Quantitative relationship between cavitation and shear rheology

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Quantitative relationship between cavitation and shear rheology[†]

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Cavitation rheology is a powerful, simple, and inexpensive technique to study the moduli of polymer gels, however its use has not yet become widespread because few studies to date have directly compared this technique to traditional oscillatory shear rheology. Herein, we report a quantitative relationship between the gel modulus determined using cavitation and shear rheology for three series of model gels whose networks are composed of (1) permanently covalent, (2) dynamic-covalent, and (3) physical hydrogen-bond crosslinks. We determine a simple proportionality constant that allows for conversion of the moduli obtained from both types of experiments and is highly dependent on the bond energy responsible for gelation. This study provides a framework for researchers in a broad range of disciplines who can exploit the ease of cavitation rheology and place their results in the context of traditional oscillatory shear rheology.

Introduction

Cavitation rheology (CR),[1–10] also known as maximum bubble pressure rheology (MBPR)[11,12] is a simple, yet powerful, technique to study polymer gels and organogels. Unlike traditional oscillatory shear rheology (SR) which requires isolated samples to be placed into the instrument, CR can be conducted on gels of any shape in their native environment, as well as in fully closed containers. This is particularly attractive when investigating samples with highly volatile solvents or biological samples where the gel properties may be disrupted if excised from their host environment.[13–16] In a cavitation experiment, a needle is inserted into the gel, pressure is applied at a constant rate, compressing the cavitation medium (typically air, although water has been used as well),[17] and at a critical pressure, the gel fails. The mechanism of failure varies depending on the material properties, and has been the subject of ongoing studies.[2,8,18,19] By modeling the gel as a neo-Hookean solid, the cavitation modulus, E_c, is easily obtained from the critical pressure, P_c, by using the relationship[4]

$$E_c = \frac{6}{5}\left(P_c - \frac{2\gamma}{r_n}\right) \tag{1}$$

where γ is the surface tension of the gel solvent, and r_n is the radius of the needle. Two similar methods that warrant brief discussion are biaxial extension[20,21] and dilatational rheology.[22]

Biaxial extension measurements are typically conducted by the compression of materials placed between two parallel plates. As the top plate is pressed downwards with constant force, normal to the material plane, the biaxial viscosity can be measured as a function of time. Biaxial extension can also be performed with multiple rotary clamps to provide highly homogeneous biaxial deformation.[23]. Bubble inflation under constant stress can also be used to measure extensional viscosity,[20] but such measurements are inappropriate for gels as a critical stress must be achieved for yielding or strain. Dilatational rheology provides information about interfacial rheological properties fluid interfaces and is especially useful for interrogating the effects of various surfactants. However, in the present systems we assume immiscibility between the air/liquid interface and the measured gel moduli are much greater than the interfacial tension, rendering its effect negligible.[22] Because the equipment for CR is extremely inexpensive compared to oscillatory shear rheometers, and sample conditions are highly versatile, CR is becoming an increasingly common tool in the arsenal of characterization techniques for polymer chemists.

However, one major drawback of the CR experiment which limits its widespread use in polymer laboratories is a lack of understanding of the relationship between gel properties obtained from CR and SR, specifically the gel modulus. Pavlovsky and coworkers used a correction factor to compare
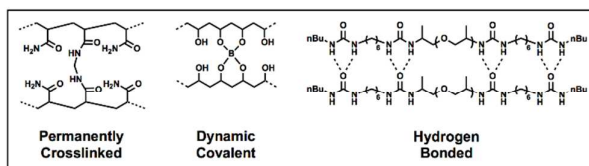
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Figure 1. Model gels used in this study, from left to right, poly[acrylamide-s-bis(acrylamide)] hydrogels, poly(vinyl alcohol)/sodium borate hydrogels, and urea-functional poly(propylene oxide) organogels.

the moduli obtained from both CR and SR in semi-dilute solutions of poly(ethylene oxide) and found that the shear modulus increased more rapidly than the cavitation modulus as the weight percent of polymer was increased.[5] However, these systems were simply dilute solutions of polymers and not polymer gels. Studies by both Kundu[24] and Cavicchi[12] used both CR and SR to study organogel systems, and their results indicated about an order of magnitude greater cavitation moduli compared to shear moduli, though the purposes of these studies were not to directly compare the two techniques.

Herein, we examine the quantitative relationship between the cavitation modulus and storage modulus for a series of model polymer gels containing: (1) permanent crosslinks, (2) dynamic-covalent crosslinks, or (3) hydrogen bonded crosslinks, as shown in Figure 1. Furthermore, we show that the ratio of the cavitation modulus to shear storage modulus is related to the strength of bonding responsible for network formation. With the information provided herein, researchers with limited access to traditional oscillatory shear rheometers will be able to access the rheological properties of their materials using simple and inexpensive instrumentation and place their results in context with traditional SR.

Experimental

Materials

Hexamethylene diisocyanate (HDI) (>99.0%), hexylamine (99.5%), acrylamide, bis-acrylamide, and oxoglutaric acid were purchased from Sigma-Aldrich and used as received. α-ω-Amine terminated poly(propylene oxide) (PPO-2000) was kindly donated by Huntsman Chemical and used as received. Polyvinyl alcohol (4 wt% solution in water) and sodium borate (4 wt% solution in water) were purchased from Flynn Scientific. Solvents were of technical grade, purchased from commercially available sources, and used as received.

Synthesis of permanently-covalent polymer hydrogels

Example synthesis of 1 wt% gel: Acrylamide (18 mg, 0.25 mmol), bis-acrylamide (2.0 mg, 0.013 mmol), and oxoglutaric acid (0.389 mg, 0.0027 mmol) were dissolved in 2 mL of deionized water and placed under UV irradiation for 1 hour.

Synthesis of dynamic-covalent polymer hydrogel

Polyvinyl alcohol solution and sodium borate solution were diluted to their corresponding concentrations (i.e. 4%, 3%, etc.) and mixed in a 10:1 ratio to a total volume of 10 mL in a 20 mL scintillation vial. Gels were equilibrated at 100 °C for 10 minutes and allowed to cool to room temperature before performing rheological measurements.

Synthesis of physically-crosslinked, hydrogen bonded polymer organogels

Example synthesis of a 0.8 wt% gel: PPO-2000 (2.17 g, 1.09 mmol) was dissolved in toluene (8.60 mL) and HDI (0.401 g, 2.39 mmol) was added dropwise and the reaction was allowed

to stir for an additional 30 minutes at room temperature to form pregel solution. Pregel solution (0.274 g) was weighed into a 20 mL scintillation vial, toluene was added (8.691 mL), and thoroughly vortexed until mixed. To form the final organogel, a stoichiometric quantity of monofunctional amine end cap was added (i.e., 995 μL of 0.060 M solution of hexylamine in toluene) via pipette and the mixture was vigorously shaken and allowed to settle at room temperature for at least 24 hours before being tested.

Cavitation rheology

Gel moduli were measured using a custom-built instrument (Figure S1, with example data Figure S2) consisting of a syringe pump (Braintree Scientific, Inc., model BS-8000) equipped with a gastight syringe (SGE Analytical Science) connected to a differential pressure transducer (Omega Engineering Inc., model PX26-005DV) and process meter (Omega, model DP-25B-S- A). Surface tension values were obtained from the *CRC Handbook of Chemistry and* Physics. A three-way valve connected the instrument to both the pressure transducer and a 22-gauge flat-tipped needle that, in a typical experiment to measure modulus, was inserted into the sample. After insertion of the needle into the sample, the syringe pump (rate = 0.40 mL min-1) was turned on to begin compressing the air inside the system and the pressure increase was recorded. A DATAQ Instruments Inc. DI-145 data recorder was used to digitize incoming signal from the pressure transducer and process meter and WinDaq software (DATAQ, v1.59) was used to manipulate the data. The experiment concluded when a failure event occurred in the sample, resulting in an instantaneous drop in pressure. The maximum pressure reached during the experiment is denoted as the critical pressure, P_c. All measurements presented are averages of three runs at different points within the sample, with error bars representing the standard deviation of the cavitation moduli. In general, error was minimized by synthesizing gel samples large enough such that the needle and subsequent cavitation event was sufficiently removed from vial wall (~2mm). Additionally, the needle was thoroughly cleaned between runs ensuring a consistent diameter was retained. Our previous report discusses in greater detail the reproducible nature of these results.[25]

Shear rheology

Shear rheology was performed on a TA Instruments Discovery HR-2 hybrid rheometer using a 20 mm parallel plate geometry. All measurements were conducted at the indicated temperature (Peltier controlled), 1% strain, with a frequency range from 0.1 to 100 rad/s. Error in storage moduli was calculated from the standard deviation of moduli of the adjacent points (plateau region) to the frequency used to report moduli.
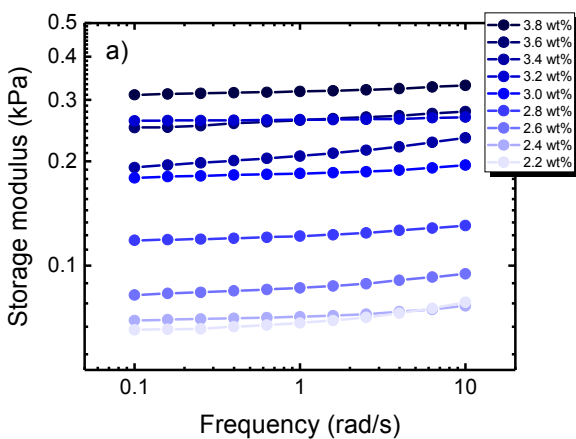
Results and Discussion

The first model system consists of poly[(acrylamide-*s-bis*(acrylamide)], permanently crosslinked gels. The SR showed

the expected frequency-independent response of storage moduli as a function of frequency, as shown in Figure 2a. Regardless of shear rate probed, due to the permanent nature of the network bonds, no difference in storage modulus was measured. In addition, the storage moduli increased as the concentration of gelator increased, ranging from approximately 0.07 to 0.31 kPa for 2.2 to 3.8 weight percent (Figure 2b, left axis). In the same series of gels, the cavitation modulus ranged from approximately 4.1 to 15.3 kPa (Figure 2b, right axis). To provide a direct, quantitative relationship between CR and SR, we introduce a simple cavitation-shear proportionality constant, k_{cs}, as determined by the ratio of the moduli obtained from the two experiments:

$$E_c = k_{cs} E_s \qquad (2)$$

where E_s is the storage modulus from oscillatory shear rheology. For permanently covalent crosslinked gels, an average cavitation-shear ratio of k_{cs}, = 39.3 ± 3.7 is observed.

covalent polyvinyl alcohol/boronic acid hydrogels. In contrast to the frequency-independent moduli for the permanently covalent hydrogels, the dynamic covalent gels showed a strong frequency dependent response in the measured storage moduli, shown in Figure 3a. The dynamic nature of the boronic ester bond allows for chain rearrangement and flow at low shear rate, resulting in reduced storage moduli for each concentration. Above a critical frequency where chain rearrangement is slower than the timescale of the oscillation, a plateau modulus is reached. Because the cavitation even occurs on the order of milliseconds,[4] the failure event can be considered to occur in the frequency-independent domain of the dynamic-covalent gels, and this is where we will make our comparison.

Shown in Figure 3b are the storage moduli (left axis) and cavitation moduli (right axis) as a function of weight percent for the dynamic covalent gels. The storage moduli in these gels ranged from approximately 0.04 to 2.51 kPa and the cavitation moduli ranged from approximately 5.13 to 21.0 kPa over the weight percent range from 2.2 to 4.0. Excellent correlation is observed between the results of the two experiments and the value of k_{cs} was determined to be 11.3 ± 2.3. The value of k_{cs}

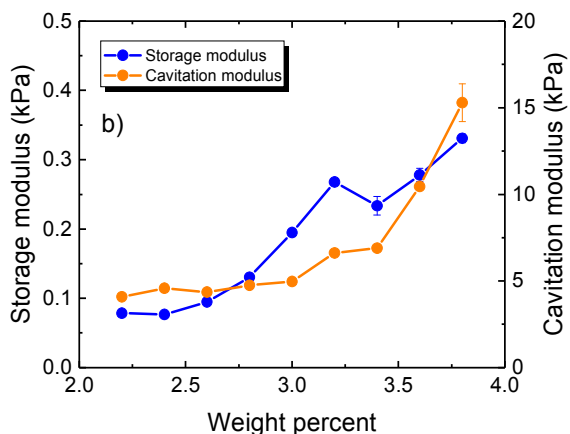The second model system is composed of dynamic

Figure 2. (a) Oscillatory frequency sweeps for permanently crosslinked gels; left. (b) Shear storage moduli (at 0.1 rad/s) are plotted on the primary axis, and cavitation moduli are plotted on the secondary axis as a function of weight percent; right.
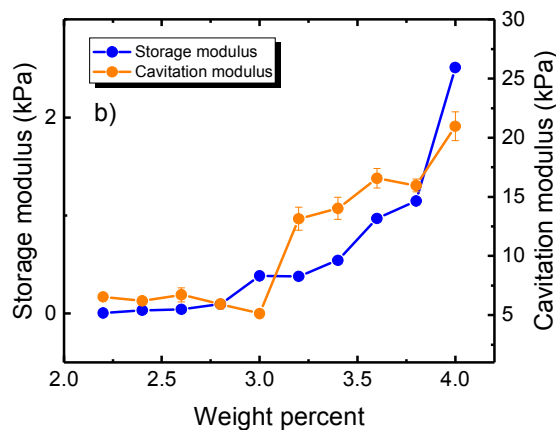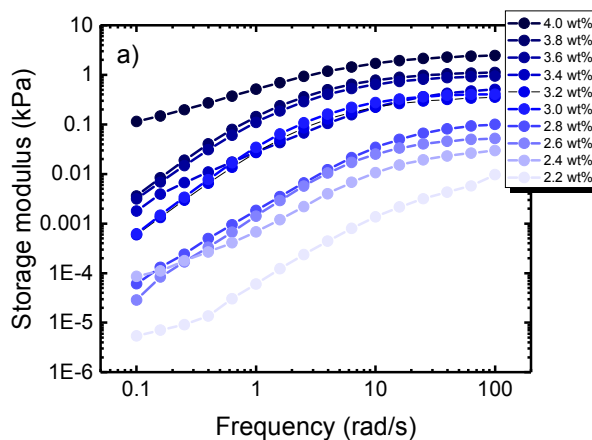
Figure 3. (a) Oscillatory frequency sweeps for dynamic covalent gels. (b) Storage moduli (at 100 rad/s) from shear rheology are plotted on the primary axis, and cavitation moduli are plotted on the secondary axis as a function of weight percent; right

for the dynamic covalent gels is nearly 3 times smaller than that of the permanently covalent gels. The magnitude of the cavitation-shear proportionality appears to be related to the relative strength of the network bonds. In general, because permanently covalent bonds have greater bond dissociation energies than dynamic covalent bonds, the pressure required to break dynamic bonds in the cavitation experiment is less than for permanently covalent networks. Indeed, this is the result observed when comparing the values of k_{cs} for the permanently covalent and dynamic covalent networks.

The third model system is composed of a series of hydrogen bond crosslinked, toluene organogels that were evaluated for their cavitation/shear relationship. Although these gels can also be considered a class of dynamic covalent gel, throughout the range probed, the storage moduli were independent of frequency (Figure 4a), indicating slow chain rearrangement over the time scale of the oscillatory experiment. Previously, we showed that the cavitation moduli of diurea end-functionalized poly(propylene oxide) gels is

strongly dependent on the nature of the solvent.[10] We showed that in non-hydrogen bonding, non-polar solvents, such as toluene, highly robust gels are formed. However, in hydrogen bonding, polar solvents such as ethyl acetate, much weaker gels result, due to competition between interchain and solvent hydrogen bonding. However, the quantitative relationship between the shear moduli and cavitation moduli in this class of gels remained unexplored until now.

In the hydrogen bonded network gels, excellent correlation between storage and cavitation moduli are again observed. The storage moduli ranged from approximately 0.03 to 4.12 kPa and the cavitation moduli ranged from approximately 1.43 to 35.4 kPa over the weight percent range of 0.2 to 0.8. The calculated k_{cs} for this gel system was found to be 10.8 ± 1.3, which is slightly lower than the value found for the dynamic covalent hydrogels, indicating similar, but slightly weaker, network bond strengths for these two classes of gels.

For the three classes of gels, the ratio k_{cs} was determined from the slope in the linear regression of a plot of cavitation modulus versus shear modulus (forced through the origin), to give a single value which can be used to interconvert between cavitation modulus and shear modulus (Figure 5). This constant, therefore, allows for the prediction of one set of moduli when the other is known. For the permanently covalent gels, dynamic covalent gels, and hydrogen bonded gels, the values of k_{cs} were determined to be 39.3 ± 3.7, 11.3 ± 2.3, and 10.8 ± 1.3 respectively. In general, the absolute magnitude of the shear and cavitation moduli are dependent on a number of factors, including weight percent of gelator and crosslinking density, but the proportionality constant provides powerful information regarding the nature of the gels and crosslinking identity.

Qualitatively, the value of k_{cs} is related to the strength if the bonds that generate the gel network. The highest value for k_{cs} in the permanently covalent system relative to the dynamic covalent and hydrogen bonded gels is to be expected. In the shear experiment, because low strains are applied (1%), little to no network bond breakage occurs. However, this is in stark contrast to the cavitation experiment where a macroscopic failure occurs, on the size scale of millimeters. In the cavitation experiment, disruption of the gel network on this length scale requires the breaking of network bonds, which in the case of the permanently covalent gels, are on the order of 400 kJ/mol. Since we observe excellent correlation between the moduli measured for the two experiments (Figure 5b), it is reasonable to interconvert between values from each experiment in this permanently covalent gel network. In moving to dynamic covalent and hydrogen bonded gels, the value of k_{cs} decreases. Again, since the cavitation process is a result of macroscopic failure and bond breakage, the lower proportionality is a direct result of the weaker bonds that form the networks. Specifically, the equilibrium modulus, G'_e, is directly proportional to the crosslink density in a given system. Because the crosslink density is held constant between the CR and SR experiments in a given gel system, the different moduli obtained from each experiment is therefore a direct consequence of the nature of the network bond.
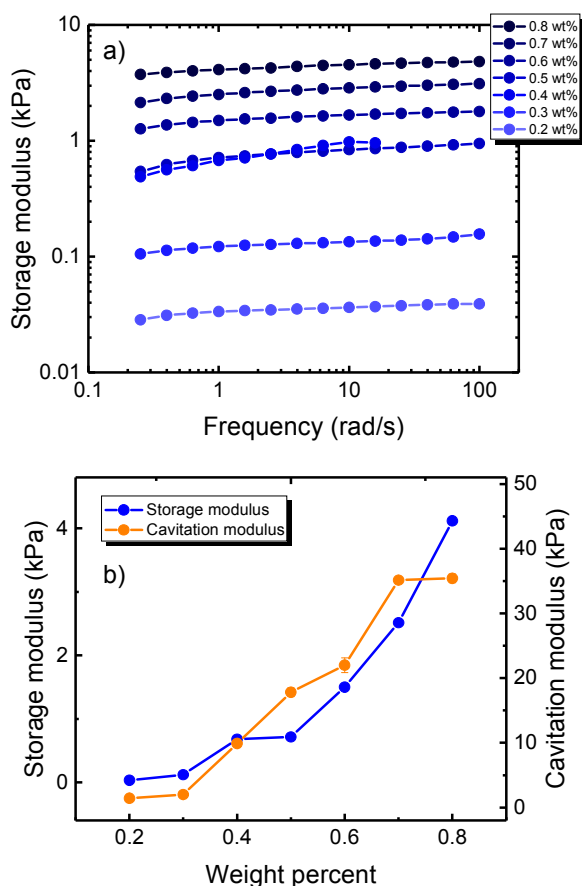

Figure 4. (a) Oscillatory frequency sweeps for hydrogen bonded gels; left. (b) Storage moduli (at 1 rad/s) from shear rheology are plotted on the primary axis, and cavitation moduli are plotted on the secondary axis as a function of weight percent; right.
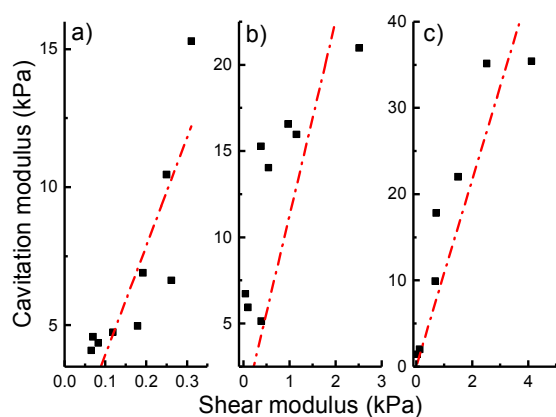
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Figure 5. Cavitation moduli versus shear moduli for (a) permanently covalent, (b) dynamic-covalent, and (c) hydrogen bonded gels. Lines are linear regression fits forced through origin. Slopes provide values of k_{CS} for each of the three gel classes. (R^2 = 0.93, 0.74, and 0.90, respectively).

In general, the scaling relationship between concentration and gel modulus is extremely complex.[25–28] As can be seen qualitatively in Figures 2b, 3b, and 4b there exists a non-linear relationship between both shear and cavitation moduli as a function of concentration. However, there is excellent correlation between shear and cavitation moduli in these systems as observed from the nearly perfect overlap in the shape of the moduli versus concentration plots. While the scaling relationship can indeed change quite dramatically depending on the nature of the gel and the solvent, this scaling becomes inconsequential for the determination of k_{cs} as both shear and cavitation moduli have roughly similar scaling relationships (Figure S3). This is especially true for both the permanently crosslinked and physically crosslinked gels, which displayed frequency independent behavior over the ranged probed. Quantitatively, in these systems, the correlation between cavitation moduli and shear moduli are excellent (R^2 > 0.9). The dynamic-covalent gel system is indeed more complicated, with a strong frequency dependence observed at lower frequencies. As the transient crosslinks have the possibility to break and reform during the characteristic period of oscillation at low frequency, the material behaves more like a traditional viscoelastic fluid. In this study, we report the shear modulus as the moduli at high frequencies when the modulus begins to plateau. In this region, the strain oscillations are fast compared with the bond breakage and reforming, thus the crosslinks behave as permanent. Indeed, the cavitation event is very rapid,[4] and thus for a frequency dependent gel such as a dynamic-covalent gel the relevant moduli with which to compare the cavitation moduli is the high frequency region in an oscillatory shear experiment. However, the exact nature between gel concentration, and relevant frequency of the cavitation event for such gels is currently the focus of future studies.
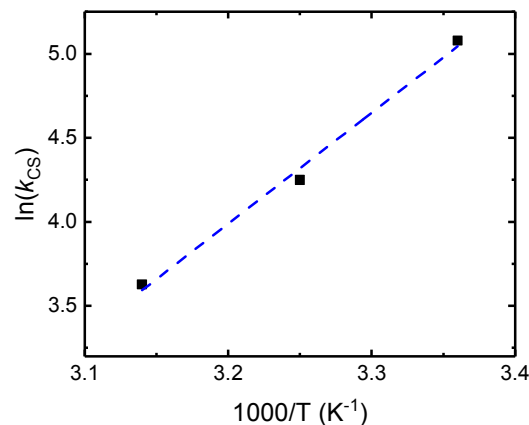

Figure 6. Arrhenius plot for dynamic-covalent gels at 2.6 weight percent. (R^2 = 0.99)

Finally, the temperature dependence of the dynamic covalent gels was studied over the range of 25 °C to 45 °C. Over this range, k_{cs} drops from 11.3 to 8.9. With increasing temperature, the boronic esters become increasingly labile, and the pressure required for a cavitation event to occur is correspondingly reduced, resulting in a lowering of k_{cs}. Additionally, an Arrhenius-type relationship was also observed in this system and was used to calculate the energy required to break the network bonds of the boronic ester crosslinks in the hydrogels studied. In Figure 6, k_{cs} is plotted as a function of inverse temperature to give a slope equal to E_a/R. From this relationship, a value of 57.3 kJ/mol was calculated as the network energy for the dynamic covalent, boronic ester crosslinks. While the homolytic bond dissociation energy for boronic esters is approximately 500 kJ/mol,[29] the energy to disrupt the network is lower, due to the ability of neighboring water molecules to hydrolyze the cleaved esters.[30]

Conclusions

In summary, this study is the first to directly compare the moduli obtained using traditional oscillatory shear rheology with cavitation rheology for polymer gels. We have shown that in model systems of polymer gels, *e.g.* covalent, dynamic covalent, and physically crosslinked, a simple proportionality constant, k_{cs}, can be utilized to interconvert between shear storage and cavitation moduli. While the results of this study, in particular the specific value of the proportionality, will not apply to every system, we hope this can serve as a useful and broad tool for researchers to adapt the powerful technique of cavitation rheology in wider use. Future work in this area will focus on the use of fluids (in contrast to air) as the cavitation medium.

Conflicts of interest

There are no conflicts to declare.

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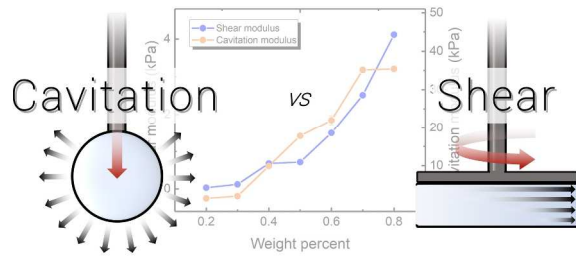
A quantitative framework is developed for comparing cavitation moduli with traditional oscillatory shear rheology for three series of model gels.