Measuring the Complex Modulus of Polyethylene Using Instrumented Indentation

Application Note

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Introduction

The mechanical properties of a material determine manufacturability, performance, and longevity; thus, knowing mechanical properties is essential for making good design decisions. Polymers are exceptionally complex materials—mechanical properties depend on chemistry, processing, and thermo-mechanical history. Specifically, mechanical properties depend on the type and length of the parent chain, branching, cross-linking, strain, temperature, and frequency, and these dependencies are generally interrelated. Further, it is likely that mechanical properties also depend on volume constraints. That is, we should not be surprised if a certain polymer manifests different mechanical properties depending on whether it is in the form of a thin film or a large block, because volume constraints can affect molecular mobility. Thus, in order to gain useful information for making sound decisions when designing with polymers, mechanical property measurements should be made on a relevant sample in a relevant context. Instrumented indentation testing makes such context-specific measurements more accessible, because samples can be small and minimally prepared.

Polymers are often employed in products because of their ability to both store and damp energy. The *complex modulus* is a phase vector which incorporates both capacities:

$$E^* = E' + iE'' \qquad \text{Eq. 1}$$

The real part (E') of the complex modulus is called the storage modulus because it quantifies the material's ability to store energy elastically. In materials with insignificant damping, the storage modulus is equivalent to Young's modulus. The imaginary part of the complex modulus (E'') is called the loss modulus, because it quantifies the material's ability to damp out energy.

Instrumented indentation can be used to measure complex modulus by oscillating the indenter while in contact with the material. The amplitude of the force oscillation (F_O) is set, and the amplitude (z_O) and phase shift (ϕ) of the resulting displacement oscillation are measured. The theory behind this

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measurement technique has been explained in another application note [1]. Here, we provide only the end of the analysis, which is that storage modulus depends substantially on the real part of the amplitude ratio:

$$E' \approx \frac{(1-\nu^2)}{d} \frac{F_o}{z_o} \cos\phi , \qquad \text{Eq. 2}$$

and the loss modulus depends substantially on the imaginary part of the amplitude ratio:

$$E'' \approx \frac{(1-\nu^2)}{d} \frac{F_o}{z_o} \sin\phi . \qquad \text{Eq. 3}$$

(Here, ν and d are the Poisson's ratio of the test material and the diameter of the contact, respectively. These are constants for a particular sample.) The dimensionless loss factor is independent of contact geometry, because it is the ratio of the loss to the storage modulus:

$$LF \equiv \frac{E''}{E'} = \tan\phi , \qquad \text{Eq. 4}$$

In this work, we demonstrate the application of the technique to the characterization of four samples of polyethylene (or more properly, "polyethene"), which is the most widely used plastic in the world. In this work, we tested high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE) and very-low-density polyethylene (VLDPE, $\rho = 0.87$ g/cm³).

Experimental Method
The four polyethylene samples (HDPE, LLDPE, LDPE, and VLDPE) were acquired from a petrochemical company. Each polyethylene sample was a small disk, having a diameter of about 8 mm and a thickness of about 1 mm. The four polyethylene samples were adhered to a glass-topped aluminum puck as shown in Figure 1. (The glass top provided a smooth and disposable surface.)

Figure 1. Four polyethylene samples, mounted for testing.

An Agilent G200 NanoIndenter, with XP-style actuator and CSM option, was used for all testing. The XP-style actuator applies force electromagnetically and measures displacement using a three-plate capacitive gage. The CSM option allows the superposition of an oscillating force.

When testing polymers, flat-ended cylindrical tips are advantageous for two reasons. First, they tend to cause deformation that is consistent with the assumption of linear viscoelasticity. Second, the contact area is known and independent of penetration depth. Two different indenter tips were used for this work. Both were flat-ended cylindrical punches made of diamond, but one had a diameter of about 100 mm and the other had a diameter of about 20 mm. The 20 mm punch was used to test the stiffer materials (HDPE, LLDPE, LDPE) and the 100 µm punch was used to test the VLDPE, which was very compliant. Indenters were chosen

with the goal of generating a contact stiffness that was large relative to the instrument stiffness.

The NanoSuite test method "G-Series XP CSM Flat Punch Complex Modulus" was used for this work. Table 1 summarizes the details of testing. All tests were conducted at room temperature. At least ten different sites were tested for each material. A single "test" consisted of bringing the indenter into full contact with the surface, and then oscillating the indenter at a number of specific frequencies between 1 Hz and 45 Hz. Thus, each test yielded complex modulus as a function of frequency for a specific test site. The amplitude of the force oscillation (F_O) was automatically determined at the beginning of each test as that value which would cause a displacement oscillation (z_O) of about 50 nm. The stiffer materials required a greater value for F_O in order to achieve this given value of z_O. Once determined, the forcing amplitude F_O was fixed for the remainder of the test.

Material	Temp, C	Freq range, Hz	Punch diam, µm	Force amp (F_O), µN
VLDPE	27.3	1-45	107.1	70
LDPE	26.8	1-45	21.15	445
LLDPE	27.3	1-45	21.15	750
HDPE	27.1	1-45	21.15	2200

Table 1. Summary of Experiments

Results and Discussion

Table 2 summarizes the results for all materials at 1Hz. Results as a function of frequency are plotted in Figures 2 and 3. In these plots, each data point represents the average result for all tests (locations) on the material at a particular frequency; error bars on the data point span one standard deviation.

With respect to the storage modulus (Figure 2), there are two important observations. First, over the frequency domain examined, the storage moduli are a weak function of frequency. Second, the storage moduli are ordered as we would expect based on chemistry. Different methods of polymerization result in dramatically different properties in part by causing more or less "branching" from the parent chain. "Branching" occurs when a polymer chain substitutes for an atom in the parent chain [2]. HDPE has relatively little branching and so polymer chains are closely packed. Thus, HDPE has a higher density, higher intermolecular forces, and on the macroscopic scale, a higher storage modulus. LLDPE, LDPE, and VLDPE have progressively more branching, respectively, and thus weaker intermolecular forces. On the macroscopic scale, these materials have progressively lower storage modulus and greater ductility for forming.

With respect to loss factor (Figure 3), the *dependence on frequency* increases with density; that is, the VLDPE shows no significant change with frequency and the HDPE shows the strongest decrease with frequency. What can we learn from this behavior? Peaks in the loss factor (tan δ) as a function of frequency or temperature are associated with phase transitions in the material. If the domain is large enough, multiple peaks in loss factor may be observed that correspond with different phase transitions. For the HDPE, LLDPE, and LDPE, the loss factor decreases with frequency. This means that for these three materials, there exists a transition at lower frequencies than those investigated in this study. The slopes observed over the present domain indicate that this transition occurs at the lowest frequency for the

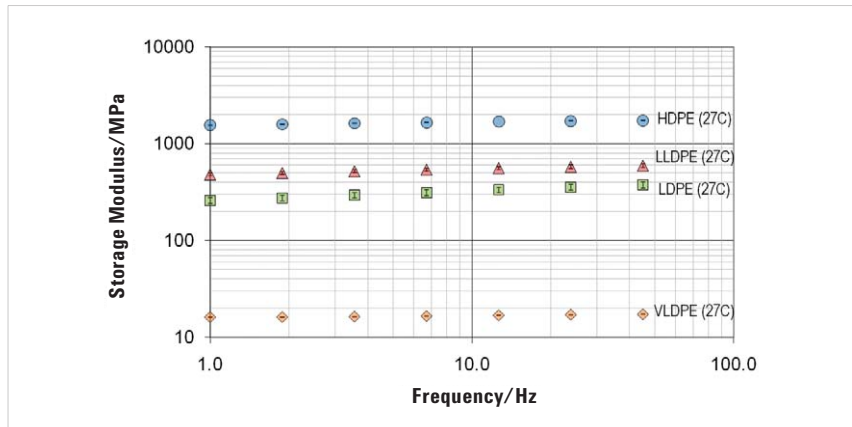| Material	E' @ 1 Hz MPa	LF @ 1 Hz Hz
VLDPE	16.2 ± 0.052	0.043 ± 0.0010
LDPE	260 ± 17.4	0.197 ± 0.0010
LLDPE	481 ± 15.1	0.150 ± 0.0020
HDPE	1554 ± 7.4	0.108 ± 0.0012

Table 2. Summary of Results

Figure 2. Storage modulus vs. frequency for the four polyethylene samples shown in Figure 1. Storage moduli are ordered as expected based on density.
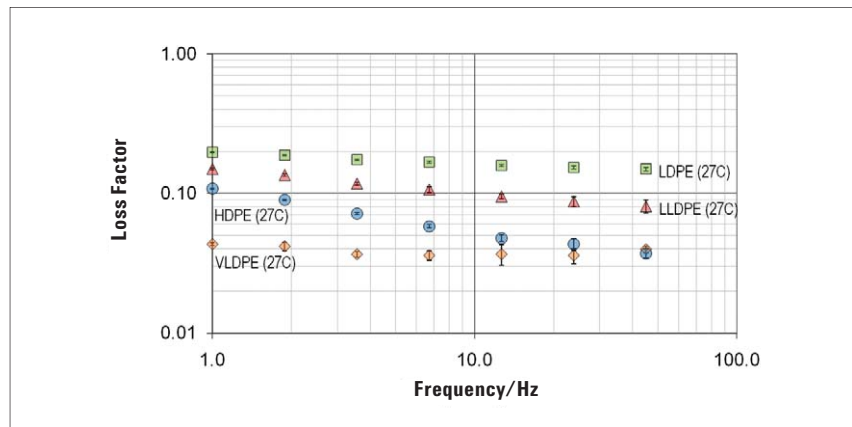

Figure 3. Loss factor (tan ϕ) vs. frequency for the four polyethylene samples shown in Figure 1. Decrease with frequency points to a phase transition at a lower frequency.

LDPE (because it has only a weak slope) and at progressively higher frequencies for the LLDPE and HDPE (because they have progressively stronger slopes). Testing over a broader frequency range would certainly clarify these results.

A more detailed discussion of these materials, including a comparison with results obtained by others, has been published elsewhere [3].

Conclusions

The Agilent G200 NanoIndenter was successfully used to measure the complex modulus of four types of polyethylene. Storage moduli were ordered as expected based on density. From the measurement of loss factor of HDPE, LLDPE, and LDPE, we deduced the existence of phase transitions at frequencies lower than the present domain.

References

1. J.L. Hay, "Using Instrumented indentation to measure the Complex Modulus of Highly Plasticized Polyvinyl Chloride," Agilent application note, available online: http://cp.literature.agilent.com/litweb/pdf/5990-6330EN.pdf.

2. P.C. Hiemenz and T. P. Lodge, *Polymer Chemistry,* 2nd ed. Boca Raton: CRC Press, 3-9 (2007).

3. J.L. Hay and E.G. Herbert, "Measuring the complex modulus of polymers by instrumented indentation testing," Accepted for publication in *Experimental Techniques* (2011).

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