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A study of mixed mode interlaminar fracture on nanoclay enhanced epoxy/glass fiber composites

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Abstract

Fiber reinforced laminate are widely used in aerospace, automobile and marine industries, despite its poor interlaminar fracture toughness (IFT), as consequence of the absence of fibers to sustain transverse load. One way recently explored with relative success in order to improve IFT is the use of nanoparticles to reinforce the matrix. Present paper intends to assess and discuss the fracture toughness on mixed mode loading of fiber glass mats/nanoclay enhanced epoxy matrix laminates. The matrix used was the epoxy resin Biresin® CR120 combined with the hardener CH120-3, the fiber glass was triaxial mats ETXT 450 and the nanoparticles were montmorillonite nanoclay (NC). The results were discussed in order to understand the effects of the percentage of nanoclay and the shear load quantified in terms of the G_{II}/G_I ratio on the total fracture toughness G. The incorporation of a small quantity of NC into matrices improves significantly mixed-mode IFT for all loading mode ratios G_{II}/G. The total fracture toughness G increases with the mode II loading component and a linear mixed-mode fracture criteria reproduces the G_c against G_{II}/G relationship.

Keywords: composite materials; nanoparticles; mixed mode; interlaminar fracture toughness

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1. Introduction

The interlaminar damage mechanism leads to the most severe type of defect since it may significantly reduce both stiffness and strength of composite materials. Crack propagation under pure mode I (opening mode) and pure mode II (shearing mode) loading has been extensively studied in the literature, but more attention must be paid to mixed mode I/II loading because it relates to most realistic situations. The Mixed-mode bending (MMB) test developed by Reeder and Crews [1] has been used for mixed-mode I/II fracture characterization of composite laminates [2, 3]. The different loading positions determine the various mixed-mode delamination ratios. The MMB test presents some advantages, including the possibility of working with a wide range of mixed-mode ratios with the same specimen geometry. The G_{II}/G, mode ratio was also found to be independent of the crack length.

The addition of nanofillers into matrix has been recently explored by many researchers to improve critical IFT, with promising outcomes. One particular area of innovation is to introduce nanoparticles nanoclay (NC) or carbon nanotubes (CNT´s)) into composite laminates to enhance their resin-dominated mechanical properties so that their delamination resistance can be substantially improved. Smectite clay minerals, especially montmorillonite (MMT), are potential candidates for platelet-type filler for

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molecular composites, since they are composed of several layers of silicates. These silicates are 1 nm thick and have a cross-sectional area of 100 nm^2, which is very small compared to conventional fillers. MMT is the most common and ubiquitous clay mineral, and it is well known that it undergoes intercalation and swelling in the presence of water. CNT´s have a nominal diameter between 2 and 100 nm and a length between tens and hundreds of a micron, depending on their manufacturing techniques and their surface functional coatings. These dimensions typically result in aspect ratio of at least two orders of magnitude.

The outcomes obtained when using NC and CNT´s in epoxy resin have also produced opposite results. Mohd Zulfli et al. [4] studied the performance of glass fiber reinforced epoxy composites containing various loadings of organo-montmorillonite (OMMT) using hand-lay-up technique. They obtained significant improvement in flexural properties in composites with OMMT content up to 4 wt%. In contrast, Kinloch et al. [5] reported that the IFT of the epoxy/clay nanocomposites is lower than that of microcomposites. This may be due to the poor clay dispersion for high concentrations, which results in the formation of big clusters of clay that reduce the plastic deformation of polymer matrix.

Marino Quaresimin et al. [6] evaluated the benefits deriving from the matrix nanomodification of composite laminates made by vacuum infusion of woven glass fabrics. The results of these authors indicate a significant improvement in the IFT and crack propagation threshold of clay-modified epoxy. Dispersion and orientation in matrices also have important role in modifying mechanical properties, particularly IFT. Kim et al. [7] reported that increasing dispersion time, the matrix becomes more viscous, difficult impregnation of the woven and the capacity of the polymer to fill the spaces between the fibers. Literature results suggest that distributing the nanoparticles into resin between layers, preferentially orientated in thickness direction, may improve the IFT of fiber reinforced laminated composites. This benefit effect was shown by Fan et al [8] in glass/epoxy composites filled with a small quantity of preferentially orientated oxidized multi-walled carbon nanotubes manufactured by a double vacuum assisted resin transfer molding method. Wicks et al. [9] evaluated the effects related to the deposition of aligned CNT´s on the surface of the fibers on the mechanical properties of composites. These authors reported an IFT increase of 76% for composites modified with aligned CNT´s. Wichmann et al. [10] also reported about 16% improvement in interlaminar shear strength while the interlaminar fracture toughness G_{Ic} and G_{IIc} was not affected. They concluded that these results were a consequence of the introduction of 0.3 wt% of CNT´s oriented in z-direction glass fiber/epoxy composites.

The goal of this current investigation is to evaluate the influence, of the incorporation of small quantities of nanoclay on IFT of glass/epoxy laminates under mixed-mode I/II loading conditions. Experimental results were compared with predictions of delamination fracture under combined loading based on literature models. The linear criterion [11] states that G_I and G_{II} normalized by G_{IC} and G_{IIC} are fitted by Eq. (1):

$$\left(\frac{G_I}{G_{IC}}\right)+\left(\frac{G_{II}}{G_{IIC}}\right)=1 \qquad (1)$$

2. Materials and experimental procedure

The laminate composite were manufactured using Biresin®CR120 as matrix, formulated by bisphenol A - (epichlorhydrin) epoxy resin 1,4 - bis (2,3-epoxypropoxy) butane, combined with the hardener CH120-3, both supplied by Sika, Stuttgart, Germany. This system has high mechanical properties, excellent adhesion and chemical resistance. The mixed viscosity a 25 ºC of epoxy and curing agent used was 240 mPas. The mixing ratio of epoxy to curing agent used was 10:3 by weight, as recommended by the manufacturer.

The matrix was nano-enhanced using organo-montmorillonite, Nanomer I.30E, an octadecyl ammonium ion modified montmorillonite with a density of 1.71 g/cm^3, supplied from Nanocor, Inc. Hoffman Estates, Illinois, USA. Nanomer I.30E nanoclay is reported to have 70-75 wt% montmorillonite and 25-30 wt% octadecyl ammonium. An average clay length 9.5 µm was measured by granulometric laser scattering analysis using a Malvern Mastersizer 2000 equipment.

The glass fiber/epoxy/nanoparticles composites were processed using 10 layers of fiber glass multiaxial woven ETXT 450, with fiber orientation 0º/+/45º/-45º of weight 450 g/m^2, supplied by Saapi, Milan, Italy. The process consists in the preparation of nanoparticles/epoxy suspensions and the impregnation of the suspension into fiber preforms. The nanoparticles were dispersed in the epoxy matrix using a high shear mixing process. The mixing of resin with the desired amount of nanoclay was carried at

average rate of about 8000 rpm for 1 h using shear blender. Then, it was degassed under vacuum for 15 minutes and afterwards, the hardener agent was added.
Composites were manufactured using vacuum bagging process (Fig. 1) with three different matrix formulations as indicated in Table 1. Fibers and modified resin were hand placed in a mold with all the fibers layers oriented in the same direction and subjected to a compression of about 0.1 MPa. Fiber glass layer and resin were applied alternately, while ensuring the complete impregnation of the fibers. The mold was put into a vacuum bag with four vacuum connectors placed properly in order to obtain a good quality of hybrid composites. To obtain good mold release of the molded plates, a film was used that promoted separation between the plate surface and the molding. The composite was cured at room temperature for 8 hours. A post cure process was carried out as follows: 55 ºC for 16 hours, 75 ºC for 3 hours and finally 120 ºC for 12 hours.

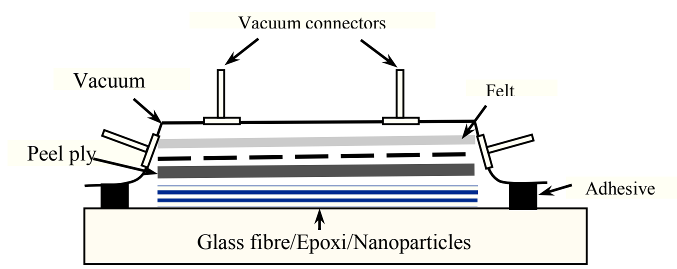

Fig. 1. Schematic view of the vacuum in mould curing process.

Table 1. Formulation of composite matrix

Reference	Epoxy (wt %)	Nanoclay (wt %)
GF/E	100	-
GF/ENC1	99	1
GF/ENC3	97	3

The delamination was simulated with a 10 μm thick Teflon layer placed at half thickness of the sample. The resulting plates were 300 mm long, 100 mm wide and 4 ± 0.1 mm thick. The final thickness of the composites shows a small change over the specimen in the order of 0.1 mm. The inclusion of nanoparticles causes an increase in viscosity of the mixture resulting in a small increase in the thickness of the inter-fiber and thus the total thickness of the laminate. This increase is however relatively small, being the maximum (about of 0.3 mm) obtained in the laminated with 3 wt% nanoclay.
Some samples were observed using Transmission Electron Microscopy (TEM) in order to analyses the dispersion of the nanoparticles into the matrix. Morphological analyses were performed in an Ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company, using a Scanning Transmission Electron Microscopy (STEM) detector and an acceleration voltage between 15 and 18.4 kV to obtain the micrographs.

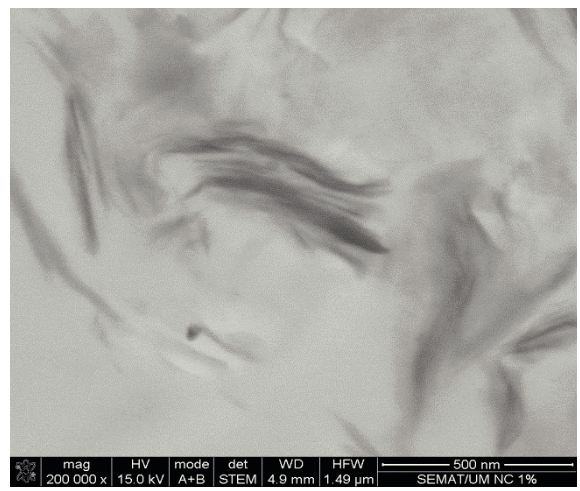

Fig. 2. TEM observation of morphology for nano-enhanced matrix.

Fig. 2 shows one of these observations for 1 wt% nanoclay nano-enhanced resin. The image shows that a good intercalation and partial exfoliation have been achieved for the nanoclay.
Mixed mode interlaminar fracture toughness was carried out for different ratios of mode I and mode II using a mixed-mode bending (MMB) apparatus. The specimens were machined from plates, nominally 300 mm long, 100 mm wide and 4 ± 0.1 mm thick. The geometry and dimensions of specimens are indicated in Fig. 3 a).
The tests were performed using a Shimadzu SLBL-5kN test machine provided by Shimadzu Corporation, Kyoto, Japan. Load and axial displacement were monitored directly from the machine software. The delamination length was also monitored along the tests using a video image camera system. Tests and specimens were conducted according ASTM D 6671 [12]. The interlaminar fracture toughness for different

ratios of mode I and mode II was evaluated using the special device built specifically for the current work as shows Fig. 3a). The ratio of the modes can be altered by changing the distance c to the load application point. The tests were performed for values of c of 137 mm, 67 mm and 47mm, which correspond to mode ratios G_{II}/G of 16%, 30% and 44% respectively, at a displacement mode with a constant displacement rate of 1 mm/min. Fig. 3 b) shows the experimental setup for MMB test.

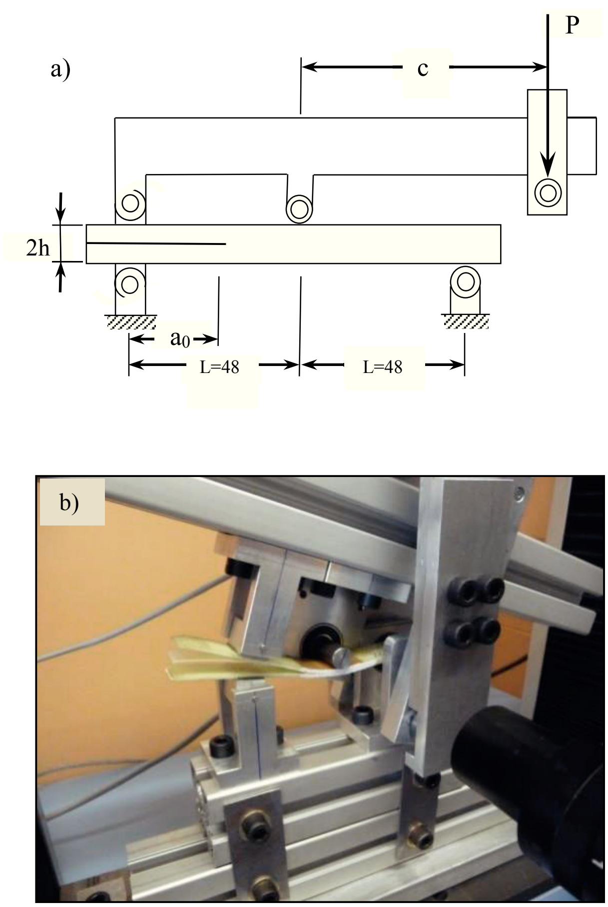

Fig. 3. Experimental setup for the a) MMB device; b) MMB test.

Mixed-mode strain energy release rate is the sum of mode I and mode II strain energy release rates.

$$G = G_I + G_{II} \quad (2)$$

The fracture toughness in terms of the strain energy components G_I and G_{II} were calculated using the Eqs (3) and (4), which are according to ASTM D 6671M standard [12]. Equations (3) and (4) rely on delamination length corrections for laminate rotation at the delamination front

$$G_I = \frac{12P^2(3c-L)^2}{16b^2h^3L^2E_{1f}}(a+\chi h)^2 \quad (3)$$

and

$$G_{II} = \frac{9P^2(c+L)^2}{16b^2h^3L^2E_{1f}}(a+0.42\chi h)^2 \quad (4)$$

where E_{1f} is the modulus of elasticity in the fiber direction measured in flexure and χ is the crack length correction parameter. The stiffness of the laminate, used in the calculation of the G_I and G_{II} was obtained using Eq. (5):

$$E_{1f} = \frac{8\,(a_0+\chi h)^3(3c-L)^2 + \left[6\,(a_0+0.42\chi h)^3 + 4L^3\right](c+L)^2}{16L^2bh^3\left(\frac{1}{m} - C_{sys}\right)} \quad (5)$$

where m is the slope of the load displacement curve and Csys is the system compliance. The crack length correction parameter, χ, was calculated by Eq.(6):

$$\chi = \sqrt{\frac{E_{11}}{11\,G_{13}}\left[3-2\left(\frac{\Gamma}{1+\Gamma}\right)^2\right]} \quad (6)$$

where Γ is the transverse modulus correction parameter, E_{11} is the longitudinal modulus of elasticity measured in tension, G_{13} is the shear modulus out of plane. The transverse modulus correction parameter, Γ, is given by Eq. (7):

$$\Gamma = 1.18\frac{\sqrt{E_{11}E_{22}}}{G_{13}} \quad (7)$$

where E_{22} is the transverse modulus of elasticity.

The critical strain energy release rate, G_C under mixed mode was obtained considering 5/M criterion that uses the point at which the compliance has increased by 5% or the load has reached a maximum value.

3. Results and discussion

Fig. 4 shows exemplary load versus displacement curves obtained in the MMB tests for GF/ENC1 composites for modes ratio 16, 30 and 44%. Curves representative of higher mode ratios, exhibit higher interlaminar failure loads which indicate benefits in terms of the mixed mode IFT.

Figs. 5 and 6 show average curves of the total fracture energy under mixed mode (G_c=G_I+G_{II}) against crack length. For all test conditions total fracture energy under mixed mode G_c increases at the beginning of the crack length and afterwards tends to stabilize.

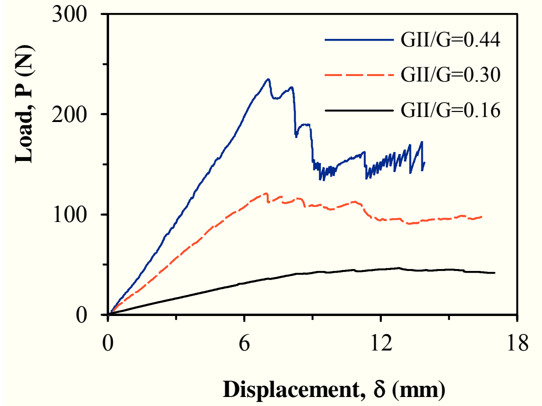

Fig. 4. Load versus displacement curves for GF/ENC1 laminates.

Fig. 5 shows the effect of the matrix composition on *R*-curves, for the mode ratio G_{II}/G=16%, observing a significant increase in G_c about 23% for GF/ENC1 in relation to neat resin composite. On the other hand Fig. 6 shows the effect of the percentage of mode II loading on *R*-curves, for the several GF/ENC1 laminate composites, observing a significant increase in the failure energy with increasing load in mode II. Total G_c increases 16% for GF/ENC1 when G_{II}/G increases from 16 to 44%.

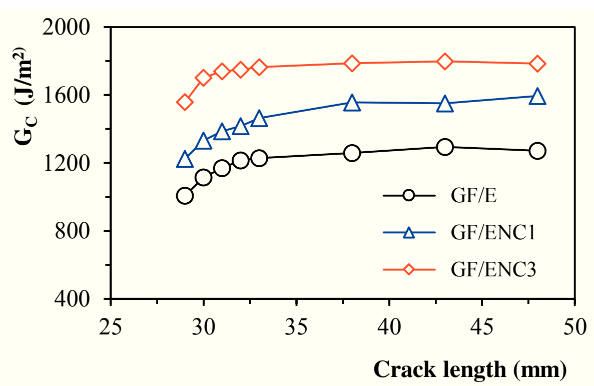

Fig. 5. Effect of the matrix composition on the fracture toughness. GII/G=16%.

Fig. 7 summarizes both effects of the incorporation of nanoclay into the epoxy matrix of the composites and of the percentage of mode II loading in mixed mode IFT. A significant IFT improvement was obtained for the composites incorporating nanoclay, reaching about 26% for GF/ENC1, for mode ratio G_{II}/G=16%. Moreover mixed mode IFT increases about 22% for GF/ENC1 when mode ratio G_{II}/G increases from 0 to 44%.

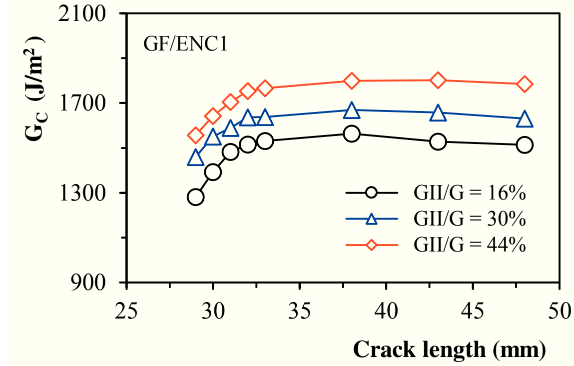

Fig. 6. Effect of the mode ratio on the fracture toughness. GF/ENC1.

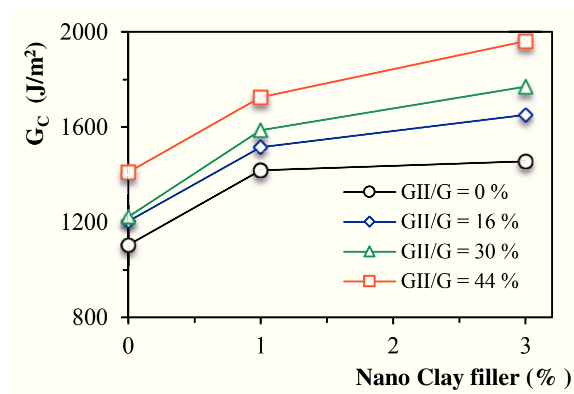

Fig. 7. Effect of nanoclay and mode ratio on the interlaminar fracture toughness.

Fig. 8 shows the representation of fracture energy of the composite materials in G_I versus G_{II} space. This representation includes the referred pure modes and the mixed-mode values measured using the MMB test. A linear fracture criterion (equation 1) was considered in order to characterize the fracture envelop. A good agreement was observed between the experimental results and the linear fracture criterion predictions.

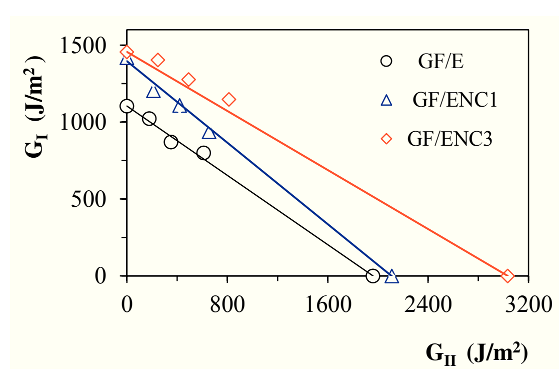

Fig. 8. Effect of nanoclay and mode ratio on the interlaminar fracture toughness.

4. Conclusions

This paper studied the interlaminar fracture toughness under mixed-mode loading of fiber glass/epoxy matrices reinforced with nanoclay, having been obtained the following main conclusions:

- The addition of small quantities of nanoclay into the matrix promotes significant improvements in IFT for all the loading mode ratios, reaching about 39% for GF/ENC3 with the mode ratio G_{II}/G=44%.
- Moreover mixed mode IFT increases about 35% for GF/ENC3 when mode ratio G_{II}/G increases from 0 to 44%.
- Experimental values of G_c increases approximately linearly with the ratio of mode II, G_{II}/G. Good agreement between the experimental results and linear fracture criteria was observed. Linear mixed-mode fracture criterion presents also globally good performance in reproducing the fracture envelop in the G_I versus G_{II} space.

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