Influence of tip indentation depth on the adhesive behavior of viscoelastic polydimethylsiloxane networks studied by atomic force microscopy

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Summary: A commercial atomic force microscope (AFM) outfitted with a custom control and data acquisition system was used to investigate the adhesive nature of a viscoelastic polydimethylsiloxane (PDMS) network. Due to the complex dependence of the adhesion of this sample on factors such as indentation, surface dwell time, applied stress and sample memory effects, total control of the applied stress profile between the AFM tip and sample was necessary. Since the force curves were analyzed automatically on-line, large amounts of data could be rapidly collected, alleviating the time-consuming task of off-line analysis. The adhesive response is shown to increase with increasing interaction time and the maximum applied load. The results are rationalized by considering the time-dependent stress relaxation behavior of the PDMS network as it is deformed by the AFM tip.

Introduction

The invention of the atomic force microscope (AFM) has enabled the detailed study of soft materials such as polymers and biological molecules with very high spatial resolution. [1] The AFM has proven to be an extraordinarily adaptable method, finding applications in almost every discipline of scientific research. Several recent reviews provide numerous examples of the latest techniques and applications of AFM. [2-4] Virtually every known type of surface force has been investigated with the AFM, usually through the use of a so-called force curve experiment. Instead of rastering the tip over the surface as is done to obtain an image, the tip is repeatedly brought into and out of contact with the sample surface. The resulting cantilever deflection data can be used to characterize materials properties such as sample stiffness, chemical functionality, and surface charge density. There exists a vast literature on this subject and the interested reader is referred to a recent review of the topic for background information and current applications. [5]

Although AFM has become a standard surface characterization technique, there has remained a relative dearth of reports related to the dynamics of contact between the

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AFM tip and the probed sample, particularly of materials with time-dependent behavior. AFM has been previously used to examine elastomer networks of differing crosslink density [6] and surface rheological properties. [7, 8] Force volume imaging has been used to determine the spatial variation of adhesion and elasticity for a polymeric network. [9] Adherence was shown to increase in magnitude as the time of contact was extended between a silica substrate and an AFM tip coated with a living yeast cell. [10] When a flourescein-coated tip was left in contact with a anti-flourescyl IgG substrate for only two seconds, no adhesion was observed. However, the pull-off deflection increased to 400 nanometers when the contact time was extended to two minutes.[11] These experiments illustrate the importance of considering how contact time influences adhesion in AFM force curve experiments.

In this article, we describe how the applied stress and contact time act to influence the adhesion of a viscoelastic polydimethylsiloxane (PDMS) network. Using custom software and electronics, we have implemented a system in which the applied stress can be controlled with an arbitrary waveform generator used to determine the position of the sample. The adherence between tip and sample is shown to depend upon the contact time as well as the maximum applied load.

Experimental

A model system was chosen for this investigation consisting of a cross-linked PDMS network and linear PDMS polymer which was present in, but not chemically bound to, the network. The functional polymer, α,ω–vinyl terminated polydimethylsiloxane (Alrdrich), was mixed with a stoichiometric amount (based upon total moles of reactive chain ends) of pentamethylcyclopentanesiloxane crosslinking agent (ABCR, Hamburg, Germany) and 40 wt% of trimethyl terminated PDMS (M_n= 62,700 g/mol, ABCR). Molecular weights were determined with size exclusion chromatography and were calibrated to polystyrene standards. Because the trimethylterminated chains possess no reactive endgroups, they were not chemically bound to the network structure, although they may be bound to the network through physical entanglements. Approximately 30 ppm cyclovinylmetalsiloxane complex (ABCR, Hamburg, Germany) was utilized as catalyst. The solution was thoroughly mixed and was placed on a clean piece of silicon wafer and allowed to crosslink overnight at 60° C. This sample was then glued to an

AFM sample holder. The bulk viscoelastic properties crosslinked PDMS networks swollen with homologous free chains have been investigated elsewhere. The presence of free chains in a crosslinked network has been shown to influence its viscoelastic properties. [12-16]

Force curve experiments were conducted with a Multimode AFM with a modified Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA Barbara) outfitted with signal access module (SAM) which was connected to an external data acquisition and control system. A data acquisition board connected to the SAM (PCI-MIO-16E-4, National Instruments, Austin, TX) was used to acquire both the normal and lateral deflection signals from the microscope and to control the piezo position with the use of a software- implemented arbitrary function generator. The waveform was sent to the controller unit for amplification and then applied to the piezo in order to move the sample. Commercial, silicon nitride tips were used as received (Nanosensors, Germany). Two tips were used during this investigation, one for Figures 1&2 and a second for Figures 3-5. Nominal spring constants were used to convert acquired voltage signals to meaningful units.

Results and Discussion

The software (LabView, National Instruments, Austin, TX, USA) developed in this study automatically analyzed each force curve for several parameters of interest. With the aid of an arbitrary function generator, each aspect of the tip-sample interaction could be controlled. However the resulting force curves are somewhat more complex than curves obtained with simple waveforms. We diverge here slightly in order to introduce some nomenclature necessary to describe the experimental techniques used to obtain the results seen in this section. The snap-on force was considered to be the force when the tip makes a spontaneous, initial contact with the surface. The approach force was considered to be the minimum force during the approach cycle and may or may not equal to the snap-on force. The maximum load was considered to be the externally applied load at the end of the approach cycle. The surface delay time was the time between the end of the approach cycle and the beginning of the retract cycle. The adherence force was the maximum force (in terms of magnitude) measured during the retraction phase of the force curve. The area between the approach and retract portions

of the force curve was calculated with numerical techniques and defined here as the adhesion hysteresis. Finally, the snap-off event was considered to be the point when the tip and surface spontaneously separate. The snap-off event was determined to be the point where the velocity of the tip reached a maximum during the retraction cycle of each force curve. As will be seen later, the adherence force and the pull-off force do not necessarily have the same value, as is often the case with elastic materials. Each force curve could be analyzed for above parameters. Only a few will be discussed here, namely the influence of the contact time and maximum load on the approach and adherence force.

A typical force curve experiment described in the previous paragraph is shown in Figure 1. In this figure, the applied piezo voltage and cantilever deflection are plotted as a function of time. The same data has been replotted as a force-distance plot in Figure 2 for clarity.

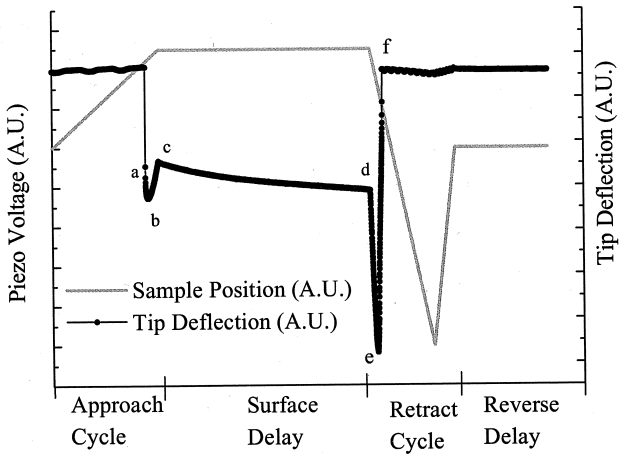

Figure 1. Typical force curve experiment with a surface and reverse delay. Although it is possible to vary the rate of approach and retraction independently, for all data shown in this report, they were equal in magnitude.

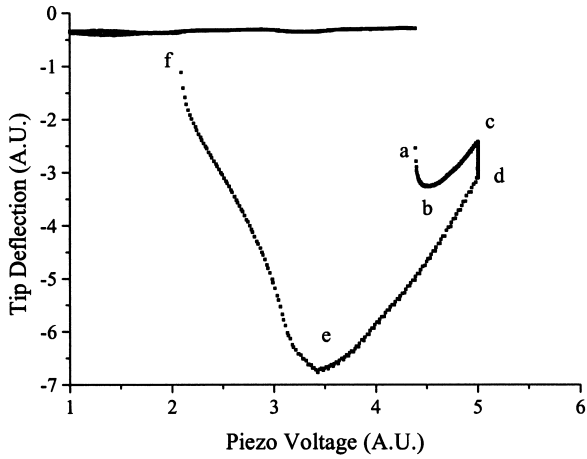

Figure 2. Force-distance plot of an AFM tip interacting with a viscoelastic PDMS network. This is the same data seen in Figure 1, replotted in terms of a force curve.

As the sample is brought into contact, the tip spontaneously jumps into contact with the surface at a point where the derivative of the surface potential is equal to the force constant of the cantilever (a). [17] Subsequently, the external force may continue to decrease until the approach force is reached (b). The sample continues its upwards motion until the maximum load is reached (c). During the surface delay period, the tip continues to penetrate further into the material due to sample relaxation (c-d). Because of the viscoelastic nature of the sample, any deformation of the material will occur over a time period determined by the relaxation characteristics of the material. After the completion of the surface delay period, the sample is lowered away from the tip and the external load passes through a minimum, defined here as the adherence force (e), and eventually snaps-off spontaneously (f).

Although the exact nature of the interface is not known, an enrichment of free chains could occur at the surface due to entropic effects. [18] The presence of free chains at the surface could lead to the formation of a capillary between the tip and sample during the retract cycle of the force-curve experiment. This can be seen in Figure 2 by the extended withdrawal of the tip from the surface. Prior to the force curve experiments

presented here, the tip was checked for possible contamination by collecting several force curves on a clean silicon wafer. In this case, the adherence force was equal to the pull-off force, as is commonly observed for non-compliant, elastic materials. Furthermore, when we performed force curve experiments with the same tip on a clean silicon surface after the force curve experiment on the PDMS network, the snap-off force was not equal to the adherence force. The external load reached a minimum, but the tip did not snap off from the surface immediately. The curves were reminiscent of force distance curves obtained for a viscous polymer film absorbed on a rigid substrate.[19] This sequence of events is consistent with the transfer of PDMS from the sample surface onto the tip, further supporting our supposition that a nanocapillary forms between the tip and sample during the retraction cycle.

In order to assess the reproducibility and quality of the measurements, numerous force curves were collected and analyzed before other parameters were varied. Because force curves were recorded and analyzed on-line, large data sets could be collected rapidly. Figure 3 comprises a histogram of 30,000 individual force curve measurements collected at the same location on the viscoelastic PDMS network after a stabilization period of several hours. Due to instrumental noise and piezo creep, the microscope was allowed to stabilize for several hours prior to collection of this data in order to minimize external influences such that the intrinsic distribution of adherence forces for a particular cantilever deflection could be determined. For these measurements, the maximum cantilever deflection was held constant with a feedback loop. This implies that the sample deformation was also constant. [20]

As seen in Figure 3, the adherence force could be characterized by a Gaussian-type statistical distribution. The mean adherence force for this particular case was 295 nN with a standard deviation of 1.39 nN or 0.47 %. Although not shown here, similar distributions were observed for a range of maximum loading values. In summary, the statistical distribution of adherence forces for a particular maximum loading value was less than 1 % of the mean, even after several thousand repeated contacts.

Due to the enrichment of chains at the surface *(vide supra)*, free chains appear to be transferred to the tip. PDMS would be expected to wet the comparatively high surface energy AFM tip which most likely composed of a mixture of silicon nitrides and oxides. It seems reasonable that the free PDMS chains contaminate the surface of the tip within the first few contacts with the surface. Because the data shown in Figure 3 was

collected after the instrument was allowed to stabilize after a period of several hours. During this stabilization period, the tip and surface were repeatedly in contact with one another. While the exact number of force curves is not known precisely, it was in excess of 40,000 based upon the length of the stabilization period (> 3 hours) and the period of each force curve cycle (~ 0.25 seconds). It can therefore be concluded that the adherence measured is actually a combination of adhesion between the AFM tip and cohesion between the PDMS adsorbed on the tip and surface layer of the PDMS network.

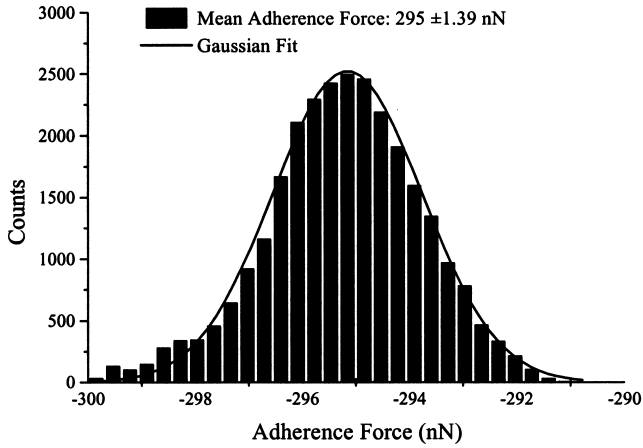

Figure 3. Distribution of adherence forces. In this experiment, over 30000 force curves were collected and analyzed. A simple sawtooth waveform was used and the maximum applied load was 0 nN.

In has been previously shown that at a constant maximum loading, the adhesion hysteresis increases dramatically with increasing surface contact time for the viscoelastic PDMS networks considered here. [21] In order to determine the effect of the indentation on the adhesive behavior of these materials, the maximum load was systematically varied over a range of sample deformations. These results are presented in Figure 4.

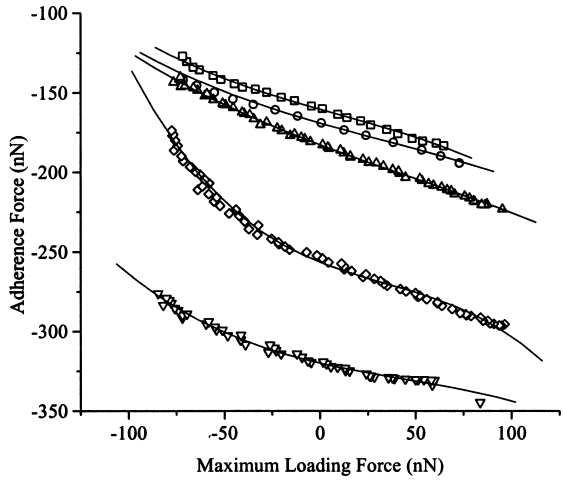

Figure 4. Effect of maximum loading force on the adherence force for various surface delay times. The maximum adherence force is plotted as a function of the maximum load for surface delay times of: 0 msec, squares; 10 msec, circles; 100 msec, up-triangles; 1000 msec, diamonds; 5000 msec, down-triangles. Lines are intended to guide the eye.

Notice also in Figure 4, that it was possible to obtain a negative value of the maximum loading force. In this case, the adhesive forces are larger than the repulsive forces at the end of the approach cycle. The shape of the force curve was similar to that seen in Figures 1 & 2, regardless of whether the maximum loading was positive or negative. However, for negative maximum loading values, the relaxation of the tip into the polymer during the surface delay period appeared to be less pronounced. By steadily increasing the maximum load, the tip will be pressed deeper into the material. Because the polymer is viscoelastic, it will tend to deform relatively slowly in response to a sudden applied stress. Increasing the surface delay time causes further penetration of the tip into the sample as the polymer relaxes in response to the applied stress. Increased indentation results in an increase in the effective surface area. As stated previously, the polymer cannot relax back to its equilibrium configuration instantaneously as the applied stress is lowered during the retraction cycle. We

postulate that these phenomena result in an imprint of the tip being formed on the surface, which leads to an increase in local surface curvature of the polymer as it conforms to the shape of the tip. This results in an increase in interfacial surface area and hence a larger adherence between the tip and the sample.[22] This effect is enhanced for longer contact times as well as deeper sample indentations.

Due to sample memory effects, the approach force also increases in magnitude with the maximum loading. At zero maximum load, the approach force decreased from 70 nN with no surface delay up to 140 nN with a five second delay. The approach forces for the data seen in Figure 4, are plotted in Figure 5 as a function of the maximum loading force. In this figure, the *n-th* approach force is plotted as a function of the *n-th* maximum load. We submit that the approach force will depend on the previous, or *(n-1)-th*, maximum loading value as well as the reverse delay time. The effect of the reverse delay was not explored here, although it has been shown elsewhere that as the reverse delay time is extended, both the approach and the adherence force decrease for a constant surface delay time and indentation. [21] In this report, because the difference in subsequent loading values was sufficiently small, this effect could be neglected.

As was the case in Figure 4, the maximum loading was increased from negative to positive. However, for this polymer, no hysteretic effects of the maximum loading scan direction were seen. Although not shown there, the curves obtained by decreasing the maximum loading from a positive towards a negative value were roughly equivalent to that seen in Figure 5. The approach force is ultimately determined by the effective compliance of the system, the surface energy, and the effective radius of curvature of the two surfaces. *(vide supra)* Because of the viscoelastic nature of this material, it cannot relax completely back to its equilibrium position between force curve cycles. As the sample is brought into contact again, the imprint left from the previous force curve cycle will result in an increase in the surface area relative to the sample's unperturbed state and therefore greater observed adherence.

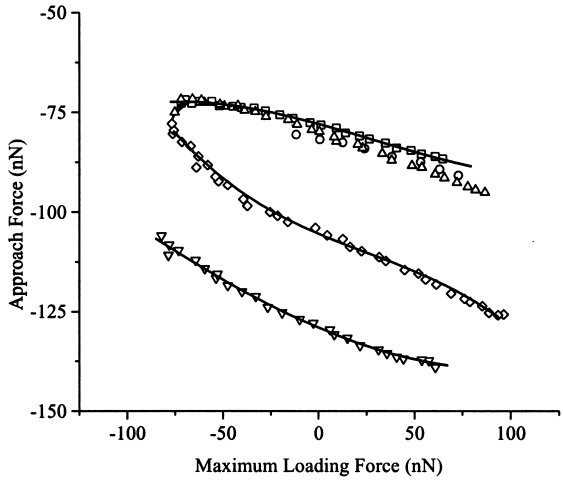

Figure 5. Effect of indentation depth on the approach force for various surface delay times. The symbol assignments are the same as in Figure 4. Lines are intended to guide the eye

Conclusions

AFM force curve measurements reveal that the adhesive behavior of a viscoelastic PDMS network depends strongly on the interaction time between the tip and sample. Repeated measurements at a constant maximum indentation were shown to have a standard deviation of less than 0.5 %, even after 30000 repeated force curves at one location. Both the adherence force and the approach force were shown to increase in magnitude with interaction time and maximum load. Because the surface of this elastomeric network is very compliant and viscoelastic in nature, the tip leaves an imprint of itself after each force curve cycle. This phenomenon acts to increase the effective surface area resulting in an increase in the overall effective adhesion between the tip and sample. The method introduced here provides new insight into the dynamic adhesive nature of compliant, viscoelastic polymer surfaces.

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