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Enhancing Fracture Toughness of Glass/Epoxy Composites for Wind Blades Using Silica Nanoparticles and Rubber Particles

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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 concurrently 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 DCB 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%.

Keywords: Fracture Toughness, Composites, Silica Nanoparticles, Double Cantilever Beam (DCB)

1. 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

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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 Tg compound, such as rubber, into the epoxy matrix (Jang and Yang 2000). Nevertheless, the drawback in doing so is the substantial reduction of the Young's modulus (Xiao and Ye 2000). 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 nano scales have recently been developed and then utilized as reinforcement in polymeric composites. Rosso et al. 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 (Rosso et al. 2006). The escalation behaviors yielded by the silica nanoparticles were also reported by Johnsen et al. (Johnsen et al. 2007). Guo and Li (Guo and Li 2007) 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.

2. SAMPLE PREPARATIONS

2.1. 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 (Adebahr et al. 2001). 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 reactive liquid rubber (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. The detailed procedure for fabricating the rubber/epoxy nanocomposites can be found elsewhere in the literature (Tsai et al. 2009).

2.2. 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 double cantilever beam (DCB) specimens, during the process, a porous film was inserted in the mid-plane of the laminates for the creation of pre-crack. 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.

3. 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.

3.1 Tensile test

The nanocomposite coupon specimens containing 10 wt% and 20 wt% silica nanoparticles, 10wt% CTBN particles, 10wt% CSR particles, 10wt% silica nanoparticles-10wt% CTBN, and 10wt% silica nanoparticles-10wt% CSR particles was employed for the tensile tests. All testes were conducted on the hydraulic MTS machine at stroke controlled mode. Experimental results indicated 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 (Xiao and Ye 2000). It was found that such 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.

3.2 Mode I fracture test of silica/rubber/epoxy nanocomposites

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 suggested based on ASTM D5045 (ASTM D5045-97 1997).

From the three point bending tests, the fracture toughness of SENB samples can be calculated using the following formulation (Anderson 1995):

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

where P_I indicates the peak load in the load and deflection curves, and x is a dimensionless value equal to the pre-crack 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 Eq. (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

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

where E is the Young's modulus and ν is the Poisson's ratio equaling to 0.34. Table 1 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.

Table 1: Fracture toughness of epoxy matrix with various particle modifications

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

3.3 Mode I interlaminar fracture toughness of glass fiber/silica/rubber/epoxy nanocomposites

Interlaminar fracture toughness was evaluated from the double cantilever beam (DCB) specimens that were made of 12-ply unidirectional laminates with a porous film inserted in the mid-plane 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. 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 pre-crack 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 (ASTM D5528-01 2001).

The interlaminar Mode I fracture toughness of the fiber composites with various silica nanoparticles and rubber particles are illustrated in Table 2. 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 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.

Table 2: 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	-
10	0	0.90	8
20	0	0.95	15
0	CTBN(10)	1.01	22
10	CTBN(10)	1.23	48
0	CSR(10)	1.66	100
10	CSR(10)	1.51	82

4. CONCLUSIONS

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.

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