illustration of how the normal force (F) acting on the cylinder changes with time as a cylinder rolls on a flat substrate. Note that the load is negative. The model system used here is Syl-184 PDMS elastomer cylinder rolling on a silicon wafer. The force on the cylinder increases as the advancing edge starts moving. It reaches a near-constant value (4.3 mN) when both the advancing and receding edges move. As the receding edge reaches the junction of the old and new contact, an instability occurs and the receding edge jumps to a new position. Consequently, the force is reduced to a very low value (0.4 mN). The width of the initial contact, i.e., before rolling, was 170 μm. During rolling, the contact width increased to 300 μm. The radius of curvature, length, and Young's modulus of the hemicylinder were 1.52 mm, 1.13 mm, and 1.31 MPa, respectively.

treatments could apply to the rolling of a sphere. The distribution of normal stress within the sphere–flat plate contact of a rolling sphere is however quite complex and no explicit equation could, so far, be developed to estimate W_a and W_r simultaneously. However, an overall energy balance approach yields the following result:

$$\frac{FS}{R} = W_r d_1 - W_a d_2 \qquad (6)$$

where d_1 and d_2 are as indicated in Figure 4.

Figure 4 captures the video images of the contact area at different phases of rolling of a PDMS (Sylgard 184) hemisphere (R = 2.47 mm) on a silicone wafer. The variation of normal load (F) during rolling is shown in Figure 5. The lack of any plateau value of the normal load, and thus torque, indicates that the rolling hemisphere maps a highly contact time-dependent adhesive zone. Here we have analyzed the situation involving only the peak value of the normal load, which ensures that the receding contact line is well within the region of original contact area. The detailed analysis of the entire profile is reserved for the future. An average of three measurements yielded the torque acting on the hemisphere as 0.316 μN m with the values of d_1 and d_2 as 0.236 and 0.3 mm, respectively. Using these values of rolling torque, d_1, and d_2 and using the value of W_a as 44 mJ/m^2, we estimate the receding work of adhesion of the PDMS hemisphere on silicon wafer to be about 600 mJ/m^2 from eq 6. This value of W_r is remarkably close to that (621 mJ/m^2) of a PDMS hemicylinder rolling on a silicon wafer (Table 1).

Conclusion

Rolling contact mechanics allows simultaneous estimation of the advancing and receding works of adhesion. The unique feature of rolling contact mechanics is that the method possesses the simplicity of peel experiment without having to deal with the complexity of peel mechanics. It has also the rigor of classical contact

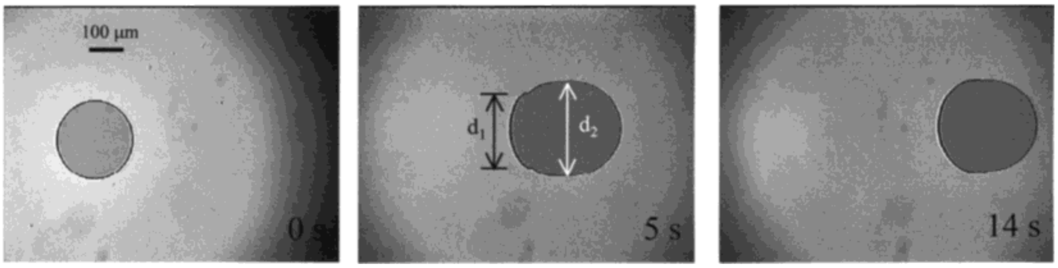

Figure 4. Video images of the rolling contact of a hemispherical PDMS (Dow Corning Sylgard-184) on silicon wafer.

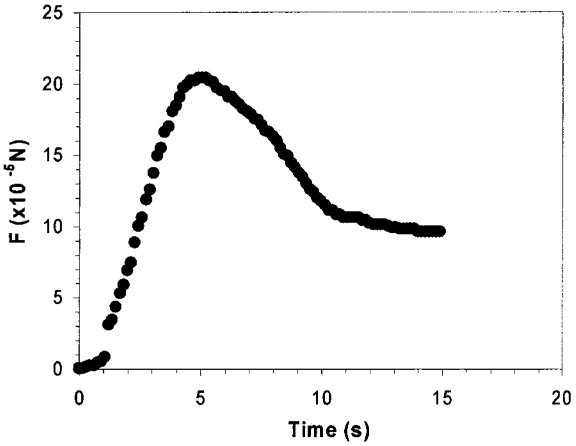

Figure 5. Illustration of how the normal force (F) acting on a PDMS hemisphere ($R = 2.47$ mm) changes with time as the hemisphere rolls on a silicon wafer.

mechanics. Rolling contact mechanics is therefore a useful method for fundamental studies in adhesion and fracture.

Experimental Section

General Information. The silicone hemicylinders were prepared using commercial kits (Dow Corning, Sylgard 184, and Sylgard 170), provided by Dow Corning Corp., Midland, MI. The silicon wafers were purchased from Silicon Quest International. The microscope used for the rolling experiment was obtained from Nikon (Nikon Optiphot), equipped with a CCD video camera module (Sony, Model XC-75), a hydraulic micromanipulator (Nikon, Model MM188), and a VCR (Sony, Model SVO-1500). An electrical motor (Ladd Research Industries, Inc.) was connected to the micromanipulator in order to control the rolling speed. A Mettler (Mettler AB104) electrobalance was used to measure the change of normal load during rolling. Plasma oxidation was carried out using a Harrick plasma cleaner (Model PDC-32G, 100 W). The chloroform (>99.8%) used to extract the elastomer in a Soxhlet extractor was obtained from Fisher Scientific. The Whatman purge gas generator (Model 75-62) was purchased from Balston Inc.

Preparation of Silicone Hemicylinder and Hemisphere. Dow Corning Sylgard 184 is composed of a vinyl end-capped oligomeric dimethylsiloxane, a methyl hydrogen siloxane cross-linker, and a platinum catalyst to carry out the hydrosilation reaction. It also contains fine silica resin for reinforcement of the elastomer. After mixing the two parts of Sylgard 184 according to Dow Corning product specification, the mixture was degassed for 1 h at low pressure. The hemicylinder was prepared by applying the degassed liquid mixture onto fluoroalkylsilane treated thin glass strips (~3 × 60 mm) using a microsyringe.[5] The liquid silicone was contained within the strips and set to an elastomer in the shape of a hemicylinder. The cross-linking reaction was carried out first at room temperature overnight, and then heated to 75 °C for an additional 2 h. The hemispheres were prepared by forming small lenses of the polymer on a silanized glass slide and curing the polymer according to the method described above. The cross-linked hemicylinders and hemispheres were Soxhlet extracted with chloroform for 2 h in order to remove the unreacted oligomeric components. They were air-dried for at least 3 days before they were used for rolling studies. The radii of curvature of the hemicylinders were in the range of 1−3 mm. Those for the hemispheres were 2−3 mm. The Young's modulus of cured Sylgard 184 elastomer is about 1.3 MPa. Sylgard 170 hemicylinders were prepared by following a method similar to that used for Sylgard 184. However, before cross-linking of the elastomer, it was freed of the opaque carbon and silica fillers. Young's modulus of Sylgard 170 elastomer is 0.65 MPa.

The silicon wafer used for the rolling studies was cut into small strips (1 × 5 cm) and cleaned in a hot piranha solution for about 2 h in order to remove the organic contaminations. Next, they were rinsed with distilled, deionized (DDI) water and dried by blowing pure nitrogen gas. Before the silicon wafer was used for a rolling contact experiment, it was briefly cleaned with an oxygen plasma for 45 s at 0.2 Torr using a Harrick plasma cleaner at the lowest power setting.

Rolling Experiment. A small PDMS hemicylinder (~ 2 mm length) was first cut out of the longer (~ 60 mm) hemicylinder using a sharp razor blade, and then its flat side was attached to a thin glass plate (~ 5 × 8 mm). The hemicylinder was then gently placed onto a clean silicon wafer, which rested on an electrobalance. After the hemicylinder contacted the silicon wafer for 10 min, it was rolled on silicon wafer by tilting one end of the thin glass plate using the micromanipulator (Figures 1 and 2). The entire rolling process was viewed using a reflection microscope and recorded in a VCR. The change of load during rolling was recorded in a computer connected to the electrobalance. The distance (S) used to calculate the torque was obtained by measuring the horizontal translation of the micromanipulator. The whole apparatus was encased inside a Plexiglas box that was constantly purged with clean dry air, which was obtained by passing compressed laboratory air through a Whatman purge gas generator. This method ensured that the humidity inside the box would remain at about 20% during the experiment. The effect of the ground vibration was minimized by placing the entire apparatus on an air-supported, vibration isolation table.

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