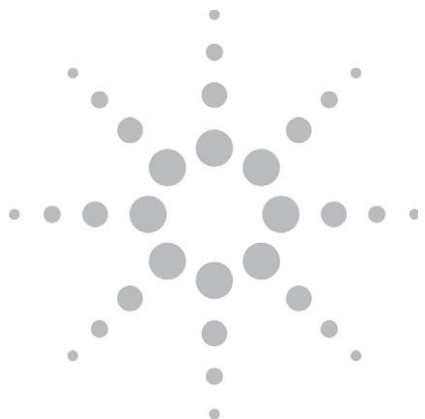




Complex Shear Modulus of Commercial Gelatin by Instrumented Indentation

Application Note

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Introduction

All gels are comprised of a three-dimensional cross-linked polymer network and a liquid filler. Because of the structure provided by the polymer network, gels can behave like solids even though they are substantially liquid by composition. Gels are classified according to their liquid fillers: hydrogels incorporate water, organogels incorporate oil, and aerogels incorporate air.

Many practical applications derive from the mechanical similarity between gel and biological tissue. For example, gels are commonly used as tissue substitutes for evaluating both ballistics and armor [1–4]. When gel is employed as a tissue substitute, mechanical characterization of both tissue and gel is essential. Ideally, one would measure the mechanical properties of the tissue that is to be mimicked and then develop a gel which behaves similarly. It is reasonable to expect that developing a tissue substitute might require testing many different gels.

Small-scale mechanical testing by dynamic instrumented indentation presents a number of practical advantages for characterizing both biological tissue and gel. First, the necessary volume of material is small. This is especially important if the application of interest constrains the material to a small volume, such as a thin film. Also, minimal sample preparation is required; only a flat surface must be presented to the indenter. Finally, instrumented

indentation holds the possibility of mapping out the spatial variation of properties in the test material; this ability is especially relevant for characterizing biological tissue.

This note presents the theory behind measuring complex shear modulus by dynamic instrumented indentation and applies that theory to the characterization of commercial gelatin using a punch which is only 100 μm in diameter. What makes these measurements so challenging is the combination of the compliance of the test material and the small contact size. Big contacts on compliant materials are not very difficult; neither are small contacts on stiff materials. Small contacts on compliant materials are extremely challenging, because the contact stiffness is small relative to the stiffness of the instrument. Thus, great care must be taken in characterizing the instrument. One gains a definite advantage by operating the instrument where it is most compliant, i.e. at its resonant frequency. But even with the instrument stiffness minimized, the instrument still dominates the measurement, so the instrument must be accurately characterized, and this characterization must be immediately relevant. That is, it should be at the same position, frequency, and temperature as the actual test. Thus, a new test method, “G-Series DCM CSM Flat Punch Complex Modulus, Gel”, is used in this work to seamlessly integrate instrument characterization and testing.



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Theory

The complex shear modulus (G^*) has real and imaginary components which manifest the intrinsic elastic and viscous natures of the material:

$$G^* = G' + iG'' \quad \text{Eq. 1}$$

When a material is indented by a flat-ended cylindrical punch, the relationship between the shear modulus (G'), Poisson's ratio (ν), elastic contact stiffness (S), and punch diameter (D) is [5]

$$G' = S(1-\nu)/(2D). \quad \text{Eq. 2}$$

Many have demonstrated the validity of an analogous definition for G'' that depends on contact damping ($C\omega$) [6–8]:

$$G'' = C\omega(1-\nu)/(2D). \quad \text{Eq. 3}$$

Proper dynamic analysis of the Agilent G200 NanoIndenter reveals that the contact stiffness (S) must be obtained by subtracting the instrument stiffness (K_i) from the total measured stiffness (K_s):

$$S = K_s - K_i. \quad \text{Eq. 4}$$

Similarly, the contact damping ($C\omega$) must be obtained by subtracting the instrument damping ($C_i\omega$) from the total measured damping ($C_s\omega$):

$$C\omega = C_s\omega - C_i\omega \quad \text{Eq. 5}$$

Logistically, stiffness and damping are obtained by oscillating the indenter. This is accomplished electromagnetically. The amplitude of the force oscillation (F_0) is set, and the amplitude (z_0) and phase shift (ϕ) of the resulting displacement oscillation are measured. The values for instrument stiffness and damping are obtained by oscillating the indenter alone—that is, not in contact with any test material. Thus the instrument stiffness and damping are given by:

$$K_i = [(F_0/z_0) \cdot \cos\phi]_{\text{free-hanging}}, \quad \text{Eq. 6}$$

and

$$C_i\omega = [(F_0/z_0) \cdot \sin\phi]_{\text{free-hanging}}. \quad \text{Eq. 7}$$

The test method “G-Series DCM CSM Flat Punch Complex Modulus, Gel” includes a “self-calibration” phase in which K_i and $C_i\omega$ are automatically evaluated according to Eqs. 6 and 7.

The system stiffness and damping are obtained by oscillating the indenter while in full contact with the test material:

$$K_s = [(F_0/z_0) \cdot \cos\phi]_{\text{in-contact}}, \quad \text{Eq. 8}$$

and

$$C_s\omega = [(F_0/z_0) \cdot \sin\phi]_{\text{in-contact}}. \quad \text{Eq. 9}$$

K_s and $C_s\omega$ are evaluated according to Eqs. 8 and 9 during the “testing” phase of the method “G-Series DCM CSM Flat Punch Complex Modulus, Gel”.

Substituting the expressions for K_i (Eq. 6) and K_s (Eq. 8) into Eq. 4, and using the resulting expression for S in Eq. 2 gives a practical expression for measuring the elastic shear modulus by instrumented indentation:

$$G' = \frac{[(F_0/z_0) \cdot \cos\phi]_{\text{in-contact}} - [(F_0/z_0) \cdot \cos\phi]_{\text{free-hanging}}}{(1-\nu)/(2D)} \quad \text{Eq. 10}$$

Likewise, the expression for the shear loss modulus is given by:

$$G'' = \frac{[(F_0/z_0) \cdot \sin\phi]_{\text{in-contact}} - [(F_0/z_0) \cdot \sin\phi]_{\text{free-hanging}}}{(1-\nu)/(2D)} \quad \text{Eq. 11}$$

Finally, the loss factor, $\tan \delta$, expresses the ratio of the loss modulus to the storage modulus:

$$\tan \delta = G''/G'.$$

For a perfectly elastic material, the loss factor would be zero. The loss factor increases with the damping capacity of the material; a loss factor greater than 1 means that the material damps more energy than it stores. In an instrumented indentation test, the loss factor is particularly useful in that it is independent of contact area and its determination.

Experimental Method

In order to contain the gels for testing, pucks that are normally used with the NanoVision (scanning) option were modified for this application. First, they were used as “cups” rather than “pucks”. Second, the rim of the cup was extended using 5-minute epoxy in order to provide an adequate surface for the cleaning material (i.e. tape). To make the epoxy rim, the cup was placed bottom-side up on a piece of Saran Wrap. Then 5-minute epoxy was mixed

and a toothpick was used to dab the epoxy around the rim. When the epoxy was fully cured, the Saran Wrap was removed.

Two versions of Knox® gelatin (Figure 1) were tested in this work. The first gel (“1X Gel”) was made following package directions: one package of Knox gelatin was dissolved in 8 fluid ounces (240 ml) of near-boiling water. Once dissolved, the gel was poured into a modified NanoVision cup, filling it to the rim. A second gel (“2X Gel”) was made by dissolving one package of Knox gelatin in only four fluid ounces (120 ml) of near-boiling water to create a “double concentration” version of the same gel. The second gel was poured to the rim of a second modified NanoVision cup, and then both cups were set on a plate. A little gel was poured on the plate around the two cups; then they were covered with a plastic container. The extra gel and covering provided a sealed, humid environment in which the gels could set without drying. The gels were poured about six hours prior to testing. Just before testing, a piece of double-sided tape was adhered to the epoxy lip. Figure 2 shows a gel sample ready for testing.



Figure 1. Standard and double-concentration versions of this gel were tested.



Figure 2. Gel sample, ready for testing in inverted NanoVision puck with extended epoxy lip.

Input	Value	Units
Clean Tip Between Tests? (yes=1; no=0)	1	
Oscillation Amplitude (in material)	500	nm
Phase Change For Contact	2	degrees
Poisson's Ratio	0.5	
Pre-test Compression	5	μm
Pre-test Compression Retracted? (yes=1; no=0)	0	
Punch Diameter	101.1	μm
Surface Approach Excitation	20	μN
Surface Approach Frequency	110	Hz
Testing Frequency	110	Hz
X Move to Cleaning Material	1.5	cm
Y Move to Cleaning Material	0	cm

Table 1. Summary of required inputs.

Sample	Temp. C	G' kPa	G'' kPa	$\tan \delta$ —
1X Gel	23.9	1.822 ± 0.023	0.446 ± 0.055	0.245 ± 0.030
2X Gel	24.0	3.811 ± 0.058	0.504 ± 0.055	0.132 ± 0.016

Table 2. Summary of results. Uncertainty range represents $\pm 1\sigma$.

An Agilent G200 NanoIndenter was used for all testing. The system was configured with a DCM II actuator, flat-ended cylindrical punch ($D = 101.1 \mu\text{m}$), and CSM option. The CSM option allowed the superposition of an oscillating force. A flat-ended cylindrical punch was employed in order to generate a contact area which was known and independent of penetration depth.

The NanoSuite test method “G-Series DCM CSM Flat Punch Complex Modulus, Gel” was used for all testing, because it seamlessly integrates dynamic self-calibration, testing, and tip cleaning. Fifteen different sites were tested on each gel. Test sites were separated by $500 \mu\text{m}$. The testing frequency was 110 Hz, because that is the resonant frequency of the DCM II actuator. (Equipment is most compliant at its resonant frequency.) Table 1 summarizes the details of testing.

Results and Discussion

Table 2 summarizes the results for this testing. Not surprisingly, the standard-concentration gel (1X) had a modulus that was about half that of the double-concentration gel (2X). Interestingly, increasing the gel concentration had

the effect of reducing the loss factor by about half. The loss factor for the 1X gel was 0.245 ± 0.030 ; the loss factor for the 2X gel was only 0.132 ± 0.016 . These results are consistent with sensory perception; that is, the 2X gel felt stiffer and more “bouncy” than the 1X gel.

Figure 3 shows the results of preliminary testing on the gel. These tests are obviously spaced too closely together ($200 \mu\text{m}$). Although these tests did not provide useful quantitative results, they did provide qualitative feedback which was valuable for performing and interpreting later tests. Fortunately, the scale bar in Figure 3 is about the same length as the diameter of the indenter face. The visible deformation occurred when the indenter was *withdrawn* from the gel. Because the gel adhered to the tip as it was withdrawn from the sample, each test left behind a protrusion of gel having about the same diameter as the tip. (The fact that it was a protrusion, not an impression, was discerned by moving the optical microscope up and down to change the focal plane.) The tensile stress induced at the surface left behind circumferential “wrinkles” when the gel finally broke away from the indenter. For these tests, the indenter was cleaned between each test. The apparent

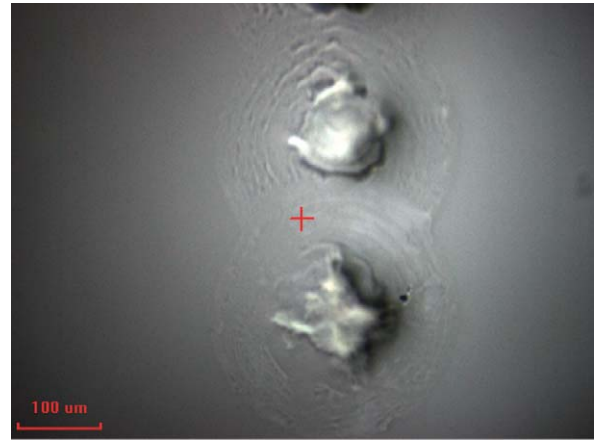


Figure 3. Residual traces from preliminary testing; scale bar is the same length as the diameter of the indenter. Tensile stresses induced by pull-off leave circumferential “wrinkles”.

adhesion verified the necessity of such cleaning. The fact that subsequent tests all left similar traces confirmed that in fact, the tip was being successfully cleaned. (If bits of gel remained on the tip from one test to another, later tests would show less adhesion than earlier tests.) As a result of these preliminary tests, the test-to-test spacing was increased to $500 \mu\text{m}$ so that there would be no interference between tests.

Conclusions

The Agilent G200 NanoIndenter was used to measure the complex shear modulus of edible gelatin. The combination of the compliance of the test material (on the order of 1 kPa) and the scale of the test ($100 \mu\text{m}$) makes these results novel in the field of mechanical testing. These extraordinary measurements required (1) a dynamically compliant actuator/transducer (the DCM II head, operating at its resonant frequency) and (2) a test method which integrated self-calibration, testing, and tip cleaning. The same equipment and test method may be used to characterize other kinds of gels and, most interestingly, biological tissue.

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