Measuring the Mechanical Properties of a Thin Polymeric Film by AFM

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INTRODUCTION

The Atomic Force Microscope (AFM) has emerged as one of the most commonly used techniques to characterize surfaces. Often, the surface is characterized by measuring the topology or surface roughness. A height standard reference is used to properly calibrate the measurement. The measurement of the mechanical properties of materials (hardness, Young's Modulus, friction) by AFM is generally more qualitative. This is due to the fact that the contact area must be inferred and the spring stiffness is difficult to measure. Also, no standards are available for calibration of mechanical properties.

Viscoelastic materials are generally described in terms of the complex modulus, composed of a storage modulus and a loss modulus. The ratio of the loss modulus to the storage modulus is given as tan δ. In these measurements, we have modified the AFM to measure tan δ. The absolute phase and amplitude response of an AFM cantilever is monitored as a polymer film is oscillated. The measured values are used to calculate tan δ as a function of frequency.

EXPERIMENTAL

Poly(n-butylacrylate), PnBA, was derived from a poly(tert-butylacrylate) parent polymer.[1] The molecular mass of the polymer was 10,000 g/mol. The polymer was heated to 50 °C to allow a thin film to be spread on a silicon substrate. The thickness of the polymer film was 100 μm ± 50 μm. Unless otherwise noted, the ± refers to one standard deviation of the measured values.

For the AFM measurement, the sample was placed on a piezo transducer that oscillated the sample sinusoidally normal to the surface. The AFM cantilever was placed on the PnBA film and the response of the cantilever resting on the polymer surface (as measured via the photodiode) was monitored. Both amplitude and phase were recorded as a function of frequency. The drive amplitude was 124 nm ± 10 nm.

A glass sphere (radius = 12 μm ± 2 μm) was glued onto the AFM cantilever to give a larger contact area.[2] The measurements were run at 25 °C.

RESULTS

The rheological model for this experiment can be given as a Kelvin element in series with a spring. The equations of motion of the cantilever and sample have been given previously.[3,4] Since the amplitude of oscillation is small relative to the probe diameter, the area of contact can be assumed constant. Solving the equations of motion gives:

$$\tan\delta = \sin\varphi/(\cos\varphi - D_{AFM}/D_{PIEZO})$$

where φ is the measured phase shift, D_{AFM} is the amplitude of oscillation of the AFM cantilever on the polymer film and D_{PIEZO} is the drive amplitude.

The AFM measurements of tan δ for the PnBA film as a function of frequency are shown in Fig. 1. Also shown in the diagram are previously reported measurements of tan δ using a hemispherical indenter in contact with the PnBA film (thickness 50 μm).[5] In these measurements, the hemispherical indenter had a radius of 4.5 mm ± 1.5 mm. The amplitude of oscillation for the indenter was 1 μm.

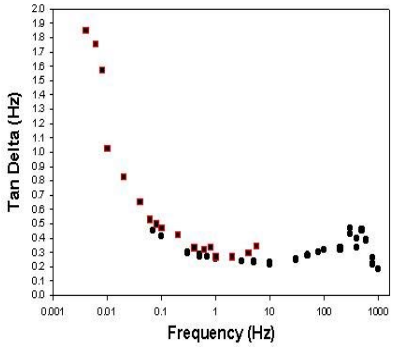

Figure 1. Measurements of the tan δ of a 50 to 100 μm thick PnBA film. The squares represent data measurements taken on a spherical indenter. The circles represent AFM measurements. For the AFM, tan δ is measured to ± 10%.

DISCUSSION

As shown in Figure 1, the AFM results are in good agreement with indenter measurements. Note that the indenter used a larger indenter radius (200 times greater) and larger oscillation amplitude (1 μm for the indenter versus 124 nm for the AFM), yet similar results were obtained. The results demonstrate that the AFM technique can quantitatively measure rheological properties of soft thin polymeric films.

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