Supplementary Information: Transient Grating Spectroscopy Nondestructively Characterizes the Mechanics of Rubbery Polymers and Soft Gels

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Supplementary information

Methods: *Microindentation*

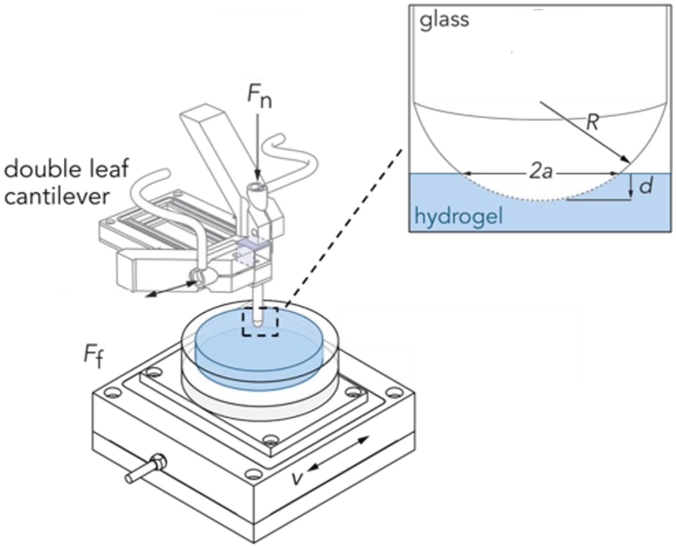

Figure S1. Schematic of custom-built tribometer used for indentation experiments [30].

A hemispherical glass probe (radius of curvature, R = 3.1 mm) attached to a double leaf cantilever with a normal spring constant of K_n = 180 μN/μm was used to indent the samples to a maximum applied normal force of F_n = 1.5 mN at an indentation velocity of v = 100 μm/s. With a probe displacement of 30 μm, this translates to a sampling frequency of ~3.33 Hz [43]. Sample stiffness was evaluated over three different locations for each sample, and five indentation measurements were performed at each location for a total of 15 indentations per sample.

Experimental data were fit up to Fn = 1 mN using Hertzian contact mechanics theory, given by the expression in equation (2.1), by minimizing the sum of squared errors to solve for E*:

$$F_n = \frac{4}{3} E^* R^{1/2} d^{3/2}$$

Where R is the probe radius of curvature, d is the indentation depth, and E* = E/(1 − v^2), where E is the compressive elastic modulus, and v is the Poisson's ratio of the sample. The reported reduced elastic moduli (and error bars) are the averages (and the standard deviation) of three total indentations on each sample. E* therefore becomes:

$$E^* = \frac{3}{4} \frac{F_n}{R^{\frac{1}{2}} d^{\frac{3}{2}}}$$

This can be used to determine macroscopic stiffness changes as the probe diameter and depth exceeds the average pore size of each of the measured polymers. The mesh sizes of the polymers are reported in Table S1. The PDMS measurements were estimated using the de Gennes[50] relationship between Young's modulus and mesh size. The PAAm mesh sizes were measured by small angle X-ray scattering as reported by Urueña et al.[29] For PHEMA, the mesh sizes were reported by McGhee et al. from swelling measurements.[51]

Table S1. Mesh sizes estimated for the polymers in this work.

Polymer	Mesh Size (nm)
PAAm	
3.75 wt%	9.4
7.5 wt%	7
10 wt%	4.4
12.5 wt%	1.7
17.5 wt%	1.3
PDMS	
10:1 – 25°C	1.5
10: - 120°C	1.3
20:1 – 25°C	2.0
20: - 120°C	1.5
PHEMA	
Swelled in 100% ethanol	2.45
Swelled in 65% ethanol	2.65
Swelled in 0% ethanol	1.75

Density Calculations

The densities for the samples used in this work are reported in Table S2. Densities were calculated by scaling the densities of individual components by their mixing ratios. The values used for the densities of individual components are 1.03 g/mL for PDMS, 1 g/mL for water, 1.12 g/mL for PAAm, 1.15 g/mL for PHEMA, and 0.79 g/mL for ethanol.

Table S2. Densities estimated for the polymers in this work.

Polymer	Density (g/mL)
PAAm	
3.75 wt%	1.0045
7.5 wt%	1.009
10 wt%	1.012
12.5 wt%	1.015
17.5 wt%	1.021
PDMS	
10:1 – 25°C	1.03
10: - 120°C	1.03
20:1 – 25°C	1.03
20: - 120°C	1.03
PHEMA	
Swelled in 100% ethanol	1.0312
Swelled in 65% ethanol	1.05546
Swelled in 0% ethanol	1.1104

Transient grating spectroscopy

The TGS setup here employs optical heterodyne detection. One arm of the probe beam is attenuated with a neutral density (ND) filter to serve as a local oscillator (the reference beam) [26]. The diffracted signal is coherently superposed with the reference beam, and then they are directed into a fast photodiode (Hamamatsu C5658). The signal is subsequently read out using an oscilloscope (Tektronix TDS784A). The relative phase of the reference beam and the probe (signal) beam can be controlled by slightly tilting a transparent glass plate placed in the probe path. Coherent superposition of the signal beam and the reference beam leads to a measured intensity that can be sensitively controlled by their relative phase. The heterodyne detection works by subtracting intensity signals measured at different relative phases and can increase the signal-to-noise (S/N) ratio, as well as yield a signal that is linear with respect to the material response, simplifying the analysis and interpretation of the measurements. The pump pulses of 515 nm and 1.3 ns pulse width (COHERENT Flare NX 515) have a fluence of 158 mJ/cm^2 with a diameter of 500 µm and a repetition rate of 2 kHz. The continuous wave (COHERENT Sapphire) 532 nm probe beam for each measurement has a power density of 4092 mW/cm^2 with a diameter of 330 µm. The time resolution of this TGS implementation is limited by the bandwidths of the photodetector and the oscilloscope and estimated to be a few nanoseconds. Due to the localized heterogeneity of each gel, for each grating period, measurements were taken for three different positions across with the average of the three used for property calculations.

To minimize steady sample heating, the pulsed and probe laser is typically modulated to be on only within the measurement time window. The power of each laser is also reduced to be at a temperature where there is minimal heating, and it is unlikely to damage the samples being measured. To prevent dehydration during measurements, hydrogels were rehydrated between measurements and samples from the same batch were interchanged to minimize wait time. In our configuration (Figure 2A), there are two achromat lenses with focal lengths being f_1 and f_2. In the limit of $\lambda << d_{PM}$ (the grating period on the phase mask), the grating period on the sample L is given by (cite [26]):

$$L = \frac{f_2}{2f_1} d_{PM}$$

In our system, f_1 and f_2 are the same so the grating period on the sample is half of that on the phase mask. The grating period on the sample L can be further calibrated by testing the spacing on different samples. One method is measuring the spacing of a burnt grating profile on a metal or dielectric film. Another is measuring the oscillation frequency (f) of the acoustic signal from an opaque sample. Given the acoustic sound velocity, v, the actual grating period on the sample can be obtained L = v/f. The actual grating was verified using the frequency of oscillations of a water sample with rhodamine dye as an absorber.

Results

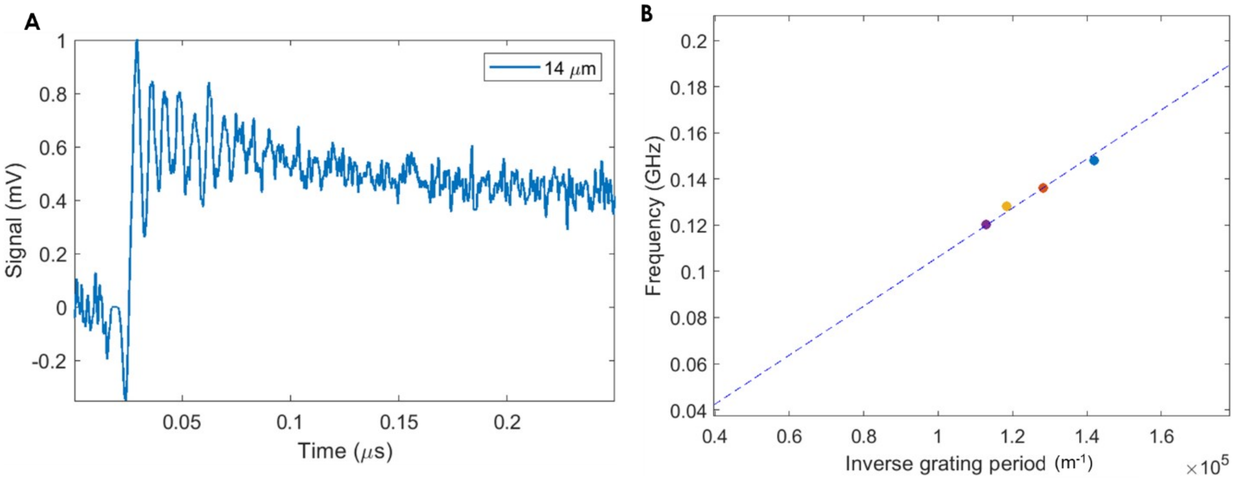

Figure S2. TGS results from the measurement of a PDMS sample with a crosslinker to monomer ratio of 20:1 cured at 120°C. The bulk acoustic wave speed is 1073 ± 69.88 m/s.

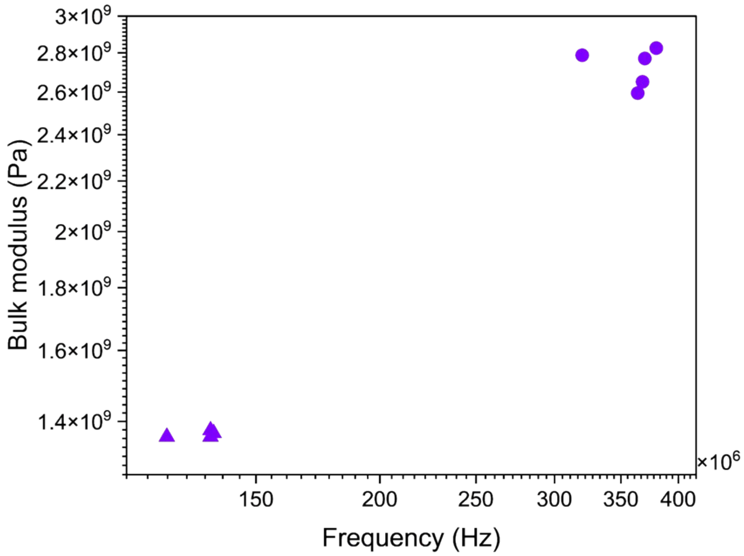

Figure S3. Bulk modulus calculations using TGS for PAAm (circle) and PDMS (triangle).

Inertial Limit

Following Ewoldt et al.,[46] the torque from a gel cylinder in a parallel plate setup should be greater than the inertial torque from the fixture

$$M_{sample} > M_{inertia},$$

where M is the moment. These two moments can be estimated as,

$$\frac{G\gamma_o \pi R^3}{2} > I\theta_o \omega^2,$$

where G is the shear modulus, γ_o is the shear strain amplitude, R is the sample radius (equal fixture radius, I is the moment of inertia of the fixture, θ_o is the angle amplitude, and ω is the frequency. Rearranging and plugging in $\gamma_o = \frac{R\theta_o}{H}$ gives,

$$\omega < \sqrt{\frac{G\pi R^4}{I\,2\,H}},$$

where H is the sample thickness. Modeling the fixture as a cylinder of steel gives,

$$I = \frac{1}{2}mR^2 = \frac{1}{2}\rho V R^2 = \frac{\pi}{2}\rho R^4 T,$$

where m is mass, ρ is density, V is volume, and T is the thickness of the cylinder. Assuming a steel fixture $\rho = 8000\frac{kg}{m^3}$ where $T = 1$ mm gives,

$$\omega < \sqrt{\frac{G}{\rho T H}} = \sqrt{\frac{G}{8H}}.$$

Finally ω can be converted to strain rate to get,

$$\dot{\gamma} \approx \gamma_o \omega < 0.01\sqrt{\frac{G}{8H}},$$

where this final form assumes a $\gamma_o = 1\%$ as is assumed in the main text.

Wave Speed Limit

Here the wave speed limit is calculated as the wave speed v over twice the size scale v of the sample to get,

$$\dot{\varepsilon} < \frac{v}{2s},$$

where $\dot{\varepsilon}$ is the strain rate. $v = 1000\frac{m}{s}$ is estimated by plugging $K = 1$ GPa and $\rho = 1000\frac{kg}{m^3}$ in to

$$v = \sqrt{\frac{K}{\rho}}.$$

Substituting in gives the final form,

$$\dot{\varepsilon} < \frac{500}{s}.$$

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