Numerical and experimental studies on the fracture behavior of rubber-toughened epoxy in bulk specimen and laminated composites

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To study the toughening mechanisms of liquid rubber (LR) and core-shell rubber (CSR) in bulk epoxy and composite laminate, experimental and numerical investigations were carried out on compact tension (CT) and double-cantilever-beam (DCB) specimens under mode-I loading. The matrix materials were pure epoxy (DGEBA), 15% LR (CTBN) and 15% CSR modified epoxies. Experimental results and numerical analyses showed that both liquid rubber (LR) and core-shell rubber (CSR) could improve significantly the fracture toughness of pure epoxy (DGEBA). However, the high toughness of these toughened epoxies could not be completely transferred to the interlaminar fracture toughness of the unidirectional carbon fibre reinforced laminate. The main toughening mechanism of CSR in bulk epoxy was the extensive particle cavitation, which greatly released the crack-tip triaxiality and promoted matrix shear plasticity. The poor toughness behavior of CSR in the carbon fibre laminate was thought to be caused by the high constraint imposed by the stiff fibre layers. No particle cavitation had been observed in LR modified epoxy and the main toughening mechanism was merely the large plastic deformation near the crack-tip due to the rubber domains in the matrix which results in a lower yield strength but a higher elongation-to-break. © 2002 Kluwer Academic Publishers

1. Introduction
The increasing demand for high performance composites has drawn much attention on how the fracture toughness of a composite can be improved. Conventionally, rubber-toughened epoxies have been successfully applied to improve the matrix toughness. Unfortunately, many studies indicated that the traditional approaches using rubber particles for matrix toughening usually do not produce expected toughness improvement in the fibre composites [1–3]. The mode-I delamination toughness of composites made with brittle epoxy is often greater than the neat-resin toughness. But composites with a ductile matrix show poor translation of resin toughness to delamination toughness [2]. The reason was partially assumed to be the constraint effect imposed by the neighboring fibres which limit the evolution of the plastic zone within the matrix resin. The stress distributions ahead of a pre-crack tip in composite laminates have been analysed by Todo and Jar [4] and Corleto et al. [5] using elastic finite element analysis. Recently, Huang and Kinloch [6] and Chen and Mai [7] have carried out extensive finite element analyses to study the toughening mechanisms in rubber-modified epoxies. Relatively little work, however, has been done to compare the changes of toughness and crack-tip stress fields in the bulk resin matrix and the composite laminate. Hence, further work is needed to obtain a better understanding of the contribution of the matrix resin to the fracture toughness of laminated composites. This allows suitable choices of matrix resins to improve the fracture toughness with minimum penalties on other mechanical properties. In this work, three different resin systems, namely pure epoxy, liquid rubber (LR) and core-shell rubber (CSR) toughened epoxies, were chosen as the matrices for carbon fibre composites. The fracture behaviors of neat resin and the corresponding laminates subjected to mode I loading were studied using compact tension (CT) and double-cantilever-beam (DCB) specimens. Elastic-plastic finite element analyses were carried out to obtain the stress-strain fields ahead of the pre-crack tip.

2. Experimental procedure
2.1. Materials
The basic resin was a diglycidyl ether of bisphenol A (DGEBA) epoxy (Araldite® GY 260, supplied by

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Ciba-Geigy, Australia). The curing agent was piperidine mixed with pure epoxy at a weight ratio of 5 : 100. Rubber-toughened epoxies were produced by adding 15% core-shell rubber (CSR) in powder form, supplied by Rohm and Haas Co., USA and liquid rubber (LR), CTBN 1300X13, supplied by BF Goodrich, USA. The average diameter of the CSR was about 0.2–0.4 μm. The CSR was first dried at 80°C for 2 h and then mixed with the pure epoxy using a mechanical mixer to achieve a uniform blend. The blend was degassed in a vacuum oven at 100°C for about 2 h. Then the vacuum was removed and piperidine was added to the mixture. For the LR rubber, the same procedure was adopted but no drying was necessary. To make the bulk epoxy specimens, the mixture was cast in a preheated mould with 12 mm thickness and then cured at 120°C for 12 h. The unidirectional prepregs were fabricated using a two-axes winding machine. The carbon fibre used in this study was Toray T300 (Advanced Composites Pty Ltd, Australia) with a specific gravity of 1.75 and the length/unit weight is 1.25 m/gm. Uncured composite laminates 280 mm × 250 mm were made by hand lay-up of twelve prepregs. A strip of 12.3 μm Teflon film (UPILEX-S, UBE Industries, Ltd., Tokyo, Japan) coated with release agent was included between the sixth and seventh plies at one end of the laminate during the laminating operation to produce a starter crack. A resin-rich layer was formed between these two plies with a thickness about 50 μm. Curing was completed in an autoclave at 120°C for 16 h under a pressure of 0.6 MPa.

2.2. Preparation and testing of specimens

For bulk epoxies, standard tensile and compact tension (CT) specimens were cut from the 12 mm thick cured plates. The stress-strain response and Young's modulus were measured using tensile specimens according to ASTM D638M-91. The dimensions of the CT specimen are shown in Fig 1a. The composite laminates were tested at room temperature using the double-cantilever-beam (DCB) specimen (ASTM D-5528). The DCB specimens were cut from the cured laminates along the longitudinal direction of the fibre using a diamond saw and then polished with fine abrasive papers. The specimen geometry is shown in Fig. 1b. All tests were conducted at a crosshead rate of 2 mm/min in an Instron 5567 testing machine. Loads and displacements were recorded continuously. The fracture surfaces for the CT and the DCB specimens were observed using optical and scanning electronic microscopes.

3. Numerical approach

Large deformation finite element analysis (FEA) was carried out with finite element code ABAQUS (Ver-
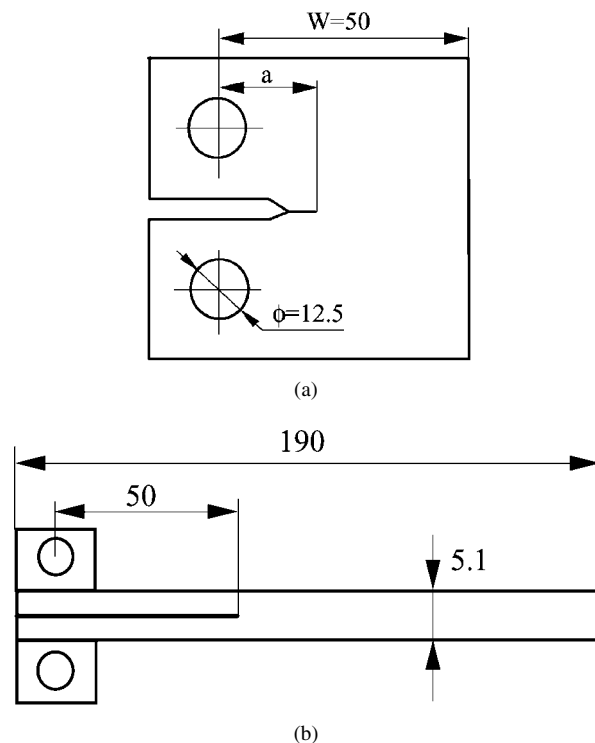

Figure 1 Compact tension specimen, and (b) double-cantilever-beam specimen (all dimensions in mm).
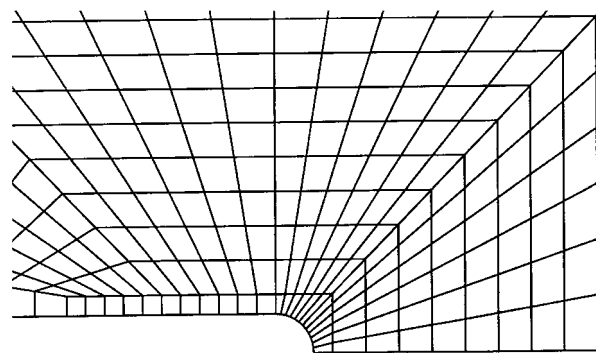

Figure 2 Finite element mesh for the crack-tip.

sion 5.8). Plane strain condition was assumed for both the CT and the DCB specimens. Only one-half of the specimen was modeled because of symmetry. The mesh details at the crack-tip are shown in Fig. 2. Rate-independent plasticity and associated flow rule were used for the material constitutive model. The stress-strain curves for the pure and rubber-toughened epoxies are shown in Fig. 3. It is clear that plastic yielding occurred before final failure. Young's moduli are 3.04, 2.12 and 2.42 GPa for pure epoxy, 15%LR and 15%CSR modified epoxies, respectively. The elastic properties of the laminates used in the FEA are shown in Table I. The resin-rich layer was treated as isotropic and the laminate orthotropic. The far field J-integral was evaluated according to the domain integral method.

TABLE I Elastic properties of laminates with different matrixes

	E_1 [GPa]	E_2 [GPa]	E_3 [GPa]	G_{12} [GPa]	G_{13} [GPa]	G_{23} [GPa]	ν_{12}	ν_{13}	ν_{23}
Epoxy	108.9 ± 3.3	7.2 ± 0.2	7.2 ± 0.2	2.3 ± 0.2	2.3 ± 0.2	3.0 ± 0.3	0.27	0.27	0.27
15%LR	107.8 ± 4.3	5.9 ± 0.4	5.9 ± 0.4	1.6 ± 0.2	1.6 ± 0.2	2.0 ± 0.2	0.27	0.27	0.27
15%CSR	105.3 ± 3.8	5.9 ± 0.3	5.9 ± 0.3	1.7 ± 0.1	1.7 ± 0.1	2.2 ± 0.2	0.28	0.28	0.28

TABLE II Critical J-integral for CT and DCB specimens (J/m^2)

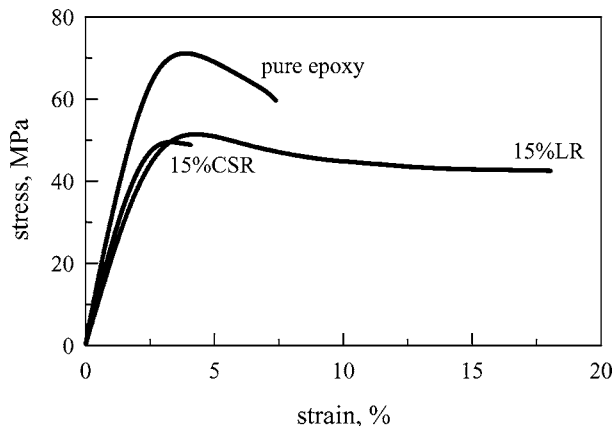|	Epoxy	15% LR	15% CSR
CT specimen (bulk material)	167	797	3140
DCB specimen (laminate)	221	529	320

Figure 3 Stress-strain relationship for the epoxies.

4. Results and discussion
4.1. Fracture toughness of bulk epoxies and laminates

Because of the plastic deformation in the toughened epoxies, the J-integral may be a more suitable parameter for fracture toughness evaluation. Keary *et al.* [8] showed that simple beam theory and experimental compliance calibration in the laminate DCB specimens gave higher values for critical strain energy release rate (G_c) than critical J-integral. The difference was attributed to non-linear material behavior and J-integral method was proposed as the most appropriate approach. In this study, critical J-integral values corresponding to fracture loads for both the bulk matrices and the composite laminates were calculated using FEA and the results given in Table II.

It can be found that for the bulk epoxies the fracture toughness is greatly improved by adding rubber particles (LR and CSR). The highest fracture toughness was associated with 15%CSR toughened epoxy in terms of the J-integral. Therefore, CSR would seem to be a more suitable rubber for toughening the epoxy matrix compared to LR. The toughening mechanisms will be discussed later.

As mentioned before, composites with ductile matrices often show a poor translation of resin toughness to delamination toughness [2]. In Table II, the interlaminar fracture toughness (J-integral) values of the laminates with CSR and LR toughened matrices are lower than those of the bulk epoxies. Especially, for the laminates with 15%CSR, the critical J value dropped from 3140 J/m^2 to 320 J/m^2, supporting a poor toughness translation from the ductile matrix to the laminate. Similar fracture toughness values are found for the pure epoxy for both bulk specimen and composite laminate (Table II). The laminate toughened by 15%LR has the largest fracture toughness. This is contrary to the fact that the maximum toughness in bulk specimens was achieved by 15%CSR toughened epoxy.

4.2. Fracture mechanisms in bulk epoxies

Possible toughening mechanisms in rubber-modified epoxy systems were reviewed by Garg and Mai [9]. Two important toughening mechanisms were identified as localized shear yielding due to stress concentration at the equator of rubber particles and dilation deformation due to the growth of voids formed by rubber cavitation. Some investigators [10–12] also reported experimental evidence of cavitation to relieve the crack-tip triaxial stress so that extensive shear deformation can be developed in the matrix. Therefore, fracture toughness is related to the plastic deformation zone ahead of a precrack tip [13, 14]. On the fracture surface of 15% CSR-modified epoxy, two distinct regions with characteristics of stress-whitening and smooth surface can be seen. In the work of Xiao and Ye [15], the fracture toughness increased with the length of the stress-whitening zone. This is consistent with the previous work of Low and Mai [16]. It was argued that stress-whitening was mainly caused by scattering of visible light from a layer of voids, i.e., cavitated rubber particles [17]. The details of the stress-whitening zone were examined using scanning electronic microscopy (SEM) and the morphology is shown in Fig. 4. Rubber cavitation is observed. For the 15%LR-modified specimen, no apparent stress-whitening zone was found. In front of the pre-crack, a plastic deformation band due to crack-tip blunting and/or stable crack growth was found, Fig. 5. The morphologies of the liquid rubber phase in the epoxy matrix were also carefully observed. No isolated rubber particles could be identified. The rubber domains had a blend structure consisting of the epoxy matrix phase. The size of the rubber domains was about 1–3 μm in diameter. The phenomenon that rubber particles did not cavitate was also found by Verchere *et al.* [18] in a system consisting of a DGEBA epoxy. The fracture surface of the pure epoxy specimen is smooth and featureless, indicating small plastic dissipation.

As mentioned before, cavitation can lead to release of constraint ahead of the crack tip and cause predominant matrix plastic deformation. Fig. 4 illustrates extensive particle cavitation took place in the 15%CSR specimen. The triaxiality (σ_m/σ_e) corresponding to the fracture load for the bulk matrices are shown in Fig. 6a, where σ_m and σ_e are mean stress and equivalent stress, respectively. The triaxiality (constraint) is released at the crack-tip to different extent for 15%LR and 15%CSR modified epoxies. A large drop of triaxiality is associated with the 15%CSR modified epoxy. This is due to the extensive plastic deformation at the crack-tip region. Fig. 6b shows the distributions of crack-tip plastic strain and a high strain is observed in the 15%CSR specimen. Fig. 6c gives the distribution of crack-tip equivalent stress (σ_e), which increases from pure epoxy to 15%LR and 15%CSR. As equivalent stress is the driving force for plastic yielding, the pure epoxy has the smallest plastic zone and 15%CSR the largest. Therefore, the high fracture toughness of the 15%CSR specimen is
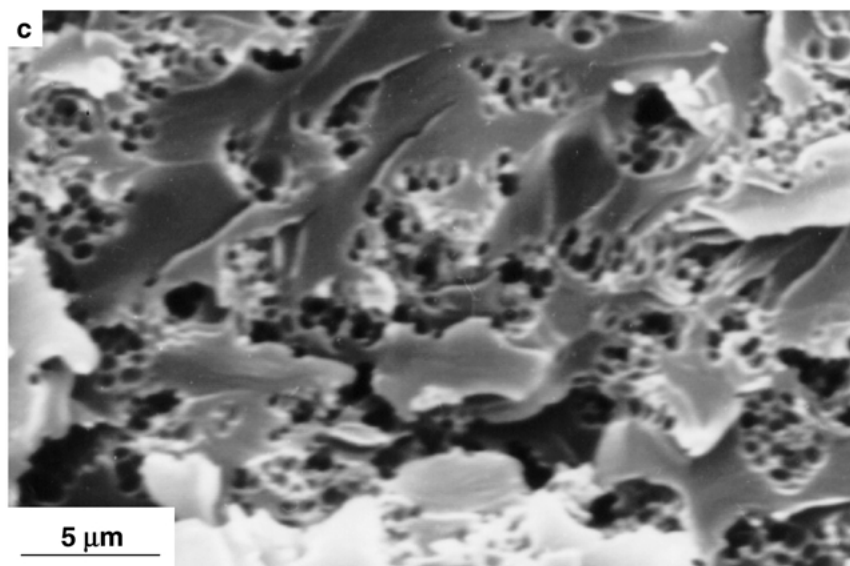
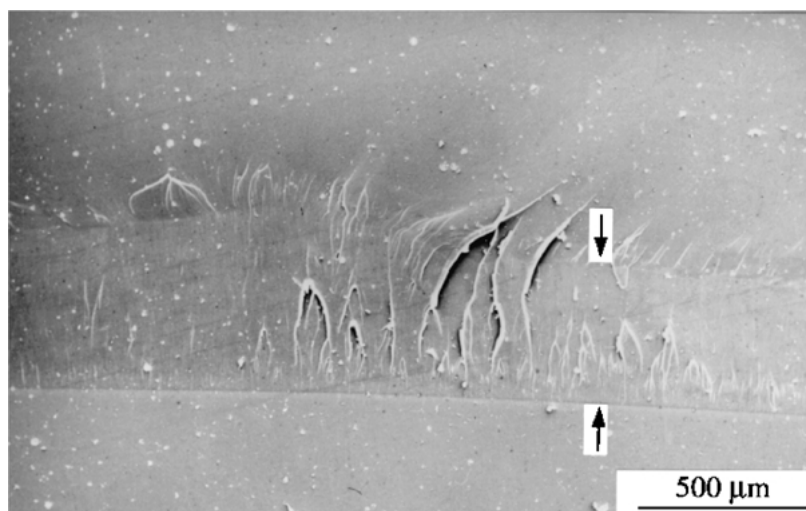*Figure 4* Fracture surface of CT bulk matrix with 15%CSR.

Figure 5 Fracture surface of CT bulk matrix with 15%LR.

due to particle cavitation, leading to constraint release near the crack-tip. For the 15%LR specimen, extensive plastic yielding was found ahead of the crack-tip (Fig. 5) although no cavitation was observed. Yee and Pearson [10] concluded that cavitation is an essential condition for subsequent plastic yielding. However, Huang and Kinloch [6] and Guild and Young [19] suggested that cavitation and matrix shear yielding are two independent processes. More recently, Chen and Mai [7, 20, 21] carried out extensive FEA to study the sequence of different toughening mechanisms of rubber modified blends. Their work has concluded that rubber cavitation and matrix shear yielding are two coexisting mechanisms. Which occurs first depends on the properties of the rubber particles and the matrix as well as the degree of constraint condition. High constraint level and high rubber bulk modulus will stimulate particle cavitation. Their results also confirm that rubber cavitation plays an important role in the toughening process. It is noted in Fig. 3 that the yield stress of 15%LR modified epoxy is lower than pure epoxy though no cavitation was observed in all 15%LR speci-

mens. Consequently, a larger plastic strain (Figs 5 and 6b) and a higher critical J-integral can be obtained by 15%LR modified epoxy in comparison to pure epoxy.

4.3. Contribution of matrix resin to the fracture toughness of laminate

In Table II, the critical J-integral values in the DCB specimens with 15%CSR and 15%LR modified matrices are lower than the corresponding toughness of the bulk matrices. The complete translation of the high toughness of the matrices to the composite laminates was not achieved. It is interesting to note that 15%LR is superior in improving interlaminar toughness of the DCB laminates compared to 15%CSR. However, fracture toughness of 15%CSR modified matrix is higher than that for the 15% LR. It is hence difficult to conclude that higher matrix toughness can lead to superior interlaminar fracture toughness.

The fracture surfaces of the laminates are shown in Fig. 7. For pure epoxy, fracture surface is smooth and brittle-like, indicating little plastic deformation
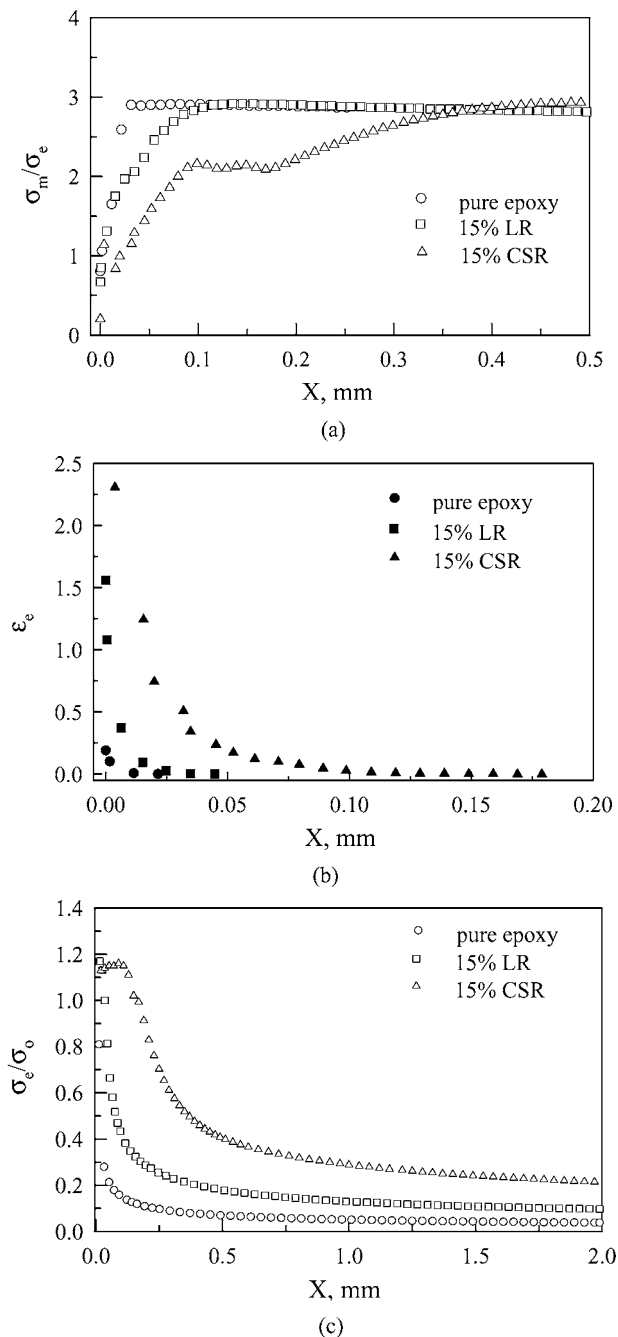
Figure 6 (a) Triaxiality, (b) plastic strain, and (c) equivalent stress ahead of crack-tip in CT specimen.

associated with fracture initiation. But many river marks and ductile matrix tearing can be seen on the fracture surface for 15%LR modified epoxy, which are indicative of the occurrence of plastic shear deformation. For the 15%CSR modified epoxy, crack growth was observed to be completely in the resin layer. At a high magnification, rubber cavitation and holes were observed in the matrix but no plastic shear bands could be found. As discussed in Section 4.2 and other studies [10–12], for bulk epoxies modified by CSR rubber, the dominant mechanism for toughening is related to the cavitation of particles, which relieves the triaxiality in front of the crack-tip, followed by dilation deformation due to the growth of voids and shear yielding of the matrix. In this study, the thickness of resin layer in the laminate is only about 50 μm. The plastic deformation within the resin layer is limited by the neighbor-
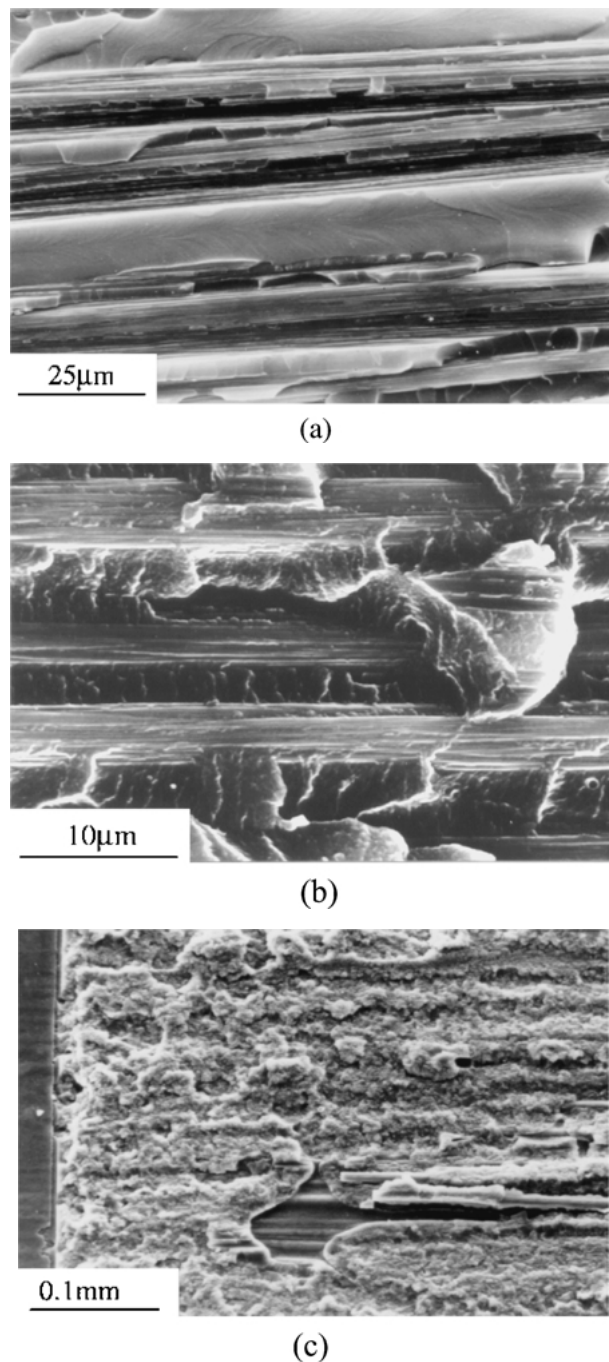

Figure 7 Fracture surfaces of DCB composite laminates with different matrices: (a) pure epoxy, (b) 15%LR modified, and (c) 15% CSR modified.

ing carbon fibre layers. The experimental investigation of Xiao and Ye [22] showed that although the plastic zone ahead of the crack tip in the 15% CSR laminate could extend over more than two fibre layers, its size was much smaller than that in the 15% CSR bulk epoxy. Consequently, dilation deformation and shear yielding are suppressed and high triaxiality is maintained at the crack-tip. Fig. 8 gives the distributions of stress triaxiality ahead of the crack-tip corresponding to the fracture loads for the DCB laminates. No apparent release of triaxiality can be seen for 15%LR and 15%CSR laminates. As pointed out by Bucknall, Karpodinis and Zhang [23], cavitation in itself cannot be regarded as an important energy-absorbing process. Cavitation itself neither provides major increase in
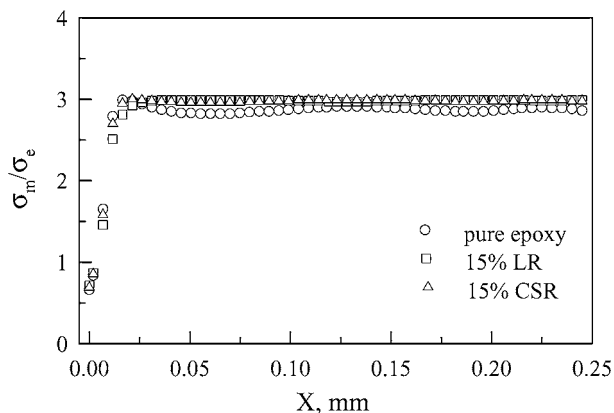
Figure 8 Triaxiality ahead of crack-tip in DCB composite laminates.

volume nor results in large energy interchange within rubber particles. The real importance of cavitation is that it reduces the resistance of the polymer to volumetric expansion in response to dilatational applied stress fields. However, due to the additional constraint by the rigid fibres in the laminate, extensive volumetric expansion may be suppressed. The work of Varias *et al*. [24] also confirmed that a very high triaxiality could cause unstable cavitation at a distance of several layer thickness ahead of the pre-crack-tip. Yee [25] also argued that high hydrostatic tensile stress tends to promote voiding and possible brittle fracture rather than shear yielding. In more recent years, there has been some argument that the mechanism of rubber-modified polymer is very similar to that occurring in metals [26, 27]. Therefore, it is reasonable to assume that if high triaxiality cannot be released ahead of a crack tip, the isolated particles whether cavitated or not, may act as crack initiation sites, which will obviously deteriorate the toughness. In this study, no *R*-curve behavior was found for the DCB composite laminates. However, Du, Thouless and Yee [28] recently observed a significant *R*-curve behavior in DGEBA epoxies toughened by different volume fractions of CTBN rubbery phase in DCB specimens. The cause of the experimental *R*-curve was directly related to the evolution of the process zone to a steady-state crack wake of constant thickness. The absence of a *R*-curve indicates a lack of energy absorption in a process zone around the crack-tip. It is expected that evolution of the process zone will be limited by
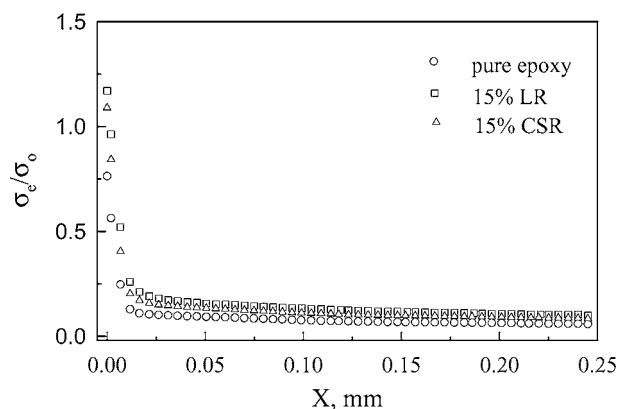
the existence of rigid fibres in a laminate. As a result, the interlaminar toughness for the 15%CSR laminate is only slightly higher than that for the laminate with pure epoxy matrix (Table II). Fig. 9 shows the distributions of equivalent stress ahead of the crack-tip for the laminates. It is clear that at the same X, the highest σ_e is obtained in the laminate with 15%LR matrix due to the lower yield strength and high elongation, which in turn has the highest interlaminar fracture toughness. The decrease of critical *J*-integral for the 15%LR laminate in comparison to the bulk matrix is also associated with the high triaxiality developed in the laminate (Fig. 8), which suppresses the plastic deformation and crack-tip blunting. Certainly, further work on the failure mechanisms for CSR modified epoxy under high constraint is needed.

5. Conclusions

1. Both liquid rubber (LR) and core-shell rubber (CSR) greatly improve the fracture toughness of pure epoxy (DGEBA). CSR is much more efficient than LR in toughening. However, the high toughness of these toughened epoxies cannot be completely transferred to the interlaminar fracture toughness of the unidirectional carbon fibre reinforced laminates. A moderate increase of interlaminar toughness can be obtained for the laminate with 15%LR matrix. A small improvement in interlaminate toughness can only be achieved by using 15%CSR as the matrix.

2. Both experimental and numerical evidence revealed that the main toughening mechanism of CSR in bulk epoxy is extensive particle cavitation, which releases the triaxiality near the crack-tip. Extensive dilation deformation and shear yielding are expected. The poor behavior of CSR in the carbon fibre laminate is considered to be the additional high constraint imposed by the stiff fibre layers.

3. No isolated rubber particles can be identified in the epoxy modified by 15% liquid rubber. The rubber domains have a blend structure, consisting of a continuous epoxy matrix phase. No particle cavitation has been observed and the main toughening mechanism is large plastic deformation near the crack-tip due to the contribution of rubber domains to the matrix, such as lower yielding strength and higher elongation. Therefore, rubber cavitation is not the only essential toughening mechanism in an epoxy matrix.

Figure 9 Equivalent stress ahead of the crack-tip in DCB composite laminates.

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