The Effect of Postcure Time on the Fracture Properties and Nodular Morphology of an Epoxy Resin

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Synopsis

The effect of different postcure times on the fracture properties and morphology of an epoxy resin was studied. The fracture energy for crack initiation and arrest was calculated for each sample and plotted as a function of the postcure time. Nodules (25–35 nm in diameter) were observed on all fracture surfaces. Of considerable interest was the alignment of nodules in the direction of crack propagation. Longer postcure times are thought to alter the fracture energy by causing additional crosslinking in the internodular matrix.

INTRODUCTION

Within the last ten years a new area of investigation of modes of failure of structural materials, known as linear elastic fracture mechanics, has been extensively developed. Methods of linear elastic fracture mechanics were used to determine the fracture energy (strain energy release rate of fracture toughness) $\mathcal{G}_{Ic}$ defined[1] as

$$\mathcal{G}_{Ic} = \frac{P_c^2}{2B}\left(\frac{dC}{da}\right)$$

The fracture energy represents a fundamental material property. The cleavage fracture test relates the fracture energy to the critical load at which an artificially produced flaw begins to propagate through the specimen, thus duplicating the behavior of structural materials in actual service.

The fracture characteristics of brittle thermosets have been of considerable interest to many investigators. Thus, the fracture toughness of two epoxy systems has been studied, in both bulk and adhesive form, as a function of the ratio of curing agent to resin content and the postcure temperature.[1,2] The fracture energy of elastomer-modified epoxy polymers, in bulk and as adhesives, has been investigated as a function of the elastomer concentration and bond thickness.[3] Recently, the durability study of an epoxy adhesive was reported.[4] The fracture energy of the joint was calculated upon exposure to an aggressive environment for different times. Apparently this type of test may be very important in predicting the long-time behavior of various structural materials.

The purpose of this study was to establish the effect of postcure time on the fracture toughness of bulk epoxy resin and also on the supramolecular structure in the form of nodules which have been observed in previous work.[5]

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EXPERIMENTAL

Tapered double-cantilever beam (TDCB) specimens were used in this experiment. The specimens were contoured in such a manner that the compliance changes linearly with the crack length. The expression for the fracture energy then becomes[1]

$$\mathcal{G}_{Ic} = \frac{4P_c^2}{EB^2} m$$

where m = constant. Furthermore, as the crack extends, the fracture energy varies only with the critical load (P_c), thus greatly simplifying the testing.

Epon 825 (Shell's liquid diglycidyl ether of bisphenol A resin, DGEBA) was used in the experiment cured with 8 phr (parts per hundred parts of resin, by weight) of diethylenetriamine (DETA). The resin and the curing agent were thoroughly mixed for 5 min, then poured into silicone rubber molds. Samples were cured for 24 hr at room temperature and subsequently postcured for times ranging from 0 to 72 hr. Side grooves and grip holes were introduced and specimens tested with an Instron tensile tester. Specimen dimensions are given in Figure 1. The cross-head rate of the machine was maintained at 0.05 in./min. Monotonically increasing load was applied, and mode I failure was studied.

C–Pt replicas of every part of the fracture surface were made and studied. A Pt bead, sitting on a carbon rod at a 30° angle to the sample surface, was evap-

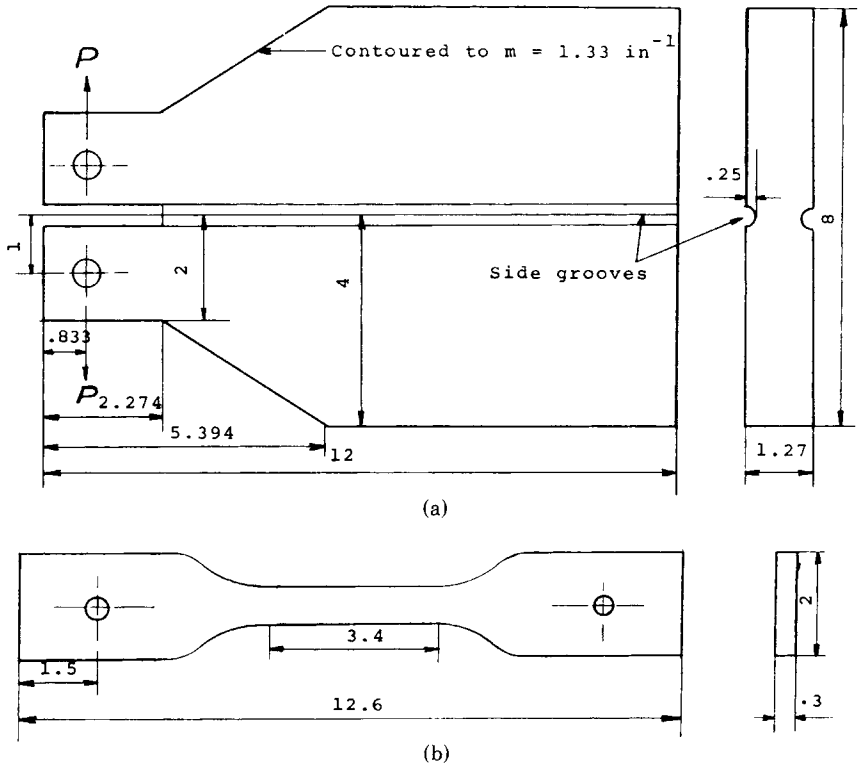

Fig. 1. (a) Tapered double-cantilever beam (TDCB) specimen for mode I fracture testing.[6] (b) Tensile test specimen.

orated onto the fracture surface. Upon shadowing, drops of poly(acrylic acid) (PAA) were placed onto spots of interest on the specimen surface. After 24 hr the hard PAA beads were peeled from the surface. The C–Pt replica adhered to PAA. The PAA was dissolved in distilled water and the replica carefully floated onto a microscope grid. Successful replicas were made of areas near the tapped-in precrack to the end of the specimen, from one end to the other along the specimen width and from both sides of the crack front. Transmission electron micrographs of the samples were taken at magnifications of 1000 to 100,000. A model JEOL 100B transmission electron microscope was used.

RESULTS AND DISCUSSION

Immediately upon the extension of the tapped-in precrack, samples were unloaded, then reloaded till the critical load for crack initiation (Pc_i) and the load for crack arrest (Pc_a) values were obtained. This procedure was repeated to obtain as many data points as possible. Only samples that gave at least three data points within the tapered region were taken into account for the calculations. The first crack obtained by tensile loading was assumed to be the extension of the precrack and was not included in the calculations. It was also assumed that the first crack was sharp enough to be a natural crack.

The crack front had a parabolic shape. In most cases the crack propagation, at least within the tapered region, occurred in the plane perpendicular to the applied load. However, in some cases, the tapped-in precrack veered out of the plane perpendicular to the applied load, and this caused the specimen arm to break off.

Values of Young's moduli obtained from the tensile test specimens were essentially independent of the postcure time, as shown in Figure 2. The $\mathcal{G}_{Ic}$ values for the initiation and arrest were calculated using the experimentally obtained values of Young's moduli. Higher values of $\mathcal{G}_{Ic}$ were observed within the first 20 hr of postcure (Fig. 3). Also a greater scatter of data occurred during this period. After approximately 20 hr the scatter of data is reduced and the value

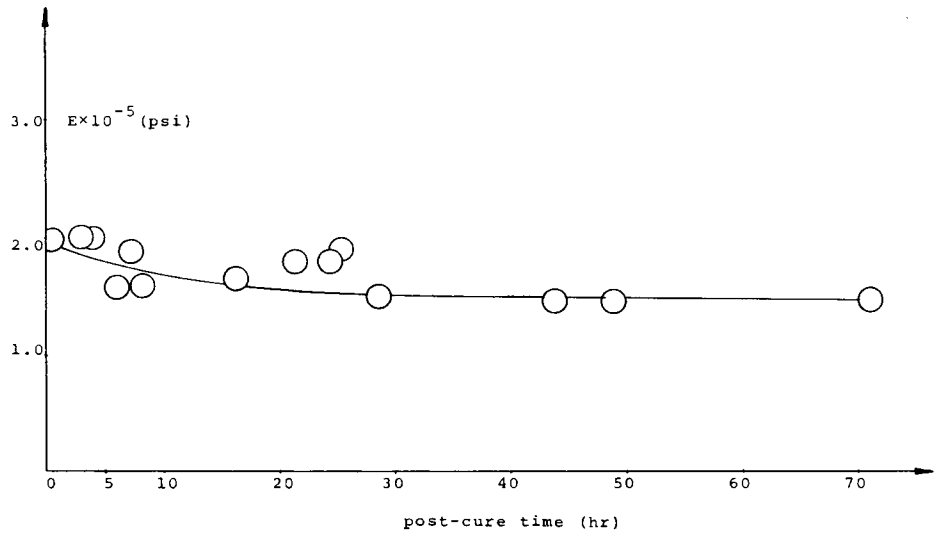

Fig. 2. Young's modulus as function of postcure time.

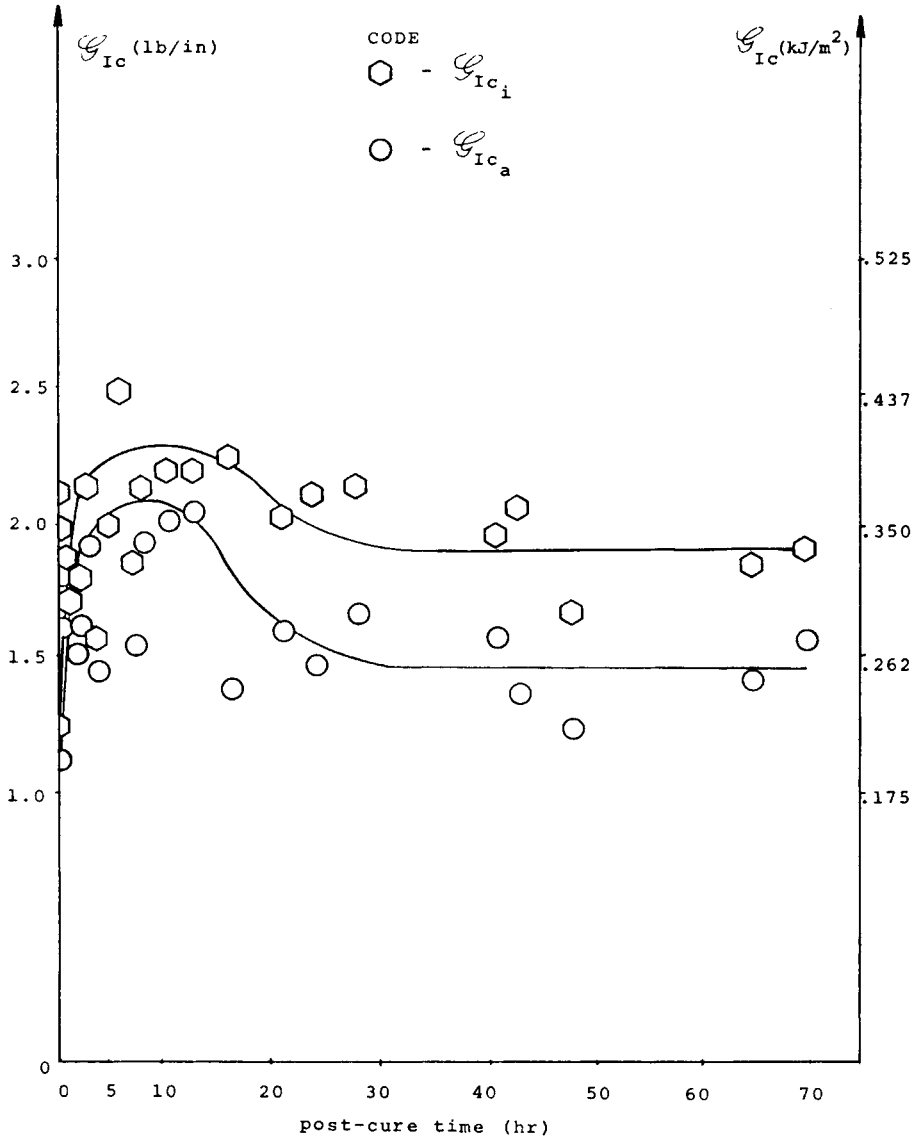

Fig. 3. Fracture energy for crack initiation ($\mathcal{G}_{Ic_i}$) and crack arrest ($\mathcal{G}_{Ic_a}$) as a function of the postcure time: (○) $\mathcal{G}_{Ic_i}$; (○) $\mathcal{G}_{Ic_a}$.

of $\mathcal{G}_{Ic}$ becomes nearly constant. Both the crack initiation ($\mathcal{G}_{Ic_i}$) and the crack arrest ($\mathcal{G}_{Ic_a}$) fracture energies follow the same pattern. As the resin becomes more brittle, $\mathcal{G}_{Ic_i}$ decreases. Also, the difference of $\mathcal{G}_{Ic_i} - \mathcal{G}_{Ic_a}$ becomes greater at longer postcure times, indicating further embrittlement of the epoxy resin, since the crack upon initiation travels for longer distance and eventually stops when the potential energy of the beams is sufficiently lowered.

Nodular structure was observed on all fracture surfaces [Figs. 4(a), (b), (c)]. Careful examination of the micrographs revealed that the fracture proceeded around nodules, indicating that the nodules are the sites of higher crosslink density in the resin. The average size of nodules, on all specimens, was between 25 and 35 nm (250–350 Å). At short postcure times a sudden increase in $\mathcal{G}_{Ic}$

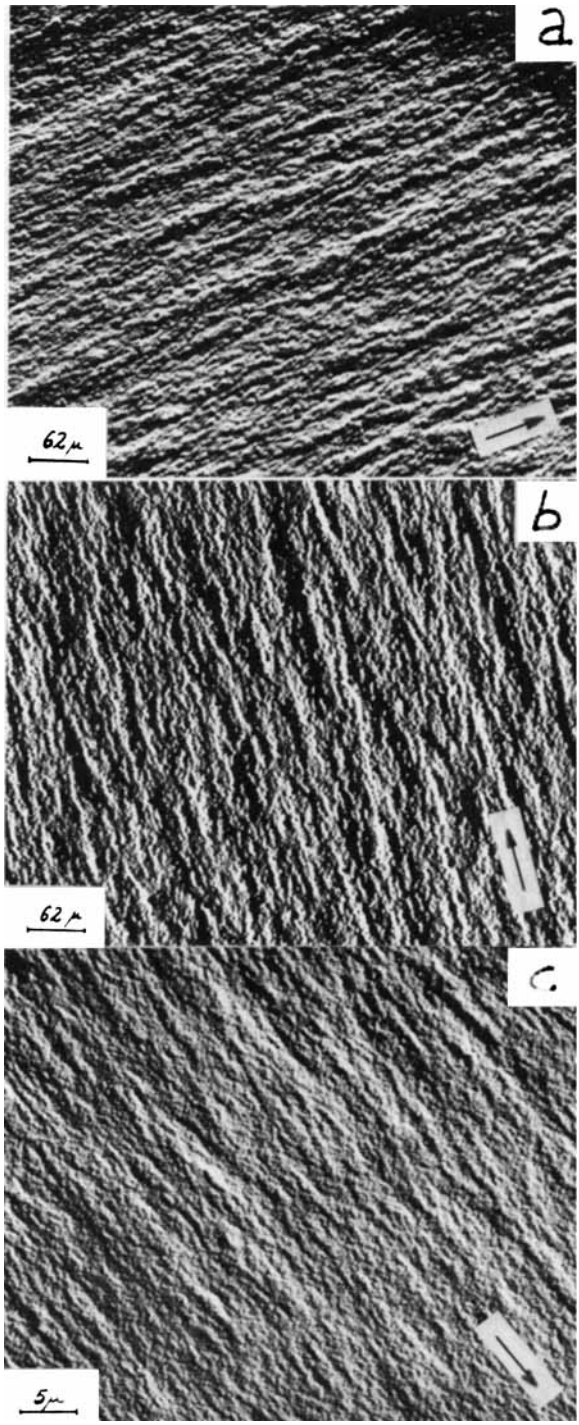

Fig. 4. Transmission electron micrographs of one-state C–Pt replicas of the fracture surfaces of Epon 825 (cured with 8 phr DETA), postcured for 35 min (a), 3 hr (b), and 65 hr (c). Arrows indicate crack propagation direction on all figures.

values was noticed. Nevertheless, no significant morphological changes were observed between samples postcured at room temperature and those postcured at 106°C. Furthermore, the shape, size, and density of the nodules did not change with different postcure times, thus suggesting that any dependence of $\mathcal{G}_{Ic}$ on the postcure times should be explained by changes in the internodular matrix. A slight subsequent decrease in $\mathcal{G}_{Ic}$ values with postcure times (as resin becomes more brittle) is probably caused by additional crosslinking in the internodular matrix; the nodules, however, remain intact. Of considerable interest was the observed alignment of nodules in the direction perpendicular to the crack front. A certain degree of plasticity is expected to exist in the system cured with 8 phr DETA (below the stoichiometric 11 phr). This is further supported by values of Young's moduli lower than those usually observed with fully cured specimens with the stoichiometric composition. It is possible that some plasticity allows flow to occur to relieve the dilational stresses which are perpendicular to the crack propagation direction. The flow is small in scale since no large fibril formation is observed.

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