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Title: The Applications of Modern Nanoindentation

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The Applications of Modern Nanoindentation

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Abstract

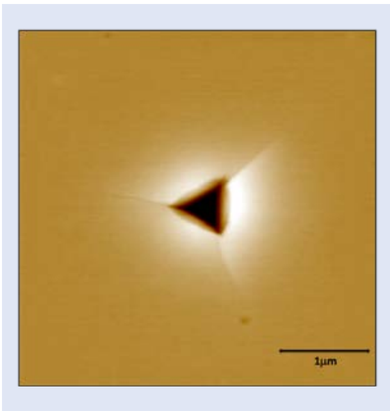
The TI-950 TriboIndenter is a nanoindentation device that obtains nanometer resolution material topography images using Scanning Probe Microscopy (SPM), modulus maps of material using nano-Dynamic Mechanical Analysis, and provides hardness measurements with a resolution of 0.2 nm. The instrument applies a force to a material through a sharp tip and used a transducer to measure the force a material applies back to the tip to derive information about the material. The information can be used to study the homogeneity of material surfaces as well as the homogeneity of the material as a function of depth and can lead to important information on the aging of the material as well as the consistency of the production of the material.

Background

Polymeric compounds present an important opportunity to achieve desired mechanical properties at low cost and have important applications in construction, automotive manufacturing, and in the production of everyday products. An example of this was when NASA adopted polyethylene (PE) as a structural material because it has the desired mechanical properties to be a support beam in spacecraft at about half the weight while providing double the radiation protection over the alternative aluminum. This resulted in much lower launch costs due to the reduced mass as well increased protection from cosmic radiation[1]. An essential part to being able to use polymers as lower cost alternatives is determining the mechanical properties needed for an application and mirroring those with a polymer compound. Examples of mechanical properties of polymers are tensile strength (a measure of the polymers integrity when stretched), compressional strength (a measure of the compressibility), elastic modulus (a measure of the elasticity or energy storage properties of the polymer, otherwise known as Young's Modulus), and hardness[2]. Currently, these properties can be measuring using techniques such as Dynamic Mechanical Analysis (DMA) and durometer shore hardness. However, these techniques generally take the bulk properties of a material by having relatively large sample sizes or areas. This presents and issue when considering the homogeneity of a material, where lack of homogeneity on the nanoscale may affect the macro properties[9]. Additionally a lack of homogeneity can indicate mechanisms or issues with the polymerization process that wouldn't be otherwise observed on larger sample sizes. Techniques that aim to observe properties at the nano-scale include visualization techniques such as Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), or nanoindentation. Generally speaking these techniques, macro or nano-scale, are done by separate instruments. But Hysitron's TI 950 Triboindenter presents an instrument that encompasses all techniques in a single instrument, all at the nanoscale, allowing for a diverse characterization of a material with high resolution. The review will discuss the theory and techniques/applications of the TI 950 Triboindenter.

Basics of the instrument

Nanomechanical characterization techniques work generally by applying a force on a polymer sample using a well-defined tip geometry and measuring the force applied versus the displacement of material. Figure 1 shows a scanning microscope probe (SPM) of the three sided pyramidal probe as well as a common force application graph.



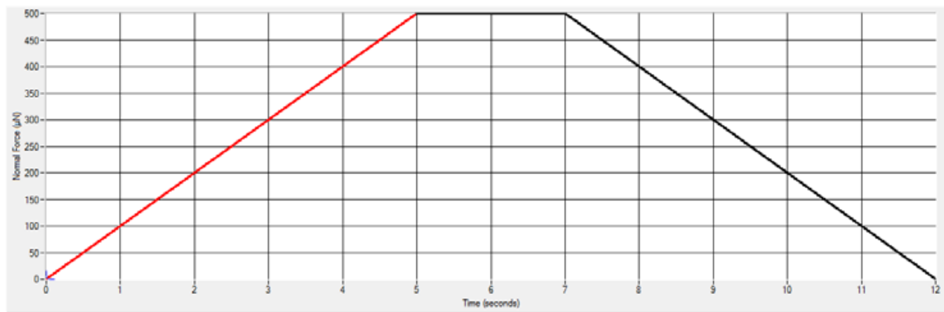


Figure 1: On the left is the SPM image of a pyramidal indentation tip that was imaged using the same tip that made the indentation. On the right is a general curve of the linear application of force, then held at the maximum force, and the linear release from the material[3].

Unlike AFM, which is cannot accurately measure lateral forces because of the configuration of the cantilever, the lateral configuration and transducer allows the TI 950 to accurately measure forces from <30 nN to 10 N. This technique general produces raw data that looks like those in figure 2. Figure 2 also contains a convenient roadmap to analyzing this data, where differences in the loading and unloading of the probe may indicate the mechanical properties of test area of the polymer sample. This information is gathered from difference between the force loading in figure 2 and the actual displacement of the sample as a result of the force. Following figure 2, various responses indicate properties such as viscous, elastic, and viscoelastic plastic responses. For example, in the second graph in the figure 2, the material is labeled brittle and this is likely because at force 500 mN there is a displacement of ~2mm at little to no change in the force indicating a break in the material. Further, there is little displacement when the force is completely removed, but when the probe hits the beginning of the break section it is displaced drastically for little to no change in force.

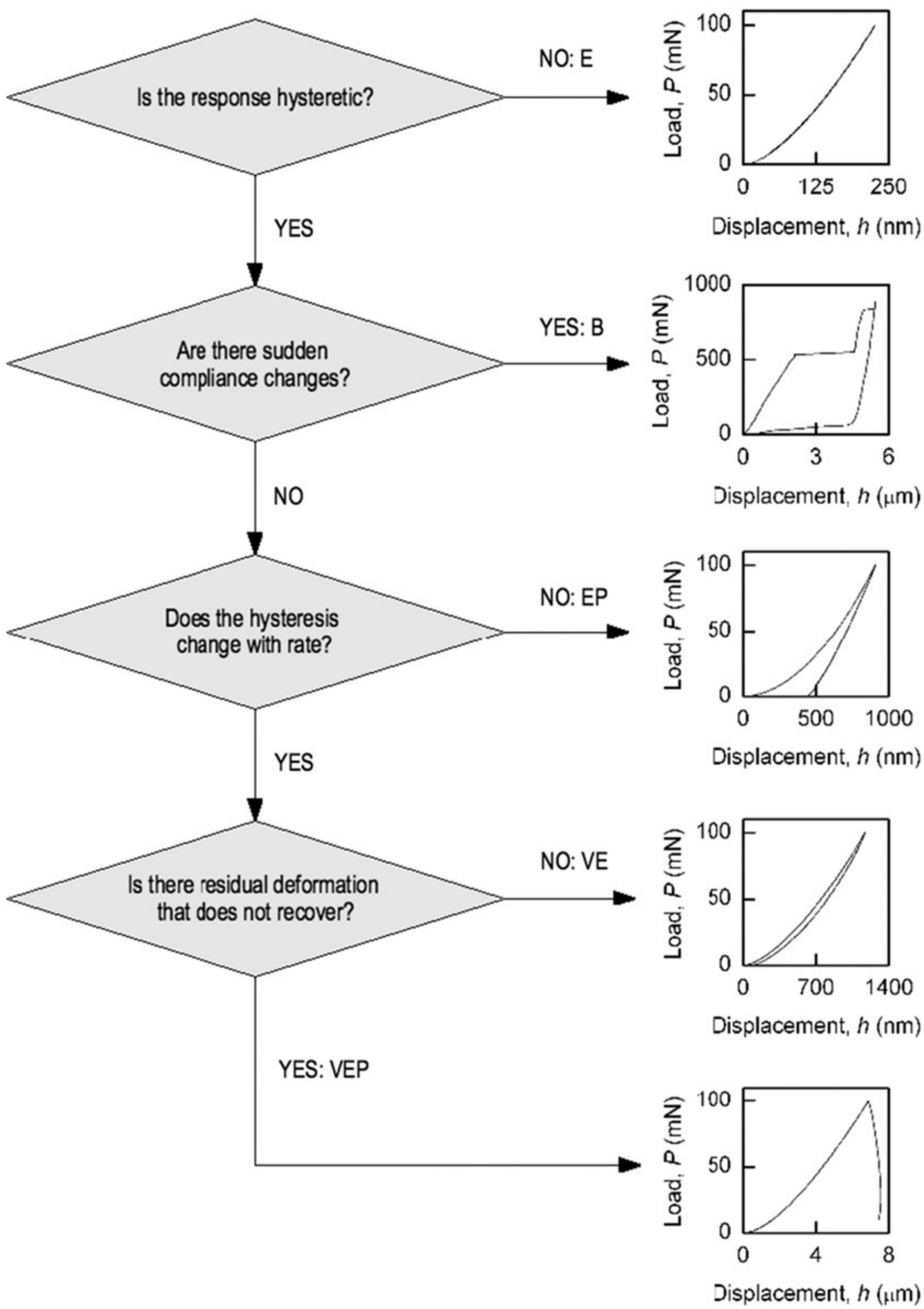


Figure 2: The displacement response of the material given a force loaded on the material. Various responses indicate different classifications of material; E: Elastic, V: Viscous, P: Plastic/Polymer, B:Brittle[4].

Modulus Mapping and NanoDMA

DMA works by applying a known dynamic force to a sample and measuring the sample's response. In many cases, the force applied is sigmoidal and elicits a sigmoidal response from the material that is slightly delayed, as can be seen in figure 3.

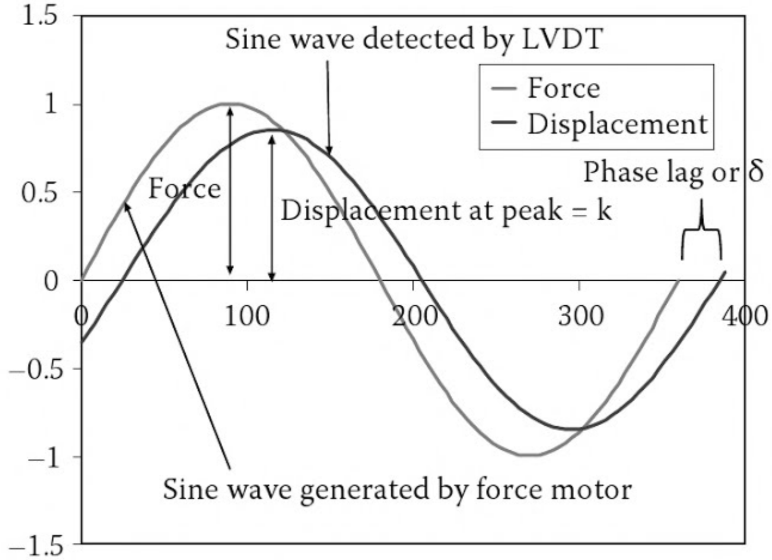


Figure 3: A representative figure of the sinusoidal force applied to a sample and its response. The difference between the two is the phase lag, and it's this information that indicates the modulus of the material[5].

Current popularized DMA techniques are done by attaching a sample to two clamps where one clamp applies a force trough a motor and the other measures force that is transferred through the sample. As previously mentioned, due to the large sample size of the technique, only the bulk properties of a material are observed. Using similar techniques, (a transducer that allows for the measurement of force from the material), the nanoindenter applies a sinusoidal force (see figure 3) to the material using the nanoindentation tip and then simultaneously measures the force the material puts back on the tip. From this, the instrument is able to extrapolate modulus information of the area of the sample the tip is in contact with. And because of the sharpness of the tip, the resolution for the modulus of the material is on the nanoscale. This allows for modulus maps, such as that in figure 4, to be created. By mapping out the storage and loss modulus, tan delta (the ratio of the storage to loss modulus), and the stiffnesses, as well as the topography of the material, you can form a holistic view of the homogeneity of the material. From this you consider the homogeneity and how it may relate to a semi-crystalline polymer, where amorphous and crystalline sections may exhibit different mechanical properties, a block polymer, where different "blocks" may exhibit different modulus, and materials that are theoretically homogenous. In addition to observing these properties at the surface of a material, there is also the capability to burrow into the material using the TI-950 triboindenter. This allows the instrument to look at hardness and modulus as function of depth in to the material being tested, into the micro-millimeter range[6].

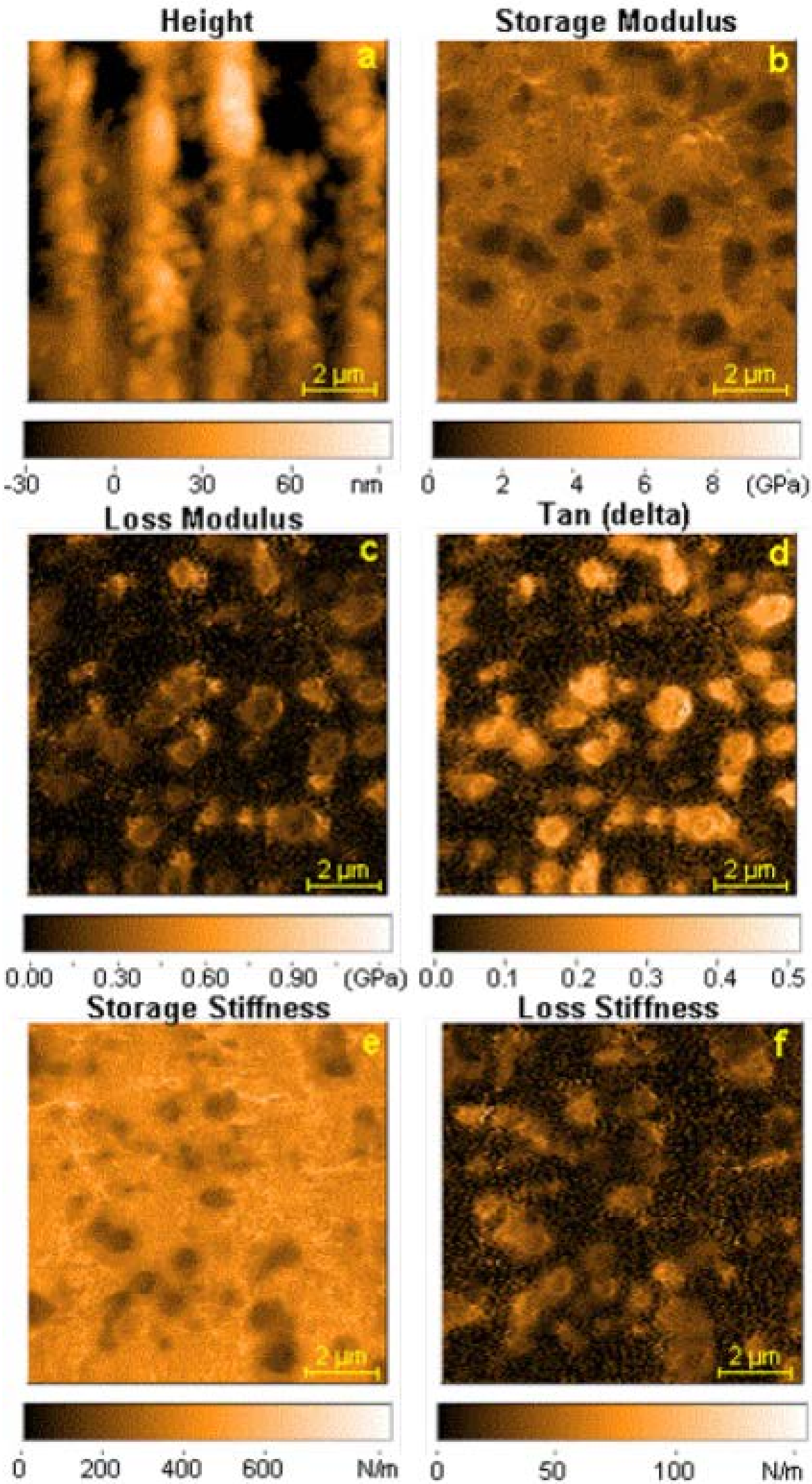


Figure 4: Using SPM and nano-DMA, the nanoindenter maps the topography (a), modulus(b and c), tan delta (d), and stiffness (e and f) of a material. The material being analyzed is a block co-polymer that exhibits different moduli based on sections on the different blocks of polymer[3].

Future Directions

In the realm of polymer science the applications of this are vast. To further characterize and visualize material better allows for better understanding of material properties, issues in production, or being able to understand a fitting application for the material. In the context of LANL technologies, the Hysitron TI 950 TriboIndenter's abilities will be utilized in understanding mechanisms of additive manufacturing (3D printing) and aging of polymers. As previously discussed, the extensive characterization techniques of the TI 950 allow for an in-depth understanding of a material. In the realm of additive manufacturing an important thing to understand is the homogeneity of the material, especially because this is generally an automated process and requires a frequent quality check to determine that the process is working as intended. In any manufacturing process a lack of homogeneity can suggest issues with the polymerization process. Specifically in powder based manufacturing processes nanomaterials tend to settle in the bed and lead to an inhomogeneous final material[7]. A lack of homogeneity could lead to parts of the material performing as intended while other sections fail, even though it is assumed to have the same properties throughout. This can be characterized using a topography characterization method such as AFM, but topography is limited in that it only provides shape information of the surface and not information on the physical properties of the material. This is important because materials may elicit the same topology information but in reality may have drastically different mechanical properties. And in the case of inhomogeneous material, a simple topography reading wouldn't observe this. Nanoindentation has a technique called modulus mapping that allows for a material to be characterized by the modulus, where a map of modulus is drawn by indenting the material to extrapolate the modulus at a certain point with a <0.2 nm resolution. With this capability, coupled with topography data from the same instrument, a very clear map of the material can be observed and information about the homogeneity can be extrapolated. This information can then be used to determine if there issues in the 3D printing process that need to be addressed.

Issues of homogeneity also apply to the aging of polymer samples. Aging in air can lead to non-homogenous aging and ultimately lead to non-homogenous degradation of the material. This can be attributed to the inhomogeneity of material before the aging studies and oxygen diffusion limitations, meaning that the oxygen may diffuse through one chemical or physical environment in the polymer and not the other[8]. This is useful information when considering the assumptions of time-temperature superposition (TTS). TTS assumes that the polymer ages by one mechanism (allowing for the same time-temperature dependence for each curve in the TTS master curve)[9] and If the polymer in not homogenous, and in consequence oxygen based aging is not homogenous, the it could be that two mechanisms are acting the on the polymer on the macro scale. Because mechanical tests take such large sample size relatively speaking this phenomena will likely not be observable. Thus, modulus mapping at the 0.2nm resolution will allow the observation of differences in the moduli on the nano-scale over time allowing for a clearer understanding of the aging mechanism(s) acting on a given polymer sample.

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