

Research paper

Energy dissipation in pH-sensitive hydrogels subjected to large amplitude oscillatory shear

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ABSTRACT

Stimuli-responsive hydrogels belong to a class of shape-memory elastomers that have gained immense popularity due to their applications in the fields of drug delivery, tissue engineering, implants, bio-sensors, and many more. The pH-responsive hydrogels 2-hydroxyethyl methacrylate (2-dimethylamino) ethyl methacrylate (HEMA-DMAEMA) and 2-hydroxyethyl methacrylate acrylic acid (HEMA-AA) exhibit swelling behavior in response to changes in pH. The present study characterizes the energy dissipation of HEMA-DMAEMA and HEMA-AA subjected to large amplitude oscillatory shear. The experiments were conducted at strain levels 0.5%, 1.0%, 1.5%, 2%, and 5% maximum amplitude strain at a constant frequency of 1 Hz. The results showed an increase in energy dissipation with an increase in shear strain for both buffer solutions. The energy dissipation obtained for the HEMA-DMAEMA samples was greater in 11.0 pH buffer solution as compared to 3.0 pH buffer solution. On the contrary, the energy dissipation for HEMA-AA samples was found to be greater in the 3.0 pH buffer solution as compared to the 11.0 pH buffer solution.

1. Introduction

Stimuli-responsive hydrogels are water-based polymers that respond to different stimuli by swelling or deswelling and are used in the fields of drug delivery (see Satish and Shivakumar, 2007, and Am-Ende and Peppas, 1997), tissue engineering (see Drury and Mooney, 2003), implants (see Refojo and Leong, 1981), bio-sensors (see Charles et al., 2004), contact lenses (see Hyon et al., 1994) and many more. The three-dimensional network structure of hydrogels and their ability to hold high water content makes them an ideal bio-material. The structural characterization of hydrogels is needed due to its biomedical applications (see Dong et al., 2006; Dong et al., 2007, and Arbabi et al., 2017). Based on the stimuli, hydrogels can be classified as temperature, pH, chemistry, shear, or electric sensitive.

The pH-responsive hydrogels are one of the promising classes of hydrogels that respond to a change in pH by either expanding or collapsing (see Gil and Hudson, 2004). Two pH-responsive hydrogels of interest are hydroxyethyl methacrylate dimethyl aminoethyl methacrylate (HEMA - DMAEMA) and hydroxyethyl methacrylate acrylic acid (HEMA-AA). The pH response of these hydrogels is due to the presence of a functional group along the backbone of the polymer. A change in the surrounding pH causes the functional group to generate electrostatic repulsive forces leading to the swelling and deswelling of the

hydrogel network. HEMA-DMAEMA is a cationic hydrogel, and HEMA-AA, on the other hand, represents an anionic hydrogel. For the efficient design of HEMA-DMAEMA and HEMA-AA in microfluidic devices, it is important to study their mechanical as well as material properties. One of the properties of these responsive hydrogels that is important to microfluidic design is the percentage of energy dissipated when work is done. Hydrogels can dissipate energy through several mechanisms. Of these processes, dissipation through the viscous nature of polymer chains and long-range migration of fluid through the cross-linked network are the most prominent. When the polymer is fully swollen, the resultant dissipation due to fluid migration is minimal, and the majority of the dissipation can be attributed to the viscous nature of the polymer chains (see Lou et al., 2018, Hu and Suo, 2012, Naficy et al., 2011, Bacca and McMeeking, 2017, Sun et al., 2012).

Many researchers have studied the ability to tune the dissipation capabilities of hydrogels (see Abdurrahmanoglu et al., 2009, Zhao, 2014, Chen et al., 2015) to take advantage of the stimuli-responsive hydrogel's unique features. A dramatic change in the amount of energy dissipated was observed between different external environments, which can be a critical factor in device designs. The significance of energy dissipation is due to the fact that it is the same for both Small Amplitude Oscillatory Shear (SAOS) and Large Amplitude Oscillatory Shear (LAOS) as the area under the hysteresis in a stress-strain curve

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does not depend on the strain amplitude. This strain independence is, therefore, a starting point by which nonlinear behavior of the hydrogels can be studied, which otherwise is difficult to capture using LAOS. The primary objective of this study is to characterize the energy dissipation of HEMA-DMAEMA and HEMA-AA stimuli-responsive hydrogels in different external environments during LAOS tests. There are many different methods of characterizing nonlinear behavior in polymers under cyclic loading. Depending on the domain investigated, (time domain (see Mac Donald et al., 1969, Onogi et al., 1970) or strain/strain rate domain (see Cho et al., 2005)), the nonlinear moduli are different and direct physical meaning can be difficult to determine. We investigate here the difference in dissipation for SAOS and LAOS tests in different hydrated environments.

2. Oscillatory shear

In general, linear viscoelasticity is only used to describe a material subjected to SAOS. A sinusoidal strain, applied at small strain amplitude, is given by,

$$\gamma = \gamma_o \sin(\omega t) \quad (1)$$

where γ_o is the strain amplitude, and ω is the frequency of oscillation, and t is time. Boltzmann's integral formulation of linear viscoelasticity is given by,

$$\tau = \int^t G(t-s) \frac{d\gamma(s)}{ds} ds. \quad (2)$$

The solution of this integral for the above applied strain can be written as,

$$\tau = G'(\gamma_o, \omega) \sin(\omega t) + G''(\gamma_o, \omega) \cos(\omega t), \quad (3)$$

where G' is the storage modulus and measures the elastic property of the material and G'' is the loss modulus and measures the viscous property. At small strain amplitude the output stress is sinusoidal, and G' and G'' have meaning. On increasing the strain amplitude γ_o , the output stress loses the sinusoidal form once it reaches non-linearity. Under these conditions, the relaxation modulus $G(t)$ can be a function of strain amplitude and the frequency of oscillation. The assumption of small strain gradients is no longer valid and a finite strain formulation is needed. To the best of this authors knowledge, a widely accepted formulation to handle LAOS behavior does not exist (see Ewoldt et al., 2008; Hyun et al., 2011, and Derkach et al., 2017).

When the strain amplitude becomes large, the stress response is no longer sinusoidal and G' and G'' lose their meaning. The point at which this transition occurs can be easily seen in a strain amplitude sweep at constant frequency. When the functions G' and G'' become functions of the strain we see that a different interpretation of the material functions is needed. One of the widely accepted nonlinear formulations for LAOS is to decompose the stress into elastic and viscous components defined as an infinite Fourier series containing only the odd harmonics (see Cho et al., 2005),

$$\tau_{\theta z} = \tau_e + \tau_v \quad \tau_e = \gamma_o \sum_{n \text{ odd}} G'_n \sin(n\omega t) \quad \tau_v = \gamma_o \sum_{n \text{ odd}} G''_n \cos(n\omega t), \quad (4)$$

where G'_1 and G''_1 are analogous to the storage and loss modulus from linear viscoelasticity, and the higher harmonics account for the nonlinear stress response (see Giacomini and Dealy, 1993). We note that there are several different methods for characterization of nonlinear viscoelastic moduli and it is important to emphasize the method of testing and the advantages and disadvantages of each method. In this work, we emphasize calculation of the percentage of energy dissipated. It is a calculation that is the same for SAOS and LAOS tests. For responsive hydrogels the difference in environmental conditions is dramatic and is shown in the data collected. For the work conducted herein we will assume a different form for the stress response (Giacomini and Dealy, 1993),

$$\underbrace{\tau_{\theta z} = \tau_o \sin(\omega t + \delta)}_{\text{linear}}, \quad \underbrace{\tau_{\theta z} = \sum_{n = \text{odd}} \tau_n \sin(n\omega t + \delta_n)}_{\text{nonlinear}} \quad (5)$$

where τ_o is the max amplitude of stress and δ is the loss angle. The loss angle is a measure of how much the stress lags behind the strain. Eq. (5) assumes a linear viscoelastic response to the applied sinusoidal strain. When the stress response is no longer sinusoidal the stress becomes a nonlinear function of strain. At this point the equations of linear viscoelasticity and the small strain assumption no longer apply. We explore the large amplitude oscillatory shear regime.

2.1. Energy dissipation

We define the stored energy W as,

$$W = \int_0^{\pi/2\omega} \tau_{\theta z} d\gamma = \int_0^{\pi/2\omega} \tau_{\theta z} \frac{d\gamma}{dt} dt, \quad (6)$$

as seen in Eq. (6) we can define the stored energy in terms of strain or strain rate, they are both equivalent. If integrated over an entire cycle the stored energy would be zero, therefore we integrate over one quarter cycle. When a sinusoidal strain is applied, given by Eq. (1), and we assume the stress is the linear response given in (5) the stored energy becomes,

$$W = \underbrace{\tau_o \gamma_o \frac{\cos \delta}{2}}_{\text{stored}} + \underbrace{\tau_o \gamma_o \frac{\pi \sin \delta}{4}}_{\text{dissipated}} = W_s + W_d. \quad (7)$$

For a material that dissipates no energy the loss angle δ is zero and Eq. (7) represents only the stored energy. When we look at the percentage of energy dissipated, which is the dissipated energy divided by the stored energy we obtain (Lakes, 2009),

$$\frac{W_d}{W_s} = \frac{\pi}{2} \tan \delta [\gamma_o, \omega]. \quad (8)$$

Note that the stored and dissipated energy depend on the maximum stress amplitude, maximum strain amplitude and the loss angle. The loss angle itself can depend on the frequency of oscillation and maximum strain amplitude. The stress calculated from oscillatory shear in a parallel plate rheometer at the upper edge is given by Barnes et al. (1989),

$$\tau_{\theta z}(R) = \frac{T}{2\pi R^3} \left[3 + \frac{d \ln(T)}{d \ln(\dot{\gamma}_R)} \right], \quad (9)$$

where T is the torque measured with the rheometer, R is the outer radius of the parallel plate, and $\dot{\gamma}_R$ is the strain rate at the edge of the plate. For a parallel plate rheometer, the term $d \ln(T)/d \ln \dot{\gamma}$ is equal to unity Bird et al.. The torque measured on a parallel plate rheometer varies as a function of radius R . For the Anton Paar MCR 302 rheometer, the average value for the torque is taken at $2R/3$. When the oscillatory stress and strain are plotted they produce what is known as a Lissajous plot as shown in Fig. 1. Eq. (8) assumed a sinusoidal stress response, however, if the stress response loses its sinusoidal characteristic the percentage of energy dissipated can no longer be calculated with (8). For all strain and stress levels the percentage of energy dissipation can be calculated graphically. The area underneath the triangle (ABC) is the stored energy and the grey area in Fig. 1 is the dissipated energy. For both small and large amplitude tests the percentage of energy dissipated to energy loss can be calculated by taking the area of the gray portion of the ellipse and dividing it by the area of the triangle (ABC). Energy dissipation is a property of all materials and shows the degree to which the viscous behavior of a material is present.

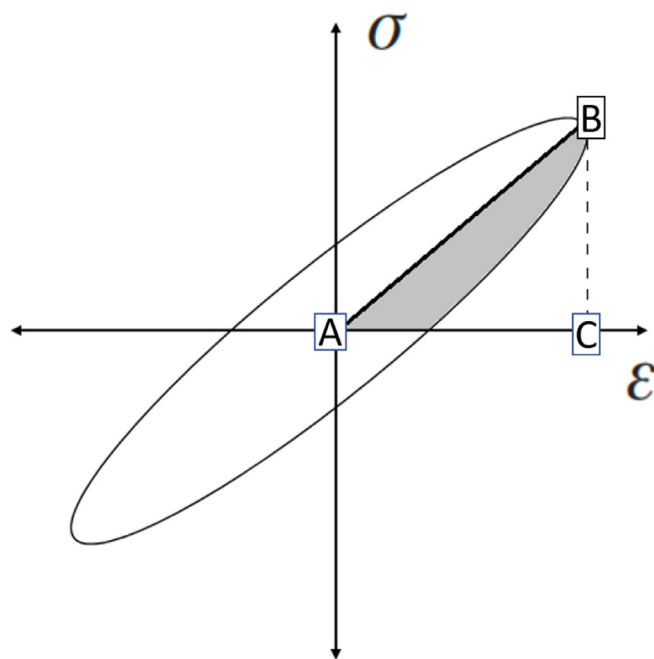


Fig. 1. A representative Lissajous plot with the gray area representing the dissipated energy for one cycle and the area under the triangle (ABC) representing the stored energy during oscillation.

Table 1

Weight % of components needed in preparation of the pre-polymer solution.

Component	HEMA-DMAEMA(wt %)	HEMA-AA (wt %)
Monomer 1	HEMA (80)	HEMA (84)
Monomer 2	DMAEMA (16)	AA (11)
Crosslinker	EGDMA (1)	EGDMA (1)
Photo-initiator	DMPA (3)	DMPA (4)

3. Material fabrication

3.1. Sample preparation

The hydrogel pre-polymer solution for HEMA-DMAEMA was prepared by mixing two monomers 2-hydroxyethyl methacrylate (HEMA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA), a cross-linker ethylene glycol dimethacrylate (EGDMA) and a photo-initiator 2,2 - dimethoxy - 2 - phenylacetophenone (DMPA) in the ratio of 27.627:5.718:0.467:1 by volume respectively. The hydrogel pre-polymer solution for HEMA-AA consisted of the same monomer, cross-linker, and photo-initiator but DMAEMA monomer was replaced by acrylic acid (AA) monomer. The weight percentage of components needed for both HEMA-DMAEMA and HEMA-AA are as shown in Table 1

Polydimethylsiloxane (PDMS) with circular wells were used for easy fabrication of hydrogel samples. The samples had the same thickness as that of the PDMS wells and thus helped in controlling the thickness of the samples. An assembly consisting of a PDMS well holding the pre-polymer solution sandwiched between two glass cover-slip was prepared and placed in a petri dish. It was ensured that no air bubbles were

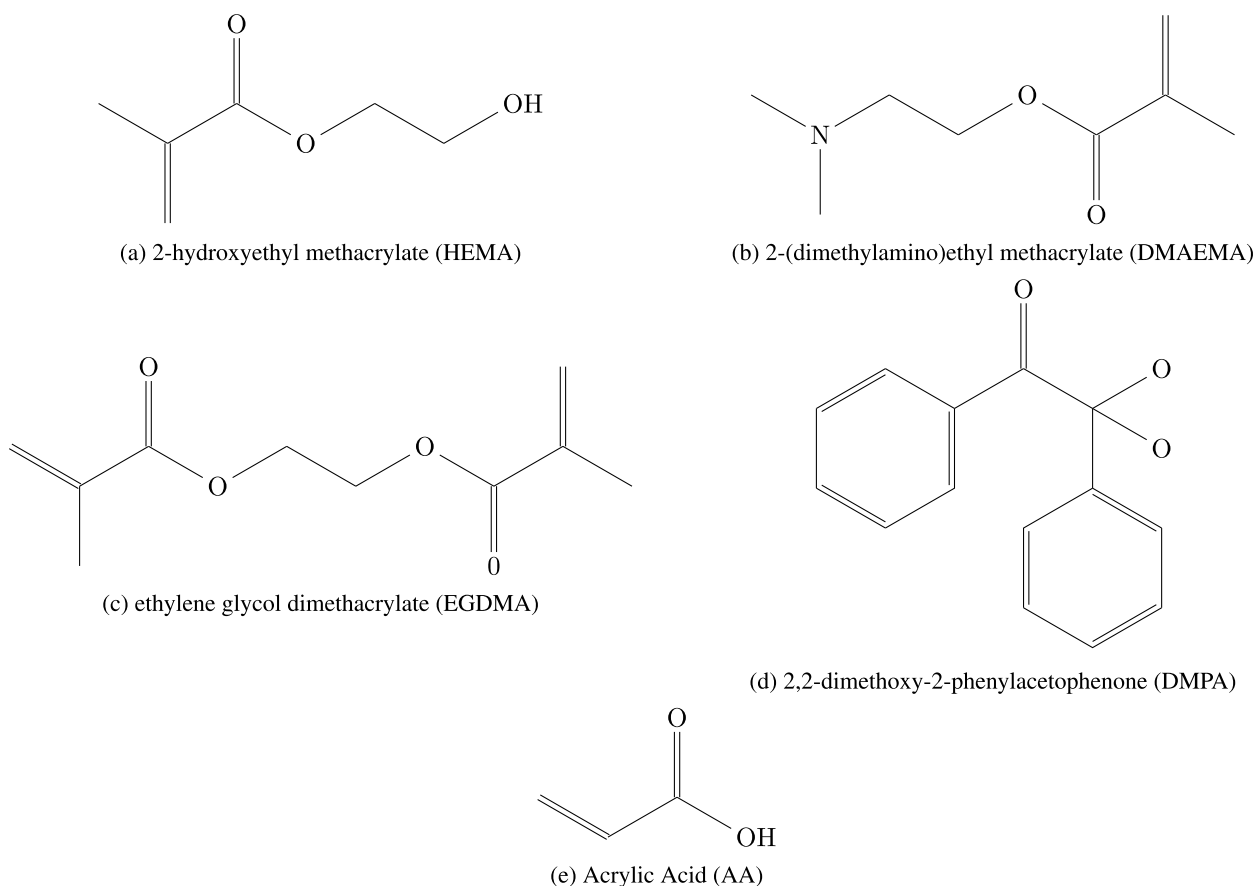


Fig. 2. The chemical formulas for a.) 2-hydroxyethyl methacrylate (HEMA), b.) 2-(dimethylamino)ethyl methacrylate (DMAEMA), c.) ethylene glycol dimethacrylate (EGDMA), d.) 2,2-dimethoxy-2-phenylacetophenone (DMPA) and e.) Acrylic Acid (AA).

formed while the glass cover-slip was placed. A photomask with a circular pattern was used for blocking the UV light such that curing occurs only in the desired pattern. The sample was then exposed to UV light using an Omnicure series 1500 at an intensity of 20 mW/cm² for 110 s which resulted in cured hydrogel samples.

3.2. Pre-conditioning

The cured hydrogel samples were first swollen in Phosphate Buffer solution for 24–48 h to easily remove the hydrogel from the glass cover-slip. The samples were then swollen in two different buffer solutions of 3.0 and 11.0 pH for 48 h, (see Davidson and Peppas, 1986, and Peppas and Franson, 1983), in which a HEMA based hydrogel was swollen and no significant changes in volume occurred after 48 hours. The pre-conditioning is conducted to minimize any additional chemical reactions between the external buffer and the hydrogel, and normal swelling from diffusion of H₂O. An illustration of the swelling behavior as seen in the two hydrogels is shown in Fig. 4. One inch samples were then punched out to meet the specifications of the parallel plate used in the rheometer for testing. The hydrogels were exposed to the atmosphere while testing since the test lasted for only 2 min.

4. Testing method

When conducting LAOS experiments it is common procedure to test at a fixed frequency (see Hyun et al., 2011). The nonlinear properties of the gel can be affected in different ways by frequency and strain amplitude. In this study we are looking to explore the effects of strain amplitude on the percentage of energy dissipation. The mechanical properties of HEMA-DMAEMA and HEMA-AA were measured by oscillatory shear tests conducted using the Anton Paar Rheometer MCR 305 with the 1-inch parallel plate setup. The samples of 1 inch diameter were punched before testing and had a thickness ranging from 1.5–2.8 mm. The samples were placed between the parallel plates, and a normal force of 1.5 N was applied to prevent slippage during the test. The tests were conducted at 0.5%, 1%, 1.5%, 2% and 5% strain and a frequency of 1 Hz. Fig. 3ii shows the experimental setup of the hydrogel in the rheometer used for testing.

5. Results

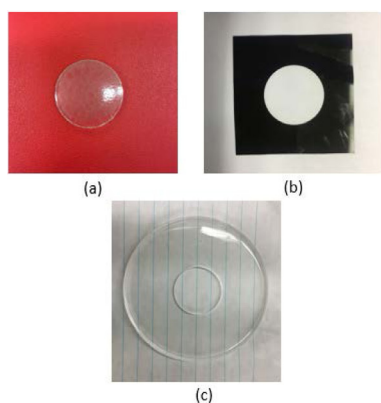
The viscoelastic properties of two pH-responsive hydrogels were studied by conducting small and large amplitude oscillatory shear tests on HEMA-DMAEMA and HEMA-AA hydrogel samples pre-swollen in 3.0 and 11.0 pH buffer solution using a parallel plate rheometer. The percentage of energy dissipated was calculated at strain amplitudes of

0.5%, 1%, 1.5%, 2%, and 5% at a frequency of 1 Hz. The shear stress and shear strain data obtained was used to plot Lissajous curves for each sample, and the energy dissipated was computed by computing the area under the curve. The percentage of energy dissipated was tabulated by taking the average of all the samples. The amplitude sweeps conducted in Fig. 5 were conducted to determine the initiation of nonlinearity, where the behavior of the hydrogels changed from the SAOS to the LAOS regime. It was determined that this change occurred after 1% strain and values for strain after 1% are in the LAOS regime.

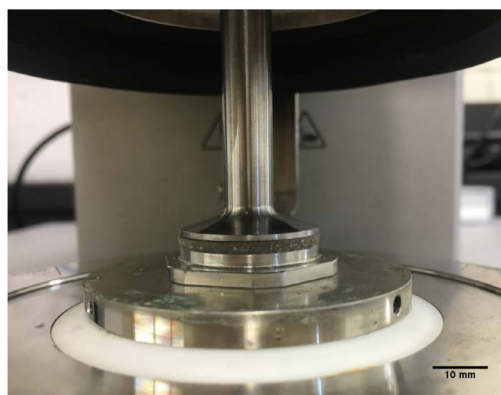
A comparison between the amount of energy dissipated by the HEMA-DMAEMA samples pre-swollen in two buffer solutions and tested at strain amplitudes of 0.5%, 1%, 1.5%, 2%, and 5% is shown in Fig. 8i, and ii respectively. The percentage of dissipated energy calculated for HEMA-DMAEMA samples was observed to increase with an increase in the strain amplitude when pre-swollen in both 3.0 and 11.0 pH buffer solutions (see Table 2 and Fig. 8i and ii). However, the percent energy dissipation obtained for these hydrogel samples was greater in 11.0 pH buffer solution as compared to 3.0 pH buffer solution. This is due to HEMA-DMAEMA samples pre-swollen in 11.0 pH buffer solution exhibiting more viscoelastic characteristics as compared to 3.0 pH samples. From Fig. 6i, the percent energy dissipation shows a jump in observed values for both 3.0 and 11.0 pH buffer solution. This change in properties after 1% strain amplitude coincides with the increase in $\tan\delta$ (the ratio between G'' and G') results obtained from an amplitude sweep test conducted on the samples as shown in Fig. 5 and the behavior predicted by Eq. (8).

Fig. 8 iii and iv displays the Lissajous plots obtained for HEMA-AA samples strained up to 0.5%, 1%, 1.5%, 2% and 5% and pre-swollen in 3.0 pH and 11.0 pH respectively. The results obtained from oscillatory shear tests conducted on HEMA-AA samples were in contrast to the HEMA-DMAEMA results. The samples pre-swollen in 3.0 pH buffer solution showed a higher percentage of energy dissipated as compared to the those pre-swollen in 11.0 pH buffer solution (see Table 2, Fig. 6). In this case, as well, the energy dissipation percentage was observed to increase when the applied strain amplitude on the samples was increased. The results obtained for HEMA-DMAEMA and HEMA-AA are similar for the opposite buffer solutions viz. acidic and basic. This phenomenon is due to the fact that the samples pre-swollen in 3.0 pH displays more viscoelastic characteristics as compared to 11.0 pH buffer solution due to the fact that this hydrogel swells in a basic medium (see Fig. 8). An amplitude sweep test (strain amplitude from 0.01% to 10%) conducted on this hydrogel showed non-linearity at a point after 1% strain amplitude (see Fig. 5).

Upon closer inspection the effects of strain amplitudes in the LAOS regime show minor hysteresis at 2.0% max strain amplitude, (see Fig. 7ii). At small strain amplitudes negligible hysteresis is observed,



(i) Preparation of hydrogel samples.



(ii) Hydrogel sample mounted in the torsional rheometer.

Fig. 3. Figure (i) shows the components used to prepare the hydrogel. a.) A HEMA-DMAEMA sample soon after curing, b.) a photomask used for curing and, c.) a PDMS well used for fabrication of hydrogel samples. Figure (ii) shows the experimental setup of hydrogel placed between the parallel plates.

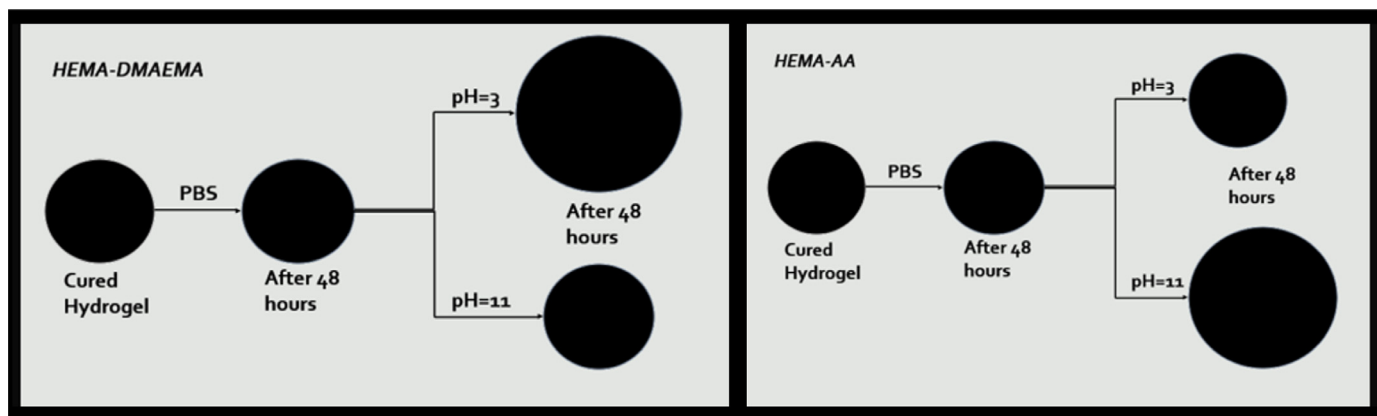


Fig. 4. Swelling behavior of the two hydrogels in 3.0 pH and 11.0 pH buffer solution

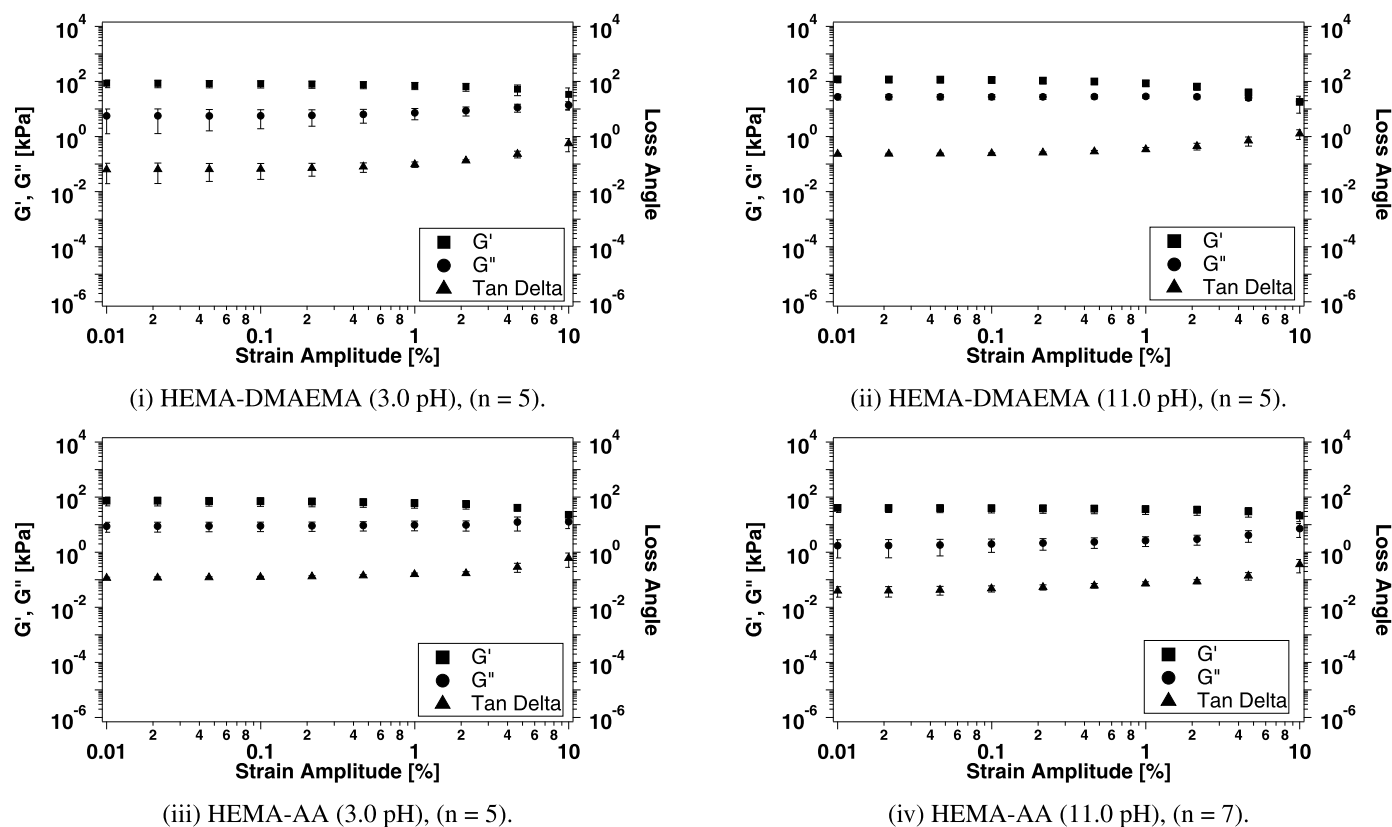


Fig. 5. This figure shows a comparison between the amplitude sweeps for HEMA-DMAEMA and HEMA-AA. The storage modulus, loss modulus and loss tangent are reported for HEMA-DMAEMA in i.) the active state (3.0 pH) and ii.) the non-reactive (11.0 pH) state. For HEMA-AA the storage modulus, loss modulus and loss angle are given for the c.) non-reactive (3.0 pH) and d.) reactive (11.0 pH) states.

(see Fig. 7i).

6. Discussion

Hydrogels have a major advantage in engineering applications due to their low cost and ease in fabrication. The ability to tune engineering properties of hydrogels, such as mechanical toughness, periodic oscillation, gelation points to name a few, make them ideal materials for the fabrication of microfluidic devices. Stimuli-responsive hydrogels represent an important class of elastomers that are hydrophilic and possess highly tunable physicochemical properties. The hydrogels HEMA-DMAEMA and HEMA-AA are pH-responsive hydrogels that are used mainly in microfluidic devices as simultaneous sensors and actuators. HEMA-DMAEMA and HEMA-AA hydrogels respond to applied loads

with changes in the conformation of the cross-linked network. The viscous nature of the polymer chains in the hydrogel and the migration of fluid through the hydrogel network contribute greatly to the dissipation process a hydrogel undergoes from these applied loads.

There are many hydrogels that display yield-stress behavior. The 'stimuli' responsive hydrogels, HEMA-DMAEMA and HEMA-AA, do not fall under this category. A yield stress fluid, (as examples toothpaste, paint, and hand lotion), display a dramatic decrease in their viscosity when a high strain rate is applied. It is the reason paint can be spread but stays on a wall after it has been applied. This decrease in viscosity is associated with shear-thinning behavior. The stimuli-responsive hydrogels HEMA-DMAEMA and HEMA-AA are not shear-thinning materials in that sense. They do not exhibit a dramatic decrease in viscosity due to a high applied strain rate. A better descriptor to the feel of a

Table 2

Energy dissipation (HEMA-DMAEMA)		
pH	Strain (%)	Energy dissipated (%)
3.0 (10 samples)	0.5	15.3 (± 2.26)
3.0 (10 samples)	1	19.9 (± 4.00)
3.0 (10 samples)	1.5	37.4 (± 9.29)
3.0 (10 samples)	2	40.9 (± 13.3)
3.0 (9 samples)	5	62.4 (± 17.8)
11.0 (10 samples)	0.5	55.1 (± 3.12)
11.0 (10 samples)	1	56.5 (± 3.77)
11.0 (9 samples)	1.5	70.4 (± 5.97)
11.0 (10 samples)	2	72.8 (± 7.63)
11.0 (10 samples)	5	83.4 (± 10.1)
Energy dissipation (HEMA-AA)		
pH	Strain (%)	Energy dissipated (%)
3.0 (8 samples)	0.5	40.6 (± 4.84)
3.0 (8 samples)	1	43.6 (± 4.61)
3.0 (9 samples)	1.5	40.3 (± 2.89)
3.0 (11 samples)	2	42.2 (± 3.42)
3.0 (8 samples)	5	55.6 (± 3.1)
11.0 (8 samples)	0.5	15.2 (± 5.03)
11.0 (8 samples)	1	21.3 (± 9.79)
11.0 (9 samples)	1.5	24.3 (± 5.53)
11.0 (9 samples)	2	30.4 (± 8.79)
11.0 (8 samples)	5	58.5 (± 20.6)

hydrogel is rubber cement, though they definitely do not have the same chemical structure. Rubber cement will not flow as paint does, and it has a strong elastic component.

The percentage of energy dissipation depends on the loss angle δ , as shown in Eq. (8). Previous research on HEMA-DMAEMA hydrogels (Benjamin et al., 2018), at a fixed strain amplitude, showed that when the hydrogel was pre-conditioned in the active (pH 3.0) medium, there was negligible frequency dependence from 0.1 Hz to 100 Hz. In the non-reactive medium (pH 11.0), HEMA-DMAEMA showed a monotonic dependence on frequency over the same range of frequencies. Data presented in this work shows an increase in the loss angle as strains increased over 1% strain for both HEMA-DMAEMA and HEMA-AA, at a fixed frequency of 1 Hz. This was observed to be the case for both HEMA-DMAEMA and HEMA-AA in the reactive and non-reactive mediums. For pH-sensitive hydrogels, such as HEMA-DMAEMA or HEMA-AA, in the reactive medium where normal fluid migration is minimized, the amount of dissipation does have a correlation with the amount of strain the material has undergone, (see Fig. 6i and ii). The percentage of energy dissipated increased as the maximum amplitude of oscillation increased. In the non-reactive medium, the percentage of energy dissipation does increase, however, the results are not conclusive as to the dependence on strain amplitude.

There is a definite point, after 1% strain, in which a marked increase in dissipation occurs (see Fig. 6i). This would agree with the

observation that the loss angle increased after 1% strain for both HEMA-DMAEMA and HEMA-AA and seen in (5) Similar studies on brain tissue (see Hrapko et al., 2006) and subcutaneous adipose tissue (see Geerligs et al., 2008) suggest the linear viscoelastic regime is up to 0.45% and 0.1% respectively. Bossard et al. (2006) showed that another DMAEMA based hydrogel behaved linearly up to a strain of 0.7%.

Results for HEMA-AA presented in Fig. 8 shows a decrease in energy dissipation with the increase in the pH value. A study by Johnson et al. (2004) shows a similar trend in the mechanical properties (Young’s Modulus, Ultimate Tensile Strength and Elongation at break) of HEMA-AA influenced by the increase in the surrounding pH value. Their results showed a maximum decrease of 42% in the Young’s modulus for samples tested at 4.0 and 12.0 pH while the maximum decrease in this paper is 62% for samples tested at 0.5% strain amplitude. The decrease in Young’s modulus of HEMA-AA was also observed by De et al. (2002) and Johnson et al. (2002).

HEMA-DMAEMA and HEMA-AA undergo swelling when exposed to buffer solutions of different pH values, and the amount of swelling depends on the type of functional group present in the polymer backbone. During the preconditioning of the HEMA-DMAEMA and HEMA-AA samples it was observed that the swelling ratio of the gels is ≈ 3.0 in the 3.0 pH buffer solution and ≈ 1.2 in the 11.0 pH buffer solution for HEMA-DMAEMA. The swelling ratio for HEMA-AA is ≈ 2.5 in the 11.0 pH buffer solution and ≈ 1.2 in the 3.0 pH buffer solution. A significant change in the volume of the hydrogel is attributed to the influx of buffer ions and water. This results in the disentanglement of the cross-links in the polymer network and reduces the degrees of freedom of motion. The additional swelling due to the influx of buffer ions in HEMA-DMAEMA and HEMA-AA occurs in the acidic and basic medium, respectively (reactive state). The hydrogel samples in the unreactive state (basic for HEMA-DMAEMA and acidic for HEMA-AA) have a highly entangled structure. This makes the hydrogels stiffer, (higher storage modulus), in the unreactive state. We believe the reason for a higher percentage of energy dissipation in the unreactive state is due to the increased degrees of freedom of motion and the higher degree of entanglement associated with the unreactive state as compared to the reactive state. The previous statement can be corroborated from the data obtained experimentally, see table (2).

The Lissajous curves obtained for the HEMA-DMAEMA (see Fig. 8i and ii) show a shift between the hardening and softening behavior of the polymer with an increase in the strain amplitude. We define hardening behavior as the increase in a materials tangent modulus as strain is increased and softening behavior as a decrease in the materials tangent modulus as the strain is increased. Shear-thinning behavior can be observed when there is a decrease in both the storage and loss modulus with an increase in strain amplitude during an amplitude sweep at a fixed frequency. Weak strain overshoot behavior is characterized by a rise and a local maximum of the loss modulus accompanied by a

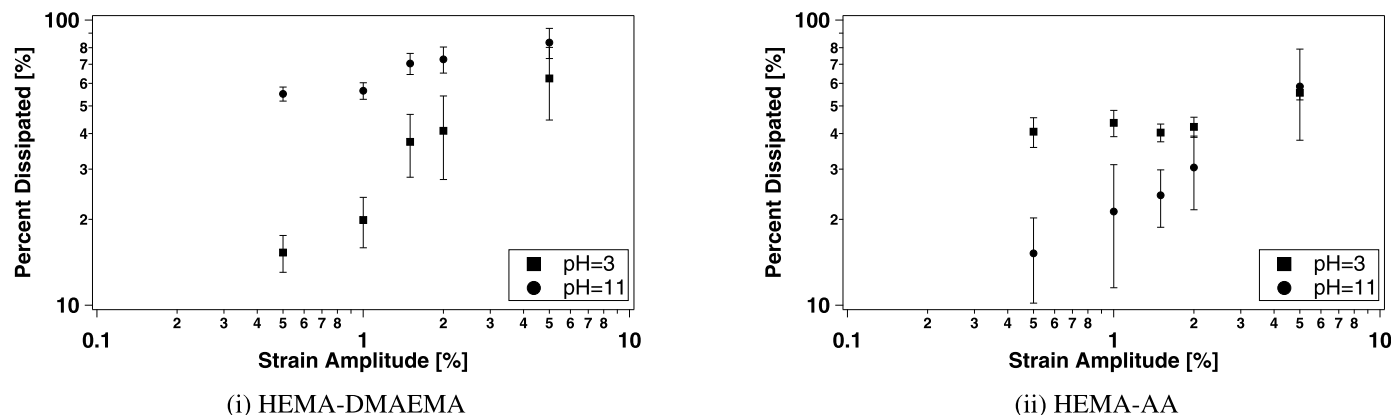
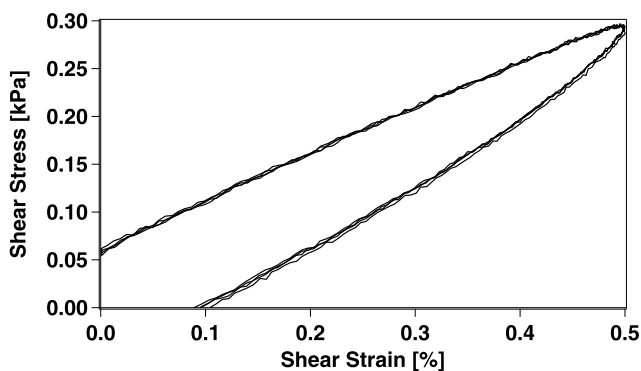
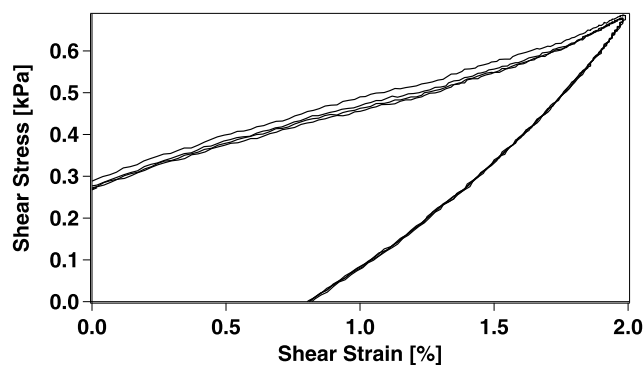


Fig. 6. Percentage of energy dissipation for HEMA-DMAEMA i.) and HEMA-AA ii.) preconditioned in 3.0 pH and 11.0 pH buffer solutions.



(i) 3.0 pH, 0.5% strain

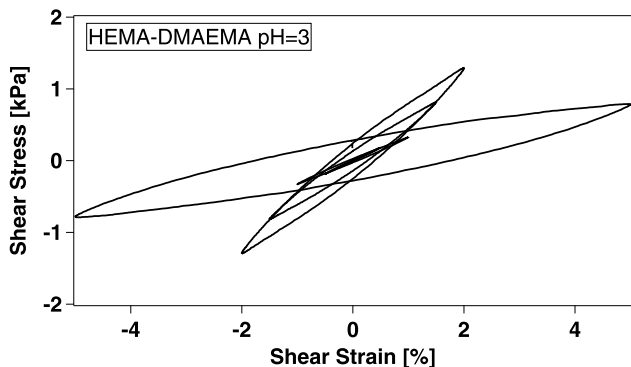


(ii) 3.0 pH 2.0% strain

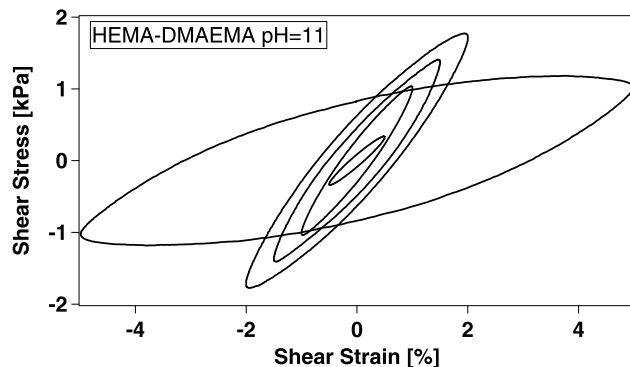
Fig. 7. Figure i.) and ii.) Show the first four cycles of testing on HEMA-DMAEMA pre-conditioned in the 3.0 pH buffer solution. Figure i.) shows negligible hysteresis at 0.5% strain after the first cycle where as ii.) does display minor hysteresis after the first cycle of strain.

decrease in the storage modulus. In Fig. 5i-iv, we see a rise in the loss modulus that may lead to a local maximum however tests conducted at higher strain amplitudes are necessary to make that definitive determination. There are certain issues associated with conducting tests at higher strain amplitudes. The connecting between the plate and the hydrogel cannot easily be maintained as higher strains, and an adhesive would be required. This leads to complication in the interpretation of the data. Careful experiments and analysis would need to be done and is the subject for another study. Weak strain overshoot can be attributed to the breaking or reforming of chain links in an elastomer (see Hyun et al., 2002). In the case of the stimuli-responsive hydrogels studied herein, there is no reformation of cross-links, at a certain strain amplitude these links are permanently broken. A shift to hardening was

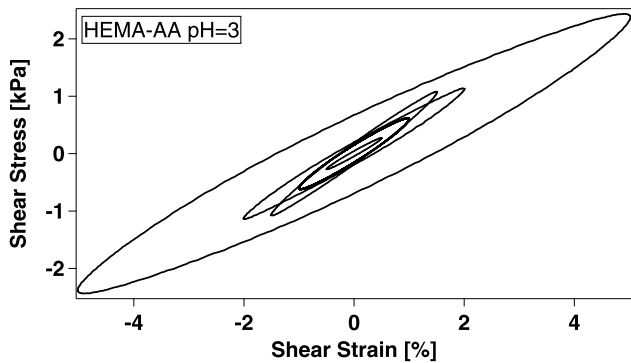
observed from 0.5% to 1%, whereas the shift to softening behavior was seen from 2% to 5%. This was observed for samples swollen in both acidic and basic mediums. As discussed before, the swelling of hydrogel causes a reduced degree of freedom of motion of the polymer network. This could be the cause of the observed hardening behavior as the strain increases. The shift to softening can be a result of the breakage of the cross-links in the network. HEMA-AA results presented (see Fig. 8iii and iv) do not show a significant shift to either softening or hardening behavior with increased strain amplitude for both buffer solutions. A possible reason for this is that no significant damage occurs to the polymer during testing. Further insight into the chemistry of the hydrogel is required to confirm this but is beyond the scope of this paper.



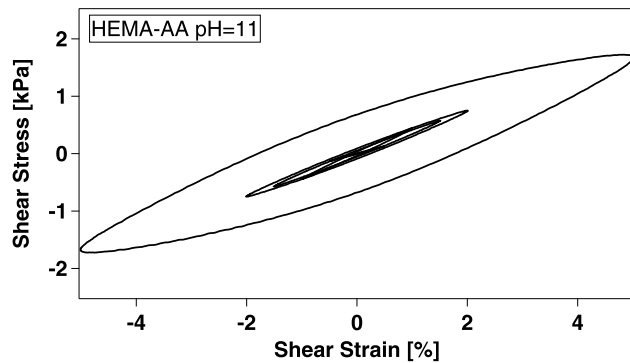
(i) HEMA-DMAEMA, reactive state.



(ii) HEMA-DMAEMA, non-reactive state.



(iii) HEMA-AA, non-reactive state.



(iv) HEMA-AA, reactive state.

Fig. 8. The Lissajous plots obtained for HEMA-DMAEMA and HEMA-AA stimuli-responsive hydrogels. The strain amplitudes ranged from 0.5% to 5%. The frequency was held constant at 1 Hz for all samples tested.

7. Conclusion

The experiments conducted herein show a strain amplitude dependence in the percentage of energy dissipated at a fixed frequency during large amplitude oscillatory shear tests. The behavior of the HEMA-DMAEMA and HEMA-AA becomes nonlinear viscoelastic after approximately 0.5% strain amplitude, and tests conducted at strains higher than 1% showed evidence of the onset of permanent chain-link rupture associated with the hysteresis observed after the first cycle of LAOS testing. Further characterization of the frequency dependence of HEMA-DMAEMA and HEMA-AA can shed further light on the structure of energy dissipation but is beyond the scope of this current study.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at [10.1016/j.mechmat.2019.103226](https://doi.org/10.1016/j.mechmat.2019.103226)

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