

Effect of Interfacial Slippage on Viscoelastic Adhesion

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Peeling of a viscoelastic adhesive from a solid substrate poses a wonderful problem of polymer flow. When the adhesive is peeled, it is also stretched in a direction normal to the substrate. The concomitant Poisson contraction creates a pressure gradient and thus induces a shear flow in the adhesive close to the delamination front. Earlier it was pointed out that the strength of viscoelastic adhesion would decrease if the shear stress in the adhesive is relaxed by a slip process at the interface. Here we report experimental results which confirm that viscoelastic adhesives do indeed slip on segmentally mobile organic surfaces at and near the crack tip regions. Evidence of slip was obtained from the interfacial displacements of small fluorescent particles when the adhesive was peeled from various substrates. While on most surfaces the slip distances were about 1–2 μm , a large slip (13 μm) was observed on segmentally mobile tethered chains of polydimethylsiloxanes (silicones). On the latter surface, slippage is so extensive that the adhesive flow pattern near the delamination zone is like plug flow. We believe it is due to the propensity of huge slippage that the silicone-containing polymers exhibit their unusually low adhesion to most materials.

Introduction

The possibility of slippage of polymers^{1–12} on rigid surfaces has long been contemplated in the context of polymer processing, melt fracture, and lubrication phenomena. Near field velocimetry by Leger¹ et al. has provided convincing evidence that polymeric fluids do indeed slip on weakly adsorbing surfaces. According to de Gennes,³ it is easier for the shear stress to concentrate at the interface between a flowing polymer melt and a passive substrate than to be distributed in the bulk causing disentanglement of polymer chains. De Gennes and Brochard⁸ recently proposed that polymer melt should always slip on solid walls as long as the applied stress overcomes a critical value. When a viscoelastic adhesive is peeled from a solid substrate, the applied stress is distributed as cleavage and shear stresses in the delamination region^{13,14} (Figure 1). Close to the crack tip, the separation of the adhesive occurs by a dewetting process,¹² where the hydrodynamic shear stress has a high value. This situation is similar to the dewetting of a liquid drop^{15,16} from a solid surface. Thompson and Robbins¹⁷ demonstrated that a Newtonian liquid drop undergoes a strong slippage on a solid surface within the length scale of a few molecular diameters near the dewetting contact line. In the case of a non-Newtonian viscoelastic polymer, strong slippage is also expected at the crack tip region. Because of polymer entanglement, however, the slip zone can be considerably higher in the viscoelastic material

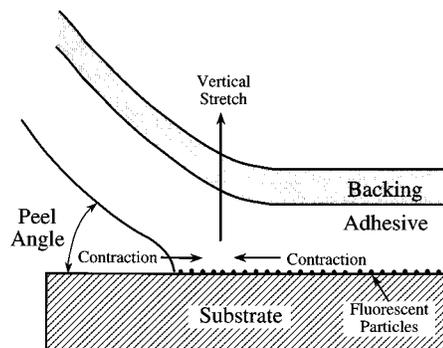


Figure 1. Simplified sketch showing that a vertical stretch in the adhesive leads to a lateral Poisson contraction, which induces a hydrodynamic flow in the delamination region. The slippage of the adhesive was investigated by studying the lateral displacements of the fluorescent particles at the interface.

than that of a Newtonian liquid. As the shear stress decreases beyond the crack tip, adhesive slippage becomes limited by the static and dynamic frictions at surfaces. The above factors cumulatively determine the amount of crack tip rotation and the associated viscous drag in typical adhesive fracture processes.¹² We have recently been developing a method to probe the velocity field in a viscoelastic adhesive using tracer particles in order to estimate quantitatively the amount of slippage that occurs at an adhesive–substrate interface. A particle-tracking method was used earlier by Galt and Maxwell² to investigate the flow pattern of polymer melts in transparent tubes. During the course of our investigation, we observed that the dimethylsiloxane polymers, i.e., silicones, fall in a special category in terms of the huge interfacial slippage that they provide. This discovery throws light on a long-standing puzzle of why the silicone polymers exhibit their unusually high release properties that we are familiar with in a number of technological applications such as antistick surfaces, mold release, and fouling control coatings.

Results and Discussion

Evidence of Slip. The adhesive tapes used in the peel experiments were prepared by sparingly coating their surfaces with small (0.5 μm) fluorescent latex particles. After these adhesive tapes were placed onto the test substrates, they were peeled at different angles (40°, 90°,

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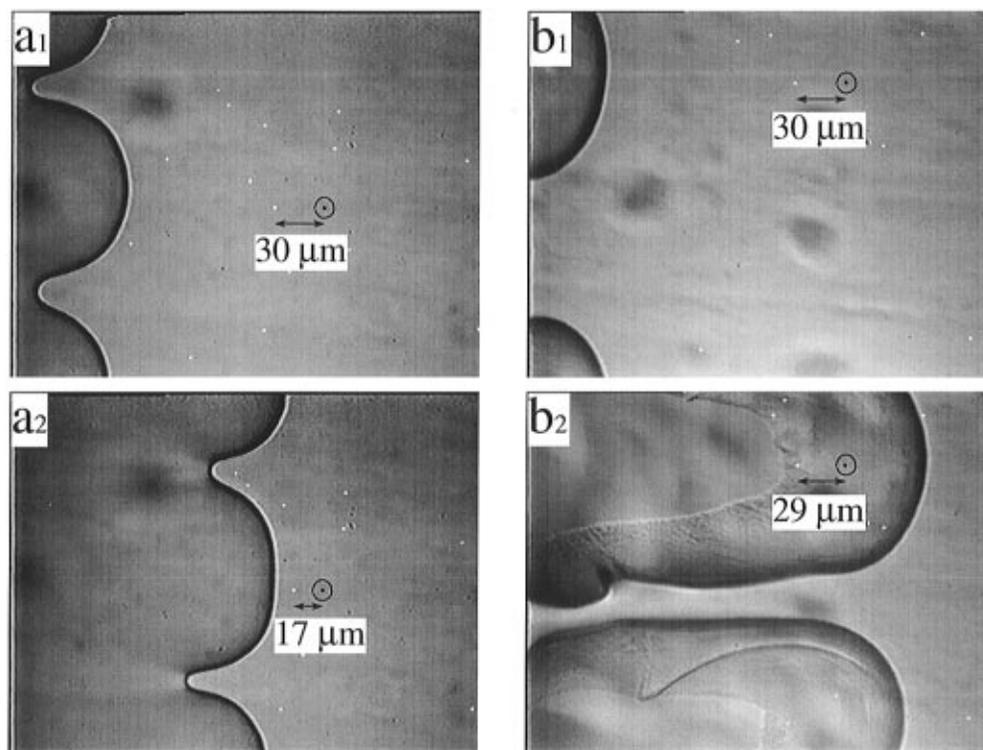


Figure 2. Interfacial slippage of a viscoelastic adhesive peeling from the PDMS (a1, a2) and fluorocarbon (b1, b2) surfaces. The crack propagates from left to right. The fluorescent particles ($0.5 \mu\text{m}$) present at the adhesive–substrate interface are seen as bright spots. In order to increase the visual clarity, the brightness of the particles has been enhanced with a computer. The black dots (circled) are artificially placed on the prints in order to provide fixed reference points for measuring the slip distances. When the crack propagates, the particles are seen to exhibit visible movement on the surface of PDMS. One of the particles is seen to move by a net distance of $13 \mu\text{m}$ laterally (from a1 to a2) before it enters the crack tip. By comparison, the lateral movement of the particle on the fluorocarbon surface is only about $1 \mu\text{m}$ (from b1 to b2).

and 180°) under a fluorescent microscope. Angle resolved X-ray photoelectron spectroscopy at a 10° takeoff angle showed that the amounts of material transfer from either the adhesive or the substrate were 1% or less, thus confirming that the loci of failure in all cases were primarily interfacial.

The slippage of the adhesive was ascertained from the lateral motion of the fluorescent particles, when the delaminating front advanced toward them. Figure 2 captures the differences in the interfacial slip behavior of the adhesive on two surfaces produced from polydimethylsiloxanes (PDMSs) and fluorocarbons (FCs) at a 40° peel angle. Although the particles displaced only by a small amount on the fluorocarbon surface, they exhibited pronounced oscillatory motion on the PDMS surface. On the latter surface, the particles first showed a movement away from the crack tip when they were as far away as $600 \mu\text{m}$ from the delamination front (Figure 3). The particles then moved toward and finally away from the crack tip before being engulfed by it. These back and forth movements of the particles close to the crack tip are due to the slippage of the adhesive in response to the Poisson contracted flow, which occurs toward the principal stretching direction from its two opposite sides. The origin of some weak oscillations of the particles far from the crack tip is not clear at present; we suspect that these are due to the secondary flows in the adhesive.

Adhesive Flow Pattern near Crack Tip. In a separate experiment, we investigated the magnitude of the shear deformation that is developed within the bulk of adhesive using a particle-tracking experiment of the type described below. In this experiment, the thickness of the viscoelastic adhesive was doubled and some fluorescent particles were introduced in the middle of the

two layers. Afterward, more particles were applied on its outer surface. During the peeling of this adhesive from a test substrate, the lateral movements of the fluorescent particles in the bulk as well as at the interface were followed. Even though the displacements of the particles were rather large in the bulk of the adhesive on a fluorocarbon surface, they were negligible at the interface (Figure 3). By contrast, these displacements were similar on the PDMS surface close to the delamination region suggesting that the adhesive flow pattern is plug flow type (Figure 3). This plug flow pattern is further supported by the fact that the adhesive slip velocities close to the crack tip are independent of the size of the tracking particles ($1, 0.5$, and $0.1 \mu\text{m}$) (Figure 4). These experiments clearly demonstrate that the shear deformation in the bulk of the adhesive is much lower on the PDMS surface than it is on the fluorocarbon surface. This pattern of shear deformation concurs with the large differences in the adhesive fracture energies observed on the two surfaces (Figure 5). Slippage is so extensive on PDMS that most of the shear stress is concentrated at the interface.³ It is therefore tempting to estimate what fraction of the total energy dissipation in fracture is due to the frictional drag acting at the PDMS–adhesive interface.

Energy Dissipation Due to Friction. The energy dissipation at the interface per unit extension of the crack area was obtained by integrating the stress power, $\sigma(v)v$, as follows:

$$Go = (1/V) \int_0^\infty \sigma(v)v dx \quad (1)$$

where v and V are the slip and peel velocities, $\sigma(v)$ is the interfacial shear stress, and x is the abscissa from the crack tip. If u is the slip displacement, the steady state

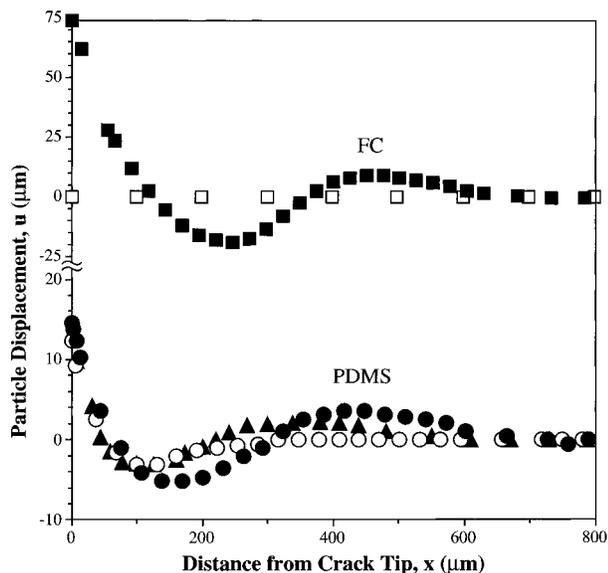


Figure 3. Oscillatory motions of fluorescent particles ($0.5 \mu\text{m}$) in the bulk of the adhesive and at the adhesive-substrate interface on PDMS and fluorocarbon. Positive displacement indicates that the particles move away from the crack tip, whereas negative displacement indicates that the particles move toward the crack tip. These slip profiles are independent of peel velocities. \blacktriangle represents the movements of a fluorescent particle at PDMS/adhesive interface when the thickness of the adhesive is $20 \mu\text{m}$. \circ and \bullet represent respectively the movements of fluorescent particles at the interface and in the bulk (midlayer) of a $40 \mu\text{m}$ thick adhesive on PDMS. Note, in this case, that the particle displacements in the bulk and at the interface are similar indicating that the adhesive flow pattern is like plug flow. In a similar experiment, \square (interface) and \blacksquare (bulk) represent the particle movements on a fluorocarbon surface.

slip velocity can be written as

$$v = V(\partial u / \partial x) \quad (2)$$

In a pure shear experiment, we found that the interfacial shear stress depends on slip velocity as follows (Figure 6):

$$\sigma(v) = kv^{0.35} \quad (\text{for } v < 100 \mu\text{m/s}) \quad (3a)$$

$$\sigma(v) = kv^{0.52} \quad (\text{for } v > 100 \mu\text{m/s}) \quad (3b)$$

Within the collected set of peel adhesion data, it was observed that the slip velocities corresponding to 40° and 90° peel angles were generally smaller than $100 \mu\text{m/s}$, whereas they were larger than $100 \mu\text{m/s}$ at a 180° peel angle. Hence, depending on the peel angles, either of eqs 3a and 3b was used to integrate eq 1. The general form of the interfacial energy dissipation is

$$Go = KV^n \int_0^\infty \left| \frac{\partial u}{\partial x} \right|^{n+1} dx \quad (1)$$

where n is 0.35 or 0.52.

The energy dissipated by friction as calculated from eq 4 comprises about 40%–60% of the total fracture energy at peel angles corresponding to 40° and 90° (Figure 7), whereas they are about 25%–40% of the total fracture energy at a 180° peel angle (Figure 7). The above statistics were derived by averaging the slippage data over at least 10 sets of experiments. A somewhat lower estimate of the frictional energy dissipation at a 180° peel angle may be explained on the basis of the fact that not all the shear stresses in this case are concentrated at the interface. In order to illustrate this point, let us examine the displacements of the particles that occur in the bulk of the adhesive

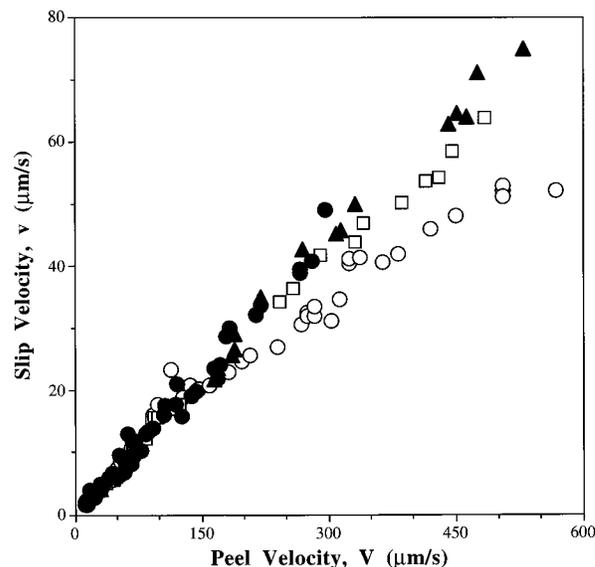


Figure 4. Slip velocities of the adhesive on PDMS increasing linearly with the peel velocity. The slippage is independent of the size of the tracer particles: $0.1 \mu\text{m}$ (\blacktriangle), $0.5 \mu\text{m}$ (\bullet), and $1.0 \mu\text{m}$ (\square). The above measurements were made on a PDMS polymer with a molecular weight of 11 080. Similar measurements on a lower molecular weight (3880) PDMS polymer (\circ) show that the slip velocities are only marginally affected by molecular weight. On the lower molecular weight polymer, the oscillatory motions of the fluorescent particles are however more suppressed (not shown here).

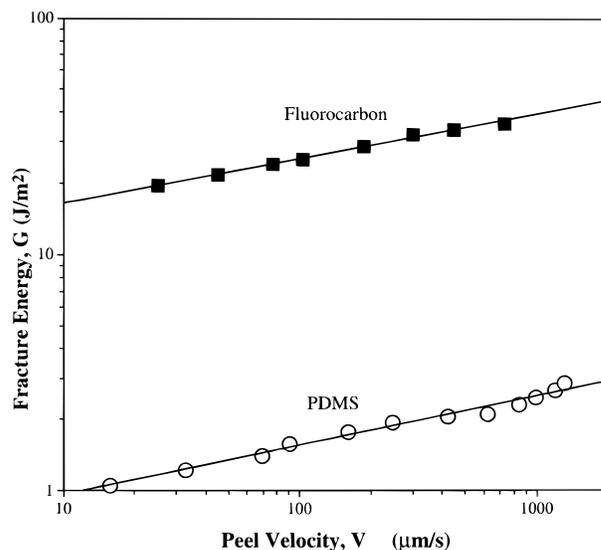


Figure 5. Relationship between adhesive fracture energy and peel velocity. Note that the fracture energy values on the fluorocarbon surface are an order of magnitude higher than those on the PDMS surface.

and at the adhesive-substrate interface (Figure 8) at a 180° peel angle. Although the displacements of the particles show that the adhesive flow pattern is like plug flow close to the crack tip, some amount of the shear stress is, nonetheless, distributed in the bulk of the adhesive. There is, therefore, a component of the energy dissipation due to the bulk shear deformation which is not included in eq 4. This situation is somewhat different from those encountered at 40° and 90° peel angles, where most of the shear stresses are concentrated at the interface. Perhaps a better way to look at the problem is to consider what happens right at the tip of the crack. The shear component of the peel force is likely to be determined by the gradient of the slip displacement of the adhesive at the crack tip, since the stress due to elastic displacement at the crack

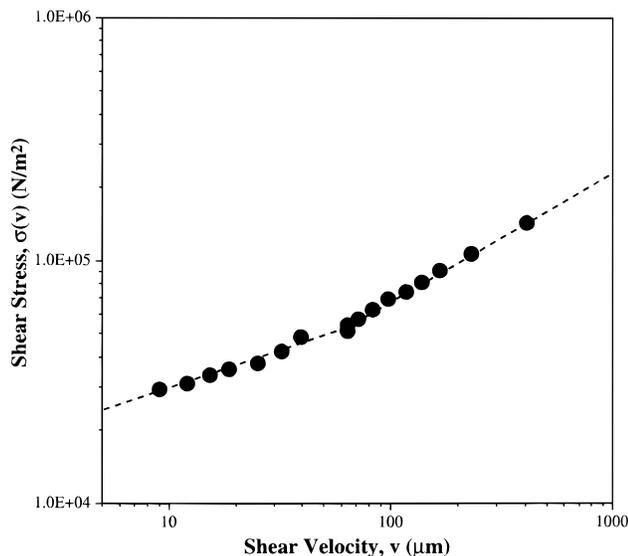


Figure 6. Interfacial shear stress as a function of sliding velocity. At low sliding velocities ($v < 100 \mu\text{m/s}$), shear stress can be expressed as $\sigma(v) = 13000 V^{0.35}$; at higher sliding velocities ($v > 100 \mu\text{m/s}$), the corresponding equation is $\sigma(v) = 6400 V^{0.52}$.

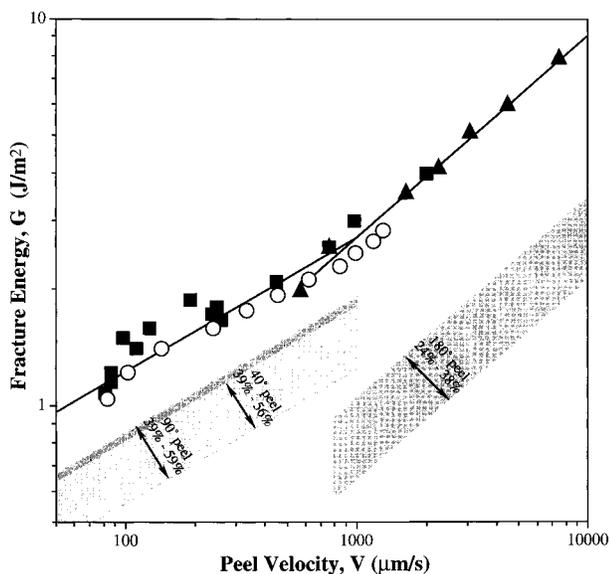


Figure 7. Increase of adhesive fracture energy with increase of peel velocity. \circ , \blacksquare , and \blacktriangle represent the adhesive fracture energies obtained at 40° , 90° , and 180° peel angles, respectively. The shaded regions represent the frictional energy dissipations calculated using eq 4. Both the total and the frictional components of the fracture energy scale with the peel velocity as $\sim V^{0.35}$ at $V < 1000 \mu\text{m/s}$, but as $\sim V^{0.52}$ at $V > 1000 \mu\text{m/s}$.

tip supports the entire interfacial friction and bulk viscous shear stresses of the adhesive in the near and far field regions. Examination of the particle displacements (Figure 9) shows that the displacement derivatives ($\partial u / \partial x$) are indeed independent of the peel angles, thus suggesting that the shear component of the peel force is independent of the peel angles as well. In the language of fracture mechanics, the phase angle ($\psi = \tan^{-1}(k_{II}/k_I)$; k_I and k_{II} are stress intensity factors of mode I and mode II, respectively) is nearly independent of the peel angle. This is perhaps why the adhesive fracture energies at three different peel angles somewhat superimpose onto each other. The near invariance of the phase angle in peel was suggested earlier by Thouless and Jensen¹⁸ in

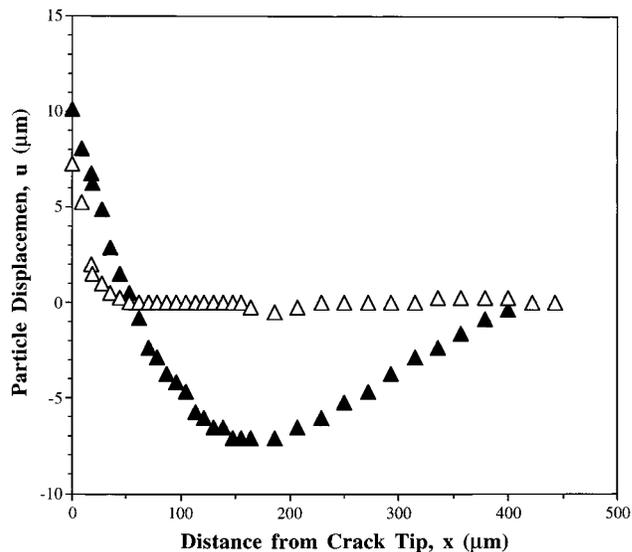


Figure 8. Displacement of the fluorescent particles ($0.5 \mu\text{m}$) in the bulk (midlayer) (\blacktriangle) of the adhesive and at the adhesive–PDMS interface (\triangle) at a 180° peel angle. The adhesive thickness is $40 \mu\text{m}$.

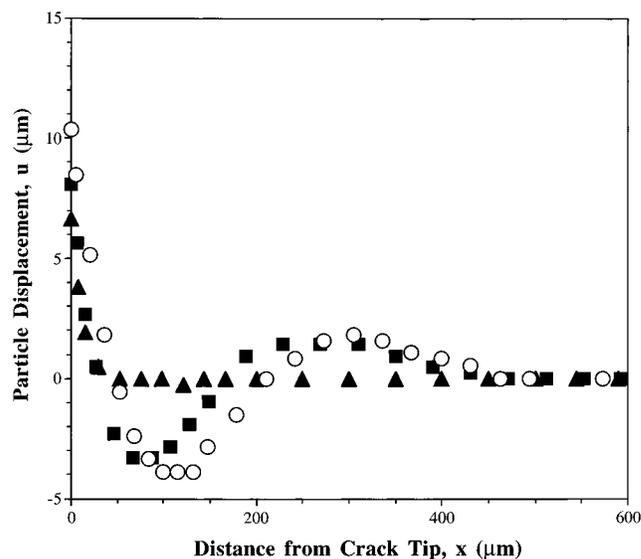


Figure 9. Displacement of fluorescent particles at an adhesive–PDMS interface obtained at three different peel angles. \circ , \blacksquare , and \blacktriangle correspond to 40° , 90° , and 180° peel angles, respectively.

a purely elastic system. These results are in striking contrast to the conventional wisdom of the peel adhesion, according to which the ψ depends significantly on peel angle. Kaelble's calculations^{13,14} predicted that the shear stress in peel adhesion varies significantly as a function of peel angle, even changing sign in going from an acute to an obtuse angle of peeling. These calculations, however, were done on the basis of pure elastic bending theory. The viscoelastic fracture cases, where a large normal stress difference can easily develop, have not yet been given proper theoretical consideration, with the exception of one study by Hill, Hasegawa, and Denn.⁷ In that study,⁷ the authors compared the melt fracture phenomenon in polymer flow to an adhesive instability of a prestressed rubber. The authors considered that a thin region of a flowing polymer melt in contact with the die wall behaves like a prestressed rubber. The equivalent of the strain energy release rate, here, is half the product of the normal stress difference ($\tau_{11} - \tau_{22}$) and the thickness (δ) of the rubbery region. When this quantity [$(\tau_{11} - \tau_{22})\delta/2$] is equal to the work of adhesion, instability occurs in polymer flow

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leading to melt fracture. In the case of the dewetting of a viscoelastic adhesive from a solid substrate, a large normal stress difference is likely to develop in the crack tip region, and it may be possible to define the strain energy release rate of the adhesive fracture similar to that proposed by Hill et al.⁷ However, in the case of strong slippage, the necessary boundary condition of fracture must invoke energy dissipative frictional processes, not just equilibrium work of adhesion.

In the standard theories of viscoelastic fracture,^{20–22} viscous drag is considered to be a bulk process. Another striking point in the current study is that the interfacial frictional drag can be as large as the drag due to the bulk viscous forces even when most of the adhesive shear stress is relaxed by an interfacial slip process. Such a local mechanism of energy dissipation in fracture was envisaged earlier by Kendall.²³ Since, on PDMS, the shear deformation in the bulk of the adhesive is minimized by an interfacial slip process, total fracture energy is reduced. What remains, in this case, is an extensional deformation in the adhesive close to the crack tip region that largely accounts for the rest of the total fracture energy.

Concluding Remarks

Surfaces exhibiting excellent release are of tremendous technological importance in areas spanning from antistick surfaces to fouling control coatings. In the past, the main design criterion to producing such a surface was based on its low surface energy. Although the low surface energy may provide the necessary condition to release, it does not provide the sufficient condition. It is important to consider the dynamic processes at the interface as well. A strong interfacial slippage may be an important criterion to the release phenomena, because it minimizes the shear deformation in the bulk, thus affording the separation of the adhesive easier in the direction normal to the substrate.

Experimental Section

General Information. The fluorescent latex particles used for this study were purchased from Molecular Probes Inc., Eugene, OR. The as-received particles were colloidal dispersions in water that were free of surfactants. Particles of three sizes were used: 0.1 [L5221], 0.5 [L5261], and 1.0 μm [L7218]. The excitation and emission wavelengths of the 0.1 and 0.5 μm particles were 490 and 515 nm respectively. The excitation and emission wavelengths of the 1.0 μm size particles were 365 and 430 nm, respectively. The adhesive tape was a standard 3M Scotch tape (No. 34-7032-3525-8). The viscoelastic part of the tape is an acrylic polymer. Hydrido-functional polydimethylsiloxanes ($\text{CH}_3(\text{CH}_2)_3(\text{Si}(\text{CH}_3)_2\text{O})_n(\text{CH}_3)_2\text{SiH}$) of two different molecular weights (3880 and 11 080) were received as gifts from Dow Corning Corporation, Japan Division. Fluoroalkylsilane (FC) ($\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$) was purchased from PCR Inc., Gainesville, FL. Silicone rubber was a commercial material (Sylgard 184) from Dow Corning. The rubber had been thoroughly cleaned with chloroform in a Soxhlet extractor and completely dried before use. The microscope used to examine the fluorescent particles was a Nikon Diaphot inverted microscope that had an epifluorescent attachment. The glass slides used for the experiments were cleaned in a Harrick plasma cleaner (Model PDC-23G, 100 W) before surface treatments.

Preparation of Low Energy Surfaces. The test surfaces were PDMS and FC grafted onto cleaned microscopic glass slides. The glass slides were first cleaned in hot piranha solution for 30 min, and then thoroughly rinsed in distilled/deionized water. After blow drying of the slides in nitrogen gas, they were further

cleaned with an oxygen plasma at a pressure of 0.2 Torr for 15–20 s. The PDMS surfaces were prepared by reacting the hydrido-functional PDMS fluid (200 μL) to glass slides in the presence of a platinum catalyst. Followed by a 20 h reaction time, the slides were cleaned with chloroform in a Soxhlet extractor. PDMS with number-average molecular weights of 11 080 and 3880 were used to yield film thicknesses of 100 and 50 Å, respectively. The film thicknesses were determined with a Geartner ellipsometer. The fluorocarbon surface was prepared by vapor phase deposition of $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$ onto glass slides at a reduced pressure (0.01–0.02 Torr) for 30 min. The details of these methods are described in refs 12 and 24.

Preparation of Adhesive for Peel Test and Slip Measurement. The adhesive tape used for the peel adhesion experiment was prepared by transferring small fluorescent latex particles on its surface. The number density of the particles was kept at low values (1 particle/1000–2000 μm^2). The as-received fluorescent colloidal dispersions (2% solid) were diluted in distilled/deionized water to attain a final concentration of 20 ppm. A small drop (10 μL) of the dilute solution was deposited on a cleaned glass slide, and it was spread uniformly by sliding the edge of another glass slide over the first one. After the evaporation of water, the fluorescent particles were randomly distributed on the glass slide. These particles were transferred onto the surface of a pre-cleaned silicone rubber (Dow Corning Sylgard 184) after pressing and removing the rubber from the glass slide. Finally, the adhesive tape was lightly pressed against the above silicone rubber. Upon removal of the tape, some of the fluorescent particles were transferred onto its surface. The main reason for transferring the particles to the adhesive tape from the silicone rubber is that the peel adhesion force, in this case, was extremely low, so that no damage occurred in the peeled adhesive.

In certain experiments it was necessary to double the thickness of the adhesive layer. This was accomplished by adhering the adhesive tape to a cleaned polystyrene Petri dish and filling the dish with pure water. After about 1/2 h, the adhesive backing began to lose its adhesion to the viscoelastic polymer, at which point the backing could be removed easily from the adhesive. After the adhesive was dried for 1/2 h, it was removed from the Petri dish with a separate fluorescent-coated adhesive tape by a fast peeling action. After allowing the adhesive to relax for 3 or 4 days, additional fluorescent particles were transferred onto its outer surface by following the method described previously.

Peel Adhesion and Slip Measurement. The adhesive tapes were peeled from the surface-modified glass slides under a microscope at different peel angles. The tapes were peeled with a string that ran over a pulley by hanging dead loads at its free end. The fluorescent particles were excited with UV light emitted from a mercury lamp. The particles were observed with a CCD video camera, and their motions were recorded by a video recorder. Later, the motions were analyzed in detail using a desktop computer. The peeling front of the adhesive was observed using transmitted light at a low intensity. Some of the peel adhesion measurements were also conducted separately outside the microscope. The adhesive fracture energy (G , J/m^2) was obtained from the peel force (P , N/m) and the peel angle (θ) using the following equation:²³

$$G = P(1 - \cos \theta) \quad (5)$$

Measurement of the Shear Stress at the Adhesive/PDMS Interface. A small portion (2.5 mm \times 12.7 mm) of an adhesive tape was slid against a PDMS coated glass surface in a pure shear configuration. When a fixed dead load (74 g) was applied, the adhesive underwent a finite shear deformation and then slid over the glass surface. The shear stress continued to increase with the increase of sliding speed. From these data, the relationship between the shear stress and the shear velocity was determined.

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