

Improving Fracture Toughness of Glass/Epoxy Composites by Using Rubber Particles Together with Zirconium Toughened Alumina (ZTA) Nanoparticles.

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ABSTRACT

The research aims to investigate the interlaminar fracture toughness of glass fiber/epoxy composites, which consist of the ZTA nanoparticles and the rubber particles. 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 ZTA nanoparticles in conjunction with the rubber particles were introduced into the epoxy matrix to form a hybrid nano composite. 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 ZTA nanoparticles. Furthermore, the fracture tests conducted on the double cantilever beam specimens revealed that the inclusion of ZTA 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 ZTA nanoparticles, the improvement of the inter-laminar fracture toughness was around 48%. It is noted that the role of the ZTA nanoparticles on the fracture toughness of fiber composites with rubber-modified epoxy matrix is different. In contrast, for the CTBN-modified epoxy matrix, the ZTA nanoparticles can synchronously improve the fracture toughness of composites.

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 [1,2,3].

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 ZTA nano-particles into the rubber-modified epoxy resin to form a hybrid epoxy matrices by taking the advantage of the ZTA nanoparticle to improve the mechanical properties of the composites and compensate the stiffness reduction caused by the rubber as well. 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 ZTA Nanocomposites for tensile and fracture tests, indicating that the addition of 5 vol% ZTA 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 ZTA nanoparticle can increase the fracture toughness of epoxy resin up to 20%; however, this improvement is less significant at larger weight fraction.

When the ZTA -modified epoxy was adopted as matrices in the fabrication of fiber composites, the mechanical properties of the fiber composites were increased accordingly. 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 ZTA nanoparticles on the fracture behaviours 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 ZTA nanoparticles and rubber particles were investigated from the simple tension tests. Furthermore, the interlaminar fracture behaviours 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 ZTA nanoparticles and liquid rubbers were established [6,7,9].

Sample Preparations

Preparation of ZTA/Rubber/Epoxy Nanocomposites

To investigate the influence of ZTA 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. Through sol-gel processing, the synthesized ZTA 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 with the diameters of around 300-3400 nm, and the other is the CTBN with 18% acrylonitrile content provided by Emerald Performance Materials. When the ZTA/CSR/epoxy nano composite samples were prepared, a desired amount of Nanopox@F400 resin was diluted with DGEBA resin, depending on the required weight percentage of ZTA 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. Then the 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 mould with Teflon coating on its surfaces to form the nano composite specimens. In the study, 10, 20 wt% ZTA nanoparticle and 10 wt% CSR particles were incorporated, respectively, in the fabrication of the nano composites. Moreover, the hybrid nano composites containing 10 wt% ZTA nanoparticles and 10 wt% CSR particles were also prepared [12,13,14].

Materials Characterization

To understand the degree of exfoliation of the ZTA nanoparticle as well as the rubber particles in the epoxy resin, the hybrid nano composite samples were examined using a transmission electron microscope (TEM). Thin film samples of ZTA/CTBN/epoxy and ZTA/CSR/epoxy nano composites (about 80 nm thick) were cut from the specimens, respectively, using a Reichert-Jung Ultra cut microtome [16].

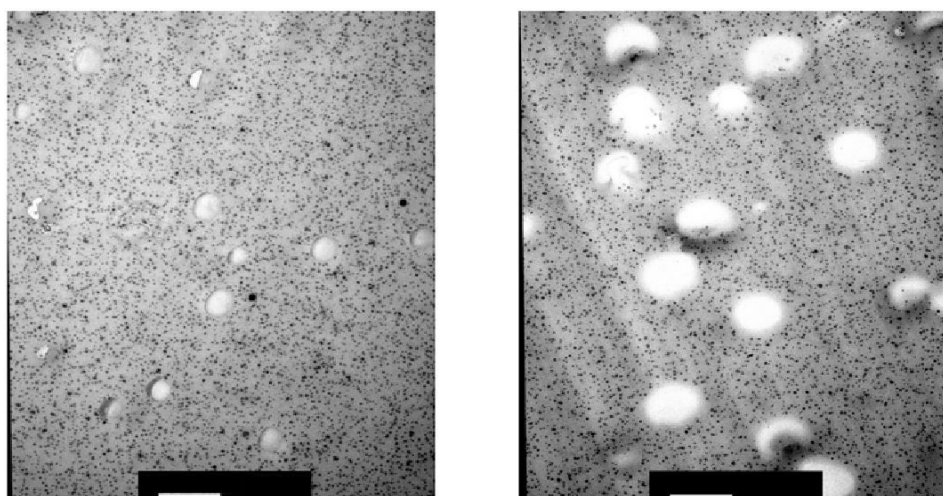


Figure 1: TEM micrographic of nano composites: (a) ZTA/CTBN nano composites, (b) ZTA/CSR nano composites.

The results with the magnification of 20 K were shown in Figure 1(a) and (b) for the two different hybrid systems, respectively. The diameters of the CTBN and CSR particles are measured as about 150-3250 nm and 300-3400 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 ZTA nanoparticles.

EXPERIMENTS

The effects of ZTA nanoparticles and rubber particles as well as their combining effects on the stress-strain curves of the epoxy nano composites 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.

Tensile Test

The nano composite coupon specimens containing 10 wt% and 20 wt% ZTA nanoparticles, 10 wt% CTBN particles, 10 wt% CSR particles, 10 wt% ZTA nanoparticles 310 wt% CTBN, and 10 wt% ZTA nanoparticles 310 wt% CSR particles was employed for the tensile tests. All tests were conducted on the hydraulic MTS machine at stroke-controlled mode. Figure 2 demonstrates the stress and strain curves for the epoxy, ZTA/epoxy, and ZTA/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 ZTA nanoparticle; however, the corresponding values decrease when only the rubber particles are included in the epoxy resin. From Table 1, it was found that such declining behaviour caused by rubber particles can be moderated by incorporating the ZTA nanoparticles into the epoxy system. The epoxy modified with CTBN and ZTA nanoparticles exhibit almost the same Young's modulus of the pure epoxy.

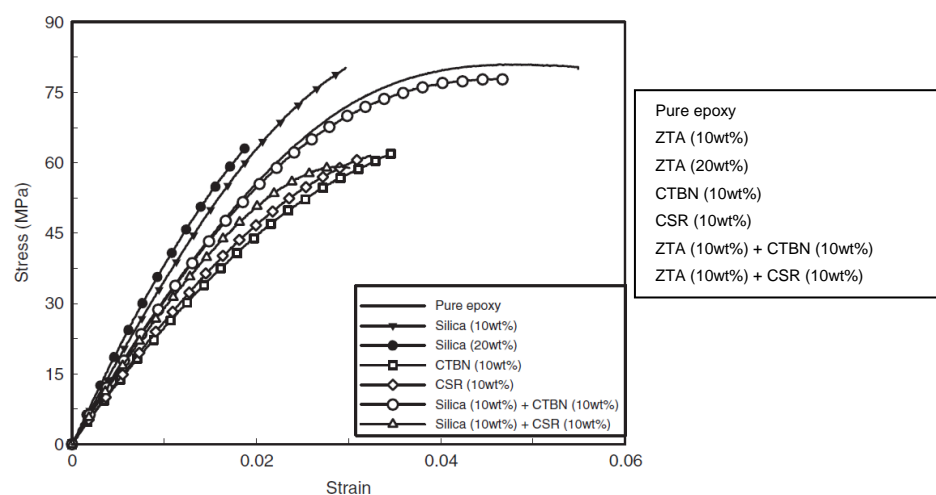


Figure 2: Stress vs strain curves of the epoxy specimens with different contents of ZTA nanoparticle and rubber particles.

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

Specimen	Young's modulus (GPa)	Increment (%)
Pure epoxy	3.25 _ 0.11	3
Epoxy + ZTA (10 wt%)	3.72 _ 0.11	14.5
Epoxy + ZTA (20 wt%)	3.93 _ 0.13	20.9
Epoxy + CTBN (10 wt%)	2.63 _ 0.02	-19.1
Epoxy + ZTA (10 wt%) + CTBN (10 wt%)	3.18 _ 0.05	-2.3
Epoxy + CSR (10 wt%)	2.73 _ 0.02	-16
Epoxy + ZTA (10 wt%) + CSR (10 wt%)	2.97 _ 0.05	-8.6

Mode I Fracture Test

From the tensile tests, results revealed that the nano composites containing both ZTA 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 ZTA 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.

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

Specimen	Tensile strength (MPa)	Increment (%)
Pure epoxy	79.74 _ 2.22	3
Epoxy + ZTA (10 wt%)	80.04 _ 7.92	0.4
Epoxy + ZTA (20 wt%)	57.65 _ 5.81	-29
Epoxy + CTBN (10 wt%)	64.43 _ 0.43	-19.2
Epoxy + ZTA (10 wt%) + CTBN (10 wt%)	76.85 _ 1.30	-03.6
Epoxy + CSR (10 wt%)	58.38 _ 2.74	-26.8
Epoxy + ZTA (10 wt%) + CSR (10 wt%)	59.01 _ 0.70	-26

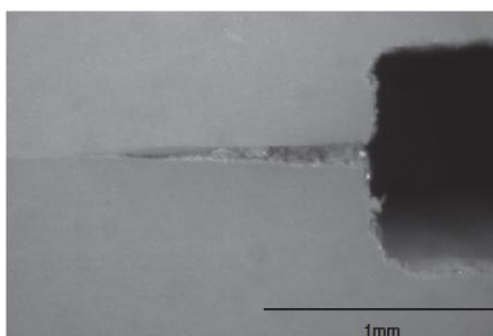


Figure 4. Sharp crack tip created by razor blade in the SENB specimens.

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]:

$$K_{IC} = \frac{P_I}{B\sqrt{W}} f(x)$$

$$f(x) = 6x^{0.5} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}}, \quad \longrightarrow \quad \boxed{1}$$

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 (1). 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:

$$G_{IC} = \frac{K_{IC}^2(1-\nu^2)}{E}, \quad \longrightarrow \quad \boxed{2}$$

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

Specimen	G _{IC} (kJ/m ²)	Increment (%)
Pure epoxy	0.19 _ 0.01	3
Epoxy + ZTA (10 wt%)	0.28 _ 0.08	47
Epoxy + ZTA (20 wt%)	0.35 _ 0.05	84
Epoxy + CTBN (10 wt%)	1.17 _ 0.17	516
Epoxy + ZTA (10 wt%) + CTBN (10 wt%)	0.93 _ 0.09	390
Epoxy + CSR (10 wt%)	1.42 _ 0.09	647
Epoxy + ZTA (10 wt%) + CSR (10 wt%)	1.03 _ 0.12	442

Where E is the Young's modulus and is obtained from Table 1, and m is the Poisson's ratio equalling to 0.34. Table 3 illustrates the variations of fracture energy of the nano-composites modified with various kinds of particles. 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 ZTA 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 ZTA nanoparticles, CTBN, and CSR rubber particles, respectively. 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].

Glass Fiber/ZTA/Rubber/Epoxy Nanocomposites

In light of the forgoing that the mechanical properties of the nano composites, such as stiffness and fracture toughness, can be improved effectively by the inclusion of the ZTA 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.

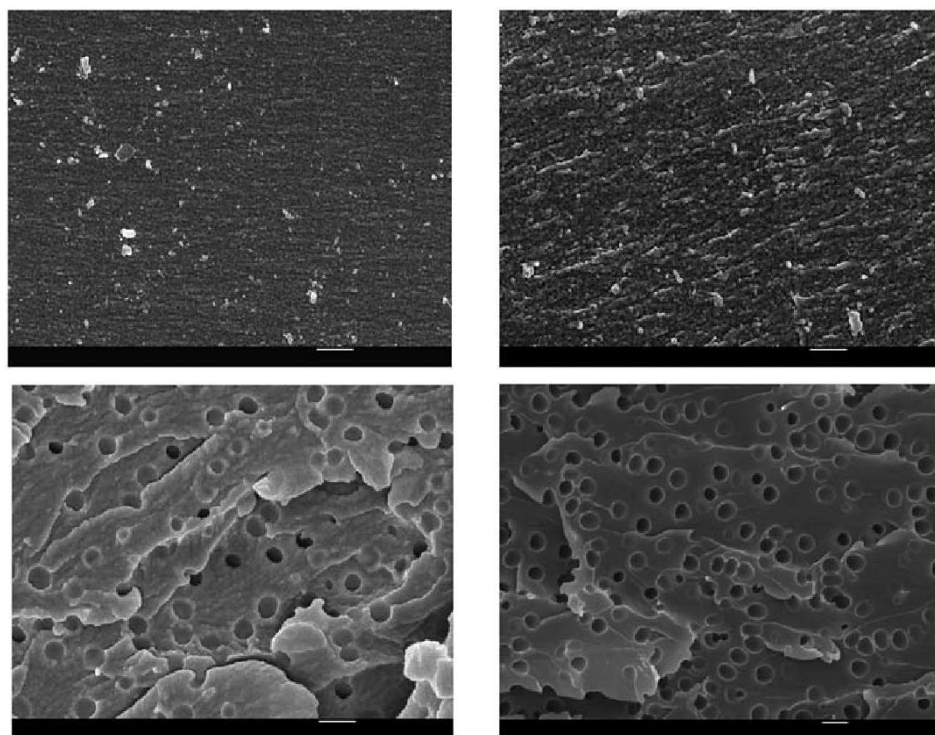


Figure 5. Fracture surface of the epoxy samples: (a) sample with neat epoxy, (b) sample with 10 wt% ZTA nanoparticles, (c) sample with 10 wt% CTBN particles, (d) samples with 10 wt% CSR particles

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

ZTA content (wt%)	Rubber content (wt%)	G _{ic} (kJ/m ²)	Increment (%)
0	0	0.83 _ 0.04	3
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

The same observations were also addressed in the literatures [8,10]. Because of the weak inter-facial 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 ZTA 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.

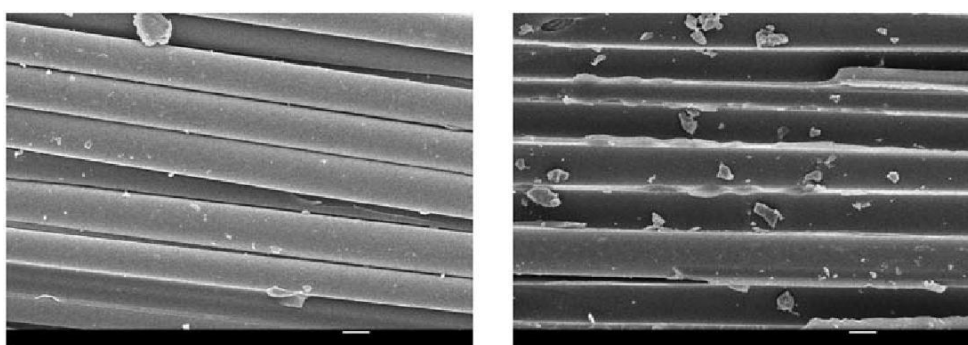


Figure 9. SEM micrograph on the fracture surfaces of the samples: (a) pure epoxy matrix, (b) epoxy matrix containing 20 wt% ZTA particles

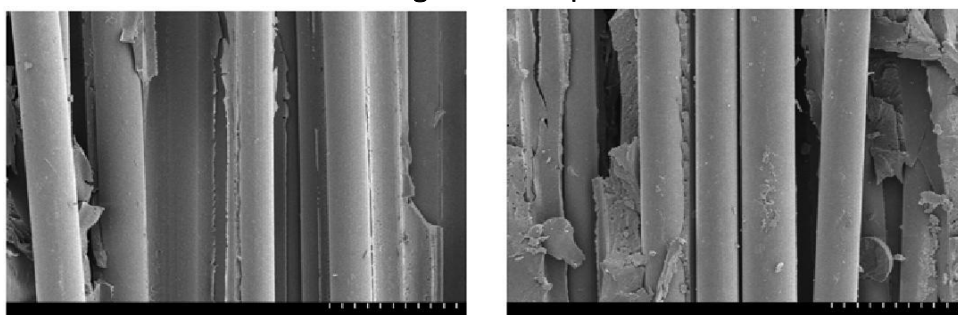


Figure 10. SEM micrograph on the fracture surfaces of the samples: (a) epoxy matrix containing 10 wt% CTBN particle, (b) epoxy matrix containing 10 wt% ZTA particles and 10 wt% CTBN particle.

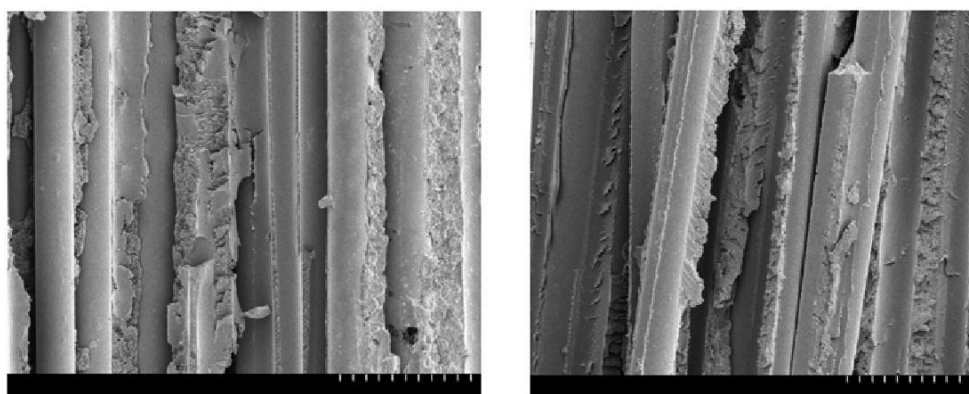


Figure 11. SEM micrograph on the fracture surfaces of the samples: (a) epoxy matrix containing 10 wt% CSR particle, (b) epoxy matrix containing 10 wt% ZTA particles and 10 wt% CSR particle.

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 ZTA 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 ZTA nanoparticles, while the hollow symbols denote their counterparts' consisting of ZTA nanoparticles. The arrows in the figure represent the tendency of the fracture energy when ZTA 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 ZTA 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 ZTA nanoparticles were introduced into CTBN-modified bulk epoxy, since the fracture energy of the modified epoxy is already 1.2 kJ/m^2 , the function of ZTA nanoparticles is destructive. On the other hand, for the CTBN-modified fiber composites, it was observed that the ZTA 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 kJ/m^2 . Finally, for the CSR-modified bulk epoxy and fiber composites, because the fracture energy is around 1.42 and 1.6 kJ/m^2 , respectively, the influence of the nanoparticle on the fracture properties becomes devastating [19,20,21].

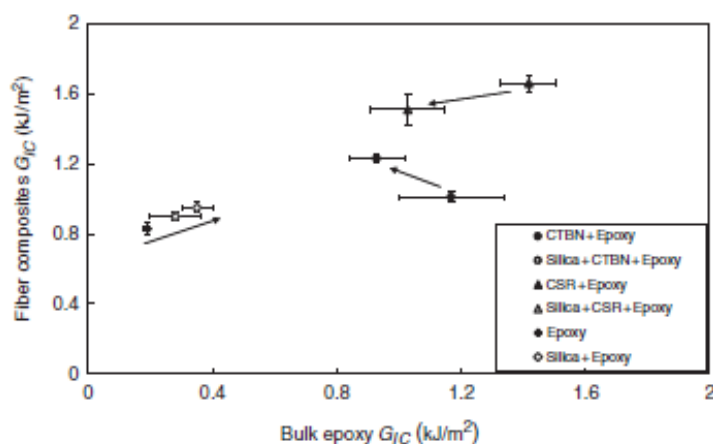


Figure 12. Effect of ZTA nanoparticles on the epoxy fracture toughness and the interlaminar fracture toughness of fiber composites.

In light of the forgoing examinations, it is suggested that when the G_{IC} value of bulk epoxy is over 1.2 kJ/m^2 , the contribution of ZTA nanoparticles may not be constructive. Similarly, for the fiber composites with higher fracture energy (greater than 1.6 kJ/m^2), the introduction of ZTA 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 ZTA 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 ZTA 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 ZTA 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 ZTA nano-particles. Moreover, for the epoxy with combination of CTBN rubber and ZTA nano-particles, 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 ZTA nanoparticles may have detrimental effects on the fracture toughness. The modified epoxy resin was then utilized as matrix to form glass fiber/epoxy compo-sites, and the merging effect of the ZTA 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 ZTA 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 ZTA nanoparticles. By considering the overall mechanical performances, the fiber composites modified with ZTA nanoparticles together with CTBN rubber particles demonstrate superior properties than other cases.

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