



# Effect of cross-linking on dynamic mechanical and fracture behavior of epoxy variants



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## ABSTRACT

Anhydride cured epoxy systems are examined to elucidate the effect of cross-linking on viscoelastic and fracture behaviour of polymers. Dynamic mechanical and quasi-static fracture tests are conducted on epoxy variants, prepared by mixing diglycidyl ether of bisphenol-A (DGEBA) and methyl tetra hydro-phthalic anhydride (MTHPA) in several proportions. The molecular weight ( $M_c$ ) of the epoxy system increases monotonically as its composition deviates from the stoichiometry, indicating decreasing cross-link density. Significant influence of constituents' proportion is observed on glassy, glass transition and rubbery states, however, the damping characteristics remain largely unaffected in adequately cross-linked epoxies. An inverse correlation is demonstrated between the glass transition temperature ( $T_g$ ) and the molecular weight of epoxy variants. A relative change in constituents' proportion from stoichiometry monotonically increases the fracture toughness ( $K_{Ic}$ ) value of the material. Fracture surface micrographs reveal distinct composition dependent toughening mechanisms. While highly cross-linked stoichiometric system provides least resistance to material fracture, crazing and plastic deformation lead to increased fracture toughness values in hardener-rich and resin-rich epoxy systems, respectively. The  $K_{Ic}$  when plotted with  $M_c$  shows increasing trend until it reaches a plateau value at higher molecular weights even if the variation distinctly differs in resin-rich and anhydride-rich cases. A model correlating  $M_c$  and  $K_{Ic}$  is proposed while addressing the effect of unreacted constituents on the fracture behaviour of epoxy system.

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## 1. Introduction

Highly cross-linked thermosetting polymers have evolved into versatile engineering materials due to their ability to attain application oriented material characteristics. Chemical and thermo-mechanical properties of polymers can be tailored by varying the combination and composition of constituent resin and curing agents; by controlling the cure kinetics, or by reinforcing secondary phase fillers. Epoxy is perhaps the most widely used resin, since the material assumed commercial importance. It has found a wide range of applications in areas including MEMS devices, aerospace and structural components and bio-mechanical systems because of its excellent thermo-mechanical, adhesive and dielectric properties. In addition, epoxy also provides favourable matrix material properties such as easy processibility and resistance to corrosion and moisture ingress.

While curing the chemical reaction between resin and the curing agent develops three dimensional cross-linked polymeric chains. It is well recognized that the degree of cross-linking, also known as cross-link density, and the flexibility of chains between cross-links control the physical and thermo-mechanical properties of epoxy systems [1]. The gelling time and (elevated) temperature at which the curing takes place are key process parameters that affect cross-linking. It is difficult to maintain a uniform temperature throughout the material while fabricating large components. Also, because of the difference in thermal properties of constituent phases in composite materials, compositional uncertainty is prevalent, especially in the vicinity of interfaces. Non-uniform cross-linking may have little effect on macroscopic properties, such as elastic modulus, but the fracture properties could be significantly influenced due to the presence of localized weaker zones, acting as the sources of failure initiation.

For understanding the dependence of material properties on the polymer cross-linking, researchers have induced variations in molecular structure of various epoxy systems by changing the

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functionality [2–4] or the chemical contents [5–7] of curing agent; by controlling the curing temperature [8–10]; or by altering the proportion of resin/hardener (R/H) mixture [11,12]. Although similar effects of molecular level material parameters on thermal properties (such as glass transition temperature) are documented [2,4,12,13], the contradictory conclusions in regards to the fracture properties can not be ignored. While some researchers have reported an increase in fracture toughness as the molecular weight decreases [2,5,8,11], others suggested either a decreasing trend [3,9] or an optimal molecular weight corresponding to the maximum fracture toughness [6,12]. Similar differences can be noticed in case of other mechanical properties. In the current investigation we have developed epoxy variants by mixing phenolic resin with anhydride based curing agent in several proportions and performed a systematic dynamic mechanical and fracture analysis. A new model, correlating molecular weight with the fracture toughness, is proposed while addressing the effect of unreacted constituents on the fracture mechanisms of epoxy systems.

## 2. Materials

The curing agent, methyl tetra hydrophthalic anhydride (MTHPA), is first liquefied by heating at 120 °C for ~20 min. The liquid MTHPA is then mixed with diglycidyl ether of bisphenol-A (DGEBA) epoxy resin and a small amount of accelerator, 2,4,5-tris [(dimethylamino)methyl]-Phenol. The mixture is stirred at 240 rpm for ~45 min before being poured into a silicone smeared aluminium mould. The curing profile consisted of two steps, a pre-curing at 85 °C for 3 h, followed by a post curing at 140 °C for 12 h. In addition to the stoichiometric composition, 100:80 R/H ratio by weight [14], a set of resin-rich and anhydride-rich epoxy systems are prepared. The two considered resin-rich systems have 100:40 and 100:60 R/H ratios, whereas 100:100, 100:120, and 100:140 R/H compositions constitute the systems with excess of anhydride. The amount of catalyst added remains 0.5% of the mixture by weight irrespective of the epoxy composition. The samples for conducting dynamic mechanical, thermomechanical and quasi-static fracture tests are prepared by machining cast sheets into the required dimensions.

## 3. Experimental methods and measurement

### 3.1. Dynamic mechanical analysis

Viscoelastic properties of epoxy variants are measured by using Dynamic Mechanical Analyzer (DMA), Diamond DMA, Perkin Elmer<sup>®</sup>. Specimens of dimension 50 mm × 10 mm × 2.5 mm are loaded in tensile mode and the temperature is gradually increased from –25 °C to 170 °C at a heating rate of 3 °C/min. Experiments are performed at 10 Hz frequency with a 5 μm dynamic displacement. Representative data obtained from a test conducted on the epoxy system with stoichiometric composition are plotted in Fig. 1(a). The variation of storage modulus ( $E'$ ) with temperature ( $T$ ), illustrated by a solid curve in the figure, shows glassy ( $T < 130$  °C), glass transition ( $130$  °C  $< T < 146$  °C) and rubbery states ( $T > 146$  °C), typically observed in polymers. In the glassy state polymer chain segments are frozen, therefore material's response is predominantly elastic whereas in the rubbery state the material provides very little resistance to the movement of polymeric chains. A rapidly decreasing  $E'$  value in the glass transition zone nearly stabilizes to a very small magnitude in the rubbery state.

The loss modulus ( $E''$ ), represented by a dashed curve in Fig. 1(a), shows bell shaped variation with temperature in the glass transition zone. The temperature corresponding to the peak of  $E''$  is

considered as the glass transition temperature ( $T_g$ ). It is observed that the measured  $T_g$  (138 °C) is marginally higher compared to the respective value when determined using the tangent method<sup>1</sup> (135 °C). The difference between the two temperatures remains less than 4 °C in all epoxy samples. The loss factor ( $\tan \delta$ ) curve also shows a bell shaped variation with temperature, however, with a peak shifted to 149 °C temperature (See, the comparative plots in Fig. 1(d)).

### 3.1.1. Molecular weight and cross-link density

With an assumption that the material will behave as an ideal elastomer in rubbery regime, average molecular weight of the material between cross-links ( $M_c$ ) is calculated based on the rubber elasticity theory, using [15–17],

$$\left(G' = \frac{E'}{3}\right) = \frac{\phi \rho R T}{M_c}, \quad (1)$$

where  $G'$  and  $E'$  are rubbery shear modulus and rubbery elastic modulus, respectively. The  $\rho$  represents the material's density at temperature  $T$ ;  $R$  is the universal gas constant, and the front factor  $\phi$  is a correction factor for free, unreacted chain ends which is defined as the ratio between mean square end-to-end distance of a networked chain and the length of a randomly coiled chain [18].

While determining molecular weight using Eq. (1) the value of  $E'$  corresponds to the temperature  $T_g + 40$  °C in the rubbery state [17,18]. The  $\rho$  is calculated by weighing test samples at room temperature,  $T = 25$  °C. The  $\phi$  is assumed to be unity as suggested in Refs. [9,18]. Pearson and Yee [19] defined  $T$  as the temperature at which  $G'$  is obtained, however, they compensated for the density measurement at room temperature by adopting a front factor of 0.75. In the current investigation no significant change is observed as far as the  $M_c$  calculation is concerned when different methods are used.

Following  $M_c$  calculations, cross-link density ( $\mu$ ) of epoxy system is determined by using kinetic theory of rubber elasticity which relates  $M_c$  with  $\mu$  by [5,20],

$$\mu = \frac{\rho N}{M_c}, \quad (2)$$

where  $N$  represents Avogadro's number.

### 3.2. Thermo-mechanical analysis

The  $T_g$  values of epoxy variants are independently measured by using Thermo-Mechanical Analyzer (TMA) – Q400, TA Instruments<sup>®</sup>. Tests are conducted by heating 6 mm cuboid shaped specimens from 20 °C to 200 °C at a constant rate of 3 °C/min. The  $T_g$  is determined by applying the tangent method (the plots are not shown for brevity).

### 3.3. Fracture analysis

ASTM Standard D5045-99 is followed to prepare single edge notch beam (SENB) specimens. First, an edge notch of 2 mm depth is machined at the midspan of 62 mm × 14 mm × 6 mm beam sample. A sharp razor blade is then placed into the notch and gently tapped with a hammer to initiate a natural crack. Care is taken to ensure that the  $a/W$  ratio is maintained between 0.45 and 0.55

<sup>1</sup> In tangent method, glassy, glass transition and rubbery state data are approximated by three straight line fits. The  $T_g$  is considered as the temperature corresponding to the midpoint of the intersection of glassy and glass transition state lines, and the intersection of glass transition and rubbery state lines (See, Fig. 1(a)).

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