Rate-Dependent Adhesion between Polymer and Surfactant Monolayers on Elastic Substrates

Marina Ruths and Steve Granick*

*Department of Materials Science and Engineering, University of Illinois,
Urbana-Champaign, Urbana, Illinois 61801*

Organic monolayers were formed on mica substrates whose detachment was rate-independent in the absence of these monolayers. The pull-off force under dry conditions was measured as a function of contact time (0.01–500 s) and separation rate (0.003–100 μm/s; corresponding lateral crack velocity approximately 0.04–1200 μm/s) using a piezoelectric bimorph attachment to a surface forces apparatus. No time or rate dependence was observed for close-packed crystalline monolayers of condensed *n*-octadecyltriethoxysilane (OTE) or the adsorbed glassy diblock copolymer poly-2-vinylpyridine (PVP)–polystyrene. Rate dependence beyond a critical separation rate was observed in monolayers whose chains were more mobile although anchored at one end to the solid surface. For loose-packed monolayers of cetyltrimethylammonium bromide (CTAB), the adhesion in excess of the constant observed at low rate increased as a power law with the square root of the separation rate. For adsorbed PVP–polybutadiene, the excess adhesion increased nearly linearly with the logarithmic separation rate. For both CTAB and PVP–polybutadiene, the critical separation rate lessened with increasing contact time before detachment. The time effects are ascribed to interdigitation between the contacting layers as a result of interdiffusion over nanoscale distances, facilitated by the low glass transition of the polybutadiene and the loose packing of the CTAB monolayers. The rate effects are ascribed to viscoelasticity during chain pull-out. The rate dependence was weaker than the simple proportionality to velocity that has been expected theoretically for chain pull-out. The oft-proposed separation of rate-dependent adhesion into the product of bulk viscoelastic response and a constant surface energy is inconsistent with these findings.

Introduction

The long history of seeking to correlate adhesion with surface energy has had mixed results.[1–11] The reason is only partially difficulty in defining the experimental system (in terms of surface roughness, chemical and mechanical homogeneity, or test criteria). More interesting difficulties stem from the fundamental distinction between the processes occurring at "loading" (compression) and "unloading" (separation). Here, using an experimental device that shows no intrinsic rate dependence, we investigate rate-dependent adhesion owing to viscoelasticity within monolayer films.

Much classical analysis in this field is predicated on fracture mechanics rather than a molecular analysis. In one prominent line of analysis,[1–11] the deformation of contacting bodies is derived from the energetic interaction between opposed surfaces. If it is attractive (e.g., arising from van der Waals attraction or chemical bonding), the energy released when two surfaces come into contact is 2γ, where γ is the surface energy of the contacting materials. The past 10 years of study show that this

approach is successful in explaining the shape of adhesive contact when solid bodies are brought together.[1–13] The pioneering "JKR" theory of Johnson, Kendall, and Roberts[1] describes the contact area and deformation of adhering elastic bodies and predicts that the contact area is finite even if no external force presses the surfaces together. There is now much experimental evidence in favor of the JKR theory under loading conditions.[14–20] The assumption of this theory, that adhesion is a balance between potential energy, surface energy, and elastic deformation within the solid bodies, therefore seems to be a good model to describe contact area during loading conditions. Dissipation and rate dependence are ignored in this line of analysis.

However, upon considering unloading, it is found experimentally that the pull-off force can exceed by several orders of magnitude the thermodynamic energy to break bonds at the geometrical surface.[10,12,13,21–23] This accounts for the usefulness of adhesives. From the work of Gent,[21]

(1) Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London, Ser. A* **1971**, *324*, 301.
(2) Derjaguin, B. V.; Muller, V. M.; Toporov, Yu. P. *J. Colloid Interface Sci.* **1975**, *53*, 314.
(3) Muller, V. M.; Yushchenko, V. S.; Derjaguin, B. V. *J. Colloid Interface Sci.* **1980**, *77*, 91; **1983**, *92*, 92.
(4) Pashley, M. D. *Colloids Surf.* **1984**, *12*, 69.
(5) Greenwood, J. A.; Johnson, K. L. *Philos. Mag.* **1981**, *43*, 697.
(6) Maugis, D.; Barquins, M. *J. Phys. D, Appl. Phys.* **1978**, *11*, 1989.
(7) Maugis, D.; Gauthier-Manuel, B. *J. Adhesion Sci. Technol.* **1994**, *8*, 1311.
(8) Johnson, K. L.; Pollock, H. M. *J. Adhesion Sci. Technol.* **1994**, *8*, 1323.
(9) Maugis, D. *J. Adhesion Sci. Technol.* **1995**, *9*, 1005.
(10) Johnson, K. L. *Langmuir* **1996**, *12*, 4510.
(11) Sridhar, I.; Johnson, K. L.; Fleck, N. A. *J. Phys. D, Appl. Phys.* **1997**, *30*, 1710.

(12) Kendall, K. *Science* **1994**, *263*, 1720.
(13) Packham, D. E. *Int. J. Adhesion Adhesives* **1996**, *16*, 121.
(14) Chaudhury, M. K.; Whitesides, G. M. *Langmuir* **1991**, *7*, 1013; *Science* **1992**, *255*, 1230.
(15) Mangipudi, V. S.; Tirrell, M.; Pocius, A. V. *J. Adhesion Sci. Technol.* **1994**, *8*, 1. Mangipudi, V. S.; Huang, E.; Tirrell, M.; Pocius, A. V. *Macromol. Symp.* **1996**, *102*, 131.
(16) Tirrell, M. *Langmuir* **1996**, *12*, 4548.
(17) Brown, H. R. *Macromolecules* **1993**, *26*, 1666; *Science* **1994**, *263*, 1411; *Faraday Discuss.* **1994**, *98*, 47.
(18) Deruelle, M.; Tirrell, M.; Marciano, Y.; Hervet, H.; Léger, L. *Faraday Discuss.* **1994**, *98*, 55. Deruelle, M.; Léger, L.; Tirrell, M. *Macromolecules* **1995**, *28*, 7419.
(19) Horn, R. G.; Israelachvili, J. N.; Pribac, F. *J. Colloid Interface Sci.* **1987**, *115*, 480.
(20) Christenson, H. K. *Langmuir* **1996**, *12*, 1404.
(21) Gent, A. N.; Kinloch, A. J. *J. Polym. Sci. A-2* **1971**, *9*, 659. Gent, A. N.; Schultz, J. *J. Adhesion* **1972**, *3*, 281. Gent, A. N. *Langmuir* **1996**, *12*, 4492.
(22) Brown, H. R. *Annu. Rev. Mater. Sci.* **1991**, *21*, 463.

among others, it is now appreciated that the separation of two solids rarely occurs strictly at the interface; energy is also dissipated in deformation of the bulk material below it.[10,21−23] Depending on the experimental setup and the materials investigated, energy may be dissipated by crazing, by breaking strands of material formed between the surfaces as they detach, and by viscoelastic losses within the bulk material itself.[10,12,13,21−24] Even when the ultimate detachment occurs at the original interface (so-called adhesive failure) rather than within the bulk material (cohesive failure), dissipation within the bulk material surrounding the contact interface often contributes prominently to the ultimate pull-off force.

Many experimental studies are rendered ambiguous by uncertainty concerning the perfection of surface−surface contact: if the surfaces are rough, the actual area of contact is much less than the nominal area of contact, but the actual area of contact might change during the course of an experiment.[7,25] This difficulty is avoided in experiments that involve spherical caps of elastomeric polymers in contact with an opposing, flat surface;[14−16] the soft elastomer conforms to the opposed surface, and molecular contact is achieved.

The magnitudes of the pull-off forces measured in these studies are generally in accordance with those expected from interfacial interactions, and the measured deformations are in good agreement with model predictions. Remaining experimental difficulties include time effects on the deformations of the relatively large and soft bodies studied,[16] which may complicate the interpretation of results on adhesion hysteresis and pull-off forces. This technique has been extended to studies of the effects of contact time and separation rate on the adhesion between an elastomer cap and a surface covered with grafted polymer chains that penetrate into the elastomer network.[17,18] Theoretical models[26,27] for such systems, based on the elastic energy and contact area of the penetrating chains being pulled out of the network, predict a linear increase in apparent adhesion or "interfacial toughness" as the separation rate is increased. This has been observed experimentally in some studies,[17] while, in other experiments,[18] the response was found to be strongly nonlinear. A limitation is that when viscoelastic or time-dependent observations are obtained on these systems, it is ambiguous whether the result is an effect of events at the surface or an effect of events within the underlying bulk material.

Alternatively, molecularly smooth solid surfaces can be employed to study adhesion experimentally. The surface force apparatus (SFA) technique[28] has been used successfully to study adhesion between surfaces separating both in air and in liquids. This technique allows for very accurate measurements of compressive and tensile forces and deformations of the interacting bodies, that is, the parameters needed for comparisons with theoretical models of contact mechanics. The time effects[16] arising from the not always uniform properties of relatively large elastomer spheres are generally avoided in the SFA, where the interacting thin surface layers are supported on a more rigid mica and glue layer on a silica disk. In addition,

the contact mechanics of these supports (without adsorbed layers) has been thoroughly studied,[11,19,20] making it easier to distinguish effects on the pull-off forces and deformations arising from different properties of the adsorbed surface layers.

The contact between the half-cylinders in the SFA can be thought of as one single asperity, and molecular contact can be achieved instantly over a macroscopic area (diameter ~50 μm) if a smooth enough surface layer with a well-defined thickness can be formed. Since the properties of the surfaces used in the SFA are easily modified by adsorption, and the separation (and thus the pressure) between the interacting bodies is well-controlled, this technique is well suited for investigations of the properties of very thin interfacial films. The surface energy obtained from adhesion experiments on polymer[29] and surfactant layers[30−32] with the SFA has in many cases been found to be very close to the expected thermodynamic surface energy.

The advantage of the SFA approach for studing adhesion is that the solid bodies themselves obey the principles of linear elasticity and, therefore, the solid fracture mechanics commonly employed to analyze adhesive unloading.[1−11] Therefore, when rate dependence is observed in a experiment, its origin lies in relaxations at the contact interface. Potentially, there is the possibility to adopt an approach more molecular than is usual in fracture mechanics to relate adhesion unloading to viscoelastic events within interfacial layers. In this spirit, much previous work has analyzed the contact radius as a function of applied load in "loading" and "unloading" experiments.[14−16,30] Hysteresis was often observed between loading and unloading, thus emphasizing the prominent effect of viscoelastic dissipation. But because of the fashion in which loading−unloading experiments are performed, variations of the detachment rate are not distinguished from effects owing to different stationary times in contact before detachment. The detachment rate is restricted in its dynamic range, especially in the direction of relatively slow detachment rates.

In this paper we describe experiments in which the separation rate between opposed molecularly smooth surfaces was varied by many orders of magnitude with independent control of the stationary contact time before detachment. The range of both separation rate and stationary contact time greatly exceeds those possible in loading−unloading "JKR" experiments. First, we employ this new device to verify that the detachment force is independent of time in contact and of separation rate, provided that the contacting surfaces are immobile over the experimental time scale (the examples here are a close-packed monolayer of surfactant and a polymer below its glass transition temperature). When the elastic solids are coated with monolayers of more mobile molecules, we find the adhesive unloading forces to be decidedly rate- and time-dependent.

Experimental Methods and Materials

Device to Apply Load and Measure Unloading Adhesion. The device[33,34] (Figure 1A) used to control the separation of the two surfaces is a modification of the support for the lower surface

(23) Brown, H. R.; Yang, A. C. M. *J. Adhesion Sci. Technol.* **1992**, *6*, 333.

(24) Baljon, A. R. C.; Robbins, M. O. *Science* **1996**, *271*, 482.

(25) Creton, C.; Leibler, L. *J. Polym. Sci., Polym. Phys.* **1996**, *34*, 545.

(26) de Gennes, P. G. *J. Phys. (France)* **1989**, *50*, 2551. *Langmuir* **1996**, *12*, 4497.

(27) Raphaël, E.; de Gennes, P. G. *J. Phys. Chem.* **1992**, *96*, 4002. Hong Ji; de Gennes, P.-G. *Macromolecules* **1993**, *26*, 520.

(28) Israelachvili, J. N.; Adams, G. E. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 975.

(29) Mangipudi, V.; Tirrell, M.; Pocius, A. V. *J. Adhesion Sci. Technol.* **1994**, *8*, 1251.

(30) Chen, Y. L.; Helm, C. A.; Israelachvili, J. N. *J. Phys. Chem.* **1991**, *95*, 10736.

(31) Peanasky, J.; Schneider, H. M.; Granick, S.; Kessel, C. R. *Langmuir* **1995**, *11*, 953.

(32) Wood, J.; Sharma, R. *J. Adhesion Sci. Technol.* **1995**, *9*, 1075.

(33) Dhinojwala, A.; Granick, S. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 619.

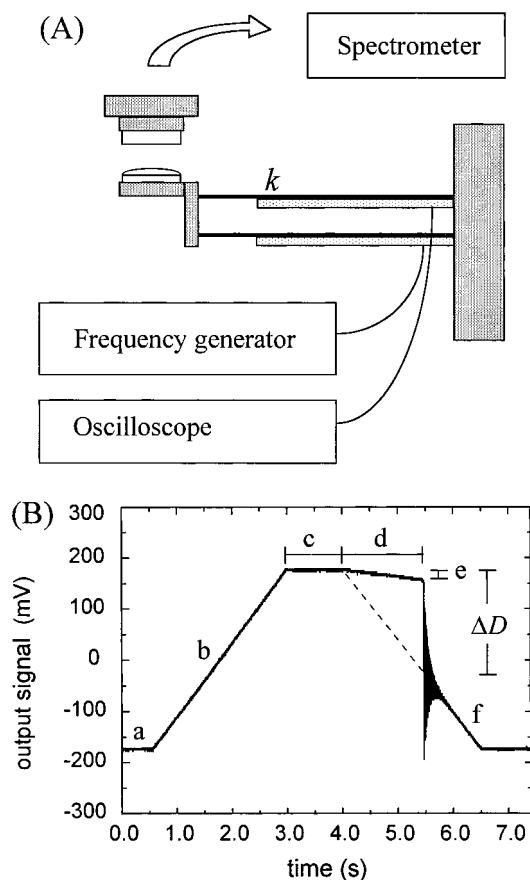(34) Dhinojwala, A.; Granick, S. *Macromolecules* **1997**, *30*, 1079.

(A)

Spectrometer

k

Frequency generator

Oscilloscope

(B)

Figure 1. (A) Double cantilever spring−bimorph device used to position the lower surface. A programmed wave form from a frequency generator is fed to the lower bimorph element. The output signal from the upper bimorph, which corresponds to the vertical displacement of the lower surface, is observed on an oscilloscope (Figure 1B) and calibrated against the surface separation observed by multiple beam interferometry. (B) Output signal from the upper bimorph (vertical displacement of the lower surface) for a trapezoidal input signal to the lower bimorph with a peak-to-peak amplitude of 9 V. The solid curve is experimental data for one approach and separation of adhering surfaces. The dashed line indicates the signal obtained on separation if the surfaces were not brought in contact (same wave form as the input signal to the lower bimorph). (a) Constant voltage; the surfaces are held apart at a constant distance. (b) The lower surface approaches the upper at a constant rate of 1.2 μm/s. Before the approach, the initial distance between the surfaces was adjusted so that they jumped spontaneously into adhesive contact at the point where region c starts. During region c, the applied voltage was constant and the surfaces were held stationary during the *contact time* (in this case 1 s), after which a separation (f, dashed line) at a constant, chosen *device separation rate* (here 1.2 μm/s) was started. The area of contact between the surfaces decreases during the *separation time* (d). The film thickness remains the same as that in section c, but deformation of the surface supports allows for a small change in deflection of the device (e). The surfaces jump apart and continue to separate freely at the chosen separation rate (f). The pull-off force is determined from the total change in displacement of the lower surface needed to separated the surfaces, ΔD, calculated from the calibrated output voltage.

in a Mark II surface forces apparatus.[28] A piezoelectric bimorph strip is glued to each of the leaf springs of the double-cantilever force-measuring spring. A programmed wave form, consisting of sections of linearly increasing, decreasing, and constant voltages, is led from a function generator to one side of the bimorph attached to the lower spring, causing the bimorph to bend and the whole double-cantilever spring assembly to deflect accordingly so that the lower surface is moved vertically. This deflection causes the bimorph on the upper spring to bend and give an output voltage, which is observed and stored on an oscilloscope

(Figure 1B). The motor-driven distance controls used in conventional SFA measurements[28] are retained and allow for additional positioning. In the absence of an applied voltage, the device can also be used as a stiff force-measuring spring (with a spring constant $k = 1.1 \times 10^4$ N/m, determined from the resonance frequency).

The separation distance of the surfaces is measured by means of multiple beam interferometry.[35] In this manner, we can ensure that the linearly increasing or decreasing output voltages observed for a linear increase or decrease in input voltage with time (Figure 1B) correspond to *constant approach and separation rates over the whole deflection amplitude*. Similarly, it was readily observed that the surfaces are indeed held at a constant separation during the sections of the input wave form that consist of a constant applied voltage. The limitations of the method are mainly thermal drifts that might occur at long measuring times (as with the standard spring assembly) and overshoots ("ringing") of the spring−bimorph device which occur upon sudden changes of position. As an example, ringing is seen after the surfaces have suddenly separated in Figure 1B. Ringing is particularly undesirable during the approach, since the surfaces might then adhere as the lower surface swings upward, even though the input amplitude might be too small to bring the surfaces in contact, had the approach been done more slowly. This was avoided by always choosing a slow approach rate, 0.1−1.5 μm/s, and varying only the separation rate in the large range seen in Figures 3−6. Since the surfaces we have studied spontaneously jumped into contact from a close distance, it was not meaningful to vary the approach rate, unless one wanted to apply a positive pressure at different rates after the surfaces were already in contact. The different regions of approach, time in contact, and separation are described further in the legend for Figure 1B.

The pull-off force, F, needed to separate the lower surface from the upper is measured as the change in deflection of the device (output voltage converted to calibrated distance) from the starting point of separation until the surfaces suddenly jump apart (cf. Figure 1B). This occurs when the derivative of the force exceeds the spring constant of the spring−bimorph assembly. This displacement is converted to force by multiplying it by the spring constant (quoted above), and it is normalized for comparison between different experiments by dividing by the radius of curvature of the undeformed surfaces, R (ca. 2 cm). The output signal also provides a measure of deformation of the adhering surfaces, since this generates a deflection in the direction of the separation (Figure 1B, region e) even while the surfaces remain in contact.

Input voltages with the trapezoidal wave form shown in Figure 1B were selected in the range 3−10 V (peak-to-peak amplitude), causing a total displacement of the lower surface of 0.9−3.3 μm and an output voltage of peak-to-peak amplitude 120−390 mV. At these large amplitudes, the output voltage can be measured with an accuracy of approximately 0.3 mV, which corresponds to an uncertainty in displacement of approximately 25 Å. (At small input voltages, the noise in the output signal is considerably smaller, and it has been demonstrated[33] that the displacement then can be measured with an accuracy of about 1 Å.) The corresponding uncertainty in the normalized pull-off force, F/R (i.e., the sensitivity if the input voltages are chosen as above), is approximately 1 mN/m. (If the forces to be measured were expected to be small, a lower input voltage could be chosen to provide higher sensitivity.) It will be seen later that since the adhesion under study here is quite strong, this uncertainty is approximately 0.5% of the measured pull-off forces. It should be noted, however, that a larger error, up to 10% of the absolute value of F/R (and the surface energy, γ, determined from F/R), arises from uncertainties in the measurement of the radius of curvature and the spring constant. These principal uncertainties in force measurement concern absolute rather than relative magnitudes, and in the data analysis presented below, we normalize out most of these uncertainties by considering how relative values of the pull-off force depend on separation rate. The noise in the output signal at these large voltages obscures the small deflection (ca. 30 Å) caused by the spontaneous inward jump of the surfaces to adhesive contact on approach that was

(35) Israelachvili, J. N. *J. Colloid Interface Sci.* **1973**, *44*, 259.

observed optically. The upper limit of the measurable pull-off force is determined by both the chosen total deflection amplitude and the radius of curvature. For example, $(F/R)_{max} \approx 1500$ mN/m for a displacement somewhat smaller than a total separation amplitude of 3.3 μm, and $R = 2$ cm.

The uncertainties in the approach and separation rates (approximately 0.5%) arise from an uncertainty of approximately 20 Å in the total displacement (0.9–3.3 μm, above), measured from the moving interference fringes during a slow approach and separation when the surface are not brought in contact. The thicknesses of the adsorbed layers (compared to contact between uncoated pieces of the same mica), which were determined from the stationary interference fringe pattern arising when the surfaces adhere, can be measured with a higher accuracy of 1–2 Å.

Formation of Adsorbed Layers. Monomolecular films were allowed to adsorb onto muscovite mica by the methods described below.

Polyvinylpyridine–polybutadiene. The diblock copolymer poly-2-vinylpyridine–polybutadiene was generously donated by H. Watanabe (Kyoto University, Japan). The M_w of the polyvinylpyridine (PVP) and polybutadiene blocks are 23 700 g/mol (polydispersity 1.05) and 38 500 g/mol (polydispersity 1.07), respectively. Adsorption solutions with a concentration of 10 μg/mL PVP–polybutadiene in toluene were prepared at least 24 h before the experiments, using Fisher toluene (purity 99.9%, with a water content <0.01% as received). The toluene was dried over Aldrich molecular sieves (pore size 5 Å) overnight and filtered through a Millex-SR filter (Millipore, pore size 0.5 μm) before the solutions were prepared.

Mica was glued onto the cylindrical silica disks used for SFA experiments with a molten 1:1 mixture of dextrose and galactose. The disks were immersed in 25 mL of polymer solution for 2 h at room temperature. Since toluene is a poor solvent for the PVP block of the copolymer, this block is preferentially adsorbed onto the mica, while the polybutadiene block extends into the solution.[36] The disks with the mica were then rinsed in approximately 40 mL of dried and filtered toluene for 2 h to remove excess (nonadsorbed) polymer, dried by blowing thoroughly with N_2 gas, and mounted in the SFA, which was purged with Ar gas for 4–5 h to remove any remaining toluene from the polymer layers. It was established that this time of purging was enough to dry the surfaces, since additional purging (for up to 16 h) did not influence the pull-off force or contact mechanics observed for the adsorbed layers. After the purging was stopped, P_2O_5 was placed on a tray in the chamber of the instrument to take up moisture. All experiments on PVP–polybutadiene were done at 23 °C within 7 h after finishing the purging.

Polyvinylpyridine–polystyrene. The diblock copolymer poly-2-vinylpyridine–polystyrene was obtained from Polymer Source, Inc. (Quebec). The M_w of the PVP and polystyrene blocks are 9200 and 55 400 g/mol, respectively, and the polydispersity of the copolymer is 1.03. Adsorption solutions with a concentration of 10 μg/mL PVP–polystyrene in dried toluene were prepared as for PVP–polybutadiene. The adsorption (by selective adsorption of the PVP block onto mica[37,38] glued onto disks with a mixture of dextrose and galactose) and rinsing procedures were also identical to the ones described above for PVP–polybutadiene. After the surfaces were mounted in the instrument, it was purged overnight with N_2 gas. P_2O_5 was placed in the chamber, and the measurements were conducted at 23 °C within 5 h.

CTAB. Cetyltrimethylammonium bromide (CTAB) (Aldrich) was allowed to adsorb from a 5×10^{-4} M aqueous solution (pH = 5.5) onto mica glued on silica disks with epoxy glue (Epon 1004F, Shell), according to the procedure described in ref 30. The solution was prepared at least 1 day before the experiment and kept at 25 °C to ensure the complete dissolution of the surfactant, since the Krafft temperature of CTAB is close to 25 °C. The disks were immersed in approximately 40 mL of the solution at 25 °C for 30 min, and after the self-assembly, the

disks with the adsorbed monolayers were rinsed for a few seconds in distilled water and thoroughly dried by blowing with N_2 gas. CTAB monolayers formed under these conditions are in the amorphous state and have a molecular area of 60 Å^2.[30] Since the cross-sectional area of a linear hydrocarbon chain is approximately 20 Å^2, the monolayer is loose-packed. After the surfaces had been mounted in the SFA, it was purged with N_2 overnight. After the purging was stopped, the humidity in the instrument was kept near zero by placing P_2O_5 in the experimental chamber in the same manner as that for the polymer layers described above. All experiments on CTAB were done at 25 °C.

OTE. Monolayers of condensed *n*-octadecyltriethoxysilane (OTE) (Petrarch Systems) were formed by self-assembly of hydrolyzed OTE onto mica substrates according to the procedure described in ref 31. In the hydrolysis step, OTE (centrifuged for 1 h) and 1.3 M hydrochloric acid were mixed in tetrahydrofuran (Baxter, spectroscopic grade, 99.9+%) to a concentration of 0.02 M OTE and 0.0066 M HCl (for discussion of the effects of other concentrations and conditions, see ref 31). The self-assembly solution was obtained by mixing hydrolysis solution with cyclohexane (Fisher, 99.9%) to an OTE concentration of 1×10^{-3} M. All solvents were used as received. For the self-assembly, the silvered mica substrates (size approximately 2 cm^2) were temporarily adhered to backing pieces of mica with a drop of water, these pieces were placed in narrow glass vials (against the wall, with the mica substrate facing down), and self-assembly solution (approximately 10 mL) was poured in. After 20 min of adsorption, the pieces were withdrawn, while the surface of the solution was being aspirated, and placed in an oven at 120 °C for 2 h to induce condensation of the silanol groups formed during the hydrolysis. The resulting close-packed monolayer has a molecular area of 20 Å^2 and an average tilt angle of the hydrocarbon chains of $13 \pm 5°$ from the surface normal.[31] The mica substrates with the OTE monolayers were glued onto silica disks with a mixture of dextrose and galactose and immediately mounted in the SFA. P_2O_5 was introduced to take up moisture, and the measurements, which were done at 25 °C, were started within 1 h after mounting the surfaces.

The glassware used in the OTE experiments was cleaned with dilute HF and rinsed thoroughly with distilled water (passed through a Barnstead Nanopure II deionizing and filtering system). All other glassware was soaked in concentrated H_2SO_4 + Nochromix for at least 1 day, rinsed with distilled water, and placed in 2 M KOH overnight and then rinsed again and dried in an oven.

Results

Force–Distance Relations. In all four systems studied, the forces measured between the surfaces on approach were monotonically attractive below a separation distance between the adsorbed layers of approximately $D = 80-90$ Å. This attraction causes the surfaces to jump into flattened contact from a separation of $D = 30-50$ Å (spring constant $k = 1.1 \times 10^4$ N/m) or, in the case of polystyrene-covered surfaces (which will be discussed further below), to come to a rounded contact (no spontaneous jump in) at a well-defined "hard-wall" separation. This closest separation distance was used as the reference point, $D = 0$, for calculations of the interaction distances and pull-off forces. In each of the systems studied, the film thickness was reproducible between different experiments. It did not decrease with contact time or normal load, nor did it increase as a negative load was applied to the surfaces prior to detachment. In addition, the interactions and film thicknesses were reproducible on subsequent approaches and separations (in general, at least 20 measurements could readily be taken at the same contact point between the surfaces), and no repulsion other than this "hard-wall" repulsion was found in any of the systems. As will be shown below, the range of the interactions is consistent with only van der Waals attraction acting across air between well-defined, smooth

(36) Watanabe, H.; Shimura, T.; Kotaka, T.; Tirrell, M. *Macromolecules* **1993**, *26*, 6338.

(37) Parsonage, E.; Tirrell, M.; Watanabe, H.; Nuzzo, R. G. *Macromolecules* **1991**, *24*, 1987.

(38) Watanabe, H.; Tirrell, M. *Macromolecules* **1993**, *26*, 6455.

(with the possible exception of the polystyrene) surfaces with a roughness of not more than a few Ångstroms. The reproducibility of the measurements of the interactions and film thicknesses during repeated measurements at the same contact spot indicates that material was not pulled out from the surfaces on repeated separations, since this would have produced a larger roughness.

Interpretation of Pull-Off Forces as Effective Surface Energy. The measured pull-off forces were related to the surface energy, γ, of the adsorbed layers by the JKR theory[1] of contact mechanics, where the relationship between the radius of the contact area, r, and the external (compressive or tensile) force, F, is given by

$$r^3 = (R/K)\{F + 6\pi R\gamma + [12\pi R\gamma F + (6\pi R\gamma)^2]^{1/2}\} \quad (1)$$

where R is the radius of curvature of the undeformed surfaces, K is the elastic constant of the interacting bodies, and γ is the surface energy ($\gamma = W/2$, where W is the adhesion energy). Some features of this model include a finite contact area at zero external force (then the radius, r_0, is $r_0^3 = 12\pi R^2\gamma/K$) and separation of the surfaces from a finite contact area, $r_{sep} = 0.63r_0$. The JKR relation is expected to be valid in a certain regime of elasticity, surface energy, and size of deformable surfaces.[1,7,9–11] It supposes that adhesion results only from field-dependent interactions and therefore does not treat the viscoelastic adhesion mechanisms that comprise the main subject of this study. In this model, the surface energy is obtained from the pull-off force,

$$\gamma = -F/3\pi R \quad (2)$$

and depends neither on the elastic moduli of the solid supports nor on the initial area of contact.

In systems where attractive forces act also in a region just outside the area of molecular contact[2–4,7] or in systems where a meniscus may gather around the contact zone,[7,19] the relationship between the pull-off force and surface energy is expected to be closer to

$$\gamma = -F/4\pi R \quad (3)$$

and the detachment then occurs at $r_{sep} = 0$. A brief summary of the effects of the properties of the elastic supports on the deformations and on the choice of the appropriate model in each case (under the assumption of no viscoelastic contribution to the adhesion) is given in ref 10.

For materials where viscoelastic dissipation contributes significantly to the adhesion, Greenwood and Johnson[5] have predicted an increase in the effective "crack length" (effective region over which surface forces act at the edge of the contact) with increasing separation rate. The result is an increased adhesive force compared to the separation of purely elastic bodies described in the JKR model.

In this paper we choose to quantify the limiting pull-off force at low separation rate by eq 2, and we use this to define a surface energy at a low detachment rate, γ_0. It will be seen from discussions below that γ_0 compares favorably with prior experiments by others on similar systems. When we consider the rate-dependent pull-off forces, it is convenient to define an effective surface energy, γ_{eff}, using eq 2. When analyzing γ_{eff} in the discussion below, we will normalize it by γ_0 such that all the constants of proportionality cancel and the result amounts to a dimensionless ratio of forces.

Previous investigations[19,20] have shown that the properties of the surface supports generally used in SFA experiments (mica supported by a glue layer of epoxy or

sugar) fall within the regime where the JKR theory is applicable. A number of adhesion experiments at slow compression and separation rates have yielded results in good agreement with the expected thermodynamic surface energies for adsorbed surfactant[30–32] and polymer[29] surfaces as well as for bare mica surfaces[19,20] contacting and separating in air. In our experiments, the surface deformations observed on approach (at the jump-in) were consistent with those expected from the JKR theory at zero external pressure ($F = 0$) for all systems except the polystyrene surfaces. On separation, the behavior observed was consistent with the prediction of separation from a finite contact area with $r_{sep} \approx 0.6r_0$ for all systems except polybutadiene, which will be discussed below.

Using the JKR theory, the elastic constant, K, of our systems can be determined from measurements of the radius of the flattened contact region at zero external pressure, r_0, and the radius of curvature, R, for a known surface energy. In all the systems studied, the surface energy arising from van der Waals attractions is around 30 mN/m (we will return to the exact values in the presentation of the results on each system). Generally, the contact radius and radius of curvature were around 20–30 μm and 2 cm, respectively. In the two systems (CTAB and OTE monolayers) where the deformations both on approach and separation appeared to be distinctively of the JKR type, we found that the elastic constant, $K = 12\pi R^2\gamma/r_0^3$, was approximately $(3.5 \pm 0.5) \times 10^{10}$ N/m² for the system containing epoxy glue (the experiments on CTAB monolayers) and $(3 \pm 1) \times 10^{10}$ N/m² for the OTE system, where a mixture of sugars was used as glue. Using the same equation, very similar values for K, $(2.4 \pm 0.4) \times 10^{10}$ N/m² and $(1.5 \pm 0.5) \times 10^{10}$ N/m², were obtained for the PVP–polybutadiene and PVP–polystyrene systems, respectively. The values are in good agreement with results reported in the literature[19,20,30] and support the assumption that all our deformable surfaces in terms of stiffness and size are in the regime where the JKR theory is expected to be valid for approaches and separations at slow "equilibrium" rates. We note that the mica–glue supports in the PVP–polybutadiene, PVP–polystyrene, and OTE systems are nearly identical (prepared in the same manner, though with possible slight variations in the mica and glue thickness), and that the observed differences in deformation of these systems on approach and separation described below thus must be due to the properties of the adsorbed layers.

The deformations and changes in the size of the contact area on separation did not depend on the time in contact, nor for any of the systems did the radius of the flattened area increase after the surfaces had come into contact. At long contact times or increased pressure, the sugar glue is, however, prone to plastic deformations, and care has to be taken to avoid permanent changes in the radius of curvature. This problem has been discussed in detail in ref 39. Interdigitation of two initially opposed surface layers occurs at a state of rest, under the action of Brownian diffusion, and therefore should not be expected to affect the radius of the contact area.

Lack of Rate Dependence in the Device, the Mica, or the Glue. The experiments with OTE and PVP– polystyrene monolayers (described below) indicate that the mechanical properties of the supports are independent of separation rate in the regime investigated. In addition, we present the following evidence. Our experimental setup allows for simultaneous measurements of the

(39) Watanabe, H.; Matsuyama, S.; Mizutani, Y.; Kotaka, T. *Macromolecules* **1995**, *28*, 6454.

deformations of the supporting surfaces and the radius of the flattened contact region (from the optical interference pattern) and the position of the base of the lower silica disk (from deflection (e) of the spring−bimorph device during the separation time (d) of the signal detected on the oscilloscope, cf. Figure 1B). In all the systems studied, the changes in deformation and the decrease in area of the flattened contact observed optically on separation were found to be the same at slow device separation rates (0.01 μm/s and less) as those at rates of up to 20−30 μm/s (above which the separation becomes too fast to be studied conclusively by eye). The displacement of the base of the lower surface during the pull off was always linear with time (section d of the trace in Figure 1B), and the final vertical displacement (deformation of the mica−glue supports), section e in Figure 1B, was constant to within ∼10% and independent of the separation rate for each experiment.

We conclude from these observations that the separation rates investigated were not large enough to affect the compliance of the combined mica and glue layer supporting the adsorbed layers compared to the situation at slow separation rates. Since the deformation of the interacting bodies is similar, the theory for quasi-static loss-free ("equilibrium") adhesion was still be assumed to be the appropriate approach to analyze the data taken at separation rates so rapid that the pull-off force depends on the separation rate. Thus, in the following, the relation $\gamma_{\text{eff}} = -F/3\pi R$ will be used to convert measured pull-off forces to surface energy at all separation times and rates studied.

Lateral separation rate estimated from the rate of change in normal force. Since the separation of two materials cannot occur everywhere at once but proceeds as a progressive reduction of the contact area, the main physical independent variable in a detachment process is the lateral separation rate. In the framework of a contact mechanics analysis,[1−13] it would be most useful to measure directly the lateral separation rate, but in our experiment it was not practical to do this.

It is worth emphasizing that the rate of change in normal force is frequently the independent variable in practical situations, since in a test rig force is applied through a device with compliance. This is especially so in situations where low adhesion (and low friction) is desired: for example, when a hard disk or an engine piston starts to slide from a position initially at rest, force is applied at a monotonically increasing rate.

An estimate of the order of magnitude of the lateral separation rate for a certain device separation rate can be obtained for a constant (rate-independent) surface energy by differentiating eq 1 with respect to time. One obtains the relationship between the time dependence of the contact radius, dr/dt, the externally applied (separation) force, F, and dF/dt:

$$dr/dt = (R/K)^{1/3}(1/3)\{F + 6\pi R\gamma +$$
$$[12\pi R\gamma F + (6\pi R\gamma)^2]^{1/2}\}^{-2/3} \times$$
$$\{1 + {}^1/_2[12\pi R\gamma F + (6\pi R\gamma)^2]^{-1/2}12\pi R\gamma\}\, dF/dt \quad (4)$$

In our experiments, F goes from approximately 0 to the pull-off force (which is formally negative), and dF/dt can be approximated by $k \times$ the device separation rate. Figure 2 shows a representative result for the (typical) parameters specified in the figure legend. On the left-hand ordinate axis, the actual contact radius relative to the contact radius under zero load is plotted against separation force; the contact radius decreases slowly as the separation force
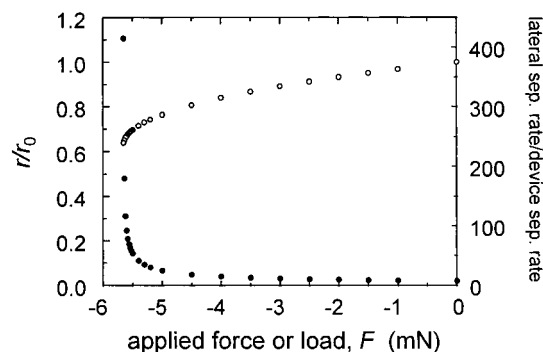

Figure 2. Estimate of the lateral separation rate for a chosen device separation rate based on the JKR theory: Contact radius of the flattened contact (eq 1) normalized by the radius at zero load (r/r_0, open circles), and ratio of lateral separation rate (dr/dt, eq 4) to device separation rate (solid circles) as functions of applied tensile force or load, F. During most of the separation, the ratio of the lateral separation rate (crack velocity) to the device separation rate is approximately 10−15 but increases to approximately 200−400 closer to detachment and then eventually diverges as $r \rightarrow 0.63r_0$. Chosen parameters: $\gamma = 30$ mN/m, $R = 2$ cm, $K = 3 \times 10^{10}$ N/m^2, and $k = 1 \times 10^4$ N/m.

is first decreased but then decreases rapidly as $r \rightarrow 0.63r_0$. On the right-hand ordinate axis, the lateral separation rate, dr/dt, produced by a spring with the stiffness we used in these experiments, is normalized to the vertical (device) separation rate. One observes that the lateral separation rate was approximately 10−15 times the device separation rate during most of the detachment process. Near the point of instability at which surface−surface detachment occurred, the ratio was approximately 200−400 times the device separation rate.

OTE Monolayers. The surfaces covered with a monolayer of OTE jumped spontaneously into a flattened, adhesive contact with a film thickness of 48 ± 2 Å (monolayer thickness 24 ± 1 Å) as soon as the separation distance was decreased to 30−40 Å. This instability occurs approximately at the point where the slope of a van der Waals−Lifshitz interaction (for a five-layer system of mica−monolayer−air−monolayer−mica[40]) exceeds the spring constant, $k = 1.1 \times 10^4$ N/m. As in the other systems described below, no repulsion other than the "hard-wall" at flattened contact was observed. The monolayer thickness is consistent with results in the literature.[31,32] On separation, the surfaces jump apart from a finite flattened area with $r_{\text{sep}} = (0.50-0.55)r_0$.

The adhesion between the OTE surfaces did *not* show dependence on the contact times (0.01−500 s) or the separation rates investigated (Figure 3). The surface energy, $\gamma_0 = 31 \pm 1$ mN/m, is the thermodynamic surface energy expected from van der Waals-Lifshitz theory (29 mN/m, for a three-layer system with a Hamaker constant of 5.9×10^{-20} J for a material with a refractive index of approximately 1.45). (The corrections introduced for a five-layer system become negligible at very close distances between the surfactant layers.[40]) In the literature, the thermodynamic surface energy for surfactant monolayers determined experimentally by various techniques is found to be in the range 23−30 mN/m.[41]

Our surface energy of the OTE surfaces is somewhat larger than the value at slow separation rates (∼0.01 μm/s) previously reported by Peanasky et al., who found that their measured value, 22.5 ± 4.7 mN/m, was in good

(40) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1991.
(41) Fox, H. W.; Zisman, W. A. *J. Colloid Sci.* **1952**, *7*, 428. Fox. H. W.; Hare, E. F.; Zisman, W. A. *J. Colloid Sci.* **1953**, *8*, 194.
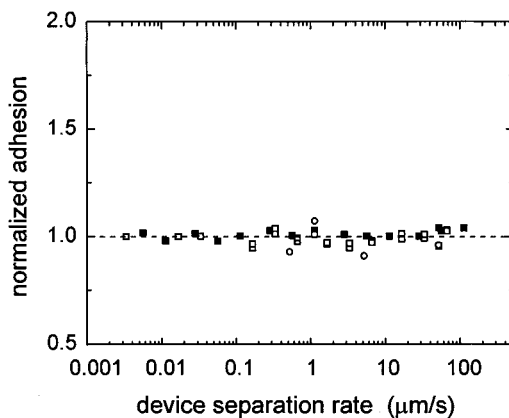
Figure 3. Normalized adhesion (pull-off force, F, normalized to the pull-off force at slow device separation rates, F_0; this is equivalent to the normalized surface energy, γ_{eff}/γ_0) plotted as a function of device separation rate for OTE surfactant monolayers at 25 °C. $\gamma_0 = -F_0/3\pi R = 31$ mN/m. Contact times: (■) 0.01 s; (□) 1 s; (●) 100 s; (○) 500 s.

agreement with the surface energy calculated from contact angle measurements: 22 mN/m.[31] A surface energy of 29 mN/m has been reported for Langmuir−Blodgett-deposited OTE layers.[32]

Peanasky et al. demonstrated that, in loading−unloading experiments, the OTE-coated surfaces do not display adhesion hysteresis,[31] which contrasts to the known behavior of CTAB-coated surfaces.[30]

The separation time (region d in Figure 1B) was found to be inversely proportional (exponent -1.00 ± 0.03) to the separation rate over the whole interval investigated (0.003−100 μm/s). Consequently, the experimentally determined average lateral separation rate ($=(r_0 - r_{sep})/$ separation time) was found to be 11−12 times the device separation rate for all data in Figure 3.

PVP−Polystyrene Films. The adsorbed PVP−polystyrene films expose a layer of polystyrene when the PVP blocks are selectively adsorbed onto mica and then dried as described in the Experimental Section. Unlike the other systems described, the polystyrene surfaces did not spontaneously jump into flattened, adhesive contact upon approach but came smoothly (with no observable interaction, whether attractive or repulsive), or with a very small inward jump, to a slightly deformed (not obviously flattened) contact at a film thickness of 53 ± 2 Å. This thickness is in good agreement with previous results on dry layers of this copolymer.[37,38] After several minutes had passed (or, alternatively, after a slight pressure had been applied), the surfaces would come to a flattened contact at this same film thickness. From the composition of the diblock copolymer and the bulk densities of the components,[42] we estimate that the thickness of the adsorbed layer on each surface (26 ± 1 Å) corresponds to approximately 3−4 Å (slightly less than one segmental diameter) of PVP and 23 Å (approximately four segmental diameters) of polystyrene. The flattened contact was adhesive upon separation and separated from a finite contact area with a radius $r_{sep} = (0.5-0.6)r_0$. Our observations of the contact mechanics in this system are consistent with previous results by Watanabe and Tirrell.[38] This behavior of the surfaces on approach is most likely because the glassy polystyrene surfaces are rougher than the polybutadiene surfaces. AFM mesurements on these systems show surface roughnesses of approximately 10 and 3 Å, respectively.[36]
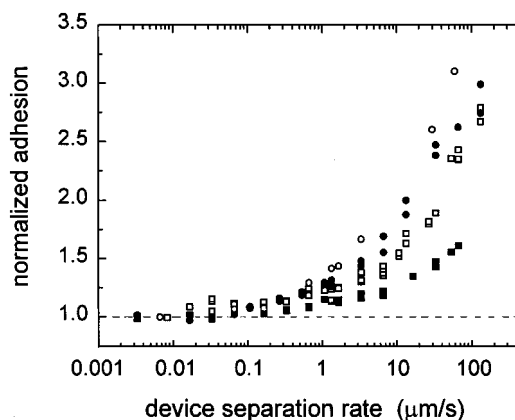
(42) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989.

Figure 4. Normalized adhesion (γ_{eff}/γ_0) as a function of device separation rate for CTAB surfactant monolayers at 25 °C. $\gamma_0 = -F_0/3\pi R = 47$ mN/m. Symbols as in Figure 3.

The slow flattening of the polystyrene surfaces with elapsed time in contact made accurate experiments at contact times shorter than ∼1 min impossible. We have studied the pull-off force at slow separation rates (around 0.01 μm/s) for contact times varying from 1 to 20 min and found the surface energy to be a constant, 26 ± 1 mN/m. This is close to the expected thermodynamic surface energy of bulk polystyrene: 32 mN/m.[38,40,42] The surface energy measured at slow separation rates for polystyrene is thus significantly lower than the one for the polybutadiene system. Our measurement for polystyrene is consistent with results found in the literature for the same system, PVP (60 000 g/mol)−polystyrene (60 000 g/mol), where pull-off experiments at separation rates of approximately 0.01 μm/s (using a weak force-measuring spring) gave $\gamma = 25 \pm 5$ mN/m, without an increase in adhesion after 1 h in contact.[38]

CTAB Monolayers. The surfaces covered with self-assembled monolayers of CTAB were found to jump into a flattened, adhesive contact with a film thickness of 36 $\pm$ 2 Å (monolayer thickness 18 ± 1 Å) from a separation of $D = 30-40$ Å. As for OTE, this is consistent with an attractive van der Waals interaction across air. The monolayer thickness is in good agreement with results found in the literature on this system.[30] The deformation of the surfaces after the jump in is as expected from the JKR theory, and on separation, the surfaces were found to jump apart from a finite area with a radius $r_{sep} = (0.65 \pm 0.05)r_0$.

At slow separation rates, the surface energy measured, $\gamma_0 = 47 \pm 2$ mN/m, is significantly larger than the thermodynamic surface energy for a hydrocarbon surfactant, 29 mN/m, obtained from van der Waals−Lifshitz theory (cf. OTE results above). However, similar values to ours for the surface energy of CTAB, $\gamma = 42-53$ mN/m, have been obtained in loading−unloading and pull-off experiments by Chen et al.[30] The separation rates in these prior investigations were slow, since the experiments employed the SFA motor controls and a weak force-measuring spring to obtain a lateral separation rate less than 1 μm/s (as measured from the change in contact area). The contact times before separation varied from 20 min to 1 h.[30]

In our experiment (Figure 4), the adhesion of the CTAB monolayers increases with increasing separation rate and also with the time in contact (0.01−500 s). The separation rate above which the increase in adhesion is observed is not well-defined but appears to be similar, around 0.05−0.1 μm/s, for all four contact times studied.

If the surface energy and compliance of the deforming surfaces show no rate dependence, the separation time

(region d in Figure 1B) should be inversely proportional to the separation rate (as observed experimentally for the OTE surfaces). In the CTAB system, the increase in apparent surface energy with increasing separation rate causes the separation of the surfaces to slow down. The average lateral peel rate was defined as the rate of decrease in the radius of the flat contact area from the initial area to separation, that is, $(r_0 - r_{sep})$/separation time, as for the OTE system. It was found that the ratio (lateral separation rate/device separation rate) was proportional to γ_0/γ_{eff}, that is, to the inverse of the curves in Figure 4. If we recall that the deformation of the supports (section e in Figure 1B) showed no change with the separation rate, this relation between apparent surface energy and average lateral separation rate ($\propto 1$/separation time) can be understood. At slow device separation rates, the ratio (lateral separation rate/device separation rate) was a constant, approximately $10-11$, in agreement with the estimate in Figure 2.

PVP–Polybutadiene Films. The total film thickness of two adsorbed, dry layers in contact was found to be 28 $\pm$ 3 Å, in good agreement with a previous report.[34] The relative volumes occupied by the constituent blocks, estimated from their molecular weights ($M_{w,PVP} = 23\ 700$ g/mol and $M_{w,PB} = 38\ 500$ g/mol) and bulk densities (1.15 and 0.96 g/cm^3, respectively[42]), suggest that the measured thickness of the dry layer on each surface (14 $\pm$ 1 Å) corresponds to approximately 5 Å of PVP (one segmental diameter) plus 9 Å of polybutadiene (two segmental diameters). It has been established by contact angle and XPS measurements that the adsorbed diblock copolymer film exposes a layer of polybutadiene,[36] so that the layer closest to the mica surface is expected to contain mostly PVP. Our measurements of film thickness, combined with the volume argument above, indicate that the adsorbed and dried polybutadiene layer is not more than $2-3$ molecular diameters thick anywhere on each surface and is very smooth, since no roughness was detected on the interference fringes for two layers in contact. The smoothness of the polybutadiene surface has been confirmed by Watanabe et al. by AFM measurements, which showed a surface roughness of 3 Å.[36]

On approach, the polymer-coated surfaces spontaneously jump in from a separation distance of $30-50$ Å to a well-defined flattened contact ($D = 0$, at dry film thickness 28 $\pm$ 3 Å). We conclude that the attraction between the polybutadiene surfaces on approach likely arises from van der Waals interactions. The size and shape of the deformed contact region at no external pressure are as expected from the JKR theory. However, on separation, the surfaces separate until the contact area is too small to be measured (radius < 2 μm) and appears as a point just before detachment occurs.

This pointed deformation of the surfaces is, however, *not* as pronounced (i.e., the shape of the separated surfaces away from the central, adhering region is not as strongly affected) as that for mica surfaces separating in a drop of a polybutadiene melt,[43] and it did not appear to change with separation rate. Throughout the separation, the film thickness remains the same as that measured on the approach, even at the pointed contact zone right before the jump apart. We tentatively ascribe this pointed deformation of the separating surfaces to possible lateral movement of the polybutadiene chains as the surfaces peel apart (though not at the point where PVP adheres to the mica), and we note that indications of lateral
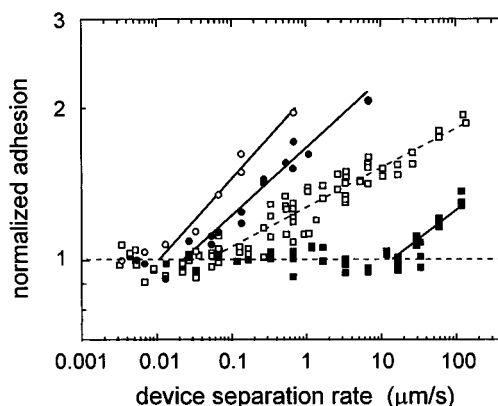
(43) Kuhl, T.; Ruths, M.; Chen, Y. L.; Israelachvili, J. *J. Heart Valve Disease* **1994**, *3*, S117.

Figure 5. Normalized adhesion (γ_{eff}/γ_0) as a function of device separation rate (plotted on logarithmic scales) for adsorbed PVP–polybutadiene at 23 °C. $\gamma_0 = -F_0/3\pi R = 55$ mN/m. Symbols as in Figure 3. The data were obtained from seven separate experiments.

movement of flexible, anchored chains have recently been seen in stiction measurements on perfluorinated polymers by Gui et al.[44] We return to this point in the Discussion.

The adhesion, expressed as (apparent) surface energy, $\gamma_{eff} = -F/3\pi R$ (shown normalized by γ_0 in Figure 5), was found to be always larger than the thermodynamic surface energy of polybutadiene, 37 mN/m, determined from van der Waals–Lifshitz theory for a three-layer system[40] of polybutadiene–air–polybutadiene. Here we use $A = 7.6 \times 10^{-20}$ J for the Hamaker constant of a material with refractive index 1.52 interacting across air. (The corrections introduced for a five-layer system become negligible at very close distances between the adsorbed polymer layers.) The experimentally determined surface energy found in the literature, for samples of bulk thickness, is between 31 and 43 mN/m.[42] In contrast, our measurements even at the slowest separation rates give $\gamma_0 = 55 \pm 3$ mN/m.

A similar increase over the thermodynamic surface energy has been observed by Watanabe and Tirrell[38] for PVP–polyisoprene. Here the experimentally determined value at 32 °C was $\gamma = -F/3\pi R = 55 \pm 10$ mN/m compared to the expected surface energy of bulk polyisoprene, 34 ± 3 mN/m. Similar experimental values were also obtained by Watanabe et al. at 20 °C.[39] In their experiment the separation rates were slow (below 1 μm/s), and no increase in adhesion was found for contact times from a few seconds up to 1 h. They also found that there was no effect of an applied pressure of up to 1×10^6 N/m^2 on the adhesion of polyisoprene at this separation rate. For the PVP–polybutadiene system, we have investigated the effect of a pressure of 6×10^5 N/m^2 at a contact time of 1 s over the whole range of separation rates in Figure 5. We also found that, under these conditions, the adhesion of the polybutadiene surfaces did not depend on applied pressure.

The adhesion of the PVP–polybutadiene layers was found to increase with separation rate above a well-defined critical separation rate for each contact time (Table 1). Empirically, we found that the adhesion showed a power-law dependence on the separation rate, unlike the case in the CTAB system, where the dependence on contact time was less pronounced and the adhesion increased initially less rapidly with increasing separation rate.

The average lateral peel rate in the PVP–polybutadiene system, $(r_0 - r_{sep})$/separation time (in this case $r_{sep} \approx 0$), decreased with increasing adhesion compared to its value

(44) Gui, J.; Kuo, D.; Marchon, B.; Rauch, G. C. *IEEE Trans. Magn.* **1997**, *33*, 932.

Table 1. Critical Separation Rate and Critical Rate of Change in Separation Force for the PVP−Polybutadiene System

| contact time (s)	device separation rate (μm/s)	$\Delta(F_s/R)/\Delta t$ (N/(ms))
0.01	11.8 ± 5.4	6.5 ± 3.0
1	0.045 ± 0.014	0.025 ± 0.008
100	0.024 ± 0.008	0.013 ± 0.005
500	0.0100 ± 0.006	0.006 ± 0.003

Figure 6. Normalized excess adhesion, $(\gamma_{eff} - \gamma_0)/\gamma_0$, for the CTAB surfaces (cf. Figure 4) plotted on logarithmic scales as a function of the device separation rate. Symbols as in Figure 3.

in the OTE system for a chosen device separation rate. It was found that the ratio (lateral separation rate/device separation rate) was proportional to γ_0/γ_{eff}, that is, inversely proportional to the normalized adhesion in Figure 5. At slow separation rates, the ratio (lateral separation rate/device separation rate) was approximately 12, in good agreement with the estimated average ratio from Figure 2.

Discussion

Previous work by others, in which differences in adhesion during loading and unloading were deduced from a JKR analysis of the contact radius, has shown time and rate effects on adhesion hysteresis.[14−18] The CTAB system was studied by Chen et al.,[30] and PVP−polyisoprene (which is similar to PVP−polybutadiene) was studied by Watanabe, Tirrell, and co-workers.[36−39] Although computer simulations show the possibility that adhesion hysteresis can reflect changes of ordering within each monolayer after they are placed in contact,[45] the prevailing interpretation[14−18,26,27,30,36−39] has been that enhanced adhesion upon unloading reflects interpenetration between opposed layers. Interpenetration is blocked if the monolayer is close-packed and crystalline (OTE) or below its glass transition temperature (PVP−polystyrene). In these respects our measurements confirm prior results.

It has been suggested that the enhanced adhesion upon unloading in the CTAB system, giving an apparent surface energy at least 10 mN/m higher than that during loading,[30] is caused by an increase in effective contact area between the loose-packed amorphous alkyl chains on opposed layers, so that the actual contact area exceeds that optically measured.[30] In this view one should expect the discrepancy to decrease as the experiment is performed more slowly, but the data in Figure 4 do not show this effect. As Chaudhury has noted (private communication) the anomalously large γ_{eff} on separation may also reflect some kind of energetically trapped state from which the system cannot escape during the experimental time.

The new aspects of the present study are two-fold: first, to vary independently the rate of unloading over a wide range and, second, to extend the period of stationary contact to times several orders of magnitude shorter than the minute or hour periods explored in previous work.[14,15,17,18,30,36−39] We now discuss the findings in turn.

Rate Dependence of Adhesion. Gent[21] and others[6,46] have postulated that rate-dependent adhesion may be expressed as the product of two terms: the surface energy, γ, and a function of viscoelastic losses within the underlying material. Support for this ansatz comes from the observation that the second term obeys the Williams−Landel−Ferry (WLF) shift factor for frequency−temperature equivalence[47] for a wide variety of adhesive polymer systems.
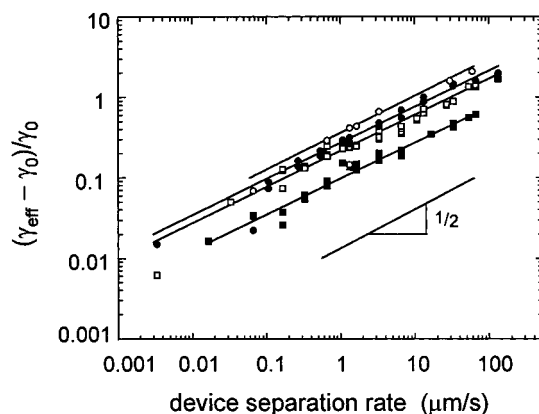
In the terminology of fracture mechanics, the adhesion we measure is the strain energy release rate, G, which can be compared to the thermodynamic work of adhesion, $W (=2\gamma)$. The normalized excess adhesion, $(G - W)/W$,[5,6] is equivalent to $(\gamma_{eff} - \gamma_0)/\gamma_0$ plotted for CTAB in Figure 6. The excess adhesion has been observed in many polymer systems to grow empirically as a power law with the crack velocity to the power 0.6.[6] Greenwood and Johnson[5] predict the excess adhesion to increase as a power law of the crack velocity to the power 0.5 for a viscoelastic material whose creep compliance is either constant or linear during the time of crack propagation. The mechanical model[5] was developed for bulk material but seems to be applicable to a viscoelastic interface without violating the theoretical assumptions.

The lateral separation rate at the crack tip was not measured in our experiments, but the considerations embodied in Figure 2 suggest that it was proportional to the rate at which normal force was applied to the system. During most of the separation, the lateral separation occurs at an average rate 10−15 times the device separation rate.

In Figure 6, the normalized excess adhesion in the CTAB system is plotted against the separation rate on log−log scales. The excess adhesion scales as a power law with the separation rate to the power 0.5, which is in agreement with the Greenwood and Johnson prediction.[5] The data extrapolates to vanishing low excess adhesion at rates that depend on the stationary contact time before detachment; we return to this point in the following section. The favorable comparison with theory is noteworthy although it is surprising that a linear viscoelastic analysis should be relevant.

It is also interesting that a similar analysis fails for the PVP−polybutadiene system. It is evident from the raw data of normalized total adhesion versus separation rate in Figure 5 that the excess adhesion $(\gamma_{eff} - \gamma_0)/\gamma_0$ rises more slowly than as a power law, and a plot of the excess adhesion on log−log scales has decided curvature (not shown). This may suggest that the viscoelastic relaxation function in these diblock copolymer layers does not satisfy the simple form assumed by the Greenwood−Johnson theory. Indeed, it is not unexpected to find indications of a complex viscoelastic response in ultrathin polymer layers.[48]

The striking common observation in both CTAB and PVP−polybutadiene systems is that the rate-dependent

(45) Karaboni, S. *Phys. Rev. Lett.* **1994**, *73*, 1668.

(46) Andrews, E. H.; Kinloch, A. J. *Proc. R. Soc. London, Ser. A* **1973**, *332*, 385.

(47) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.

(48) Van Alsten, J.; Granick, S. *Macromolecules* **1990**, *23*, 4856.

regime has a velocity dependence far weaker than simple proportionality. This contrasts with predictions for the excess adhesion to be expected from chain pull out from an opposed layer; the theories which model chain pull out have presumed this friction to be *linearly* proportional to velocity.[26,27] The discrepancy between theory and experiments might in principle arise from an inability to produce a low enough crack velocity to achieve a linear viscoelastic response. However, if this is the case, the linear regime is not experimentally relevant, since effects in this regime must be overwhelmed by the larger constant work of adhesion from energetic interactions that is always observed when the rate is low.

We note that a similar power-law relation between the adhesion and separation rate as for PVP−polybutadiene has been found in experiments on an elastomer cap interacting with a flat surface covered with anchored polymer chains.[18] However, in the experiments on elastomer, the adhesion depended on rate even at the slowest separation rates. The difference might reflect the longer contact times (1 h[18]) in those experiments.

Estimates of Critical Separation Rates for Other Experiments. From the observed scaling in Figures 4 and 5 and the critical device separation rate needed to induce an increase in adhesion (from the "equilibrium" value, γ_0) after different contact times (given for PVP−polybutadiene in Table 1), one may estimate the contact time needed to observe, for example, a 10% or larger increase in the measured adhesion (from the equilibrium value) for different experimental setups.

For comparison between different types of experiments (different contact geometries or devices with different spring constants) it is convenient to convert the separation rate (the abscissa in Figures 3−5) to the rate of change in (external) separation force by multiplying the separation rate by the spring constant of the device, k. The variable obtained can be further normalized by dividing by the radius of curvature, R (approximately 2 cm). In most adhesion experiments found in the literature using an SFA device, the lower motor in the SFA was used to control the separation. In such cases, the separation rate is around 0.01 μm/s, and for comparison with our results, the rate of change in separation force, $\Delta(F_s/R)/\Delta t$, is then easily obtained from the spring constant and radius of curvature of each experiment.

For a spring constant of 10^3 N/m and a separation rate of 0.01 μm/s, which is commonly used in SFA adhesion experiments in the literature, the contact time needed to observe an increased adhesion in the PVP−polybutadiene system would be a few hours. This estimate is consistent with the observation by Watanabe et al.[39] that, for such experimental conditions, no increase in the adhesion was observed for PVP−polyisoprene (which is expected to be similar to PVP−polybutadiene) after a contact time of up to 1 h.

Role of Stationary Time in Contact. In both the CTAB and PVP−polybutadiene systems, some rate-independent adhesion in excess of that expected from the thermodynamic surface energy is always observed for even the briefest stationary time in contact, implying that some interdiffusion between the contacting layers probably always occurs on the time scales investigated. The shortest contact time investigated was 0.01 s (cf. Figures 3−5), and the shortest detachment time was approximately 0.02 s (at the largest separation rates). The adsorbed polybutadiene layers are, however, very thin (approximately 9 Å on each surface) and tethered to the surface. In such a system we expect local segmental rearrangements rather than unconstrained diffusion in

the bulk. For contacts between thick films (0.2−0.7 μm) of poly(methyl methacrylate) or polystyrene ($M_w = 100\,000−200\,000$ g/mol), the mutual diffusion coefficient at temperatures approximately 30−50 °C above the glass transition temperature is around 10^{-16} to 10^{-15} cm^2/s.[49,50] At such diffusion rates, the maximum interdiffusion possible in our system (to an interfacial width comparable to the thickness of the whole sample) would occur already at the shortest contact time investigated (0.01 s). Since the polymer in our experiment is of lower M_w and the difference in temperature from the glass transition temperature is larger than that in the examples above, the bulk diffusion coefficient might be even larger. It has, however, recently been shown by Lin et al.[51] that the diffusion between one thin, supported and one thicker, covering layer of poly(methyl methacrylate) ($M_w = 143\,000$ g/mol) in contact 35 °C above T_g does not scale as $t^{1/2}$ (where t is the contact time), as for diffusion across the interface between bulk samples,[52,53] but develops considerably more slowly for very thin ($0.4R_g$) supported layers. For such thin layers, an effective diffusion constant almost 2 orders of magnitude lower than that in the bulk was determined. The slower development of the diffusion in time (approximately proportional to $t^{1/8}$) was attributed to a larger number of contacts with the supporting (silicon) surface per chain and restricted polymer conformation, slowing down the diffusion. The results by Lin et al. support our interpretation that a slowly developing interdiffusion and interdigitation occurs between our two thin, supported polybutadiene layers in contact at temperatures above T_g. In our experiment, the polymer layer is even thinner ($0.2−0.3R_g$), and there are the further complications of both layers being supported and one end of each polymer chain being bound to the surface, further restricting the mobility.

The CTAB monolayers show more rapid development of the adhesion and less dependence on contact time and separation rate. These differences are likely due to the loose packing of the CTAB monolayers and the abundance of mobile chain ends at the interface. The free ends of the surfactant molecules may penetrate rapidly into the available space between the chains of the opposing monolayer; but since no change in thickness of the two contacting layers was detected even during the longest times in contact, the depth of this interpenetration must be small (not more than a few Å). The interpenetration and interdigitation of the short, anchored chains of the CTAB monolayers most likely occur only close to the contact interface. They thus differ from the rearrangements in the polybutadiene system where the polymer, to increase its conformational entropy, might (given a long enough diffusion time) explore the whole gap between the surfaces without a change in thickness of the confined film. The differences in absolute magnitude of the surface energies measured in the PVP−polybutadiene ($\gamma_0 = 55$ mN/m) and CTAB ($\gamma_0 = 47$ mN/m) systems may be caused by different penetration depths and numbers of interdigitated chains but may also be influenced by the difference in their thermodynamic surface energies, 37 and 29 mN/m, respectively.

It is natural to inquire into the quantitative shifts of our data with elapsed time in contact, since the length of

(49) Brochard, F.; Jouffroy, J.; Levinson, P. *Macromolecules* **1983**, *16*, 1638.

(50) Yukioka, S.; Nagato, K.; Inoue, T. *Polymer* **1992**, *33*, 1171.

(51) Lin, E. K.; Wu, W. L.; Satija, S. *Macromolecules* **1997**, *30*, 7224.

(52) de Gennes, P. G. In *Microscopic Aspects of Adhesion and Lubrication*; Georges, J. M., Ed.; Elsevier: Amsterdam, 1982.

(53) Jud, K.; Kausch, H. H.; Williams, J. G. *J. Mater. Sci.* **1981**, *16*, 204.

diffusive interpenetration between layers might in the simplest approach be expected to scale with $t^{1/2}$. Such a dependence has been predicted[52] and observed[53] for the interdiffusion of polymer chains to the point of entanglement with subsequent chain pull out. As discussed above, the diffusion between two thin, supported layers is likely slower than that for the same polymer in the bulk. Unfortunately our data available to date are too few and scattered to allow a quantitative comparison. A systematic study addressing this question is in progress.

Contact Area at Adhesive Instability. In the JKR theory[1] the surfaces detach from a nonzero contact radius, $r = 0.63r_0$, where r_0 is the contact radius under zero force. This has been confirmed for many systems in the literature, and we also observed it in the OTE, PVP–polystyrene, and CTAB systems.

A different relationship was observed in the PVP–polybutadiene system; however, the contacting surfaces remained stable down to a contact radius less than 2–3 μm. The interference fringes thus became slightly pointed, with a contact area too small to be measured, right before the jump apart. We found that it was possible to halt the detachment process at small contact radii ($r < 0.6r_0$) and maintain a stable junction (the longest times investigated were around 5 min), implying that if the difference from the JKR prediction reflects sluggish viscoelastic processes, these processes took longer than 5 min.

The polybutadiene chains in this experiment were rather long; the extended length for $M_w = 23\,700$ g/mol exceeds 0.1 μm. Although these chains were tethered to the solid substrate such that a fluid transport of the polymer to form a meniscus toward the middle of the contact zone was impossible (as confirmed by visual inspection of the interference fringes and by the repeatability of the experiments), the microscopic fluidity of the segmental polybutadiene repeat units may be relevant to explain the origin of this phenomenon.

Discussion of the Instrumental Approach. In future work it should be possible to image the propagating crack directly with a high-speed camera during the course of the experiment and in this way avoid the indirect estimate of lateral crack velocity that we present in Figure 2. An advantage of this experimental approach in which force is applied at a constant rate, which differs from the classical constant-load or constant-displacement experiments,[6] is its closeness to the common experimental situation where anomalously high adhesion occurs between surfaces that are intended to slide over one another.

The longest time in contact investigated (500 s) does not constitute an upper limit for the possible contact times, and it is likely that the development of the adhesion continues further, especially in the PVP–polybutadiene system. However, experimental difficulties such as thermal drift and plastic deformation of the supporting glue layer appear at longer contact times, which may affect the accuracy of the measurements of pull-off force at very long times and slow rates. The large adhesion measured at high separation rates is, likewise, not an upper limit for the adhesion. If the separation rates are larger than those shown in this study, the requisite deflection of the device produces extra noise in the output signal, perhaps owing to nonlinearities in the piezoelectric circuitry for input signals larger than 10 V. In addition, we observed a decrease in the output signal at large amplitudes during fast separations (or approaches) that we ascribe to air damping of the movement of the lower surface.

One might speculate that there would be a change in the increase of the adhesion if a fast separation caused damage to the adsorbed layer or even the supporting mica. We did, however, not reach a separation rate that would have caused any observable damage to the surfaces in any of the systems studied, provided that they were kept dry. During one experiment on PVP–polybutadiene, the atmosphere inside the instrument was deliberately allowed to take up humidity from the laboratory air overnight. The adsorbed PVP–polybutadiene layers could then be removed from the mica surfaces, so that a gathering of material in the contact region was observed on the interference fringes during detachment. This type of damage was most prone to happen at low separation rates. The adhesion of damaged films was not investigated.