CRACK PROPAGATION STUDIES OF A RUBBER-TOUGHENED EPOXY RESIN IN THE SCANNING ELECTRON MICROSCOPE

S. Bandyopadhyay and V. M. Silva

Materials Research Laboratories, Melbourne Defence Science & Technology Organisation, PO Box 50, Ascot Vale 3032, Victoria, Australia

ABSTRACT

The crack tip micromechanics in a commercial, rubber toughened epoxy resin have been studied by conducting crack propagation experiments in a scanning electron microscope. The method gives a clear picture of crack tip deformation and crack tip opening displacement. The critical crack shear opening displacement provides a satisfactory estimate of the critical strain energy release rate G_{Ic} of this material. Also, the material exhibits a maximum shear strain of about 47% at the crack tip.

KEYWORDS

Rubber Toughened Epoxy, Crack Tip Opening Displacement, Scanning Electron Microscope, Tensile Stage, Fracture Energy, Crack tip shear strain

INTRODUCTION

Epoxy resins are extensively used as structural adhesives and as the matrix phase in composite materials. Although epoxies possess adequate strength and stiffness for load bearing purposes, their inherently brittle nature can be of serious concern both in adhesive joints and in regard to matrix controlled properties in composites. The fracture energy, G_{Ic}, of these resins is often as low as 0.1-0.2 kJ/m^2 implying that a flaw or flaws present in these materials can propagate easily, leading to fracture. In order to combat this problem, elastomer (rubber) modified epoxy resins have been developed with minute rubber particles being formed in situ during the early stages of epoxy polymerisation and distributed throughout the epoxy matrix. Carboxyl terminated acrylonitrile butadiene (CTBN) elastomers are used most commonly for this purpose where the rubber particles are believed to form chemical bonds with the matrix (Siebert and Riew, 1971). Fracture energies of an order of magnitude higher than that of the original resin have been reported for elastomer containing epoxies (Sultan and Co-workers, 1971, Bascom and Co-

were obtained with a 2.5 mm diameter hemispherical probe, loaded with 20 g, at a heating rate of 5°C/min. The DSC curves were obtained at 20°C/min. The glass transition (Tg) of the epoxy system was well defined in both TMA and DSC curves : Tg (TMA) was 50°C while Tg (DSC) was in the range of 53-69° with inflection temperature 59°C and the DSC studies suggested that the curing reaction was virtually complete at room temperature during cure. No unequivocal evidence was obtained for a transition that could be attributed to the rubber phase in the range -70° to 30°C. However, the TMA results indicated a very slight but persistent effect at -8°C which may be the rubber Tg.

The rubber content of this resin is not specified, however, the yield strength of the material was found to be 40 MPa, and one may assume the rubber content to be between 10 and 15%. In unnotched tensile testing, deformation was mostly by shear yielding, but stress whitening was also observed.

RESULTS AND DISCUSSION

Crack Tip Characteristics

A typical load displacement curve of crack propagation is shown in Fig. 2. From an examination of a number of test specimens the load-displacement curve can be approximately divided into three regions: crack tip opening, slow crack growth, and rapid failure.

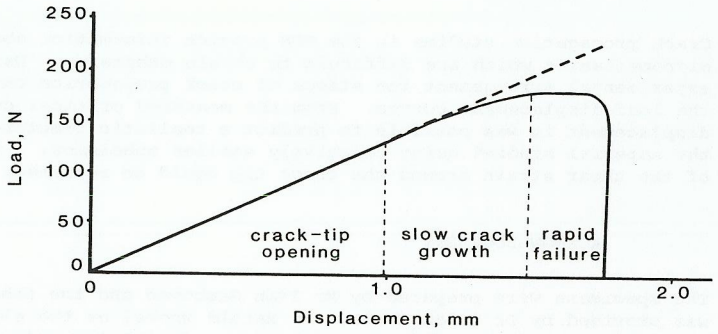

Fig. 2. A typical load-displacement curve

Representative crack tip appearances are presented in the following figures.

Figure 3 shows an initial crack tip in a specimen prior to loading, where the bright squares are due to the discrete blocks of gold that have been vapour deposited onto the specimen through the 17 μm grid copper mesh. Upon loading, this crack tip starts deforming and opening (blunting), as shown in Fig. 4, until a maximum crack tip opening (δ_c) is attained when the material ahead of the crack tip fails and a crack initiates in the specimen resulting in the

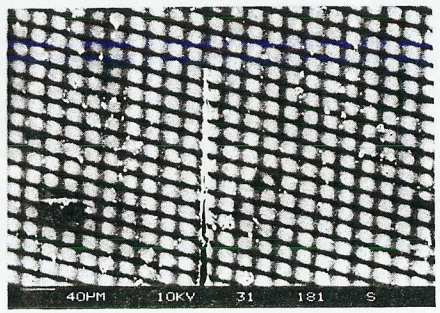

Fig. 3. The crack tip region prior to loading

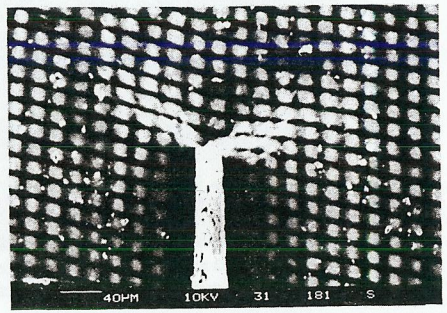

Fig. 4. The crack tip under tension in the crack opening stage

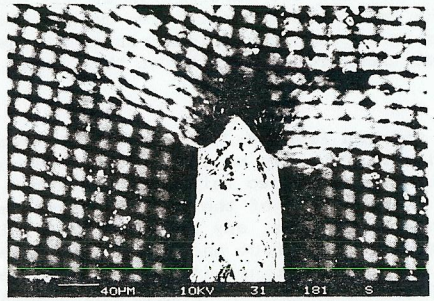

Fig. 5a. Crack tip appearance during slow crack growth

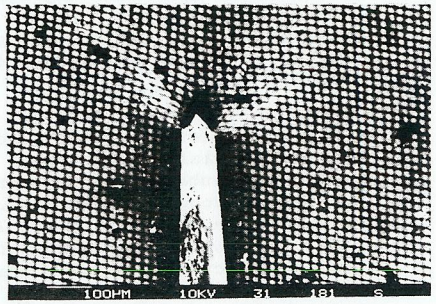

Fig. 5b. Showing a wider region around the crack tip

onset of slow crack growth. Figures 5(a,b) show a crack tip situation in the slow crack region at two magnifications. There is distinct evidence of shear deformation, shown by the displacement of the grid, in the crack tip region, the maximum shear strain being about 47%. In Figs. 4 and 5 the bright (v-shaped) areas which are seen at the crack tip approximately ±60° to the crack line, show the plastic zone boundary. (The increase in brightness in these areas may be due to voltage contrast developed by some type of piezoelectric effect as is known to occur in certain polymeric materials). Examination of Fig. 5 also shows the presence of small voids and craze-like features near the crack tip. At this stage, the specimen in consideration was unloaded and allowed to relax for 24 hours. The deformed zone at the relaxed crack tip is shown in Fig. 6 which also shows evidence of crack tip closure. The overall shape of the deformation zone shown in Figs. 4, 5 and 6 has similarity with the crack tip plastic zone predicted by Tuba (1966).

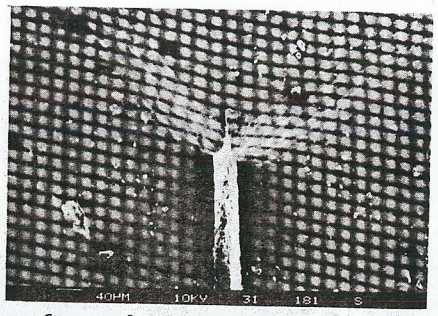

Fig. 6. Relaxed crack tip (no load) showing permanent deformation

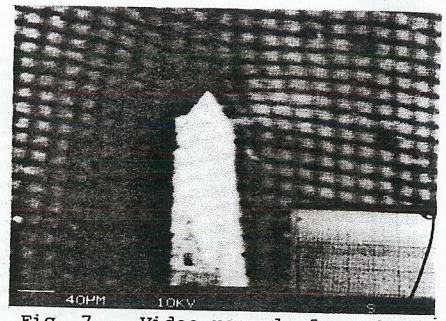

Fig. 7. Video record of crack tip during slow crack growth

The crack tip features shown in Figs. 3-6 were photographed in the normal SEM mode, Figs. 4 and 5 being taken under load by stopping the crosshead movement at the respective stages. The crack tip situation shown in Fig. 7 has been reproduced from the video record, during slow crack growth in another specimen. Although the quality of photograph of Fig. 7 is not so good as that of Figs. 3-6, the crack tip appearance and the deformation around the crack tip are visible. The state of the load-displacement curve corresponding to this crack tip situation can be seen in the lower right corner of the figure. There is significant deviation from linearity at this stage of crack growth.

A closer inspection of the crack tips in Figs. 4-7 reveals the presence of fibrous material between crack edges. This may be due to the stretching (and tearing) of rubber particles or it may be due to failure of asbestos filler particles through fibrillation. An SEM study of the fracture surfaces confirmed the presence of the latter. However, any stretched and failed rubber particles would almost immediately retract and possibly not be seen by study of fracture surfaces. Bascom and co-workers (1975) had considered a possible link between high G_{Ic} of rubber toughened epoxies and presence of a large number of energy dissipating (rubber) particles at the crack tip.

Crack Tip Opening Displacement (CTOD) and Fracture Energy

A number of workers have used the concept that fracture occurs when the CTOD exceeds a critical value (δ_c) and this approach has also been used in polymeric materials by Williams (1972). Now, following Burdekin and Stone (1966), for stresses small compared to yield stresses:

$$CTOD = \frac{G_I}{\sigma_{ys}}$$ Where σ_{ys} is the yield stress; and 1

$$\delta_c = \frac{G_{Ic}}{\sigma_{ys}}$$, for onset of crack propagation 2

where G_{Ic} is the critical strain energy release rate for plane strain conditions. δ_c can be estimated at the onset of slow crack growth and it can be defined at the intersection of the plastic boundary and the crack edges (Broek, 1974). In most routine tests it is difficult to measure δ_c but in the present work this information can be directly obtained. For this reason an estimate of G_{Ic} has been made in this material by using equation (2) as follows. With specimens 1.1 mm or more in thickness it was possible to obtain almost plane strain failure; δ_c for such specimens was 40±5 μm, the corresponding stresses being less than $\sigma_{ys}/3$. By using equation (2) and using σ_{ys} = 40 MPa, a G_{Ic} value of 1.6±0.2 kJ/m^2 is obtained. Sultan, Laible and McGarry (1971) reported G_{Ic} between 1.6 and 2 kJ/m^2 for Epon 828 resin containing 10% CTBN. G_{Ic} reported by Bascom and co-workers (1975) for DGEBA resin with 10% CTBN is about 2 kJ/m^2 and that with 15% CTBN is 2.5 kJ/m^2. A similar value of G_{Ic} was quoted by Kinloch, Shaw and Hunston (1982) for an epoxy resin with 15% CTBN. Considering the enormous variation in Tg, modulus of elasticity and σ_{ys} that can be produced by using different curing agents and curing temperatures in these different resins, the value of the fracture energy G_{Ic} obtained in the present paper from critical CTOD approach is considered quite satisfactory.

The ability to measure crack length extension at the same time as load and load-point displacement makes this method a potential tool for estimation of J_{Ic}. However, for single edge notched specimens an allowance for deformation for the material away from the notch tip has to be incorporated. These aspects are currently being examined and use of other specimen geometries, such as compact tension is also being contemplated.

CONCLUSION

Crack propagation studies in the SEM provide information about crack tip micromechanics which are difficult to obtain otherwise. Using the present experimental arrangement the stages of crack propagation can be identified on the load-displacement curves. From the measured critical crack tip opening displacement it was possible to predict a realistic fracture energy G_{Ic} for the material studied using relatively smaller specimens. Also, the magnitude of the shear strain around the crack tip could be measured.

ACKNOWLEDGEMENT

The specimens were prepared by Mr Ivan Grabovac and the thermal analysis data was provided by Dr Brian Ennis. Mr Harald Wrobel of the electron microscopy unit established the conditions for vapour depositing gold through the copper grid and also gave valuable technical help. Thanks are due to Dr Derry Doyle for providing the video recorder used in this study and to Mr Jim Nicholls for carrying out the live video superimposition. The authors would also like to thank Dr Peter Burchill and Mr Peter Pearce for helpful discussion and Dr Graham Clark and Dr Carolyn Morris for reading the manuscript. The photographic prints were produced by Ms Julian Thompson.

REFERENCES

Bandyopadhyay, S. (1984). Crack Propagation Studies of Bulk Polymeric Materials in the Scanning Electron Microscope. J. Mater Sci Lett., 3, 39.

Bascom, W.D., R.L. Cottington, R.L. Jones, and P. Payser (1975). J. Appl. Polym Sci., 19, 2545.

Broek, D. (1974). Elementary Engineering Fracture Mechanics. Noordhoof, Leyden.

Burdekin, F.M. and D.E.W. Stone (1966). J. Strain Analysis, 1, 145.

Kinloch, A.J., S.J. Shaw and D.L. Hunston (1982). 5th International Conference on Deformation, Yield and Fracture of Polymers, Cambridge, England, 29 March - 1 April.

Kunz-Douglass, S., P.W.R. Beaumont, and M.F. Ashby (1980). J. Mater Sci., 15, 1109.

Riew, C.K., E.H. Rowe, and A.R. Siebert (1976). Rubber Toughened Thermosets, Toughness and Brittleness of Plastics. Adv. Chem. Ser., 154, 326.

Siebert, A.R., and C.K. Riew (1971). A.C.S., Division of Organic Coatings and Plastic Chemistry, 31, 1, 552.

Sultan, J.N., R.C. Laible, and F.J. McGarry (1971). Appl Polym Symp. 16, 127.

Tuba, I.S. (1966). J. Strain Analysis, 1, 115.

Williams, J.G. (1972). Int. J. Fract Mech. 8, 393.