Dynamic Mechanical Analysis (DMA) of Polymers by Oscillatory Indentation

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Abstract

This application note teaches the theory and practice of measuring the complex modulus of a polymer by means of oscillatory indentation. We demonstrate the technique by using the **iNano** indentation system produced by Nanomechanics, Inc. to test a sample of highly plasticized polyvinyl chloride (HP-PVC), a material which is commonly used in industry to damp out mechanical vibrations. The complex modulus measured by oscillatory indentation compares well with previously published DMA measurements on the same material [1].

Introduction

Dynamic mechanical analysis, abbreviated as "DMA," is a common technique used to characterize the mechanical properties of bulk polymer specimens. Typically, an oscillatory stress is imposed on the sample, either in tension, compression, or torsion, and the resulting strain, which is also oscillatory, is measured. The outcome of a DMA test is the storage modulus, E', which characterizes the polymer's ability to store energy elastically, and the lost modulus, E'', which characterizes the polymer's ability to dissipate energy as heat. Taken together, E' and E'' are the *complex modulus* of the material. Phasor analysis of DMA mechanics reveals that the storage and loss modulus are concisely related through the loss factor, which is the tangent of the phase angle, δ, by which the strain lags the stress:

$$loss\ \ factor \equiv \tan\delta = E''/E' \tag{1}$$

In practice, E', E'', and $tan\ \delta$ are measured by DMA as a function of frequency and temperature. Reporting any two of these parameters is sufficient for knowing all three.

When the polymer is in the form of a thin film or other volume which is too small to be tested by DMA, analogous measurements can be made by means of an oscillatory indentation test. As the indenter is pressed into the sample, an oscillating force is imposed on the sample through the indenter, and the resulting displacement oscillation is measured. By presuming the same kind of constitutive form which DMA employs, and by interpreting the indentation data in light of established contact models, one can measure equivalent values of E' and E'' by oscillatory indentation.

Oscillatory indentation has additional advantages over DMA, even when the material is available in quantities large enough to be tested by DMA. The moving mass of an indenter is much smaller than the moving mass of a traditional DMA instrument, which means that the indenter can be made to oscillate at much higher frequencies. Thus, oscillatory indentation can be used to characterize a larger frequency range than DMA. Further, because the volume of required material is smaller, the temperature of that volume can be changed faster, and with less heat, relative to DMA. Finally, sample preparation for indentation testing is generally easier than for DMA.

Theory

The theory of oscillatory indentation is informed both by elastic contact models and constitutive forms used to comprehend the mechanical behavior of polymers in DMA testing. Ian Sneddon was the first to derive a general relation between force, displacement, and elastic modulus for an axisymmetric indenter in contact with a flat surface [2]. Oliver, Pharr, and Brotzen showed that a derivative form of Sneddon's relation is actually independent of the geometry of the indenter [3]. This derivative relation, commonly used to interpret instrumented indentation data, is

$$\frac{E''}{1-\nu^2} = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}} \tag{2}$$

where E' is the storage modulus of the material, ν is the Poisson's ratio, S is the elastic stiffness of the contact and A is the contact area. If the material response is substantially elastic, then the storage modulus is identical to the better known Young's modulus, E. Later, Loubet, Lucas, and Oliver invoked the same constitutive material form used in DMA[1] and deduced an analogous relationship between the loss modulus, E'', and contact damping, $D_s\omega$ [4]:

$$\frac{E''}{1-\nu^2} = \frac{\sqrt{\pi}}{2}\frac{D_s\omega}{\sqrt{A}} \tag{3}$$

For oscillatory indentation, the loss factor is particularly advantageous, because the contact area is eliminated as an unknown:

$$\tan\delta = E''/E' = D_s\omega/S \tag{4}$$

Thus, the task of measuring the complex modulus of a polymer by oscillatory indentation is that of measuring the contact stiffness, S, and contact damping, $D_s\omega$.

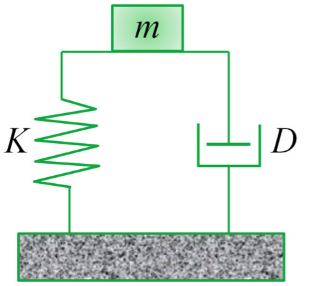

Figure 1. Simple harmonic oscillator used to model the indentation system alone or in contact with a sample.

The **iNano** indentation system manufactured by Nanomechanics, Inc. has been deliberately designed to behave like the simple-harmonic oscillator illustrated in Figure 1, so that by oscillating the system with a force amplitude, F_0, and angular frequency, ω, and measuring the resulting displacement amplitude, z_0, and phase shift, φ, we may know the values of all the components of the model: K, D, and m. Specifically,

$$K - m\omega^2 = \frac{F_0}{z_0}\cos\phi, \text{ and} \tag{5}$$

$$D\omega = \frac{F_0}{z_0}\sin\phi. \tag{6}$$

[1] *The Kelvin-Voigt model of a spring and dashpot in parallel*

When the indenter is free-hanging, or not in contact with any material, then K, D, and m are the stiffness, damping, and mass of the indentation system alone, or K_i, D_i, and m_i. In fact, this is how K_i, D_i, and m_i are determined by a factory calibration: by oscillating the indenter when it is free-hanging. When the indenter is in contact with a test material, the parameters K, D, and m comprehend the combined effect of both the indentation system *and* the contact. Thus, the fundamental values of F_0, z_0, and φ must be compensated for the known influence of the instrument in order to isolate the influence of the contact. During an experiment, we obtain the contact stiffness for use in Eq. 2 as the combined stiffness less the instrument stiffness, or

$$S = K - K_i = \frac{F_0}{z_0}\cos\phi - (K_i - m_i\omega^2) \quad (7)$$

and we obtain the contact damping for use in Eq. 3 as the combined damping less the instrument damping, or

$$D_s\omega = D\omega - D_i\omega = \frac{F_0}{z_0}\sin\phi - D_i\omega \quad (8)$$

When testing polymers, flat-ended cylindrical tips are advantageous for two reasons. First, they promote deformation that is consistent with the assumption of linear viscoelasticity. Second, the contact area, A, which appears in Eqs. 2-3, is known and independent of penetration depth. Generally, punch diameter should be selected with consideration for the microstructure, desired spatial resolution, material properties, and the sensitivity and capacity of the testing instrument. The microstructure of the material often dictates the desired spatial resolution. That is, the punch face should be large enough to cover relevant features that determine mechanical behavior, but the punch must not be so large that the instrument cannot provide enough force to bring the punch face into full contact with the test material and then oscillate. A smaller punch should be chosen for more spatially resolved measurements, yet the punch diameter must be large enough that the contact, and not the instrument, dominates the measured response.

Experimental Method

We tested a highly plasticized polyvinyl chloride (HP-PVC) sold commercially as a mat for damping out noise and vibration. The HP-PVC came to us in the form of a small square sheet, approximately 15 cm on a side and 6 mm thick. From this sheet, a small section was potted in epoxy and metallographically polished as shown in Figure 2.

The **iNano** indentation system produced by Nanomechanics, Inc. was used to measure the complex modulus as a function of frequency. For these measurements, the system was fitted with a 60o frustum having a face diameter of 52.5 µm. All the tests were conducted at room temperature using the test method, “Dynamic Flat Punch Complex Modulus”.

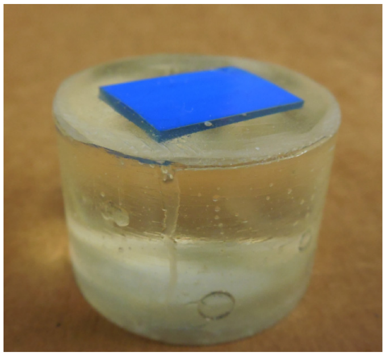

Figure 2. Simple harmonic oscillator used to model the indentation system alone or in contact with a sample.

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This test method performed the following automated steps at each test site:

1. The indenter face was brought into full contact with the surface.
2. The amplitude of the force oscillation (F_0) was determined which would cause a displacement oscillation (z_0) of about 50 nm at 100Hz. Once determined, F_0 was fixed for the remainder of the test.
3. The system sequentially imposed the prescribed frequencies, ω, and measured the resulting displacement oscillation, z_0, and phase shift, φ, at each frequency.
4. Contact stiffness and damping were calculated for each frequency by Eqs. 7 and 8, and the storage modulus, loss modulus, and loss factor were calculated by Eqs. 2 - 4.

The above process for a single test was repeated at 15 different test sites over the surface of the sample.

Results & Discussion

In Figure 3, we compare our results from oscillatory indentation (green trace) to those obtained by Herbert et al. [1] on another sample of the same material using DMA (blue trace). The repeatability of our measurements is notable: error bars which span one standard deviation are barely visible—they are about the width of the green trace. Given the profound differences in equipment and sample geometry, the agreement between oscillatory indentation and DMA is outstanding. The "wobble" in the DMA results at about 30 Hz is likely due to an inadequate accounting for instrument influence, although Herbert et al. report that the instrument was calibrated according to the manufacturer's instructions.

The properties for the HP-PVC are a strong function of frequency. As expected, the loss factor (tan δ) for this material is particularly high. At higher frequencies, the loss factor approaches unity, which means that the material damps out as much energy as it stores and returns elastically.

Peaks in the loss factor (tan δ) as a function of frequency or temperature imply phase transitions in the material, such as the glass transition. If the domain is large enough, multiple peaks in loss factor may be observed that correspond with different phase transitions. In the HP-PVC, the loss factor increases sharply with frequency over the testing domain. This implies that the material is approaching (in frequency space) a phase transition.

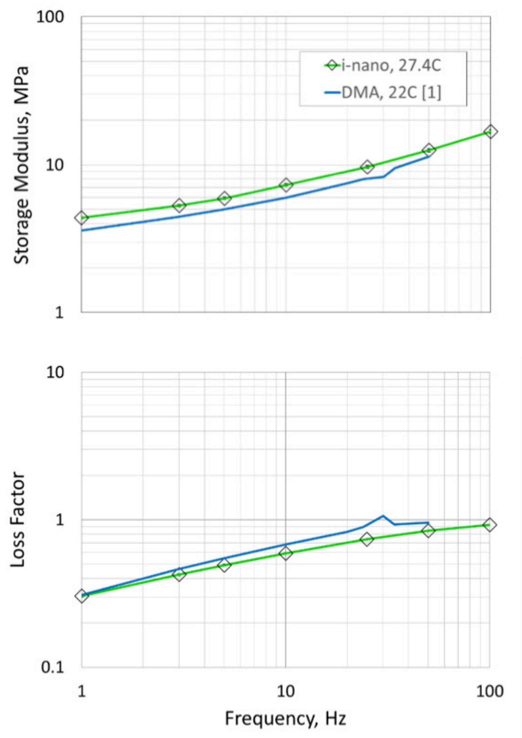

Figure 3. Storage modulus (top) and loss factor (bottom) of highly plasticized polyvinyl chloride as measured by oscillatory indentation (green trace) and dynamic mechanical analysis (blue trace).

Conclusions

The mechanical properties of polymers depend on many variables of production and excitation. Oscillatory indentation makes relevant testing more accessible, because only a small amount of material is needed and sample preparation is minimal. The **iNano** indentation system produced by Nanomechanics, Inc. can measure complex modulus as a function of frequency. The results are comparable to those achieved by the DMA over the same domain.

References

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