Effects of matrix ductility on rubber/matrix interfacially modified epoxy resins

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The effects of changing matrix ductility are studied for rubber-toughened epoxy resins with modification of the rubber/matrix interfacial zone. The interfacial modification results in a large and more deformable interfacial zone, which gives rise to a further increased fracture toughness. Various microstructural parameters and the deformation and fracture behaviours of the rubber-toughened epoxy resins are quantified. Epoxy resins with moderate ductility are more effective in increasing further toughness after modification of the rubber/matrix interfacial zone. The further increased toughness results solely from the increased cavitation that arises in the modified rubber/matrix interfacial zone. On the other hand, the size of the plastic deformation zone in the vicinity of the crack tip is independent of the degree of rubber cavitation, but it is significantly increased by multiple but localized shear yielding, caused by the increase in matrix ductility. In addition, the degree of multiple but localized shear yielding is independent of the degree of cavitation in the present investigation.

(Keywords: epoxy resin; fracture toughness; carboxyl-terminated butadiene–acrylonitrile; matrix ductility; rubber/matrix interfacial modification)

INTRODUCTION

Epoxy resins are highly crosslinked thermosetting polymers that are brittle in nature. They are therefore frequently toughened by dissolving a reactive liquid rubber in the liquid epoxy system before curing. While curing proceeds, the rubbery phase separates out from the resin mixture and forms a fine dispersion of rubbery particles with diameters of a few micrometres or less. The enhanced crack resistance that results with the multiphase microstructure arises from two energy-dissipating deformations[1–8] occurring in the vicinity of the crack tip. The deformation processes are (1) cavitation in the rubber, or at the rubber/matrix interface, and (2) multiple but localized shear yielding in the matrix. Theoretical model calculations show that cavitation reduces the octahedral shear stress to yield[9], and they generate and promote the formation of localized plastic shear yielding between voids[4,9,10]. Localized shear deformation is enhanced in such a voidy solid[2,4,10,11].

In a previous study[12] the relationship between the properties of the rubber/matrix interfacial zone and the fracture toughness of a rubber-modified epoxy resin was studied. It was found that the addition of a long-chain flexible epoxide (DER732) end-capped carboxyl-terminated butadiene–acrylonitrile copolymer (CTBN) caused the rubber particles to contain a large and more deformable interfacial zone, which in turn significantly enhanced the fracture toughness by giving rise to a greater degree of rubber cavitation occurring in the plastic deformation zone in the vicinity of the crack tip. Recently, the effects of matrix properties on the toughness of rubber-modified epoxy resins have been studied[7,8,13]. Yee *et al.*[7] and Kinloch *et al.*[8] studied the effect of segmental molar mass between crosslinks, $\bar{M}_c$, of the matrix phase. Both groups indicated that epoxy resins with high $\bar{M}_c$ values exhibit greater ductility and, correspondingly, greater toughenability. Chen and Jan[13] emphasized the overall glass transition temperature of the matrix and indicated that, without altering the rubber phase microstructure, the effect of increasing matrix ductility (i.e. decreasing matrix T_g) was to enlarge the plastic deformation zone in the vicinity of the crack tip and hence increase toughness. In the present investigation the effects of changing matrix ductility are examined further when the rubber/matrix interfacial zone is modified. Various microstructural parameters and the deformations are quantified.

EXPERIMENTAL

Materials

The base epoxy prepolymer was a low-molar-mass liquid diglycidyl ether of bisphenol-A (DGEBA; Epon828 from Shell Co.). Two other epoxy prepolymers used for modifying the matrix ductility were tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM; MY720 from Ciba-Geigy Co.) and diglycidyl ether of propylene glycol (DGEPG; DER732 from Dow Chemical Co.). DER732 was also used for rubber/matrix interfacial modification. The structures of Epon828, MY720 and DER732 are

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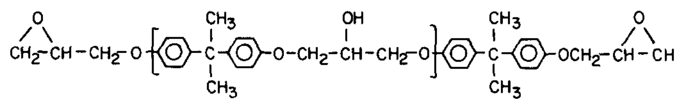
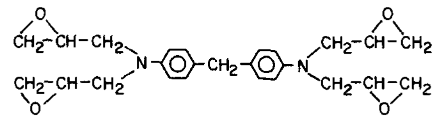
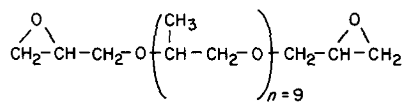
given as follows:



Epon828



MY720



DER732

The hardener was reagent-grade piperidine and was a product of Merck Chemical Co. The reactive liquid rubber was a random acrylonitrile–butadiene copolymer (Hycar 1300 × 8 by B. F. Goodrich) with an acrylonitrile content of 18 wt%. The molar mass of the rubber was 3500 g mol^{-1} and the carboxyl content was 2.37 wt%. For rubber/matrix interfacial modification, each mole of CTBN was reacted with 2 mol of DER732 beforehand. Thus, a DER732 end-capped CTBN was produced. The reaction conditions and the characterization of this end-capped CTBN product were described in our previous study[12]. Resins and rubber were mixed together at 60°C until the solution was completely homogeneous and then degassed in a vacuum oven at 60°C until frothing stopped. When the mixture was cooled to about 30°C, the piperidine was stirred in gently to minimize air entrapment. The mixture was then poured into a preheated glass mould, cured at 120°C for 16 h and allowed to cool down slowly. The blending formulations, with or without rubber/matrix interfacial modification, are summarized in *Table 1*. The specimens obtained from the moulded resin plaques were used in the following experiments for the studies of the microstructure and mechanical properties.

Table 1 Formulations for rubber-toughened epoxy resins

Designation	Resin composition (wt%) Epon828	MY720	DER732	Type of CTBN rubber	Amount of rubber (phr)
MY-20-(10)	80	20	0	CTBN[a]	10
MY-15-(10)	85	15	0	CTBN	10
MY-10-(10)	90	10	0	CTBN	10
MY-5-(10)	95	5	0	CTBN	10
Epon-(10)	100	0	0	CTBN	10
DER-5-(10)	95	0	5	CTBN	10
DER-10-(10)	90	0	10	CTBN	10
DER-15-(10)	85	0	15	CTBN	10
DER-20-(10)	80	0	20	CTBN	10
MY-20-(10)-I	80	20	0	CTBNI[b]	10
MY-15-(10)-I	85	15	0	CTBNI	10
MY-10-(10)-I	90	10	0	CTBNI	10
MY-5-(10)-I	95	5	0	CTBNI	10
Epon-(10)-I	100	0	0	CTBNI	10
DER-5-(10)-I	95	0	5	CTBNI	10
DER-10-(10)-I	90	0	10	CTBNI	10
DER-15-(10)-I	85	0	15	CTBNI	10
DER-20-(10)-I	80	0	20	CTBNI	10

[a] CTBN represents the CTBN1300x8 rubber
[b] CTBNI represents the modified CTBNI1300x8 rubber obtained from end-capping of 2 mol of DER732 to 1 mol of CTBN 1300x8

Thermal properties

The glass transition temperature T_g of the matrix phase was measured by a differential scanning calorimeter (DuPont 9900), which was conducted over temperatures ranging from ambient to +150°C at a heating rate of 20°C min^{-1}.

Microstructural analysis

To ascertain the volume fraction, particle size and particle size distribution of the rubbery phase, and the properties of the rubber/matrix interfacial zone in rubber-modified epoxies, we obtained transmission electron micrographs from specimens that had been microtomed to a thickness of less than 100 nm and stained with 1% (w/v) osmium tetroxide. The Schwartz–Saltykov method[14] was employed to analyse the TEM micrographs to deduce the volume fraction, particle size and particle size distribution of the rubber phase. Samples of at least 100 rubber particles were needed for these analyses.

Mechanical properties and fracture energy

Tensile testing was performed by an Instron 1302 tensometer and an Instron 2620-602 extensometer. Dumb-bell specimens were machined from a 3 mm resin plaque in accordance with ASTM D638-64T. Fracture toughness was measured and expressed in terms of critical strain-energy release rate, G_{Ic}. This value was determined from a tapered double cantilever beam (TDCB) specimen, which was developed by Mostovoy[15] and is shown in *Figure 1*. The advantage of this specimen is that G_{Ic} given by the measured load P is independent of crack length. Thus, the G_{Ic} value can be easily calculated by the following equation:

$$G_{Ic} = 4P^2m/Ebb' \qquad (1)$$

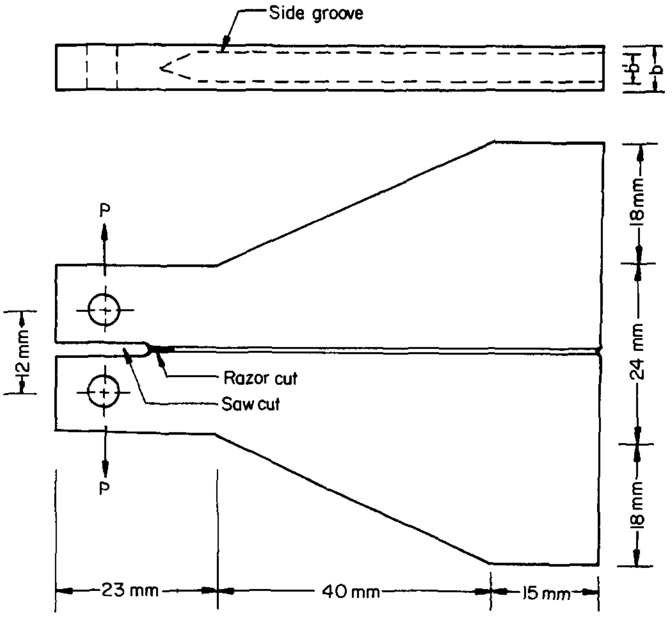


Figure 1 Tapered double cantilever beam specimen for fracture energy measurement

where P is the load required to propagate the crack, E is the Young's modulus, b is the specimen thickness, b' is the side groove width, and m is a constant, which depends on the shape of the specimen and has a value of 3.27 cm^{-1} for the TDCB specimen shaped according to *Figure 1*. Before the fracture energy testing, a sharp crack was formed at the base of the slot by carefully tapping a fresh razor blade on the base, thus causing a sharp crack to grow naturally for a short distance ahead of the razor blade. Fracture energy tests were conducted by an Instron 1302 tensometer with crosshead moving at 1 mm min^{-1}. Temperature for the test was held at 25°C.

Fractography

The fracture surfaces were examined under a Hitachi S-750 scanning electron microscope operated at an accelerating voltage of 20 kV. Prior to examination, the fracture surfaces were coated with a thin evaporated layer of gold in order to improve conductivity of the examined surfaces and prevent electron charging on them.

RESULTS

The effects of matrix ductility on rubber-toughened epoxy resins with rubber/matrix interfacial modifications are compared with those without interfacial modifications. Results on microstructures, mechanical properties and fracture behaviours of the rubber-toughened epoxy resins are described as follows.

Rubbery phase morphology

TEM micrographs for rubber-toughened epoxy resins with varying matrix ductility and with rubber/matrix interfacial modification are shown in *Figures 2a* to *2c*. Those with varying matrix ductility but without rubber/matrix interfacial modification are shown in *Figures 2d* to *2f*. The rubber particles in *Figures 2a* to *2c* seem to show a somewhat diffused interfacial zone as compared with those shown in *Figures 2d* to *2f*. The diffused interfacial zone may indicate that a larger and more deformable interfacial zone was produced. From several micrographs containing at least a total of 100 rubber particles, the particle size distributions were calculated by using the Schwartz–Saltykov quantitative method[14]. The calculated results are shown in *Figures 3a* to *3f*. It is observed that all the resin systems have similar unimodal particle size distributions with all the particle diameters ranging from 1 to 3 μm. Based on these particle size distributions, the number-average particle diameter and the particle number per 1000 $\mu\mathrm{m}^3$ for some of the resin systems were plotted against resin composition and are shown in *Figures 4* and *5*, respectively. Rubber particles with or without interfacial modification resulted in very similar particle size and similar particle numbers throughout all the epoxy resins. Furthermore, resin composition does not measurably affect the particle size nor the particle number.

Rubber volume fractions of each epoxy system were calculated separately from the particle size distributions by the method suggested by Guy[16]. The results are shown in *Figure 6* for various epoxy resins. It is observed that equivalent volume fractions of the rubbery phase with or without interfacial modification were obtained throughout all the epoxy resins. Furthermore, resin composition does not measurably affect the volume fraction. Consequently, the microstructures of the rubbery phase for all the epoxy systems are equivalent. This would greatly simplify the discussion on the present subject.

Matrix ductility

The current toughening mechanism[1–8] highlights the role of the inherent ductility of the matrix in influencing the toughness of the rubber-modified epoxy resin. As might be expected, those factors which lead to an increase in matrix ductility (e.g. high $\bar{M}_c$ values, low interchain attractive force and high chain flexibility, etc.) also lead to a low value of matrix T_g. In this investigation, various amounts of matrix-modifying epoxides were blended separately into the DGEBA–piperidine epoxy system in order to change the matrix ductility. The matrix modifiers were the rigid and polyfunctional tetraglycidyl-4,4′-diaminodiphenylmethane (MY720) and the flexible diglycidyl ether of propylene glycol (DER732). MY720 is expected to decrease the $\bar{M}_c$ value and chain flexibility in the matrix phase. Thus, decreasing matrix ductility and increasing matrix T_g can be achieved simultaneously by increasing the amount of MY720. DER732 is expected to decrease the interchain attractive forces and to increase the average chain flexibility. Thus, increasing matrix ductility and decreasing matrix T_g can be achieved simultaneously by increasing the amount of DER732. The values of matrix T_g for various modified epoxy resins with or without rubber/matrix interfacial modification were all measured by d.s.c. analysis and are shown in *Figure 7*. It is observed that all the values of matrix T_g are strongly affected by resin composition. The directions for the changes are the same as discussed above. In addition, for all the epoxy resins toughened with DER732 end-capped CTBN, matrix T_g is on average 3°C lower in comparison with the T_g of the epoxy resins toughened by unmodified CTBN. Hence, the end-capped CTBN is slightly more soluble in the matrix phase.

Mechanical properties

The tensile stress and tensile modulus for all the epoxy systems are plotted in *Figures 8* and *9*, respectively. The tensile stress varies greatly with the matrix ductility. The tensile modulus remains quite constant throughout all the resin compositions. Both properties are not affected by rubber/matrix interfacial modification.

Fracture toughness

Figure 10 shows the effect of resin composition upon fracture energy G_{Ic} for the epoxy resins toughened with either unmodified CTBN or DER732 end-capped CTBN. The results indicate that the fracture toughness is strongly dependent upon the matrix ductility, and the rubber particles with interfacial modification always enhance the toughening effect for all the epoxy resins at various compositions. Furthermore, epoxy resins with moderate ductility are more effective in improving further toughness after interfacial modification.

DISCUSSION

According to the currently well accepted toughening mechanism[1–8], the energy dissipation deformation processes in the vicinity of the crack tip are cavitation and multiple but localized shear yielding. In discussing the

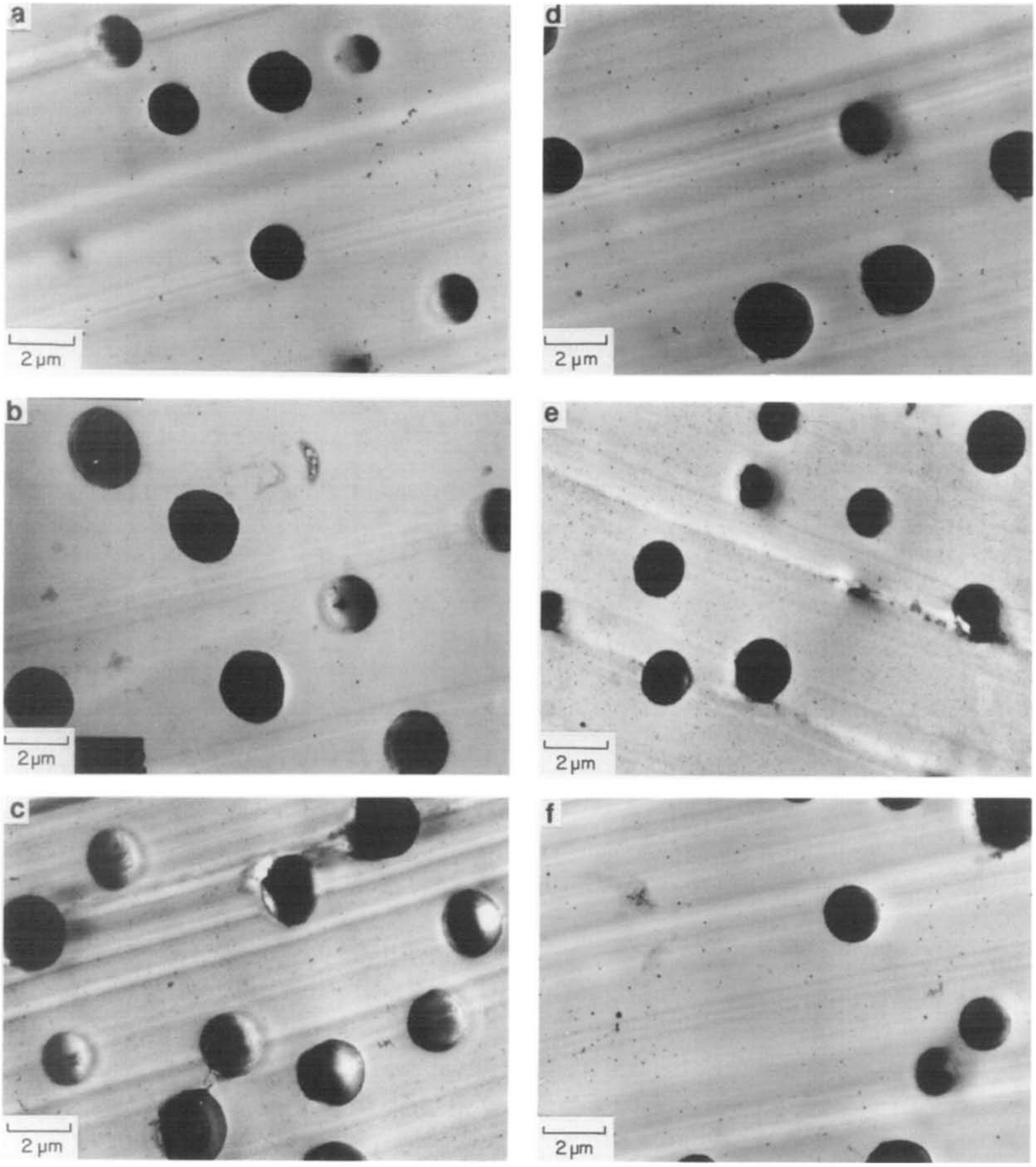


Figure 2 TEM micrographs of rubber-toughened epoxy resins with varying matrix ductility and with or without rubber/matrix interfacial modification: (a) MY-20-(10)-I, (b) Epon-(10)-I, (c) DER-20-(10)-I, (d) MY-20-(10), (e) Epon-(10) and (f) DER-20-(10)

fracture behaviour, the examination of these two processes should be emphasized.

Examination of the degree of cavitation can be obtained by comparison between the diameter of the fractured rubber cavity and the diameter of the undeformed rubber particle[5]. The cavity diameter is measured directly from SEM micrographs of the fracture surface by assuming that the rubber particles were all broken on equatorial planes by the crack front owing to the stress concentration on these planes[17]. The diameter of an undeformed rubber particle is calculated from TEM micrographs and was discussed previously. In general, the diameter of the rubber cavity is always larger than the diameter of the undeformed rubber particle[2,4,5], and the difference between them is considered as the degree of cavitation that has occurred while the crack initiates[5]. *Figure 11* shows the degree of cavitation for each toughened epoxy resin. It is observed that the degree of cavitation is much greater for those toughened epoxy resins with rubber/matrix interfacial modification. The greater toughening effect (*Figure 10*) that resulted from the interfacial modification was attributed to the greater cavitation and has been discussed in our previous paper[12]. The present results indicate that similar phenomena can be found in the epoxy resins with various matrix compositions. Furthermore, *Figure 11* also shows that the degree of further cavitation for the interfacially modified epoxy resins increases steadily as the matrix ductility increases, but *Figure 10* shows that the resin composition with intermediate ductility exhibits

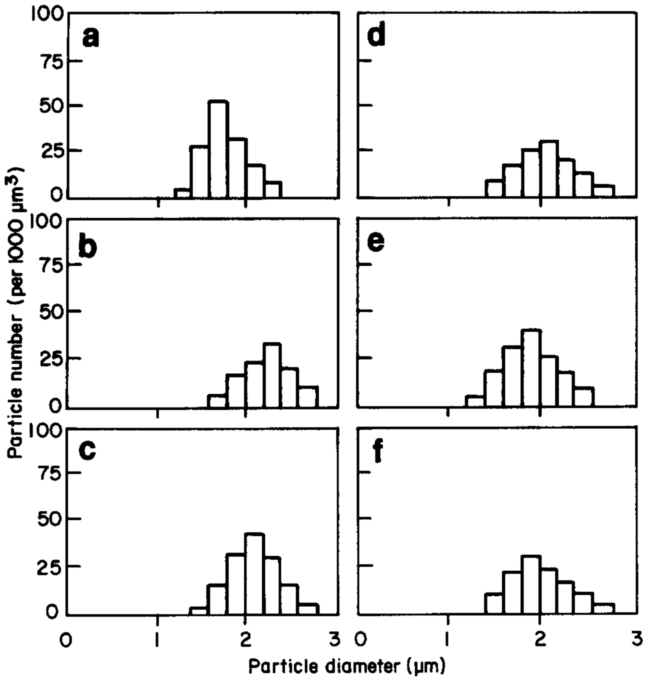


Figure 3 Rubber particle size distribution for (a) MY-20-(10)-I, (b) Epon-(10)-I, (c) DER-20-(10)-I, (d) MY-20-(10), (e) Epon-(10) and (f) DER-20-(10)

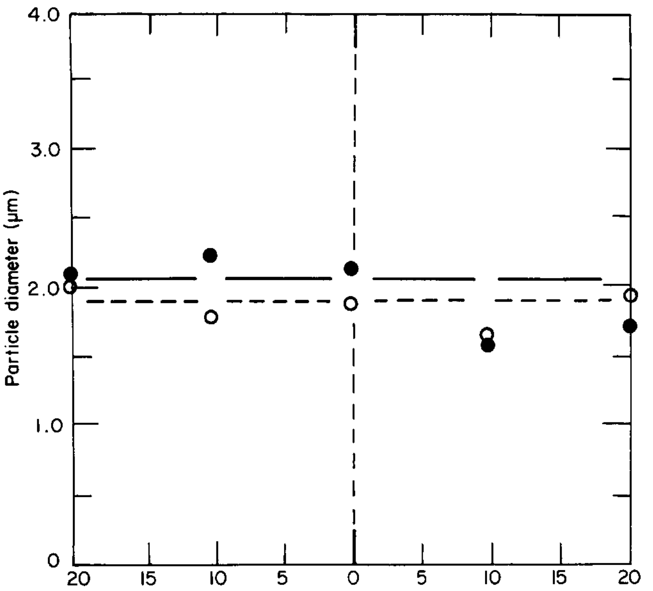


Figure 4 Dependence of number-average particle diameter upon the resin composition: (--○--) rubber particles without interfacial modification; (—●—) rubber particles with interfacial modification

greater toughness enhancement after interfacial modification. Because different matrix compositions may affect the interfacial composition, without knowing the detailed interfacial composition, it is difficult to discuss the relationship between the further cavitation and the further toughness that result from the interfacial modification.

Although evidence of localized shear yielding has been provided by polarized optical micrographic studies on the sublayer damage just below the fracture surface by Yee and Pearson[5,7], quantitative analysis of the localized shear yielding has not been carried out. Since the cavitation process involves the initiation and growth of voids in the rubbery particles, which gives rise to the phenomenon of stress whitening[2], and there is an interaction[2,12,13] between cavitation and shear yielding, any stress whitening must be accompanied by shear yielding. Therefore, it may be reasonable to assume that the size of the stress-whitening zone will correspond to the deformation volume containing total plastic shear yielding in the vicinity of the crack tip. (This assumption may be made for the present systems with all the rubber particles greater than 1 μm, which is large enough to diffract visible light.) The size of the stress-whitening zone is identified by the length and depth of this zone on the

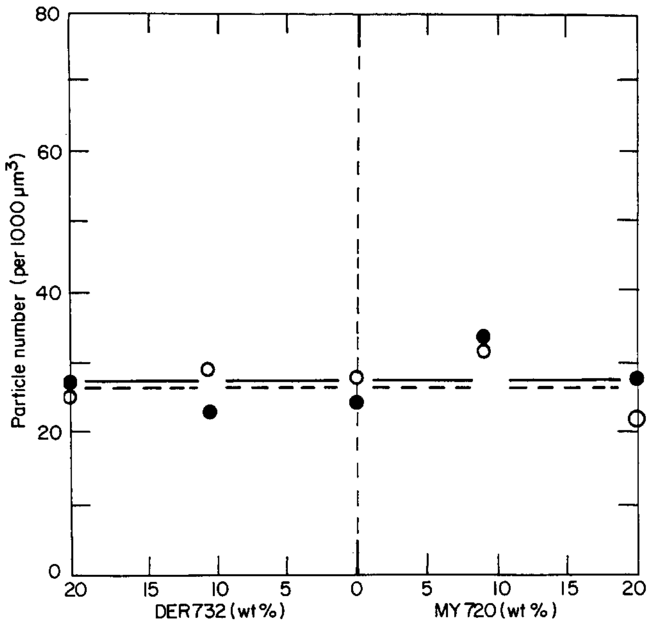


Figure 5 Dependence of particle number per 1000 μm³ upon the resin composition: (--○--) rubber particles without interfacial modification; (—●—) rubber particles with interfacial modification

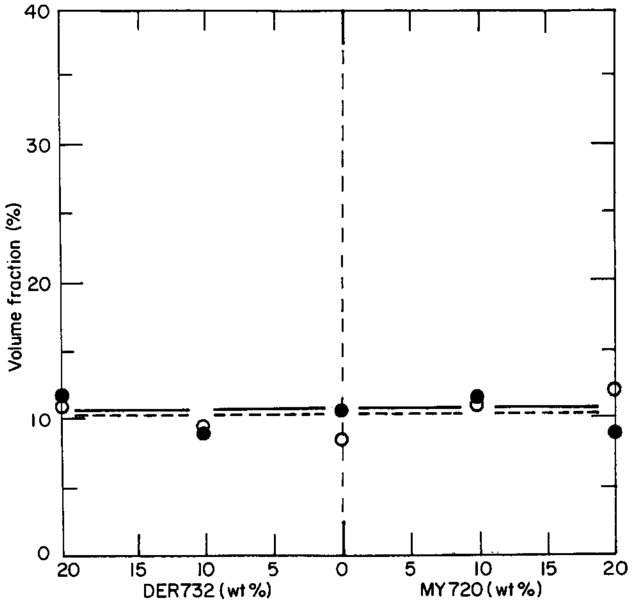


Figure 6 Dependence of precipitated rubber volume fraction upon resin composition: (--○--) rubber particles without rubber/matrix interfacial modification; (—●—) rubber particles with rubber/matrix interfacial modification

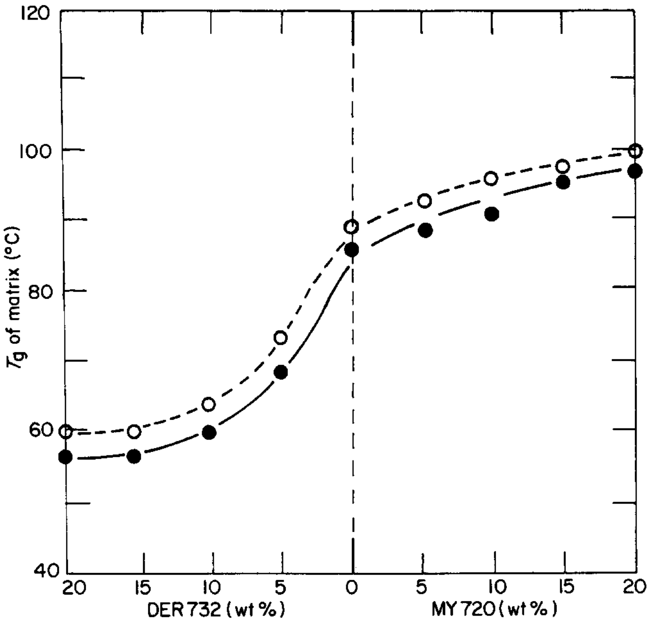


Figure 7 Dependence of matrix T_g upon resin composition: (—○—) resin systems without rubber/matrix interfacial modification; (—●—) resin systems with rubber/matrix interfacial modification

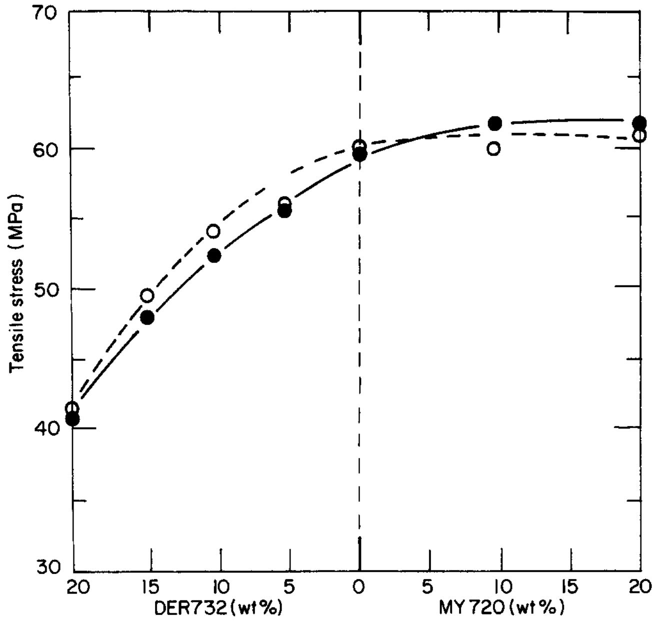


Figure 8 Dependence of tensile stress upon resin composition: (—○—) resin systems without rubber/matrix interfacial modification; (—●—) resin systems with rubber/matrix interfacial modification

fracture surface, and was measured under an optical magnifier. The stress-whitening length was measured directly from the fracture surface of the stress-whitening region in the direction of crack propagation. The stress-whitening depth was measured from a plane perpendicular to the fracture surface of the stress-whitening region. This plane was made by grinding the fractured specimen to the central portion. If the length and the depth increase, the zone size and hence the fracture toughness should increase[18]. *Figures 12* and *13* show the stress-whitening length and stress-whitening depth, respectively, for the rubber-toughened epoxy resins with and without interfacial modification and at various resin compositions. For all the epoxy resins, it is observed that the same stress-whitening sizes are obtained for epoxy resins toughened with or without interfacial modification, while their matrix compositions are the same. Combined with the result of greater cavitation observed in *Figure 11* for the interfacially modified epoxy resins, one may realize that variation in the degree of cavitation in this investigation (i.e. under constant rubbery phase morphology) does not measurably affect the size of the stress-whitening zone. Since there are only two major toughening processes, the other toughening process, i.e. multiple but localized shear yielding, must predominantly determine the size of the stress-whitening zone. Because the stress-whitening sizes

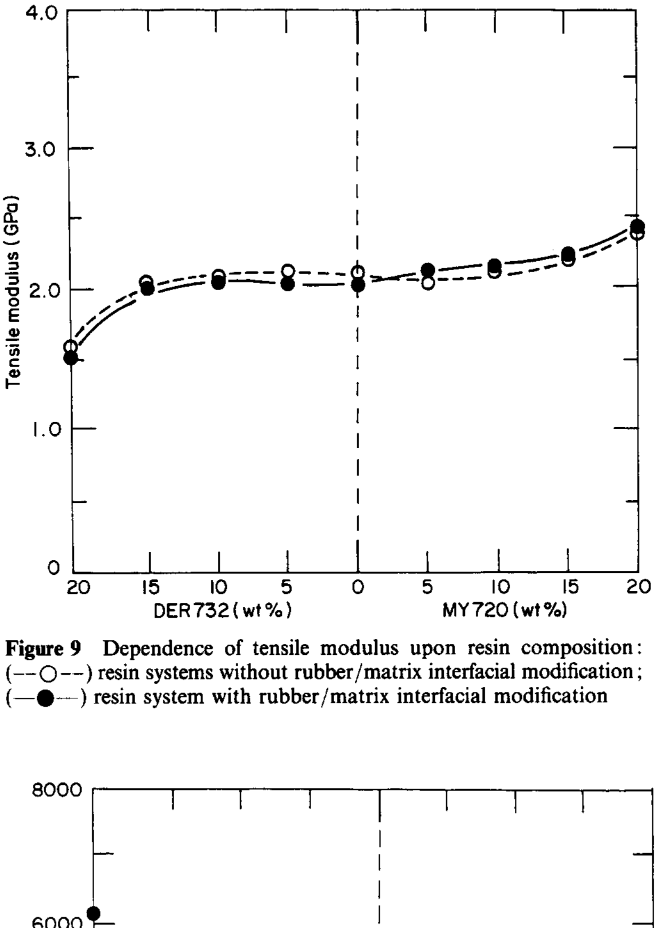


Figure 9 Dependence of tensile modulus upon resin composition: (—○—) resin systems without rubber/matrix interfacial modification; (—●—) resin system with rubber/matrix interfacial modification

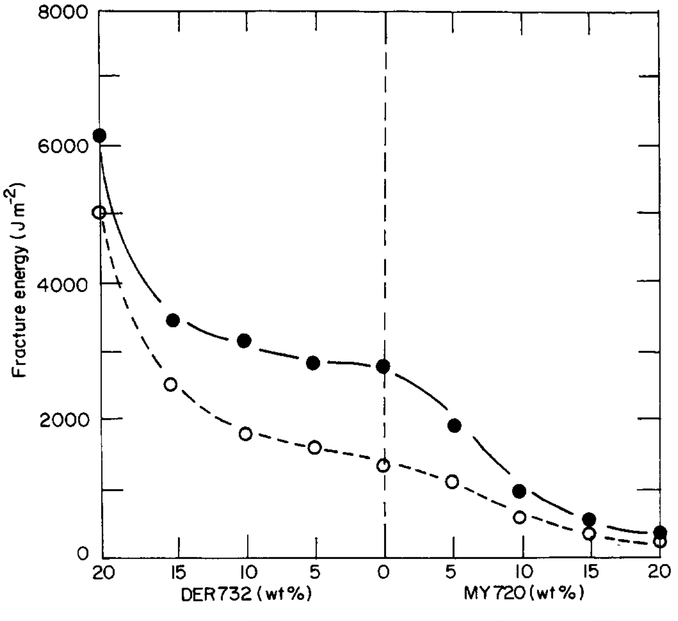


Figure 10 Dependence of fracture energy upon resin composition: (—○—) resin systems without rubber/matrix interfacial modification; (—●—) system with rubber/matrix interfacial modification

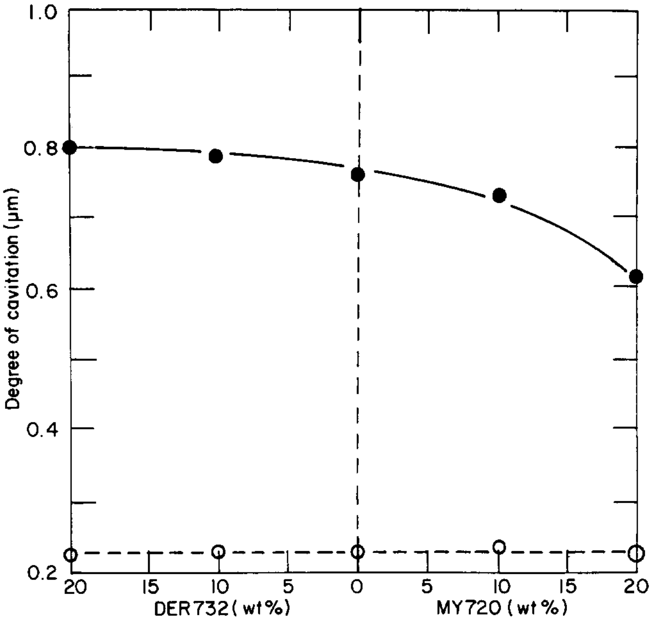


Figure 11 Dependence of degree of cavity upon resin composition: (—○—) resin systems without rubber/matrix interfacial modification; (—●—) resin systems with rubber/matrix interfacial modification

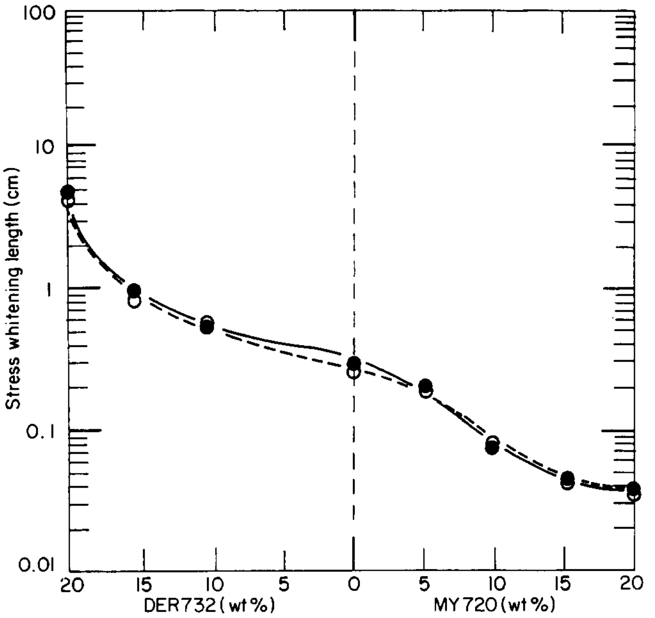


Figure 12 Dependence of stress-whitening length upon resin composition for rubber-toughened epoxy resins: (—○—) resin system without rubber/matrix interfacial modification; (—●—) resin system with rubber/matrix interfacial modification

are the same for the toughened epoxy resins with or without rubber/matrix interfacial modification and at the same matrix composition, their degrees of multiple but localized shear yielding must also be the same. Thus, the energy dissipating process of cavitation itself may solely account for the greater increment in fracture energy from interfacial modification. Furthermore, the above discussion may also imply that the degree of localized shear yielding is independent of the degree of cavitation in the present investigation.

On the other hand, *Figures 12* and *13* indicate that the stress-whitening zone size increases significantly as the matrix ductility increases. Since cavitation does not affect the stress-whitening zone size, the effect of increasing matrix ductility on increasing the size of the stress-whitening zone is to cause multiple but localized plastic shear yielding to occur more extensively.

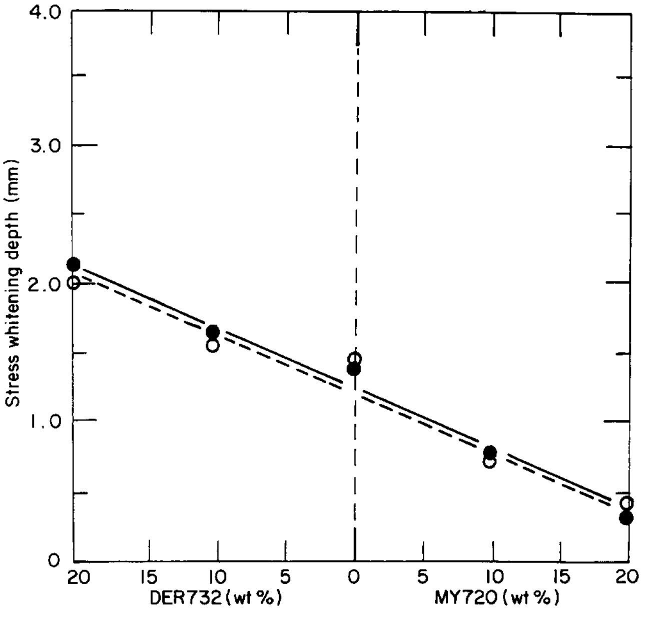


Figure 13 Dependence of stress-whitening depth upon resin composition: (—○—) resin systems without rubber/matrix interfacial modification; (—●—) resin systems with rubber/matrix interfacial modification

CONCLUSIONS

Pre-reaction of CTBN rubber with twice molar quantities of flexible DER732 resin results in a DER732 end-capped CTBN. The end-capped CTBN (10 phr) or the unmodified CTBN (10 phr) were blended with various epoxy resins, distinguished by various compositions and hence various matrix ductilities. Both series of rubber-toughened epoxy resins result in similar rubbery phase microstructures, but the rubber/matrix interfacial zone of the end-capped CTBN rubber particles is larger and more deformable. This modified rubber/matrix interfacial zone gives rise to a further toughness for various epoxy resins. Moreover, epoxy resins with moderate ductility are more effective in improving further toughness via this modified interfacial zone. The further toughness is simply a result of further cavitation of the rubber particles in the plastic deformation zone ahead of the crack tip. Different resin compositions may affect the interfacial composition, but, without detailed knowledge of the interfacial composition, the quantitative relationship between the further increased toughness and the further increased cavitation is difficult to ascertain. The size of the plastic deformation zone is independent of the degree of rubber cavitation, but is significantly increased by the increase in multiple but localized shear yielding. The effect of increasing matrix ductility on increasing the size of the plastic deformation zone is by causing multiple but localized plastic shear yielding to occur more extensively.

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