Interlaminar Fracture Toughness and Fatigue Delamination Growth of CF/EP Composites with Matrices Modified by Nano-silica and CTBN rubber

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Abstract Experimental investigations were conducted to characterize mode I interlaminar fracture and fatigue delamination growth behaviors of carbon fiber-reinforced epoxy (CF/EP) laminates with modified epoxy matrices using nano-silica particles, a reactive CTBN liquid rubber and a hybrid of nano-silica particles and CTBN liquid rubber. The CF/EP composites were fabricated using unidirectional carbon fibre and a DGEBA epoxy by means of a vacuum resin infusion technique. The mode I interlaminar fracture toughness (G_{IC}) of the CF/EP laminates was increased significantly after the additives were incorporated in the matrices, especially for the laminates containing the hybrid particles of nano-silica and CTBN liquid rubber. Furthermore, nano-silica and CTBN liquid rubber were also found to effectively improve the fatigue performance of the CF/EP laminates by noticeably decreasing the fatigue crack propagation rates, particularly for the laminate with the matrices modified by the hybrid of nano-silica and CTBN liquid rubber. The results confirm that the enhancement in the fracture toughness due to the incorporation of the nanoparticles to the epoxy matrices has been partially transferred into the improvement of the interlaminar fracture resistance of the CF/EP composites, under both static and cyclic loadings.

Keywords Interlaminar fracture, fatigue delamination growth, nano-silica, CTBN liquid rubber

1. Introduction

Interlaminar fracture toughness and delamination growth resistance play a major role in determining long-term service life of carbon fibre-reinforced epoxy (CF/EP) composite structures. A large number of research efforts have been carried out to improve interlaminar properties of CF/EP composite laminates, including the use of toughened matrices, stitching, Z-pining, etc [1-7]. Toughened epoxy matrices can normally result in high interlaminar fracture toughness and delamination growth resistance [8-11]. Recently, nano-sized silica particles produced by a sol-gel process and CTBN liquid rubber have been reported to significantly increase the toughness of epoxies and also the mode I interlaminar fracture toughness for carbon fiber reinforced epoxy composites [12]. As a result of the unique combination of the additives, the hybrid epoxy matrices may also improve the interlaminar fatigue crack growth resistance of CF/EP composites.

The present paper presents the experimental results of a study in exploring the role of silica nano-particles and CTBN liquid rubber in the epoxy matrices of CF/EP composites. Mode I interlaminar fracture toughness and fatigue delamination growth rate are evaluated and possible mechanisms are discussed.

2. Experimental

2.1. Materials

A DGEBA epoxy (Araldite-F, Huntsman) was used for the study. Piperidine was used as hardener for curing the epoxy. The modifiers for the epoxy were a SiO_2 nano-particle dispersed epoxy (Nanopox XP, Nanoresins, Germany) and a CTBN liquid rubber (Hycar CTBN 1300X13). Nanopox

XP consists of surface-modified silica nano-particles (40 wt%) with an average particle size of 20nm. T300 unidirectional carbon fibre fabrics (FGI Fibre Glass International, Australia) were used.

2.2. Fabrication of CF/EP composites

The CF/EP composites were fabricated from the unidirectional carbon fibre fabric using a vacuum assisted resin infusion molding (VARIM) process. Neat epoxy and modified epoxies with 10 wt% silica nano-particles and/or 10 wt% rubber were premixed at 80^{o}C and later used in VARIM. Piperidine was added at a ratio of 5:100 (hardener/epoxy) in weight. The laminates consisted of 20 unidirectional carbon fiber layers. A polyimide thin film (50 μm in thickness and 120 mm in length) was inserted between the 10th and 11th layers at one end of the laminate, to serve as a “pre-crack” for the interlaminar fracture tests. Two loading blocks of 20 mm in width were bonded to up and bottom sides of one end of the specimen for load applying.

2.3. Mechanical tests

Double cantilever beam (DCB) specimens (dimensions of 20 mm in width, 240 mm in length, 4 mm in thickness and 50 mm in initial “pre-crack” length) were prepared for the interlaminar fracture tests of the laminates under static and fatigue loadings. For static testing on an Instron 5567 universal testing machine, a displacement rate of 1 mm/min was used. Mode I interlaminar fracture toughness (G_{IC}) of unidirectional CF/EP composites was determined by the Modified Beam Theory (MBT) Method, according to ASTM D5528,

$$G_{IC} = \frac{3P\delta}{2b(a+|\Delta|)} \tag{1}$$

Where b is the specimen width, P is the applied load, δ is the displacement of the load-point and $|\Delta|$ is the modification of actually measured crack length a. Two values of G_{IC} were defined, namely G_{IC} (init.), at the point when the delamination was observed visually to propagate from the pre-crack tip, and G_{IC} (prop.), the plateau value of the resistance curve (R-curve).

The fatigue tests were carried out on an MTS-810 servo-hydraulic machine in reference to ASTM D6115 to measure the interlaminar delamination growth rate. During fatigue testing, the displacement ratio (R) of the minimum to the maximum displacements was kept constant (R = 0.1), and a cyclic frequency of 1 Hz was adopted. At least 3 specimens were tested for each group starting from the maximum cyclic strain energy release rate at the peak of displacement cycle being 60% of mode I interlaminar fracture toughness measured from quasi-static tests of the corresponding CF/EP laminates. The maximum cyclic strain energy release rate can be calculated from:

$$G_{\mathrm{I}max} = \frac{3P_{\max}\delta_{\max}}{2b\left(a+|\Delta|_{av}\right)} \tag{2}$$

Where $P_{\max}$ is the maximum cyclic load, $\delta_{\max}$ is the maximum value of cyclic displacement, $|\Delta|_{av}$ is the average value of $|\Delta|$ from static tests. The crack length was determined by visual observation during the crack propagation. The corresponding number, N, of fatigue cycles required to generate delamination growth in the CF/EP laminates were recorded during the fatigue tests, thus allowing the crack growth rate, da/dN, to be calculated.

3. Results and discussion

3.1. Interlaminar fracture toughness

Typical curves of mode I interlaminar growth resistance as a function of crack length (R-curves) under static loading are shown in Figure 1 for CF/EP laminates with unmodified and modified matrices. The corresponding mode I interlaminar fracture properties are shown in Table 1. It can be seen that both G_{IC} (init.) and G_{IC} (prop.) increased after the epoxy matrix was modified. The presence of 10 wt% nano-silica particles or 10 wt% CTBN rubber, showed a significant effect on the interlaminar fracture toughness, leading to increases in both G_{IC}(init.) and G_{IC}(prop.). The combined use of the nano-silica particles and the CTBN rubber with the epoxy, to form a “hybrid” epoxy matrix, gives a further enhancement to the fracture toughness, with the maximum values of 649 J/m^2 for G_{IC} (init.) and 1323 J/m^2 for G_{IC} (prop.) being recorded.

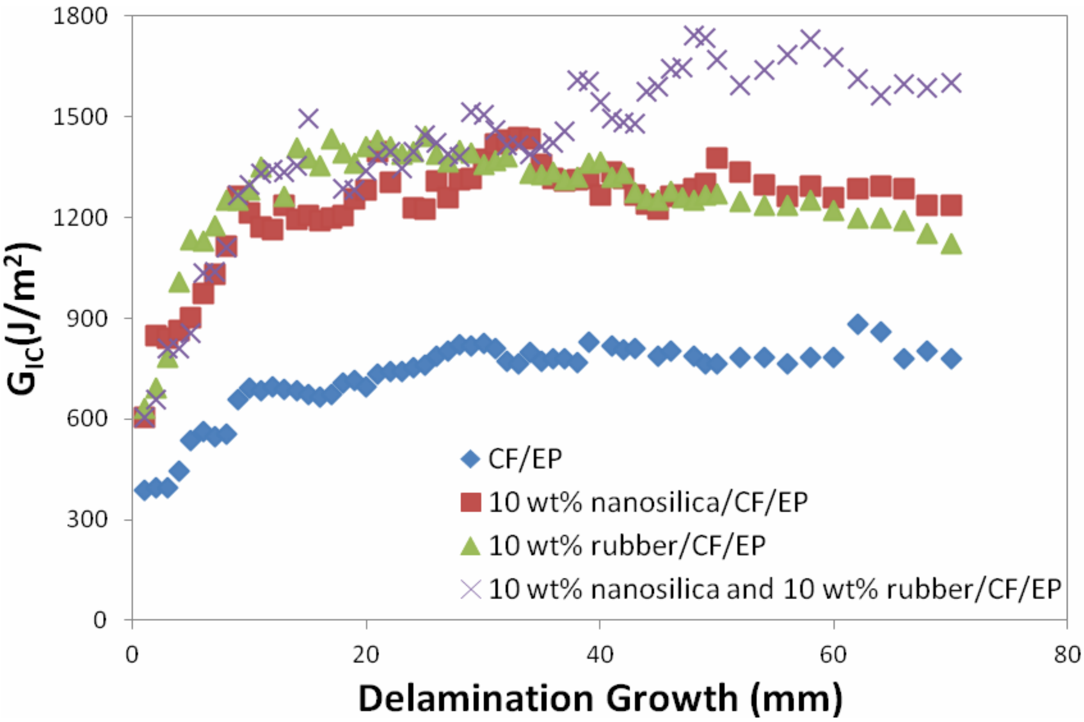

Figure 1 Typical R-curves for mode I interlaminar fracture of CF/EP laminates

Table 1. Mode I interlaminar fracture properties of CF/EP laminates

Laminates	G_{IC} (init.)[J/m^2]	G_{IC}(prop.)[J/m^2]
CF/EP	389±20	741±70
10 wt% nano-silica/CF/EP	602±4	1130±93
10 wt% rubber/CF/EP	629±31	1256±37
10 wt% nano-silica and 10 wt% rubber/CF/EP	649±112	1323±101

3.2. Fatigue delamination resistance

The crack growth rate (da/dN) versus delamination length curves are shown in Figure 2 for CF/EP laminates with unmodified and modified matrices. The results show that the fatigue delamination resistance in composite laminates with the matrix modified by nano-silica, CTBN rubber and the hybrid of these additives was greatly improved. Generally, the rate of delamination propagation was initially high and then decreased as the delamination growth because of reduced strain energy release rate under the constant peak displacement. In particular, the CF/EP composite laminate with the matrix modified by the hybrid of 10wt% nano-silica and 10 wt% rubber have the slowest delamination growth rate, being about almost two orders lower than that of the laminates with the neat epoxy at the early stage of delamination growth.

As shown in Figure 3, the da/dN-G_{Imax} curve characterized the relationship between delamination growth rates and the maximum delamination energy (G_{Imax}) used for different group of CF/EP laminate specimens. It can be seen that the plots for the four groups of CF/EP laminates show the same trend, i.e., a high growth rate corresponds to a high G_{Imax}. Furthermore, it requires higher G_{Imax} for the same delamination growth rate for the CF/EP laminates with modified matrices. Particularly, the CF/EP laminate with the matrix modified by the hybrid of 10 wt% nano-silica and 10 wt% rubber, requires the highest G_{Imax} for the same delamination growth rate, compared with other three groups of CF/EP laminates without modification, with 10 wt% nano-silica or 10 wt% rubber, respectively.

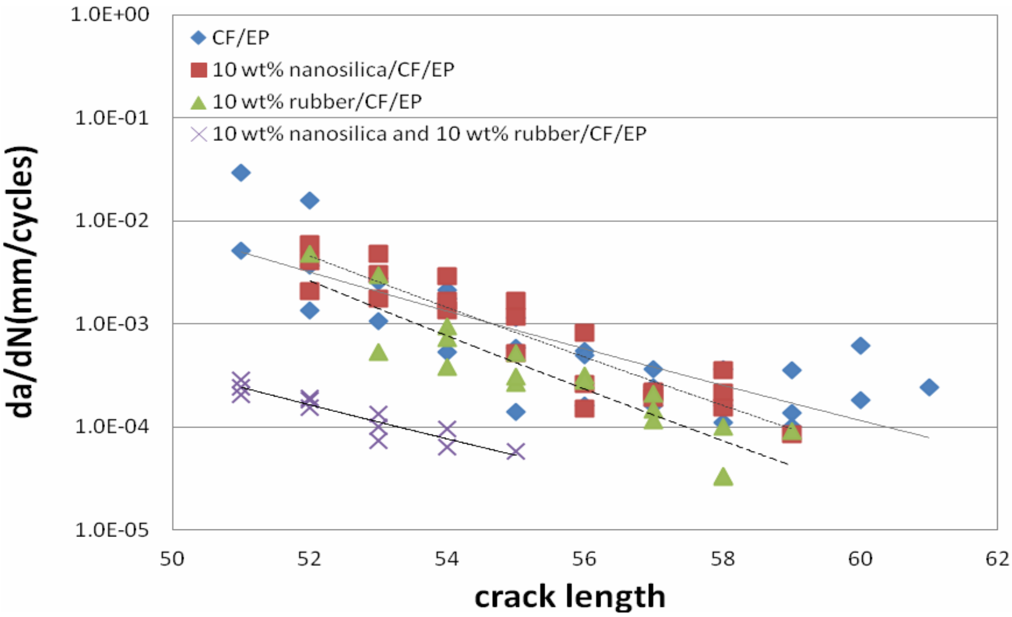

Figure 2 Propagation rate versus delamination length under cyclic fatigue for the CF/EP laminates

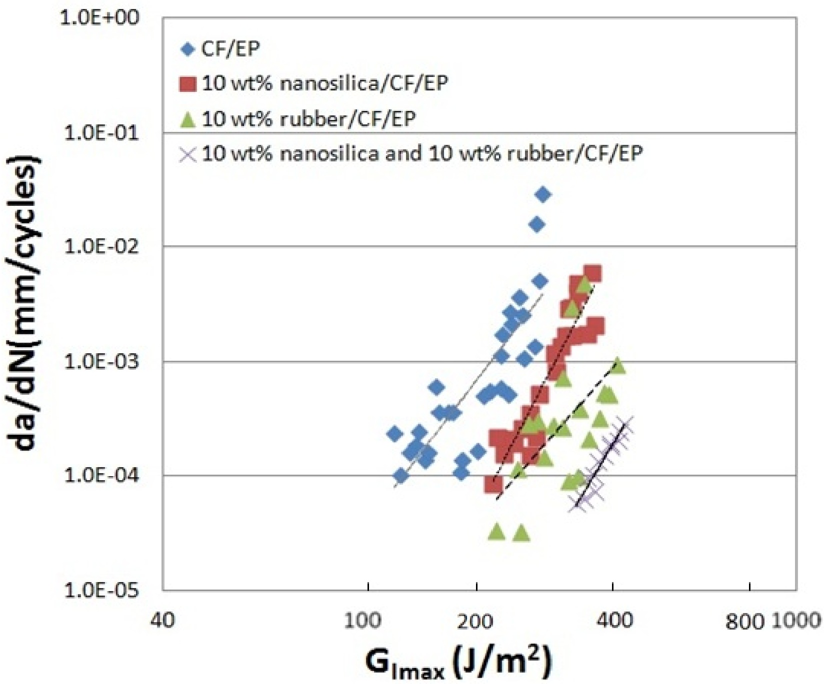

Figure 3 Propagation rate versus G_{Imax} under cyclic fatigue for the CF/EP laminates

SEM photographs in Figure 4 show the morphology of fracture surfaces in the initial region of crack growth for the fatigue delamination growth in CF/EP laminates. For the neat epoxy laminate, in Figure 4 (a), exposed fibres can be seen being completely stripped of matrix resin, indicating an interfacial failure in the unmodified CF/EP laminate. However, more matrix resin remains on the exposed fibre surfaces in the 10 wt% nano-silica modified CF/EP laminate, in Figure 4 (b), showing better adhesion at fibre-matrix interface. The same phenomenon were also reported by Tang et al [9], who investigated mode I and II interlaminar fracture toughness in CF/EP laminated modified with nano-silica particles under static loading. The increasing fatigue delamination resistance for 10 wt % nano-silica CF/EP laminates can be attributed to the toughening mechanisms in the matrix induced by nano-silica ahead of delamination tip. It was observed that the plastic void growth around the nano-silica particles makes a contribution to the fracture energy of the epoxy modified by nano-silica during the delamination propagation, reported by Hsieh et al [12]. Enhanced plastic deformation can also be observed for the matrix modified with 10 wt% rubber, as shown in Figure 4(c), indicating shear flow of the matrix resin due to the increased ductility. The hybrid matrix containing both 10 wt% nano-silica and 10 wt% rubber presented a rougher matrix surface that may be resulted from a synergistic effect of plastic void growth and shear yielding mechanisms, which correlates well with the highest delamination growth resistance under both static and cyclic loading.

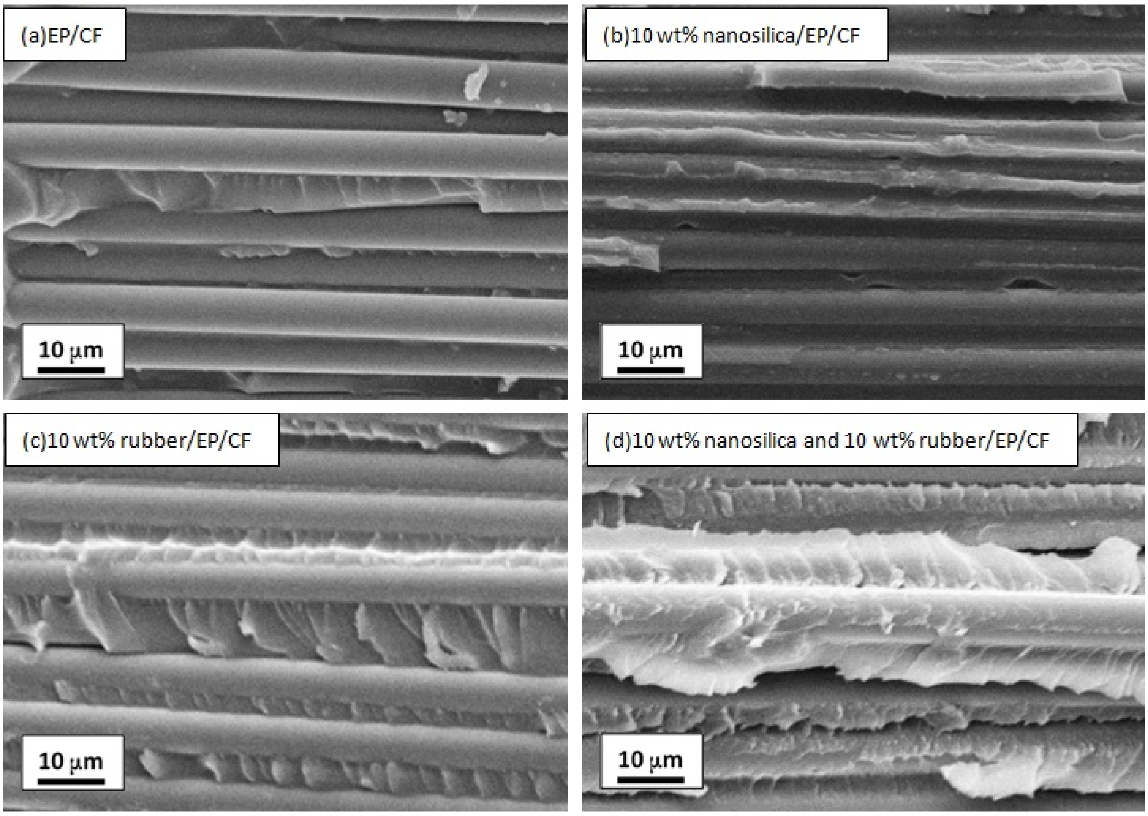

Figure 4 SEM photographs of fracture surfaces for fatigue tested CF/EP laminates

4. Conclusions

(1) The mode I interlaminar fracture toughness of CF/EP laminates under static loading was significantly improved after the epoxy matrix was modified with 10 wt% nano-silica particles or 10 wt% CTBN rubber. In particular, for the CF/EP laminate with the matrix modified by the hybrid of 10 wt% nano-silica and 10 wt% rubber, the interlaminar fracture toughness was further improved.

(2) The fatigue delamination growth resistance of the CF/EP laminates was also improved after the matrix was modified by nano-silica and/or CTBN rubber. It was observed that the CF/EP laminate with the matrix modified by the hybrid of 10 wt% nano-silica and 10 wt% rubber achieved the highest resistance to fatigue delamination growth, attributed to the synergistic contribution of toughening mechanisms induced by nano-silica particles and CTBN rubber, respectively.

References

[1] Y. Zeng, H.Y. Liu, Y.W. Mai, X.S. Du, Improving interlaminar fracture toughness of carbon fibre/epoxy laminates by incorporation of nano-particles. Compos Part B-Eng, 43 (2012) 90-94.

[2] K.A. Dransfield, L.K.Jain, Y.W. Mai, On the effect of stitching in CFRPs-I. Mode I delamination toughness. Compos Sci Technol, 58(1998) 815-827.

[3] Q. An, A.N. Rider, E.T. Thostenson, Electrophoretic deposition of carbon nanotubes onto carbon-fiber fabric for production of carbon/epoxy composites with improved mechanical properties, Carbon, 50 (2012) 4130-4143.

[4] N. Ghafari-Namini, H. Ghasemnejad, Effect of natural stitched composites on the crashworthiness of box structures, Mater Design, 39 (2012) 484-494.

[5] F. Mujika, G. Vargas, J. Ibarretxe, J.D. Gracia, A. Arrese, Influence of the modification with MWCNT on the interlaminar fracture properties of long carbon fiber composites, Compos Part B-Eng, 43(2012) 1336-1340.
[6] P. Robinson, S. Das, Mode I DCB testing of composite laminates reinforced with z-direction pins: a simple model for the investigation of data reduction strategies. Eng Fract Mech, 71 (2004) 345-364.
[7] A.P. Mouritz, P. Chang and M.D. Isa, Composites: aerospace structural design comsiderations, J Aerosp Eng, 24 (2011) 425-432.
[8] Y. Ye, H. Chen, J. Wu, C.M. Chan, Interlaminar properties of carbon fiber composites with halloysite nanotube-toughened epoxy matrix, Compos Sci Technol, 71(2011) 717-723.
[9] Y. Tang, L. Ye, D. Zhang, S. Deng, Characterization of transverse tensile, interlaminar shear and interlaminate fracture in CF/EP laminates with 10 wt% and 20 wt% silica nanoparticles in matrix resins, Compos Part A-Appl S, 42(2011) 1942-1950.
[10] D. Zhang, L. Ye, S. Deng, J. Zhang, Y. Tang, Y. Chen, CF/EP composite laminates with carbon black and copper chloride for improved electrical conductivity and interlaminar fracture toughness, Compos Sci Technol, 72 (2012) 412-420.
[11] N. Hu, Y. Li, T. Nakamura, T. Katsumata, T. Koshikawa, M. Arai, Reinforcement effects of MWCNT and VGCF in bulk composites and interlayer of CFRP laminates, Compos Part B-Eng, 43 (2012) 3-9.
[12] T.H. Hsieh, A.J. Kinloch, K. Masania, J.S. Lee, A.C. Taylor, S. Sprenger, The toughness of epoxy polymers and fibre composite modified with rubber microparticles and silica nanoparticles, J Mater Sci, 45 (2010) 1193-1210.