Cohesive Failure in Partially Cured Epoxies

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ABSTRACT: The critical stress intensity factors of partially cured epoxies were measured with notched three-point bend fracture specimens and exhibited a strong dependence upon cross-link density, increasing by more than an order of magnitude over the wide range in extent of reaction probed. In fact, the critical stress intensity factor appears to vanish at the gel point with a critical exponent, reminiscent of predictions from percolation theories of gelation.

I. Introduction

We need to offer a good reason for presenting yet another investigation into the cross-link dependence of thermoset cohesive failure given the huge number of studies already performed. While the literature does abound with such investigations,[1−5] we feel that two key features have been neglected. First, it is imperative to probe this dependence at a fixed temperature difference below the glass transition temperature to normalize viscoelastic relaxations. Second, a wide range of cross-link densities must be probed to determine this dependence accurately. These two requirements are obviously linked, since the glass transition temperature, T_g, is a function of cross-link density, and gross differences in cross-link densities imply clearly distinct T_g's.

It seems necessary to explain the need for performing these failure tests at a constant $T-T_g$ since few experiments follow this rule. Certainly, it is agreed that plastic deformation (nonlinear viscoelastic relaxation) is important in determining the magnitude of the critical stress intensity factor. It is also well-established[6] that the linear viscoelastic relaxation spectra for polymers of differing T_g's are identical at their respective T_g's. We will show below that the nonlinear relaxation spectra scale with T_g as well. Therefore, it is reasonable to break polymers at a constant $T-T_g$ to ensure identical viscoelastic conditions if we wish to investigate only the cross-link density dependence of fracture. The T_g of our epoxy in this study changed by almost 60 °C as cross-link density was varied, and failure to test at constant $T-T_g$ would cloud the cross-link density dependence with a nonnegligible temperature dependence.

The cross-link density dependence will also certainly be more apparent if a wide range in cross-links is probed. A number of experimental approaches have been employed to vary the network cross-link density. In perhaps the most common approach, the molecular weight of the precursor resin is varied, and the reaction is cured to completion.[1] While easily accomplished, the change in cross-link density that can be achieved is quite small. For example, readily available epoxy resin molecular weights vary by a factor of roughly 5. One could instead change the reactant stoichiometry and cure to completion,[2] and the variation in cross-link density is now much greater. However, a more subtle problem arises. As we change stoichiometry, the local molecular environment changes which, in turn, induces a change in the viscoelastic friction factor. For example, the constants in the WLF equation[6] describing the temperature dependence of the relaxation times change with stoichiometry. This makes our efforts to normalize viscoelastic relaxations more difficult, since even holding $T-T_g$ constant does not ensure identical conditions. Similar concerns arise if the type of resin or cross-linker is varied to affect the change in cross-link density.[3]

By quenching the cross-linking reaction,[4,5] we can induce a huge change in cross-link density. This technique is obviously simple and avoids gross changes in the friction factor. In addition, it actually represents the change in the thermoset during cure and is practically important. It may seem to suffer from two flaws, however. First, the system must react slowly enough to enable us to halt the reaction completely by a quench into the glass at a well-defined time. Fortunately, many such systems are available. Second, the relationship between extent of reaction and the structure and viscoelasticity of the network may seem unclear. We have recently elucidated these relationships[7] and will summarize them below.

II. Evolution of Viscoelasticity during Cross-Linking

For several years now, we have investigated the evolution of structure and viscoelasticity during the cure of thermosets.[7] A brief summary of these findings could be useful in interpreting our fracture data. The gel point of cross-linking systems defines the topological transition from a liquid to a solid. Before the gel point, the sol clusters increase in size which, in turn, increases the viscosity. At the gel point, one of these clusters spans the reaction vessel, and yet, almost all monomers are still in the sol. As the reaction progresses past the gel point, these unattached sol clusters react with the infinite cluster, increasing the gel fraction and the equilibrium modulus of the gel. At the gel point, the system simultaneously exhibits a inifinite viscosity and infinitesimal modulus.

From experiments on several epoxies, we have determined that percolation theory adequately describes the

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evolution of structure in thermosets. In percolation computer simulations, one mimics reaction by placing monomers on nodes of a lattice and then randomly connecting them. The computational bond probability is related to the chemical extent of reaction. Percolation proposes several interesting structural features for the evolving thermoset. Most important is that the critical gel (i.e., the systems exactly at the gel point) exhibits topological self-similarity. That is, the structure of a piece of the critical gel examined at successively higher magnifications is independent of the magnification (until molecular details emerge). A mathematical consequence of this self-similarity is that evolving structural quantities adopt power-law functional dependences on the reduced bond probability. For example, the weight-averaged molecular weight (as measured by static light scattering) diverges as it approaches the gel point by the functional form $M_w \sim \epsilon^{-\gamma}$. The reduced bond probability, ϵ, is given by $|b - b_c|/b_c$ where b is the current bond probability and b_c is that at the gel point. Experiments at Sandia have validated these relationships with quantitative agreement for the exponents.

This structural self-similarity has implications for *viscoelasticity*, and dynamic quantities should also display power-law divergences. For example, the viscosity should diverge as $\eta \sim \epsilon^{-k}$. We have modified the simple bead–spring (Rouse) model of polymer dynamics to account for the fractal nature and broad polydispersity of the percolation clusters and developed a unique theory for gel *dynamics* which now predicts the magnitudes of these critical exponents. Again, experiments agree well with these predictions through the entire course of reaction.

One such validated viscoelastic prediction[7] states that the equilibrium modulus, G_∞, increases past the gel point as

$$G_\infty = G_\infty^{f}\left(\frac{b - b_c}{1 - b_c}\right)^{2.67} = G_\infty^{f}\epsilon^{2.67} \qquad (1)$$

where G_∞^{f} is the modulus at reaction completion. Equation 1 can be rewritten as $G_\infty = f\rho RT/M_z$ where f is the gel fraction (that fraction of the monomer attached to the infinite cluster at a given extent of reaction past the gel point) and M_z is the z-averaged molecular weight of the sol fraction. This relationship is commonly used in the literature for nearly fully reacted networks in the form $G_\infty = \rho RT/M_c$ where M_c is the "molecular weight between cross-links".

We hope that this brief summary suggests that actually quite a bit is known about the structure and viscoelasticity of curing thermosets, and therefore, performing fracture tests on partially cured epoxies is more controlled than perhaps previously assumed. From an historical viewpoint, our interest in the cohesive failure properties during cure originated from these gelation studies. We routinely prepared partially cured samples for these investigations by curing to a given time and then quickly tossing them into a freezer to quench the reaction. To our initial surprise, it was extremely difficult to extract samples quenched near the gel point from the molds since they would break so readily. Whereas fully cured epoxies were even difficult to break with bare hands, these critically gelled samples would fracture at the slightest touch. It seemed reasonable to investigate this dramatic qualitative effect more closely.

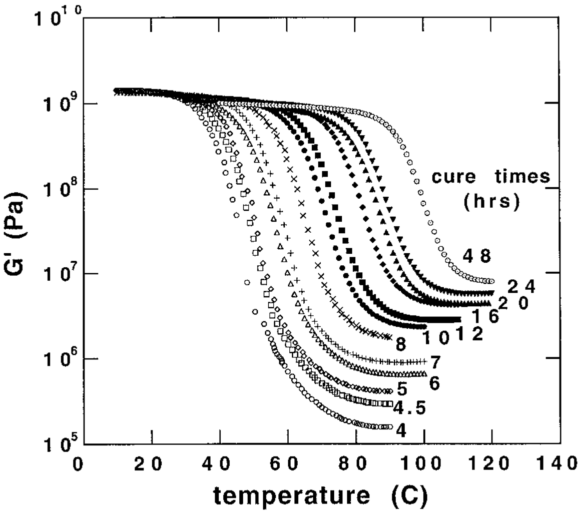

Figure 1. Dynamic shear storage moduli, G', of an epoxy cured for various times at 90 °C. The glassy moduli are unchanged by cure while the rubbery moduli increase with cure.

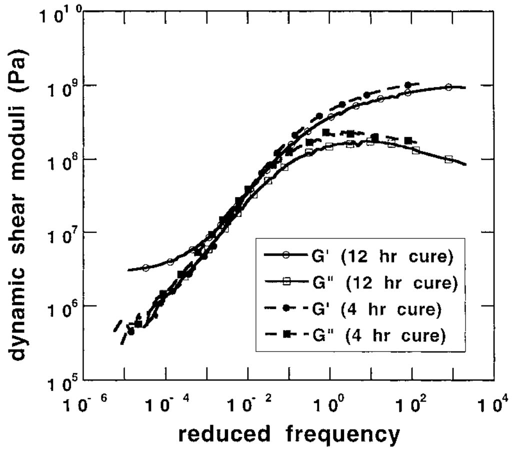

Figure 2. Stress relaxation moduli, $G(t)$, of an epoxy cured for 4 and 12 h at 90 °C. The spectrum of relaxation times is unchanged by cure.

III. Viscoelasticity and Fracture in Partially Cured Thermosets

Let us examine the fracture process in partially cured thermosets more closely to understand the role of this evolving viscoelasticity. For clarity, we focus on a notched three-point bend fracture specimen. The bulk of the sample responds elastically (as required for a valid fracture mechanics analysis) with the glassy thermoset modulus, since we are by definition below T_g. In Figure 1, we show that the glassy shear moduli for our partially and fully cured epoxies (diglycidyl ether of bisphenol A cured with diethanolamine) as measured by the dynamic shear storage modulus, G', are very similar, which is not surprising since the glassy modulus reflects the topologically independent van der Waals interactions.

Near the crack tip, nonlinear viscoelastic relaxations (plastic deformation) appear. Our theory of the evolution of linear viscoelasticity during cure[7] predicts that the spectrum of relaxation times is unaffected by cure if the reference temperatures are chosen as the respective T_g's. In Figure 2, we show the validity of this prediction by plotting the stress relaxation moduli for the partially and fully cured epoxies against reduced time ($T_{ref} = T_g$).

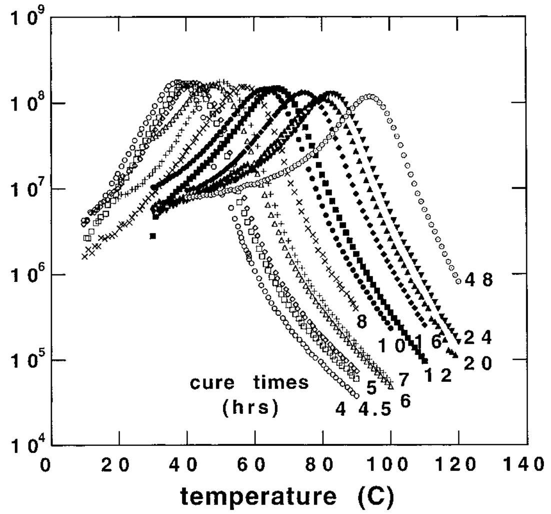

Figure 3. Dynamic shear loss moduli, G'', of an epoxy cured for various times at 90 °C. The normalized spectrum of relaxation times is unchanged by cure, but T_g (maximum in G'') increases with cure.

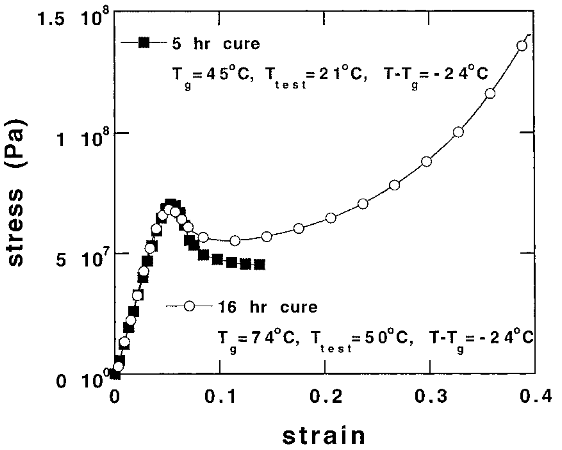

Figure 4. Stress−strain curve from a constant strain rate test (rate = 10^{-3} s^{-1}) at $T-T_g = -24$ °C for partially and fully cured epoxies.

The curves overlap until the distinct equilibrium moduli of the two samples (which do reflect the changing network topology) dominate. Figure 3 demonstrates this behavior as well. Here, we plot the dynamic shear loss modulus as a function of temperature. The curves have identical curvature reflecting the invariant relaxation spectra and are simply shifted along the temperature axis due to the change in T_g with cure.

The nonlinear viscoelastic relaxation spectra likewise seem unaffected by cure as can be demonstrated in a number of ways. Perhaps the constant strain rate test is the most familiar method. In Figure 4, the "yield stresses" from compressive strain ramps on partially and fully cured epoxies at *constant* $T-T_g$ are are identical. The concept of a true "yield stress" is fundamentally incorrect since it is tied to a particular test. The phenomenon is more accurately described as the onset of nonlinear viscoelastic relaxations just as T_g is related to the onset of linear viscoelastic relaxations.

Therefore, we see that, in the bulk of the sample, the elastic glassy responses of the partially and fully cured epoxies are identical, and in the "plastic zone" near the crack tip, the nonlinear viscoelastic relaxations are identical for the two if we test at constant $T-T_g$. At this point, we have little reason to believe that a severe dependence of the critical stress intensity factor on state of cure actually could exist. As the applied strain near the crack tip becomes large enough, however, all nonlinear relaxations will be exhausted, and the resulting stress will be supported by the equilibrium modulus which does depend on extent of reaction as described by eq 1. We must now be approaching the crack initiation event, and we require a mechanism for failure. Perhaps a hydrostatic instability occurs, even though observations of crazing in epoxies are controversial. Perhaps, we simply overextend the network chains and break bonds. It is not overly pessimistic to assert that we do not have a very clear mechanistic view of thermoset failure. We hope that the data collected in this study could help develop this picture.

IV. Experimental Procedure and Results

We now quantify the dramatic fragility of partially cured epoxies which we previously described qualitatively. In overview,[8] we partially cured epoxy bars, notched them to create three-point bend specimens, and broke them at a prescribed $T-T_g$. The digylcidyl ether of bisphenol A (Shell Epon 828) was reacted with diethanolamine (Fisher Chemical) at a ratio of 100 parts by weight to 12 parts. The reactants were thoroughly mixed and degassed, poured into silicone rubber molds (producing 0.25 in. × 0.5 in. × 2.0 in. samples), degassed again, cured to a specified time at 90 °C, and placed into the freezer to quench further reaction. To illustrate the lethargy of this reaction, the sample gelled at 90 °C in roughly 3 h.

One sample from each reaction time was reserved for linear viscoelastic analysis while the rest were notched to a depth of 0.25 in. with a diamond wafering blade (Buehler 11-4244) and returned to the freezer. The three-point bend specimens were then *not* precracked with a wedge or similar device but simply scribed with a sharp razor blade.[9] The least cured samples were very fragile, and attempts at precracking were highly unsuccessful.[10] Therefore, we could have either precracked only the more highly cured samples or precracked none. We believed the latter path to be a more consistent path to elucidate the cure dependence. On fully cured samples, we did measure critical stress intensity factors, K_{IC}, for both cut and precracked specimens and noticed a factor of 3 difference in the results (compared to a factor of 20 increase in K_{IC} during cure presented later). Therefore, the effect of not precracking is significant, but we optimistically hope that it is similar for all samples and does not alter the physical mechanism responsible for our observed cross-link dependence.

We measured the linear viscoelastic dynamic shear moduli for each reserved sample at each cure time as a function of temperature at a frequency of 10 Hz using a Rheometrics ARES. The results were presented previously in Figures 1 (G') and 3 (G''). From Figure 1, we obtain the equilibrium modulus, or equivalently the extent of reaction, at each cure time, and from Figure 3, we obtain the relative T_g as defined by the clear maximum in G''. These quantities are listed in Table 1 for each sample.

The loads at failure for the remaining samples were measured with an Instron 1122 using a liquid nitrogen cooled, controlled temperature chamber, and a displace-

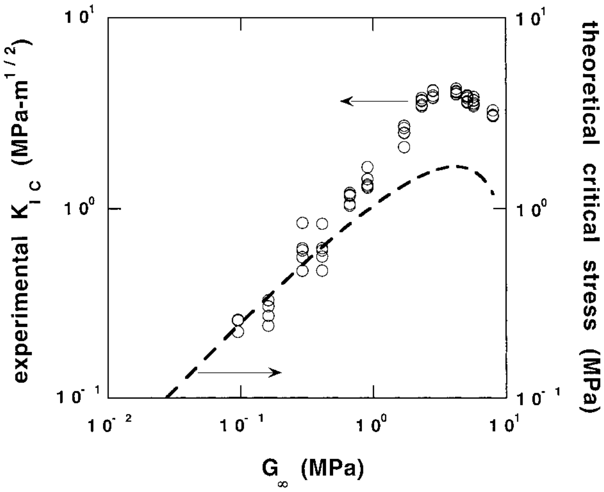

Figure 5. Experimental critical stress intensity factor and the theoretical stress required to fully stretch a percolation network cluster as a function of cure (represented by the rubbery modulus).

Table 1. Experimental Data

cure (h)	G_∞ (MPa)	cacld[14] extent of rxn	T_g (°C)	load at failure (N)	K_{IC} (MPa m$^{1/2}$)
3.5	0.095	0.729	36	17.9 ± 1.3	0.246 ± 0.020
4	0.16	0.745	38	20.8 ± 2.7	0.286 ± 0.039
4.5	0.29	0.767	41	27.2 ± 2.3	0.618 ± 0.139
5	0.41	0.782	45	44.3 ± 9.7	0.617 ± 0.134
6	0.66	0.806	48	81.8 ± 5.7	1.14 ± 0.08
7	0.90	0.923	50	102.1 ± 10.8	1.41 ± 0.15
8	1.7	0.863	57	179.8 ± 16.7	2.51 ± 0.24
10	2.3	0.886	63	262.2 ± 11.2	3.65 ± 0.15
12	2.8	0.901	67	287.3 ± 12.1	3.99 ± 0.17
16	4.2	0.936	75	291.5 ± 8.6	4.10 ± 0.11
20	5.1	0.954	80	261.8 ± 26.4	3.79 ± 0.14
24	5.7	0.965	83	252.9 ± 9.7	3.68 ± 0.12
48	8.0	1.00	94	206.8 ± 5.9	3.14 ± 0.09

ment rate of 0.2 in/min. K_{IC} was determined from[11]

$$K_{IC} = \frac{P}{B\sqrt{W}} f\left(\frac{a}{W}\right) \tag{2}$$

with

$$f(x) = \frac{3Sx[1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)]}{2W(1 + 2x)(1 - x)^{3/2}}$$

where P is the load, a is the crack length, and B, W, and S are the thickness, width, and spanning length, respectively. The samples were tested at 50 °C below the measured T_g as determined by the maximum in G''.

We present our results in Figure 5 and Table 1. In Figure 5, note that two measured properties are cross-plotted. We instead could have reported the critical stress intensity factors as functions of calculated extent of reaction (see Table 1) but felt that observables are always preferred. A dramatic increase in load at failure is observed as the cross-link density increases from the gel point (65% reacted) toward reaction completion. Phrasing this differently, the load at failure plummets as cross-link density decreases. In fact, it appears that the load at failure vanishes at the gel point with a critical exponent

$$K_{IC} \sim G_\infty^{\ 7/8} \sim \epsilon^{7/3} \tag{3}$$

where we have employed the scaling relationship in eq 1. This power-law functional dependence is hauntingly familiar from our investigations on epoxy gelation and may imply that the self-similar concepts of percolation apply somehow to fracture as well. At an extent of reaction of roughly 94%, however, this dependence reverses, and the load at failure decreases gradually with further reaction.

V. Speculations on a Failure Mechanism

With such a clear dependence of K_{IC} on network topology, we unfortunately feel obliged to offer an explanation. From the discussions in section III, we hypothesize that a thermoset crack initiates when the network spanning clusters are stretched beyond their maximum extensibility. Since percolation predicts that the network clusters are fractal and highly polydisperse, it is necessary to parametrize a cluster size carefully as a function of extent of reaction. Fortunately, such identification is clear from percolation; all evolving network static and dynamic quantities scale with the z-averaged molecular weight or size of the network spanning clusters. The maximum extensibility of the network is thus the ratio of the fully stretched length of a network cluster with z-averaged weight, L_z, to its unperturbed dimension, R_z. Standard scaling relations[12] predict the dependence of these quantities on the cluster mass,

$$R_z \sim M_z^{\ 1/D} \quad \text{and} \quad L_z \sim M_z^{\ 1/\zeta} \tag{4}$$

where $D = 2.52$ is the fractal dimension and $\zeta = 1.87$ is the topological exponent.

A very crude estimate for the local Cauchy tensile stress at failure is then

$$\sigma_c = G_\infty\left(\lambda_c^{\ 2} - \frac{1}{\lambda_c}\right) \tag{5}$$

with

$$\lambda_c \sim \frac{L_z}{R_z} = C_1 \frac{L_z}{R_z}$$

where C_1 is just a constant. Note that we have used the equilibrium modulus, G_∞, rather than the glassy modulus. One final percolation result[13] is required,

$$M_z \sim \epsilon^{-2.25} \tag{6}$$

We can now combine eqs 1 and 4–6 such that

$$\begin{aligned}\sigma_c &= G_\infty\left[\left(C_1\frac{L_z}{R_z}\right)^2 - \left(\frac{R_z}{C_1 L_z}\right)\right] \\ &= G_\infty\left[(C_2 G_\infty^{-0.11})^2 - \left(\frac{1}{C_2 G_\infty^{-0.11}}\right)\right] \\ &= C_2^2 G_\infty^{0.78} - \frac{G_\infty^{1.11}}{C_2}\end{aligned} \tag{7}$$

At low cross-link densities, the critical stress scales as $G_\infty^{7/9}$ and goes through a maximum at a critical value for the equilibrium modulus equal to $0.343C_2^{\ 8.52}$. The results of eq 7 for $C_2 = 6.6$ are shown in Figures 5 and 6 and are strikingly similar to our experimental data given such a crude model. Such similarity certainly does not prove our assumed failure mechanism (in fact, it

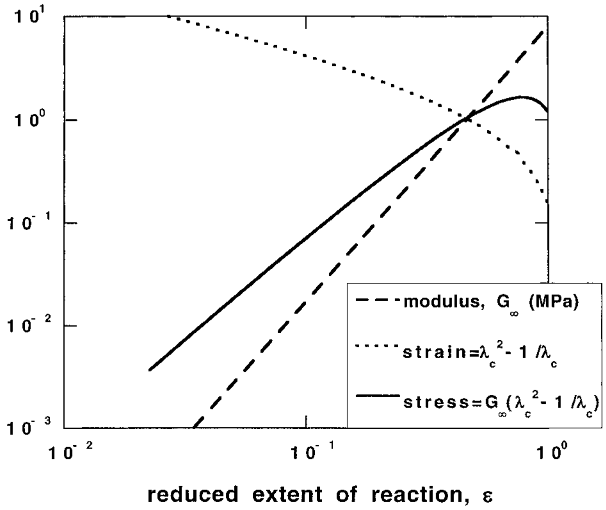

Figure 6. Equilibrium modulus, critical extension ratio, and critical stress as functions of reduced extent of reaction, $\epsilon = (p^2 - p_c^2)/(1 - p_c^2)$ for $C_2 = 6.6$.

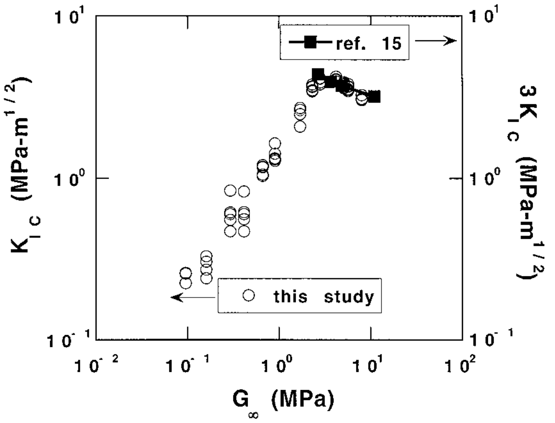

Figure 7. Comparison of our data and that of ref 15 showing the importance of probing a wide range in extent of reaction.

even surprises us) but does suggest that it might be interesting to investigate further the correlation of fracture with extent of reaction from a percolation framework.

VI. Conclusions

It is worth restating the uniqueness of this study; all tests were conducted *at a constant* $T-T_g$, thereby normalizing viscoelastic relaxations, and an *extremely* broad range in cross-link density was explored by quenching cure. This combination was critical in order to distinguish unambiguously a dramatic increase in K_{IC} as cross-link density increased. From the literature, one can find numerous studies to support a conclusion that K_{IC} increases, decreases, or is independent of cross-link density. However, in most of these studies, a relatively narrow range of cross-link densities was probed, and since most measurements were performed at a constant temperature, results included both thermal and topological effects.

Those studies indicating a decreasing trend typically probed a narrow range in cross-link densities skewed toward high densities. For example, we plot both our data and the data from ref 15 in Figure 7 (note that we multiplied the data in ref 15 by 3 for better comparison, again reflecting the influence of not precracking our notches). The study in ref 15 did in fact perform measurements at constant $T-T_g$ but supported the decreasing trend since the cross-link densities examined were quite high. In our investigations, we too observed this decreasing trend but only *for those highly cured networks*. The dramatic fragility of thermosets was only apparent at low cross-link densities, which is probed most easily by quenching the reaction. Moreover, since this lower cross-link density regime clearly displays power-law behavior, it may offer insight into failure mechanisms previously unrecognized.

The fragility of epoxies near the gel point is actually of practical interest to Sandia. We not only use the DEA-cured epoxy studied here but also use an aromatic amine-cured epoxy with a much higher ultimate T_g. This epoxy cures so fast to such a high T_g that it typically vitrifies during cure. As luck would have it, our historical production schedule brings the epoxy to the gel point almost simultaneously with its vitrification. Therefore, we are generating stresses from cure shrinkage and thermal expansion in a glassy epoxy right at the gel point where it is most fragile. The cure profile has since been changed.

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References and Notes

(1) See for example: Bos, H. L.; Nusselder, J. J. H. *Polymer* **1994**, *35*, 2793. Cherry, B. W.; Thomson, K. W. *J. Mater. Sci.* **1981**, *16*, 1913. Cherry, B. W.; Thomson, K. W. *J. Mater. Sci.* **1981**, *16*, 1925. Van der Sanden, M. C. M.; Meijer, H. E. H. *Polymer* **1993**, *34*, 5063. Narisawa, I.; Murayama, T.; Ogawa, H. *Polymer* **1982**, *23*, 2921.

(2) See for example: Mostovoy, S.; Ripling, E. J. *J. Appl. Polym. Sci.* **1966**, *10*, 1351. Bell, J. P. *J. Appl. Polym. Sci.* **1970**, *14*, 1901. Espuche, E.; Galy, J.; Gerard, J.-F.; Pascault, J.-P.; Sautereau, H. *Macromol. Symp.* **1995**, *93*, 107. Yamini, S.; Young. R. J. *J. Mater. Sci.* **1979**, *14*, 1609. Yamini, S.; Young, R. J. *J. Mater. Sci.* **1980**, *15*, 1814. Selby, K.; Miller, L. E. *J. Mater. Sci.* **1975**, *10*, 12. Broutman, L. J.; McGarry, F. J. *J. Appl. Polym. Sci.* **1965**, *9*, 609.

(3) See for example: Nusselder, J. J. H.; Bos, H. L. *Macromol. Symp.* **1995**, *93*, 17. Phillips, D. C.; Scott, J. M.; Jones, M. *J. Mater. Sci.* **1978**, *13*, 311. Scott, J. M.; Wells, G. M.; Phillips, D. C. *J. Mater. Sci.* **1980**, *15*, 1436.

(4) Jordan, C.; Galy, J.; Pascault, J.-P. *J. Appl. Polym. Sci.* **1992**, *46*, 859.

(5) Noordam, A.; Wintraecken, J. J. M. H.; Walton, G. In *Crosslinked Epoxies*; Sedlacek, B., Kahovee, J., Eds.; W. de Gryter and Co.: Berlin, 1987.

(6) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.

(7) See our review and references therein: Adolf, D. B.; Martin, J. E.; Chambers, R. S.; Burchett, S. N.; Guess, T. R. *J. Mater. Res.* **1998**, *13*, 530.

(8) For more detail see: Weeks, T. S. Fracture Properties as a Function of the Extent of Reaction for an Epoxy Network. Thesis, New Mexico Tech, Socorro, NM, 1997.

(9) A similar procedure was used in ref 4 on partially cured epoxies.

(10) Upon reflection, perhaps we could have precracked partially cure compact tension samples more easily by placing the unnotched end under compression.

(11) Anderson, T. L. *Fracture Mechanics*; CRC Press: Boca Raton, FL, 1995.

(12) Martin, J. *J. Phys. A: Math. Gen.* **1985**, *18*, L207.

(13) Stauffer, D. *Introduction to Percolation Theory;* Taylor and Francis: London, 1985.

(14) Calculated from eq 1 where the epoxy extent of reaction, α, and the bond probablity, *b*, are related by $b = \alpha^2$ since two epoxies must react with the cross-linker to form a true percolation bond. The gel point for this system occurs at $\alpha = 0.65$.

(15) LeMay, J. D.; Swetlin, B. J.; Kelley, F. N. In *Characterization of Highly Cross-linked Polymers*; ACS Symposium Series No. 243; Labanna, S. S., Dickie, R. A., Eds.; American Chemical Society: Washington, DC, 1984.

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