INTERFACIAL FORCE MICROSCOPY: APPLICATION TO POLYMER SURFACES

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Introduction

Scanning-probe microscopies (SPM) are presently widely used in remarkably diverse applications and, as evidenced by this symposium, these techniques are rapidly expanding into the important areas of polymer surfaces and interfaces. The Atomic Force Microscope (AFM) is presently the most widely used of the scanning-probe techniques. However, the AFM’s range of application suffers from an inherent mechanical instability in its deflection force sensor. The instability problem has been overcome by the development of the Interfacial Force Microscope (IFM), which utilizes a force-feedback sensor concept. In the following, we present several examples of polymer applications to illustrate the utility of the IFM sensor concept.

Experimental

Interfacial Force Microscopy (IFM) is a scanning probe technique similar to the AFM but distinguished by its use of a stable and quantitative force sensor. The sensor (shown schematically in Fig. 1) consists of a differential capacitor involving a common plate (CP) suspended above two capacitor pads C1 and C2 by torsion bars. A tip is placed on one end of the CP and interfaces forces between it and a sample surface rotates the CP, increasing one capacitance and decreasing the other. This displacement is detected by an RF bridge circuit and the force balanced by placing the appropriate voltages on C1 and C2. Within the frequency response of the controller that establishes the proper voltages, the force measurement is made without tip movement and is, thus, stable. In addition, since the force-voltage relationship only depends on the capacitor values, the measurement is quantitative. These attributes give rise to a degree of measurement control that permits the study of a broad spectrum of materials properties.

Results and Discussion

One of the modes of IFM operation, which has been extensively used on metal, self-assembling monolayer and polymer surfaces, is that of a nanoindenter. In this mode, a parabolic hard probe tip (such as diamond or tungsten) is used in a classic “Hertzian” indentation experiment. This allows measurements of the elastic modulus (both real and imaginary), the yield stress at the plastic threshold and both creep and relaxation. Normal indentation experiments take the form of force profiles, i.e., force applied to the tip versus tip displacement (stress-strain curves) while approaching and withdrawing from the surface at a constant rate. Such profiles are illustrated in Fig. 2 in a direct comparison of the surfaces of polyethylene (PE) and (a)

poly(methyl methacrylate) (PMMA). After contact, the behavior on approach initially appears elastic closely following the Hertzian elastic force/deformation relationship, F - kR2 where k is the tip radius, E* is the indentation modulus and d is the deformation. Figure 2a shows the behavior for PE taken with 2500 Å W tip. The E* value calculated from this data turns out to be 44 MPa and the deviation from the Hertzian curve signals the plastic threshold, which occurs at ~15 MPa of average applied stress. These figures compare reasonably well with the range of values (95-260 MPa and 4-16 MPa, respectively) given for low density PE. After a further deformation of more than 2000 Å, the withdrawal curve shows hysteresis, which signals a “permanent” deformation (a dent). However, the concave nature of the withdrawal curve indicates a considerable level of healing as the tip is removed leaving an indentation depth of about 1000 Å (over time, this indentation significantly heals). Thus, the hysteretic behavior is anelastic—energy is lost but recovery is significant. In contrast, Fig. 2b shows the force profile for PMMA, which indicates a much less compliant surface and very little hysteresis. In addition, a significant level of adhesive interaction is observed, which is largely responsible for the hysteresis (i.e., adhesive hysteresis). The modulus value calculated from this data is almost 17 GPa, which is high compared to the handbook value of ~3 GPa. However, the surface deformation here is only about 70 Å and the high E* value indicates the presence of a thin but stiff skin on the sample surface.

The relaxation behavior alluded to in Fig. 2a for the PE surface can be characterized by performing a creep test. This measurement begins with the tip “hovering” in light contact with the surface (~100 nN). The hover force is then suddenly increased to ~4 μN (above the plastic threshold in Fig. 2a) and the motion of the tip is recorded. The results are shown in Fig. 3. The increase in force causes the tip to suddenly push into the surface by almost 4000 Å and as the sample relaxes it continues to push into the surface, over a period of ~6 sec, by an additional ~1500 Å. This relaxation can be adequately characterized by two time constants with values of about one and six seconds, essentially splitting the relaxation displacement equally. Materials such as PE are usually nonlinear, which means that the creep behavior will depend on the degree of deformation.

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Figure 3. Creep data taken on a polyethylene sample where at time equals zero the force is suddenly stepped to 4 μN. The tip displaces into the sample in order to maintain the constant-force value.

Another useful mode of IFM operation, especially for heterogeneous materials, involves applying a small modulation of the tip/sample separation and synchronously detecting the signal to obtain a single-frequency value of the ac modulus, i.e., the slope of the stress-strain curve at a given level of applied force. This procedure permits images to be obtained in the normal repulsive-force mode while also acquiring 2D information on the ac modulus. Figure 4a shows an example of an ac modulus image taken on a sample consisting of 10 μm glass fibers embedded in an epoxy matrix. The terrace in the upper right-hand corner is on the edge of the glass fiber and the brighter color indicates a higher value of the ac modulus than for the epoxy in the lower left-hand terrace. The flatness of the two terraces shows that the modulus is constant in these areas. The crossing pattern in the area separating the terraces could be taken as part of the "interphase" region. However, the constant repulsive-force image in Fig. 4b shows that it results from morphology variations. The sample polishing procedure has left an uneven boundary between the fiber and matrix. This result clearly illustrates the value of taking simultaneous modulus/morphology data since measured modulus values depend on the local surface structure.

In earlier work on the glass/epoxy system, individual force profiles were measured along a line perpendicular to the interface. Results were compared for systems with varying thickness of interfacial silane coupling agents between the glass and epoxy. They showed considerable systematic variation in the measured modulus as a function of distance from the fiber surface. In general the modulus initially decayed to one-half the bulk modulus then rose to two times the bulk modulus before decaying to the value of the modulus in the bulk as shown in Fig. 5. The distance over which this occurred was 2 to 8 microns depending on the surface treatment. This is in agreement with the Williams et al. but in considerably excess of the thickness of adsorbed coupling agent. This is a clear indication that the interfacial interaction is playing a significant role in altering matrix properties over an extended range. Being able to measure these changes as a function of the chemical nature of the coupling agent will have a significant impact on effective fiber reinforced composite design.

Figure 4. (a) A 1 μm x 1μm ac modulus image of a 10 μm glass fiber embedded in an epoxy matrix. The higher modulus glass appears as a brighter color than the false color image, (b) a constant repulsive-force image of the same region showing that the epoxy has been distorted near the interface by the polishing procedure.

Figure 5. Modulus is shown to vary as a function of position from the fiber surface.

Conclusions
In this brief discussion, we have tried to cover a few examples of IFM applications to polymer surfaces to illustrate its unique capabilities. Its chief strengths are its ability to obtain quantitative information on interfacial forces in a controllable manner. The ability to control the sensor makes it possible to perform measurements to determine a wide variety of materials parameters. In addition, the "zero-compliance" nature of the sensor ensures that no energy is stored during the act of measuring the force. Thus, for systems which involve relaxation phenomena (so prevalent in polymer materials), the sensor does not mask individual processes by dumping its stored energy at the onset of relaxation. These unique capabilities, coupled with the advantages inherent in being able to study materials properties on a very local level, make the IFM a very appealing tool for advanced polymer research.

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