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BRIEF TECHNICAL NOTE

Ballistic and Blast-Relevant, High-Rate Material Properties of Physically and Chemically Crosslinked Hydrogels

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Abstract

Background Hydrogels are one of the most ubiquitous polymeric materials. Among them gelatin, agarose and polyacrylamide-based formulations have been effectively utilized in a variety of biomedical and defense-related applications including ultrasound-based therapies and soft tissue injury investigations stemming from ballistic and blast exposures. Interestingly, while in most cases accurate prediction of the mechanical response of these surrogate gels requires knowledge of the underlying finite deformation, high-strain rate material properties, it is these properties that have remained scarce in the literature.
Objective Building on our prior works using Inertial Microcavitation Rheometry (IMR), here we present a comprehensive list of the high-strain rate ($> 10^3$ 1/s) mechanical properties of these three popular classes of hydrogel materials characterized via laser-based IMR, further showing that the choice in finite-deformation, rate-dependent constitutive model can be informed directly by the type of crosslinking mechanism and resultant network structure of the hydrogel, thus providing a chemophysical basis of the the choice of phenomenological constitutive model.
Methods We analyze existing experimental gelatin IMR datasets and compare the results with prior data on polyacrylamide.
Results We show that a Neo-Hookean Kelvin-Voigt (NHKV) model can suitably simulate the high-rate material response of dynamic, physically crosslinked hydrogels like gelatin, while the introduction of a strain-stiffening parameter through the use of the quadratic Kelvin-Voigt (qKV) model was necessary to appropriately model chemically crosslinked hydrogels such as polyacrylamide due to the nature of the static,covalent bonds that comprise their structure.
Conclusions In this brief we show that knowledge of the type of underlying polymer structure, including its bond mobility, can directly inform the appropriate finite deformation, time-dependent viscoelastic material model for commonly employed tissue surrogate hydrogels undergoing high strain rate loading within the ballistic and blast regimes.

Keywords Finite-deformation · Hydrogel · High strain rate · Cavitation

Introduction

Efforts to better understand internal organ injury due to high rate mechanical loading like those encountered in automobile crashes, military blasts, ballistic, and blunt impact scenarios often utilize soft hydrogels as surrogates for human tissues. Among them, gelatin, agarose and polyacrylamide formulations are some of the most commonly used materials as they replicate many of the physical traits, primarily the soft (i.e., elastic modulus < 100 kPa), viscoelastic properties of native tissues.

Hydrogels display a wide range of mechanical properties that are influenced by various factors that collectively shape the gel microstructure. This microstructure is primarily determined by the interactions between polymer chains as well as the density and type of primary crosslinks involved, either physical or chemical. Physical crosslinks can include chain entanglement, hydrophobic interactions, hydrogen bonding, or other ionic-type bonding. Chemical crosslinks, however, refer predominantly to covalent bonding [1, 2]. Beyond physical and chemical crosslinking, the chain interactions can be dynamic or static, which refers to the ability or inability of a bond to disassociate and reconnect with other binding sites. These factors collectively

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shape the bulk mechanical properties of various hydrogel formulations. The polymer chains within the hydrogel may originate from synthetic polymers or naturally occurring biopolymers, contributing to a diverse range of hydrogel properties and applications.

Here, we compare three commonly used biomimetic hydrogels: polyacrylamide (PAAm), gelatin, and agarose. PAAm is a chemically crosslinked gel comprised of static-covalent bonds [3]. Gelatin and agarose, however, both have physically bonded network structures. In gelatin, the polymer chains form into a triple helix structure via dynamic, hydrogen bonds [4]. While agarose is also formed from hydrogen bonds, its polymer chains form into double helices [5, 6] that aggregate extensively into a side-by-side, almost fibrillar structure. Each of these agarose aggregate structures contains between 10 to 10^4 helices [7]. These distinct microstructural differences significantly influence the mechanical behavior of the gels, necessitating the use of various constitutive models to accurately predict their behavior under different conditions.

In hydrogels with microstructures featuring static bonds, deformation energy is suggested to dissipate through the straightening and elongation of polymer chains [3], which will compound as more crosslinks become involved. This necessitates the inclusion of a strain-stiffening term in the constitutive model. Conversely, hydrogels comprised of dynamic bonds are characteristically weak because of the bond's ability to disassociate and rearrange in response to deformation [9]. While the weakness of these dynamic bonds is important for their self-healing capability, it almost always results in an inability to achieve a region of strain-stiffening before the network ruptures [8]. To examine these microstructural differences in the context of high-rate deformation mechanics, our study employs two constitutive models: the finite deformation Neo-Hookean Kelvin-Voigt model (NHKV) with a Neo-Hookean spring in parallel with a Newtonian dashpot, and the quadratic Kelvin-Voigt (qKV) model featuring a strain-stiffening hyperelastic spring alongside a Newtonian dashpot.

In the context of high strain-rate loading conditions, specifically ballistic and blast scenarios (i.e., $\dot{\epsilon} > 10^3$ 1/s), determining the finite-deformation viscoelastic properties remains challenging, largely due to the high compliance and large bulk (K) to shear modulus (μ) ratios, which render classical impact-based material characterization tests, such as Kolsky and pressure shear tests, difficult to implement [10–13]. To address this, we developed inertial microcavitation rheometry (IMR), which decouples the pressure and deviatoric stress fields, providing accurate means of estimating a material's shear modulus, even for large K/μ ratios. While IMR provides a general framework for the characterization of any transparent soft polymer (including tissues and hydrogels), it requires the user to select a particular constitutive model a priori. In return, this can create a lengthy optimization problem for identifying a best-fit material model. In response, we demonstrate that the underlying microstructure of the hydrogel cannot only inform an appropriate constitutive model choice, but also ensure that the best fit material properties from the bespoke constitutive model are physically representative and meaningful.

Methods

The laser-induced cavitation (LIC) data presented in Figs. 1 and 2, and Table 1 for both soft and stiff polyacrylamide gels was adapted from Yang et al. [14]. The raw bubble LIC data, i.e., bubble radius vs. time traces, for gelatin

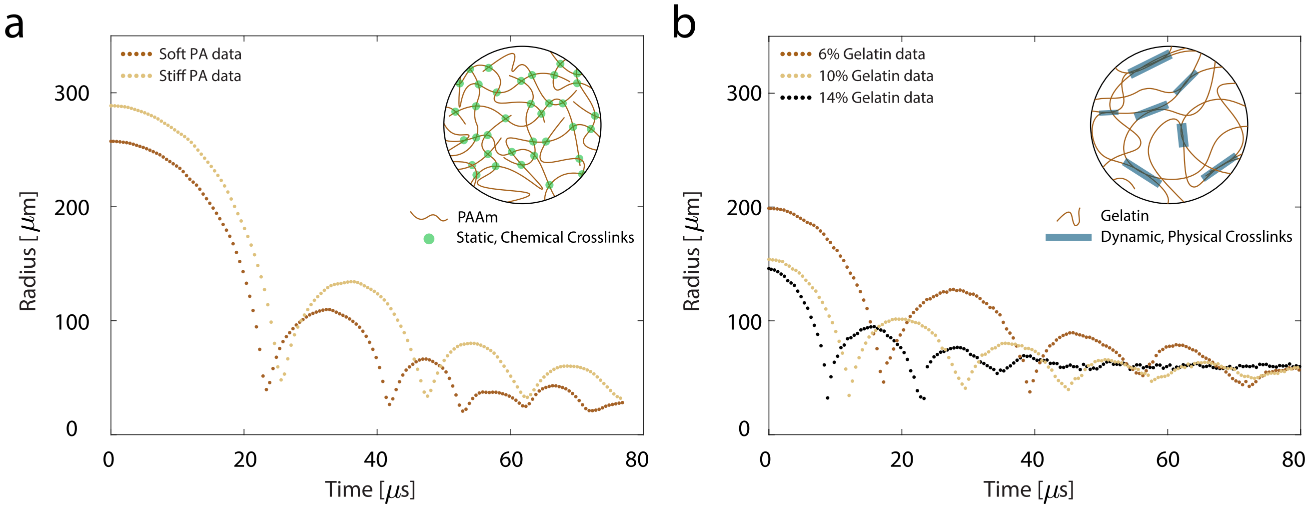

Fig. 1 Representative radius versus time curves alongside the appropriate microstructure in **a**) soft and stiff polyacrylamide and **b**) 6%, 10%, and 14% gelatin (data obtained from [13, 14])

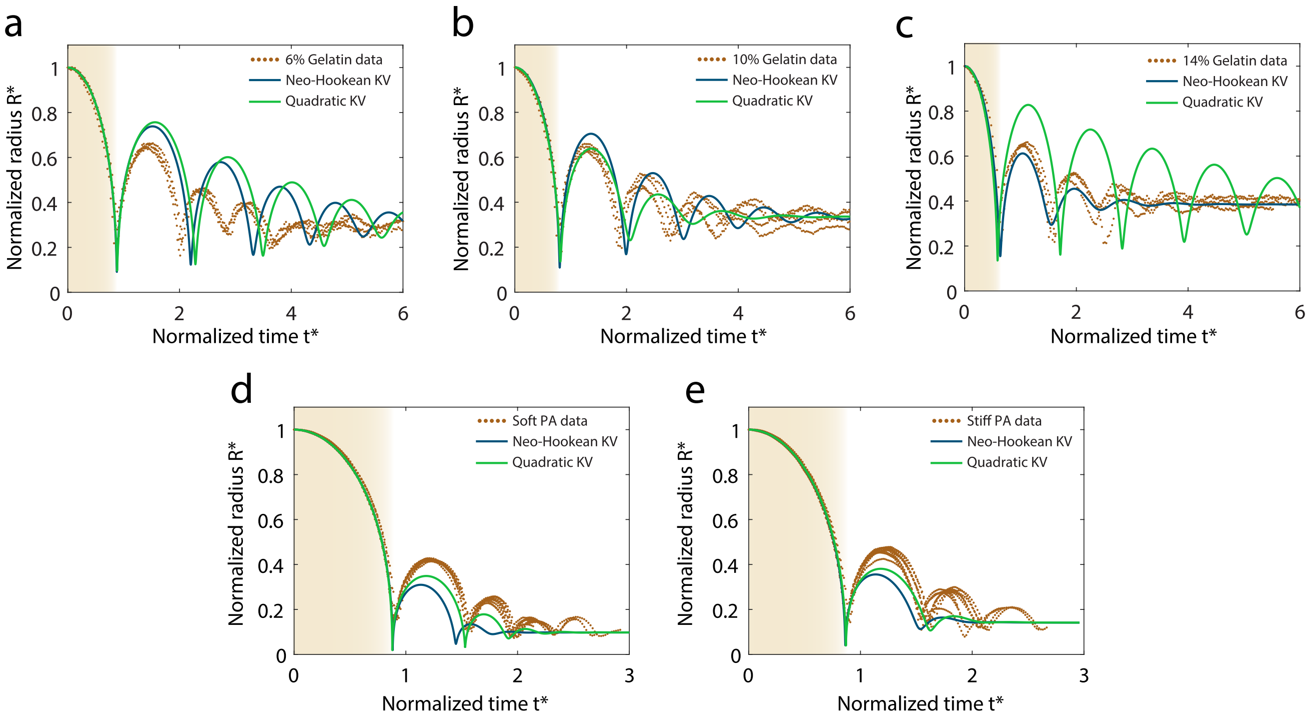

Fig. 2 Normalized bubble radius versus time curves with NHKV and qKV single peak material model fits overlaid for **a**) 6% Gelatin, **b**) 10% Gelatin, **c**) 14% Gelatin, **d**) Soft PAAm, and **e**) Stiff PAAm

gels were obtained from McGhee et al. [15] and analyzed in this brief via Eqs. (1)-(3) to determine the best constitutive material model and best-fit viscoelastic material properties (reported in Table 1). Finally, all LIC data on agarose gels reported in Table 1 was extracted from Yang et al. [16].

The theoretical framework of IMR has been detailed in our prior work [13–17], and is followed closely in this study to determine the viscoelastic material properties of gelatin gels. Briefly, within the IMR analysis framework, the cavitation bubble is modeled from its maximum radius to first collapse, where thermodynamic equilibrium is assumed and the 1D Keller-Miksis equation is used to describe the spherically symmetric motion of the bubble, which is provided in Eq. (1) [14, 16, 18, 19].

$$\left(1-\frac{\dot{R}}{c}\right)R\ddot{R}+\frac{3}{2}\left(1-\frac{\dot{R}}{3c}\right)\dot{R}^2=\frac{1}{\rho}\left(1+\frac{\dot{R}}{c}+\frac{R}{c}\frac{d}{dt}\right)\times\left(p_b-\frac{2\gamma}{R}+S-p_\infty\right) \tag{1}$$

R, $\dot{R}$, and $\ddot{R}$ are the bubble radius and its first and second time derivatives respectively. c is the longitudinal wave speed, ρ is the mass density of the surrounding material, p_b is the internal bubble pressure, γ is the surface tension, S

Table 1 Summary of IMR-fitted viscoelastic material properties for various soft materials over a strain rate envelope of $10^3\ \mathrm{s}^{-1} \sim 10^6\ \mathrm{s}^{-1}$

Material	Model	Concentration[%]	G_∞[kPa]	G[kPa]	μ[Pa· s]	α
Polyacrylamide[14]	qKV	3 (v/v)	0.57	-	0.060±0.057	0.96±0.058
	qKV	8 (v/v)	2.77	-	0.186±0.194	0.48±0.14
Agarose[16]	qKV	0.5 (w/w)	2.11±0.11	-	0.054±0.015	0.88±0.147
	qKV	1 (w/w)	12.38±0.14	-	0.21±0.032	0.46±0.051
	qKV	2.5 (w/w)	81.05±0.17	-	0.19±0.105	0.104±0.006
	qKV	5 (w/w)	333.63±0.11	-	1.06±0.053	0.054±0.006
Gelatin	NHKV	6 (w/v)	0.74±0.02	12.78±3.69	0.027±0.022	-
	NHKV	10 (w/v)	3.08±0.01	29.85±6.20	0.055±0.061	-
	NHKV	14 (w/v)	6.71±0.03	101.50±4.01	0.166±0.208	-

is the stress integral for the chosen material model, and p_∞ is the ambient pressure. For brevity, detailed descriptions of the composition of the internal bubble pressure, p_b, and its equation of state can be found elsewhere [13–17]. From our prior literature two particular constitutive formulations within the Kelvin-Voigt arrangement accurately represent the material stress integral term. The first, highlighted by Eq. (2), is the Neo-Hookean Kelvin-Voigt model (NHKV) featuring a hyperelastic, Neo-Hookean spring in parallel with a constant viscosity dashpot. The second is a simplification of the generalized Fung model, called the quadratic Kelvin-Voigt (qKV) model, which incorporates strain-stiffening, characterized by the parameter α into the hyperelastic spring (Eq. (3)) [14].

$$\begin{aligned} S_{NHKV} &= 2\int_R^\infty \frac{\sigma_{rr}-\sigma_{\theta\theta}}{r}dr \\ &= -\frac{G}{2}\left[5-\left(\frac{R_0}{R}\right)^4-4\left(\frac{R_0}{R}\right)\right]-\frac{4\mu\dot{R}}{R} \end{aligned} \tag{2}$$

$$\begin{aligned} S_{qKV} = &\frac{(3\alpha-1)G}{2}\left[5-\left(\frac{R_0}{R}\right)^4-4\left(\frac{R_0}{R}\right)\right]-\frac{4\mu\dot{R}}{R} \\ &+2\alpha G\left[\frac{27}{40}+\frac{1}{8}\left(\frac{R_0}{R}\right)^8+\frac{1}{5}\left(\frac{R_0}{R}\right)^5\right. \\ &\left.+\left(\frac{R_0}{R}\right)^2-\frac{2R}{R_0}\right] \end{aligned} \tag{3}$$

G is the rate dependent shear modulus (for NHKV), μ is the viscosity, R is the bubble radius, and R_0 is the equilibrium bubble radius. The same follows for qKV with a modification that G is now the rate independent ground state shear modulus, and α is a non-dimensional parameter governing the material's strain-stiffening.

Results & Discussion

To investigate whether a priori knowledge of the type of microstructure that exists in a given hydrogel could inform the best choice of phenomenological constitutive model, we evaluated prior obtained experimental data [14, 15] for gelatin and PAAm gels to contrast two conventional examples of statically bonded and dynamically bonded network structures. Figure 1(a) and (b) show representative curves for soft and stiff PAAm gels and various concentration gelatin gels respectively.

For networks with dynamic bond structures that are capable of rearranging in response to deformation, G can be represented by a Neo-Hookean spring (Eq. (2)-NHKV). However, to represent the chain elongation that occurs in networks comprised of static bonds, a fixed, ground state shear modulus alongside α, a non-dimensional parameter representing the degree of strain stiffening (Eq. (3)-qKV), is more appropriate phenomenologically. Recall that the dynamic shear modulus in the NHKV model is rate-dependent while the qKV model employs a rate-independent, ground state shear modulus. These hydrogel chemistries are depicted schematically in Fig. 1 and the stress integrals for the NHKV and qKV models are provided in Eqs. (2) and (3) respectively.

To evaluate which constitutive model best describes the inherent gel behavior, we fit the normalized radius-time curve starting from the point of maximum bubble radius to the first collapse using both the qKV and NHKV material models within the IMR framework (Eq. (1), Fig. 2). The results for Gelatin and PAAm hydrogels are presented in Fig. 2(a)–(e) respectively with normalized root mean squared errors given in Table S1.

In all cases the first collapse is similar between the curve fits, but model simulations utilizing the material properties obtained from those fits diverge appreciably beyond the first collapse. The reader should keep in mind that the current IMR theoretical framework depicted by Eq. (1) does not account for any type of material damage or explicit shock physics, meaning that any deviation of the data from a given radius vs. time past the first bubble collapse could have contributions of such physics present but currently not represented by the model. That is why all of our constitutive data fitting is generally constrained to the region from maximum bubble expansion to first collapse (Fig. 2, shaded region). In the case of gelatin, which features a highly dynamic bond structure, the NHKV model provides a much better representation of the material than the qKV model (Fig. 2(a)–(c)). There are pronounced visual similarties between the qKV and NHKV models as well as the NRMSE values associated with them, which seem in contradiction to our claims; however, the fits reflect unrealistically large and non-physical values for the qKV model [Table S1]. This result is consistent with the understanding that dynamic bonds rearrange in response to deformation [9] and are, in most cases, too weak to achieve a region of strain stiffening prior to yielding [8, 20]. Both 'soft' and 'stiff' PAAm hydrogels, however, show a strong preference to the qKV model when compared to NHKV (Fig. 2(d) and (e)). Literature regards PAAm as a strain-stiffening material, postulating it as a consequence of the static bond structure and subsequent polymer chain elongation [3, 8]. Thus, these results are in clear agreement with existing literature. Finally, the best fit material parameters for each most appropriate constitutive model are provided in Table 1.

It is noteworthy to discuss how agarose diverges from the conventional dynamic bond response presented in this brief. Agarose, at its core, is formed from dynamic, hydrogen bonds, not unlike gelatin. However, the double helical polymer chains in agarose will aggregate extensively into a fibrillar-like structure [7]. This will significantly reduce the ability of the hydrogel to rearrange while increasing its strength and presenting a response more akin to a network of static bonds. As a result Yang et al. showed that while both the qKV and NHKV models could be used to characterize agarose gels, the qKV model provides slightly better agreement with experimental data over the range of reported (Table 1) concentrations, which is consistent with prior literature reporting significantly constrained polymer chain mobility in agarose gels [5].

Conclusion and Future Directions

We present high strain rate ($\dot{\epsilon} > 10^3$ 1/s) constitutive properties of commonly employed polyacrylamide, agarose and gelatin gels across the ballistic and blast relevant regimes obtained via IMR. Our study demonstrates that understanding the microstructure and crosslinking mechanism, such as physical with dynamic or static links vs. chemical with static links, can have significant implications in selecting the appropriate constitutive model for a specific hydrogel. In the context of IMR, this prior knowledge can efficiently estimate the most suitable material model, saving significant time and effort and ensuring that the determined high strain-rate material properties are accurate and physically meaningful.

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Declarations

Conflicts of Interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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