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## MODE I AND II INTERLAMINAR FRACTURE TOUGHNESS OF NANOCCLAY-REINFORCED EPOXY/GF COMPOSITES

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### Abstract

Of prime importance in fiber reinforced composites is the interfacial strength between glass fiber reinforcement and matrix. A potential benefit of nanoclays (NC) is to improve the matrix-reinforcement stress transfer due to their positive interactions with glass. Double cantilever beam (DCB) and end-notch flexural (ENF) tests were performed to evaluate the interfacial fracture toughness ( $G_c$ ) in mode I and II, respectively, of GF composites with a NC/epoxy matrix. Results show no benefit of NC on mode I toughness while a significant 20%+ improvement on mode II was obtained. Given the non-optimal chemistry of the epoxy/GF laminate used, this result is encouraging.

### Introduction

Epoxy resin reinforced with nanoclays has received increasing attention recently because of the possibility of obtaining improved properties in terms of stiffness, strength, fire resistance, dimensional stability, shrinkage, etc. [1]. Most of the works have relied on the chemical compatibility between clay and matrix to control the exfoliation. However, it seems that the thermodynamic is not always sufficient to drive the resin into the highly oriented clay stacks to obtain fully exfoliation. Ngo *et al.* has demonstrated the shear force contribute a very important factor in bring down the number of stack layer in the clay nanoparticles, thus facilitating the exfoliation [2]. By improving the dispersion of the nanoclays in the epoxy matrix, it is believed that the modulus and strength are also increased. However, the benefits of increasing the properties of already fairly rigid glassy epoxy to the cost of brittleness and fracture properties can be questioned. On the other hand, a nanoclay reinforcement well dispersed into a glassy epoxy in a continuous glass fiber composite, where matrix strength and rigid contributes more than strain at break or toughness to the overall composite properties, might be of interest.

The goal of this study is to investigate mode I and mode II interlaminar fracture of epoxy/nanoclay glass fiber composites. It is hypothesized that nanoclay presence improves glass-matrix interfacial strength which could translate into improved matrix-reinforcement stress transfer.

### Materials and Method

The matrix used was based on a diglycidylether of bisphenol-A (DGEBA) epoxy resin (Epon 828) and an amine hardener (Epikur 3046), both supplied by Resolution Performance Products LLC (Houston, TX). The organoclay chosen, recommended for use with amine-cured epoxy systems, was Cloisite 30B (montmorillonite treated with methyl tallow bis-(2-hydroxyethyl) quaternary ammonium) supplied by Southern Clay Products (Gonzales, TX). To prepare the clay reinforced nanocomposites, 3 wt% of clay was mixed to the epoxy by moderate mechanical mixing first at room temperature for 30 min and then at 160°C for 2 hours. The amine hardener was added by mechanical mixing at room temperature at a level of 40 phr. Details about processing and materials can be found elsewhere [2].

The glass reinforcement used consisted in a non crimp glass fabric (22 oz/yd<sup>2</sup>), with sizing recommended for DGEBA epoxy resins, supplied by JB Martin (St-Jean, Canada). The non crimp fabric was chosen to facilitate delamination either by mode I or mode II interlaminar fracture. The plates of epoxy glass fabric were laminated by hand lay-up. Six plies of NCS fabrics were used to obtain 6 mm thick laminates for fracture testing and three plies were used to obtain 3 mm thick laminated for tensile and flexural testing.

The final glass and void content were measured from density measurements using Archimedes' method (water-immersion) and by weighing the epoxy/nanoclay glass fiber composites before and after pyrolysis (4 h at 450°C) to get rid of the epoxy resin (results from triplicates).

Both tensile and three-point bending tests were performed on the epoxy/nanoclay glass fiber composites following recommendations of ASTM D3039 and D790 standards. An electromechanical Instron tester (model 1123) was used in both cases. Tensile testing was done at a crosshead speed of 5 mm/min using a video extensometer. Three-point bending tests were done at a crosshead speed of 2 mm/min. Load-displacement curves were recorded in both cases, from which the elastic modulus, the strength (maximum stress here) and yield strain were determined.

Mode I and mode II interlaminar testing was performed on the epoxy/nanoclay glass fiber composites following recommendations of ASTM D5528 and the end-notched flexure (ENF) method [3], respectively. The DCB specimens (Fig. 1a) was chosen to determine the strain energy release rate associated with mode I interlaminar cracking,  $G_I$ . Details about the testing procedure have been disclosed previously [4]. The ENF specimen consists in a three-point bending specimen with an embedded through-width delamination crack present at one end (Fig. 1b) from which the strain energy release rate associated with mode II interlaminar cracking,  $G_{II}$ , can be measured. Details about the testing procedure have been disclosed previously [5]. For both types of interlaminar fracture specimen, a polyethylene terephthalate film, 50 mm thick, was inserted prior to molding at mid-thickness of one end of the composite to act as a starter crack. Both tests were done at room temperature on the mechanical tester previously described.

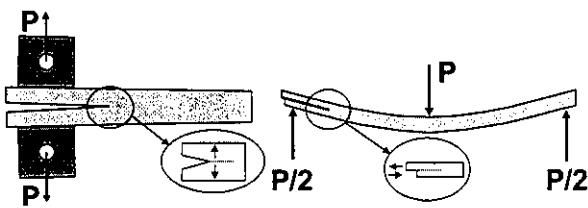


Fig. 1 DCB (a) and ENF (b) specimens with schematized crack tip loading configuration (mode I and II respectively).

The strain energy release rate in mode I and mode II can be determined following Eq. 1:

$$G_{I,II} = \frac{P^2}{2b} \cdot \frac{dC}{da} \quad (1)$$

where  $P$  is load at propagation,  $b$  is the specimen width,  $C$  is the specimen compliance at crack length  $a$ . The compliance in mode I and mode II can be related to the crack length following Eqs. 2 and 3:

$$C_I = \frac{64a^3}{Ebh^3} \quad (2)$$

$$C_{II} = \frac{16L^3 + 3a^3}{64Ebh^3} \quad (3)$$

where  $E$  is the elastic modulus,  $h$  is the thickness of the laminate and  $L$  is the support span. From the load-displacement curves, the critical strain energy release rate  $G_{Ic}$  and  $G_{IIc}$ , defined at the onset of crack propagation, and the strain energy release rate associated with further crack propagation can be determined.

Finally, the mode I and mode II interlaminar fracture surfaces were observed using a scanning electron microscope (SEM, JEOL JSM 6100). Prior to SEM

observation, the surfaces were coated with a thin gold-palladium layer by physical vapor deposition.

## Results

The glass and void content obtained were respectively 53.5% and 8.9% for the epoxy glass fiber composites and 49.9% and 8.0% for the epoxy/nanoclay glass fiber composites, with a 1.4% in nanoclay. All glass and void content values were within 0.7%. The respective component contents differ from their nominal contents, as a result of the manual lamination method used. However, the glass contents between both composites are very close, within 3.5 points of %, which allows for mechanical comparison between both types of composites. Observations of the composite cross-section revealed the presence of large voids within the matrix between the glass laminates.

Tensile and flexural tests were performed on the epoxy glass fiber composites with and without nanoclay. The results, shown in Table 1, indicate that the mechanical properties of both composites are not significantly different from each other. This lack of difference suggests that whether the addition of nanoclay did not lead to significant changes in mechanical properties of the epoxy-based matrix or that the mechanical behavior is dominated by the glass fabric reinforcement or by the interface between the latter and the matrix. Previous results using the same epoxy/nanoclay system and preparation method showed that static properties were very similar with and without nanoclay [2].

Table 1. Tensile and flexural properties of the epoxy glass fiber composites with and without nanoclay

Property	Epoxy glass fiber composite	Epoxy/nanoclay glass fiber composite
Tensile modulus (GPa)	14.6 ± 0.7	13.8 ± .7
Tensile strength (MPa)	229 ± 11	230 ± 10
Tensile yield strain (%)	7.8 ± 0.4	8.6 ± 0.3
Flexural modulus (GPa)	13.1 ± 0.7	12.9 ± 0.6
Flexural strength (MPa)	380 ± 19	350 ± 20

The DCB tests were then performed on both composites. The load-displacement curves were recorded to determine the critical load at onset of crack propagation,  $G_{Ic,onset}$ , and the load associated with further crack propagation,  $G_{Ic,prop}$ . A discontinuous load-displacement curve was obtained in mode I (Fig. 2), indicative of a discontinuous crack propagation process.

Each step on the latter curve corresponds to a sudden crack propagation, to which is associated a critical load and a crack length. From Eqs. 1 and 2, the  $G_{Ic}$  vs. crack propagation curve can be obtained (Fig. 3). Crack propagation results show that the  $G_{Ic,onset}$  values only slightly decreases by 12% when organoclay is added to the epoxy glass fiber composite. The results also indicate that upon propagation,  $G_{Ic}$  progressively increases toward a plateau value as higher energy is required to further propagate the crack, indicative a tough behavior for both composites. The composite with and without nanoclay show non significantly different  $G_{Ic,prop}$  (plateau) values.

These mode I fracture values are similar with values of  $G_{Ic,onset}$  of 200-400 kJ/m<sup>2</sup> reported for continuous glass/epoxy composites [6,7]. The lack of difference between the mode I fracture values of the composite with and without nanoclay is in agreement with their similar tensile and flexural properties.

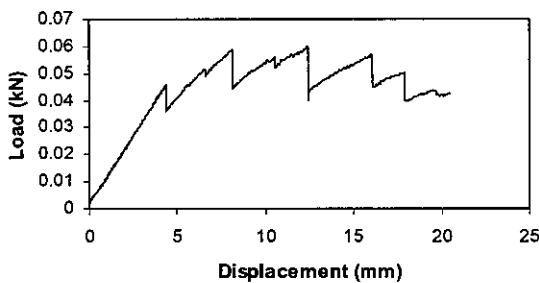


Fig. 2 Typical load-displacement curve in mode I.

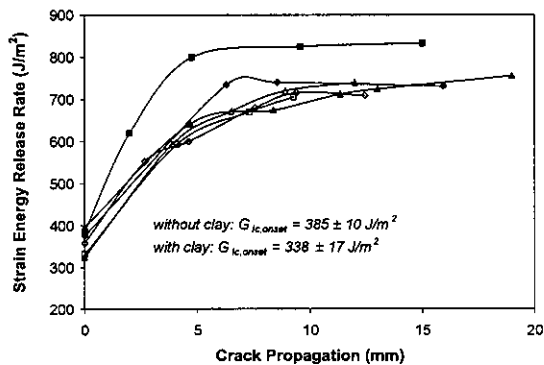


Fig. 3 Mode I fracture toughness expressed as strain energy release rate vs. crack propagation for epoxy glass fiber composites (open symbols) and epoxy/nanoclay glass fiber composites (closed symbols).

The ENF tests were also performed on both composites. The load-displacement curves were also recorded to determine the critical load at onset of crack propagation,  $G_{IIc,onset}$ , and the load associated with further crack propagation,  $G_{IIc,prop}$ . Contrary to mode I crack propagation, the load-displacement curve obtained in mode II (Fig. 4) was progressive, indicative of a

continuous stable crack propagation process; additional energy was required for the crack to further propagate. From Eqs. 1 and 3, the  $G_{IIc}$  vs. crack propagation curve can be obtained (Fig. 5). Mode II crack propagation results show a slight (6%) but significant increase in  $G_{IIc,onset}$  when nanoclay was added to epoxy glass fiber composites. They also show that upon crack propagation,  $G_{IIc}$  progressively increased until failure occurs for both composites, but also that the rate of  $G_{IIc}$  increase was significantly higher when nanoclay was added to the composite, *i.e.*, the difference between  $G_{IIc}$  of epoxy/nanoclay glass fiber composites and epoxy glass fiber composites increased as the crack propagated. Final  $G_{IIc,prop}$  were  $1800 \pm 83$  J/m<sup>2</sup> with nanoclay and  $1449 \pm 125$  J/m<sup>2</sup>, a significant difference of 24%.

These slight improvement in  $G_{IIc,onset}$  and considerable improvement in  $G_{IIc,prop}$  reveal an increased crack propagation resistance when nanoclays are added to the epoxy matrix in the composites. Since the flexural modulus was the same for both composites with and without nanoclays, a very plausible cause for this higher crack propagation resistance is an improved interfacial strength between the glass fabric and the matrix resulting in improved matrix-reinforcement stress transfer. Also, the mode II interlaminar fracture toughness is known to be very sensitive to the fiber-matrix interfacial strength and less to the properties of the matrix itself [8], which is in agreement with the important effect of clay addition to the epoxy glass fiber composite on interlaminar fracture toughness in mode II.

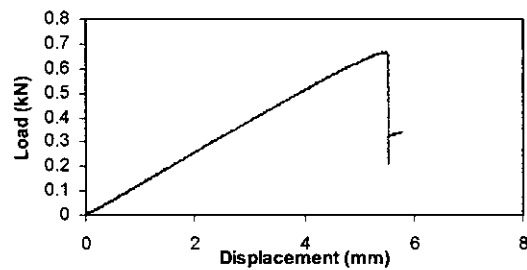


Fig. 4 Typical load-displacement curve in mode II.

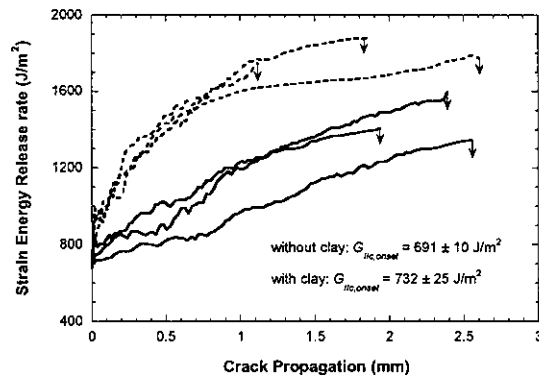


Fig. 5 Mode II fracture toughness expressed as strain energy release rate vs. crack propagation for epoxy glass fiber composites (solid line) and epoxy/nanoclay glass fiber composites (dotted line). Arrow indicates failure.

The fracture surface of the epoxy glass fiber composites with and without nanoclays was studied to confirm the presence of indications of improved interfacial strength between the glass fabric and the matrix. Mode II interlaminar fracture surface of both composites are shown in Figs 6 and 7. Comparison of the fractographic features of epoxy glass fiber composite and epoxy/nanoclay glass fiber composite indicates that the surface of the glass fibers appears perfectly smooth while the glass fiber surface revealed remaining matrix. Nonetheless, the presence of cusps or shear fracture induced defects, associated with cavities interacting with the crack tip and indicative of good matrix-reinforcement stress transfer [9], is noted in both epoxy glass fiber and epoxy/nanoclay glass fiber composites (Fig. 8).

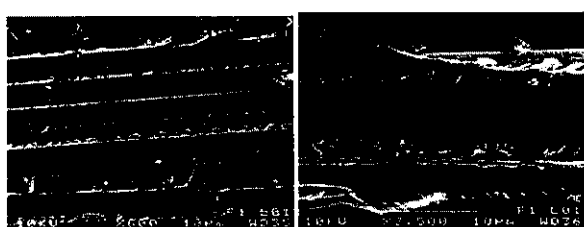


Fig. 6 SEM of mode II interlaminar fracture surface of epoxy glass fiber composite at low and high magnification.

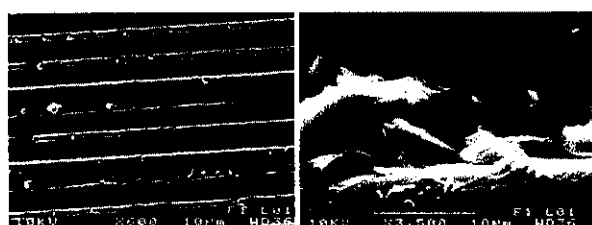


Fig. 7 SEM of mode II interlaminar fracture surface of epoxy/nanoclay glass fiber composite at low and high magnification.

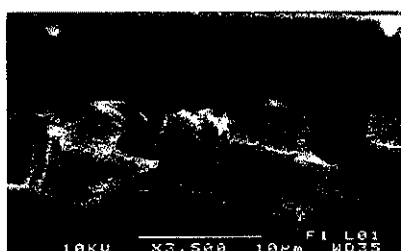


Fig. 8 Shear cusps observed on the mode II interlaminar fracture surface of epoxy glass fiber composites.

## Discussion

Although they have been studied at length in the last years, clay-based epoxy nanocomposites have not demonstrated the improvements expected in fracture-governed properties (tensile strength, toughness, etc.) when glassy epoxy system were used. This lack of effect can be attributed to the desired dispersed structure of the nanoclay reinforcement that increases the rigidity of the 3D molecular cross-linked network of the epoxy matrix, which comes at the cost of increasing brittleness. However, in a continuous glass fiber epoxy composite, increasing the rigidity of the matrix while maintaining its strength and, most importantly, the fiber-matrix interfacial strength, as a result of the affinity between hydrophilic clays and glass fibers, would translate into improved glass reinforcement-matrix stress transfer. Therefore, nanoclays were added to the epoxy glass fiber composite in the goal of improving its interlaminar fracture toughness.

As expected, tensile and flexural properties of the epoxy glass fiber composite were not improved by nanoclay addition. In agreement with the latter observation, their mode I interlaminar fracture toughness was not importantly affected by the nanoclay addition. The effect observed showed a trend of slight reduction of mode I interlaminar fracture toughness, sensitive to the matrix properties, caused by the reduced toughness of the matrix. Both static tests and mode I interlaminar fracture tests indicate that in the epoxy glass fiber composite system studied, the matrix properties were not sufficiently improved by nanoclay addition to result into improved composite properties. This conclusion is in agreement with a previous study on the same epoxy/nanoclay system that showed no significant differences in static properties with and without nanoclay.

On the contrary, mode II interlaminar fracture toughness showed a slight increase in  $G_{IIc,onset}$  and important increase in  $G_{IIc,prop}$  when nanoclays were added to epoxy glass fiber composites. Fracture surface observations showed signs of improved fiber-matrix interfacial strength. The latter fracture toughness increase and fractographic observations in conjunction with the known sensitivity of mode II interlaminar fracture toughness to the fiber-matrix interface lead to conclude that nanoclay addition to epoxy glass fiber composites has the potential to improve glass fiber-matrix interfacial strength and resulting stress transfer between the nanoclay-reinforced epoxy matrix and the glass fibers. It is hypothesized that these improvements are attributed to the affinity of clays for glass fibers, both hydrophilic in nature.

## Conclusions

Nanoclay was introduced in the epoxy matrix of a continuous glass fiber composite in the goal of improving its fiber-matrix interfacial strength as a result of the potential affinity between hydrophilic clays and glass fibers. Interlaminar fracture toughness testing was used to assess this interfacial strength improvement. Matrix-dependent mode I interlaminar fracture toughness was not significantly affected by nanoclay addition; whereas as mode II interlaminar fracture toughness showed significant improvements upon nanoclay addition. It is concluded that nanoclay-reinforced epoxy glass fiber composites can demonstrate improved glass fiber-matrix interfacial strength, resulting higher stress transfer and interlaminar fracture toughness.

## References

1. J. M. Brown, D. Curliss, and R. A. Vaia, *Chem. Mater.*, **12**, 3376 (2000).
2. T.-D. Ngo, M.-T. Ton-That, S.V. Hoa, K.C. Cole, *Polym. Eng. Sci.*, **47**, 649 (2007).
3. A. J. Russell, and K. N. Street, *ASTM STP*, **876**, 349 (1985).
4. F. Perrin, M. N. Bureau, J. Denault and J. I. Dickson, *Compos. Sci. Techn.*, **63**, 597 (2003).
5. M. N. Bureau, J. Denault and J. I. Dickson, *J. Thermopl. Compos. Mater.*, **14**, 374 (2001).
6. P. Davies, and M. L. Benzeggagh. *Interlaminar mode-I fracture testing*. In: K. Friedrich (Ed.). Application of fracture mechanics to composite materials, vol. 6. Amsterdam: Elsevier Science Publishers (1989).
7. N. Alif, L. A. Carlsson, and J. W. Gillespie. *ASTM STP*, **1242**, 82 (1997).
8. M. N. Bureau, F. Perrin, J. Denault, and J. I. Dickson, *Intern. J. Fatigue*, **24**, 99 (2002).
9. D. Purslow. *Composites*, **17**, 289 (1986).

Key Words: Continuous glass fiber, Composites, Epoxy, Nanocomposites, Clay, Interlaminar fracture toughness.