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Adhesion and Deformation of a Single Latex Particle

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The rupture of contact between a single latex particle and an atomic force microscope tip has been investigated at nanoscopic scales by monitoring retracting force−distance curves. The particle is highly elongated, and an intermittent rupture proceeds at the tip/latex interface. The minimal force of detachment, the separation energy, and the long distance shape of the curve depend on the tip velocity and are strongly sensitive to the presence of nearby particles. This indicates that viscoelastic dissipations occur over spatial scales depending on the particles organization. The formation of long nanofilaments seems to be a specific dissipative mechanism prominent for isolated particles.

Introduction

Latex particles are nanometric polymer beads, generally used as binding or coating agent. Depending on the processing conditions, the particles can either aggregate to form clusters and films or remain isolated.[1] This degree of aggregation could influence the mechanical and adhesive properties of the latex particles. Investigating the behavior of a single particle having a size of a few hundred nanometers is a typical field of application for atomic force microscopy (AFM).

Owing to the nanometric spatial resolution of AFM, the wetting and spreading of latex particles have already been studied.[1−3] Using force−distance curves ($F-d$ curves), Fretigny et al. have shown that the mechanical properties of thin latex layers (10 μm) do not differ from macroscopic ones.[4] Unertl reported that the work of adhesion of one latex particle can be determined by $F-d$ curves and found no difference between an isolated particle and a continuous thin film of particles.[3]

In the present study, on the basis of AFM imaging and $F-d$ curves, we show that the adhesive behavior of single latex particles can differ from that of ultrathin latex layers.

Experimental Section

(1) Preparation of Latex Samples. Core−shell latex, with a core of partially cross-linked styrene/butadiene and a copolymerized shell of neutralized carboxylic acids, was used. For the experiments discussed here, the glass transition temperature (T_g) and the gel fraction are −2 °C and 75%, respectively. The average diameter of the particles is 160 nm (quasi-elastic light scattering). A 25 μL portion of an ultrafiltrated and diluted aqueous latex dispersion (0.05% in mass) was poured on a flat silicon wafer, previously cleaned by a mixture of H_2O_2 and H_2SO_4 (surface energy $\gamma_s > 70$ mJ·m^{-2}). The slow evaporation of the water in a humid atmosphere (RH = 95%) leads to various latex particle organizations, multilayers, monolayers, and isolated particles, that can be visualized through AFM imaging. When adsorbed on the silica surface, the particles are about 30 nm high. Before testing, samples were stored at 20 °C with silica gel.

(2) AFM Measurements. To image the latex and perform the force−distance curves, a Park Autoprobe CP AFM was employed. We used a Si_3N_4 tip mounted on a gold-coated cantilever with a nominal spring constant equal to 0.5 N·m^{-1} (Park, Microlever). The samples were first imaged in contact mode, keeping the applied force constant at 5 nN. Then $F-d$ curves were monitored at a chosen spot of the sample. The lateral resolution of the force mode and the small radius of curvature of the tip (35 ± 5 nm, determined by imaging an silicon grating (NT-MDT Ultrasharp TGT01)) allow $F-d$ curves to be monitored, with the tip touching only one latex particle, either isolated or embedded in a cluster. The $F-d$ curves protocol consisted of two stages: first, the latex particle was indented under a maximal normal force of 150 nN; in a second stage on which we focus, the sample was moved away from the tip (retraction). To do so, the piezoelectric actuator carrying the sample performed a vertical displacement sweep. Simultaneously, the deflection of the cantilever was monitored (by reflection of a laser spot) and converted into a force signal using the spring constant of the cantilever. A force versus actuator position curve was thus acquired. To translate it into a force versus distance curve, the real distance between the sample and the tip was calculated by subtracting the deflection of the cantilever from the measured actuator displacement. This protocol corresponds to a single cycle of the usual periodic sweeps used in force spectroscopy. The vertical displacement speed was varied (between 40 and 2000 nm·s^{-1}) by keeping the amplitude of the actuator sweep constant and changing the setting frequency (between 0.02 and 1 Hz). The test temperature was $T = 27 \pm 2$ °C. Using a sealed chamber under dry nitrogen flux, we have checked that the behaviors reported below are not due to the presence of a water film on the sample, even if the mechanical properties of the latex depend on humidity. All data reported here were obtained during one single series of experiments with the same tip and under the same conditions (cantilever, electronic settings, and atmospheric parameters).

Results and Discussion

Typical retraction $F-d$ curves acquired on an isolated particle for different sweep frequencies are presented in Figure 1. We first concentrate on the general trends of the curves. After a relatively rigid response at small distances, the latex particle yields (there is no abrupt jump out of contact), a plastic threshold is overcome, and the latex is strongly deformed. At higher distances, force steps appear and finally the contact is broken. The rupture is located at the latex/tip interface, as demonstrated by comparing $F-d$ curves performed on bare silica before and after the $F-d$ sequence on the latex. These curves on silica appear identical, indicating that the tip is unspoiled. Before this interfacial failure, the strong deformation supported by the particle (at least five times larger than the initial thickness of the particle) can be associated to the formation of a long nanofilament between the tip and the particle. Indeed, the remains of this nanofilament can be seen on topographical images captured immediately after the rupture of contact, as shown in Figure 2. An isolated latex

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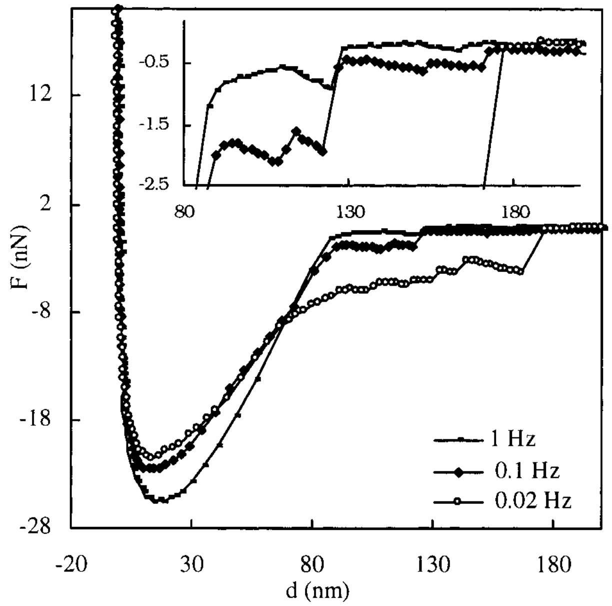

Figure 1. Typical force−distance curves for one isolated particle probed at different frequencies. The embedded figure is a zoom on the long distances behavior.

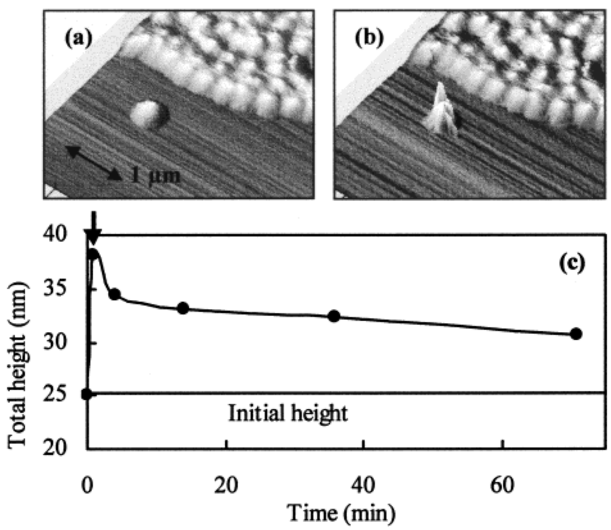

Figure 2. Protrusion of a latex particle due to the elongation of the material during the withdrawal of the tip: (a) before the test; (b) after the test; (c) height relaxation of the protrusion after the rupture of contact.

particle lying on a silicon wafer is imaged before (Figure 2a) and after (Figure 2b) having supported a $F-d$ cycle. After the rupture of contact, a protrusion accompanied by instabilities of the topographical signal have appeared at the point of contact with the tip. The protrusion relaxes with time (Figure 2c).

The last striking feature of the $F-d$ curves is the succession of steps in the force values at long distances. Such steps in $F-d$ curves have already been observed for polymers or biological materials. They were interpreted in terms of extraction of single polymer chains and bond rupture[5,6] or in terms of fracture mechanics in bulk or at interfaces.[7] In our case, an interplay between the cohesive behavior of the latex (rheological properties) and the

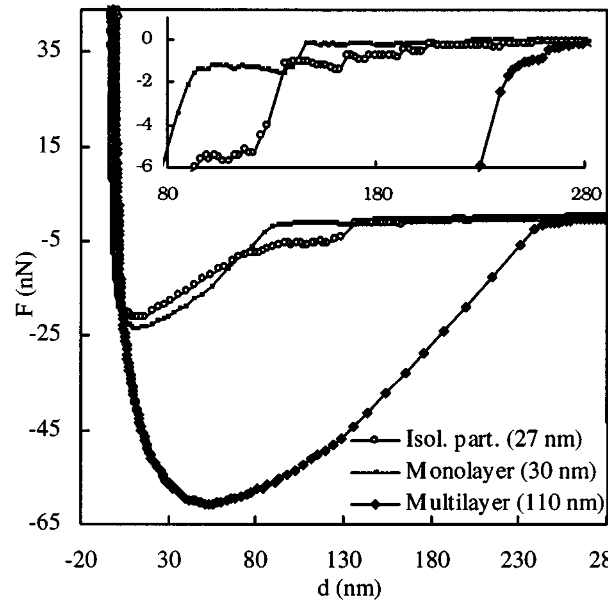

Figure 3. Typical force−distance curves for one latex particle with different neighborhoods at a sweep frequency equal to 0.02 Hz. The thickness of the layers is indicated between parentheses. The embedded figure is a zoom on the long distances behavior.

strength of the interface could account for the nonmonotonic shape of the final part of the retraction curve. During the stretching of the filament, elongation strengthening occurs and the force increases slightly (in absolute value). At a critical point, enough strain energy is stored to allow the interfacial failure to propagate. This relaxes stress, and the force falls abruptly. If the failure stops (due to relaxation) before the full rupture of contact, elongation takes place again. At the present stage of the experiment, we cannot exclude the formation of multiple filaments. The steps could then correspond to successive detachments of different filaments.

In any case, even if the failure processes cannot be directly visualized, the general features of the $F-d$ curves discussed above are qualitatively similar to what is obtained in a macroscopic tack experiment,[8,9] except for the length scales.

The detailed shape of the retraction curves depends on the test frequency (Figure 1), indicating that the contact is not purely elastic. Hence the minimal force at which the rupture of contact between the tip and the particle occurs cannot be related to the thermodynamical work of adhesion by a JKR analysis.[10−12] Moreover, the framework of the tack test cannot be used because the contact area is not under control in our AFM experiment. Therefore, to characterize our results, we have chosen to examine the following parameters: the minimal separation force F_S and the separation energy E_S (the area enclosed by the curve and the $F = 0$ axis).

We have presented in Figure 1 the retraction curves obtained on isolated particles for different sweep frequencies. In Figure 3, curves monitored at a fixed frequency

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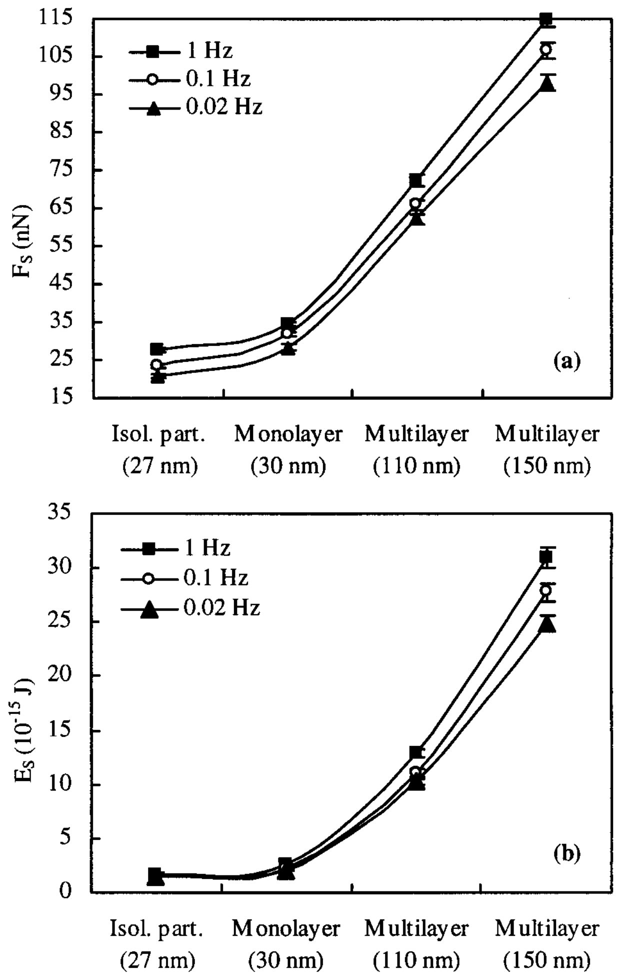

Figure 4. Effects of the frequency and of the neighborhood on the average values of: (a) the minimal separation force F_S; (b) the separation energy E_S. The thickness of the layers is indicated between parentheses. Each data point is the average of 15 measurements, standard deviation is less than 4%.

on latex particles with different neighborhoods (isolated particle, particle pertaining to a monolayer or to a multilayer) are displayed. The elongation and the stick–slip process are more pronounced for lower frequencies (Figure 1) and for an isolated particle (Figure 3). Figures 1 and 3 also highlight the fact that the minimal separation force F_S and the separation energy E_S depend on the frequency and on the neighborhood of the particle. This is summarized in Figure 4 which presents F_S and E_S for three different frequencies and four different neighborhoods. Each data point represents an average value over 15 experiments.

Both F_S and E_S grow when the frequency rises. Increasing the frequency results in two antagonistic effects: the scanner velocity increases but the contact time decreases. These two parameters cannot be decorrelated with our AFM apparatus. But they are known to act in the same way on the viscoelastic adhesive behavior: the adhesive energy increases with the velocity [13] and with the contact time.[8,9] The observed augmentation of F_S and E_S with frequency is thus an indication for the predominant role of the velocity. This velocity dependence of F_S and E_S shows that energy is dissipated vicoelastically at the fracture head and/or in the bulk of the sample during the whole pulling process. A more subtle effect can be noticed: although the sweep velocity (frequency) affects F_S (Figure 4a), it has no effect on E_S for an isolated particle and a minor effect for a particle pertaining to a monolayer (Figure 4b). This results from the fact that, at low frequencies, the contribution of the force steps becomes significant (Figure 1). The fraction of area associated to the steps can represent more than 20% of E_S. The increase of the step length when decreasing the frequency can be qualitatively understood: the filaments are longer at low pulling rates because the latex is softer (relaxation of the modulus). The corresponding increase of the step amplitude is more delicate to explain because the effect of the frequency on the contact area is uncontrolled.

The most striking observation is that both F_S and E_S increase when the number of neighbors (in lateral and/or in vertical dimension) is increased. This clearly indicates that, when the number of neighbors is high, the strain and stress fields induced in the sample by the retraction of the tip extend to several particles. The global dissipation volume is thus broader. Nevertheless, the sensitivities of E_S and F_S to the lateral nearby particles appear to be different: E_S is almost the same for an isolated particle and a particle pertaining to a monolayer, while the corresponding F_S values are quite distinct (Figure 4). This can also be attributed to the preferential appearance of the force steps. For the retraction curve corresponding to the isolated particle, the steps are more numerous and longer than those for the monolayer (Figure 3). A tentative explanation of this behavior is that filaments are preferentially formed when the stress cannot propagate to lateral neighbors (confinement effect). In this case, the latex locally undergoes higher stress, leading to a strong elongation and thus to a specific energy dissipation. This specific dissipation mechanism can compensate for the smaller available volume for bulk dissipation.

Conclusion

We have used force–distance curves to investigate directly the adhesive behavior of nanoscopic latex particles. Under the presented experimental conditions, the rupture of contact occurs at the AFM tip/latex interface. During the retraction test, viscoelastic and plastic energy is dissipated in a volume which can extend to several nearby particles, and a strong deformation of the probed particle is observed. This elongation can become the prominent contribution to the separation energy for an isolated particle and low separation velocities. The adhesive behavior of latex particles appears drastically affected by their tendency to readily yield and elongate.

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