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Fracture toughness improvement of CFRP laminates by dispersion of cup-stacked carbon nanotubes

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ABSTRACT

Several techniques are introduced to enhance the interlaminar fracture toughness of CFRP laminates using cup-stacked carbon nanotubes (CSCNTs). Prepared CSCNT-dispersed CFRP laminates are subject to Double Cantilever Beam (DCB) and End Notched Flexure (ENF) tests 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 the improvement of fracture toughness. All CSCNT-dispersed CFRP laminates exhibit higher fracture toughness, and specifically, CSCNT-dispersed CFRP laminates with thin epoxy interlayers containing short CSCNTs have three times higher fracture toughness than CFRP laminates without CSCNT. SEM observation of fracture surfaces is also conducted to investigate the mechanisms of fracture toughness improvement. Crack deflection mechanism is recognized in the CSCNT-dispersed CFRP laminates, which is considered to contribute the enhancement of interlaminar fracture toughness.

1. Introduction

Many nano-fillers (carbon nanotubes, nanoclays, etc.) have been considered to be applied as the modifiers of the traditional polymers in order to enhance the mechanical, thermal, electric, and gas/liquid barrier properties or to add multi-functionality [1–8]. Among them, carbon nanotubes (CNTs) have been reported to possess exceptional mechanical properties (e.g. extensional stiffness ~1 Tpa for multi-walled CNTs, MWCNTs) [3] and considered to be the most promising class of nano-fillers.

Cup-stacked carbon nanotube (CSCNT) also attracts a great deal of attention as a superior candidate for the polymer modifier [9]. Fig. 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 of the present CSCNTs is about 80 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 is expected to have the advantage in the load transfer between CSCNT and polymer matrix to prevent the graphene sheet sliding. It was reported that 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 contribute to 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 [11–18].

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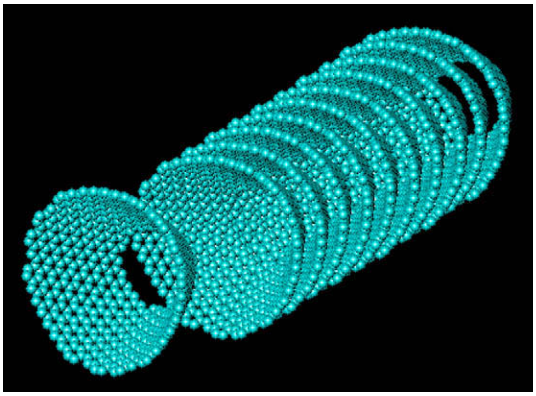

Fig. 1. Cup-stacked carbon nanotube, CARBERE®.

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 interlaminar fracture toughness. Several techniques are proposed for the improvement of the interlaminar fracture toughness of CFRP, and prepared samples are subject to DCB and ENF tests in order to evaluate the mode-I and mode-II interlaminar fracture toughness. Comparative study of the fracture toughness of CSCNT-dispersed CFRPs and traditional CFRP (without CSCNT) is presented.

2. Experimental procedure

2.1. Strategy for the improvement of interlaminar fracture toughness

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, in-plane properties may be sacrificed (e.g., compressive strength decreases 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 in-plane properties. In addition, existence of thin layers of CSCNT-dispersed resin between the plies of CFRP is expected to contribute the enhancement of interlaminar fracture toughness with minimal loss of in-plane properties. 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.

Note that the interlayer method similar to the former method was recently investigated by Arai et al. [18], and the improvement of interlaminar toughness of CFRP was reported. This study investigates the effectiveness of the presented methods for the improvement of interlaminar fracture toughness of CFRP using CSCNTs with different aspect ratios, and effects of the interlayer method and the aspect ratios of CSCNT used for interlayers are 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 (control)	–	–
B	CNT in epoxy No CNT in interlayer	AR10, 5 wt%	–
C	CNT in epoxy CNT sprinkle	AR10, 5 wt%	AR10, 10 g/m^2
D	CNT in epoxy CNT-dispersed film	AR10, 5 wt%	AR10, 10 wt%
E	CNT in epoxy CNT sprinkle	AR10, 5 wt%	AR100, 10 g/m^2
F	CNT in epoxy CNT-dispersed film	AR10, 5 wt%	AR100, 10 wt%

2.2. Materials and sample preparation

The CSCNTs used in this study were CARBERE® (GSI Creos Corporation), see Fig. 1. The average diameter ranged from 70 to 80 nm. In order to control the lengths of CSCNTs, CSCNTs were subject to the dry mill using ceramic beads. Two kinds of CSCNTs with aspect ratio of about 10 (designated as AR10) and 100 (designated as AR100) were prepared. This information was obtained by direct measurement of CSCNTs using SEM. The details of this measurement are given in Ref. [19]. 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, and then, CSCNTs were dispersed using the wet mill with ceramic beads for 45 min. 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 wt% were prepared.

Unidirectional prepregs were developed using T700SC-12K fibers and the above-mentioned epoxy filled with 0 and 5 wt% CSCNTs. The prepreg fiber areal weight was set to be 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 (10 wt%) were prepared using AR10 and AR100 CSCNTs.

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

(A) CFRP without CSCNT (control),
(B) CFRP using 5 wt% CSCNT-dispersed epoxy,
(C) CFRP using 5 wt% CSCNT-dispersed epoxy with 10 g/m^2 sprinkle of AR10 CSCNT between layers,
(D) CFRP using 5 wt% CSCNT-dispersed epoxy with 10 wt% AR10 CSCNT-dispersed film between layers,
(E) CFRP using 5 wt% CSCNT-dispersed epoxy with 10 g/m^2 sprinkle of AR100 CSCNT between layers, and
(F) CFRP using 5 wt% CSCNT-dispersed epoxy with 10 wt% 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 subject to a pressure of 490 kPa and the curing temperature of 130 °C for the duration of 2 h. The resulting volume fractions of the carbon fiber were about 60% for all composites.

2.3. Test procedure

In order to evaluate mode-I and mode-II interlaminar fracture toughness, 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 with 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 apparatus of DCB and ENF tests are shown in Fig. 2.

The mode-I interlaminar fracture toughness was measured as a function of the crack growth using the experimental compliance method according to JIS K 7086 standard [20]. Crack lengths were visually observed from both sides of the specimens, and the average length was regarded as the crack length in this study. In this method, the relationship between the crack length, a, and the compliance, λ (crack opening displacement divided by applied force, P) is approximated as

$$\left(\frac{a}{2H}\right) = \alpha_1 (B\lambda)^{\frac{1}{3}} + \alpha_0 \tag{1}$$

where $2H$ and B are the total thickness and the width of the specimen, respectively, and α_1 and α_0 are fitted parameters. The mode-I fracture toughness can be obtained by

$$G_{IC} = \frac{3}{2(2H)}\left(\frac{P}{B}\right)^2 \frac{(B\lambda)^{\frac{2}{3}}}{\alpha_1} \tag{2}$$

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 standard [20].

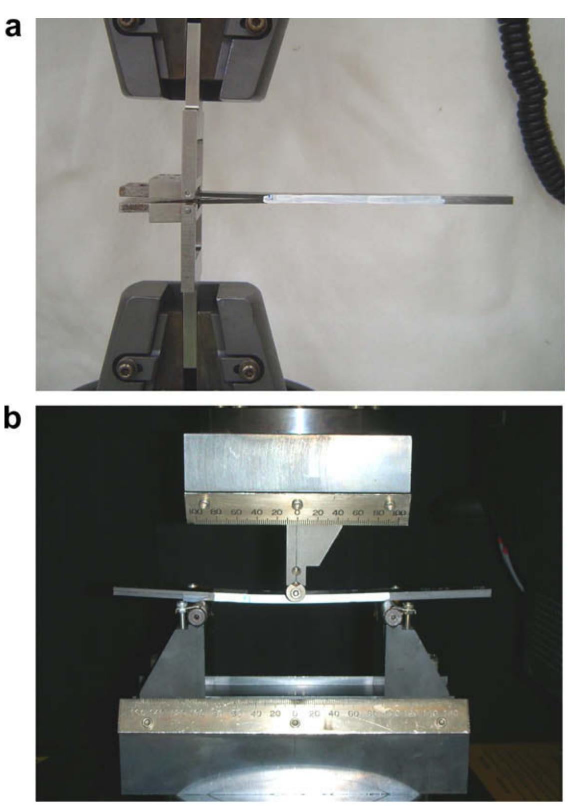

Fig. 2. Test apparatus: (a) DCB test, and (b) ENF test.

$$\begin{aligned} G_{IIC} &= \frac{9a_1^2 P_1^2 C_1}{2B(2L^3 + 3a_1^2)} \\ a_1 &= \left[\frac{C_1}{C_0} a_0^3 + \frac{2}{3}\left(\frac{C_1}{C_0} - 1\right) L^3\right]^{\frac{1}{3}} \end{aligned} \tag{3}$$

Here $2L$ is the span length of the supporting rods, C_0 and C_1 are the initial compliance and the compliance at crack propagation of ENF test, respectively, a_0 is the initial crack length from the supporting rod, P_1 is the applied load at crack propagation.

3. Experimental results

3.1. 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 samples 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 and 60 mm are averaged and summarized in Fig. 4 for all samples. The error bars correspond to the maximum and minimum values. All CSCNT-dispersed CFRPs (samples B–F) have high fracture toughness compared to CFRP without

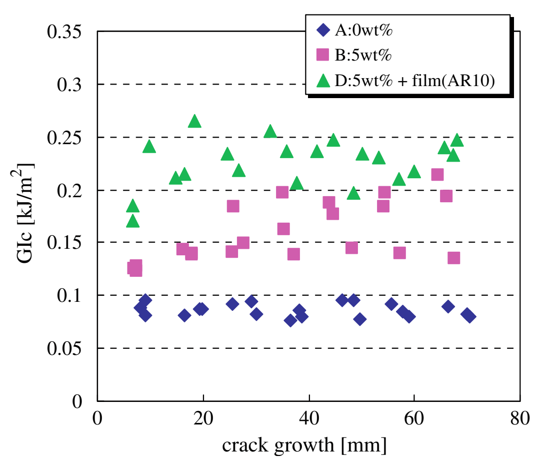

Fig. 3. Comparison of R-curves in DCB tests among samples A, B, and D.

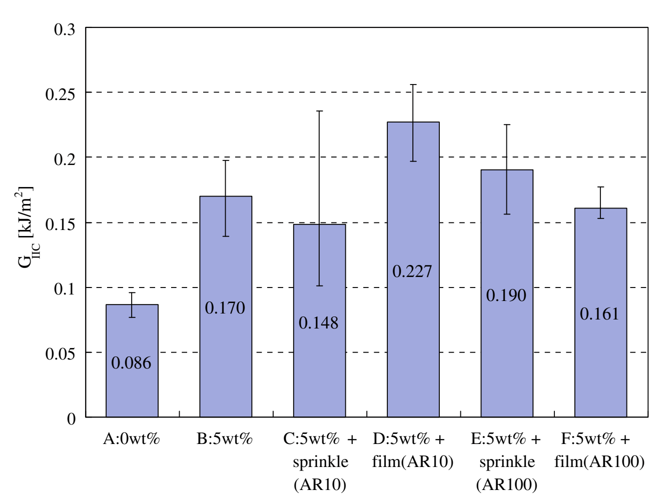

Fig. 4. Comparison of mode-I fracture toughness.

CSCNT (sample A). Specifically, sample D exhibits the highest fracture toughness. Note that only use of CSCNT-dispersed epoxy (sample B) contributes to increase in mode-I interlaminar fracture toughness.

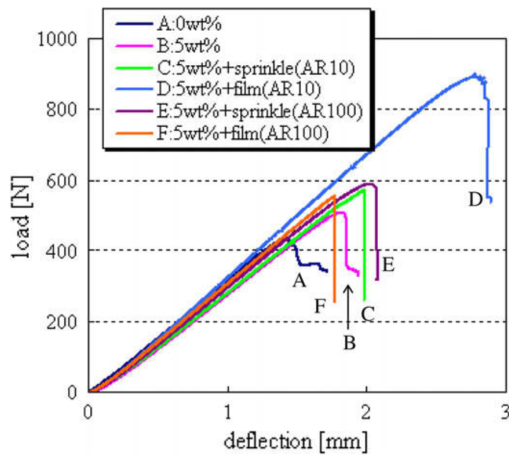

Fig. 5. Comparison of load–deflection curves in ENF tests.

3.2. 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.

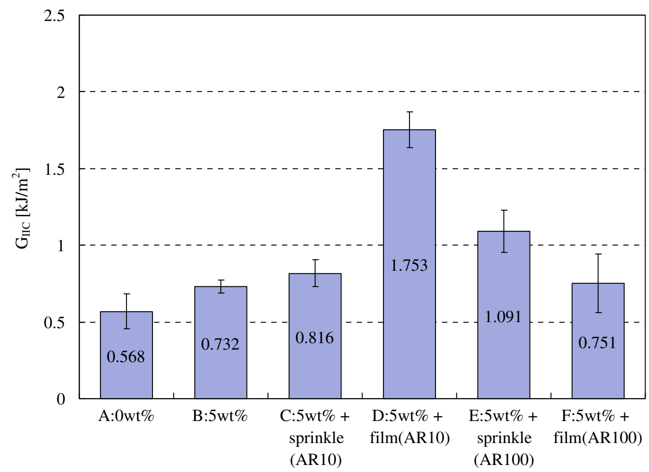

Fig. 6. Comparison of mode-II fracture toughness.

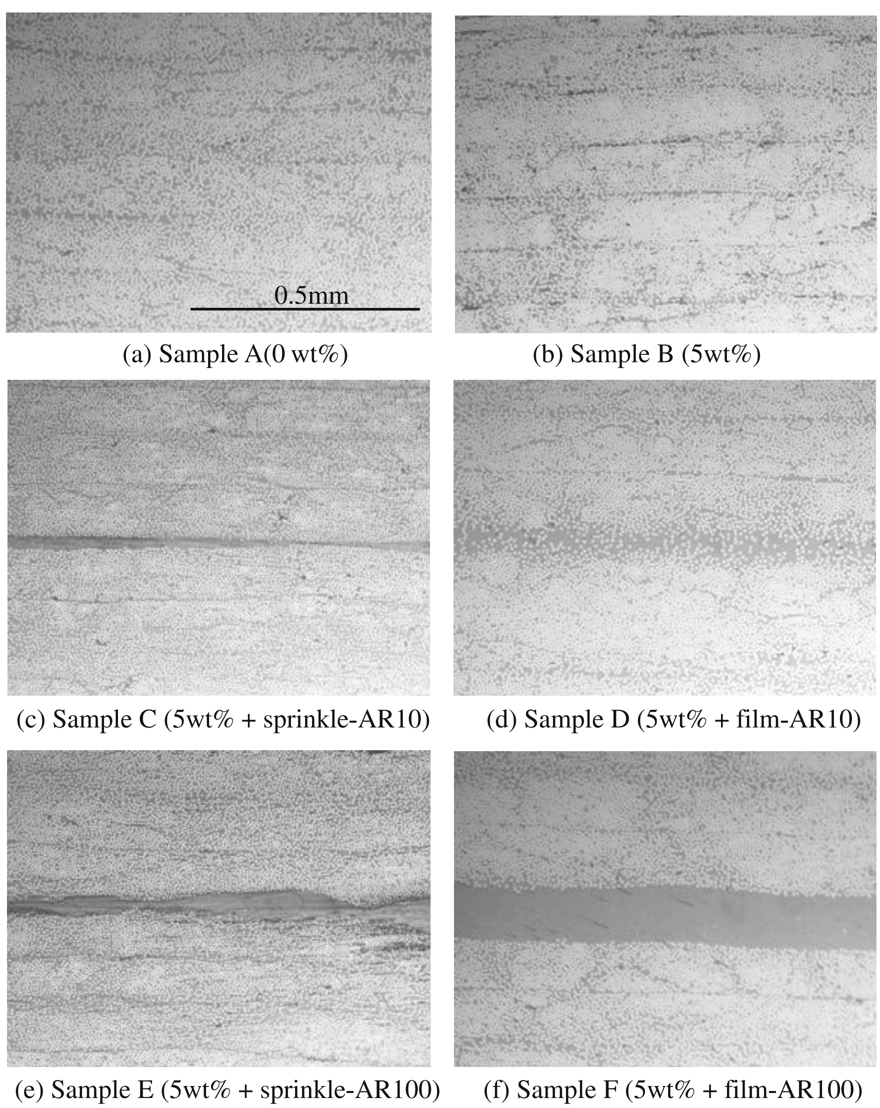

Fig. 7. Comparison of cross-sectional views perpendicular to fiber direction.

All CSCNT-dispersed CFRPs (B–F) have high fracture toughness compared to CFRP without CSCNT (A). 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.

3.3. 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 (0° direction) were observed and compared among six laminates as shown 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. In contrast, use of CSCNT-dispersed films results in uniform interlayers. Sample D (using AR10 CSCNT-dispersed film) has resin-rich interlayers containing carbon fibers, which might be the reason of significant increase in fracture toughness. Sample F (using AR100 CSCNT-dispersed film) has thick uniform interlayers, and this situation might reduce the in-plane mechanical properties. Thus, it is concluded that sample D has preferable manufacturing quality for the improvement of interlaminar fracture toughness.

The thickness of interlayer is considered to depend on the used CSCNTs. Comparison of Fig. 7d and f (or c and e) indicates that

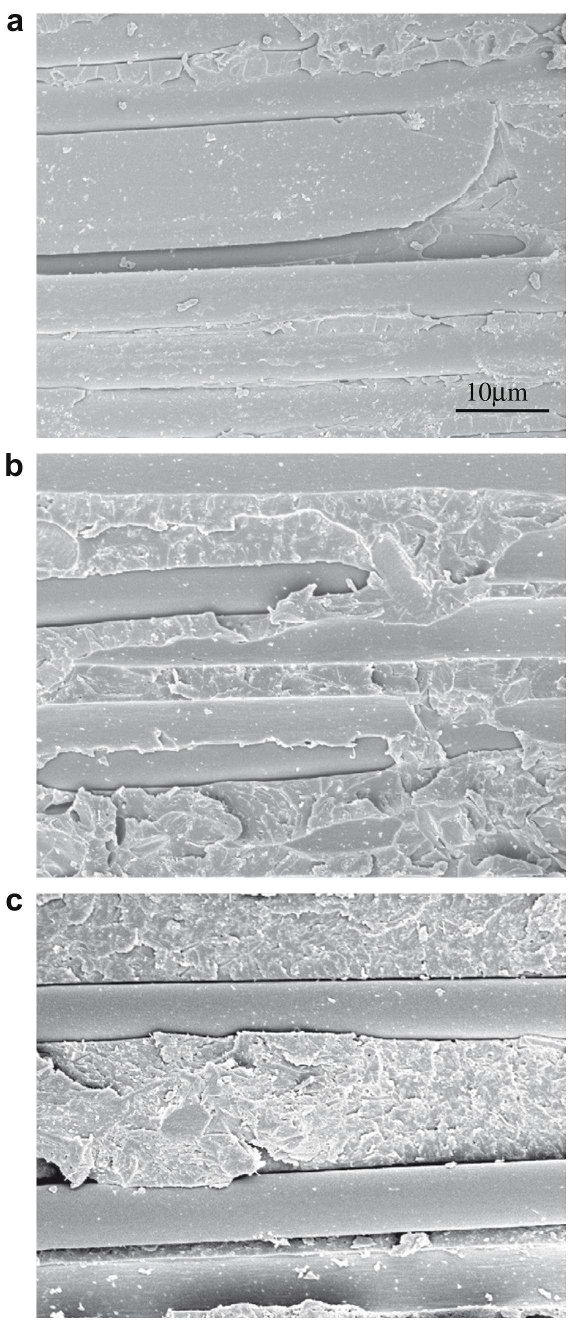

Fig. 8. SEM images of fracture surfaces of DCB specimens: (a) sample A (0 wt%), (b) sample B (5 wt%), and (c) sample D (5 wt% + film-AR10).

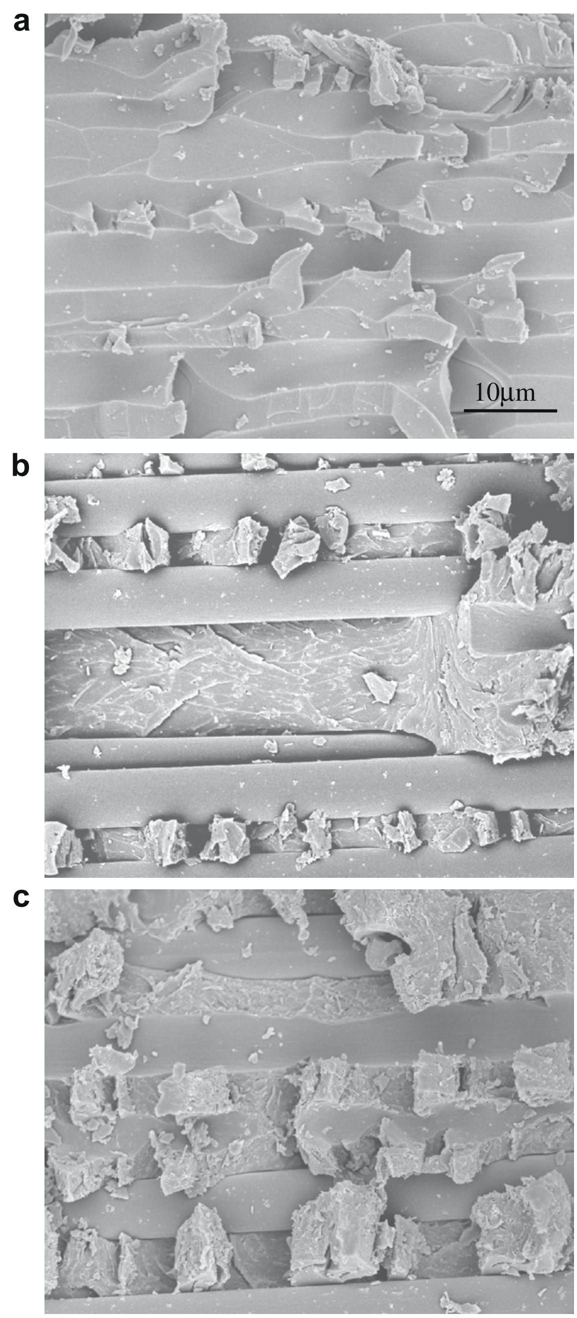

Fig. 9. SEM images of fracture surfaces of ENF specimens: (a) sample A (0 wt%), (b) sample B (5 wt%), and (c) sample D (5 wt% + film-AR10).

AR10 CSCNT-dispersed samples have thinner interlayers. AR10 CSCNT might be superior to AR100 CSCNT for the improvement of interlaminar fracture toughness of CFRP without loss of in-plane properties.

3.4. 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 samples 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 for samples A, B and D. This figure reveals that samples 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 (5 wt% + film-AR10) is most effective for the improvement of fracture toughness.

4. 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 without CSCNT), and DCB and ENF tests were performed. The evaluated results indicated that interlaminar fracture toughness 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 the enhancement of mode-I and mode-II fracture resistance. SEM observations of fracture surfaces indicated that samples with high measured toughness have rough surfaces compared to the control sample. 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.

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References

[1] Schadler LS. Polymer-based and polymer-filled nanocomposites. In: Nanocomposite science and technology. Weinheim: Wiley-VCH; 2003. p. 77–153.
[2] Kojima Y, Usuki A, Kawasaki M, Okada A, Fukushima Y, Kurauchi T, et al. Mechanical properties of nylon 6-clay hybrid. J Mater Res 1993;8:1185–9.
[3] Thostenson ET, Reng Z, Chou T-W. Advances in the science and technology of carbon nanotubes and their composites: a review. Compos Sci Technol 2001;61:1899–912.
[4] Gojny FH, Wichmann MHG, Fiedler B, Schulte K. Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites–a comparative study. Compos Sci Technol 2005;65:2300–13.
[5] Delozier DM, Watson KA, Smith JG, Connell JW. Preparation and characterization of space durable polymer nanocomposite films. Compos Sci Technol 2005;65:749–55.
[6] Liu W, Hoa SV, Pugh M. Fracture toughness and water uptake of high-performance epoxy/nanoclay nanocomposites. Compos Sci Technol 2005;65:2364–73.
[7] Kim JK, Hu C, Woo RSC, Sham M-L. Moisture barrier characteristics of organoclay-epoxy nanocomposites. Compos Sci Technol 2005;65:805–13.
[8] Ogasawara T, Ishida Y, Ishikawa T, Aoki T, Ogura T. Helium gas permeability of montmorillonite/epoxy nanocomposites. Composites A 2006;37:2236–40.
[9] Endo M, Kim YA, Hayashi T, Fukai Y, Oshida K, Terrones M, et al. Structural characterization of cup-stacked-type nanofibers with an entirely hollow core. Appl Phys Lett 2002;80:1267–9.
[10] Choi Y-K, Gotoh Y, Sugimoto K, Song SM, Yanagisawa T, Endo M. Processing and characterization of epoxy nanocomposites reinforced by cup-stacked carbon nanotubes. Polymer 2005;46:11489–98.
[11] Timmerman JF, Hayes BS, Seferis JC. Nanoclay reinforcement effects on the cryogenic microcracking of carbon fiber/epoxy composites. Compos Sci Technol 2002;62:1249–58.
[12] Siddiqui NA, Woo RSC, Kim J-K, Leung CRY, Munir A. Mode I interlaminar fracture behavior and mechanical properties of CFRPs with nanoclay-filled epoxy matrix. Composites A 2007;38:449–60.
[13] Subramaniyan AK, Sun CT. Enhancing compressive strength of unidirectional polymeric composites using nanoclay. Composites A 2006;37:2257–68.
[14] Thakre PR, Lagoudas DC, Zhu J, Barrera EV, Gates TS. Processing and characterization of epoxy/SWCNT/Woven fabric composites. AIAA Paper 2006–1857; 2006.
[15] Wichmann MHG, Sumfleth J, Gojny FH, Quaresimin M, Fiedler B, Schulte K. Glass-fibre-reinforced composites with enhanced mechanical and electrical properties–benefits and limitations of a nanoparticle modified matrix. Eng Fract Mech 2006;73:2346–59.
[16] Iwahori Y, Ishiwata S, Sumizawa T, Ishikawa T. Mechanical properties improvements in two-phase and three-phase composites using carbon nano-fiber dispersed resin. Composites A 2005;36:1430–9.
[17] Yokozeki T, Iwahori Y, Ishiwata S. Matrix cracking behaviors in carbon fiber/epoxy laminates filled with cup-stacked carbon nanotubes (CSCNTs). Composites A 2007;38:917–24.
[18] Arai M, Noro Y, Sugimoto K, Endo M. Mode I and mode II interlaminar fracture toughness of CFRP laminates toughened by carbon nanofiber interlayer. Compos Sci Technol 2008;68:516–25.
[19] Yokozeki T, Aoki T, Arai A, Ishibashi M, Yanagisawa T, Imai K, et al. Effect of CNT length distribution on mechanical properties of nanocomposites: measurement and estimation. In: Proceedings of 13th US-Japan conference on composite materials, 2008, CD-ROM.
[20] JIS K7086. Testing methods for interlaminar fracture toughness of carbon fibre reinforced plastics. Tokyo: Japanese Standards Association; 2004.