Correlation Between Stress-Whitening and Fracture Toughness in Rubber-Modified Epoxies

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SYNOPSIS

Fracture toughness of rubber modified epoxy systems was evaluated in relation to stress-whitening. The epoxy systems consisted of diglycidyl ethers of bisphenol A (DGEBA)-based epoxy resin, 4,4' diaminodiphenyl sulphone (DDS) as curing agent, and carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber. It was found that a peak value of fracture toughness occurs at a small amount of rubber content (~ 4 phr) and closely corresponds to that of stress-whitening size. Other properties such as flexural strength and flexural modulus were also found to display maxima at a similar amount of rubber content. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Epoxies have been used for structural adhesives, matrix materials for composites, etc. Such epoxies have been modified for better performance. Failure of rubber-modified epoxies involves a number of phenomena such as cavitation, shear banding at the crack tip, shear banding between rubber particles, debonding between matrix and rubber particles, and rubber particle tearing.[1-3] Major deformation, although responsible for the improvement of fracture toughness, includes the first three of those. Also, the epoxy systems that can be effectively toughened are confined to those with relatively low crosslink density. The molecular mobility of these epoxy systems is higher than that of those with high crosslink density, which results in increased ductility, thus efficiently improving the toughness.[4]

Epoxies with a high crosslink density have advantages including good resistance to chemical attack and high glass transition temperature (T_g).[2] However, the molecular mobility in these epoxies is limited, resulting in limited plastic deformation. Hence, there has been little progress in the toughening of such epoxies by rubber modification.[5,6]

The deformation in polymers is generally accompanied by stress-whitening. The stress-whitening referred to here is distinguished from that in fracture surface.[1] The term "stress-whitening" describes subsurface discoloration of the material in response to deformation. It is due to the scattering of light from free surfaces created during deformation. It has been shown that the formation of stress-whitening in rubber-modified epoxies is caused by hydrostatic stress.[7] Although stress-whitening often occurs in polymers,[8-10] its study in quantitative relation to the fracture toughness of epoxy has not been reported. In this work, as a step toward the improvement of toughness in rubber-modified epoxies with high T_g's, further results to our previous work[7] are presented for a correlation between stress-whitening and fracture toughness.

EXPERIMENTAL

The material used was a diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin (GY250, Ciba-Geigy) cured using 4,4'-diaminodiphenyl sulfone (DDS). The rubber used for the modifications was Hycar CTBN rubber (1300 × 13). The curing schedule for all the rubber-modified epoxy/DDS systems was as follows: The rubber, first, and, then, DDS was mixed with the epoxy resin and stirred up at 135°C until the DDS was dissolved; the systems were cured for 24 h at 120°C, followed by 4 h postcure at 180°C. The control epoxy was cured in the same schedule.

Molded sheets of the epoxies were cut into test specimens. Three-point bending tests for fracture toughness (Fig. 1), flexural strength, and flexural modulus were carried out at a crosshead speed of 1 mm/min. At least three specimens were used for the tests. Precracks were produced on three-point fracture test specimens by tapping a razor blade. The following expression[11] for the critical stress intensity factor, K_{IC}, based on linear-elastic fracture mechanics, was used for calculations of fracture toughness:
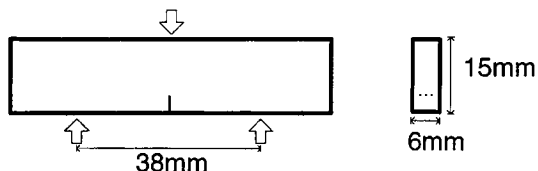
Figure 1   Dimensions of three-point fracture specimen.

$$K_{IC} = \frac{P_C S}{B W^{3/2}} Y \qquad (1)$$

where P_C is the critical fracture load, which in the current study corresponds to the maximum load, S is the span, B is the geometry factor given by

$$Y = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W)}{2(1 + 2a/W)(1 - a/W)^{3/2}} \qquad (2)$$

$$\frac{(2.15 - 3.93a/W + 2.7a^2/W^2)]}{}$$

and a is the crack length. For stress-whitening measurements, U-notched specimens (Fig. 2) were loaded until one of the notches fractures at a crosshead speed of 0.5 mm/min. Glass transition temperature for each rubber content is given in Table I.

The survived U-notches of rubber-modified specimens were used for measurements of the vertical extent of stress-whitening. The control specimens did not display any detectable stress-whitening. For rubber-modified epoxies, it was observed that the maximum stress-whitening at the root of U-notch occurs at the "midsection" (see Fig. 2). The maximum vertical extent of the stress-whitening from the root of U-notch was plotted as a function of rubber content, as shown in Figure 3. It is seen that the extent of stress-whitening decreases with increasing rubber content.
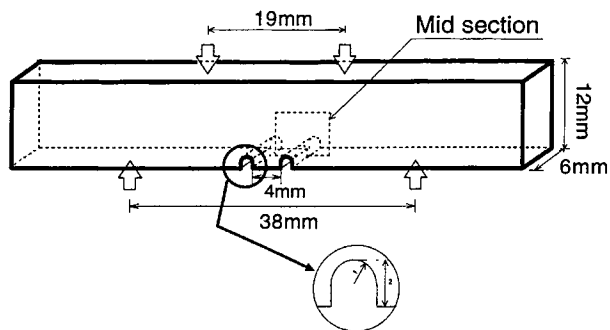
Table I   Glass Transition Temperatures and Rubber Contents for Modified Epoxies[7]

Rubber (phr)	DDS (phr)	T_g (°C)[a]
0	32	222[†]
2	32	—
4	32	—
5	32	217[†]
8	32	—
10	32	195[‡]
15	32	216[†]

[a] Determined by differential thermal analysis at 20°C/min using either powder samples for those marked by "[†]" or block samples for those marked by "[‡]" (phr denotes parts per hundred of resin by weight).

RESULTS AND DISCUSSION

The relationship between fracture toughness and rubber content obtained from three-point bend tests is illustrated in Figure 4. The fracture toughness appears to be maximum at a small amount of rubber (about 4 phr). This accounts for a 27% increase in toughness of the control. The trend is quite different to that reported by other investigators.[1,2] Most epoxies cured using piperidine (which is relatively less brittle than is the current DDS cured epoxies)
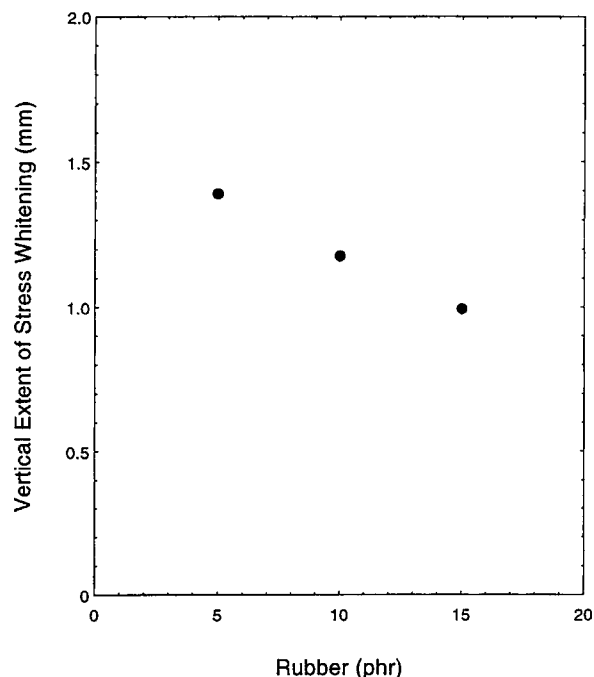

Figure 2   Double U-notched specimens with dimensions.

Figure 3   Vertical extent of stress-whitening at "midsection" vs. rubber content.[7]
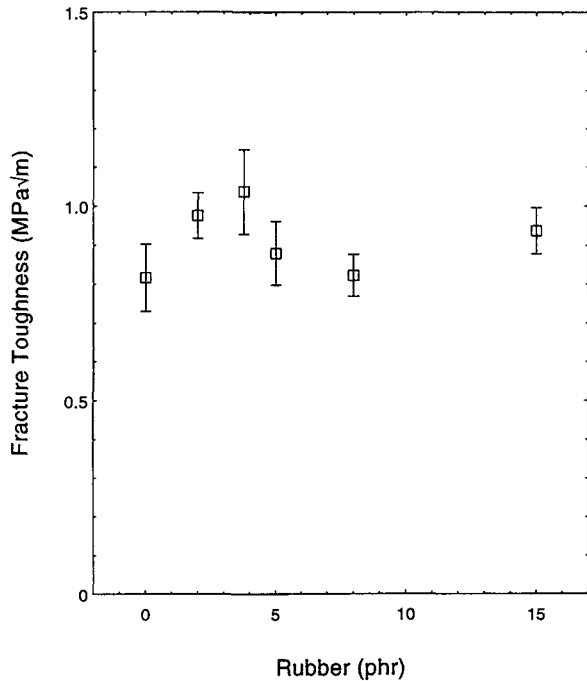
Figure 4 Fracture toughness of rubber-modified epoxies vs. rubber content.

can be effectively toughened with about 15 phr of rubber content[1,2] unless they are toughened by the dissolution of rubber in the epoxy matrix.[12] The peaks of fracture toughness (Fig. 4) and stress-whi-
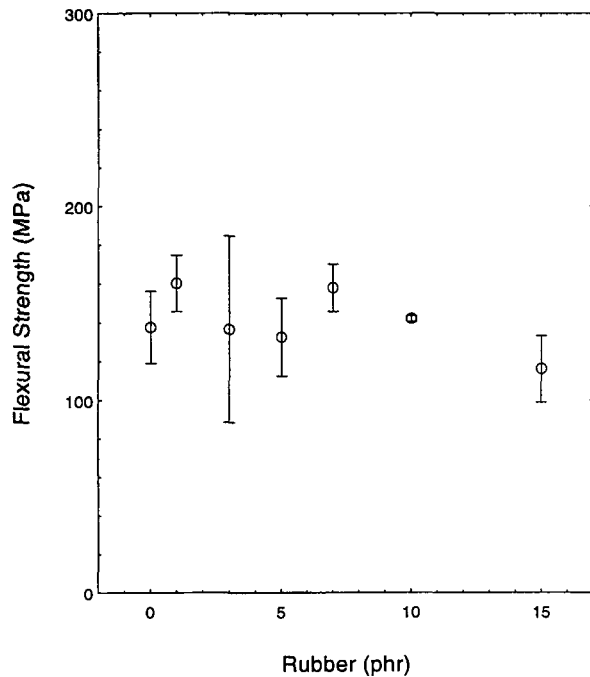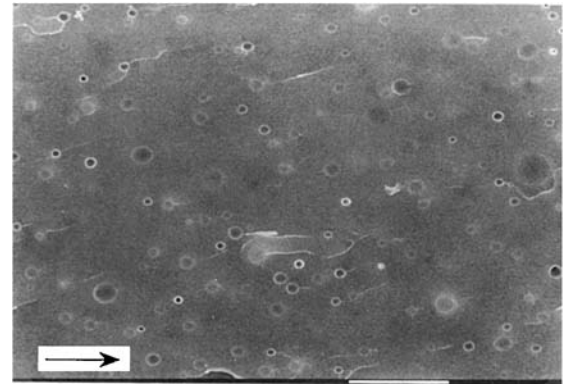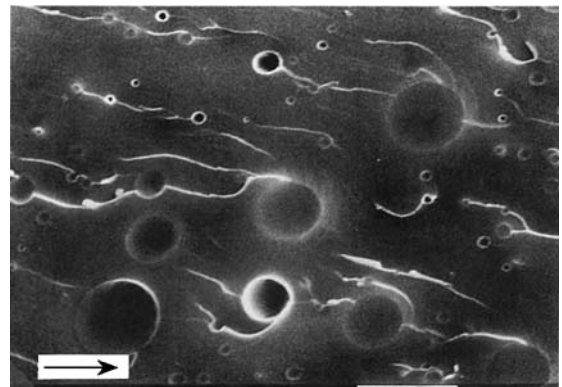

Figure 6 Flexural strength of rubber-modified epoxies vs. rubber content.

(a)

(b)

Figure 5 SEM micrographs of three-point bending fracture surface of rubber-modified epoxies: (a) 4 phr rubber; (b) 8 phr rubber. The arrow indicates crack growth direction. Each scale bar represents 10 μm.

tening size (Fig. 3) closely match each other, indicating that the improved toughness is associated with the stress-whitening. The stress-whitening was previously shown to be due to cavitation caused by hydrostatic stress.[7]

Figure 5 shows micrographs taken by a scanning electron microscope (SEM) for fracture surfaces of the region created mainly by slow cracking prior to fast propagation. At 4 phr rubber content, where the maximum toughening effect was exhibited, the fracture surface is characterized by its smoothness. By contrast, at 8 phr rubber content, where the minimum toughening effect was exhibited, the fracture surface contains more and larger welts that resulted from the occurrence of microcracking or bifurcation, which can produce a modest toughening effect. A further difference between the two rubber contents
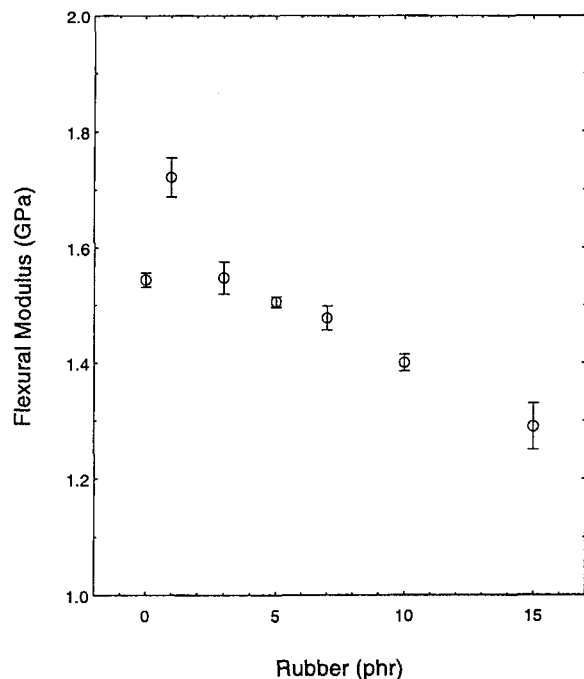
Figure 7 Flexural modulus of rubber-modified epoxies vs. rubber content.

is found in rubber particle size. Rubber particle sizes ($\approx$1–2 μm) at 4 phr are smaller than those at 8 phr. Pearson and Yee[13] showed that small particles are more efficient in producing a toughening effect than are large particles, because particles greater than the process zone size in the vicinity of a notch would not cavitate. This particle-size effect seems to be reflected in the increase in toughness. Furthermore, it is noted that flexural strength (Fig. 6) and flexural modulus (Fig. 7) are noticeably improved initially with increasing rubber content and then reduced afterward. The improvements in these two properties also coincide closely with the maximum toughness. Thus, the usefulness of toughening at the small amount of rubber is seen to be enhanced.

CONCLUSIONS

Toughening of rubber-modified epoxies in relation to stress-whitening has been studied. The fracture toughness of rubber-modified epoxies with high glass transition temperatures can be considerably improved with a small amount of rubber without sacrificing strength and stiffness. The toughening effect in the epoxies is closely associated with the size of stress-whitening occurring in U-notched specimens.

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