# FRACTURE TOUGHNESS IMPROVEMENT OF CFRP LAMINATES BY DISPERSION OF CUP-STACKED CARBON NANOTUBES

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**Keywords**: *CFRP, Cup-stacked carbon nanotube, fracture toughness, interlayer*

## *Abstract*

*Several techniques are introduced to enhance the interlaminar fracture toughness of CFRP laminates using cup-stacked carbon nanotubes (CSCNTs). Five types of CSCNT-dispersed CFRP laminates are prepared and Double Cantilever Beam (DCB) and End Notched Flexure (ENF) tests are performed in order to obtain mode-I and mode-II interlaminar fracture toughness. The measured fracture toughnesses are compared to that of CFRP laminates without CSCNT to evaluate the effectiveness of CSCNT dispersion for fracture toughness improvement. All CSCNT-dispersed CFRP laminates exhibit higher fracture toughness, and specificcaly, CSCNT-dispersed CFRP laminates with thin epoxy interlayers containing short CSCNTs have three times higher fracture toughness compared to CFRP laminates without CSCNT. SEM observation of fracture surfaces were also conducted to investigate the mechanisms of fracture toughness improvement.*

## 1 Introduction

Extensive attention has been paid to nanofibers and nanoparticles as the superior reinforcements of engineering polymers. Many nano-fillers (carbon nanotubes, nanoclays, etc.) have been incorporated into the traditional polymers in order to enhance the mechanical, thermal, electric, and gas/liquid barrier properties as well as to add multi-functionality[1-8].

Cup-stacked carbon nanotube (CSCNT) (or commonly named carbon nano-fiber) is also considered to be a superior candidate for the polymer modifier[9]. Figure 1 shows the schematic view of the used CSCNT, CARBERE® manufactured by GSI CREOS Corporation in Japan. This type of CNT has novel structural characteristics such as a larger hollow core and a larger portion of open ends than other CNT's. Several layers of truncated conical graphene sheets are stacked and placed in relation to each other like metal bellows. The diameter range of the present CSCNT's is 80–100 nm and their length could be up to 200 μm. The growth conditions of CSCNT can be precisely controlled in a production method of chemical vapor deposition (CVD) with the use of a floating reactant method[9]. Stacking morphology of truncated conical graphene sheets exhibits an angle to the fiber axis and almost every portion of the graphene sheet edges are exposed to the outside. This nano-structure of CSCNT suggests the advantage in the load transfer between CSCNT and polymer matrix to prevent the graphene sheet sliding. Therefore, dispersion of CSCNTs into the polymers results in the improvement of the mechanical and electric properties of the polymers[10].

The incorporation of nano-fillers into the polymers is also expected to result in the improvement of the mechanical properties of three-phase nanocomposites consisting of traditional long fibers and nano-fillers-dispersed polymers. Although researches on two-phase nanocomposites consisting of nano-fillers and polymers have been extensively performed using many types of nano-fillers and polymers based on several dispersion techniques including surface treatment of nano-fillers, successful processing and characterization of three-phase nanocomposites have been rarely reported[11-17].

The goal of this research is mainly to improve the weak points in mechanical properties of CFRP laminates by using nano-reinforcements. As the conventional CFRP laminates have enough tensile properties, exceptional strength improvement of resin in tension is not necessary in our concept. Instead, compressive properties and fracture resistance of CFRP laminates would be improved by using nano-fillers. Therefore, CSCNTs are selected as nano-fillers because of their merit in load transfer between CNT and polymer. As the previous researches indicated the improvement of compressive strength and resistance against matrix crack accumulation of CFRP by using CSCNTs[16,17], this study focuses on the improvement of interlaminar fracture toughness. Several techniques are introduced to enhance the interlaminar fracture toughness of CFRP, and DCB and ENF test are performed. Comparative study of the fracture toughness of CSCNT-dispersed CFRPs is presented.

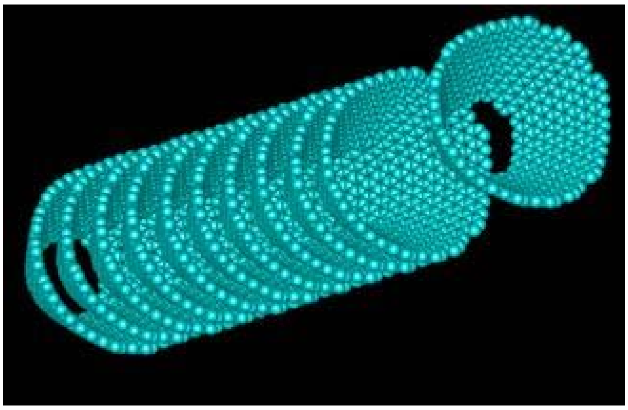


Fig. 1. Cup-stacked carbon nanotube, CARBERE®.

## 2 Strategy

It is widely recognized that tough resin and tough interlayers have been used in order to improve the fracture toughness of CFRP. Although interlaminar toughness is improved by using tough resin, compressive strength may decrease due to decrease in stiffness of the used resin. The authors expect that dispersion of CSCNTs into epoxy results in increase in fracture surface due to crack deflection without loss of compressive stability. In addition, existence of CSCNT-dispersed resin between the layers is expected to contribute the enhancement of interlaminar fracture toughness. In order to place CSCNT-dispersed resin between the layers, the following methods are introduced herein.

- Sprinkle of CSCNTs between the layers during layup
- Placement of CSCNT-dispersed resin films between the layers during layup

This study investigates the effectiveness of the presented methods for the improvement of interlaminar fracture toughness of CFRP. The effect of the aspect ratio of CSCNT used for interlayers is also examined. Therefore, six types of CFRP were prepared in this study, as shown in Table 1. The following sections include the explanation of the prepared samples, the experimental procedures and the experimental results.

Table 1. Prepared samples

| Sample | Type | CSCNT in epoxy | CSCNT in interlayers |
|---|---|---|---|
| A | No CNT<br>(Control) | - | - |
| B | CNT in epoxy<br>No CNT in interlayer | AR10<br>5wt% | - |
| C | CNT in epoxy<br>CNT sprinkle | AR10<br>5wt% | AR10<br>$10g/m^2$ |
| D | CNT in epoxy<br>CNT-dispersed film | AR10<br>5wt% | AR10<br>10wt% |
| E | CNT in epoxy<br>CNT sprinkle | AR10<br>5wt% | AR100<br>$10g/m^2$ |
| F | CNT in epoxy<br>CNT-dispersed film | AR10<br>5wt% | AR100<br>10wt% |

## 3 Experimental Procedure

### 3.1 Materials and Sample Preparation

The CSCNTs used in this study were CARBERE® (GSI Creos Corporation), see Fig. 1. In order to control the lengths of CSCNTs for successful dispersion into the epoxy, CSCNTs were subjected to the dry mill using zirconia beads. The resulting nominal aspect ratio of CSCNTs was 10 (designated as AR10) and 100 (designated as AR100). No surface treatment was applied to CSCNTs within this study. The resins used were bisphenol-A based epoxy, EP827 (Japan Epoxy Resin Co. Ltd), and dicyandiamide was used as the curing agent. In order to disperse CSCNTs into the epoxy resin, two-step mixing procedures were employed; EP827 epoxy and CSCNTs were combined using the planetary mixer at 70°C, and then, CSCNTs were dispersed using the wet mill with zirconia beads at 70°C for 45 minutes. The blended CSCNT-dispersed epoxy was diluted with EP827, and the curing agent was added to the compounds. Three types of CSCNT-dispersed epoxy with weight fractions of CSCNTs to the compound of 0, 5 and 10 were prepared. All these processes were conducted by GSI Creos Corporation.

Unidirectional prepregs were developed using T700SC-12K fibers and the above-mentioned epoxy filled with 0 and 5wt% CSCNTs. The prepreg fiber areal weight was set to 125 g/m$^2$ and the nominal resin content including CSCNTs was 33 wt%. The nominal ply thickness was 0.12 mm. In addition, CSCNT-dispersed epoxy films (10wt%) were prepared using AR10 and AR100 CSCNTs.

Six types of unidirectional CFRP were prepared (see Table 1);

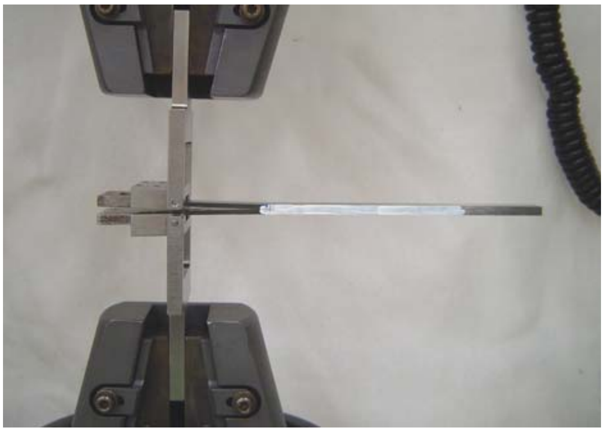
A) CFRP without CSCNT (control)
B) CFRP using 5wt% CSCNT-dispersed epoxy
C) CFRP using 5wt% CSCNT-dispesed epoxy with 10g/m$^2$ sprinkle of AR10 CSCNT between layers
D) CFRP using 5wt% CSCNT-dispersed epoxy with 10wt% AR10 CSCNT-dispersed film between layers
E) CFRP using 5wt% CSCNT-dispesed epoxy with 10g/m$^2$ sprinkle of AR100 CSCNT between layers
F) CFRP using 5wt% CSCNT-dispersed epoxy with 10wt% AR100 CSCNT-dispersed film between layers

Unidirectional $[0]_{36}$ laminates were stacked and fabricated using an autoclave. Placement of interlayers and CSCNT sprinkle were only performed between the middle layers where crack propagates in this study. In order to induce the initial cracks between the middle layers, thin release films were partially placed during fabrication. The laminates were subjected to a pressure of 490 kPa and the curing temperature of 130°C for the duration of two hours. The resulting volume fractions of the carbon fiber were about 60% for all composites.

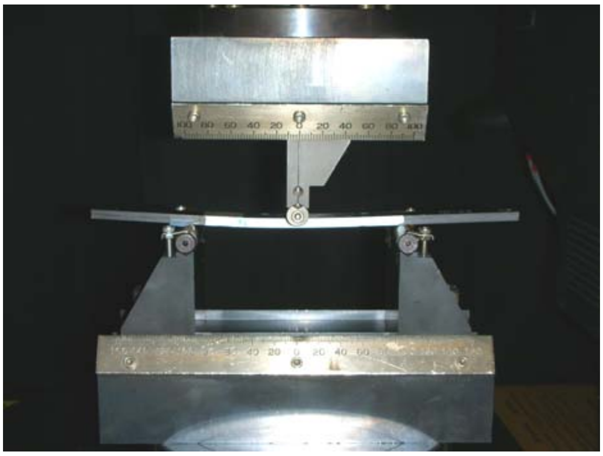
## 3.2 Test Procedure

In order to evaluate mode-I and mode-II interlaminar fracture toughnesses, DCB and ENF tests were performed, respectively, for the six types of laminates using a mechanical testing machine (5882, Instron Co. Ltd.) at RT. Specimens of 200 mm length and 12.7 mm width were cut from the fabricated $[0]_{36}$ panels, and pre-cracks were carefully introduced in order to avoid blunt crack tips.

The mode-I interlaminar fracture toughnesses were measured as a function of the crack growth using the experimental compliance method acording to JIS K 7086 standard. Crack lengths were visually observed from both sides of the specimens. In ENF test, three point bending was applied to the specimens with the span length of 100 mm. The mode-II interlaminar fracture toughness was evaluated using the equation based on the beam theory with crack length correction in reference to JIS K 7086. The apparatus of DCB and ENF tests are shown in Fig. 2.



(a) DCB test



(b) ENF test
Fig. 2. Test apparatus.

## 4 Results and Discussions

### 4.1 Mode-I Interlaminar Fracture Toughness

Typical R-curves (crack growth vs. mode-I interlaminar fracture toughness) are plotted in Fig. 3, which shows the comparison among sample A, B and D. Although almost no increase in fracture toughness in conjunction with crack growth in the case of sample A (CFRP without CSCNT), slight toughness increase can be observed in other CFRPs. The evaluated fracture toughnesses between the crack growth length of 20 mm and 60 mm are averaged and summarized in Fig. 4. The error bars express the standard deviations. All CSCNT-dispersed CFRPs (B~F) have high fracture toughness compared to CFRP without CSCNT. Specifically, sample D exhibits the highest fracture toughness. Note that only use of CSCNT-dispersed epoxy (sample B) contributes to increase in fracture toughness.

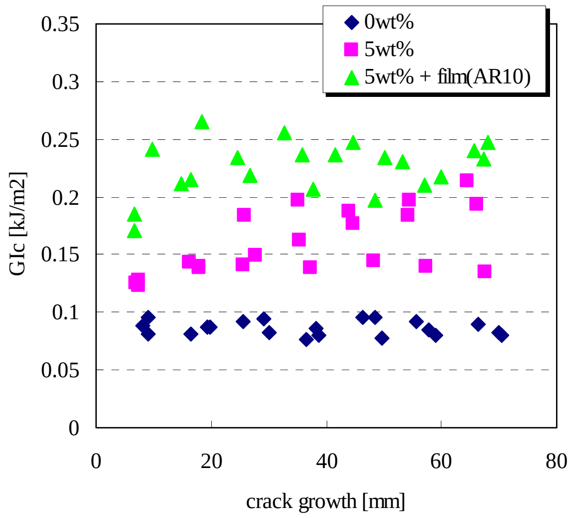


Fig. 3. R-curves in DCB tests.

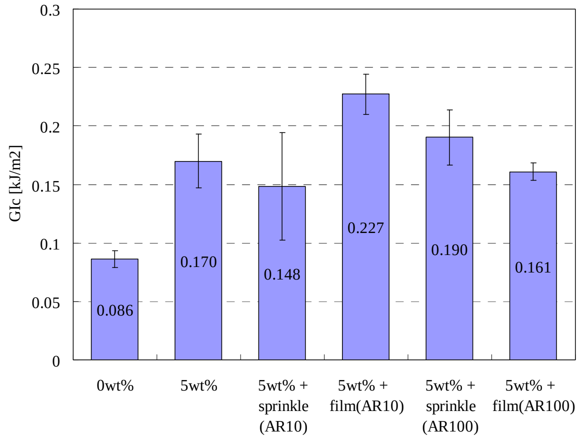


Fig. 4. Comparison of mode-I fracture toughness.

## 4.2 Mode-II Interlaminar Fracture Toughness

Typical load-deflection curves are summarized in Fig. 5. The evaluated mode-II fracture toughnesses are summarized in Fig. 6. All CSCNT-dispersed CFRPs (B~F) have high fracture toughness compared to CFRP without CSCNT. Specifically, sample D exhibits the highest fracture toughness (about three times higher than sample A), which coincides with the trend in the case of mode-I toughness. The results of DCB and ENF tests exhibit similar improvement of fracture toughness by using CSCNTs.

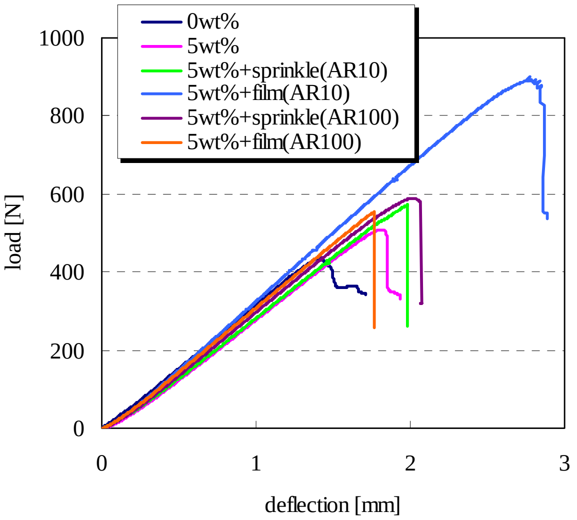


Fig. 5. Load-deflection curves in ENF tests.

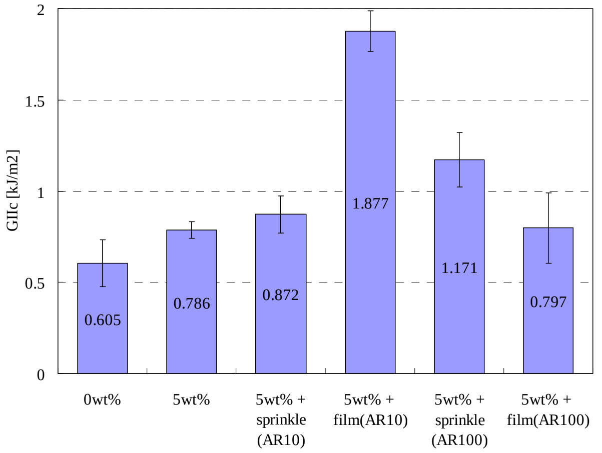
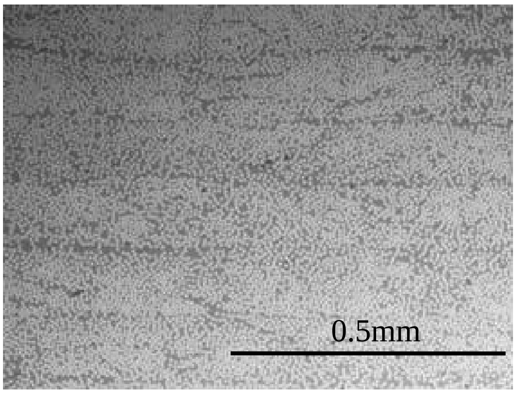


Fig. 6. Comparison of mode-II fracture toughness.

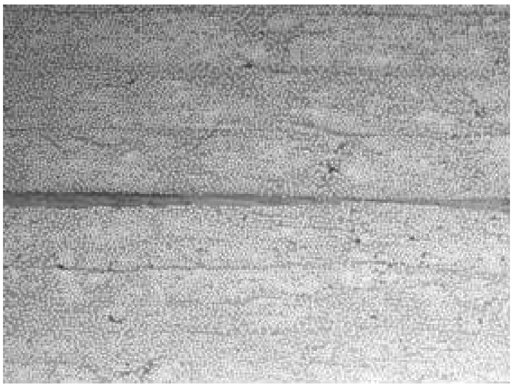
## 4.3 Cross-sectional Observation

In order to discuss the quality of the prepared samples, cross-sectional views were checked using an optical microscope. Cross-sections including interlayers perpendicular to the fiber direction were observed and compared among six laminates in Fig. 7. It is recognized that manufactured composite laminates have good quality except interlayer regions. CSCNT sprinkle seems to induce non-uniform thickness of the interlayers, which causes slight improvement and large scatter (see Fig. 4) in fracture toughness due to fiber bridging, whereas use of CSCNT-dispersed films results in uniform interlayers. Note that Sample D (using AR10 CSCNT-dispersed film) has resin-rich interlayers containing carbon fibers, which might be the reason



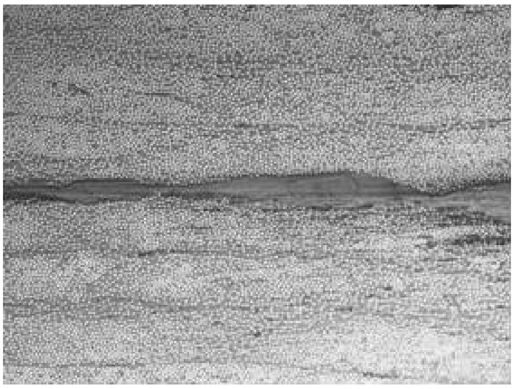
(a) Sample A (0wt%)

(b) Sample B (5wt%)



(c) Sample C (5wt% + sprinkle-AR10)

(d) Sample D (5wt% + film-AR10)



(e) Sample E (5wt% + sprinkle-AR100)

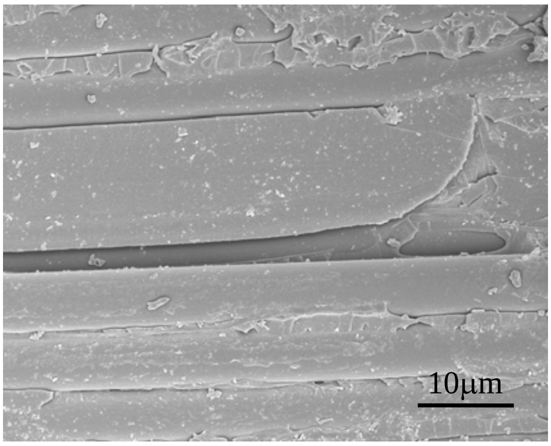
(f) Sample F (5wt% + film-AR100)

Fig. 7 Comparison of cross-sections

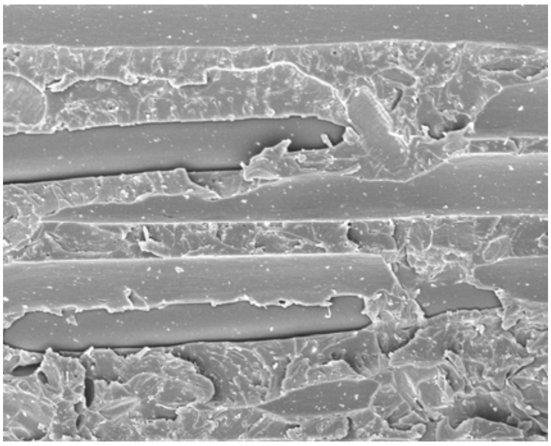
of significant increase in fracture toughness. In contrast, Sample F (using AR100 CSCNT-dispersed film) has thick interlayers, which might result in slight improvement compared to Sample D.

## 4.4 SEM Observation of Fracture Surfaces

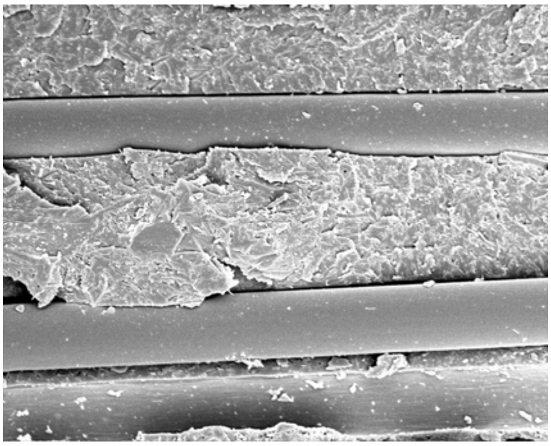
Fracture surface observation by SEM (S-4700, Hitachi Ltd.) was conducted to investigate the mechanism of the enhancement of the fracture toughness. Fracture surfaces of DCB specimens are compared among laminates A, B and D, as shown in Fig. 8. Sample B and D have clearly rough surfaces compared to Sample A. The SEM images of the ENF specimens are also presented in Fig. 9 (Sample A, B and D). This figure reveals that Sample B and D have rougher surfaces than Sample A, and specifically, Sample D have much rougher fracture surfaces. These results of fracture surface observation coincides with the experimental results that the measured fracture toughnesses of Sample B and D are higher than that of Sample A, and mode-II toughness of Sample D is much higher than that of Sample A. Other types of laminates have rough surfaces compared to Sample A. This result indicates that the incorporation of CSCNT into the conventional CFRP creates fracture surface increase due to crack deflection, which may cause the enhancement of interlaminar fracture toughness. It is demonstrated that Sample D (5wt% + film-AR10) is most effective for fracture toughness improvement.



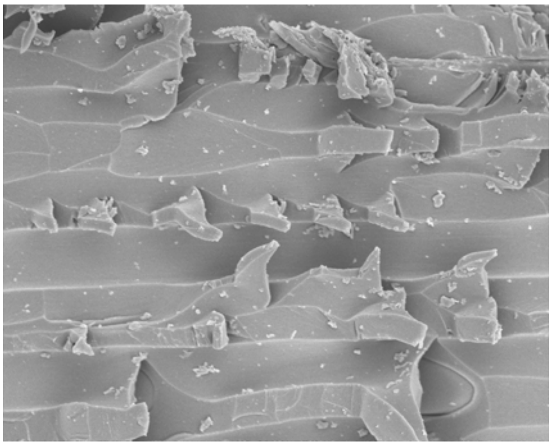
(a) Sample A (0wt%)



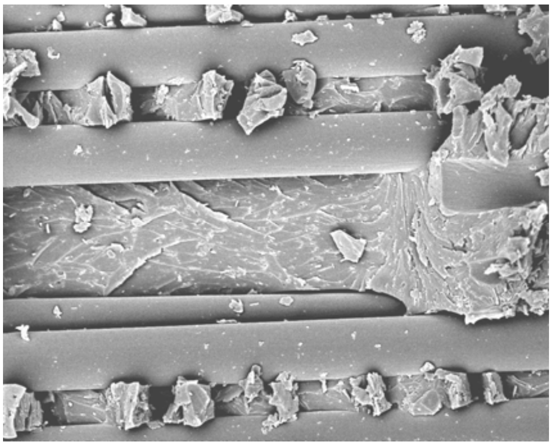
(b) Sample B (5wt%)



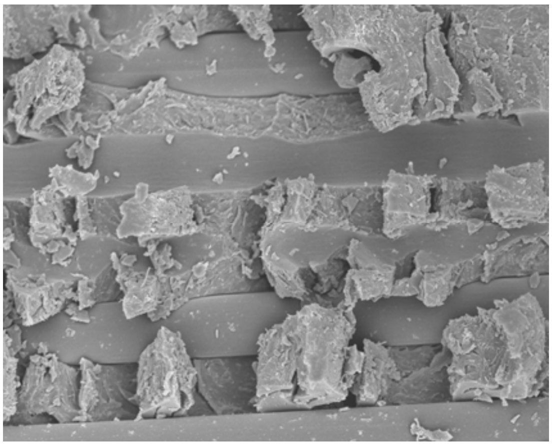
(c) Sample D (5wt% + film-AR10)
Fig. 8 SEM images of fracture surfaces of DCB specimens



(a) Sample A (0wt%)



(b) Sample B (5wt%)



(c) Sample D (5wt% + film-AR10)
Fig. 9 SEM images of fracture surfaces of ENF specimens

## 5 Conclusions

This study focuses on the improvement of interlaminar fracture toughness of CFRP using CSCNT-dispersed resin. Five types of specimens using interlayer techniques were prepared in addition to control samples (traditional CFRP), and

DCB and ENF test were performed. The evaluated results indicated that interlaminar fracture toughnesses can be improved using CSCNT-dispersed resin (up to 300%). The use of CSCNT-dispersed epoxy resulted in fracture toughness improvement, and the placement of CSCNT(AR10)-dispersed films was most effective for enhancement of fracture resistance. SEM observations of fracture surfaces indicated that samples with higher measured toughness have rough surfaces. It is considered that the incorporation of CSCNT into the conventional CFRP creates fracture surface increase due to crack deflection, which may cause the enhancement of interlaminar fracture toughness.

## Acknowledgement

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