Journal of Composite
Materials

**Enhancing Fracture Toughness of Glass/Epoxy Composites by Using Rubber
Particles Together with Silica Nanoparticles**

Jia-Lin Tsai, Bao-Hung Huang and Yi-Lieh Cheng

The online version of this article can be found at:
http://jcm.sagepub.com/content/43/25/3107

Additional services and information for *Journal of Composite Materials* can be found at:

Email Alerts: http://jcm.sagepub.com/cgi/alerts

Subscriptions: http://jcm.sagepub.com/subscriptions

Reprints: http://www.sagepub.com/journalsReprints.nav

Permissions: http://www.sagepub.com/journalsPermissions.nav

Citations: http://jcm.sagepub.com/content/43/25/3107.refs.html

>> Version of Record - Nov 25, 2009

OnlineFirst Version of Record - Sep 9, 2009

What is This?

Enhancing Fracture Toughness of Glass/Epoxy Composites by Using Rubber Particles Together with Silica Nanoparticles

Jia-Lin Tsai,* Bao-Hung Huang and Yi-Lieh Cheng

Department of Mechanical Engineering
National Chiao Tung University, Hsinchu, Taiwan, 300

ABSTRACT: The research aims to investigate the interlaminar fracture toughness of glass fiber/epoxy composites, which consist of the silica nanoparticles and the rubber particles. Two kinds of rubber particles, one is the reactive liquid rubber (CTBN) and the other is the core-shell rubber (CSR), were employed to modify the fracture toughness of epoxy resin. In general, the disadvantage of adding rubber particles into polymeric resin is the dramatic reduction of stiffness although the toughness could be modified accordingly. In order to enhance the fracture toughness of the fiber composites without sacrificing their stiffness, the silica nanoparticles in conjunction with the rubber particles were introduced into the epoxy matrix to form a hybrid nanocomposite. Experimental results obtained from tensile tests on bulk epoxy confirm the presumption that the reduction of the epoxy stiffness because of the presence of rubber particles can be effectively compensated by the silica nanoparticles. Furthermore, the fracture tests conducted on the double cantilever beam specimens revealed that the inclusion of silica nanoparticles together with the CSR particle can appreciably increase the fracture toughness of the glass/epoxy composites up to 82%. On the other hand, when the epoxy matrices were modified with CTBN rubber particles and silica nanoparticles, the improvement of the interlaminar fracture toughness was around 48%. It is noted that the role of the silica nanoparticles on the fracture toughness of fiber composites with rubber-modified epoxy matrix is different. For the CSR-modified epoxy matrix, the contribution of silica nanoparticle on the fracture toughness is destructive. In contrast, for the CTBN-modified epoxy matrix, the silica nanoparticles can synchronously improve the fracture toughness of composites.

KEY WORDS: fracture toughness, composites, silica nanoparticles, double cantilever beam (DCB).

---

*Author to whom correspondence should be addressed. E-mail: jialin@mail.nctu.edu.tw
Figure 8 appears in color online: http://jcm.sagepub.com

INTRODUCTION

WITH THE FEATURES of high stiffness, strength, and low weight, the high-performance composites have been extensively utilized not only in the aerospace industry but also in marine, armor, automotive, and civil engineering applications. However, for the laminated composites, the interlaminar delamination is the main failure mode, which results in the unacceptable reduction of material performances. Therefore, modifying the delamination fracture toughness of high-performance composites, especially for composites made of brittle matrices, is an essential task for the applications of the materials with safety.

In an attempt to enhance the fracture toughness of composites, the typical approach is to add a lower T_g compound, such as rubber, into the epoxy matrix [1,2]. Nevertheless, the drawback in doing so is the substantial reduction of the Young's modulus [3]. The main objective of the study is to improve the fracture toughness of composites with minimum penalties on the other properties. As a result, we proposed to incorporate the silica nanoparticles into the rubber-modified epoxy resin to form a hybrid epoxy matrices by taking the advantage of the silica nanoparticle to improve the mechanical properties of the composites and compensate the stiffness reduction caused by the rubber as well.

The silica nanoparticles have been employed to modify the epoxy resin for many years. In general, the dimensions of these particles are in micron ranges. However, with the advance of nanotechnology as well as the processing techniques, various types of particles in nanoscales have recently been developed and then utilized as reinforcement in polymeric composites. Rosso et al. [4] employed the well-dispersed silica nanocomposites for tensile and fracture tests, indicating that the addition of 5 vol% silica nanoparticles could improve the stiffness and fracture energy to 20 and 140%, respectively. Chen et al. [5] indicated that small weight percent (1 wt%) of silica nanoparticle can increase the fracture toughness of epoxy resin up to 20%; however, this improvement is less significant at larger weight fraction. Moreover, for silica weight percent less than 5 wt%, the toughening mechanism is the surface roughening; whereas for 15 wt% silica loading, matrix yielding is the main toughening mechanism. The escalation behaviors in fracture toughness yielded by the silica nanoparticles were also reported by Johnsen et al. [6]. In their study, the debonding of the nanoparticles from the surrounding matrix and the subsequent plastic void growth were believed to be responsible for the increased fracture toughness in the nanoparticle-modified samples. Guo and Li [7] performed compressive loading on the SiO_2/epoxy nanocomposites under different loading rates, revealing that the compressive strength of the composites with silica nanoparticles is higher than pure epoxy at higher strain rates; nevertheless, there is no clear connection between the compressive strength and the nanoparticle contents at lower strain rates. The comprehensive effectiveness of silica nanoparticles on the property enhancement was demonstrated in the literature [8].

When the silica-modified epoxy was adopted as matrices in the fabrication of fiber composites, the mechanical properties of the fiber composites was increased accordingly. The effect of particle aspect ratio, particle modulus, and interparticle distance on the strengthening of particle-reinforced polymer was studied by Zhao and Hoa [9] using finite element analysis. Zheng et al. [10] investigated the silica nanoparticle effect on the epoxy resin and glass/epoxy composites showing that a comprehensive enhancement in the properties of the composites was reached by the particles. Such improvement was believed to be attributed to the prompted bonding forces between the glass fiber and matrices modified by the silica nanoparticles. Yan et al. [11] studied the toughening mechanisms of reactive liquid rubber (CTBN) and core shell rubber (CSR) in bulk epoxy and composites laminates using compact

tension and double cantilever beam (DCB) specimens, respectively. It was found that for bulk epoxy, CSR is much more efficient in toughening the fracture behaviors than the CTBN. In contrast, the CTBN can provide better interlaminar fracture toughness in fiber composites than CSR. The influence of silica nanoparticles together with the CTBN rubber on the mechanical responses of glass and carbon fiber composites was examined by Kinloch et al. [12,13]. It was shown that the fracture toughness of the composites was enhanced effectively by the addition of the hybrid particles into the epoxy matrix. A comprehensive review regarding the polymer–matrix composites modified by the nanoscale reinforcement was provided by Hussain et al. [14].

In this study, two kinds of rubbers, one is the CTBN and the other is the CSR, were employed to modify the fracture toughness of bulk epoxy as well as the epoxy-based fiber composites. The merging effects of the rubber particles with silica nanoparticles on the fracture behaviors of bulk epoxy were investigated using single-edge notch bending specimens, and the corresponding fracture mechanisms were determined from the scanning electron microscopy (SEM) observation on the failure surfaces. Meanwhile, the stiffness of the bulk epoxy in terms of the combined effects of silica nanoparticles and rubber particles were investigated from the simple tension tests. Furthermore, the interlaminar fracture behaviors of the fiber composites with the modified epoxy were characterized through Mode I fracture tests on DCB specimens. In accordance with the experimental data, the correlation of the fracture toughness between the bulk epoxy and the fiber composites associated with different contents of silica nanoparticles and liquid rubbers were established.

SAMPLE PREPARATIONS

Preparation of Silica/Rubber/Epoxy Nanocomposites

To investigate the influence of silica nanoparticles and rubber particles on the mechanical properties of epoxy nanocomposites and the glass fiber/epoxy composites, the samples containing various particle loadings have to be prepared in the beginning. The epoxy resin used in this study is Nanopox@ F400 supplied from Hanse Chemie, Germany. Basically, it is a diglycidyl ether of bisphenol A (DGEBA) resin consisting of 40 wt% silica nanoparticles. Through sol–gel processing, the synthesized silica particles with diameters of around 25 nm were dispersed uniformly in DGEBA resin [15]. Two different kinds of rubbers were introduced in this study in an attempt to alter the fracture toughness of bulk epoxy. One is the CSR particles (PARALOID EXL-2314) obtained from Rohm and Hass with the diameters of around 300–400 nm, and the other is the CTBN (Hycar CTBN 1300x8) that is a carboxyl-terminated butadiene–acrylonitrile copolymer with 18% acrylonitrile content provided by Emerald Performance Materials. The curing agents are H-100 (modified cycloaliphatic amine) supplied by the Yun Teh Corporation of Taiwan.

When the silica/CSR/epoxy nanocomposite samples were prepared, a desired amount of Nanopox@ F400 resin was diluted with DGEBA resin, depending on the required weight percentage of silica nanoparticles. The mixture was then sonicated using a sonicator with a cooling system around the sample container so that the nanoparticles were displaced uniformly in the epoxy resin. The epoxy–silica mixture was degassed at room temperature in a vacuum oven for 10 min and then mixed with the CSR rubber. The mixture was blended at 80°C for 360 min using a mechanical stirrer, followed by the degassing process for another 5 min in the vacuum oven. After cooling down into the room temperature, the

final compounding was mixed with the curing agent using the mechanical mixture for 10 min. Afterward, the mixture was poured into the designed steel mold with Teflon coating on its surfaces to form the nanocomposite specimens. Subsequently, the samples were cured at 100°C for 3 h with an additional 3 h at 125°C for postcuring. In the study, 10, 20 wt% silica nanoparticle and 10 wt% CSR particles were incorporated, respectively, in the fabrication of the nanocomposites. Moreover, the hybrid nanocomposites containing 10 wt% silica nanoparticles and 10 wt% CSR particles were also prepared.

On the other hand, for the preparation of the silica/CTBN/epoxy nanocomposite, the desired amount of the Nanopox@ F400 resin together with DGEBA resin and CTBN were mixed evenly using the mechanical mixture for 10 min at room temperature followed by the sonication for another 20 min. Subsequently, the degassing was carried out on the mixture in the vacuum oven for 120 min at 100°C. After the compounding is cooled down, it was blended with the curing agent for 10 min and then the whole mixtures were degassed at room temperature for 10 min. For the sake of comparison with CSR-modified nanocomposites, 10 wt% CTBN particles were included in the preparation of the nanocomposites. In addition, the combination of 10 wt% silica nanoparticle and 10 wt% CTBN particles were also integrated in the fabrication of hybrid nanocomposites.

Fabrication of Glass Fiber/Silica/Rubber/Epoxy Nanocomposites

When the epoxy resins modified with different contents of particles were prepared through vacuum-assisted hand lay-up procedures, they were diffused into unidirectional fibers to form the glass fiber/silica/rubber/epoxy composites. The process is that the final mixture epoxy resin with the H-100 curing agent was poured on one dry unidirectional glass fiber layer (provided by Vectorply®, E-LR0908-14 unidirectional E-glass fiber) and then impregnated into the dry fibers with the assistance of a hand roller until the fiber bundles were permeated completely by the resin. Then, another ply of dry fiber was stacked on it. The repeating process continued until the 12 layers of glass fibers were fabricated. Since the interlaminar fracture toughness of composites was measured from the DCB specimens, during the process, a porous film was inserted in the midplane of the laminates for the creation of precrack. The entire stacking was then sandwiched between two steel plates with porous Teflon fabric on the surfaces and then sealed within a vacuum bag. The whole laminates were cured in a hot press with a suggested temperature profile under vacuum conditions. It is noted that the vacuum is an essential process for forming nanocomposites because it can facilitate the removal of the tiny bubbles trapped in the nanocomposites. The contents of the silica nanoparticles and rubber particles in the composites are the same as those in the bulk epoxy.

MATERIALS CHARACTERIZATION

To understand the degree of exfoliation of the silica nanoparticle as well as the rubber particles in the epoxy resin, the hybrid nanocomposite samples were examined using a transmission electron microscope (TEM). Thin film samples of silica/CTBN/epoxy and silica/CSR/epoxy nanocomposites (about 80 nm thick) were cut from the specimens, respectively, using a Reichert-Jung Ultracut microtome, and the associated morphology was imaged using a JEOL 200CX TEM at an accelerating voltage of 120 KV. The results with the magnification of 20 K were shown in Figure 1(a) and (b) for the two different
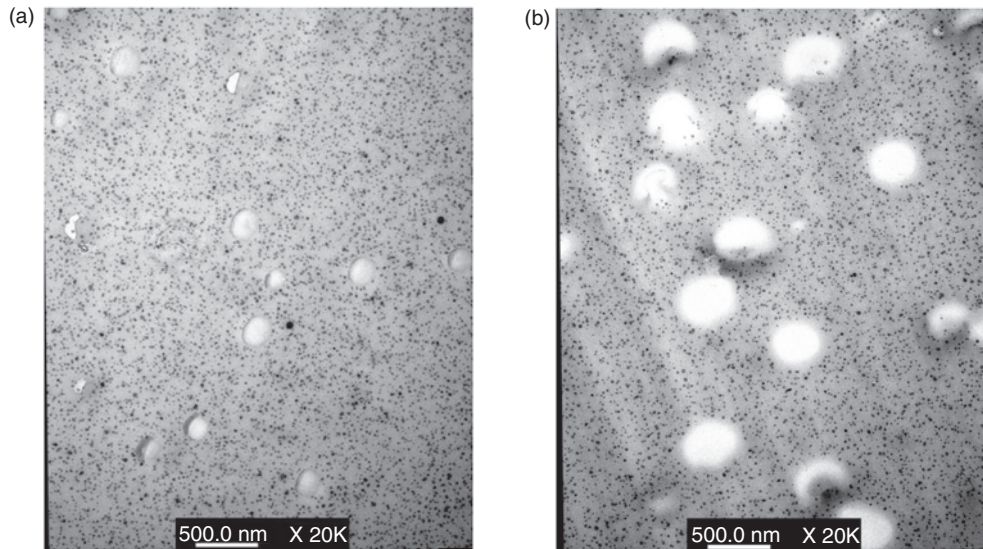
Figure 1. *TEM micrographic of nanocomposites: (a) silica/CTBN nanocomposites, (b) silica/CSR nanocomposites.*

hybrid systems, respectively. From the micrographs, the diameters of the CTBN and CSR particles are measured as about 150–250 nm and 300–400 nm, respectively. Moreover, it can be seen that these rubber particles are dispersed well in the samples. Because the rubber particle is greater than the thickness of the TEM samples such that the rubbers are to be easily detached during the microtome cutting, finally only the holes are left on the TEM micrographs. In addition, the small black dots shown on the background of the photos denote the silica nanoparticles. It seems that the silica nanoparticles are also homogeneously distributed in the nanocomposites. Therefore, from the TEM observations, it was concluded that the two samples were regarded as the nanocomposites with fully exfoliated silica nanoparticles and rubber particles.

EXPERIMENTS

The effects of silica nanoparticles and rubber particles as well as their combining effects on the stress–strain curves of the epoxy nanocomposites were assessed from the tensile tests on the coupon samples. In addition, the fracture behaviors of the samples were investigated using Mode I fracture tests on the single-edge notch bending (SENB) specimens. After the characterization of the bulk epoxy, the fracture behaviors of the fiber composites in terms of the particle modified epoxy as matrices were determined from Mode I fracture tests on DCB specimens.

Silica/Rubber/Epoxy Nanocomposites

TENSILE TEST

The nanocomposite coupon specimens containing 10 wt% and 20 wt% silica nanoparticles, 10 wt% CTBN particles, 10 wt% CSR particles, 10 wt% silica nanoparticles–10 wt%

CTBN, and 10 wt% silica nanoparticles—10 wt% CSR particles was employed for the tensile tests. All tests were conducted on the hydraulic MTS machine at stroke-controlled mode. Back-to-back strain gages were adhered on the center of the specimens to eliminate the possible bending effect and to measure the strain history during the tensile tests. The corresponding stress histories were obtained from the load cell mounted on the loading fixture. Figure 2 demonstrates the stress and strain curves for the epoxy, silica/epoxy, and silica/rubber/epoxy material systems. The moduli and the tensile strengths of the epoxy samples with various particle inclusions are summarized, respectively, in Tables 1 and 2. It was shown that Young's modulus of the epoxy increases with the inclusion of silica nanoparticle; however, the corresponding values decrease when only the rubber particles are included in the epoxy resin. The phenomena that rubber particles can result in the reduction of the stiffness were also reported in the literatures [3]. From Table 1, it was found that such
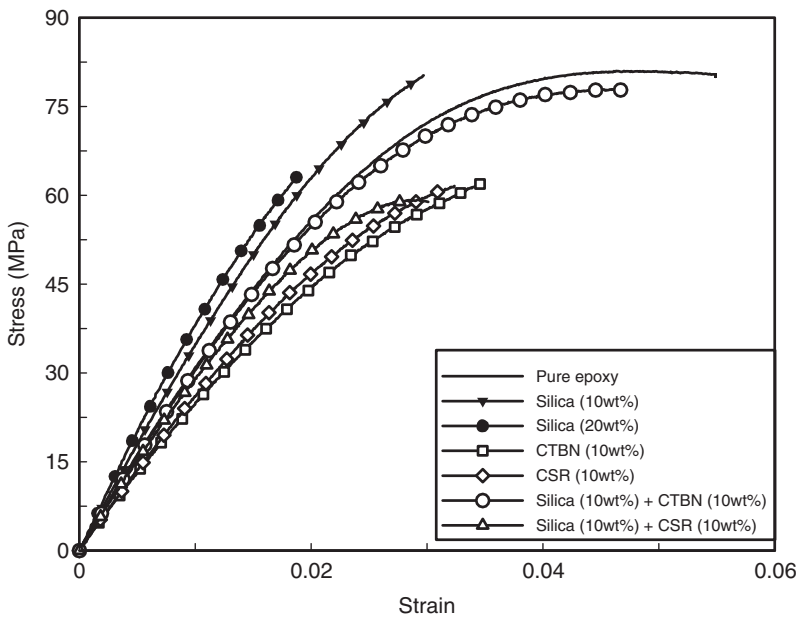

Figure 2. *Stress—strain curves of the epoxy specimens with different contents of silica nanoparticle and rubber particles.*

Table 1. Young's modulus of epoxy matrix with various particle modifications.

Specimen	Young's modulus (GPa)	Increment (%)
Pure epoxy	3.25 ± 0.11	–
Epoxy + Silica (10 wt%)	3.72 ± 0.11	14.5
Epoxy + Silica (20 wt%)	3.93 ± 0.13	20.9
Epoxy + CTBN (10 wt%)	2.63 ± 0.02	−19.1
Epoxy + Silica (10 wt%) + CTBN (10 wt%)	3.18 ± 0.05	−2.3
Epoxy + CSR (10 wt%)	2.73 ± 0.02	−16
Epoxy + Silica (10 wt%) + CSR (10 wt%)	2.97 ± 0.05	−8.6

declining behavior caused by rubber particles can be moderated by incorporating the silica nanoparticles into the epoxy system. The epoxy modified with CTBN and silica nanoparticles exhibit almost the same Young's modulus of the pure epoxy. Nevertheless, for the epoxy resin containing CSR and silica nanoparticles, although the Young's modulus is also improved by the silica nanoparticle, it is still around 16% less than the pure epoxy resin. In addition, it was observed from Table 2 that for the epoxy resin with the nanoparticles, rubber particles or both, the corresponding tensile strengths generally are lower than those in pure epoxy. This decreasing behavior could be due to the defect/void generated during the fabrication process when the particles were included into the epoxy system. It was found that when the CSR rubber particles were introduced into the brittle epoxy matrix, the compound would become very sticky, making it difficult to fully eradiate the embedded bubbles. In addition, the high-viscosity behavior was also observed in the samples with 20 wt% silica nanoparticles. As a result, the corresponding tensile strengths of the epoxy specimens with either 20 wt% silica nanoparticle or CSR particles would be relatively lower than the other cases.

MODE I FRACTURE TEST

From the tensile tests, results revealed that the nanocomposites containing both silica nanoparticles and rubber particles demonstrated higher Young's modulus than those with only rubber particles, and their Young's modulus are more or less close to that in pure epoxy. To further investigate the effect of the silica particles together with the rubber particles on the Mode I fracture toughness (K_{IC}) of the nanocomposites, the SENB specimens were fabricated and then employed in the three-point bending tests. The dimensions of the SENB specimens are illustrated in Figure 3 where B denotes the thickness, and W is the height of the sample. In an attempt to produce a sharp precrack tip, the precrack length (a in Figure 3) was created by a jewel saw followed by a new razor blade. A close-up photo of the crack tip is illustrated in Figure 4. It seems that the crack tip is quite sharp and the entire crack length is straight. The correlations of the dimensions $W = 2B$ and $a = B$, suggested by ASTM D5045 [16], were followed during the preparations of SENB specimens with the thickness B around 5 mm. Moreover, in order to measure a valid fracture toughness, the following inequality equation for the specimen size must also be satisfied [17]:

$$B, a, (W - a) > 2.5(K_{IC}/\sigma_y)^2, \tag{1}$$

where σ_y is the yielding stress of the materials, which is determined using the offset method with 0.002 offset strains in the stress–strain curves shown in Figure 2.

Table 2. Tensile strengths of epoxy matrix with various particle modifications.

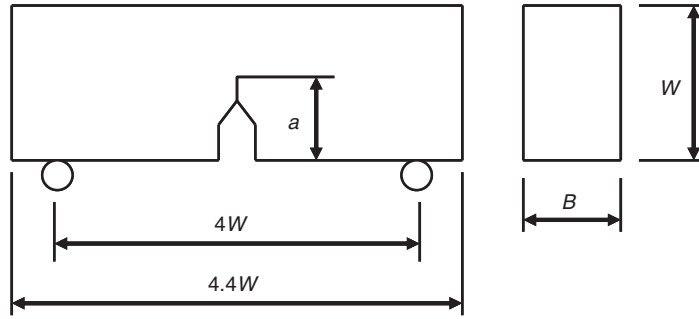| Specimen	Tensile strength (MPa)	Increment (%)
Pure epoxy	79.74 ± 2.22	—
Epoxy + Silica (10 wt%)	80.04 ± 7.92	0.4
Epoxy + Silica (20 wt%)	57.65 ± 5.81	−29
Epoxy + CTBN (10 wt%)	64.43 ± 0.43	−19.2
Epoxy + Silica (10 wt%) + CTBN (10 wt%)	76.85 ± 1.30	−3.6
Epoxy + CSR (10 wt%)	58.38 ± 2.74	−26.8
Epoxy + Silica (10 wt%) + CSR (10 wt%)	59.01 ± 0.70	−26

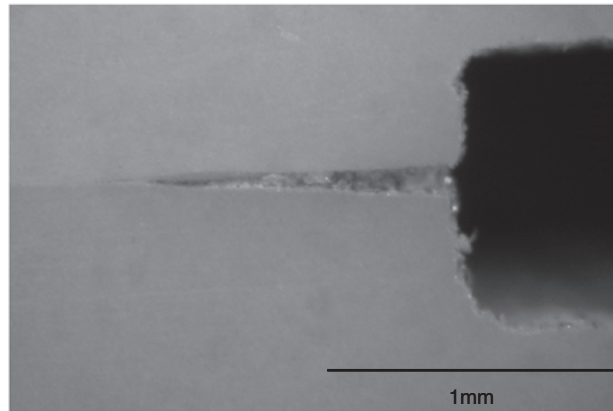**Figure 3.** *SENB specimens for Mode I fracture tests.*

Figure 4. *Sharp crack tip created by razor blade in the SENB specimens.*

During the experiments, at least four specimens were tested in each case for the measurements of fracture toughness.

From the three-point bending tests, the fracture toughness of SENB samples can be calculated using the following formulation [17]:

$$
\begin{aligned}
K_{IC} &= \frac{P_I}{B\sqrt{W}} f(x) \\
f(x) &= 6x^{0.5} \frac{\left[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)\right]}{(1+2x)(1-x)^{3/2}},
\end{aligned}
\tag{2}
$$

where P_I indicates the peak load in the load and deflection curves, and x is a dimensionless value equal to the precrack length, a, divided by the sample height, W. The fracture tests were carried out on the servo-electrical control machine (HT-2102BP) at a displacement rate of 0.05 mm/min. The peak value of the force was regarded as the failure load, P_I, and employed in the calculation of the fracture toughness given in Equation (2). For the linear elastic materials, the fracture toughness K_{IC} can be related to the fracture energy G_{IC} in terms of the material constants as follows:

$$
G_{IC} = \frac{K_{IC}^2(1 - \nu^2)}{E},
\tag{3}
$$

Table 3. Fracture toughness of epoxy matrix with various particle modifications.

Specimen	G_{IC} (kJ/m^2)	Increment (%)
Pure epoxy	0.19 ± 0.01	—
Epoxy + Silica (10 wt%)	0.28 ± 0.08	47
Epoxy + Silica (20 wt%)	0.35 ± 0.05	84
Epoxy + CTBN (10 wt%)	1.17 ± 0.17	516
Epoxy + Silica (10 wt%) + CTBN (10 wt%)	0.93 ± 0.09	390
Epoxy + CSR (10 wt%)	1.42 ± 0.09	647
Epoxy + Silica (10 wt%) + CSR (10 wt%)	1.03 ± 0.12	442

where E is the Young's modulus and is obtained from Table 1, and v is the Poisson's ratio equaling to 0.34. Table 3 illustrates the variations of fracture energy of the nanocomposites modified with various kinds of particles. Apparently, for the bulk epoxy, the fracture energy of nanocomposites increases with the addition of the silica nanoparticles, and the enhancement can be improved significantly as the rubber particles are added. Nevertheless, for the nanocomposites with hybrid particles, the fracture toughness is lower than those with only rubber particles included. Therefore, it was concluded that introducing the rubber particles into epoxy resin is the most effective way to enhance the fracture toughness of bulk epoxy, and moreover, the effectiveness of the rubber particles could be moderated once silica nanoparticles are also included in the samples.

In order to understand the failure mechanism associated with the enhancement of fracture toughness when the rubber particles were included, the failure surfaces of the specimens around the crack tips were examined using SEM. Figure 5 illustrates the neat epoxy sample and the epoxy samples modified with silica nanoparticles, CTBN, and CSR rubber particles, respectively. All fractography was conducted outside the process zone. It is clearly seen that in the rubber modified cases, the fracture surfaces are very rough and filled with lots of cavitations that may be caused by the localized plastic deformation of the epoxy accompanied by the interfacial debonding between the particles and surrounding matrix. As compared to the pure epoxy resin where smooth and featureless fracture surfaces were observed, these kinds of failure mechanisms may complicate the fracture process and dissipate more fracture energy for crack initiation, resulting in high fracture toughness [18]. It is noted that the similar failure mechanisms were also found in the hybrid systems when both silica nanoparticles and rubber particle were included in the epoxy.

Glass Fiber/Silica/Rubber/Epoxy Nanocomposites

In light of the forgoing that the mechanical properties of the nanocomposites, such as stiffness and fracture toughness, can be improved effectively by the inclusion of the silica nanoparticles together with the rubber particles, the improvement made by the particles should be effectively transferred into the fiber composites. In an attempt to validate the above inspiration, the unidirectional fiber composites with the modified epoxy as matrices were prepared, and the effect of the particles on the interlaminar fracture toughness of the fiber composites was evaluated from Mode I fracture tests.
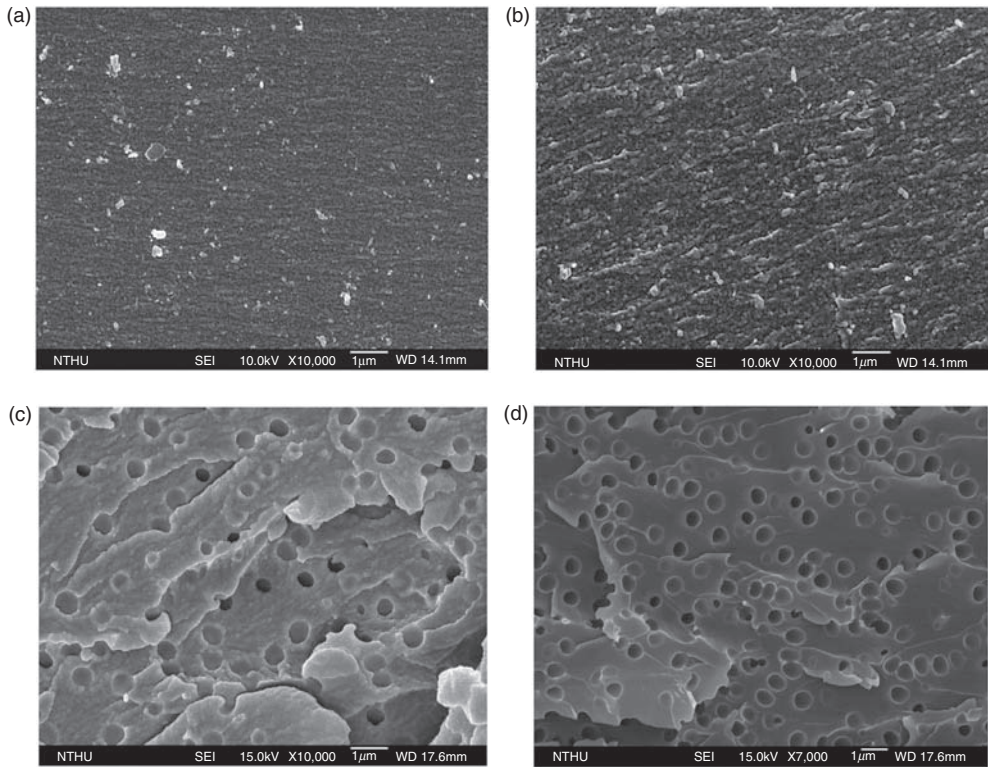
Figure 5. Fracture surface of the epoxy samples: (a) sample with neat epoxy, (b) sample with 10 wt% silica nanoparticles, (c) sample with 10 wt% CTBN particles, (d) samples with 10 wt% CSR particles.

MODE I INTERLAMINAR FRACTURE TOUGHNESS

Interlaminar fracture toughness was evaluated from the DCB specimens that were made of 12-ply unidirectional laminates with a porous film inserted in the midplane during the lay-up process for creating the initial crack. The dimensions of the DCB specimen are 230 mm long, 20 mm wide, and 3.3 mm thick as shown in Figure 6. Symmetric loadings applied in opposite directions were transferred into the cracked end of the specimens through a pair of hinges bonded on the specimen surfaces resulting in the Mode I crack extension. Prior to the fracture tests, the DCB specimens were pulled out such that the precrack can extend around 4 mm penetrating the resin-enriched area and reach the 'true' crack tip where the fracture toughness begin to be measured. During testing, the initial crosshead rate is 3 mm/min and then reduced to 0.5 mm/min before the onset of delamination extension. All specimen preparations and experimental procedures were performed based on ASTM standard D5528-01 [19]. The corresponding fracture toughness was calculated using the modified beam theory as [20] follows:

$$G_{IC} = \frac{3P\delta}{2B(a + \Delta)}, \tag{4}$$

where P is the load when cracks begin to propagate, and δ is the displacement associated with the load P; B is the width, and a is the initial crack length of the specimen. Figure 7 illustrates the typical load–displacement curves of the composites with 20 wt% silica
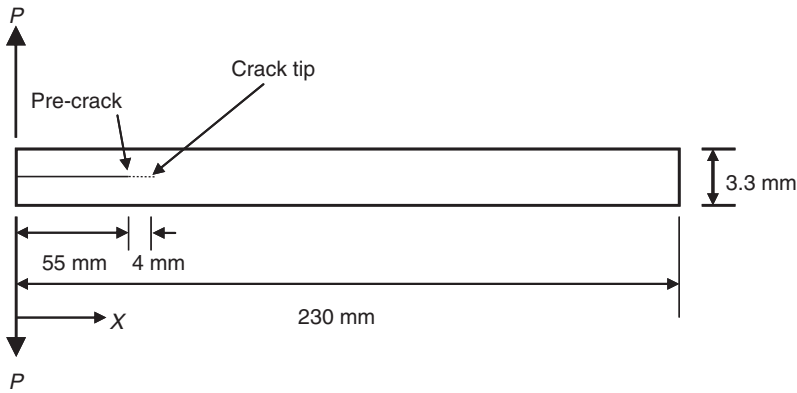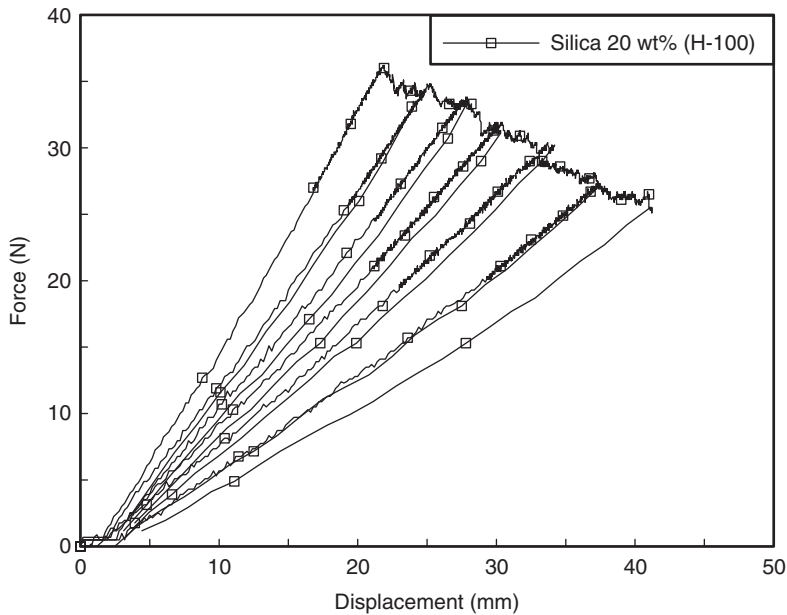
Figure 6. *Dimension of DCB specimens.*

Figure 7. *Typical load–displacement curves in the DCB tests.*

nanoparticles in the DCB tests. In the conventional beam theory, fracture toughness was calculated based on the assumption that the specimen is clamped at the delamination crack front. However, in reality, the DCB specimen is not a perfectly built-in cantilever, but it exhibits rotation and deformation around the crack tip. To compensate for the deformation and ration effect, the beam theory was modified with a slightly longer crack length $a + \Delta$, where Δ can be evaluated experimentally from the plot of the cube root of compliance with respect to the crack length as shown in Figure 8. The interlaminar Mode I fracture toughness of the fiber composites with various silica nanoparticles and rubber particles are illustrated in Table 4. It is shown that the interlaminar fracture toughness of the fiber composites increases consistently as the silica loading increases. Moreover, for the fiber composites with CTBN and silica nanoparticles, the fracture toughness is even higher
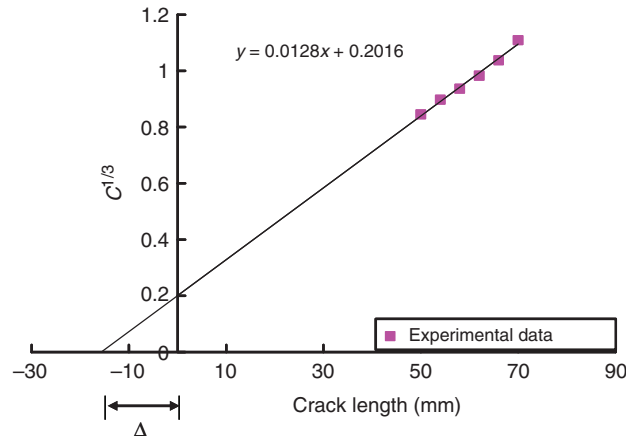
$$y = 0.0128x + 0.2016$$

Figure 8. *Determination of the parameter Δ in the modified beam theory.*

Table 4. Fracture toughness of fiber composites with various particle modifications.

Silica content (wt%)	Rubber content (wt%)	G_{IC} (kJ/m^2)	Increment (%)
0	0	0.83 ± 0.04	–
10	0	0.90 ± 0.02	8
20	0	0.95 ± 0.03	15
0	CTBN (10)	1.01 ± 0.03	22
10	CTBN (10)	1.23 ± 0.02	48
0	CSR (10)	1.66 ± 0.05	100
10	CSR (10)	1.51 ± 0.09	82

than that of the fiber composites, where only CTBN rubbers are contained. As a result, it is conceived that the silica nanoparticle has a constructive effect on the fracture toughness of the fiber composites with pure epoxy or CTBN-modified epoxy. On the contrary, the silica nanoparticle effect would become detrimental when the fiber composites are already modified by CSR rubber. The details will be discussed in the next section. SEM observations on the fracture surfaces of the fiber composites containing 20 wt% silica nanoparticles and those without any modifications are compared in Figure 9. Apparently, the enhancing mechanism because of the presence of the silica nanoparticles is the improved interfacial bonding between matrices and fiber as well as the induced plastic deformation (matrix yielding) in the matrix. The same observations were also addressed in the literatures [8,10]. When the CTBN rubber particle is added into the matrix, the dominant failure mechanism becomes the cavitations together with the local plastic deformation of the epoxy around the rubber particles [21] as shown in Figure 10. Because of the weak interfacial bonding between the fiber and CTBN-modified matrix [1], the fiber surfaces exhibited on the fracture plane are quite smooth, and thus, the interlaminar fracture toughness cannot be improved significantly. Furthermore, it was found that the addition of silica nanoparticles basically may not alter the fracture mechanisms of the CTBN-modified fiber composites. Figure 11 is the SEM micrographs of the fiber composites with CSR rubbers.
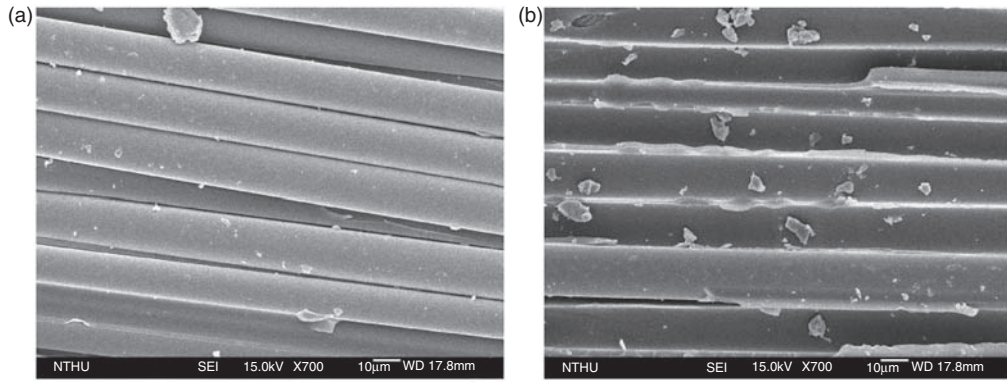
Figure 9. *SEM micrograph on the fracture surfaces of the samples: (a) pure epoxy matrix, (b) epoxy matrix containing 20 wt% silica particles.*
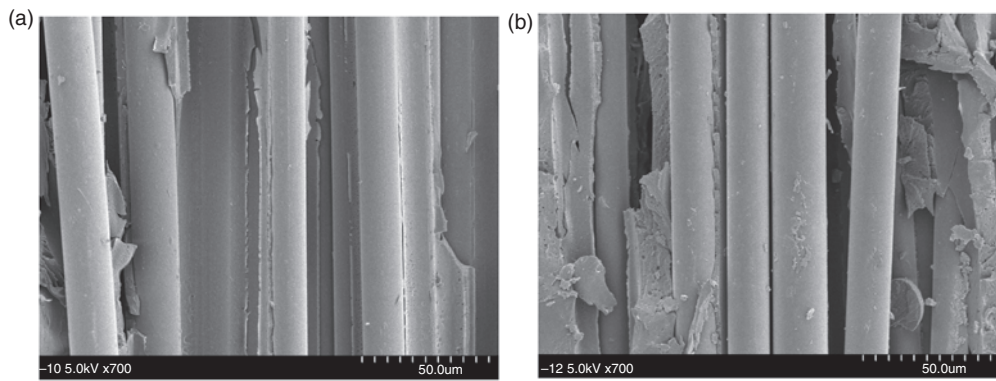

Figure 10. *SEM micrograph on the fracture surfaces of the samples: (a) epoxy matrix containing 10 wt% CTBN particle, (b) epoxy matrix containing 10 wt% silica particles and 10 wt% CTBN particle.*
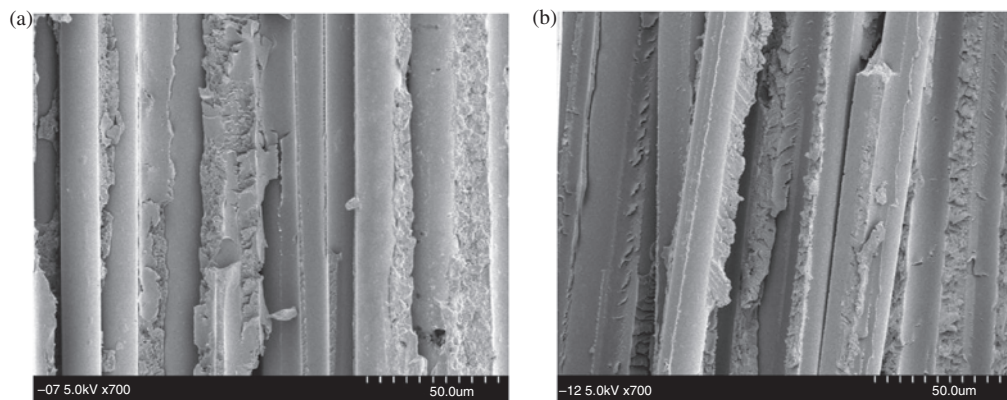

Figure 11. *SEM micrograph on the fracture surfaces of the samples: (a) epoxy matrix containing 10 wt% CSR particle, (b) epoxy matrix containing 10 wt% silica particles and 10 wt% CSR particle.*

In contrast to the CTBN-modified samples, the CSR-modified fiber composites demonstrate better bonding between the fiber and surrounding matrix. Moreover, the cavitations accompanied with the severe rough fracture surface on the matrices were believed to be the main toughening mechanism in the CSR-modified composites. As a result, the CSR-modified fiber composites exhibit better interlaminar fracture behaviors than the CTBN-modified samples. It is noted that this tendency is contrary to that presented in the literature [11].

DISCUSSIONS

To understand the effect of the silica nanoparticle on the bulk epoxy fracture toughness as well as the interlaminar fracture toughness of the fiber composites, the experimental data shown in Tables 3 and 4 was replotted in Figure 12. It is noted that in the figure, the solid symbols indicate the samples without silica nanoparticles, while the hollow symbols denote their counterparts' consisting of silica nanoparticles. The arrows in the figure represent the tendency of the fracture energy when silica nanoparticles were included. For the brittle epoxy system (diamond symbol), the G_{IC} value of fiber composites is greater than the bulk epoxy fracture toughness, and the addition of silica can efficiently enhance the epoxy toughness and the interlaminar toughness of composites as well. When the CTBN rubber was utilized to modify the epoxy, a significant toughening effect was found in the bulk epoxy (solid circle symbol); however, the incremental increase in the fiber composites is not so significant. Once the silica nanoparticles were introduced into CTBN-modified bulk epoxy, since the fracture energy of the modified epoxy is already $1.2 \, \text{kJ/m}^2$ (pretty ductile), the function of silica nanoparticles is destructive. On the other hand, for the CTBN-modified fiber composites, it was observed that the
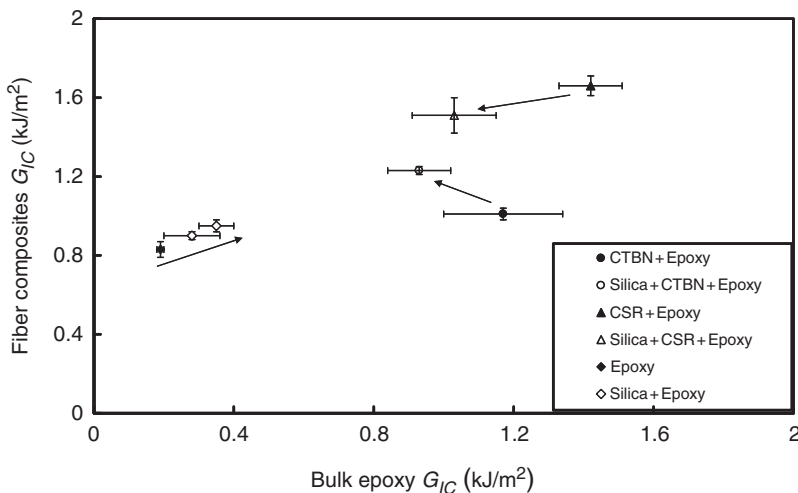

Figure 12. *Effect of silica nanoparticles on the epoxy fracture toughness and the interlaminar fracture toughness of fiber composites.*

silica nanoparticles still have a toughening effect on the interlaminar fracture toughness, although the fracture energy of the CTBN-modified fiber composites is around $1.0 \, \text{kJ/m}^2$. Finally, for the CSR-modified bulk epoxy and fiber composites, because the fracture energy is around 1.42 and $1.6 \, \text{kJ/m}^2$, respectively, the influence of the nanoparticle on the fracture properties becomes devastating. In light of the forgoing examinations, it is suggested that when the G_{IC} value of bulk epoxy is over $1.2 \, \text{kJ/m}^2$, the contribution of silica nanoparticles may not be constructive. Similarly, for the fiber composites with higher fracture energy (greater than $1.6 \, \text{kJ/m}^2$), the introduction of silica nanoparticles would reduce the corresponding fracture toughness. In addition, from Tables 3 and 4, it is shown that the *increment* of the fracture energy in bulk epoxy is always greater than that in fiber composites associated with the same amount of the particle modification. As a result, the translation of bulk epoxy toughness to the interlaminar fracture toughness of fiber composites is poor when the rubber particles and silica nanoparticles were included in the epoxy systems.

Furthermore, when comparing the mechanical properties of the fiber composites prepared based on different combinations of the particle modifications introduced in the study, the CTBN rubber in conjunction with the silica nanoparticles, which can achieve a 48% increment in the interlaminar fracture toughness with only a 2% reduction in Young's modulus of the matrix part is recommended as reinforcement in fiber composites. Although CSR particles can provide the better fracture toughness, the overall mechanical properties, such as strength and stiffness, are still inferior to those in the CTBN-modified system.

CONCLUSIONS

The tensile and fracture behaviors of the epoxy matrix modified by silica nanoparticles and rubber particles were investigated from the simple tension tests and the three-point tests, respectively. Results indicate that the reduction of Young's modulus in epoxy resin caused by the addition of CTBN and CSR rubbers can be moderated by the silica nanoparticles. Moreover, for the epoxy with combination of CTBN rubber and Silica nanoparticles, the Young's modulus is about 2.3% less than the pure epoxy resin. Both CSR and CTBN rubbers can dramatically enhance the fracture of the epoxy resin, while in such cases, the addition of silica nanoparticles may have detrimental effects on the fracture toughness.

The modified epoxy resin was then utilized as matrix to form glass fiber/epoxy composites, and the merging effect of the silica nanoparticle and rubber particles on the interlaminar fracture toughness was examined. Similar to the bulk epoxy, the fracture energy of the fiber composites can be improved by either CTBN or CSR rubber particles. However, for the hybrid epoxy matrix modified by CTBN and silica nanoparticles, the fracture energy of the fiber composites is higher than those containing only CTBN rubber particles. On the contrary, the CSR-modified epoxy matrix can provide higher fracture energy than the hybrid matrix with both CSR particles and silica nanoparticles. By considering the overall mechanical performances, the fiber composites modified with silica nanoparticles together with CTBN rubber particles demonstrate superior properties than other cases.

ACKNOWLEDGMENT

REFERENCES

1. Jang, J. and Yang, H. (2000). Toughness Improvement of Carbon-fiber/Polybenzoxazine Composites by Rubber Modification, *Composites Science and Technology*, **60**(3): 457–463.
2. Yee, A.F. and Pearson, R.A. (1986). Toughening Mechanisms in Elastomer-modified Epoxies, *Journal of Materials Science*, **21**: 2462–2474.
3. Xiao, K. and Ye, L. (2000). Rate-effect on Fracture Behavior of Core-Shell-Rubber (CSR)-modified Epoxies, *Polymer Engineering and Science*, **40**(1): 70–81.
4. Rosso, P., Ye, L., Friedrich, K. and Sprenger, S. (2006). A Toughened Epoxy Resin by Silica Nanoparticle Reinforcement, *Journal of Applied Polymer Science*, **100**(3): 1849–1855.
5. Chen, Q., Chasiotis, I., Chen, C. and Roy, A. (2008). Nanoscale and Effective Mechanical Behavior and Fracture of Silica Nanocomposites, *Composites Sciences and Technology*, **68**(15–16): 3137–3144.
6. Johnsen, B.B., Kinloch, A.J., Mohammed, R.D., Taylor, A.C. and Sprenger, S. (2007). Toughening Mechanisms of Nanoparticle-modified Epoxy Polymers, *Polymer*, **48**(2): 530–541.
7. Guo, Y. and Li, Y. (2007). Quasi-static/Dynamic Response of SiO_2–Epoxy Nanocomposites, *Materials Science and Engineering: A*, **458**(1–2): 330–335.
8. Chen, C., Justice, R.S., Schaefer, D.W. and Baur, J.W. (2008). Highly Dispersed Nanosilica-Epoxy Resin with Enhanced Mechanical Properties, *Polymer*, **49**: 3805–3815.
9. Zhao, Q. and Hoa, S.V. (2007). Effect of Stress Shielding on Strengthening of Particles-dispersed Polymer, *Journal of Composite Materials*, **41**(21): 2615–2624.
10. Zheng, Y., Ning, R. and Zheng, Y. (2005). Study of SiO2 Nanoparticles on the Improved Performance of Epoxy and Fiber Composites, *Journal of Reinforced Plastics and Composites*, **24**(3): 223–233.
11. Yan, C., Xiao, K., Ye, L. and Mai, Y.W. (2002). Numerical and Experimental Studies on the Fracture Behavior of Rubber-toughened Epoxy in Bulk Specimen and Laminated Composites, *Journal of Materials Science*, **37**(5): 921–927.
12. Kinloch, A.J., Mohammed, R.D., Taylor, A.C., Sprenger, S. and Egan, D. (2006). The Interlaminar Toughness of Carbon-fiber Reinforced Plastic Composites Using 'Hybrid-toughness' Matrices, *Journal of Materials Science*, **41**(15): 5043–5046.
13. Kinloch, A.J., Masania, K. and Taylor, A.C. (2008). The Fracture of Glass-fiber-reinforced Epoxy Composites Using Nanoparticle-modified Matrices, *Journal of Materials Science*, **43**(3): 1151–1154.
14. Hussain, F., Hojjati, M., Okamoto, M. and Gorga, R.E. (2006). Review Article: Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview, *Journal of Composite Materials*, **40**(17): 1511–1565.
15. Adebahr, T., Roscher, C. and Adam, J. (2001). Reinforcing Nanoparticles in Reactive Resins, *European Coatings Journal*, **4**: 144–149.
16. ASTM D5045-97. (1997). *Standard Test Methods for Plane-strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials: Annual Book of ASTM Standard*, ASTM, Philadelphia.
17. Anderson, T.L. (1995). *Fracture Mechanics: Fundamentals and Applications*, CRC Press, Boca Raton.
18. Tsai, J., Hsiao, H. and Cheng, Y. (2009). Investigating Mechanical Behaviors of Silica Nanoparticle Reinforced Composites, *Journal of Composite Materials* (in press).

19. ASTM D5528-01 (2001). *Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional Fiber-reinforced Polymer Matrix Composites: Annual Book of ASTM Standards*, ASTM, Philadelphia.
20. Hashemi, S., Kinloch, A.J. and Williams, J.G. (1989). Corrections Needed in Double-cantilever Beam Tests for Assessing the Interlaminar Failure of Fiber-composites, *Journal of Materials Science Letters*, **8**(2): 125–129.
21. Pearson, R.A. and Yee, A.F. (1991). Influence of Particle Size and Particle Size Distribution on Toughening Mechanisms in Rubber-modified Epoxies, *Journal of Materials Science*, **26**: 3828–3844.