# ADVANCING NANOSCALE INDENTATION MEASUREMENTS TOWARD QUANTITATIVE CHARACTERIZATION OF POLYMER PROPERTIES

by

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The ultimate objective of instrumented indentation testing is to obtain absolute measurements of material properties and behavior. To achieve this goal, accurate knowledge of the shape of the indenter tip is required. For indentation measurements involving sub-micrometer scale contacts, accurate knowledge of the tip shape can be difficult to achieve. In this presentation, a technique referred to as blind reconstruction is applied to the measurement of tip shapes of indenters used with the atomic force microscope (AFM) to indent polymeric materials.

The AFM has been used recently to make nanoscale indentation measurements and is particularly useful for evaluating the mechanical response of polymeric materials. These measurements can be made using AFM cantilever probes and operating the AFM in force mode with some modifications to account for lateral tip motion. Because the AFM was not specifically designed as an indentation device, other complications can arise due to instrumental uncertainties such as piezo hysteresis, piezo creep, and photodiode nonlinearities. Certain precautions must be taken to limit these errors. However, one of the important advantages of AFM indentation regarding polymers is the ability to choose a probe spring constant that allows for meaningful indentation measurements of a given polymer or set of polymers at the nanoscale. Traditional indentation devices, including recently developed depth-sensing devices, often do not have the sensitivity to produce measurements at the nanoscale for important polymer systems due to low machine compliance and the inability to detect initial contact loads less than 1 $\mu$N. Thus, these systems have limited capabilities for studying materials such as polymer thin films, multi-phase polymers, and multi-component polymers. The ability to measure the responses from microscopic and nanoscopic regions can be a key to understanding the performance of these technologically important material systems.

Because of the lack of information regarding the tip shape of AFM probes, AFM indentation measurements made to date have been relative measurements. Tip shape calibration procedures used for instrumented indentation devices normally include indentation of a reference sample, such as fused silica, at a variety of loads and penetration depths. However, the AFM has limited capabilities to indent a material like fused silica, and a good reference material for indention that has a modulus under 10 GPa is difficult to find. Also, determining tip shape directly from indentation measurements of a reference sample can have large measurement uncertainties. Therefore, a material-independent method for tip shape calibration is suggested based on blind reconstruction. An image produced by scanning a surface with a particular probe tip will contain 3-dimensional information about the tip's shape. In blind reconstruction, this information is extracted and used to produce an estimate of the tip shape. This estimate is an outer bound, because the sharpest surface features have finite dimensions that broaden the image of the tip. To limit this broadening effect, so-called tip characterizer surfaces are imaged that contain features with nominal radii of curvature of 10 nm or less. Also, erosion processes can be performed on the data to reduce this broadening effect.

An image of a particular tip characterizer sample that contains an array of spike-like features is shown in Figure 1a. This image was taken by scanning the sample with a Berkovich tip, and the Berkovich geometry is evident in the image. In fact, the spikes essentially image the tip such that the tip geometry, broadened by the finite size of each spike, is produced several times in the image. The area-depth relationship for this tip was calculated from blind reconstruction results. In Figure 1b, this result is compared to that from an indentation tip-shape analysis, in which fused silica was indented at a variety of loads and penetration depths with this same Berkovich tip. In a similar study, a diamond-tipped AFM cantilever was used to scan a set of tip characterizers and indent a glassy polymeric material at a variety of loads and penetration depths. An AFM image of the plastic impressions left in the polymer are shown in Figure 1c and the load-indentation depth curves corresponding to one row of indents is shown in Figure 1d. In Figure 1e, the area-depth relationships calculated from the blind reconstruction results and from a tip-shape analysis using the polymer indentation results are compared. In both Figures 1b and 1e, significant discrepancies are observed between the two methods of tip shape characterization. These discrepancies will be discussed in terms of measurement uncertainties and material behavior, and suggestions will be made for standardization of indentation testing and analysis, particularly with regard to polymeric materials.

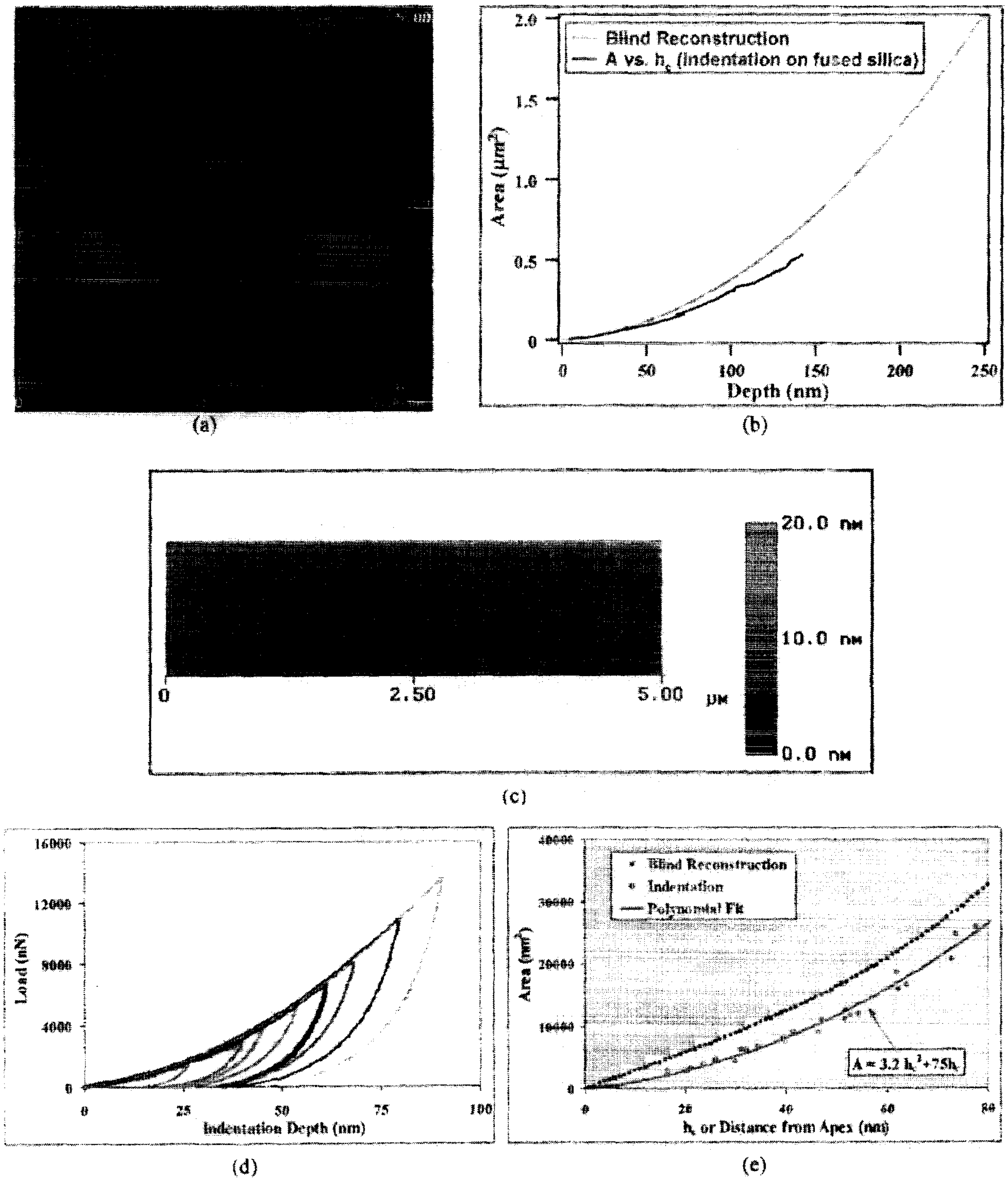


FIG 1. (a) AFM topographic image generated by scanning a spike-type characterizer sample with a Berkovich indentation tip; (b) plot of the area-depth relationship for the Berkovich tip in which blind reconstruction results are compared to results from an indentation tip-shape analysis; (c) AFM topographic image showing three rows of indents made on the polymer sample, each row containing indents produced at eight different loads; (d) plot of load versus indentation depth for one of the rows in (c); (e) plot of the area-depth relationship for the AFM indentation tip in which blind reconstruction results are compared to results from an indentation tip-shape analysis.

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