Adhesion between Solid Surfaces in Polymer Melts: Bridging of Single Chains

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ABSTRACT: The adhesion of solid surfaces across polymer melts has been studied with an atomic force microscope (AFM). As polymers we used poly(dimethylsiloxane) (PDMS, $M_w = 18\,000$), poly(ethylmethylsiloxane) (PEMS, $M_w = 16\,800$), and a diblock copolymer (PDMS-*b*-PEMS, $M_w = 15\,100$). Upon retraction, adhesion peaks were observed which we interpret as bridging of single polymer chains. Bridging occurred seldom (in each 20th force curve) in PDMS and more often in PEMS (in each 8th force curve) and was most prominent in the diblock copolymer, where a typical force curve contained 5−10 adhesion peaks. The mean detachment force decreased with increasing retraction velocity, indicating that the bond to the surface or tip is not a direct contact with the solid surface.

There are two basic mechanisms for the stabilization of colloids in liquids: charge stabilization and steric stabilization. The latter is due to the adsorption of polymers onto the surface of colloidal particles, leading to a steric repulsion between them. Under certain circumstances, however, high molecular weight polymer can adsorb on two separate particles and draw them together. This is known as polymer bridging flocculation.

Steric stabilization can also occur in a polymer melt. For an attractive interaction between the solid surface of the particle and the polymer chain the polymer forms a pinned, rubberlike, immobilized layer of few nanometers thickness on the surface.[1−10] This immobilized layer prevents particles in a melt to aggregate, which is important in the production of composite materials. It is not clear whether to expect bridging in a polymer melt. Two effects hinder polymer bridging: First, the immobilized layer should prevent single polymer chains from reaching the solid surface of the particle. Second, even if a polymer chain adsorbs directly to the surface of the particle, if it is removed its place should immediately be taken by another chain, leading to no change in the free energy of that system.

Here we show that nevertheless bridging can occur and that it can lead to a significant adhesion between solid surfaces in polymer melts. This finding is of direct relevance for a better understanding of polymer adhesives. Force vs distance curves were measured between the tip of an AFM (Multimode, Veeco Instruments, Fremont, CA) and a planar substrate in different polymer melts. Rectangular cantilevers with microfabricated silicon tips (Ultrasharp, length 130 μm, thickness 1 μm, Anfatec, Oelsnitz, Germany) and V-shaped cantilevers with silicon nitride tips (length 100 μm, thickness 0.6 μm, Veeco Instruments, Fremont, CA) were used. Both materials are naturally oxidized. They were cleaned in a plasma cleaner for 8 min at 30 W before each measurement. Tip radii of curvature were measured by imaging a silicon grating (TGT01, Mikromasch, Oelsnitz, Germany) to be between 31 and 150 nm. Cantilever spring constants ranged from 0.2 to 0.6 N/m as determined from thermal noise. As substrates we used naturally oxidized silicon wafers (oxide layer thickness ≈2 nm, Wacker-Chemie, Burghausen, Germany) and mica (PLANO, Wetzlar, Germany). Polymers were synthesized by anionic polymerization. Molecular weights M_w and polydispersities M_w/M_n were determined by gel permeation chromatography. The zero shear viscosity η was measured with a rheometer (ARES, Rheometric Scientific). We used poly(dimethylsiloxane) (PDMS, $M_w = 18\,000$ g/mol, $M_w/M_n = 1.04$, $\eta = 0.482$ Pa s, mean contour length $\bar{L} = 63$ nm), poly(ethylmethylsiloxane) (PEMS, $M_w = 16\,800$ g/mol, $M_w/M_n = 1.14$, $\eta = 2.328$ Pa s, $\bar{L} = 45$ nm), and a diblock copolymer consisting of 1:1 wt % PDMS:PEMS (PDMS-*b*-PEMS, $M_w = 15\,100$ g/mol, $M_w/M_n = 1.08$, $\eta = 1.056$ Pa s, $\bar{L} = 47$ nm). Molecular weights were above the entanglement molecular weight (12 000 g/mol for PDMS).[11] Wetting properties were measured with a sessile drop setup. PDMS spreads on silicon oxide and mica (advancing contact angle zero). PEMS forms a finite advancing contact angle of ≈10° on mica and ≈25° with silicon oxide. This indicates a stronger interaction of PDMS with the substrate than PEMS.

In a force measurement, the substrate was first mounted onto the piezoelectric AFM scanner. Then, the AFM head with the liquid cell, O-ring, and cantilever were mounted, and the liquid cell was completely filled with polymer melt. The surface was periodically moved up and down at constant velocity at 40 nm/s (if not mentioned otherwise). The cantilever is deflected by forces between the tip and the surface. The result of such a measurement is a curve, showing cantilever deflection vs height position of the scanner. A force vs distance curve, briefly called "force curve", is calculated by multiplying the cantilever deflection with the spring constant to obtain the force and subtracting the cantilever deflection from the height position to obtain the distance. Experiments were done at 23 °C.

Formation of the immobilized layer can take several hours.[4,6,10,12,13] This is reflected in force curves, which changed significantly during the first ≈10 h. Just after filling PDMS into the AFM cell a repulsive, oscillatory force was observed on approach (Figure 1). The period of the oscillation was 0.8−1 nm, which corresponds roughly to the diameter of the PDMS strand and

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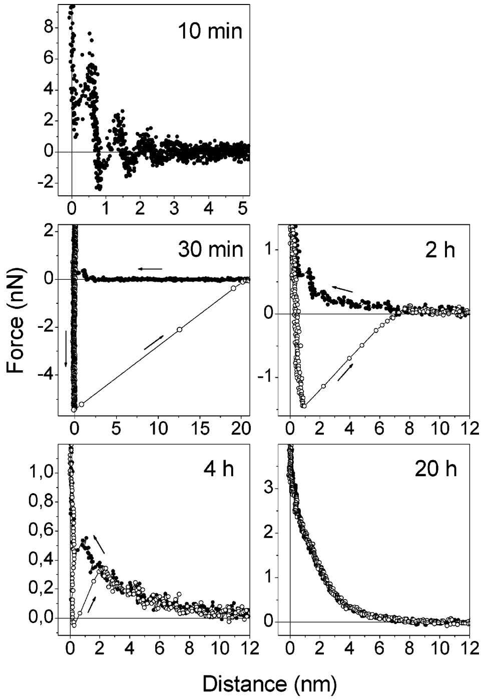

Figure 1. Typical sequence of force curves recorded 10 min, 0.5 h, 2 h, 4 h, and 20 h after filling the AFM cell with PDMS on silicon oxide. Approaching (●) and retracting (○) force curves are shown. Negative forces are attractive and positive forces repulsive. The first plot is shown at a different scale to highlight the oscillations on approach.

indicates a layered structure. After ≈1 h a monotonically increasing repulsive force became visible and grew in strength. After typically 10 h it completely dominated the total force, and no oscillation could be observed anymore. Annealing for 1 h at 50 °C by a heating plate mounted on top of the scanner always had the same effect as waiting for more than 10 h. In some cases also a long-range attraction occurred just after filling the cell. After waiting for few hours it disappeared and the same repulsion was observed as when starting with a layered structure. When retracting the tip from a freshly immersed silicon oxide surface, it experienced a strong adhesion force of typically 5 nN. The adhesion decreased with time. After waiting more than ≈10 h the adhesion disappears, and completely reversible force curves were measured. This increase of repulsion upon approach and the disappearance of adhesion demonstrates the stabilizing effect of the immobilized layer on colloidal dispersion.

Figure 1 shows typical force curves. In roughly 6% of the force curves, however, characteristic adhesion peaks at distances of up to 80 nm were observed during the retraction of the tip from the silicon oxide substrate (Figure 2). Forces measured in PDMS on mica were similar except that very few stretching events were observed. These adhesion peaks were probably caused by the stretching of individual polymer chains connecting tip and substrate. A polymer chain which is bound to the substrate (or the tip) partially adsorbs to the tip (or substrate) when both are close together. When the tip is retracted, the polymer chain is first stretched until either the bond to the substrate or the bond to the tip detaches. In solvents bridging of single polymer chains connecting the surface and the tip is frequently observed.[14,15] We know, however, of no report on bridging of single molecules in a melt.

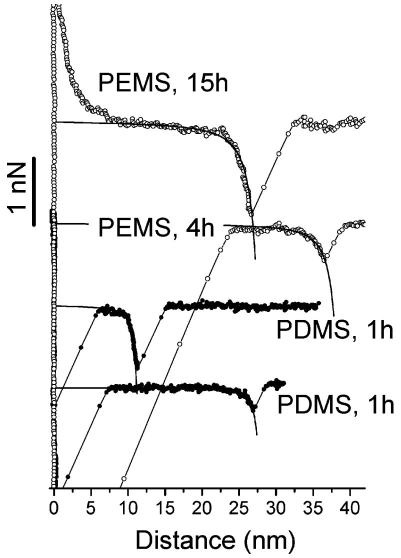

Figure 2. Selected force curves recorded in PEMS (15 and 4 h after filling the melt into the AFM cell) and PDMS (after 1 h) when retracting the tip from silicon oxide. The curves are shifted along the force axis so that individual events can be distinguished. Continuous lines are fits with the WLC model (eq 1).

When using PEMS on silicon oxide, the same dependence on the incubation time was observed: the repulsion increased on approach, and the adhesion decreased on retraction. More bridging events (12%) than in PDMS were detected. Maximal stretching forces (from now on called detachment forces) were widely distributed, and we found no indication that they are multiples of a discrete number. On mica we did not observe bridging with PEMS.

A direct conclusion from this result is that we have to distinguish between two different kinds of adhesion phenomena: contact adhesion, which describes the release from direct contact between the solid surfaces, and bridging adhesion, which is connected with the detachment of bridges between the two solid surfaces. What are the typical energies required to overcome contact and bridging adhesion? In contact adhesion the energy required to release the tip from the surface is equal to the bending energy of the cantilever just before it snaps off contact: $W_C = K\Delta x^2/2$. Here, K is the spring constant of the cantilever and Δx is the deflection of the cantilever just before it snaps off the surface. The adhesion force is $F_C = K\Delta x$, which leads to $W_C = F_C{}^2/2K$. Contact adhesion energies were typically 30×10^{-18} J just after immersing the surfaces in the polymer melt and decreased to zero after several hours. The bridging adhesion energy was obtained by integrating attractive forces with respect to distance. Typical energies of bridging adhesion were $(0.5-5) \times 10^{-18}$ J for a single event.

When measuring forces in PDMS-*b*-PEMS on silicon oxide bridging events were more frequently observed, and almost all force curves showed adhesion peaks. Usually multiple adhesion peaks were observed (Figure 3a). Thus, with the diblock copolymer multiple polymer chains were pulled off one by one during the retraction. The total bridging adhesion energy was typically $(100-200) \times 10^{-18}$ J and exceeded contact adhesion energies observed directly after immersing the surfaces with the melt. When plotting many individual force curves together (Figure 3b), the plot shows a maximum of the

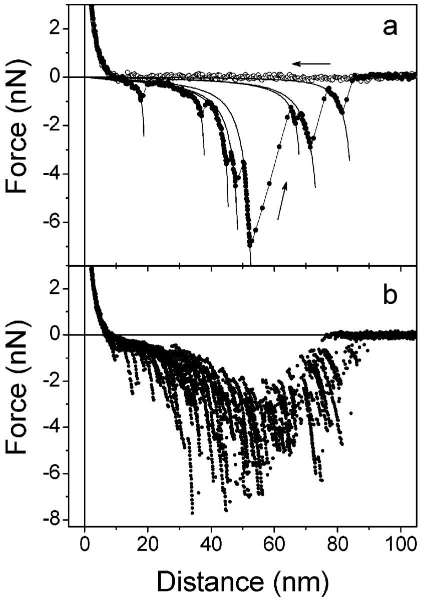

Figure 3. (a) Typical force curve measured in PDMS-*b*-PEMS on silicon oxide. Approaching (○) and retracting parts (●) are shown. Each adhesion peak is stepwise fitted with the WLC model (eq 1, continuous lines). (b) Superposition of 20 individual force curves (retracting parts).

stretching force at a distance of ≈60 nm. This value agrees with the mean contour length of 46 nm, considering that longer chains are more likely to be detected.

Three questions arise: First, what is the stretching process, and how can we describe it? To analyze the stretching process quantitatively, forces were fitted with the wormlike chain (WLC) and the freely jointed chain (FJC) models. In the WLC model the polymer is an elastic cylinder with a constant bending elasticity and of constant length L.[16] The force required to stretch a WLC with persistence length l_P and length L to a distance x is given by[17,18]

$$F(x) = \frac{k_B T}{l_P}\left[\frac{x}{L} + \frac{1}{4(1 - x/L)^2} - \frac{1}{4}\right] \qquad (1)$$

Here, k_B is Boltzmann's constant and T is the temperature. In the FJC model the polymer is divided into rigid elements of length l_K, the Kuhn length, through perfectly flexible joints without any interactions. When stretching a FJC a force is required because its entropy is decreased. Force and distance are related by[19-21]

$$\frac{x}{L} = \coth\left(\frac{Fl_K}{k_B T}\right) - \frac{k_B T}{Fl_K} \qquad (2)$$

Adhesion peaks could be fitted with the WLC model (eq 1). For PDMS a persistence length of 0.44 ± 0.13 nm was obtained, which agrees with literature values (0.4−0.5 nm).[22-25] Also, the stretching of PEMS chains could be fitted with the WLC model, resulting in a smaller persistence length of 0.17 ± 0.07 nm. A fit with the FJC model was possible, but the Kuhn lengths obtained of typically 0.1−0.2 nm were too small. Since the maximal forces were relatively high, we also took elastic contributions into account in both models.[26] This did not lead to a significant improvement. In accordance, typical elastic moduli obtained were relatively high (1000 nN).

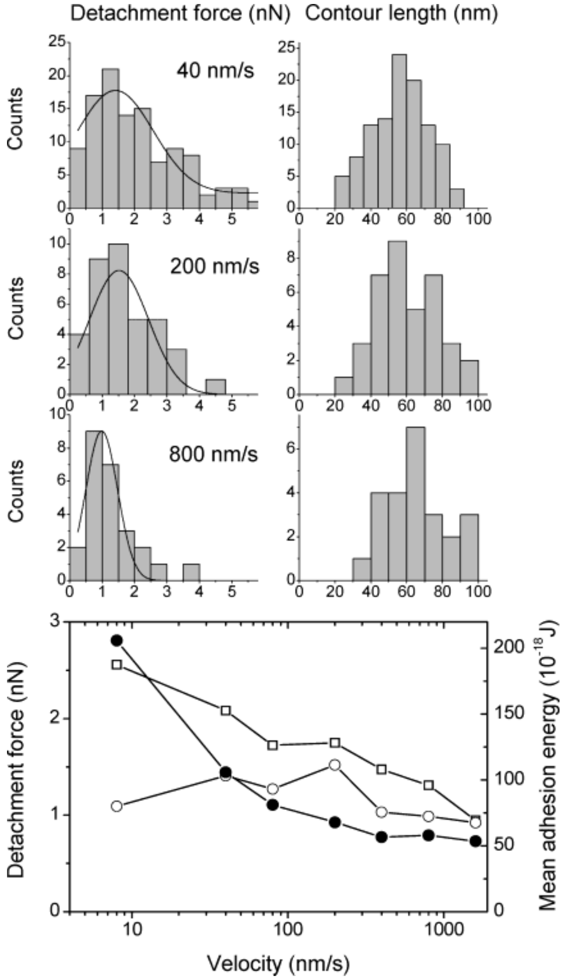

Figure 4. (top) Distribution of detachment forces and contour lengths at three approaching/retracting velocities for PDMS-*b*-PEMS on silicon oxide. Values were obtained after stepwise fitting with the WLC model. In all cases the maximal load was 50 nN. (bottom) Mean detachment forces (□), maximal detachment force obtained from a fit of the distribution with a Gaussian (○), and mean adhesion energy (●) plotted vs approaching/retracting velocity.

Force curves of PDMS-*b*-PEMS could also be fitted with the WLC (and FJC) model. It led, however, to small persistence lengths of 0.08 ± 0.06 nm ($l_K \approx 0.1$ nm). To account for the fact that each force curve contained multiple adhesion peaks, we assumed that the total force is the sum of several independent bridging events. Starting from the adhesion peak at the largest distance the peak was fitted and the fit was subtracted from the force curve. In this way the "background" force for the second adhesion peak was removed. Then the peak at the second largest distance was fitted, the fit subtracted, etc., until all adhesion peaks were fitted. By this stepwise fitting multiple adhesion events could partially be decoupled. However, because of "hidden", undetected adhesion peaks, the procedure does not lead to a perfect decoupling. Detachment forces might still be overestimated.

The second relevant question is: what is the nature of the bond between polymer and solid surface? To get more information, force curves were measured at different approaching/retracting velocities for PDMS-*b*-PEMS. The detachment force *decreased* when increasing the retracting velocity (Figure 4). In accordance the adhesion energy decreased. The mean contour length

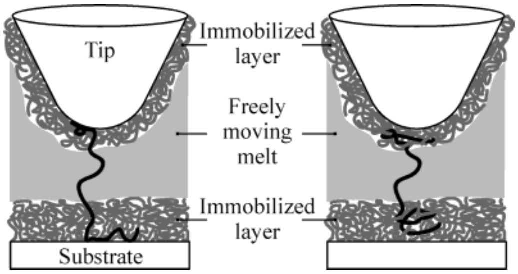

Figure 5. Bridging polymer chains either bind directly to the solid surfaces (left) or are entangled in the immobilized layers (right). The bridging polymer chain is in black while the polymers in the immobilized layer are gray. The homogeneous gray region represents the mobile polymer melt.

as obtained from the fit increased slightly from 56 nm at 8 nm/s to 67 nm at 1600 nm/s.

A decreasing detachment force with increasing retracting velocity is surprising because it is well-known that the rupture force for a single bond should increase with increasing retracting velocity.[30−32] In addition, if a direct bond between the polymer chain and silicon oxide or silicon nitride was broken (Figure 5, left), we expect to find a defined value for the detachment force or multiples of it.[27−29] Even if the polymer binds at a number of sites, one binding point after the other should rupture when pulling on the polymer, each with a defined strength. Instead, a wide distribution of detachment force was observed. This indicates that the detachment is not dominated by the rupture of a defined single bond to the solid surface. An alternative hypothesis is that the bridging polymer chain is partially entangled in the network of the immobilized layer (Figure 5, right). When pulling hard enough it is released from this network.

The third question is: why does bridging occur so often in the diblock copolymer as compared to the homopolymers, and why is it more likely in PEMS than in PDMS? At this point we can only speculate about possible reasons. The attractive interaction of PDMS with silicon oxide and mica is stronger than the interaction of PEMS with these surfaces. This could lead to a more entangled immobilized layer of PDMS into which the bridging polymer might not be able to penetrate. The less strongly bound immobilized layer of PEMS might give a polymer chain a higher chance to diffuse partially into the layer and form a bridge. A factor, which might contribute to the high bridging probability of PDMS-*b*-PEMS, is the higher ordering and a possible tendency to form a lamellar structure at a sold surface despite the fact that in bulk only PDMS-*b*-PEMS of much higher molecular weight orients in a lamellar phase.[33] The PDMS block tends to orient toward the silicon oxide or mica surface while the PEMS block points away from it. Such a surface-induced preorientation could increase the likelihood to bridge the two surfaces. The fact that the diblock copolymer showed such a strong tendency to form bridges might give important insights into how to design adhesives.

Conclusion. Polymer chains can form bridges between two solid surfaces in a melt. Bridging adhesion is conceptually different from contact adhesion. While contact adhesion is only acting when the two solid surfaces are in direct contact (zero distance), bridging adhesion has a maximum at a distance of the order of the contour length of the polymer. The energy required to overcome bridging adhesion can be high compared to contact adhesion. Block copolymers, which are preoriented at surfaces, can show significantly enhanced bridging adhesion.

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