

CORRELATION OF THE CRACK INITIATION STRESS WITH EPOXY NETWORK TOPOLOGY

Douglas Adolf,

Sandia National Laboratories,
Albuquerque, NM

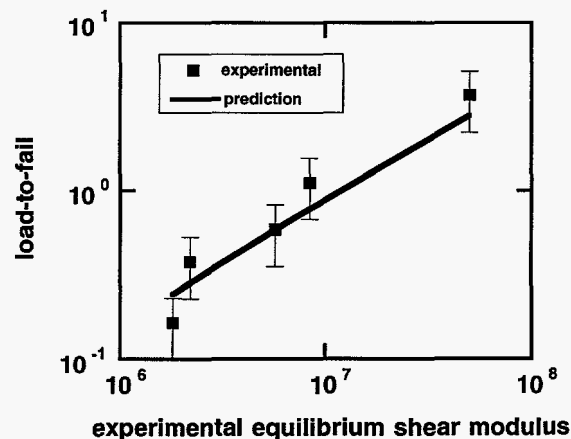
Timothy Weeks and John McCoy
New Mexico Tech
Socorro, NM

Much controversy surrounds the dependence of stress intensity factor of glassy thermosets, epoxies in particular, with crosslink density. One could scan the literature and find references that claim K_{Ic} increases with crosslink density, decreases with crosslink density, or is independent of crosslink density.

We feel that two factors contribute to this confusion. First, a typical method for assessing this dependence relies on modifying the crosslink density by changing the precursor epoxy molecular weight. Unfortunately, this procedure results in relatively small changes in crosslink density ($\sim x2$). On the other hand, one could change stoichiometry or quench the reaction at intermediate extents of reaction to obtain large changes in crosslink density. However, most studies have not measured the resulting stress intensity factor of these partially cured systems at constant $T-T_g$, where T_g is the glass transition temperature of the epoxy. Since T_g can change

significantly with cure and since fracture processes at the crack tip are dissipative, we must work at constant $T-T_g$ to ensure that the nonlinear viscoelastic mechanisms are fairly compared.

In this study, we quenched the reaction of the diglycidyl ether of bisphenol A (DGEBA) and diethanolamine (DEA) at various stages past the gel point and measured the three-point-bend stress intensity factor at a constant $T-T_g = -50^\circ\text{C}$. The results are shown below where we have plotted the measured stress intensity factor against the measured equilibrium modulus (a metric of crosslink density).



The trend is clear and significant; increasing crosslink density directly increases the load-to-fail.

Now we need to explain why this trend exists. Unfortunately, this requires quite a bit of background information which we will cover quickly. First, we wish to relate the macroscopic load-to-fail,

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F_c^{meas} , to the local stress-to-fail at the crack tip, σ_c^{local} . We would hope that $F_c^{\text{meas}} = C \sigma_c^{\text{local}}$, where the proportionality constant, C , is independent of crosslink density. For this to be true, the epoxy glassy modulus and yield stress (or more accurately, the stress at the onset of nonlinear viscoelastic behavior) must be independent of crosslink density at constant $T-T_g$. These quantities are constant thus ensuring that the stresses outside the crack plastic zone are independent of crosslink density.

Inside the plastic zone, nonlinear viscoelastic relaxations occur. From our previous investigations on the evolution of viscoelasticity with cure, we have found that the spectrum of shear relaxation times is independent of extent of reaction and is described by a power-law, $G(t) \sim t^{-\Delta}$. This curious fact is a result of the self-similar topological structures formed by the condensation gelation reactions, which can be modelled by percolation theory. At the gel point, simple scaling arguments lead to the result that $\Delta=2/3$. Experiments have shown that this relationship extends to the fully-cured network, implying that the topology of the fully-cured network is more subtle than the three-dimensional net typically envisioned.

Therefore, the only viscoelastic property that changes with cure (at constant $T-T_g$) is the equilibrium

modulus, which is a direct measure of the network connectedness. We now propose a failure criterion in which the crack initiates when the network spanning chains are stressed beyond their maximum extensibility. The local maximum extension ratio is then $\lambda_c \sim L/R$ where R is the unstrained end-to-end distance of the spanning chains and L is their fully-stretched length. L is obviously proportional to N , the number of monomers in the chain, and from percolation theory, $R \sim N^{4/5}$.

Following this line of reasoning, $\sigma_c^{\text{local}} \sim G_\infty(\lambda_c - 1)$, where G_∞ is the equilibrium shear modulus which itself scales as $G_\infty \sim \rho RTf/M_z$, with M_z as the z -averaged molecular weight between crosslinks and f as the gel fraction ($f \sim M_z^{-1/5}$). Since $\lambda_c \sim M_z^{1/5}$ and $G_\infty \sim M_z^{-6/5}$ from above, we can relate λ_c to G_∞ as $\lambda_c \sim G_\infty^{-1/5}$. Therefore, $F_c^{\text{meas}} \sim \sigma_c^{\text{local}} \sim G_\infty^{5/6}$ and we have a relationship between two observables, the measured load-to-fail and the measured equilibrium modulus. As seen in the Figure above, the data agree well with this prediction.

The practical implications of this relationship are clear; at the gel point, the glassy epoxy is extremely fragile, which is consistent with the behavior of B-staged epoxies. During cure then, one must take care that cracks do not develop in this fragile state that may propagate into the cured system.