SUPPORTING INFORMATION

Thermoresponsive Supramolecular Hydrogels with High Fracture Toughness

Fei Wang and R. A. Weiss*

Department of Polymer Engineering, University of Akron, Akron, OH 44325

Part 1: Video of pure shear test for notched NF10 hydrogel.

Part 2: Calculation of crosslink density of the NFx hydrogels.

An effective crosslink density of the supramolecular hydrogels was calculated from the phantom network model[1] for rubber elasticity using the tensile modulus data, assuming a Poisson ratio of 0.5 and using the volume of the swollen hydrogel as the reference volume.

$$G = \frac{E}{3} = \left(1 - \frac{2}{f}\right) \nu_e RT \phi_2^{\frac{1}{3}} \qquad (S1)$$

where G is the shear modulus, ν_e is the crosslink density, f is the functionality of the crosslinks and ϕ_2 is the volume fraction of polymer in the fully swollen hydrogel,

$$\phi_2 = \left[1 + \frac{(q-1)\rho}{d}\right]^{-1} \qquad (S2)$$

Where q is the swelling ratio (mass of hydrogel/mass of dry polymer), d is the solvent (water) density (1.00 g·cm^{-3}) and ρ is the density of the dry NFx copolymers (1.21 g·cm^{-3}, 1.25 g·cm^{-3}, 1.28 g·cm^{-3} and 1.34 g·cm^{-3} for NF5, NF8, NF10 and NF14, respectively).

Each FOSA group is attached to two NIPAM chains, so each FOSA—FOSA supramolecular bond produces four network chains. Thus the functionality, f, of a nanodomain crosslinks is twice the number of FOSA groups within the nanodomain (N_{agg}). Values for N_{agg}, determined by small angle neutron scattering[2] for NF5, NF10 and NF10 hydrogels at temperatures between 9°C and 13°C vary from ~29 – 59, values of f for the NFx hydrogels used in the present study were estimated to be $f = 2N_{agg}$ ~60 – 120. Thus, the $2/f$ term in Equation (1) is essentially negligible and

$$\nu_e \approx \frac{E}{3RT\phi_2^{1/3}} \qquad (S3)$$

Part 3: Tensile tests of samples with various notch sizes (crack lengths)

Pure shear tests following the method described by Rivlin and Thomas[3] and using the same type of specimen used for the pure shear tests described in the paper, except that the crack length, c, was varied were used to calculate the fracture energy of the NF10 hydrogel. Figure S1 shows the measured tensile force, F, vs. strain for NF10 specimens with initial crack lengths of 1 – 9 mm. The work, W, required to deform that sample to a specific strain, ε_L, is the area under the F-ε curves integrated to $\varepsilon = \varepsilon_L$. Figure S2 shows the initial crack length dependence on W measured at a constant strain of $\varepsilon_L = 476\%$, which was the fracture strain for the sample with the 9 mm notch. The W-c data were fit with a linear least squares regression, solid line in Figure S2, and the slope of the line was $\left(\frac{\partial U}{\partial c}\right)_{\epsilon_L}$ = -(4.62 ± 0.76) J/m. The fracture energy is given by equation (S4)[3].

$$\Gamma = -\frac{1}{t}\left(\frac{\partial U}{\partial c}\right)_{\epsilon_L} \qquad (S4)$$

where t = specimen film thickness. In this case Γ = 6.3 ± 1.0) kJ/m^2, which is comparable to the value determined from the pure shear analysis of Suo et al.[4] of Γ = 7.8 ± 1.1) kJ/m^2.

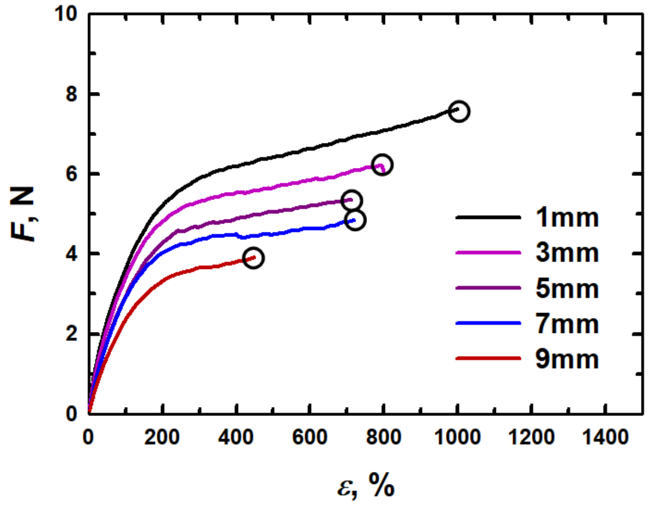

Figure S1. *F* versus strain curves at 5°C for NF10 hydrogel samples with various notch length. The circles indicate the strain at which the notch began to propagate.

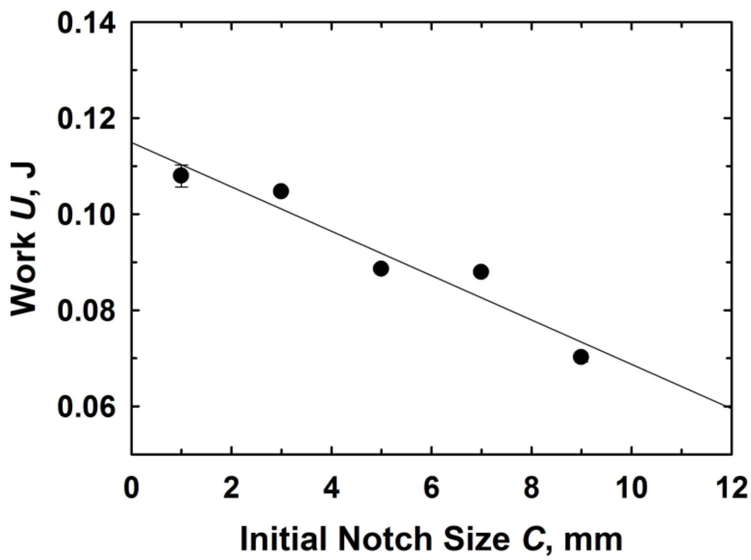

Figure S2. Work *U* versus initial notch size *C* for the NF10 hydrogel at 5°C. A linear least squares fit is shown. The slope is $\left(\frac{\partial U}{\partial c}\right)_{\epsilon_L}$ = -(4.62 ± 0.76) J/m.

References

1. Treloar, L. R. G. *The Physics of Rubber Elasticity*; Oxford University Press, 1975.

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3. Rivlin, R. S.; Thomas, A. G. Rupture of rubber. I. Characteristic energy for tearing. *J. Polym. Sci.* 1953, *10*, 291.

4. Sun, J.-Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H. O.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. Highly stretchable and tough hydrogels. *Nature* **2012**, *489*, 133.