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IMPROVING FRACTURE TOUGHNESS OF CARBON FIBRE/EPOXY COMPOSITE FILLED WITH NANO-CELLULOSE MODIFIED WITH LIQUID RUBBER

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ABSTRACT

In certain application of fiber reinforced polymer composites fracture resistance is required. The aim of this study was to improve the interfacial adhesion between plain woven carbon fiber (CF) and epoxy matrix filled with 0.3% of nano-cellulose (microfibrillated cellulose-MFC) modified with liquid rubber (carboxyl-terminated butadiene acrylonitrile-CTBN) with different contents. CF/Epoxy/MFC/CTBN composite was characterized by different techniques, namely tensile, fracture toughness (mode I) test and scanning electron microscope (SEM). The results reveal that at a fibre content 0.3% of MFC and 1%CTBN, initiation and propagation interlaminar fracture toughness in mode I improved significantly by 39% and 57% respectively which could be attribute to strong adhesion between filled epoxy, carbon fibre and rubber. This can be explained by SEM at given weight as well; SEM images showed that in front of the tip, fiber breakage during initiation delimination as well as the extensive matrix deformation between fibers accounting for increase fracture toughness.

KEY WORDS

Carbon fibres; Micro-fibrillated cellulose; Mechanical properties; Fracture toughness.

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INTRODUCTION

Composite materials formed by natural fibers and polymeric matrices constitute a current area of interest in composites research. A great development in this field has been noticed, mainly driven by the automotive industries. Cellulose, the most abundant natural homopolymer, is considered to be one of the most promising renewable resources and an environmentally friendly alternative to products derived from the petrochemical industry. Plant derived cellulose has been widely used as either reinforcement [1-3] or matrix [2] and even as the sole component to prepare all-cellulose composites [4].

Recently the identification of nano-sized cellulose microfibrils which called microfibrillated cellulose (MFC) increases the choices of fibers and expands their use because of their excellent mechanical properties in composites. Using MFC as reinforcement with polymer matrix gives significant effect on the mechanical properties for the composite [5, 6, 7, 8]. Takagaki et al. [9] showed that addition of 0.1, 0.3wt% MFC contribute slightly to improve the static properties of MFC-CFRP-Epoxy composite. They also stated that addition of MFC contribute to improve fatigue life of the composite. However, the low interlaminar strength of composite laminates is one of major disadvantages, which delayed the widespread use of composite laminates in primary aircraft structures. Interlaminar fracture or delamination becomes a fatal damage frequently observed in composite structures in service. For this reason, many efforts have been made to improve the interlaminar strength. Kazuya Okubo et al. [10] stated that if small amount of MFC added into the bamboo fiber composite, tangled MFC fibers prevented the growth of micro crack along the interface between bamboo fiber and matrix. Kazuya Okubo et al [11] showed significant improvements in the strain energy until fatal failure when the PLA matrix enhanced with 1 wt% of MFC. Yamashita Naoya et al. [12] showed that addition of small amount of MFC into polylactic acid/bamboo short fiber (PLA/BF) composites contribute to improve the fracture toughness and impact strength.

In this study, polymer matrix composites (PMCs) are produced using an epoxy resin as matrix. Epoxy resins are characterized with outstanding performances such as, rigidity, high temperature performance, chemical resistance, adhesive properties, formulation latitude, and reactivity with a wide variety of chemical curing agents [13]. The resin forms a highly cross-linked network structure having relatively high stiffness and glass transition temperature (T_{a}) with high chemical resistance. However, the inherent toughness of the network polymer is low. Elastomeric modification is one of the most frequently used and widely accepted methods for improving properties of epoxy networks. The copolymer of acrylonitrile and butadiene with end carboxyl functional groups, CTBN, can react with the epoxide groups, and hence are popularly employed as a modifier to epoxy. A high level of interfacial adhesion and property improvements are achieved by this elastomer. The great majority of the studies [14,15] involve the chemical modification of epoxy resin with reactive liquid rubber, particularly carboxyl-terminated butadiene acrylonitrile copolymer (CTBN). The liquid rubber enhances the toughness of the unmodified epoxy considerably with only a minimal modification to thermal and mechanical properties [16]. Carbon fiber reinforced plastic (CFRP) is a type of reinforcement which applied in this study. CFRP possesses admirable properties low weight, high



fracture toughness with relatively high strength that makes them suitable for such applications. In previous work [17], we studied the interlaminar fracture toughness for CFRP/Epoxy modified with MFC as hybrid reinforced composite. We concluded that interlaminar fracture toughness improved with addition MFC up to 2wt% of MFC [17].

The main objective of the present study was to improve the interlaminar fracture toughness of CFRP/Epoxy filled with 0.3% of microfibrillated cellulose by addition 1, 3, and 5 phr of CTBN as liquid rubber as well as study the effect of natural fiber on carbon fiber reinforced epoxy modified with liquid rubber. The effect of addition liquid rubber on CFRP/Epoxy filled with MFC on Mechanical properties has been investigated.

EXPERIMENTAL

Material

Micro Fibrillated Cellulose (MFC, Celish KY110G, water slurry containing 10 wt% fiber, Daicel Chemical Industries, Ltd., Japan) was used as filler. Plain-woven carbon cloth (Pyrofil TR3110M: Mitsubishi Rayon CO., LTD.) was used as reinforcement. Epoxy resin and modified aliphatic polyamines (Japan Epoxy Resins Co., Ltd) were used as matrix and curing agent respectively. Liquid rubber Carboxylated acrylonitrile butadiene copolymer (CTBN, Nipol DN601, acrylonitrine 20%, Zeon Chemicals, Japan) was used as modifier.

Preparation of MFC

MFC was solvent exchange with ethanol to remove water and then filtered by vacuum pump to obtain the sheet of MFC. The filtered sheet of MFC was stirred with additional amount of ethanol then sonicated for 10 minutes by using ultrasonic homogenizer.

Sample Preparation

MFC 0.0, 0.3 wt% were prepared to examine the effect of addition cellulose fibers on the mechanical properties of the composite modified with CTBN. The desired amount of epoxy was added into MFC ethanol suspension mixed for five minutes. The modifier content was 1, 3 and 5 phr based epoxy. Epoxy MFC rubber mixtures were mixed at room temperature for 10min. The mixture heated for three days at 85 °C in an electric oven. The calculated amount of curing agent was added and the mixture was stirred for 5min and then degassed in a vacuum oven for 10min. The mixture was hand lay-upped with plain woven carbon fiber which its fraction of volume was the 50 \pm 2%.

Tensile Tests

The tensile properties of samples were measured using a Shimadzu Autograph universal testing machine. The specimen gage length was 100mm and the testing speed was set to 1mm/min. The specimen dimension was 200x25x2 according to

JIS K7073, glass fiber reinforced plastic (GFRP)/Epoxy tabs were attached at both ends of specimen by adhesive.

Fracture Toughness Test

The Double Cantilever Beam (DCB) mode I fracture specimen (JIS K 7086) was employed to characterize the delimination resistance. The corrections for the endblock, DCB arm bending and root rotation were considered. DCB tests are conducted using a universal mechanical testing machine. The recommended specimen size is at least 150mm long and 20mm wide with an initial crack length (i.e. the length of the insert from the load line) of 50mm (see Fig. 1). Hinges of the same width as the specimen were attached to allow load application. The Mode-I interlaminar fracture toughness G_{IC} and G_{IP} , for each MFC and CTBN content was calculated using the modified compliance calibration (MCC) method [18].

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

where G_{lC} is fracture toughness at initial crack stage, G_{lP} is fracture toughness at propagation stage, P_p is the applied load, δ_p is displacement, *C* is Compliance corresponding to each crack length, *a* is crack length, P_c is the initial maximum load, *B* is specimen width, *2h* is the thickness, *N* is end block correction factor, *F* is large displacement correction factor, and *m* is the slope of a plot of $(BC/N)^{1/3}$ versus (a/2h).

Scanning Electron Microscopy Observations

Fractured surfaces obtained from mechanical tests were examined by scanning electron microscopy (SEM) using JSM-7001FD equipment. Prior to SEM observation, all samples were sputter coated with a thin layer of gold to avoid electrical charging.

RESULTS AND DISCUSSION

Tensile Properties

The effect of the CTBN contents on the large strain behavior of CF/Epoxy composites filled with MFC was investigated up to their failure. Table 1 shows the tensile strength and strain at break. For unfilled composite, the tensile strength decreased with addition 1phr CTBN and maintained its decrease at 3, and 5phr. A gradual increase for composites filled with 0.3% MFC at 1, and 3phr CTBN followed by slight decrease with addition 5phr CTBN. This may be due to the increase in the relative amount of dissolved rubber as rubber content increases [16]. Although there is tendency to increase strength for composite filled with addition of MFC, the increase was no significant. Qingzheng cheng et al [19] prepared polyvinyl alcohol (PVA) nanocomposite reinforced with different types of cellulose fibrils. They also reported that there is no significant difference for tensile strength and young's modulus with addition 2 wt% MFC to PVA compared to neat PVA which agree with the results obtained for the effect of MFC in this study. The improvements of tensile strength as well as strain at break due to the addition of MFC were not as high as those of microfibers generated from wood pulp [20] and soybean [21]. Most reports

	MFC (%)	CTBN (phr)	Tensile Strength (Mpa)		Strain at break (%)	
CF/Ep/MFC ₀ /CTBN ₀	0	0	640	± 23	5.191	± 0.11
CF/Ep/MFC _{0.3} /CTBN ₀	0.3	0	640.043	± 43	5.367	± 0.21
CF/Ep/MFC ₀ /CTBN ₁	0	1	632	± 31	5.285	± 0.07
CF/Ep/MFC ₀ /CTBN ₃	0	3	631	± 41	5.897	± 0.09
CF/Ep/MFC ₀ /CTBN ₅	0	5	628.781	± 29	4.977	± 0.12
CF/Ep/MFC _{0.3} /CTBN ₁	0.3	1	667.428	± 44	6.315	± 0.19
CF/Ep/MFC _{0.3} /CTBN ₃	0.3	3	683.033	± 39	5.553	± 0.15
CF/Ep/MFC _{0.3} /CTBN ₅	0.3	5	637.797	± 41	5.336	± 0.09

Table 1. Tensile strength and break at strain of each CTBN weight at different ratios of MFC.

have attributed the strong reinforcing effect of the cellulose to the formation of a networked structure above percolation threshold resulting from hydrogen bonding [22]. In this work, possibly no network structure was formed due to low MFC loadings. The reinforcing effect of MFC is a direct result of the interaction of the fiber and polymer, as well as the rigidity of the web-like structure. A higher concentration threshold is required to introduce interactions between fibrils so that a network can be formed [23]. The strain at break, determined from the typical stress-strain curve, showed little decrease for composites modified with 5phr while, showed a slight increase for composites filled with MFC at 1phr CTBN.

Mode-I Interlaminar Fracture Toughness

Double cantilever beam (DCB) tests were performed and the mode I interlaminar fracture toughness, G_{lc} was determined. The typical load displacement curves recorded during the interlaminar fracture test for CF/epoxy composite filled with MFC contents modified with CTBN are shown in Fig. 2. Step by step variations in the crack opening load of all specimens are observed. Severe steps are clearly observed for unfilled unmodified CF/Epoxy. It's seen that the specimens filled with MFC contents showed more stable and gradual crack growth than unfilled specimens. It was more pronounced that at 0.3% MFC and 1% CTBN, the crack propagates more stable and gradually as well as almost all peaks rather than first peak showed closed values which could be attribute to higher crack closure force exerted incorporating MFC and CTBN with carbon fibers.

The delamination resistance curves (R-curves) are drawn between crack length (a) and the corresponding fracture toughness as shown in Fig. 3. High deviations are noted particularly for some fabric composites, probably as a consequence of the complex translaminar crack growth mechanism acting in the material. It has been observed that inside unfilled unmodified resin rich layers the crack growth rate propagates smoothly as a result of the relatively low tenacity of the polymeric phase with carbon fiber; on the other hand, in the resin rich layers filled and modified with

MFC and CTBN, the crack is deflected and pinned by the reinforcing obstacles so that more energy is required, resulting in increasing fracture toughness.

The G_{lc} value corresponding to first crack initiation is determined from the load point at which the initiation of delamination is microscopically observed on the specimen edge. In this investigation, both delamination initiation and delamination propagation mode I fracture toughness values are plotted in Fig. 4 and Fig.5. The delamination initiation mode I fracture toughness values reported throughout this investigation correspond to first peak load in the load–crack opening displacement curves, while the delamination propagation mode I fracture toughness values are taken from the plateau region of the R-curves.

Various reasons such as intra-laminar delamination, fiber-bridging, micro-cracking, residual stresses, or a combination of these effects of lamina at interface caused the development of transverse intralaminar and unstable crack propagation in DCB tests [24]. The experimental results show that addition of CTBN to composite filled with MFC affects the G_{IC} and G_{IP} . As shown in Fig.4, the initial fracture toughness was increased about 18% from 407J/m² for unfilled unmodified CF/Epoxy to 497J/m² for 0.3%wt addition of MFC, while with addition 5phr of CTBN, the fracture toughness was increased by 15% from 407J/m² for unfilled unmodified CF/Epoxy to 466J/m² using MCC method. A more significant increase was observed for the initial fracture toughness increased about 39% from 407J/m² for unfilled unmodified CF/Epoxy to 565J/m². The propagate fracture toughness was further improved by 57% from 337J/m² for unfilled unmodified CF/Epoxy to 529J/m². These results suggest that CF/Epoxy composite filled with 0.3% MFC modified with 1phr CTBN gives better results which agree with other researches [13].

SEM Observations

Two distinct regions exist in Fig 6(a) showing micrograph of CF/Epoxy filled 0.3%MFC modified 1phr CTBN: the first is the rough region showing reinforced adhesion, while the second one in front of the tip of film insert contains remnants of the CFRP substrate. The rough areas of the CFRP suggest a stronger bond exists at the interface as a result of the strengthening effect resulting from the dispersed nanofillers with liquid rubber. In front of the tip, fiber breakage takes place during initiation delimination. Fiber breakage results from fiber–polymer interaction, fiber–fiber interaction, and fiber contact with surfaces of processing equipment. Fiber–polymer interaction promoted a large number of carbon fiber to break at the fracture surfaces resulting in consuming substantial fracture energy.

The micrographs in Fig. 6(b), CF/Epoxy filled 0.3 MFC modified 3phr CTBN, show stepwise topography at the end of the insert film and fiber/matrix interface debonding, indicating that delamination initiation was dominated by the failure of the fiber/matrix interface. The distinct feature of the fracture surface is matrix deformation between clean fibers devoid of the matrix, indicating tearing (or drawing) of the matrix and interfacial debonding.

In Figure 6(c), the fracture surface at CF/Epoxy filled 0.3% MFC modified 5phr CTBN consists mainly of resin microflow lines and river patterns, which are characteristic of

brittle cleavage matrix fracture. However, the river marks in the matrix fracture area of the composite appear not to coincide with the macroscopic crack growth direction, which may indicate various directions of local microcrack growth due to interference of fibers during interlaminar crack growth. The matrix deformation between fibers with interfacial debonding remains the dominant fracture feature accounting for increase fracture toughness.

Figure 6(d) show that addition 1phr CTBN to CF/epoxy resulted in high wettability leading to improve interfacial bonding between fiber and matrix. With addition 3, and 5phr CTBN the fracture occurred predominantly at the fiber/matrix interface as reflected by the bare fibers and cavities left by fibers on the fracture surfaces as shown in Fig.6(e, and f), which indicates poor fiber/matrix adhesion. Although some broken fibers are observed on the fracture surfaces, the fiber bridging mechanisms, common in mode I fracture of unidirectional composites [25], appear not to be a major energy-absorbing mechanism for the plain weave composite.

The matrix failure for CF/epoxy modified filled with 0.3% MFC as shown in Fig 6(g) appears very similar to the plastic deformation associated with shear lip formation for fracture surface of CF/Epoxy filled 0.3% MFC modified 1% CTBN (see Fig. 6(a)). The extensive matrix deformation between fibers with interfacial debonding as well as fiber breakage noted to be the dominant fracture feature.

CONCLUSION

In this study, we focused our attention to the to improve the interfacial adhesion between plain woven carbon fiber (CF) and epoxy matrix filled with microfibrillated cellulose (MFC) modified with carboxyl-terminated butadiene acrylonitrile (CTBN) as liquid rubber. The work concentrated on the experimental determination of the tensile, and fracture toughness properties of the CF/Epoxy/BC/CTBN composite. The results reveal that a given weight of MFC fibre content 0.3% and 1phr CTBN plays a major role to improve initiation and propagation interlaminar fracture toughness in mode I significantly by 39% and 57% respectively which could be attribute to strong adhesion between filled epoxy, carbon fiber and rubber. This can be explained by SEM at given weight, in front of the insert film, fiber breakage takes place during initiation delimination resulting in consuming substantial fracture energy as well as the rough areas of the CFRP confirm a stronger bond between fiber and matrix.

Although there is tendency to increase tensile strength for composite filled with addition of MFC, the increase was no significant.

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Fig. 1. Geometry of DCB specimen (all dimensions in mm).









Fig. 3. R-curves for each content of MFC and CTBN.





Fig. 4. Initiation fracture toughness for each weight of CTBN at different contents of MFC.



Fig. 5. Propagation fracture toughness at each weight of CTBN for different contents of MFC.

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Fig. 6. SEM for different ratios of MFC% / CTBN phr, (a)0.3/1, (b)0.3/3, (c)0.3/5, (d)0/1, (e) 0/3, (f) 0/5, (g)0.3/0, (h)0/0 showing the delamination direction at insert tip from the bottom to the top.