

# Effect of molecular weight between crosslinks on fracture behaviour of diallylterephthalate resins

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The effect of molecular weight between crosslinks,  $\bar{M}_c$ , on the fracture toughness and fracture behaviour of diallylterephthalate resin was investigated. As  $\bar{M}_c$  increased, the fracture toughness increased rapidly up to a maximum value and then decreased gradually. Scanning electron micrographs showed that the fracture toughness increased with an increase in the length of the slow crack growth, i.e. plastic deformation zone. Also, fracture toughness was found to have a close relation to crack opening displacement. Such a correlation reveals that the difference in fracture toughness with  $\bar{M}_c$  was due to the different sizes of the plastic zone. It is suggested that diallylterephthalate resin could undergo deformation via shear yielding at the crack tip with subsequent crack blunting. There was no evidence that crazes occurred in the fracture process.

(Keywords: diallylterephthalate resin; fracture; crosslinks)

## INTRODUCTION

It is well known that average molar mass between crosslinks,  $\bar{M}_c$ , affects the mechanical properties and fracture behaviour of thermosetting resins such as epoxy, phenolic and unsaturated polymers<sup>1,2</sup>. Many studies have been done on the mechanical properties and fracture behaviour of epoxy resins using amine-cured epoxy systems with various  $\bar{M}_c$  controlled by stoichiometry. The results showed that fracture toughness increases up to maximum value and then decreases<sup>3,4</sup>. It was also observed that glassy thermosetting resins undergo deformation by shear yielding rather than crazing<sup>1-4</sup>. However, in these cases unreacted excess components remain in the cured epoxy resin and may act as a plasticizer or structural defects. Then they can affect the mechanical properties and fracture behaviour of epoxy resins.

Matsumoto *et al.* investigated the mechanical properties of diallylphthalate resins co-crosslinked with glycol bis(allylphthalate) resin<sup>5</sup>. They controlled crosslink density by changing the content of diallylphthalate resin and the molecular weight of the co-crosslinker. They found that as crosslink density increases, fracture energy decreases and concluded that the fracture energy of co-crosslinked diallylphthalate resins is essentially governed by the crosslink density. However, in the case of high molecular weight co-crosslinker, microgel formation occurs in the

initial stage of the curing process and the microgels agglomerate, to become macrogels resembling colloidal particles, in the final product. Therefore these macrogels may act as a secondary phase and affect the fracture energy. However, they did not consider these effects.

Thus many authors have investigated the effect of  $\bar{M}_c$  on mechanical properties and fracture behaviour of thermosetting resins but have passed over other factors such as plasticization and macrogel formation.

Several authors have investigated the deformation mechanism of thermosetting resins during the fracture process<sup>6-9</sup>. They expected a transition from crazing to shear yielding to occur in the deformation mechanism as crosslink density increased, i.e.  $\bar{M}_c$  decreased. Van den Boogaart reported that crazes are formed around the crack tip in under-cured epoxy resin, the shape of the crazes appearing to be identical to those found in poly(methyl methacrylate)<sup>6</sup>. Morgan and O'Neal also observed craze-like entities in strained epoxy films<sup>7</sup>. However, the crazes were relatively short and although they seemed to be bridged by drawn polymers they are not well-defined crazes as observed in thermoplastics. On the other hand, Young<sup>8</sup> and Yee and Pearson<sup>9</sup> insisted that crazing cannot occur in the deformation of thermosetting resins. Thus there is little conclusive evidence that crazes are formed during the fracture process of thermosetting resins. Moreover, the reason why thermosetting resins are deformed by shear yielding rather than crazing has not been explained fully.

In this study, the effect of molecular weight between

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crosslinks on the mechanical properties and fracture behaviour of thermosetting resins has been investigated using a series of glycol bis(allylterephthalate) resins. For this purpose, the fracture toughness was measured and the deformed zone was examined by electron microscopy. The structure of the allylterephthalate resins could be systematically varied to control  $\bar{M}_c$  and the length of the glycol unit was short to prevent phase separation.

## EXPERIMENTAL

### Materials and specimen preparation

The materials for this study were a series of unsaturated ended prepolymers, which were prepared by transesterification<sup>10</sup>. First, a prepolymer was formed by reacting 1,3-butanediol (1,3-BG) with an excess of diallylterephthalate (DAT) in the presence of monobutyltin as a catalyst. The content of catalyst was 1000 ppm to diallylterephthalate. The reaction proceeded for 4 h at 190°C in vacuum to remove allyl alcohol. After reaction, unreacted reactant and low molecular weight oligomer were removed in high vacuum. The prepolymer chain length was controlled by the stoichiometry, which is defined by the mole ratio of diallylterephthalate to 1,3-butanediol. The synthetic reaction of prepolymers is shown in Figure 1.

To prepare plates for mechanical tests, prepolymer and dicumylperoxide as an initiator were mixed by a mechanical stirrer at 80°C and degassed. The content of initiator was 2 phr. Then the mixture was cast into a poly(tetrafluoroethylene) (Teflon) coated aluminium mould and cured in an oven. The curing steps included heating the sample at 135°C for 12 h and at 170°C for 2 h under nitrogen atmosphere to obtain a fully cured sample. After curing the cured sheets were slowly cooled and then machined to the desired size.

### Testing procedure

Molecular weight between crosslinks,  $\bar{M}_c$ , was calculated using equation (1) based on rubber elasticity<sup>11</sup>.

$$\bar{M}_c = \rho RT/G \quad (1)$$

where  $\rho$  is the density,  $R$  is the gas constant,  $T$  is absolute temperature and  $G$  is the shear modulus. The shear modulus  $G$  in the rubbery plateau region was measured by dynamic mechanical testing at 1 Hz in the single cantilever bending mode between 30 and 200°C, using a Polymer Laboratories DMTA apparatus. In this study, dynamic modulus  $E'$  was determined at  $T_g + 40^\circ\text{C}$  (where  $T_g$  is the glass transition temperature) and the shear modulus  $G$  was taken as  $E'/3$ . Fracture toughness  $K_{IC}$  was measured by

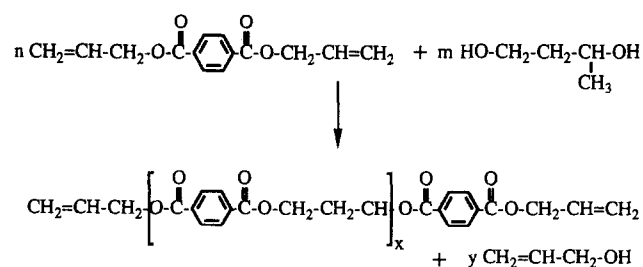


Figure 1 Synthetic reaction for preparing prepolymer

Table 1 Effect of mole ratio of reactant on glass transition temperature and molecular weight between crosslinks

Mole ratio (DAT/1,3-BG)	$T_g$ (°C)	$\bar{M}_c$ (g mol <sup>-1</sup> )
1.2/1	93	1668
1.3/1	103	746
1.4/1	114	610
1.6/1	130	276
1.8/1	148	190
2.0/1	153	183

a three-point bending test. The dimensions of the specimens were 5 mm × 10 mm × 50 mm (span 40 mm). The measurements were carried out using a universal test machine (Instron model 4202) at room temperature with a crosshead speed of 1.28 mm min<sup>-1</sup>. The specimens were sharply notched as follows. First, a blunt notch was produced using a machine with a V-shaped tool and then a sharp notch was made by a razor blade. The final notch depth was measured by an optical microscope after fracture. The fracture surfaces were examined by means of a scanning electron microscope (Hitachi S-570). The surfaces were coated with gold.

To examine the deformed zone in front of the crack tip, double notched four-point bending testing was employed<sup>12</sup>. A thin section of the specimen cut from the deformed zone in the front of the crack tip was polished and then examined using an optical microscope. Yield behaviour of the resins was determined by uniaxial compression testing using cylindrical specimens with a height-to-diameter ratio of 2:1. The specimens were deformed in uniaxial compression mode at a crosshead speed of 1.28 mm min<sup>-1</sup> using the Instron apparatus.

## RESULTS AND DISCUSSION

The effect of mole ratio on the glass transition temperature  $T_g$  and molecular weight between crosslinks  $\bar{M}_c$ , measured by dynamic mechanical thermal analysis, is shown in Table 1. As the mole ratio increased,  $\bar{M}_c$  decreased but  $T_g$  increased as expected. It is well known that increasing  $\bar{M}_c$  leads to increasing chain flexibility and then results in decreasing glass

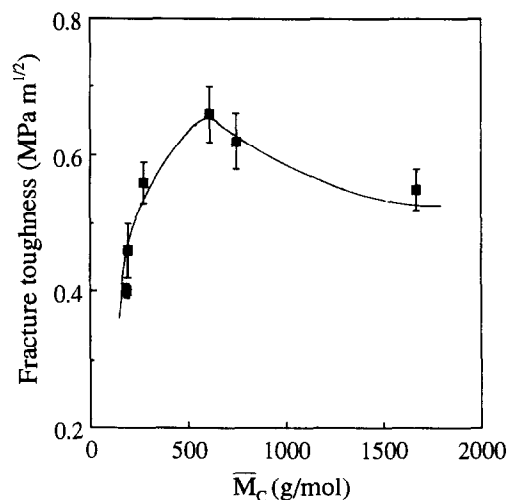


Figure 2 Variation of fracture toughness  $K_{IC}$  as a function of  $\bar{M}_c$  for a diallylterephthalate resin

transition temperature<sup>1</sup>. These results indicated that the length of the prepared prepolymer was well controlled, as expected. This was also confirmed by the fact that, as mole ratio decreased, the viscosity of the prepolymer increased due to increasing molecular weight.

Figure 2 shows the variation of fracture toughness  $K_{IC}$  measured by the three-point bending test as a function of  $\bar{M}_c$ . As  $\bar{M}_c$  increased fracture toughness increased rapidly up to an  $\bar{M}_c$  value of  $610 \text{ g mol}^{-1}$  and then decreased gradually with increasing  $\bar{M}_c$ . This is the typical dependence of fracture toughness on  $\bar{M}_c$  in thermosetting resins with narrow molecular weight distribution<sup>4</sup>. If the molecular weight distribution is broad, the fracture toughness is almost constant irrespective of  $\bar{M}_c$ <sup>4</sup>. The above phenomenon revealed that the molecular weight distribution of the prepared prepolymer in this study was narrow. It is known that plastic deformation is localized at the crack tip during crack propagation in highly crosslinked thermosetting resins<sup>13</sup> and large plastic deformation occurs if crosslinking is relatively light<sup>4</sup>. Therefore increasing fracture toughness with  $\bar{M}_c$  in Figure 2 might be mainly attributed to large plastic deformation resulting from easy chain flow. However, the reason for decreasing fracture toughness at larger  $\bar{M}_c$  is not yet clear.

Although it is well known that plastic deformation is localized at the crack tip in highly crosslinked thermosetting resins, it is extremely difficult to show directly that it takes place. According to Kinloch and Young<sup>13</sup>, it is possible to observe blunt cracks with tip radii of several micrometres but it is extremely difficult to observe the plastic zone which is believed to be present in front of the crack tip. Figure 3 presents optical micrographs of a thin section of the crack tip region for a specimen with maximum fracture toughness. Phase separation was not observed in Figure 3, and absence of this phenomenon was also confirmed by scanning electron micrographs. Therefore, the effect of a secondary phase on fracture toughness and fracture behaviour could be excluded. Optical micrographs of specimens with lower fracture toughness were found to be similar to that shown in Figure 3; there was no evidence that plastic deformation occurred at the crack tip region even in the specimen of high fracture toughness. Thus it is not possible to explain differences in fracture toughness by considering deformation of the

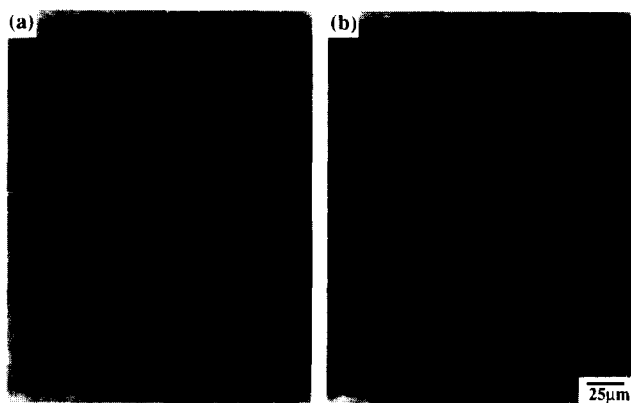


Figure 3 Optical micrographs of a thin section of the crack tip region for a specimen with maximum fracture toughness ( $K_{IC} = 0.66 \text{ MPa m}^{1/2}$ ): (a) bright field; (b) cross polar field

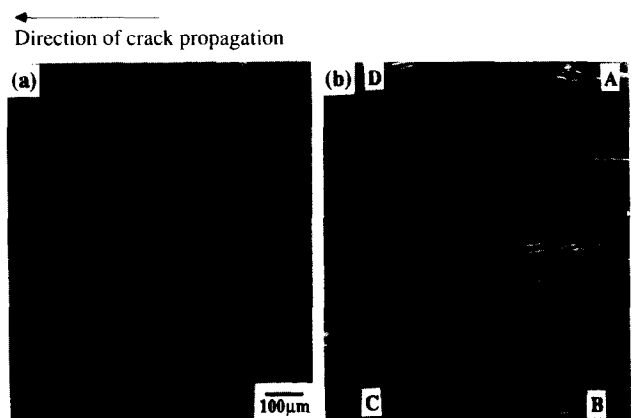


Figure 4 Scanning electron micrographs of fracture surface in the crack tip region for three-point bending specimens with different fracture toughness: (a)  $K_{IC} = 0.4 \text{ MPa m}^{1/2}$  ( $\bar{M}_c = 183 \text{ g mol}^{-1}$ ); (b)  $K_{IC} = 0.66 \text{ MPa m}^{1/2}$  ( $\bar{M}_c = 610 \text{ g mol}^{-1}$ )

crack tip region. As mentioned above, the same phenomena are observed in the fracture of other neat thermosetting resins such as epoxy and unsaturated polyester<sup>13</sup>. So the reason why fracture toughness varied with  $\bar{M}_c$  should be discussed in other ways.

Figure 4 shows scanning electron micrographs of the fracture surfaces in the crack initiation region for three-point bending specimens with different fracture toughnesses. The specimen in Figure 4a exhibits a smooth and relatively featureless fracture surface which can be associated with fast crack propagation. On the other hand, the specimen in Figure 4b showed considerable deviation of the crack from the main fracture plane at an arrest zone (ABCD) and the two halves of the crack surface in the vicinity of the arrest zone tended to interlock. Beyond line CD, the fracture surfaces showed only the presence of fine longitudinal lines parallel to the crack propagation direction. These phenomena illustrate that crack propagation occurred by slow growth through the arrest zone (ABCD) followed by rapid growth through the specimen. Kinloch and Young<sup>13</sup> defined the slow crack growth zone as the plastic zone and Yamani and Young<sup>14</sup> found a correlation between the length of the slow crack growth zone,  $l_s$ ,

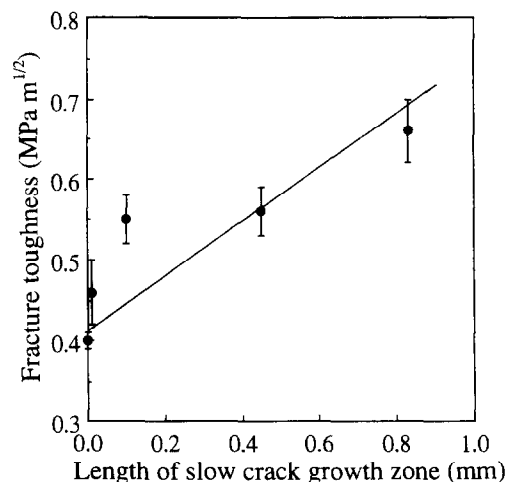


Figure 5 Variation of fracture toughness as a function of length of the slow crack growth zone

**Table 2** Yield behaviour of diallylterephthalate resins with  $\bar{M}_c$ 

$\bar{M}_c$ (g mol <sup>-1</sup> )	Yield strength (MPa)	Yield strain (%)
183	66 ± 1.4	3.97 ± 0.18
190	78 ± 6.0	3.77 ± 0.16
276	84 ± 3.5	3.89 ± 0.20
610	79 ± 0.6	3.71 ± 0.26
1668	83 ± 0.4	3.74 ± 0.04

and fracture toughness for epoxy resin. Another report for an epoxy/polycarbonate blend also demonstrated that the length of the slow crack growth zone  $l_s$  is related to the fracture toughness  $K_{IC}$  measured by the three-point bending test<sup>15</sup>. In our study, the length of the slow crack growth zone of the specimen with low fracture toughness was very short (Figure 4a); however, this length increased with increasing fracture toughness (Figure 4b). Also deviation of the crack at the arrest zone from the main fracture plane became larger with increasing fracture toughness.

Figure 5 shows the variation of fracture toughness as a function of the length of the slow crack growth zone. Fracture toughness increased linearly with the length of the slow crack growth zone, i.e. with the size of the plastic zone, as in previous work<sup>14</sup>. Therefore these results confirmed that plastic deformation occurred at the crack tip region and the difference in fracture toughness was attributed to the different sizes of the plastic zone.

For the allylterephthalate resin in this study, there was no decisive evidence of craze formation. So it is supposed that the plastic zone around the crack tip was most likely produced via shear yielding rather than crazing. It seems that a localized plastic zone developed at the crack tip and the crack blunted during crack arrest<sup>3</sup>. This blunted crack grows slowly until sufficient strain energy is stored. On continuous loading the crack propagates rapidly through the specimen. Therefore it might be speculated that localized yielding at the crack tip with subsequent crack blunting is the main mechanism of energy dissipation during the fracture process.

To prove the above discussion, the yield behaviour of the allylterephthalate resins was investigated in detail. Since these materials fractured before yielding when

tested in uniaxial tension, their yield behaviour was determined in uniaxial compression. Values of yield and fracture toughness data were used to calculate the degree of crack blunting. Assuming that the radius of blunt crack,  $\rho_c$ , is equivalent to the crack opening displacement,  $\delta_c$ , it can be calculated using the relation<sup>3</sup>:

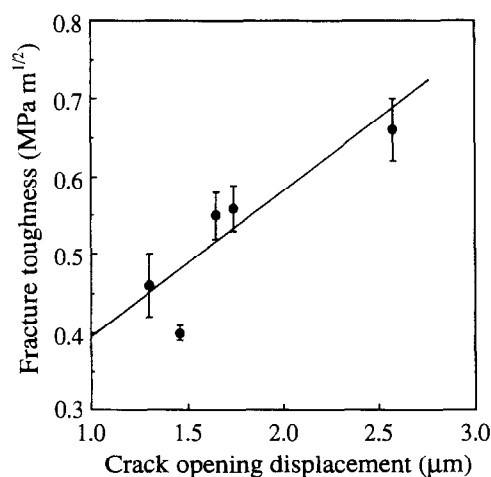
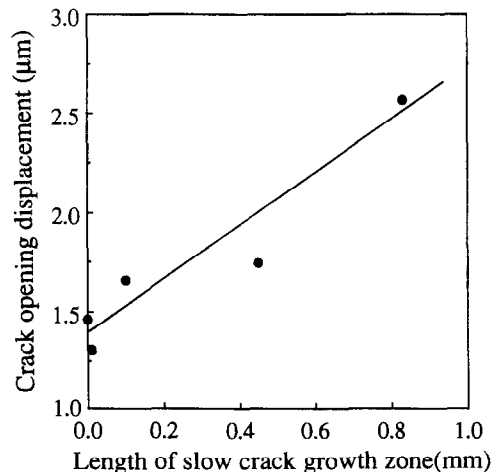
$$\rho_c = \delta_c = (K_{IC}/\sigma_y)^2 \epsilon_y \quad (2)$$

where  $\sigma_y$  is the yield stress and  $\epsilon_y$  is the yield strain. The yield behaviour of the materials is illustrated in Table 2. The yield strength was almost constant irrespective of  $\bar{M}_c$ , except at an  $\bar{M}_c$  value of 183 g mol<sup>-1</sup>. It is not clear why yield strength was minimum at low  $\bar{M}_c$  and is contrary to expectation.

Fracture toughness  $K_{IC}$  as a function of crack opening displacement is shown in Figure 6, which reveals that the fracture toughness increased with crack opening displacement. As shown in Figure 7, the length of the slow crack growth zone had a close relation to the crack opening displacement. Therefore these results demonstrate that localized yielding at the crack tip and subsequent crack blunting was the main mechanism governing the degree of plastic deformation during the fracture process and the difference in fracture toughness was due to the different size of the plastic deformation via shear yielding.

Many studies have been done on the deformation mechanism of polymers. Donald and Kramer have suggested that molecular entanglements influence the deformation mechanism of polymers<sup>16</sup>. They found that polymers with large chain contour length,  $l_e$  between entanglements tend to undergo fibrillation readily and are deformed by crazing<sup>16</sup>. Wu proposed that polymers tend to be brittle and that crazing is the dominant deformation mode when the entanglement density is lower than 0.15 mmol cm<sup>-3</sup> and the characteristic ratio is higher than 7.5, otherwise shear yielding occurs<sup>17</sup>. Both these conclusions were confirmed by experimental investigation using various thermoplastics.

It is accepted that thermosetting resins undergo plastic deformation via shear yielding rather than crazing<sup>8,9</sup>. This is attributed to high crosslink density and small  $l_e$ . As mentioned above, thermosetting resins must have a low crosslink density and a large chain

**Figure 6** Variation of fracture toughness as a function of crack opening displacement**Figure 7** Correlation between crack opening displacement and length of the slow crack growth zone

contour length,  $l_c$  between crosslinks to be deformed by crazing. It is also known<sup>18</sup> that crosslinking reduces  $l_c$ . In this study the value of crosslink density ranged from 0.75 to 6.84 mmol cm<sup>-3</sup> and this value was too high for the materials to form crazes. Although much lower crosslink density than those of this study may be obtained by changing the stoichiometry, the materials might be ductile and tend to yield. Matsumoto *et al.*<sup>5</sup> showed that the glass transition temperature is about 20°C and the elongation at break measured by uniaxial tension is about 40% in co-crosslinked diallylphthalate–poly(ethylene glycol) bis(allylphthalate) resins (50 : 50 mole ratio). They also found that as crosslink density decreases, the materials become ductile. Their results verify the above discussion.

In fact, total effective entanglements are composed of physical entanglements and chemical crosslinks<sup>19</sup>. If the molecular weight between double bonds of the prepolymer in this study was larger than the molar mass  $\bar{M}_c$  of physical entanglements, it is probable that physical entanglements were formed before network formation and permanently trapped during the curing process<sup>19</sup>. Hence lowering of the effective entanglement density by changing the stoichiometry was limited and it was difficult to acquire a crosslink density that coincided with the craze criteria due to physical entanglements. Therefore it is supposed that diallylterephthalate resins were deformed via shear yielding, like other thermosetting resins, because of high crosslink density and small  $l_c$ .

## CONCLUSION

In this study, the effect of molecular weight between crosslinks on mechanical properties and fracture behaviour was investigated using diallylterephthalate resins. It was found that the fracture toughness passed through a maximum as  $\bar{M}_c$  was varied. Scanning electron micrographs showed that fracture toughness increased with the length of the slow crack growth zone, i.e. the plastic deformation zone. Fracture toughness was found to have a close relation to the

degree of crack blunting. Therefore the main deformation mechanism was localized shear yielding at the crack tip and subsequent crack tip blunting, which was confirmed by yield behaviour and fractography of the crack initiation region. There was no evidence that crazes occurred during the fracture process.

## ACKNOWLEDGEMENT

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