A Local-Probe Analysis of the Rheology of a "Solid Liquid"

by **J. E. Houston**

Motivation—Polymer composites have become increasingly important in materials science and engineering and have found ever-broadening application in commercial products. Fiber and particulate-reinforced composites show considerable improvement in overall performance. However in both cases, matrix aging can cause serious degradation in long-term performance. In order to study the details of the aging process it is necessary to go beyond bulk mechanical testing methods and explore the local adhesive and viscoelastic properties in the interphase region near the dispersed-agent/matrix boundary and local-probe techniques offer potential in this area.

Accomplishment—We have recently taken advantage of the unique capabilities of the Sandia-developed Interfacial Force Microscope (IFM) to demonstrate its application to the local viscoelastic properties of a material which is often referred to as a "solid liquid" but is more commonly known as Silly Putty™ (SP) (Registered trademark of Binney and Smith, Inc.). This material was chosen as a test case, not only because of its interesting properties, but because it represents a "worst-case" example of a viscoelastic material from an experimental standpoint. As any child born after 1950 knows, SP readily bounces off a hard surface but when sitting on the same surface it gradually deforms into a thin pancake. In addition, it tends to stick to most any surface. This combination makes the material very difficult to study and certain strategies have to be developed in order to produce quantitative results.

In recent experiments, we have used a 50 micron diameter spherical tip, Fig. 1, and relaxation measurements in order to acquire the frequency response of the material. We first establish an initial contact, the dimensions of which can be measured optically (Fig. 2). After this contact is established, the tip is then suddenly pushed further into the surface by a small amount, while recording the force as the SP responds to being deformed. The result is shown in Fig. 3. From this data we see that the material will support a high force over only short times, but rapidly relaxes to insignificant levels within a few seconds. The relaxation data can be made quantitative in terms of the material's relaxation function, i.e., stress as a function of time, through the use of a classic contact-mechanics formalism by knowing the shape and size of the tip, the initial contact dimensions and the extent of the step deformation. In addition, the time dependence of Fig. 2 can be cast in terms of the frequency response for both the real and imaginary components of the shear modulus through the use of a standard Fourier analysis. Figure 4 shows the results of this process directly compared to those obtained by a commercial vibrating pendulum rheometer. In this instrument, a bulk SP sample is placed between two pads, one of which oscillates with the pendulum and the data of Fig. 4 consists of 10 individual measurements of amplitude and phase of the SP deformation at each frequency. In contrast, the IFM results were done on a relatively local level and the data acquisition for the entire frequency response took less than 10 sec. Although these measurements were not taken at a level necessary to analyze the interphase of a typical fiber-reinforced composite, there is no reason why this level cannot be achieved with the present instrument.

Significance—This work shows that truly nano-scale rheology is possible with presently available IFM technology.

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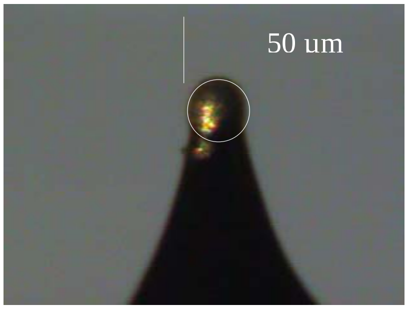

Figure 1. The IFM tip is a flame-annealed glass rod Au platted to enable coating with a passivating film.

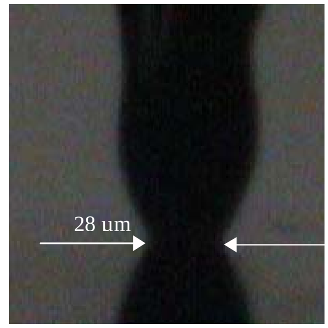

Figure 2. The IFM tip is at the top in contact with SP at the arrows indicating the contact diameter. Below is the reflection of the tip off the SP surface.

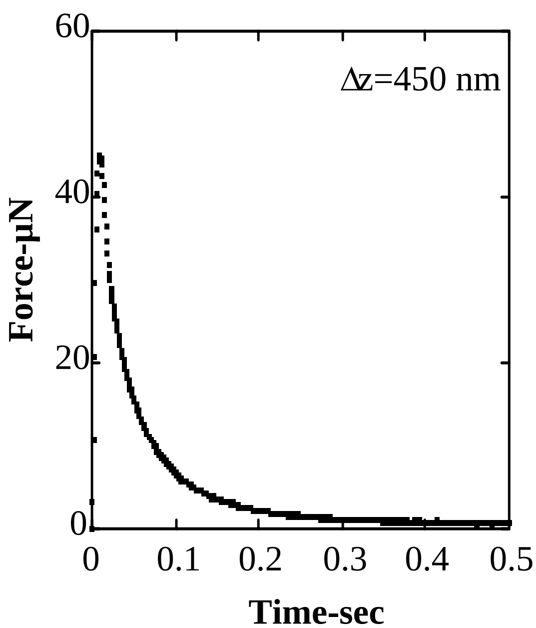

Figure 3. Relaxation results for a 450 nm step deformation at t=0 sec showing a rapid exponential relaxation after reaching a high initial force.

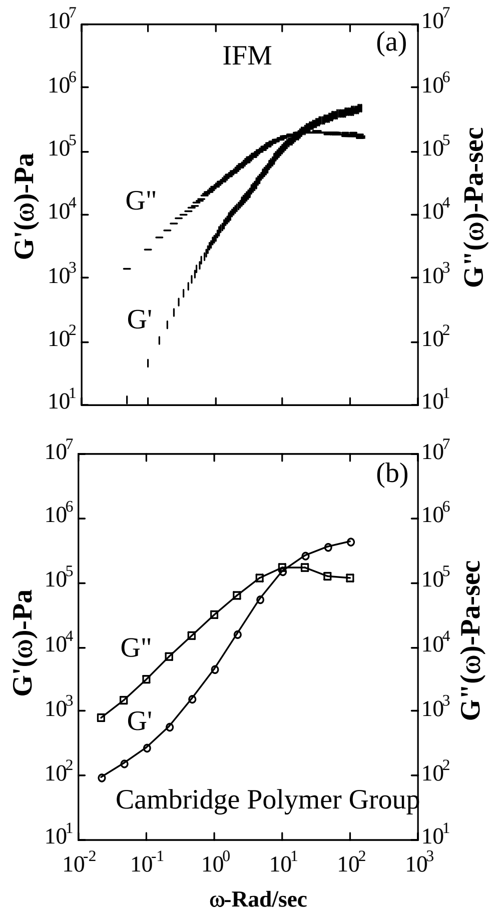

Figure 4. (a) the SP frequency response obtained from the analysis and (b) the point-by-point response obtained with a commercial vibrating-pendulum rheometer by the Cambridge Polymer Group, Boston, MA.