

Crosslink density and fracture toughness of epoxy resins

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A series of networks of diverse crosslink density were prepared using bifunctional epoxide prepolymers of different molecular weight, crosslinked with diamine diphenyl sulphone, and their fracture behaviour investigated. The same set of resins was also modified with a reactive rubber. The fracture toughness regularly decreased on increasing the crosslink density for all formulations. The addition of the rubber gave rise to a marked increase in toughness, though it magnified the influence of the molecular weight of the prepolymer. Tests performed with blunt notches showed that the fracture toughness was maximum at medium crosslink densities. A dispersion of rubber particles caused a toughness increase through the formation of microcavities ahead of the crack tip. Failure was preceded by a rapid volume increase caused by void coalescence.

1. Introduction

Bisphenol-A based bifunctional prepolymers (DGEBA) represent the most widely utilized class of epoxy resins. At room temperature they can be either liquid or solid depending upon their molecular weight (MW). Liquid resins are more readily utilizable, while for the high-MW grades the use of solvents or high processing temperature are needed. Typical areas of employment of solid resins are therefore prepreg manufacturing and powder coating.

Many of the properties of thermosetting polymers, including brittleness, arise from their highly cross-linked structure. Toughness in fact substantially relies on plastic flow processes capable of dissipating energy within the crack tip region. Such processes are strongly hindered by the formation during cross-linking of chemical links which limit the number of molecular conformations attainable under stress. Although much more fragile than linear polymers, epoxy resins possess the highest fracture energy among crosslinked glassy polymers. This is one of the reasons for their widespread use in the field of composite materials and structural adhesives. The present work shows some aspects of the fracture resistance of epoxy resins, related to the role of the molecular weight of the epoxy prepolymers.

2. Materials and methods

Commercial bisphenol-A prepolymers were used with molecular weights of 380, 980, 1700 and 3700 approximately (Epon 828 EL by Shell and Eposir 7161, Eposir 7170/P, Eposir 7180 by SIR, respectively). The prepolymers will be indicated in the following by the letter E followed by the molecular weight. Diamine

diphenyl sulphone (DDS), in stoichiometric quantity, was used as the hardener. A reactive carboxyl-terminated rubber (BF Goodrich CTBN 1300 × 13) was used as the toughener (content 10 vol %). Curing was carried out at 180 °C for 12 h.

Elastic moduli were determined, as a function of temperature, with a polymer Laboratory DMTA analyser at the frequency of 1 Hz. Glass transitions temperatures, T_g , were determined from the $E'-T$ curves.

Fracture tests were performed at room temperature on prismatic specimens (12 mm × 15 mm × 80 mm) in three-point bending. The critical parameter K_{Ic} was determined by the relation

$$K_{Ic} = \sigma_c Y a^{1/2} \quad (1)$$

where σ_c is the load at crack propagation, a is the crack length and Y a geometric factor.

Volume changes were calculated by measuring longitudinal and lateral deformations, ϵ_{11} and ϵ_{22} , during tensile creep tests according to

$$\delta V/V_0 = (\epsilon_{11} + 1)(\epsilon_{22} + 1)^2 \quad (2)$$

3. Results and discussion

3.1. Network characterization

The reaction of bifunctional epoxy prepolymers with primary diamines gives rise to networks with trifunctional knots due to the presence of nitrogen atoms. However, since crosslinking had to be carried out at high temperature (180 °C) the hydroxyl groups possibly contributed to crosslinking, particularly for the high molecular weight prepolymers whose epoxy equivalent is high. Additionally, incomplete crosslinking could have resulted from the sluggish reactivity of the

hardener. The use of the prepolymer molecular weight to characterize the network is consequently unreliable. Networks examined in this work have been therefore characterized by evaluating the density of the elastically active junctions through measurement of elastic moduli in the rubbery state (50° above T_g). According to the theory of rubber elasticity the equilibrium elastic modulus is given by

$$G_r = \phi dRT/M_c \quad (3)$$

where d is the density, R the molar gas constant, T the absolute temperature and M_c the average molecular weight of chain segments between crosslink points. The actual value of the first factor ϕ is uncertain. In fact the concentration of inactive chains is unknown and tight networks are no longer Gaussian. To a first approximation it can be assumed [1-4] that when $G_r < 10^7$ Pa, ϕ is close to unity. For $G_r > 10^7$ Pa the non-Gaussian character becomes more and more predominant on increasing the crosslink density and Equation 3 no longer holds. In this study it was therefore preferred to use an approximate relation that better describes the elastic properties of dense epoxy networks [5, 6]:

$$\log G_r = 6 + 293 (d/M_c) \quad (4)$$

The crosslink density, μ , therefore given by

$$\mu = dN/(1.5 M_c) \quad (5)$$

with N = Avogadro's number. A variation of μ causes a variation of the long-range segmental mobility and therefore of the glass transition temperature. Fig. 1 shows that for the materials examined the relationship between μ and T_g was substantially linear. This agrees with a theoretical relationship developed by Fox and Loshaek [7] to describe the dependence of T_g on molecular weight and entanglement concentration in linear polymers. By extrapolating the line in Fig. 1. to $\mu = 0$ it is possible to estimate the glass transition temperature of the uncrosslinked polymer, $T_{g\infty} = 80^\circ\text{C}$. This value is identical to that reported by

Murayama *et al.* [8] who used the same resin but a different hardener. The accord is due to the fact that for $M_c \rightarrow \infty$, $T_{g\infty}$ only depends upon the chemical nature of the prepolymer since the hardener content tends to zero. A higher value, $T_{g\infty} = 99^\circ\text{C}$, was obtained by Lau *et al.* [9] using tetrafunctional prepolymers.

A consequence of the linear relation in Fig. 1 is the fact that dense networks, those obtained with low-MW prepolymers, are rather sensitive to the resin to hardener ratio. Fig. 2 shows that T_g of non-stoichiometric formulations rapidly decreased for the resin E380. On the contrary, E1700 was almost insensitive to composition. The relation $T_g = T_{g\infty} + m\mu$, representing the line in Fig. 1, may be rearranged as

$$\frac{\delta T_g}{\delta M_c} = - \frac{mdN}{1.5 M_c^2}$$

In the case of non-stoichiometric mixtures the molecular weight between crosslinks increases [10], giving rise to T_g variations inversely proportional to M_c and to the prepolymer molecular weight as well.

3.2. Fracture

The fracture resistance progressively decreased with increasing the crosslink density. From data in Fig. 3b one can easily extrapolate the value of K_{Ic} for the resin of infinite molecular weight ($2.2 \text{ MPa m}^{1/2}$). This value is close to that of many thermoplastic polymers.

The yield stress did not appreciably vary with MW. This result is similar to that reported by Bell [11] for the fracture stress of a series of resins in which M_c was varied by using non-stoichiometric formulations. The reduction in toughness caused by crosslinking can be attributed either to the decrease of the volume of the plastic zone at the notch tip or, above all, to a lack of post-yield deformability as confirmed by tensile tests.

The influence of the crosslink density becomes more complex in the case of blunt notches. The local stress at the crack tip is a function of the radius of curvature,

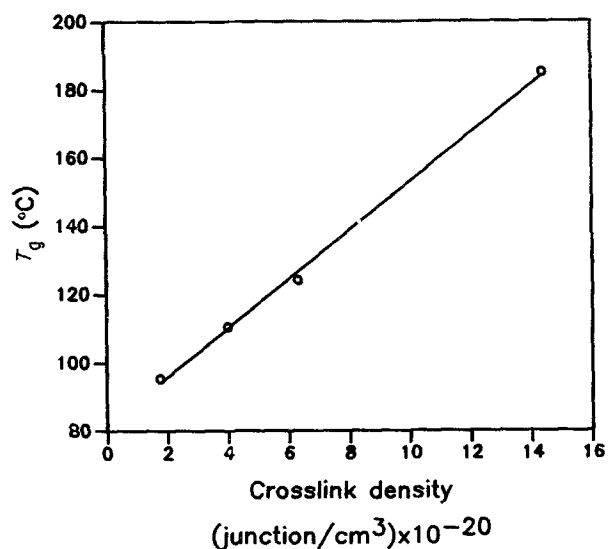


Figure 1 Glass transition temperature as a function of crosslink density.

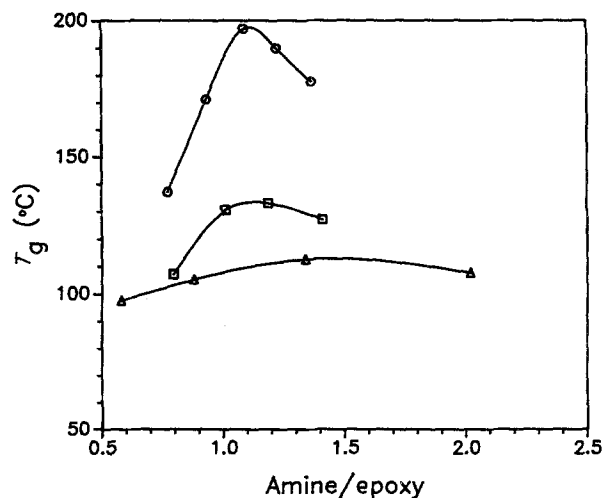


Figure 2 Glass transition temperature as a function of amine to epoxide equivalent ratio for specified prepolymers: (○) E380, (□) E980, (Δ) E1700.

r . The stress normal to the crack axis, σ_{yy} , at a distance δ from the tip is given by [12]

$$\delta_{yy} = \delta_0 \left(\frac{a}{2\sigma} \right) \frac{1 + (r + \delta)}{[1 + (r/2\delta)]^{3/2}} \quad (6)$$

It has been proposed [12] that crack propagation occurs when a certain critical stress is reached at a distance δ from the notch tip. Equation 6 can be recast as

$$\frac{K_{Ib}}{K_{Ic}} = \frac{[1 + (r/2\delta)]^{3/2}}{1 + (r/\delta)} \quad (7)$$

The ratio K_{Ib}/K_{Ic} therefore increases with increasing r (δ may be regarded as an adjustable parameter). For $r \gg \delta$, K_{Ib}/K_{Ic} depends almost linearly on $r^{1/2}$.

As shown in Fig. 4, the dependence of K_{Ib} on $r^{1/2}$ is similar for all materials. A well-established fracture criterion assumes that crack propagation occurs when the tip reaches a critical aperture, CTOD, given by

$$\text{CTOD} = \frac{K_{Ic}^2}{E\sigma_y} \quad (8)$$

where σ_y is the yield stress.

A sharp crack will undergo blunting before propagation until its radius of curvature reaches approx-

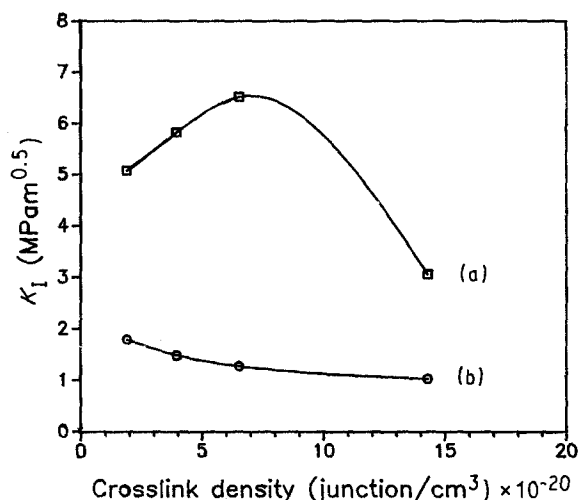


Figure 3 Stress intensity factor, K_I , against crosslink density for the neat resins: (a) tip radius $500 \mu\text{m}$ (K_{Ib}), (b) sharp crack (K_{Ic}).

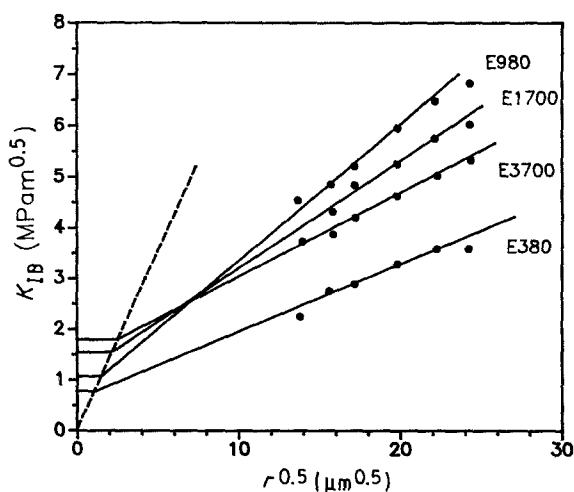


Figure 4 Stress intensity factor, K_{Ib} , as a function of the radius of curvature; (---) $K_{Ic}/(2E\sigma_y)^{0.5}$.

imately the value of CTOD/2. For this reason interpolating lines in Fig. 4 were not drawn to $r^{1/2} = 0$. Equation 8 is plotted in Fig. 4 (dotted line).

The fact that the $K_{Ib}/r^{1/2}$ lines are not parallel has the interesting consequence that the materials rank differently in terms of fracture toughness, depending on the severity of the defect. While the resin with the highest crosslink density is invariably the most fragile, the E980 resin is the toughest in the presence of mild defects. This is better shown in Fig. 3a that collects data relative to $r = 500 \mu\text{m}$. The origin of this is unknown and could be related to viscoelastic effects during the slow crack growth that precedes the unstable fast propagation. It can be observed that in principle there is no reason to predict a monotonous dependence of K_{Ib} or r . The trend shown in Fig. 3b is similar to the dependence of resilience on M_c observed by Bell [11] and by Kim *et al.* [13] using non-stoichiometric blends.

The addition of reactive liquid rubbers (RLP) substantially mitigates the fragility of epoxy resins [14–19]. Typically these rubbers are low molecular weight butadiene-acrylonitrile copolymers, MW ≈ 3500 to 5000 , with the important property of being soluble in low molecular weight epoxy resins. Due to the presence of reactive end-groups they can also react with the epoxy prepolymers. The solution of an RLP in the prepolymer becomes unstable since the increase of the molecular weight of the resin, as crosslinking goes on, causes the free energy of mixing to decrease. As a consequence, the rubber separates, before gelation, in the form of minute spherical particles, diameter 1 to $5 \mu\text{m}$ depending on the type of rubber and cure temperature. For the same reason the initial solubility of the CTBN in the epoxy prepolymers decrease with increasing molecular weight of the resin. In the case of E3700 complete solubility of CTBN in the prepolymer was not observed even at high temperature ($\approx 200^\circ\text{C}$). However, this does not appear to have affected to a large extent the final morphology. The presence of reactive terminal groups is important for it enables the formation of a mechanically stable interface between the rigid matrix and the particles. It is known that the absence of these links renders ineffective, at least at high strain rates, the rubbery phase.

K_{Ic} data for the modified systems are shown in Fig. 5b. The trend is similar to that in Fig. 3b though the values are higher. The fracture toughness of E3700/CTBN is close to that of polycarbonate tested in plane stress. It is worth noting that the influence of the crosslink density is much higher in the case of rubber-modified formulations. The same effect was found by Yee and Pearson [20] although they found a linear dependence of the fracture energy upon the molecular weight of the epoxy prepolymer. As in the case of the neat resins, the rubbery phase produced a decrease in yield stress that slightly depended upon the crosslink density of the matrix polymer.

Curves relative to blunt notches (Fig. 5a) are substantially similar to those shown in Fig. 3a. The increase in fracture toughness is, however, smaller than that found with sharp cracks, which indicates that the

slope of $K_{Ib}/r^{1/2}$ lines are lower for the modified materials, as confirmed from data in Fig. 6 that refer to the E3700 resin. The toughest material has a higher natural radius of curvature (higher COD) and a lower rate of increase of K_{Ib} with $r^{1/2}$. This suggests that for high values of the tip radius the toughness of the unmodified material could become higher than that of the corresponding rubber-modified formulations. This effect, also known in thermoplastic polymers, has been given no convincing interpretation so far.

Upon loading a cracked specimen a triaxial stress develops in the crack region as the tip radius decreases. As a consequence, a negative pressure is generated which promotes the nucleation and growth of holes inside or around the rubber particles. In the plastic zone at the crack tip the material plastically deforms reaching a maximum strain, ϵ_{max} , that can be estimated by the equation [21]

$$\epsilon_{max} \approx \frac{3}{4}\epsilon_y \left(1 + \frac{K_{Ic}^2}{\sigma_y^2 r} \right) \quad (9)$$

in which ϵ_y is the deformation at yield. Equation 9 can

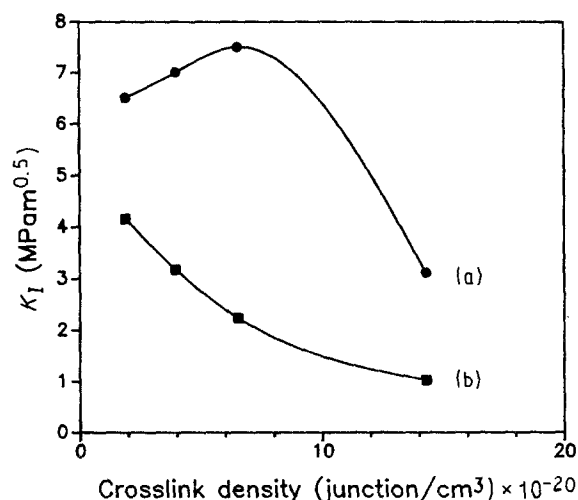


Figure 5 Stress intensity factor, K_I , against crosslink density for the rubber-modified resins: (a) tip radius 500 μm (K_{Ib}), (b) sharp crack (K_{Ic}).

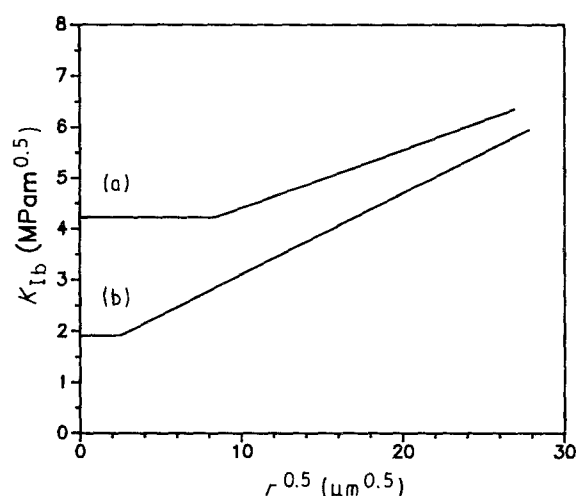


Figure 6 Stress intensity factor, K_{Ib} , as a function of the radius of curvature for (a) E3700, (b) E3700/CTBN.

be rearranged as

$$K_{Ic} \approx \sigma_y \left(\frac{4\epsilon_{max}}{3\epsilon_y} - 1 \right)^{0.5} r^{1/2} \quad (10)$$

Equation 10 gives important information. Fracture toughness varies linearly with $r^{1/2}$ in agreement with experimental evidence. Moreover, K_{Ic} depends upon the maximum deformability of the material. ϵ_{max} , which in the present case can be related to the maximum network extensibility and therefore to M_c [22]. The formation of microcavities in the region of crack propagation locally reduces the yield stress. Consequently the slope of the K_{Ic} against $r^{1/2}$ line decreases (see Equation 10). On the other hand, the triaxiality becomes less important as the tip radius increases. As a consequence the rubber will no longer be able to cavitate in the tip region and no crack shielding will be in action. One should therefore expect that at high $r^{1/2}$ values the rate of increase of K_{Ic} (the slope of lines in Fig. 6) should increase. This effect, not observed in our tests, was probably masked by the plastic collapse caused by the high loads necessary to the propagation of non-sharp notches.

The toughness of rubber-modified resins increases because a series of energy-consuming events take place in the stressed regions. Some depend on the deviatoric component of the stress tensor, others on the hydrostatic one. All materials dilate when stressed in tension and the volume change is initially truly elastic: $\delta V/V_0 \approx (1 + 2\nu)\epsilon_{11}$, ν being Poisson's ratio (≈ -0.4 for the polymers examined). In the case of multicomponent systems, microholes are easily generated as a consequence of interface or particle failure so that the volume of the material exceeds the elastic dilation. At an early stage of deformation the volume of the holes increases at a higher rate compared to that of the matrix. The growth rate, however, decreases as voids become elliptical in shape. When the length of the cavities is close to the particle spacing, slip lines form and the matrix fails in shear [23]. The condition for void coalescence is then met and a rapid increase of volume takes place prior to fast propagation (Fig. 7). These processes are active in the tip region and give

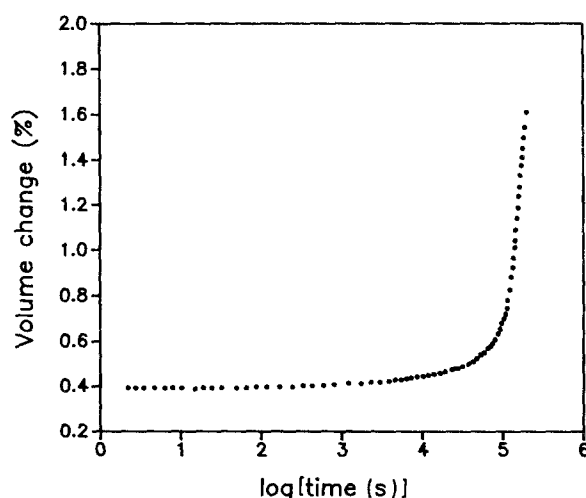


Figure 7 Volume deformation against time during tensile creep for E3700/CTBN.

rise to contradictory effects. At the beginning crack shielding takes place with the consequence of rendering more difficult the transfer of strain energy to the tip zone. However, after coalescence has taken place the crack can easily enter the tip region since a fracture path originates in the region before the crack.

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