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Study on interlaminar fracture toughness of biocomposites based on epoxy resin/bacterial cellulose reinforced glass fibers

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Abstract: In this papper, the influence of bacterial cellulose (BC) prepared from Vietnamese nata-de-coco via an alkaline pre-treatment followed by a solvent exchange process on inter-laminar fracture toughness, of glass fibers reinforced epoxy composites. The inter-laminar fracture toughness measured from the double cantilever beam (DCB) at BC contents up to 0.4 wt. % BC. The fracture toughness of the bio-based composites was compared with those of the virgin epoxy resin, G_{IC} values (G_{IC} and G_{IP} - MBT method) of the 0.3wt % BC/epoxy composites were 815.7 J/m^2 and 1277.7 J/m^2, respectively. These values represent the improvement of 102.3% and 95.0%, respectively, compared to a virgin epoxy resin. Scanning electron microscopy revealed the presence of BC in epoxy resin prevents and/or changes the direction of cracks in the material.

Keywords: Epoxy, bacterial cellulose, fracture toughness, mechanical property

I. Introduction

Because of many advantages like high mechanical properties, good corrosion resistance, heat resistance, durability, good adhesion to many materials, low shrinkage after curing; epoxy resin was widely used in many areas of the industry. However, the disadvantage of epoxy resin is crispy, that limited its application in a number of areas. The combination of epoxy resin with fibers into composite materials increased significantly the mechanical properties of the materials [1-4].

Composite materials with glass fiber as reinforcement are one of the most widely used in structural components. However, the low load capacity and low shear strength of this material is one of the biggest drawbacks, which delays its application in the details. One of the best ways to increase the toughness of the material is the addition of micro/nano sized reinforcements such as carbon nanotubes, nano clay, nano silica, silver nanoparticles, and recently bacterial cellulosic (BC). Therefore, in this work, BC was selected as an object to improve the durability of epoxy resin and composite materials.

Numerous studies have focused on the fabrication of bio-based composite materials by using BC as green reinforcement filler in materials such as polylactic acid (PLA) and poly (vinyl alcohol) (PVA) [5,9,10,11]. Luddee et al. [12] used BC as reinforcement filler for fabricating PLA biocomposites and stated that the tensile strength and elongation of a PLA/BC biocomposite decreased with increase in the BC particle size. Gea et al. [13] prepared bio-nanocomposites via an in-situ growth process through the direct addition of PVA to an *Acetobacter xylinum*-inoculated medium and compared the results with composites made by impregnating BC gels with a PVA solution. Mechanical property tests showed that PVA in the BC acts as a plasticizer, interrupting the hydrogen bonding between the cellulose fibrils within the BC network. This resulted in a reduction in the Young's modulus and an increase in the toughness relative to pure BC sheet, especially for in-situ grown samples, reporting that the mechanical properties of the PLA composites reinforced with surface-functionalized BC showed significant improvements when compared to unmodified PLA and BC-reinforced PLA. Quero et al. [14] showed that the Young’s modulus and stress at failure of transparent, predominantly amorphous poly(L-lactic) acid (PLLA) films were found to increase by 100% and 315%, respectively, with an 18% volume fraction of BC fibers. Gabr et al. [16] showed that, for a BC fiber content of 0.5% in epoxy matrix, the initiation and propagation Mode – I interlaminar fracture toughness were improved by 84% and 72%, respectively. The addition of 0.5% BC to the composite, modified with 10% liquid rubber, improved the storage modulus by 28% at 200°C. Concurrently, epoxy resin (EP) was successfully used as the matrix of composites for various industrial applications such as aircraft (half of the total weight of the Boeing 787 Dreamliner is epoxy-based composite), marine craft, and the chemical industry. However, given the intrinsic brittleness of EP after curing, as caused by its high crosslinking density, fiber reinforced epoxy composites such as glass-fiber (GF) reinforced epoxy composite can be broken by even low external impact energy. This problem can be solved by the introduction of Nano scale reinforcement material filler.

In the present study, a suspension of BC in ethanol was initially fabricated and employed as a source of green filler, and its effects on the fracture toughness, morphology of glass fiber reinforced epoxy composites were investigated.

II. Experimental

2.1. Materials

- Nata-de-coco from Dang Khoa coconut company, Ben Tre Province, Vietnam, with a 10 wt% dry content.
- Epoxy Epikote 828 (epoxy content: 22.63%, molecular weight: 383 g/mol, viscosity: 12 ÷ 13 Pa.s, density: 1.16 g/cm^3 at 25^0 C) was supplied by Shell Chemical.
- Methylhexahydrophthalic anhydride (MHHPA) procured from Jiaxing Alpharm Fine Chemical Co., China, was used as the curing agent.
- 1-Metylimidazol (NMI) and polyol (BASF, Germany) were used as the accelerators.
- (3-Glycidyloxypropyl)trimethoxysilane (GS) was purchased from Sigma-Aldrich. Ethanol and acetone were used as the solvent without further purification.
- Glass fibers type Woven Roving 400g/m^2 (China) were used as the reinforcement.

2.2. Dispersion of BC in epoxy resin

Nata-de-coco was maintained in a 2.5M NaOH solution for 8h at room temperature to remove the bacterial cells, followed by washing with distilled water to natralize. The alkaline pre-treated nata-de-coco was well blended by using a mixer for 20 mins to obtain a cellulosic pulp. In the next step, the water in the slurry was removed using a vacuum filter before obtaining the BC sheet containing approximately 80 wt% water and 20 wt% BC. Subsequently, the BC sheet was immersed in ethanol and blended by using a mixer for 20 mins again and filtered with the help of a vacuum filter. This processing was repeated three times to get the suspension of 20 wt% BC in ethanol. The obtained suspension was used for the preparation of EP/BC mixtures as well as bio-based composite materials.

In this study, high speed mechanical stirrer and ultrasonic technique were used to disperse BC in epoxy resin. The suspension of BC in ethanol was dispersed in epoxy resin using a high speed mechanical stirrer at 2000 rpm, at 70–80 C for 5 hours. Subsequently, the resulting mixture was agitated by ultra sonication for 30 or 60 mins. An ice bath was also used in this step to prevent the evaporation of ethanol. Finally, the ethanol in the mixtures was removed completely by using a vacuum oven at 60^0 C for 3 hours.

2.3. Preparation of composite materials

The epoxy resin was well mixed with a curing agent of MHHPA (ratio of epoxy resin/MHHPA: 1.0/0.8 mol/mol), accelerators of NMI and polyol (1.5 wt% with respect to the total mass of the MHHPA/EP mixture) at 60^{o}C for 60 minutes, using a magnetic stirrer. The mixture was degassed, poured into a mold coated with a release agent and cured in a vacuum oven via two steps: at 80^{o}C for 60 min followed by 100^{o}C for 60 min. Similar procedures were used to prepare the bio-based composite materials containing 0.1, 0.2, and 0.3 wt% BC in the epoxy resin.

2.4. Characterization

To measure the mode-I interlaminar fracture toughness, a mode I double-cantilever beam test was carried out as described in ASTM: D5528–01. This standard recommends a specimen size of at least 157 mm (L) by 20 mm (W) with an initial crack length (i.e. the length of the insert from the line) of 50 mm. Hinges of the same width as the specimen were attached to allow the application of the load. The load and displacement were then related to the delamination length as measured with a ruler at the specimen edge. The mode-I interlaminar fracture toughness G_{IC} and G_{IP} for each BC content were calculated using the modified compliance calibration method and Eqs. (1) And (2):

$$\mathbf{G_{IC} = \frac{3m}{2(2h)} \cdot \left(\frac{P_c}{B}\right)^2 \cdot \left(\frac{BC}{N}\right)^{\frac{2}{3}} F} \qquad (1)$$

$$\mathbf{G_{IP} = \frac{3m}{2(2h)} \cdot \left(\frac{P_P}{B}\right)^2 \cdot \left(\frac{BC}{N}\right)^{\frac{2}{3}} F} \qquad (2)$$

Where G_{IC} is the fracture toughness at the initial crack stage, G_{IP} is the fracture toughness at the propagation stage, Pp is the applied load, C is the compliance corresponding to each crack length, a is the crack length, Pc is the initial maximum load, B is the specimen width, h is the thickness, N is the end-block correction factor, F is the large-displacement correction factor, and m is the slope of a plot of (BC/N)1/3 versus (a/2h). The sample dimensions and testing processing can be seen in Figs. 1 and 2.

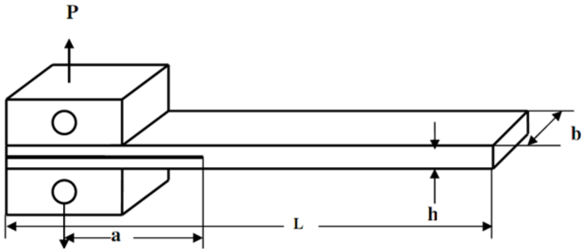

Figure 1: Geometry of interlaminar fracture toughness specimen (L=150 mm; h= 3÷4mm; b=20 mm; a=50 mm)

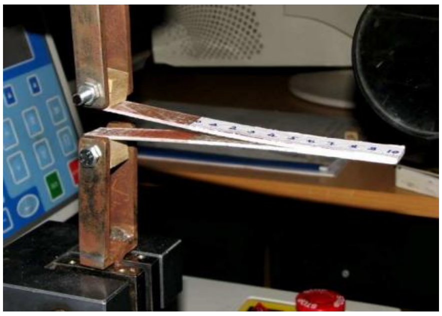

Figure 2: Picture of the mode-I interlaminar fracture toughness testing

The fractured surfaces of the test specimens were observed by scanning electron microscopy (SEM) using a Jeol JSM-6360LV, Japan. Prior to the SEM observations, all the samples were coated with a thin layer of platinum to avoid the build-up of an electrical charge.

III. Results and Discussion

The ability to resist cracks development of composite materials is usually characterized by fracture toughness (the energy required to form a new surface). The fracture toughness of composites is determined by the separation energy (G_{IC}) during the separation of the two layers of composites materials. The results in Fig. 3 showed the curves of the applied load versus displacement during interlaminar fracture toughness test.

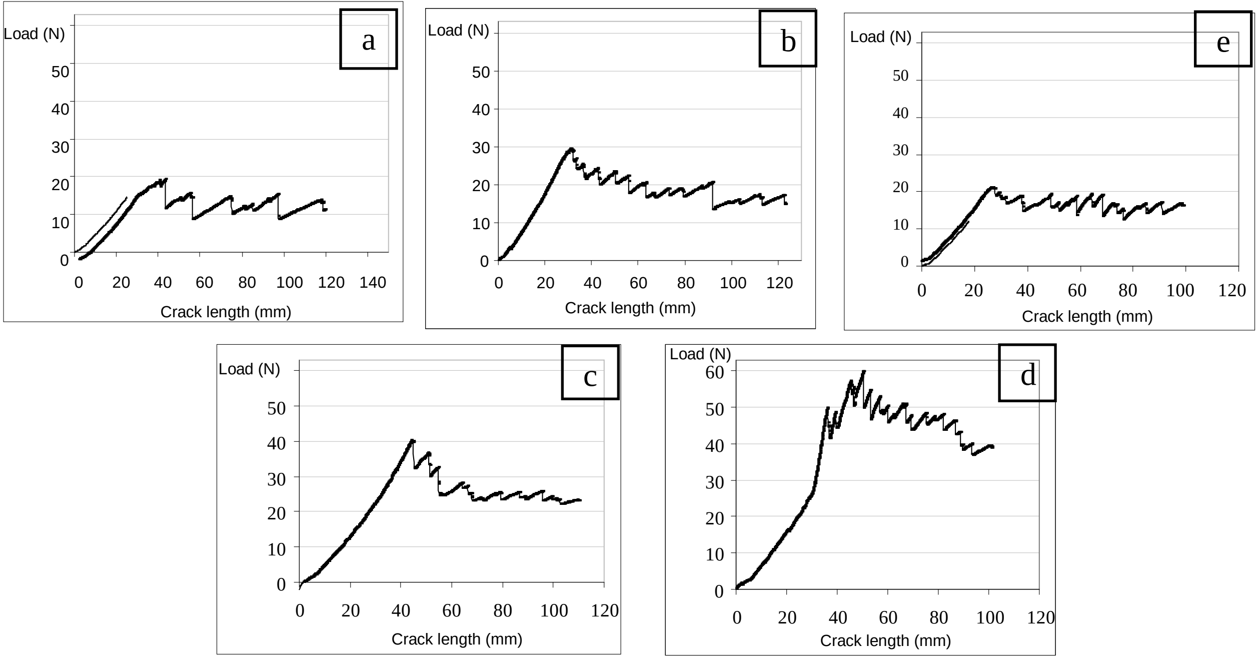

Figure 3: Applied force versus displacement curves for each content of BC: (a) 0%BC,(b) 0,1%BC, (c) 0,2%BC, (d) 0,3%BC, (e) 0,4%BC

As showed in Fig. 3, all curves were zigzag plots, the force increased gradually to maximum value and then decreased. The BC has significant effects on the force required for layers separation in epoxy/fiberglass composite materials: whithout BC, the force required was in the range of 10÷20N, with BC contents from 0.1 to 0.4 wt %, the force were 15N to 60 N, respectively. At the BC content of 0.3 wt %, the force required for layers separation in the composites materials is highest at 60 N. This also means that the presence of BC in epoxy matrix enhanced the ability to resist cracks development of composite materials, which increased fracture toughness of the epoxy/fiber glass composite.

In addition, the all curves in Fig. 3 shown that cracks development that occurred due to layer separation is a discontinuous process, they occurred step by step. With composite materials without BC, crack development steps occurred irregularly, they grown quickly and vigorously (the step of cracks and force dropt very strongly) but also a slow development, the force is reduced slowly. In the presence of 0.1 to 0.3% wt BC, the cracks development progresses more steadily, the shorter the separation steps and the reduction in force. The layer separation is also significantly reduced. With material of 0.4% wt BC, even though the separation force is equivalent to the sample without BC fiber but the crack development step is shorter and more uniform.

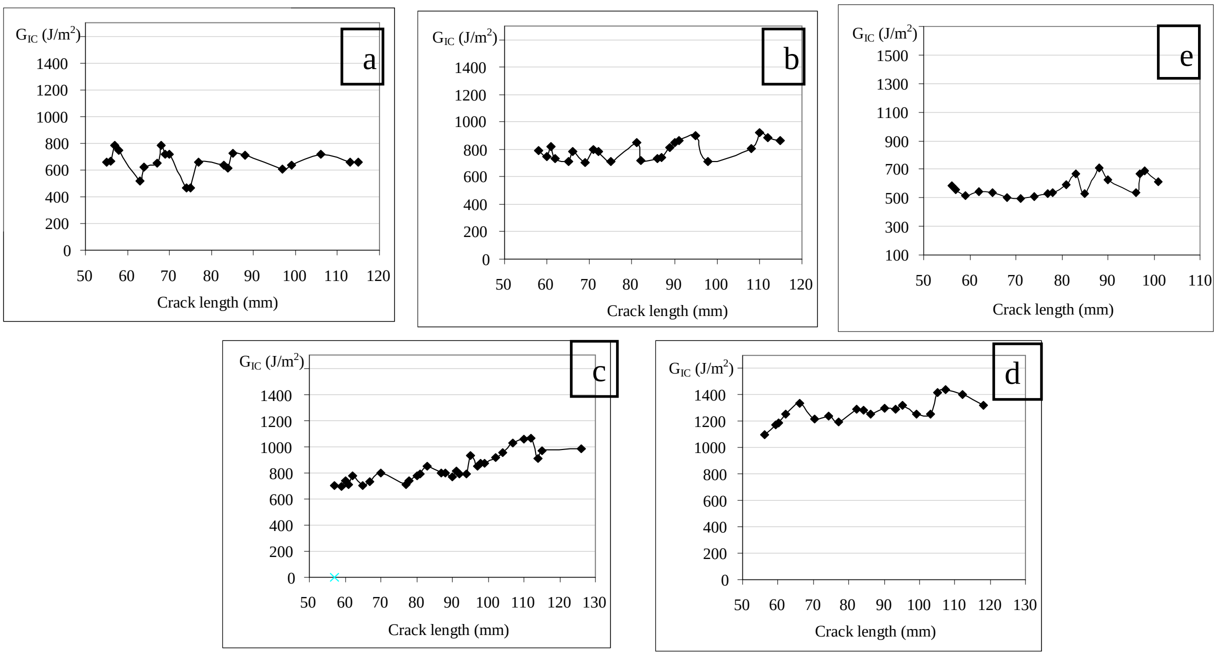

Figure 3: G_{IC}-curves for each content of BC (a) 0%BC,(B) 0,1%BC, (c) 0,2%BC, (d) 0,3%BC, (e) 0,4%BC

The G_{IC} values calculated by the Modified Beam Theory (MBT) method and Modified Compliance Calibration (MCC) method were presented in Table 1.

Table 1: Initiation fracture toughness (G_{IC}) and propagation fracture toughness (G_{IP}) for each contents of BC

Contents of BC, **wt %**	**G_{IC} (MBT) J/m^2**	**G_{IC} (MCC) J/m^2**	**G_{IP} (MBT) J/m^2**	**G_{IP} (MCC) J/m^2**
0.0	403.2	439.3	655.2	670.7
0.1	594.6	515.9	792.5	802.0
0.2	707.4	736.5	831.0	885.4
0.3	**815.7**	**747.0**	**1277.7**	**1267.7**
0.4	437.3	485.6	595.0	636.9

The results in Fig. 3 and Table 1 shown that the development steps of the cracks in composites using BC were shorter and more regular than that of non-fiber BC materials. The G_{IC} value increased when putting BC into the resin and G_{IC} (G_{IP}) reached the highest value at the content of BC is 0.3 wt %.

The increasing of G_{IC} value can be explained that BC microfiber may change direction or event stop cracks inside the material under external load applied. Hence, the energy required to keep the cracks growing will be higher.

Specifically, the delamination initiation value (G_{IC}) of the 0.3wt % BC composite (815.7 J/m^2) increased 102.3% compared to the samples without BC (403.2 J/m^2) calculated by MBT method. The delamination propagation value (G_{IP}) of the 0.3wt % BC composite increased 95.0% compared to composite samples without BC (1277,7 J/m^2 versus 655.2 J/m^2). However, at the BC content of 0.4wt %, the G_{IC}, G_{IP} values were significantly reduced, nearly equivalent to those without BC.

The data in Table 1 demonstrates the role of BC during the formation and development of cracks of composites by significantly increasing the force and energy values required for development the cracks in the material system.

The SEM images of the composites surface after determining interlaminar fracture toughness were shown in Fig. 4.

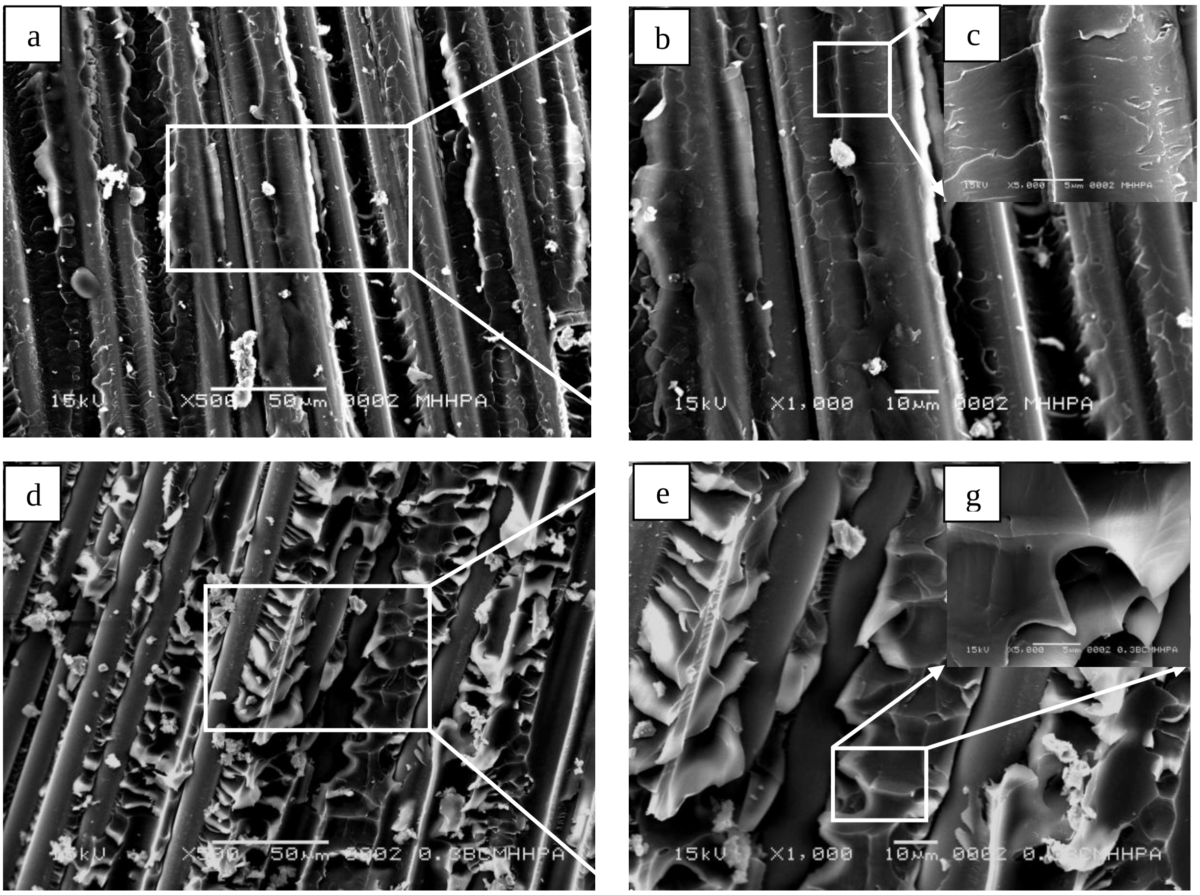

Fig. 4: SEM images obtained after interlaminar fracture toughness of composite without BC (a, b, c) and 0.3 wt% BC filled epoxy/glass fiber composite (dreg)

From the results in Fig. 4, the difference in the destruction of the material resulting from layer separation is shown in the following points: rougher surface of composites materials with the present of BC (Fig. 4d, e, g) than samples without BC (Fig. 4a, b ,c).

On the crack characteristics: the number of cracks per area unit of the BC/epoxy/glass fiber composites materials (Figure 4g) is higher than the sample without BC (Figure 4c), however the cracks on the surface of the BC filled epoxy/glass fiber composites are quite short and not in a certain direction while in the sample without BC, cracks mainly developed in certain directions. Thus, the layer separation at the composites without BC is due to a number of long cracks in certain directions causing rapid decomposition. In the BC filled composites materials, the cracks can be stopped or take time to change direction continuously due to the interference of BC so the needed energy to develop the cracks also increases. Thus, the separation energy of the material with 0.3wt % BC is higher than that of non-BC materials.

IV. Conclusion

The BC extracted from nata-de-coco was used as reinforcement to improve interlaminar fracture toughness of glass fibers reinforced epoxy composites. The results shown that, at the BC content of 0.3 wt%, BC plays an important role in enhancing the interlaminar fracture toughness (G_{Ic}, G_{IP}); increasing by 95.0% and 102.3%, respectively. The presence of BC in epoxy resin prevents and/or changes the direction of cracks in the composites materials, thus enhancing the fracture toughness the composites.

V. Acknowledgements

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