COVALENT METROLOGY

Application Note

Dynamic Mechanical Analysis of Polymer coatings by Nanoindentation

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Introduction

Nanoindentation probes the mechanical properties of materials like elastic modulus and hardness at the nanoscale. Its high resolution in both force and depth makes it a powerful tool for a wide range of applications from thin films to micro-electronic devices. Nanoindentation measures the normal force vs. penetration depth yielding a force-displacement curve. The material properties are calculated according to the Oliver and Pharr method [1]. The indenter tip area is calibrated against fused quartz, which has a well-known hardness and elastic modulus. The tip area is fit to polynomial function of contact depth, h_c:

$$A(h_c) = C_o h_c^{\,2} + C_1 h_c^{\,1} + C_2 h_c^{\,1/2} + \ldots$$

The contact depth h_c can be calculated from the maximum indentation depth h_{max}, the permanent indentation depth h_p, and ε, a geometric constant.

$$h_c = (h_c - h_c) + \varepsilon$$

Indentation hardness, H_{IT} is calculated as:

$$H_{IT} = \frac{F_{max}}{A(h_c)}$$

The reduced elastic modulus, E_r is calculated as:

$$E_r = \frac{1}{\beta}\frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A(h_c)}}$$

Where β is a geometric constant of the indenter and S is the slope of the unloading curve. E_r can easily be converted to Young's modulus if one knows the Poisson's ratio of the material. **Figure 1a** and **1b** show an illustrated schematic of an indenter indenting into a material with a normal force F to a maximum penetration depth, h_{max}. A typical result from nanoindentation is a force-displacement curve, as shown in **Figure 1c**.

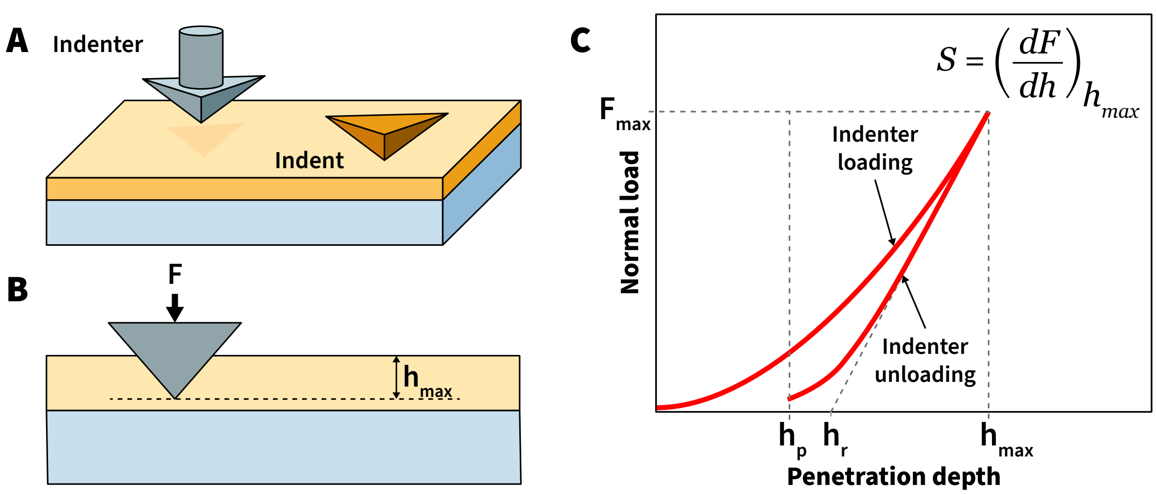

Figure 1. *(A) and (B) show schematics of indentations; (C) shows a force-displacement curve.*

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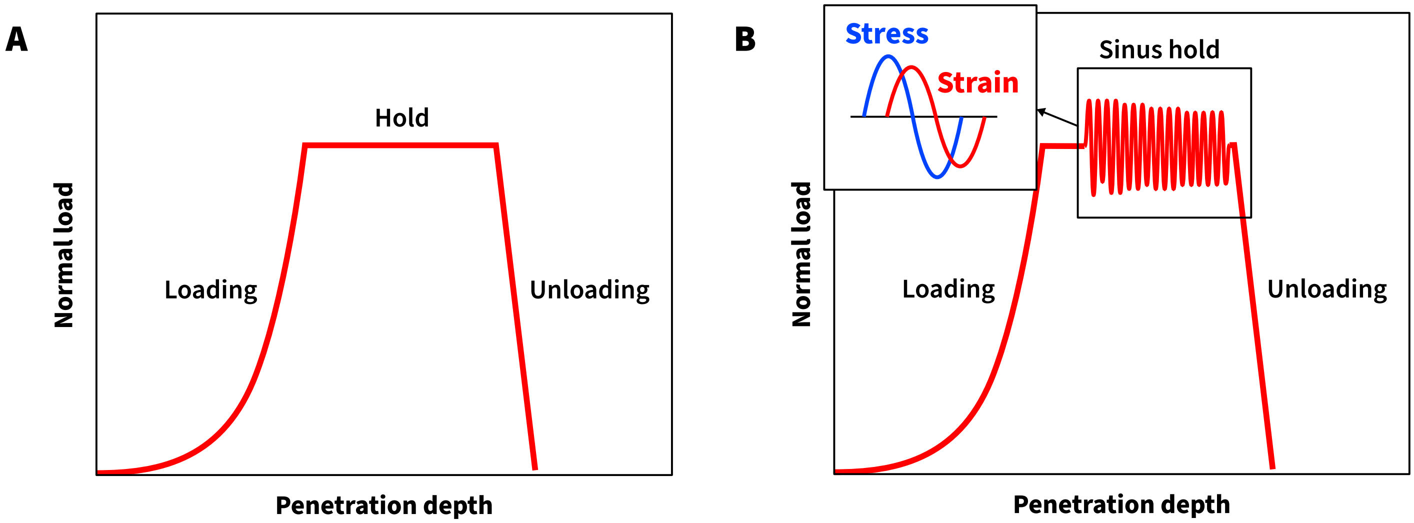

Figure 2. *(A) Quasi-static loading; and (B) Loading profile with sinus-hold*

Hard materials such as nitrides, thermal oxides, or ceramics require sharp indenters and/or higher loads to penetrate sufficiently through the material and calculate H and Er accurately. However, soft materials such as polymers will show significant plastic deformation with sharp indenters and/or high loading. Furthermore, polymers exhibit viscoelastic (dynamic) properties. To characterize the dynamic properties of polymers within the linear viscoelastic region, the load and indenter geometry are important considerations.

Sinus mode combines nanoindentation and DMA to calculate storage modulus, loss modulus, and tan delta (E', E'', tan δ). It employs a sinusoidal load that is superimposed on a quasi-static load, and subsequently measures the phase shift δ between the normal load and displacement. **Figure 2a** shows a typical quasi-static loading profile while **Figure 2b** shows a loading profile with a sinus hold. A heating stage (RT to 200°C) allows investigation of thermally induced phenomena such as glass-transition and curing. In this application note, we investigate the curing process of an epoxy adhesive film using Sinus mode.

Dynamic Properties vs. Temperature of an Epoxy Adhesive Film

Background

We investigated the dynamic mechanical behavior of an epoxy adhesive film (60 µm thick) on a substrate under elevated temperatures. Epoxies are widely used adhesive materials whose mechanical properties depend on the degree of cure. Incomplete curing of epoxy can lead to downstream problems such as delamination. While thermal analysis methods such as Differential Scanning Calorimetry (DSC) are commonly used for measuring the degree of cure, it is constrained by sample mass (at least 5-10 mg is needed). However, such amount of adhesive film is rarely available. On the other hand, minimal sample preparation is required for nanoindentation of a thin film. From previous DSC work, we found the cure onset temperature to be ~150 °C. In this study, we used Sinus mode to characterize E', E'', and tan δ near the cure state of the epoxy. From this investigation, we were able to better understand the relationship between temperature and epoxy curing.

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The Anton Paar UNHT3 (Ultra Nanoindentation Tester) incorporates active top referencing via a reference indenter to mitigate mechanical and thermal drift. The reference approaches the sample first and maintains contact with the sample during the entire test. After reference contact, a 20 µm diameter spherical indenter approaches the sample and applies the load function as shown in **Fig. 2B**, including dynamic oscillations at predefined force.

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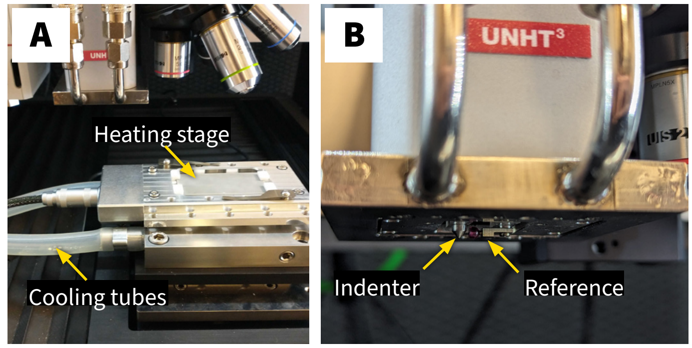

Figure 3. *(A) Front view of Anton Paar UNHT3 with Heating Stage; and (B) Bottom view.*

The heating stage, cooling block, and indenter shield were installed, and samples were secured to stubs clamped on the heating stage. A front view of the stage is shown in **Figure 3a** along with a bottom view in **Figure 3b**. To minimize thermal drift due to curing, indentations were performed in 'quick mode', i.e. with the surface reference in permanent contact with the sample. This way the thermal equilibrium could be maintained at various temperatures. A total of 5 indentations were performed at each temperature. The loading profile (shown in Figure 2b) consisted of a constant strain rate of 0.1 s^{-1} to a max load of 75 mN, followed by a pause for 15 s to accommodate the creep. A pause sinus was applied for 30 s at 1 Hz frequency and a sinus amplitude of 7.5 mN.

E', E'', and tan δ were averaged across the sinus hold. The tests were carried out at 3 different temperatures: 150°C, 175°C and 200 °C. The temperatures were verified to be within ± 0.1 °C of the setpoint using a thermocouple placed on the surface of the sample. **Figure 4** shows the trends in E' (Storage Modulus), E'' (Loss Modulus) and tan δ (loss factor) as a function of temperature and sinus cycles during the oscillation period.

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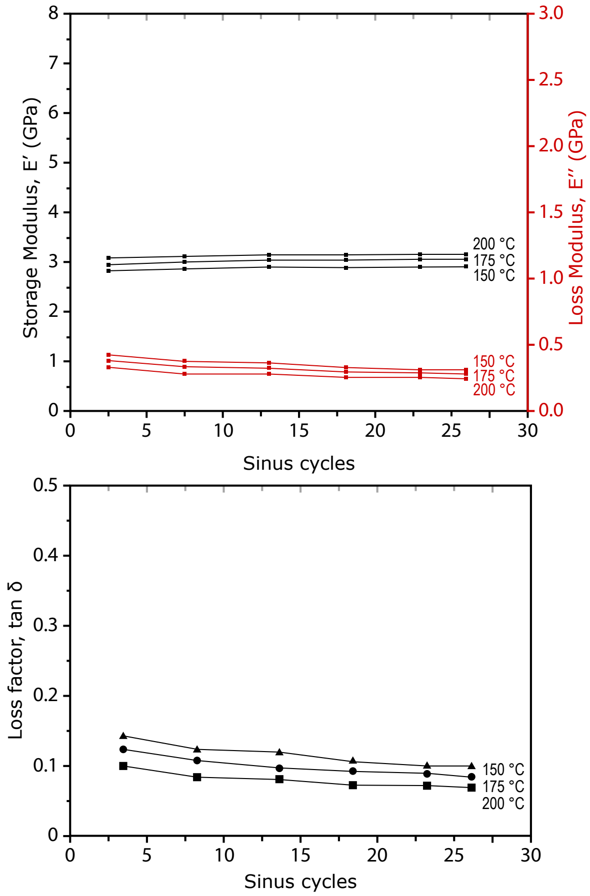
Figure 4. *(A) Storage Modulus and Loss Modulus vs. cycle #; and (B) tan δ vs. cycle #.*



Discussion

1. Effect of Temperature on Storage and Loss Modulus: The observed increase in storage modulus (E') with temperature indicates that the adhesive becomes stiffer as the temperature rises. The storage modulus represents the elastic stored energy in the material. This can be attributed to the reduced mobility of polymer chains as curing progresses, leading to enhanced elastic behavior. Conversely, the decrease in loss modulus (E'') representing the viscous deformation energy, with rising temperature suggests that the adhesive exhibits reduced viscous deformation energy at elevated temperatures. This confirms the change of state of the epoxy adhesive to a stiffer material with predominantly elastic behavior.

2. Relationship between Cure Stage and Mechanical Properties: The progressive increase in storage modulus (E') and decrease in loss modulus (E'') as the material progresses into advanced stages of curing indicate, i.e. higher temperature, a transition towards a more rigid state. This transition is reflected in the drop in tan δ, which represents the material's damping capacity, and which is related to the ratio E''/E'. A more rigid adhesive is typically associated with higher strength and improved load-bearing capacity, which are desirable attributes in many bonding applications.

3. Quality Control and Process Optimization: Monitoring the changes in storage modulus (E'), loss modulus (E''), and tan δ during the curing process can serve as a valuable tool for quality control and process optimization of thin film adhesives. By assessing these parameters at different stages of curing, manufacturers can ensure consistent adhesive performance and identify opportunities for improving process efficiency and product quality.

Conclusion

Understanding properties such as E', E'', tan δ, curing, glass-transition etc. is crucial for assessing the performance and durability of polymer films. Dynamic nanoindentation is the only technique suitable for advanced characterization of mechanical and viscoelastic properties of polymer films as very little sample preparation is required and the measurements are performed within a short time. It is however important that the measurement system has thermal equilibrium, which can be easily achieved by using the quick mode of the UNHT3.

References

[1] Oliver, W. C., & Pharr, G. M. (1992): "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments." *Journal of materials research*, 7(6), 1564-1583.

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