JOURNAL OF MATERIALS SCIENCE 16 (1981) 2657–2664

# The fracture of an epoxy polymer containing elastomeric modifiers

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The fracture energies of elastomer-modified epoxy polymers have been determined over a range of strain rates from $10^{-2}$ to $10^3$ sec$^{-1}$. The modifiers included a liquid carboxy-terminated butadiene acrylonitrile and a solid rubber. They were used alone and also in combination. In all cases, the modifiers increased the toughness of the base resin by orders of magnitude and one combination of liquid and solid rubber increased toughness by 60 times. There was a general decrease in fracture energy with increasing strain rate but even during impact testing the modified epoxys were 10 to 20 times tougher than the base polymer. Scanning electron microscopy revealed that, when combined with the liquid rubber, the solid rubber induced a localized shear yielding.

## 1. Introduction

The effect of elastomeric modifiers on the fracture behaviour of epoxy polymers has been described by McGarry *et al.* [1, 2], Siebert *et al.* [3–5], Bascom *et al.* [6–8] and others [9, 10]. These workers have investigated epoxy resins modified with liquid carboxy-terminated butadiene acrylonitriles (CTBN) in which the CTBN co-polymerizes with the epoxy prior to gelation to form a dispersed phase of particles having diameters of a few micrometres or less. These particles enhance the toughness of the unmodified epoxy by orders of magnitude by mechanisms that involve triaxial dilation of the particles in the plane-strain stress field at a crack tip [2, 6–8], plastic flow of the epoxy matrix [11] and elongation of the particles [11, 12].

Riew *et al.* [5] have shown that a bimodal distribution of particle sizes enhances epoxy polymer toughness more than a mono-dispersed formulation. Some commercial elastomer–epoxy formulations utilize both a liquid CTBN and a solid rubber in an effort to achieve a multi-modal distribution of particle sizes and greater toughness. In the study reported here, a commercial epoxy resin formulation, Hexcel F-185 (Hexcel Corp. Dublin, CA), which contains both liquid and solid elastomeric additives is examined to determine the effect of these additives on the fracture behaviour of an epoxy polymer.

## 2. Experimental procedure

The composition of the epoxy resin without elastomeric modifiers is given in Table I. The four polymer compositions which were fracture tested are listed in Table II and include the unmodified base epoxy and the base epoxy modified with a liquid CTBN (HYCAR® 1300 x 13, B. F. Goodrich Chemical Co., Cleveland, OH) or a solid rubber (HYCAR® 1472) or both. The solid rubber was pre-cooked with the epoxy resin components of Table I by heating in methylethyl ketone solution.

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0022–2461/81/102657–08$02.80/0

TABLE I Composition of the base epoxy resin (205)

| Component | Approximate weight % |
|---|---|
| Epoxides | 73 |
| (diglycidyl ether of bisphenol A) | |
| (epoxidized novolac, epox. eq. wt. 165) | |
| Diphenols | 20 |
| (bisphenol-A) | |
| (tetrabromobisphenol-A) | |
| Catalysts | 7 |
| (dicyandiamide) | |
| (substituted urea) | |

TABLE II Elastomer content of test resins

| Composition number | Liquid CTBN[a] (HYCAR® 1300 × 13) | Solid rubber[b] (HYCAR® 1472) |
|---|---|---|
| 205[c] | None | None |
| 206 | 8.1 wt% | None |
| 207 | 8.1 wt% | 1.0 |
| 210 | None | 8.1 |
| 185 | 8.1 wt% | 5.4 |

[a] Average molecular weight of 3500.
[b] Average molecular weight of 260 000.
[c] Base epoxy.

The resins were cast and cured into plates approximately 15 cm by 10 cm by 0.6 cm at 82 to 88° C for 4 to 8 h and then at 121° C for 1 h. Most of the fracture tests were conducted using compact tension (CT) specimens [13] cut from the cast plates. The CT specimen geometry is shown in Fig. 1 and the equation used to calculate the fracture energy ($\mathscr{G}_{\mathrm{I_c}}$, strain energy release rate) is

$$\mathscr{G}_{\mathrm{I_c}} = Y^2 \frac{P_c^2 a}{E W^2 b^2}, \qquad (1)$$

where $P_c$ is the failure load, $E$ is the bending modulus, $Y$ is a geometry factor given by

$$Y = 29.6 - 186\,a/W + 656\,(a/W)^2 - 1017\,(a/W)^3 + 639\,(a/W)^4 \qquad (2)$$

and $a$, $b$ and $W$ are the crack length and specimen dimensions as shown in Fig. 1. Precracks were made in the elastomer–epoxy composition specimens by notching the end of the saw cut with a razor blade. Specimens of the unmodified epoxy were too brittle to use this notching method and so it was necessary to machine a dove-tail at the end of the saw-cut and tap the edge of the dove-tail with a sharp blade to initiate a starter crack. The CT specimens were tested for $\mathscr{G}_{\mathrm{I_c}}$ at 25° C and various loading rates using a mechanical test machine (Instron Corp.). The bending modulus, $E$, was determined using the three-point bending method.

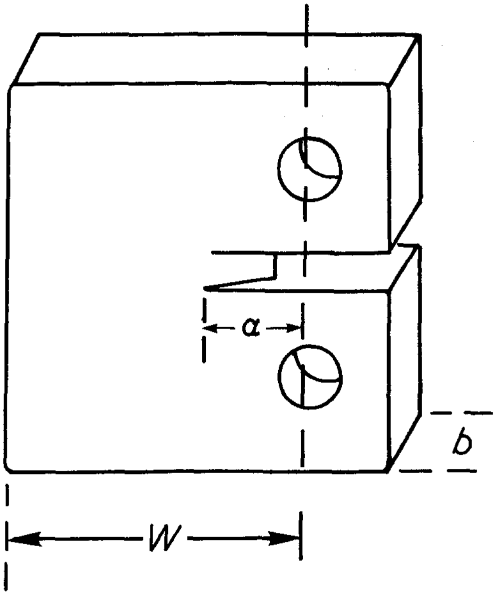

*Figure 1* Compact tension test specimen.

Fracture tests at strain rates considerably higher than can be attained with a conventional mechanical machine were carried out using the standard Izod impact test method. Specimens measuring 5.5 cm × 1.0 cm × 1.0 cm were centre notched and a razor cut was made at the base of the notch. This razor cut avoids the ambiguities associated with "blunt" notch and also the data scatter was considerably reduced [14]. The impact load and the impact energy were recorded simultaneously as functions of impact time. The load was found to increase linearly with impact time until fracture which allows the use of linear elastic fracture mechanics for data analysis [15]. The impact energy data were converted to $\mathscr{G}_{\mathrm{I_c}}$ using the method of Plati and Williams [16]. Plots were made of impact energy against specimen cross-sectional area (Fig. 2), the slopes of which give the fracture energy directly. The net cross-sectional areas of the specimens were varied by varying the notch depth.

Post-failure examinations of the specimens were made using scanning electron microscopy (SEM).

## 3. Results

The fracture energies obtained over a range of loading rates for the four epoxy and epoxy–

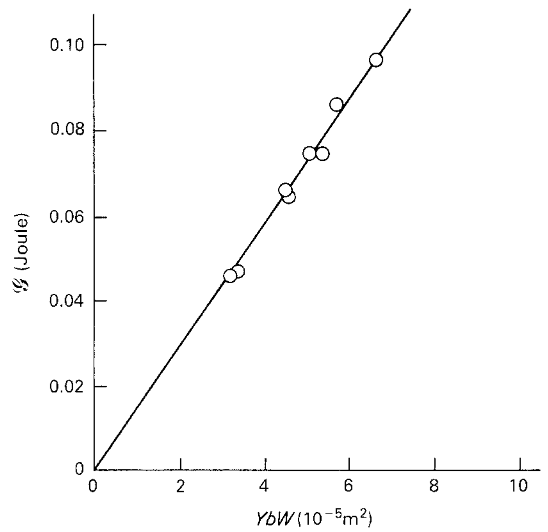

*Figure 2* Impact energy against specimen cross-sectional area.

elastomer compositions listed in Table II are plotted in Fig. 3. Four aspects of Fig. 3 should be noted: (a) elastomer additives, both liquid and solid, increase the fracture energy of the epoxy by orders of magnitude at all strain rates; (b) used alone, the liquid CTBN and the solid rubber have about the same effect on toughness; (c) when both elastomeric additives are present the fracture energy is increased further by a factor of as much as two times; and (d) all elastomer–epoxy compositions show a general decrease in fracture energy with increasing strain rate but there was no strain rate effect evident for the base epoxy polymer.

Associated with the high toughness of the elastomer–epoxy compositions is the development of a stress whitening at the crack tip prior to fracture. On the other hand, the base, unmodified epoxy specimens showed no visible evidence of stress whitening. The extent of stress whitening increased with increasing toughness. In a preliminary report of this work [17], it was shown that the extent of stress whitening and toughness increased as the weight per cent of the solid rubber was increased (at a fixed concentration of the liquid CTBN of 8.1 wt%). Specimens of the 185 compositions showed the largest area of stress whitening. In Fig. 4 specimens of the 185 compositions that had been tested at different strain rates are shown and it is evident that the stress whitening decreases significantly as the strain rate is increased and, in fact, the impact specimen shows no evidence of stress whitening.

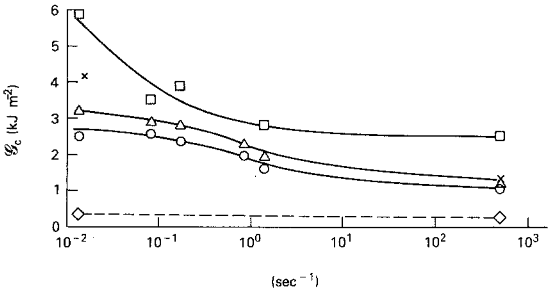

*Figure 3* Fracture energy against strain rate. ◇, 205; ○, 206; ×, 207; △, 210; □, 185.

The fracture specimens were given a detailed, post failure SEM examination. Fig. 5a is an SEM view of the unmodified epoxy specimen at the boundary between the pre-crack (LHS) and the region of slow crack growth (RHS) as the fracture initiated. The region of slow growth shows considerable plastic deformation of the epoxy polymer. Further to the right, where the crack was moving very rapidly, the surface was smooth which indicates much less yielding of the material. A stress-whitened region of the specimen containing only the liquid CTBN additive (composition 206) showed evidence of massive shear yielding as shown in Fig. 5b at low magnification and at high magnification small holes are evident (Fig. 5c and d) having diameters of a few tenths of a micrometre.

SEM examination of the stress-whitened region of the specimens containing both elastomeric additives (composition 185) revealed two characteristic features. At low magnification, as shown in Fig. 6a, there is localized shear yielding that appears to be associated with holes a few micrometres in diameter. At high magnification (Fig. 6b), small holes are observed similar to those seen in the stress-whitened regions of the specimen containing only the liquid CTBN (Fig. 5c and d).

The preceding SEM observations were made on specimens tested at the lowest strain rate (~ $10^{-2}$, $\sec^{-1}$). At increasing strain rate there was a gradual diminishing of the severity of the deformation. This change can be seen by comparing Fig. 7a with Fig. 5d. Although the small holes are still evident on the fracture surface of the impact specimen (Fig. 7a) they are shallower and less distinct than on the specimen tested at the low strain rate (Fig. 5). Similarly, the localized shear yielding and the associated holes are still evident on the impact specimen of the 185 composition material (Fig. 7b) but the degree of yielding is clearly reduced

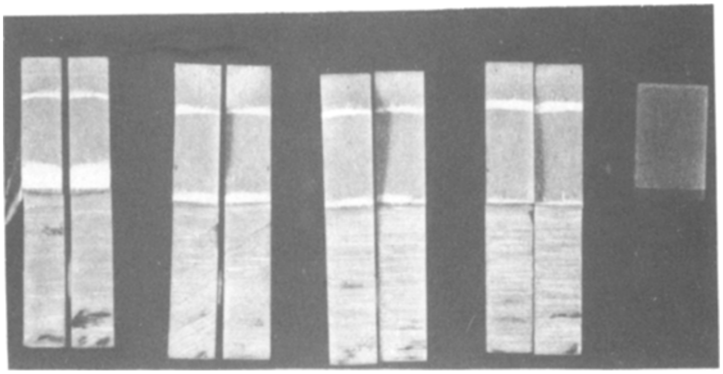

*Figure 4* Decrease in stress-whitened area with increasing strain rate. Strain rate increases from left to right.

compared to that of the specimen tested at a low strain rate (e.g. Fig. 6a).

When the solid rubber is present at a low concentration, e.g. 1 wt% instead of 5.4 wt%, the extent of micro-yielding is reduced. This can be seen by comparing Fig. 8 with Fig. 6a and noting that there is a difference in magnification of 5×. Although there are regions of localized shear yielding evident in Fig. 8, it is not as extensive as in Fig. 6a. Also, on the fracture surfaces of the 206 composition (no solid rubber), occasional regions of local yielding could be observed, associated with large inclusions, as shown in Fig. 5b. These inclusions are most likely to be unreacted dicyanamide or other constituents or impurities that did not become fully dissolved or blended.

Finally, the fractography of the specimens containing only the solid rubber revealed neither

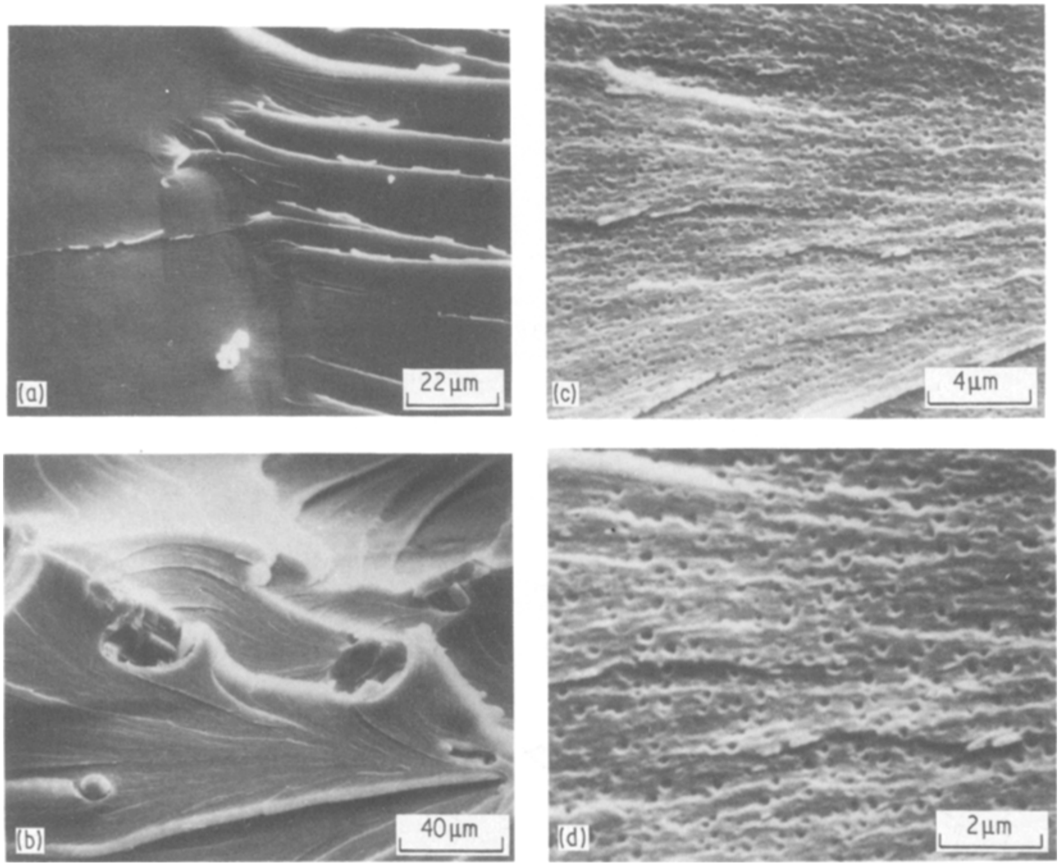

*Figure 5* SEM photomicrographs of the crack tip deformation zone for the base epoxy (a) and the stress-whitened zone on 206 composition fracture specimens (b to d, $2.0 \times 10^{-3}$ cm sec$^{-1}$).

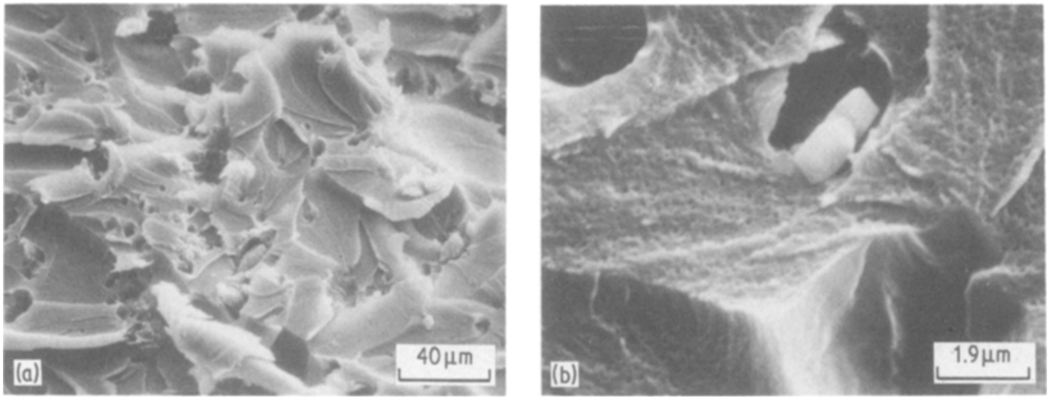

*Figure 6* SEM photograph of the stress-whitened zone on 185 composition fracture specimens ($2.0 \times 10^{-3}$ cm sec$^{-1}$).

the small holes evident on the specimens containing only the liquid rubber nor the massive localized yielding evident on the specimens containing the liquid rubber plus 5.4 wt% solid rubber. Instead, there was considerable multi-level cracking indicative of crack branching.

## 4. Discussion

The magnitudes of the increases in fracture toughness of the epoxy by the liquid and solid elastomeric modifiers are consistent with the results already in the literature. By itself the liquid CTBN increased toughness by 30 times which is similar to the results reported for this elastomer at a concentration of approximately 10 wt% [6]. In combination with the solid rubber the toughness was increased further by a factor of 2 times at the lowest testing rate and this is consitent with the result of Riew *et al.* [5] for an epoxy–CTBN composition having a bimodal distribution of particle sizes. Indeed, at low strain-rate testing, the contribution of the two types of modifiers appears to be additive. At these low rates, the F-185 composition has a toughness which exceeds most thermoplastic polymers [18] with only a modest (20%) decrease in modulus from that of the unmodified epoxy. Using the liquid CTBN alone, the toughness of the epoxy is as high as that of polysulphone [19].

The effect of increasing strain rate on $\mathscr{G}_{\mathrm{I_c}}$ was a modest but discernable decrease in fracture energy for all of the elastomer-modified compositions. The exception to this general statement is the very large decrease $\mathscr{G}_{\mathrm{I_c}}$ exhibited by the F-185 composition when tested at $8.5 \times 10^{-2}$ cm sec$^{-1}$ compared to the value obtained at $2.0 \times 10^{-3}$ cm sec$^{-1}$. Admittedly, this sharp decline in toughness depends heavily on the datum point taken at the lower strain rate but this decrease in toughness over a surprisingly short range of strain rates is believed to be real especially since the low strain rate toughness value is easily repeat-

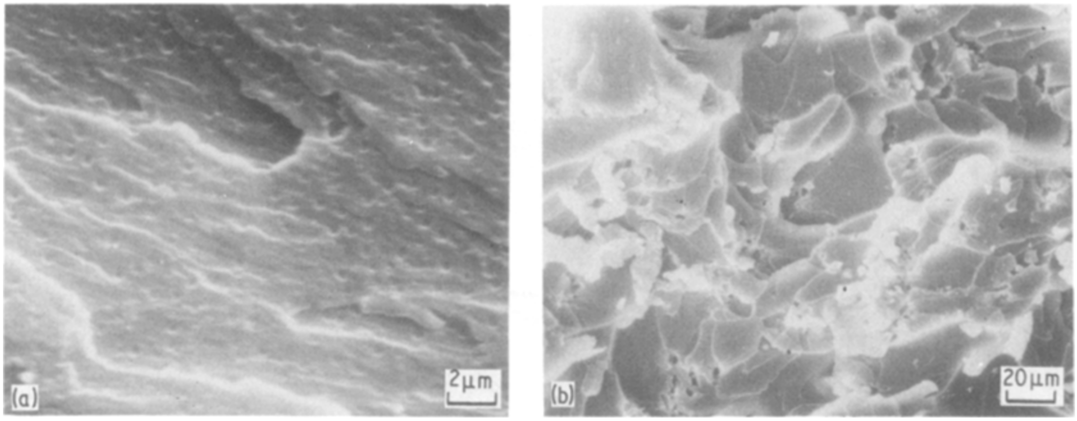

*Figure 7* SEM photographs of the deformation on 185 composition impact test specimens.

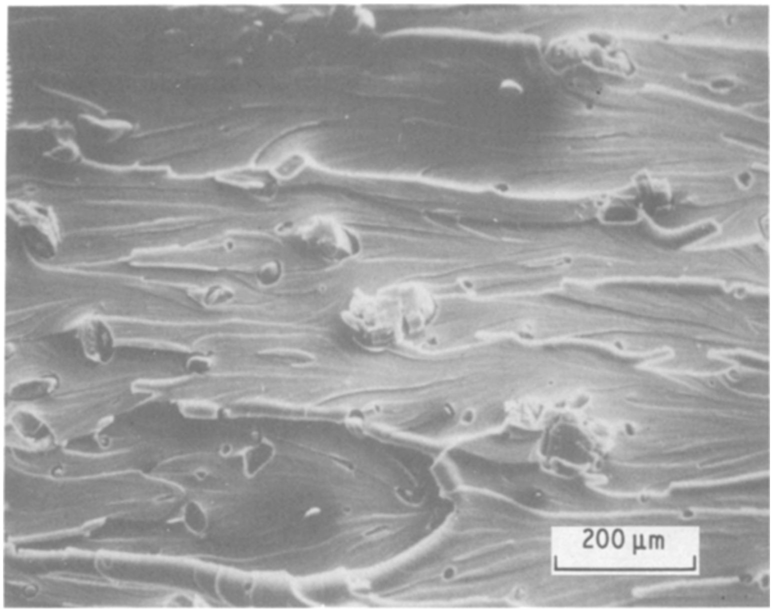

*Figure 8* SEM photograph of the stress-whitened region on 206 composition fracture specimen ($2.0 \times 10^{-3}$ cm sec$^{-1}$) showing local shear yield around adventitious inclusions.

able. Nonetheless, it is clear that with increasing strain rate the additional toughness attained by adding the solid elastomer is very significantly reduced.

The general decrease in toughness with increasing loading rate is consistent with a decreasing capacity for viscoelastic and plastic deformation which polymers exhibit with increasing strain rate. However, it is interesting that even over ten decades of time the decline in toughness is relatively modest, e.g. about 50% for the composition containing 8 wt% of the liquid CTBN.

Post-failure examinations of the specimens containing only the liquid rubber revealed holes slightly larger than the original particle size and yielding of the matrix resin around the particles. The same features have been observed in other studies of the fracture of CTBN modified epoxies and are generally attributed to the dilatational deformation of the elastomer particle and the shear yielding of the surrounding matrix. When the solid elastomer is included in the formulation along with the liquid CTBN another deformation mechanism appears to come into operation. Fig. 6a, for example, shows the fracture surface of the F-185 composition having 5% of the solid rubber and the scallop-like features around relative large holes. It would appear that the large particles have induced localized shear yielding and that this yielding is facilitated by the presence of the smaller elastomer particles. This additional deformation could explain the high toughness of the modified epoxy containing both liquid and solid rubber.

However, careful scrutiny of the fracture surface of the F-185 composition failed to reveal any evidence for a particle associated with the solid rubber additive. Presumably, these large particles are in some way connected with the large holes seen in Fig. 6 and it is conceivable that the particle underwent such a severe dilational deformation that it is no longer recognizable as a particle or that it was completely ejected out of and away from the fracture surface. Neither of these explanations is especially convincing. Careful examination of the fast crack region of the F-185 fracture specimen beyond the stress-whitening region revealed only an occasional particle a few tens of micrometres in diameter but not in sufficient numbers that would correspond to a 5% solid rubber content.

When the solid rubber was present at a 1 wt% level, the fracture surface again showed regions of massive localized yielding again associated with a hole. The extent of this deformation was much reduced compared to the composition containing 5 wt% of solid rubber and the fracture toughness was correspondingly lower.

The fracture surfaces of the 210 composition which contained only the solid rubber showed none of the above mentioned fracture markings. There was evidence of large particles but no distinct localized deformation associated with these particles. There had been considerable yielding of the epoxy matrix but this was rather randomly distributed throughout the stress-whitened region. It is possible that when the solid rubber is formulated into the epoxy that a certain portion is dispersed either as a more or less homogeneous blend or as extremely small particles of the order of 50 nm. The presence of this finely dispersed phase could be responsible for the toughening action of the solid elastomer. Sayre *et al.* [20] have presented evidence that in epoxies modified with liquid CTBN elastomers, in addition to particles of a few tenths of a micrometre, the rubber is also present as a finely dispersed phase of particles having diameters of the order of 50 nm.

All of these fractography features were most evident on the specimens tested at the lowest strain rate. As the strain rate was increased there were no changes in the type of surface markings but there was a gradual decrease in the extent of deformation. There was also a systematic decrease in the length of the stress-whitened zone (Fig. 4). However, the fact that the impact specimen of the F-185 composition showed no stress whitening is somewhat deceiving. Examination of this surface using SEM revealed localized yielding similar in appearance to that observed on the specimen tested at low strain rates but diminished in the extent of yielding that had taken place. The fact that no stress whitening was observed on the impact specimen indicates that the layer of deformation was too thin to produce any detectable light scattering.

## 5. Conclusions

It has been shown that the modification of an epoxy resin by both a liquid and a solid elastomer improves the toughness of the base epoxy to a greater extent than when either modifier is used alone. This enhanced toughness was observed over a wide range of strain rates (including impact testing) and that the effect of adding the solid rubber was greatest at the lowest strain rate of $2.0 \times 10^{-3}\,\text{cm sec}^{-1}$. All of the rubber-modified epoxy compositions showed a systematic decrease in fracture energy with increasing strain rate but even at impact testing the fracture energies were 10 to 20 times greater than the unmodified epoxy.

Post-failure examination of the fracture specimens using SEM indicated that the liquid elastomeric additive had formed particles 0.3 to 0.5 $\mu$m in diameter. In the crack tip deformation zone these particles undergo dilatational deformation and induce shear yielding in the surrounding matrix. These are the two deformational mechanisms generally accepted as being responsible for inducing toughness in elastomer-modified epoxy polymers. The introduction of the solid rubber introduces a new deformational mechanism which appears to involve a local shear yielding of the epoxy induced by particles having diameters of 2 to 4 $\mu$m. The evidence for these larger particles are holes in the fracture surface from which the localized shear yielding appears to have emanated. The actual large particles themselves could not be found even after extensive SEM examination.

When the epoxy resin was modified with the solid rubber elastomer alone, the fracture energy was almost as high as when the liquid elastomer was used. However, the mechanism of the toughening action when the solid elastomer was the only modifier, is not clear. Post-failure SEM examination showed the presence of large (2 to 5 $\mu$m) particles but there was no specific localized yielding associated with these particles. Instead, there had been a random shear yielding of the epoxy matrix.

## Acknowledgements

The authors wish to thank Mr R. L. Cottington of the Naval Research Laboratory for his help in conducting the majority of the tests reported here.

## References

1. J. N. SULTAN, R. C. LAIBLE and F. J. McGARRY, *J. Appl. Polymer. Sci.* 6 (1971) 127.
2. J. N. SULTAN and F. J. McGARRY, *Polymer. Eng. Sci.* 13 (1973) 29.
3. E. H. ROWE, A. R. SIEBERT and R. S. DRAKE, *Mod. Plastics* 47 (1970) 110.
4. A. R. SIEBERT and C. K. RIEW, *ACS Preprints, Organic Coatings and Plastics Div.* 31 (1971) 555.
5. C. K. RIEW, E. H. ROWE and A. R. SIEBERT, in "Toughness and Brittleness of Plastics" edited by D. Deanin and A. M. Crugnola, ACS Adv. in Chem. Ser. 154 (American Chemical Society, 1976) p. 326.
6. W. D. BASCOM, R. L. COTTINGTON, R. L. JONES, and P. PEYSER, *J. Appl. Polymer Sci.* 19 (1975) 2545.
7. W. D. BASCOM and R. L. COTTINGTON, *J. Adhesion* 7 (1976) 333.
8. W. D. BASCOM, R. L. COTTINGTON and C. O. TIMMONS, *J. Appl. Polymer Sci. Appl. Polym. Symp.* 32 (1977) 165.
9. A. C. SOLDATUS and A. S. BURHANS, *I&EC Prod. R&D* 9 (1970) 296.
10. J. M. WALKER, W. E. RICHARDSON and C. H. SMITH, *Modern Plastics* 53 (1976) 62.

11. W. D. BASCOM and D. L. HUNSTON, "Toughening of Plastics", (Plastics and Rubber Institute, London, 1977).
12. S. KUNZ-DOUGLASS, P. W. R. BEAUMONT and M. F. ASHBY, *J. Mater. Sci.* **15** (1980) 1109.
13. J. F. KNOTT, "Fundamentals of Fracture Mechanics", (Butterworths, London, 1973) p. 130.
14. R. Y. TING and R. L. COTTINGTON, *J. Appl. Polymer Sci.* **25** (1980) 1815.
15. P. E. REED, "Developments in Polymer Fracture", (Butterworths, London, 1973) p. 132.
16. E. PLATI and J. G. WILLIAMS, *Polymer Eng. Sci.* **15** (1975) 470.
17. W. D. BASCOM, R. J. MOULTON, E. H. ROWE and A. R. SIEBERT, *Organic Coatings and Plastics* **39** (1978) 164.
18. E. H. ANDREWS, in "The Physics of Glassy Polymers", edited by R. H. Howard, (Wiley, Chichester, 1973) p. 394.
19. R. D. R. GALES and N. J. MILLS, *J. Eng. Fract. Mech.* **6** (1974) 93.
20. J. A. SAYRE, R. A. ASSINK and R. R. LAGASSE, *Polymer* **22** (1981) 87.

Received 20 January and accepted 5 March 1981.