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Cavity growth in a triblock copolymer polymer gel

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Cavitation rheology is a recently developed measurement method for studying the mechanical properties of polymer gels from sub-micron to millimeter length scales at arbitrary locations within the network material. Current knowledge has focused on understanding the relationship between materials properties, such as modulus or fracture strength, and the maximum pressure for initiating cavitation. After the maximum pressure is reached, the growth of the bubble and the associated pressure drop is sudden and uncontrolled. We develop methods to control the growth of the bubble and to understand the relationship between cavity growth, pressure drop, and the material properties of the surrounding polymer network. We conduct these measurements on swollen networks of a triblock copolymer of poly(methyl methacrylate)–poly(*n*-butyl acrylate)–poly(methyl methacrylate) (PMMA–PnBA–PMMA).

1 Introduction

Cavitation is the unstable growth of a defect within a material. For an elastic material, this sudden growth occurs when the pressure inside the defect reaches a critical value related to the Young's modulus of the material and the initial size of the defect.¹ This critical pressure P_c is described by²

$$P_c \approx \frac{5}{6}E + \frac{2\gamma}{r_n} \quad (1)$$

for a neo-Hookean material with E the Young's modulus of the material, γ the surface tension between the material and the media inside the defect and r_n , the typical size of the defect.

Recently, this simple relationship has led to the development of the cavitation rheology technique (CRT), which can determine the mechanical properties and surface tension of soft materials across a large range of length scales. Similar methods have previously been used for soils,^{3–5} and have also been studied in liquids.^{6,7} For model tissues, Brujan and Vogel⁸ used a laser to induce cavitation in polyacrylamide gels. They showed that the oscillation of a bubble created by a laser pulse was linked to the elastic properties of the gel, and how the propagation of a shock wave during the experiment could damage the tissue during laser surgery for example. The cavitation rheology we use in this paper creates a small defect, or bubble, by inserting a needle into a soft material, and increasing the pressure in the bubble until the critical value is reached (Fig. 1).

This critical pressure is associated with a pressure drop due to the rapid growth of the bubble. The growth, described by the extension ratio $l = \frac{r_b}{r_n}$ with r_b defined as the bubble size and r_n the radius of the needle, typically reaches values beyond 100 as shown in Fig. 1d and previously.^{9,10} Most importantly, this

Fig. 1 a) Schematic of a cavitation rheology experiment. b) Pictures and schematic of the events at the tip of the needle: 1 during the compression; 2 just before the cavitation; 3 after the cavitation. c) Pressure recorded during a typical experiment of cavitation. The pressure increases while the gas is compressed, and drops at $P_{\max}$ when the gas expands. d) Extension ratio of the bubble size, l , during the same experiment of cavitation. The size of the bubble increases suddenly when the pressure is close to $P_{\max}$.

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maximum extension ratio is uncontrolled and excessively large, especially in the context of measurements in biological tissues which have been reported recently.^{9,11} In this paper, we wish to determine whether or not a finite air volume influences the results in such a way that limits the validity of this technique.

To answer this question, we modify the CRT by limiting the reservoir of the cavitating medium to a finite volume. This is simply accomplished by filling the syringe and needle with a liquid, such as water, and then drawing a finite volume of air into the tip of the needle (Fig. 2). This approach is largely based upon recent theoretical calculations of Zhu *et al.*¹²

In brief, they consider a volume V_0 of air initially in the needle at the pressure P_0 . When the critical pressure P_c is reached, the volume is V_c and is smaller than V_0 due to the compression of the gas. As growth occurs, the gas expands and the bubble is formed. The bubble volume is V_b and its pressure is P_b . The conservation of the number of molecules dictates that, in the context of an ideal gas,

$$P_0\lambda_0 = P_c\lambda_c = P_b(\lambda_c + \lambda_b) \quad (2)$$

Fig. 2 Bubble growth, for two different sizes of chamber, 9 images s^{-1} , needle outer diameter 0.47 mm. a) For an infinite chamber, the bubble is larger than one with a finite volume of chamber, as in b). c) Schematic of the events during the experiment at the tip of the needle filled partially with air. Initially, a volume V_0 at a pressure P_0 is trapped in the needle. During the compression, the volume of air is reduced, and the pressure increases, until it reaches the maximal pressure P_{max} . The volume is then V_c . The bubble is formed, the total volume of air is then $V_c + V_b$, and the pressure is P_b . d) Pressure measured during an experiment: blue squares for a needle filled with air (pictures in a), orange circles for a syringe partially filled with water (pictures in b). The maximal pressure is P_{max} , and the critical pressure in air is $P_c = P_{max} - P_0$. $P_b + P_0$ is the pressure at the end of the experiment. Inset: measure of P_b and P_0 with a sensor with higher sensitivity.

with the non-dimensional volumes being $\lambda_i = \frac{V_i}{r_n^3}$, with r_n the radius of the needle.

Accordingly, the fewer molecules that are available, the smaller the size of the bubble. In this paper we confirm this proposed relationship, experimentally showing that P_c is not a function of the finite volume and link P_b to the material properties of the cavitating system.

2 Experimental

2.1 Materials

We use a swollen polymer network formed by the physical association of a triblock copolymer in a selective solvent for the midblock segment. The selected triblock copolymer is poly-(methyl methacrylate)-poly(*n*-butyl acrylate)-poly(methyl methacrylate) (PMMA-PnBA-PMMA). Two different triblock copolymer architectures were kindly provided by Kuraray Co. Ltd. One copolymer, referred to as PMMA₉, has PMMA endblocks with a molecular weight of 9 000 $g\ mol^{-1}$. The midblock PnBA has a molecular weight of 53 000 $g\ mol^{-1}$. The second copolymer material, referred to as PMMA₂₅, has PMMA endblocks with a molecular weight of 25 000 $g\ mol^{-1}$ and a PnBA midblock molecular weight of 116 000 $g\ mol^{-1}$.

To make triblock copolymer gels, the copolymers are dissolved in 2-ethyl-1-hexanol (Sigma Aldrich) at a temperature of 60 °C. At this temperature, both PMMA and PnBA domains are soluble in the solvent. After mixing for two hours at this temperature, the copolymer solution is cooled to room temperature, 20 °C. As the solution cools, the PMMA endblocks

Fig. 3 a) Microscopic structure of the triblock copolymer PMMA-PnBA-PMMA. The PMMA endblocks organize in micelles, linked by the PnBA midblocks. b) At 20 °C, for the triblock PMMA₂₅ at a polymer concentration of 5% G' red circle and G'' blue triangles. Elasticity is predominant in the range of deformation between 0.1 $rad\ s^{-1}$ and 100 $rad\ s^{-1}$. c) At 20 °C for the triblock PMMA₉ at a polymer concentration of 7%. d) At 25 °C, for the triblock PMMA₉ at a polymer concentration of 7%, the increase of temperature increases the energy of the system, and then decreases the deformation rate to observe the second viscous regime.

become insoluble, forming micelles which are linked by the PnBA midblocks, Fig. 3a. Conveniently, these gels are thermoreversible, thus allowing the samples to be heated to temperatures above 60 °C to heal deformation zones induced during cavitation and subsequent reuse of the sample materials. The properties of such triblock copolymer gels have been reported extensively by the Shull group.^{13–15}

The mechanical properties of the swollen gels depend strongly on the polymer concentration.¹³ Here, we primarily study two concentrations. For PMMA₉, the polymer volume fraction is equal to 7%. For PMMA₂₅, the polymer volume fraction is equal to 5%. At room temperature (20 °C), both of these concentrations produce gels with storage moduli significantly greater than the loss moduli, as measured using shear rheometry on a rheometer (AR2000, TA instruments) in a parallel plate geometry (Fig. 3b, c and d). At 25 °C, a 7% PMMA₉ gel exhibits rheological properties typical of a polymer solution near the critical gel transition (Fig. 3d).

2.2 Cavitation rheology

Cavitation rheology is performed on the experimental setup introduced by Zimmerlin *et al.*¹⁰ in our laboratory at 20 °C. We use steel needles purchased from Hamilton with radii ranging between 0.1 mm and 0.6 mm and glass needles from WPI with radii ranging between 0.01 to 0.1 mm. We fill the syringe and part of the needle with water to control the amount of air, V_0 , at the tip of the needle (Fig. 2c). The pressure is increased by compressing the volume of the cavitating media *via* a syringe pump (NE100 from New Era). The flow rate was varied from 1 $\mu\text{L s}^{-1}$ to 10 $\mu\text{L s}^{-1}$ in the experiments reported here, but no significant dependence on flow rate was observed over this range. The pressure is measured by a pressure sensor (Omega Engineering PX26-001GV), the critical pressure is measured with the 0 to 5 psi model and for more precise measurements (for the final pressure into the bubble) we used a 0 to 1 psi. The bubble growth is imaged by a video camera (Edmunds Optics). We measured the volumes of the bubbles by measuring the area of the two-dimensional image of the bubble and calculating the average radius, which was then used to calculate the volume assuming a spherical geometry. The value of V_0 is calculated with the measured volume into the glass needle, we checked that this volume is the same as the volume dispensed by the syringe pump. This is measured *a posteriori*, we add to the volume dispensed to form the bubble to the volume dispensed to fill the needle with liquid. For the time scales relevant to these measurements, we consider the swollen gels to behave as incompressible materials.

2.3 Contact mechanics measurements

A custom-built contact mechanics instrument is also used to measure the elastic modulus of the sample. A cylindrical glass probe of 3 mm in diameter compresses the gel until the compression force reaches a fixed value of 5 mN. The probe is then retracted. The velocity of the probe during forward and reverse motion is 5 $\mu\text{m s}^{-1}$. The force and displacement of the resulting contact between the probe and the swollen gel is recorded continuously throughout the experiment. The elastic modulus, E , of the gel is determined by $E = \frac{3kd}{4}$, where k is the

slope of the measured force–displacement relationship, and d is the diameter of the cylindrical probe.¹⁶

3 Results

3.1 Critical pressure

As Fig. 2b demonstrates, the size of the bubble upon cavitation can be controlled by the initial volume, V_0 . Pressure *versus* time, for these experiments with different initial volumes of air, V_0 , curves are shown in Fig. 2d. In both cases, the pressure increases until it reaches the critical value for cavitation, P_{max} , and then drops suddenly. Three primary differences are observed for the two representative experiments. First, the initial pressure, P_0 , is larger for the system with a smaller V_0 compared to the experiment with $V_0 = \infty$. As there is a meniscus of water into the needle, the pressure measured (in water) is not the same that the actual pressure in air. To calculate the pressure in air, we subtract P_0 from the measured values of P . We then have the critical pressure in air $P_c = P_{\text{max}} - P_0$. In the infinite V_0 experiment, water is not used to confine a volume of air at the tip of the needle, so the initial pressure, P_0 , is equal to atmospheric pressure. The second difference, which is evident in the different slopes, is the time required to reach P_{max} . This time difference is associated with the different levels of compression that are required to achieve P_{max} , depending on V_0 , the compression rate of the syringe pump, and the difference between P_0 and P_c . The third difference is the different values of P_b , the pressure inside the bubble after cavitation.

We compare the values of P_c for finite initial volumes, $P_{c \text{ finite}}$, to P_c values for infinite initial volumes, $P_{c \infty}$. As presented in Fig. 4, we observe no difference between $P_{c \text{ finite}}$ and $P_{c \infty}$. Therefore, the critical pressure does not change with V_0 .

3.2 Critical pressure for cavitation

As the critical pressure does not depend upon V_0 , the value of P_c from a cavitation rheology experiment with a finite volume can

Fig. 4 Critical pressure measured for the experiment with a finite volume of air in the needle $P_{c \text{ finite}}$ compared to the measured critical pressure when the syringe and the needle are filled with air $P_{c \infty}$. The range of volume of air in the case of a finite volume is of order 0.3 mm³ to 4 mm³.

be used to quantify the elastic modulus of the swollen triblock copolymer gels, and the surface tension of the gel/media interface. P_c is plotted as function of $\frac{1}{r_n}$ in Fig. 5. Fitting a line to this data according to eqn (1), we find that the surface tension for the air/gel interface is 23 mN m^{-1} , which compares favorably to the surface tension listed in literature for the solvent, 2-ethyl-1-hexanol.¹⁷ The fitted line also provides a measurement of $E = 5.0 \text{ kPa}$ for the 7% PMMA₉ triblock gel. This measurement of E compares favorably to independent measurements of the elastic modulus using contact mechanics measurements and shear rheometry, assuming that the gel can be considered as incompressible. This agreement is observed across gels of various concentrations, as shown in Fig. 5b.

3.3 Final bubble volume λ_b

As schematized in Fig. 2c, the molecules of air are initially confined in a volume, V_c , at the threshold, at which point they are redistributed into a volume $V_c + V_b$. This implies that the pressure P_b in this new volume is smaller than P_c . To compare the volume of the bubble, V_b , to the initial volume of air, V_0 , from eqn (2):

$$\frac{P_0 \lambda_0}{P_c} + \lambda_b = \frac{P_0 \lambda_0}{P_b} \quad (3)$$

where we have converted the volumes, V_i , to non-dimensional parameters, $\lambda_i = \frac{V_i}{r_n^3}$.

This gives us measured values of λ_b which are presented in Fig. 6. This relationship shows that the initial volume of air in the needle controls the size of the final bubble during a cavitation experiment, but the predicted scaling in eqn (3) does not fully describe the relationship between the initial and final bubble volumes. Our data suggests a scaling that is weaker than linear for the combined data sets between the two triblock gels. This discrepancy may be associated with the slightly non-spherical shape of the final bubble (Fig. 2b) or with other deformation

Fig. 5 a) Measurement of the surface tension of the 7% triblock copolymer PMMA₉. The slope of the line indicates that $\gamma = 23 \text{ mN m}^{-1}$, the intercept gives $E = 5 \times 10^3 \text{ Pa}$. b) Triangles: elastic moduli measured with cavitation rheology for PMMA₉ gels as a function of polymer volume fraction, ϕ . Square: the elastic modulus provided by the storage modulus measured with shear rheometry at 20°C (Fig. 3d). Circles: elastic moduli measured with contact mechanical measurements conducted at room temperature.

Fig. 6 a) Initial volume of air related to the volume of the bubble and of critical pressure. The relationship is linear as predicted by eqn (3). b) The pressure in the bubble at the end of the experiment follows a Laplace law (green line) which can only be applied for a liquid. Orange circles represents the values for triblock PMMA₉ at 7%, blue triangles represents the values for PMMA₂₅ at 5%.

mechanisms, such as fracture,² which have not been considered in developing eqn (3).

3.4 Pressure P_b

The final volume of air in the bubble is related to the final pressure in the bubble, which is the pressure P_b measured after the drop in Fig. 2d. We can see on the same figure that this value is not significantly different from the initial pressure P_0 . We will now focus on the parameters which controls P_b .

We plot P_b as a function of the final bubble radius, r_b . We measure that pressure inside the final bubble increases with decreasing final bubble radius. Interestingly, this observed trend can be fit with a line defined by the Laplace law, such that $P_b = \frac{2\gamma}{r_b}$. In this plot, we use $\gamma = 23 \text{ mN m}^{-1}$, which is measured in Fig. 5a and consistent with the surface tension of the solvent.¹⁷ This observed correlation suggests that the final pressure in the bubble is controlled by the liquid properties of the triblock copolymer solution, and not the elasticity of the network.

4 Discussion

The results above present several clear lessons. The final bubble size for cavitation rheology measurements can be controlled by using a finite initial volume of the cavitating medium. The critical pressure for cavitation does not depend upon the size of the finite volume. The critical pressure for cavitating a swollen triblock copolymer gel, with crosslink junctions defined by the micelles of endblock domains, can be quantitatively related to the elastic properties of the network and the surface tension between the cavitating media and the gel. The final bubble size can be related to the initial volume and the pressure at cavitation. Finally, we also observe that the pressure in the final bubble appears to follow the Laplace law for a triblock copolymer gel.

The pressure in the final bubble volume being defined by the Laplace law is unexpected, and we hypothesize that this result is related to the specific network structure of the triblock copolymer gels. Specifically, we hypothesize that the energy associated

with cavitation, and the rapid expansion of the air, breaks the micelles.

To measure the deformation rate during a cavitation experiment, we have used a high speed camera (Photron) to image the growth of the bubble in a PMMA₉ gel with a volume fraction of 7%. Images of the growth and measured values of radius as a function of time allows us to calculate the velocity of bubble growth $v = \frac{dr_b}{dt}$, as shown in Fig. 7. From this data, we estimate

the deformation rate, defined as $S = \frac{dr_b(t)}{dt} / r_b(t)$, to be between 10^3 Hz and 10 Hz. These measurements are begun after the first 40 ms after the critical pressure is reached; therefore, deformation rates may even approach as high as 10^4 Hz, at earlier times. This upper bound would be the sound velocity for the material, $v_s = \sqrt{\frac{E}{\rho}}$, which is approximately 1 m s^{-1} for the gels. This deformation rate is larger than the deformation rate we can test with a standard rheometer.

To understand why the gel becomes liquid at large deformation rates, we consider the fact that glassy PMMA domains can be disintegrated at high stress. Seitz *et al.*¹⁸ consider that when the pressure is higher than 2×10^6 Pa, the micelles of the gel can be destroyed. In our experiment, the pressure in the gel during bubble formation can be larger than the pressure applied with the syringe pump. When the bubble is formed the flow rate is imposed by the material itself, and as we can see in Fig. 7a is large (about $10^3 \text{ mm}^3 \text{ s}^{-1}$) compared to the flow rate of the syringe pump (about $10 \text{ mm}^3 \text{ s}^{-1}$). This flow rate implies a deformation rate of the material defined as $\frac{dr_b(t)}{dt} / r_b(t)$, which ranges between 10^3 s^{-1} and 10 s^{-1} during the first 40 ms after the critical pressure. To estimate the stress experienced by the gel during expansion, we consider that the friction in the gel can be quantified by the viscosity in the viscous regime η_{gel} , which is about $10^3 \text{ kg m}^{-1} \text{ s}^{-1}$ (Fig. 3c). Accordingly, we estimate the shear stress of the gel during bubble formation to be $\sigma \sim \eta_{\text{gel}} \dot{\gamma}$, ranging between 10^6 Pa and 10^4 Pa. At the beginning of the bubble formation process, the energy of friction in the gel is of the order of magnitude of the energy needed to destroy the micelles, hence the gel is liquid during this short time and the bubble shape is fixed by the surface tension.

Therefore, we believe that our results indicate that the Laplace law dependence of P_b is a property of the thermoreversible

triblock copolymer gels, and not necessarily a general result for the cavitation of elastic materials.

5 Conclusion

We studied triblock copolymer PMMA–PnBA–PMMA gels using cavitation rheology measurements. We verified that the critical pressure for cavitation is dependent upon the elastic modulus and surface tension of the gel, and not a function of the initial volume of the cavitating medium. We confirmed that the final bubble size after cavitation can be controlled by the initial volume of the cavitating medium. For the thermoreversible triblock copolymer gels, the final pressure in the bubble is defined by the Laplace law, due to the likely breakage of the micelles of PMMA endblocks upon rapid expansion. These results have important implications in the future implementation of cavitation rheology in confined systems and living biological tissues, where final cavity size needs to be controlled to minimize damage to surrounding material. Furthermore, the observation of breakage of micelles at high deformation rates is important in the future design of protective devices for high rate impacts.

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Fig. 7 a) Growth velocity of the bubble $v = \frac{dr_b}{dt}$ for a 7% PMMA₉ at room temperature. b) Ratio of the radius of the bubble and the radius of the needle r_b/r_n (brown triangles) and deformation rate S for the same experiment (blue circles).