Soft Matter

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Supplementary Information: Linking Cavitation and Fracture to Molecular Scale Structural Damage of Model Networks

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1 Supplementary Videos

The supplementary videos associated with this paper are listed below.

- Supplementary Video SV4_1: Video of NIC on a PEG gel when $RE/G_c = 0.84$.
- Supplementary Video SV4_2: Video of NIC on a PEG gel when $RE/G_c = 0.37$.
- Supplementary Video SV4_3: Video of NIC on a PEG gel when $RE/G_c = 0.27$.
- Supplementary Video SV4_4: Video of NIC on a PEG gel when $RE/G_c = 0.02$.

2 Scaling the Elastofracture Length

The scaling in Equation 6 of the main text is derived by taking the ratio of Equations 4 and 5.

$$\frac{G_{c,RENT}}{E_{RENT}} = \frac{\nu R_{ee,o} NU \left(\frac{F_{eff}}{F_{eff}-2}\right)^{\frac{1}{2}}}{3\nu k_b T \left(\frac{\phi_o^{\frac{1}{3}} R_{ee,o}}{\phi^{\frac{1}{3}} R_{ee}}\right)^2 \left(\frac{F_{eff}-2}{F_{eff}}\right)}$$

ν cancels and F_{eff} terms combine to get,

$$\frac{G_{c,RENT}}{E_{RENT}} = \frac{R_{ee,o} NU \left(\frac{F_{eff}}{F_{eff}-2}\right)^{\frac{3}{2}}}{3k_b T \left(\frac{\phi_o^{\frac{1}{3}} R_{ee,o}}{\phi^{\frac{1}{3}} R_{ee}}\right)^2}.$$

As the materials are tested at the reaction conditions and no additional swelling or drying step is used $\phi = \phi_o$, which cancels the term in the denominator.

$$\frac{G_{c,RENT}}{E_{RENT}} = \frac{R_{ee,o} NU \left(\frac{F_{eff}}{F_{eff}-2}\right)^{\frac{3}{2}}}{3k_b T}.$$

The end-to-end distance $R_{ee,o}$ has a weak ϕ dependence in a good solvent $R_{ee,o} = b\sqrt{N}\phi_o^{-\frac{1}{8}}$.[1]

$$\frac{G_{c,RENT}}{E_{RENT}} = \frac{b\sqrt{N}\phi_o^{-\frac{1}{8}} NU \left(\frac{F_{eff}}{F_{eff}-2}\right)^{\frac{3}{2}}}{3k_b T}.$$

Combining N terms gives the final scaling relationship presented in Equation 6 of the main text.

$$\frac{G_{c,RENT}}{E_{RENT}} = \frac{bN^{\frac{3}{2}}\phi_o^{-\frac{1}{8}} U \left(\frac{F_{eff}}{F_{eff}-2}\right)^{\frac{3}{2}}}{3k_b T} \sim N^{\frac{3}{2}}\phi_o^{-\frac{1}{8}} \left(\frac{F_{eff}}{F_{eff}-2}\right)^{\frac{3}{2}}$$

3 DMA of PEG Gels

The dynamic response of the PEG gels was characterized on a TA Instruments Discovery DMA 850. The gels had 4.5 mm and 1.6 mm radius and height, respectively, and were compressed between two steel platens. Frequency sweeps were performed over the range of 0.01-100 Hz. The 4 kg/mol PEG gel was formed at 50 mg/mL and probed with a preload of 1 N and a strain amplitude of 0.08%. The 12 kg/mol PEG gel was formed at a concentration of 100 mg/mL and probed with a preload of 1 N and a strain amplitude of 0.092%. Note that the 12 kg/mol PEG gel was formed at a concentration of 100 mg/mL which is higher than the concentration used in NIC (77 mg/mL).

Plots of storage E' and loss E'' modulus against frequency are

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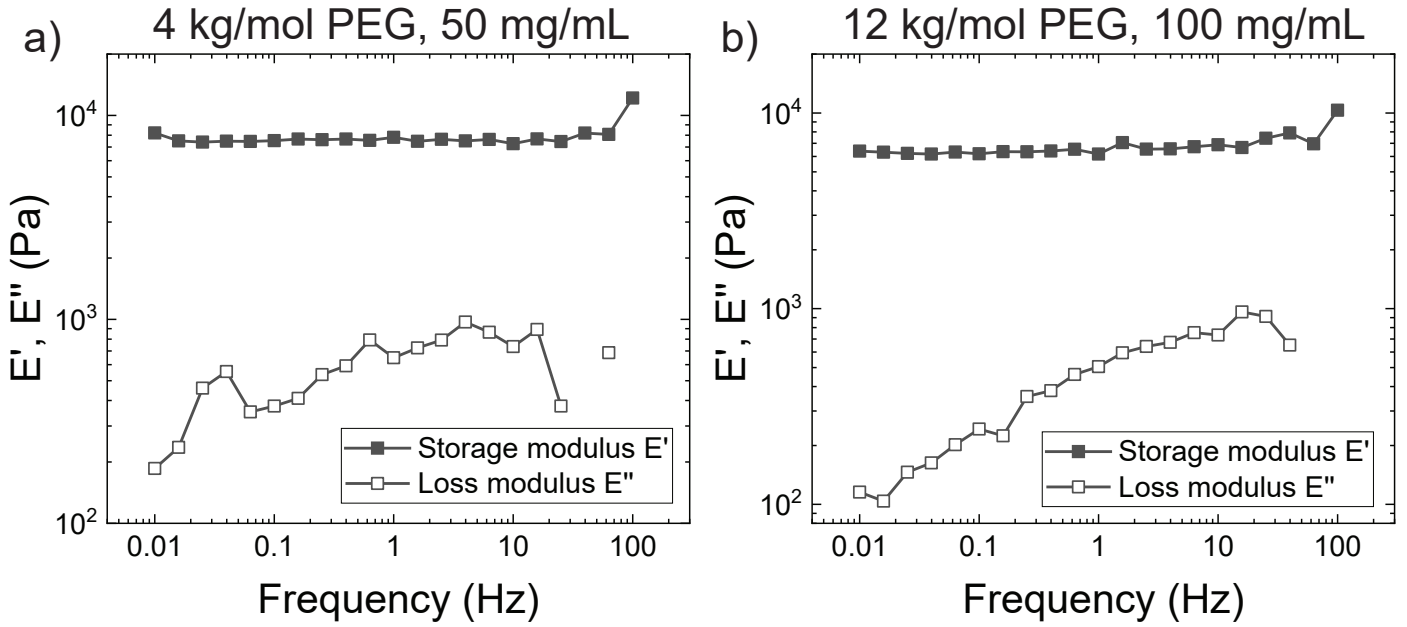

Fig. S1 Frequency sweep DMA data for a) 4 kg/mol PEG gel formed at a concentration of 50 mg/mL and b) 12 kg/mol PEG gel formed at a concentration of 100 mg/mL.

shown in Figure S1 for a) the 4 kg/mol PEG gel formed at 50 mg/mL and b) the 12 kg/mol PEG gel formed at 100 mg/mL. The 4 kg/mol PEG gel is observed to be highly elastic with E' being an order of magnitude greater than E'' over the entire frequency range. E' is also observed to be largely independent of frequency in the 4 kg/mol PEG gels. The 12 kg/mol PEG gel is observed to be highly elastic with E' being an order of magnitude greater than E'' over the entire frequency range. E' is also observed to be largely independent of frequency in the 12 kg/mol PEG gels.

4 Ultimate Extension of PEG Networks

The maximum stretch that a polymer network can achieve in the presence of solvent $\lambda_{max,wet}$ has been considered previously by Akagi et al.[2] In the dry state, this quantity can be estimated by taking the ratio of the contour length to the end-to-end distance of a polymer chain in the reference state (taken as the dry state in this model).

$$\lambda_{max,dry} = \frac{R_{ee,max}}{R_{ee,o}} \tag{1}$$

A network chain has a constant finite length so any change in maximum stretch must be driven by an increase in the unstrained end-to-end distance. Here we estimate this change through the use of a swelling ratio λ_s.

$$\lambda_{max,wet} = \frac{R_{ee,max}}{\lambda_s R_{ee,o}} \tag{2}$$

Estimating $\lambda_s = \phi^{-\frac{1}{3}}$ and substituting in for $R_{ee,max}$ and $R_{ee,o}$ gives

$$\lambda_{max,wet} = \phi^{\frac{1}{3}} \frac{b\frac{V_{PEG}}{V_{Ref}}N}{b\sqrt{\frac{V_{PEG}}{V_{Ref}}N}} = \phi^{\frac{1}{3}}\sqrt{\frac{V_{PEG}}{V_{Ref}}N}, \tag{3}$$

where $V_{PEG} = 0.069\ nm^3$ is the PEG monomer volume, $V_{Ref} = 0.1\ nm^3$ is the reference volume, and N is taken as the number of PEG monomers.[3] The convention here of taking the ratio of a monomer volume to a reference volume is taken from Eitouni and Balsara[3] which enables the estimation of the number of Kuhn segments from the number of chemical monomer units.

Note that Equation (3) is different from that estimated by Akagi et al. where a semi-empirical scaling argument was used to estimate the altered end-to-end distance.

$$\lambda_{max,wet} \sim N^{\frac{2}{3}}\phi_o^{\frac{1}{3}} \tag{4}$$

Each estimate of $\lambda_{max,wet}$ is plotted as an explicit model against the maximum stretch data gathered by Akagi et al. from uniaxial extension on tetra-PEG hydrogels in Figure S2.[2] In Figure S2a), the dark gray squares show a comparison to the model developed in this work while the red squares show a comparison to the model, developed only as a scaling relationship and not an explicit model, by Akagi et al.[2] A comparison between each model and data shows that the model developed in this work gives a better estimate than the scaling relationship developed by Akagi et al.[2] Figure S2b) shows the data from Akagi et al. plotted against only the model from this work. It is apparent from the agreement that this model is a reasonable estimation of the maximum stretch of a network in the presence of solvent. Estimating $\lambda_{max,wet}$ for the 12 kg/mol PEG gels used in this work give a value of 5.5.

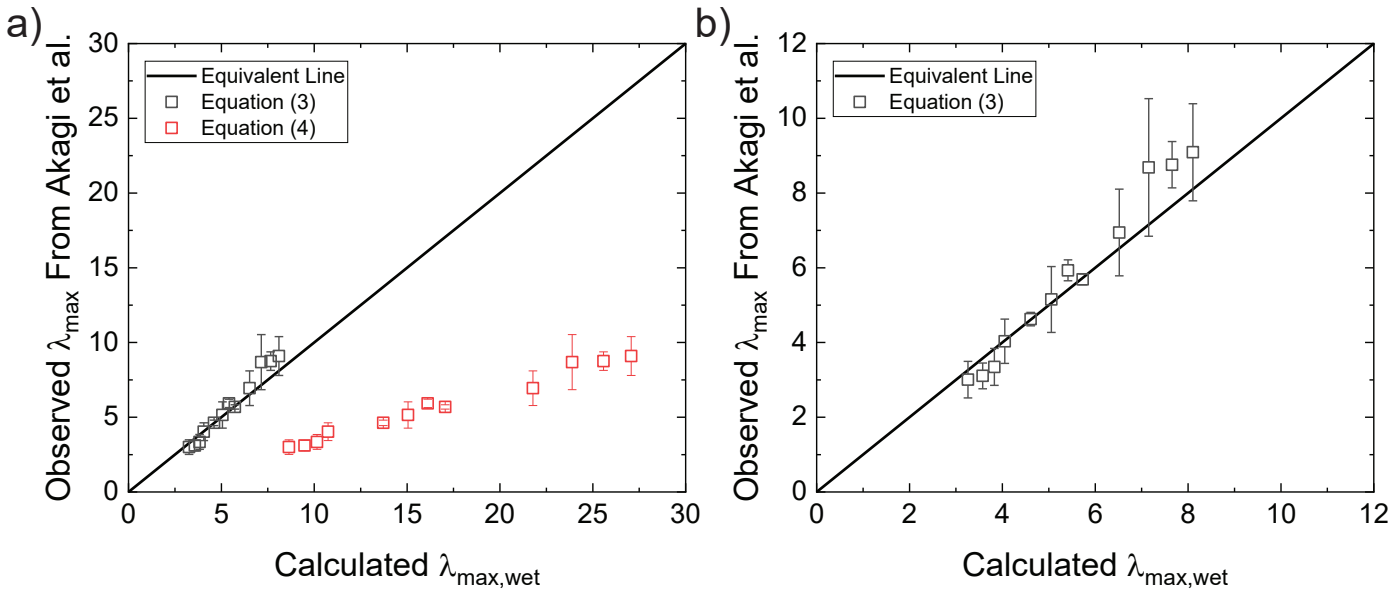

Fig. S2 a) Plot of the maximum observed stretch during uniaxial extension of tetra-PEG hydrogels gathered by Akagi et al.[2] against the max stretch calculated from the model in this work (Equation (3)) and the scaling relationship from Akagi et al. b) Plot of the same data against only the model developed in this work (Equation (3)).

5 Summary Data

Table 1 contains a summary of the data gathered in this work.

Table 1 Summary of data gathered in this work.

E (kPa)	G_c (N/m)	$\frac{RE}{G_c}$	P_c (kPa)
9.8	8.12	0.89	4.18
9.4	8.12	0.85	6.52
9.2	8.12	0.84	6.31
9.7	8.12	0.28	9.04
13.1	8.12	0.37	10.57
10.1	8.12	0.29	4.90
14.0	8.12	0.27	12.5
9.5	8.12	0.18	17.02
14.4	8.12	0.28	11.35
4.6	40.5	0.017	7.53
5.8	40.5	0.022	7.32
5.5	40.5	0.021	8.58
6.6	40.5	0.025	9.61

References

1 S. P. Obukhov, M. Rubinstein and R. H. Colby, *Macromolecules*, 1994, **27**, 3191–3198.

2 Y. Akagi, T. Katashima, H. Sakurai, U. I. Chung and T. Sakai, *RSC Advances*, 2013, **3**, 13251–13258.

3 H. B. Eitouni and N. P. Balsara, *Physical Properties of Polymers Handbook*, 2006, pp. 339–356.