Viscoplastic Fracture Transition of a Biopolymer Gel

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1 Volume fraction

The volume fraction (ϕ) of the gelatin component can be calculated based on the measured mass of the gelatin ($m_{gelatin}$) and water (m_{water}), and the density for gelatin ($\rho_{gelatin} = 1.35 g/cm^3$) and water ($\rho_{water} = 1.00 g/cm^3$).

$$\phi = \frac{\frac{m_{gelatin}}{\rho_{gelatin}}}{\frac{m_{gelatin}}{\rho_{gelatin}} + \frac{m_{water}}{\rho_{water}}} \tag{1}$$

2 Elastic modulus

2.1 Shear modulus of gelatin from CMT

From CMT, we can obtain the plane-strain elastic modulus, $E = \bar{E}(1-\nu^2)$ (assuming an incompressible elastic solid, $\nu = 0.5$). This is easily obtained by relating the stiffness from the load (p) vs. displacement (δ) plot,

$$\frac{\Delta p}{\Delta \delta} = 2\bar{E}a \tag{2}$$

From Eq. (9.37) of Rubinstein & Colby[1], we can derive relationships between shear modulus and polymer network dimensions. Specifically, the shear modulus (μ) is related to the polymer volume fractions (ϕ_0, ϕ) and the average number of monomer units per chain (N). For a polymer network that is swollen in a good solvent ($T > \theta$) and θ-solvent ($T = \theta$),

$$\mu \approx \frac{k_B T}{a^2 \xi} \tag{3}$$

a is the diameter of the Edwards tube and $a^2\xi$ is the occupied volume of either a network strand of an unentangled network ($N < N_e$) or an entangled network ($N > N_e$), thus,

$$a^2\xi \approx \begin{cases} \xi^3 & \text{for } T > \theta, N < N_e \\ a_1^2 \phi^{-\frac{4}{3}} \xi & \text{for } T = \theta, N > N_e \end{cases} \tag{4}$$

where a_1 is the Edwards tube diameter in the melt state. Recall from the manuscript that,

$$\xi \approx \begin{cases} R_F \left(\frac{\phi^*}{\phi}\right)^{\frac{3}{4}} = b\left(\frac{\mathrm{v}}{b^3}\right)^{-\frac{1}{4}} \phi^{-\frac{3}{4}} & \text{for } T > \theta \\ b\phi^{-1} & \text{for } T = \theta \end{cases} \tag{5}$$

Substituting Eq. (3) and Eq. (4) into Eq. (2) yields,

$$\mu \approx \mu_o \begin{cases} \phi^{\frac{9}{4}} & \text{for } T > \theta, N < N_e \\ \phi^{\frac{7}{3}} & \text{for } T = \theta, N > N_e \end{cases} \tag{6}$$

For an isotropic material, the shear modulus is related to the Young's modulus (E) by the Poisson's ratio (ν),

$$E = 2(1+\nu)\mu \tag{7}$$

In other words, $\bar{E}$ scales similarly with the polymer volume fraction.

3 Fracture energy

3.1 Determination of energy release rate from CR

From CR, we can measure the critical pressure (P_f) when a flaw grows into an unstable crack of infinite size[2],

$$G_c \cong \frac{3P_f^2 r}{\pi E} \tag{8}$$

Once E is quantified and r is measured, we can use Eq. (14) to quantify G_c.

3.2 Lake-Thomas fracture theory for gels

G_c has been empirically shown numerous times that it is a testing rate-dependent quantity. The generic form for elastomers is,

$$G_c = G_o(1 + \Phi(a_T V)) \tag{9}$$

Eq. (9) assumes that 1) chain scission occurs and 2) the material ahead of the crack tip experiences a range of strain rates across its entire relaxation spectrum thus the assumption of bulk viscoelasticity (WLF shift factor, a_T) is the appropriate mode of energy dissipation here.

For gels whose fracture behavior can be considered as non-dissipative, we can use the Lake-Thomas theory to describe the fracture of gelatin. According to the Lake-Thomas theory, the zero-rate energy release rate (G_o) (according to H. Xin *et al.*[3]) is defined as,

$$G_o = N\Gamma U \tag{10}$$

where N is again the number of monomers that make up a polymer chain that is loaded in tension prior to fracture, Γ is the areal density of polymer chains that crosses the crack plan per area of crack, and U is the bond dissociation energy (J/mol.). In comparing Eq. (9) and Eq. (10), $G_c(V = 0) \cong G_o$.

N and Γ are the parameters that scale with gelatin concentration and solvent quality. As suggested by Baumberger *et al.*[4],

$$\Gamma \cong \frac{1}{\xi^2} \tag{11}$$

From Eq. (6) and Eq. (8) of Obukhov *et al.*[5], N is related to ϕ as,

$$N \approx \begin{cases} \phi^{-\frac{5}{4}} & \text{for } T > \theta, N < N_e \\ \phi^{-\frac{4}{3}} & \text{for } T = \theta, N > N_e \end{cases} \tag{12}$$

Substituting Eq. (5), Eq. (11), Eq. (12) into Eq. (10) yields,

$$G_c \approx \Gamma N U \approx \frac{U}{b^2} \begin{cases} (1-2\chi)^{\frac{1}{2}} \phi^{\frac{1}{4}} & \text{for } \phi \leq \phi_e \\ \phi^{\frac{2}{3}} & \text{for } \phi > \phi_e \end{cases} \tag{13}$$

3.3 Poroelastic-type fracture of gels

For gels that display dissipative fracture behavior such as viscoelasticity or poroelasticity, rate dependent effects can play a significant role. Previously, Baumberger and coworkers[4] showed that gelatin gels undergo viscoplasticity during fracture. This viscoplastic process is a poroelastic-type process since the authors used Biot's theory of poroelasticity for gels to derive the relevant relationships, and we will refer this mechanism of fracture in gelatin gels as a poroelastic fracture process.

Specifically, the fracture energy (G_{vis}) is related to the hydrodynamic friction of the gelatin chains being pulled out of the network junctions and then traversing across effective "tubes" formed by the gelatin mesh network. The dimensions of these "tubes" is defined by the mesh size (ξ_M) of the gelatin network. The stress at the crack tip is defined as,

$$\sigma_{tip} \approx \sigma_o + \sigma_{vis} \tag{14}$$

We can safely assume that the gelatin/water motions are diffusive, thus the pull-out of the chain across the mesh can be described as poroelasticity, *i.e.* motion of the chain relative to fluid motion. Therefore, we can approximate σ_{vis} as,

$$\sigma_{vis} \approx l\nabla P \tag{15}$$

where l is the contour length of the gelatin chain and ∇P is the pore pressure in Darcy's law. According to Darcy's law, the pore pressure is related to the volumetric flow rate (J) and mesh size according to the following,

$$J = -\frac{{\xi_M}^2 A}{\eta}\nabla P \tag{16}$$

Here, A is the total area of permeation and η is the fluid viscosity. Note that this flux is the fluid flux but we are interested in the motion of the gelatin chains, which means the sign should be the opposite, which implies this is a cooperative exchange process between the solvent and the polymer chain. Additionally, this derivation assumes dilute/semi-dilute solution conditions. If the polymer chains were entangled, l is likely not the relevant length-scale since polymer reptation has to considered. Thus this model should not be applicable for entangled polymer gels.

We don't have direct information about J but we can approximate it using an average chain pull-out velocity, $\dot{\delta} = \beta V$. In other words, we will assume that,

$$\frac{J}{A} \approx \dot{\delta} \tag{17}$$

Substituting Eq. (20) and Eq. (21) into Eq. (19) yields,

$$\sigma_{vis} \approx \beta\eta V\left(\frac{l}{{\xi_M}^2}\right) \tag{18}$$

The fracture energy expression is defined by Eq. (9). For this poroelastic fracture model, the relationship is,

$$G_c \approx G_o + G_{vis} \tag{19}$$

where $G_{vis} = \sigma_{vis} l$ accounts for the energy dissipation due to viscoplasticity. Both terms in Eq. (19) are derived based on a Dugdale-type fracture model. The expression for G_{vis} is,

$$G_{vis} \approx \beta\eta V\left(\frac{l}{\xi_M}\right)^2 \tag{20}$$

In terms of ϕ when $\phi \leq \phi^*$,

$$G_{vis} \approx \beta\eta V\left(\frac{l}{b}\right)^2 \phi^{\frac{3}{2}} \tag{21}$$

In Biot's theory of poroelasticity, the hydraulic permeability for a polymer gel is the mesh size (ξ_M^2), which is related to the materials properties of the gel as,

$$\xi_M{}^2 \approx \frac{\eta D_c}{\mu} \tag{22}$$

Substituting Eq.(**??**) into Eq.(24),

$$G_{vis} \cong \frac{\beta V l^2}{D_c} \mu \tag{23}$$

If we assume that D_c is independent of the polymer concentration, which is one of the assumptions in Biot's theory of poroelasticity[6], Eq.(23) implies that G_{vis} is directly correlated with μ. Experimental results suggest that D_c is primarily concentration independent at low to moderate polymer fraction[7,8].

Since we know the scaling relationship between μ and ξ, Eq.(23) becomes,

$$G_{vis} \cong \frac{k_B T \beta V l^2}{D_c \xi^3} \tag{24}$$

In relation to ϕ,

$$G_{vis} \cong \frac{k_B T \beta V l^2}{D_c b^3} \phi^{\frac{9}{4}} \tag{25}$$

We note that the derivation to this poroelastic-dominated fracture mechanism is only valid according when $\phi < \phi_e$.

4 Kratky Plots

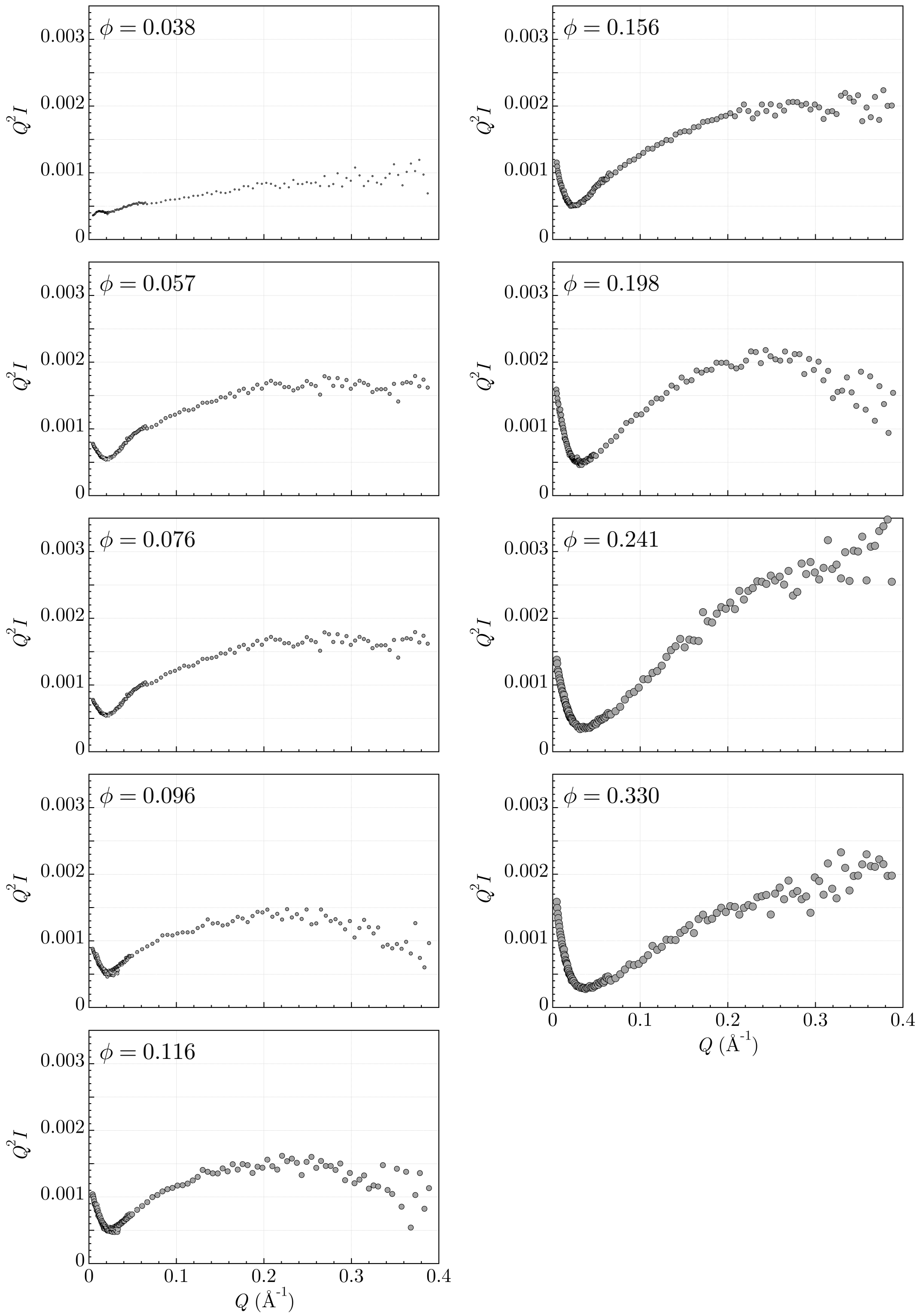

Figure S1: Kratky plots ($Q^2 I(Q)$ vs. Q) of the gelatin gels.

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