Fabrication of CNTs grafted hierarchical multiscale composite and evaluation of its mechanical properties

T. Kim[a*], M. Kameya[a], J. Natori[a], H. Kawada[b]

[a]*Dept. of Applied Mechanics, Graduate School of Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan*
[b]*Dept. of Applied Mechanics and Aerospace Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan*
**sayoitu1126@akane.waseda.jp*

Keywords: CNTs, multiscale composite, interfacial property, carbon fiber

Abstract

In this study, CNTs were grafted onto carbon fibers using Ni deposited film as the catalyst, and their interfacial properties were evaluated for the purpose of figure out the significant effect of CNTs introduced at the fiber/resin interface in CFRP laminates. CNTs were grafted onto carbon fiber surfaces without any significant degradation of tensile properties. CNT-grafted fibers also showed the remarkable interfacial and interlaminar properties. Interfacial shear strength of CNT-grafted fibers indicated 224% improvement compared with as-received ones. Furthermore, hierarchical CFRP laminate was fabricated and intelaminar shear strength was studied. As a result, interlaminar shear strength has increased by 32%. Those beneficial results derive from an anchor effect of CNTs introduced to the fiber/resin interfaces.

1. Introduction

In recent years, carbon nanotubes (CNTs) have attracted a lot of interest as an additional component in fiber reinforced plastics (FRP) to enhance the mechanical properties. Particularly, CNTs grafted onto fiber surfaces are expected to improve the interfacial adhesion and to prevent the debonding at the interface due to their anchor effect.

The method of grafting CNTs onto carbon fiber and the evaluation of its morphology are studied. It is well known that CNTs are hardly grafted onto carbon fiber without several steps of appropriate preparations. Some researchers [1,2] think the functional groups onto fiber surfaces as the key to grafting CNTs. They functionalized carbon fiber surfaces using strong acid such as nitric acid or mixed acid, and grafted CNTs by CVD method. Hu et al. [1] reported that those functional groups onto fiber surfaces are necessary to promote the adhesion of catalyst to the fiber surfaces and to improve the weak catalyst-carbon interaction. However, their method has the crucial problem of causing damages onto fibers especially during the acid treatment. For example, in Hu's report, tensile strength of carbon fiber indicated 35% degradation after grafting CNTs.

At the same time, some reported that CNTs were grafted onto carbon fibers with a simple thermal preparation. They utilized the previously-functionalized raw fiber surfaces. Naito [3] and Kin [4] synthesized CNTs onto carbon fibers and reported the improvement of tensile strength. Kim [4] and Peng [5] also studied the interfacial property by fiber fragmentation test. However, it haven't rarely been done yet to fabricate a hierarchical CFRP and to figure out the effect of CNTs introduced at the fiber/resin interface in the CFRP laminates, mainly because of the difficulty of grafting CNTs onto carbon fibers in bulk, and without any degradation of their tensile properties.

The method of grafting CNTs onto carbon fiber surfaces without causing any damages to fibers was established. Thermal preparation and CVD method are adopted, and also nickel (Ni) deposited film is used as the catalyst with the substitution for iron compounds mainly used as the catalyst for grafting CNTs elsewhere [1-3,5-7]. In addition to the tensile mechanical properties, the interfacial properties are also evaluated by fiber fragmentation test. Furthermore, the hierarchical CFRP is fabricated to characterize the bulk sized composite.

2. Materials and testing methods

2.1 Materials

Polyacrylonitrile (PAN)-based carbon fibers (T700S, Toray Industries, Inc.) were used as the specimen in single fiber tensile test and as the reinforcement of multiscale FRP. Table 1 shows the properties of T700S. The bisphenol epoxy resin (jER 828) was used as matrix for the single fiber composite (SFC). The epoxy resin was mixed with the curing agent (jER cure 113) with the ratio of 100:32, and then cured with the condition of 80°C for 1h and 150°C for 3h.

Table 1. Mechanical properties of PAN-based carbon fiber.

Grade	T700S
Nominal diameter μm	7
Tensile strength MPa	4900
Young's modulus GPa	230
Tensile strain %	2.1
Density g/cm^3	1.8

2.2 Synthesis of CNTs onto carbon fibers

To remove the sizing agent on the fiber surface, carbon fibers were heat treated at 750°C for 40minutes in vacuum (Gauge pressure 0.01MPa) in the CVD apparatus. And then, the fibers were Ni coated as the catalyst-introducing step using a vacuum deposition equipment (EBX-6D, ULVAC). The thickness of Ni film was set to 7nm, which is technically the minimum thickness of even films produced by metal-film deposition method. After the deposition step, carbon fibers went through an annealing step, in which fibers were heated again 750°C for 5minutes. As is well known, the annealing treatment has an important role to align crystals and to relax the internal residual strain in the material. Finally, CNTs were synthesized on to carbon fibers by CVD method in a vacuum (Gauge pressure 0.01MPa). Ethanol was used as a carbon source and the grafting condition was at 750°C for 10minutes.

2.3 Single fiber tensile test and fragmentation test

The tensile properties of as-received fiber (AR), heat-treated fiber (HT), Ni-deposited fiber (Ni), annealing treated fiber (AT) and CNT-grafted fiber (CNTG) were measured by universal testing machine (AG-I-10kN, SHIMAZU). The tensile strength of each specimen was evaluated by calculating Weibull parameters. The interfacial properties of AR and CNTG were measured by fragmentation test apparatus equipped with a micro-tension apparatus and a microscope. Figure 1 shows the Geometry of SFC specimen used in fragmentation test. The interfacial shear strength (IFSS) of each specimen was calculated by equation 1 based on the Kelly-Tyson model. Where d denotes the fiber diameter, L_0, the fiber length; and σ_{fb}, the theoretical strength of the fiber whose length is L_0.

$$\tau_{\mathrm{IFSS}} = \frac{\sigma_{\mathrm{fb}} d}{2L_{\mathrm{c}}} \tag{1}$$

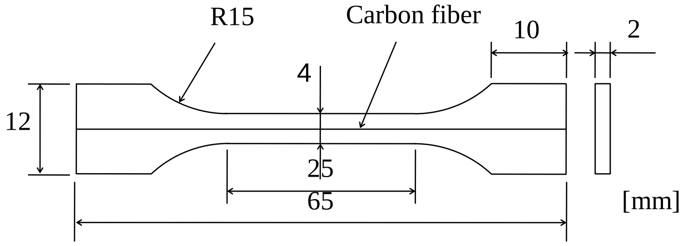


Figure 1. Geometry of SFC specimen.

2.4 Fabrication of multiscale FRP and evaluation of interlaminar shear strength

Multiscale CFRP laminate was fabricated to confirm the interlaminar shear strength (ILSS) by short beam specimen. B-stage resin sheets (Sanyu Rec Co., Ltd.) were melted at 100°C for 3minutes with CNT-grafted carbon fiber bundles aligned between them, and that formed a hierarchical prepreg. Then, 16 prepregs were stacked and a unidirectional CFRP laminate with 2mm in thickness was fabricated by compression molding at 150°C for 1hour. The three-point flexural test about short beam specimen (20mm, 5mm and 2mm in length, width and thickness) cut out from CFRP laminate was conducted by universal testing machine (AG-IS-100kN, SHIMAZU). Figure 2 shows geometry of jig for three-point flexural test.

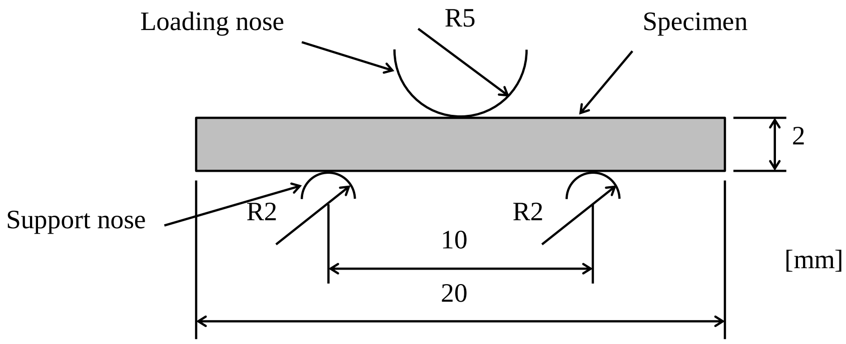


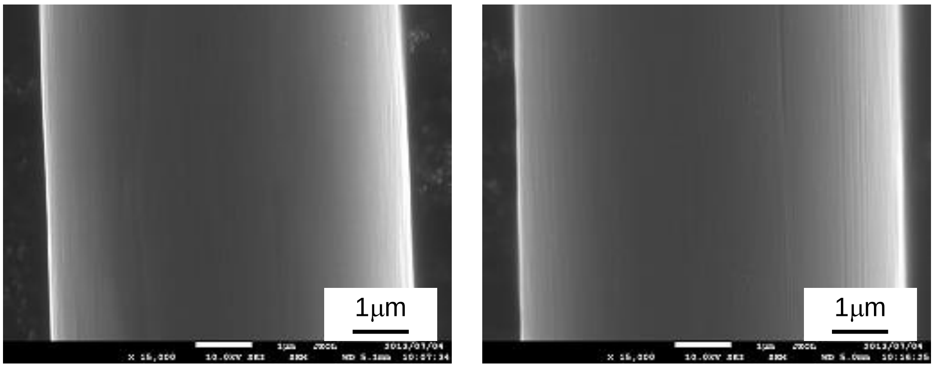
Figure 2. Geometry of jig for three-point flexural test.

3. Results and discussions

3.1 The influence of pretreatment on fiber surface condition

Surface morphologies and FTIR spectra of AR and HT are shown in Figure 3 and Figure 4, respectively. Comparing two images in Figure 3, the surface morphology is almost unchanged after the heat treatment. With those images only we cannot discuss whether the sizing has completely removed after the thermal treatment, however, those images are at least suggesting that the carbon fibers remain undamaged after being heated up to 750°C. Two spectra in

Figure 4 show the obvious difference. The spectrum of AR has two strong peaks around 1200-1100cm-1 and 900-800cm-1, and those peaks cannot be detected from the one of HT. The former peak is characteristic for C-O bonds, and the latter one indicates the presence of epoxy group. Therefore, the result shows that the epoxy-based sizing has been removed from the HT surface, and that the thermal treatment has been successfully conducted. Moreover, broad and weak peaks which tell us the presence of hydroxyl and carboxyl groups on the fiber surface are identified in both spectra, the one of AR and of HT. Those functional groups will be necessary to promote the adhesion of catalyst to the fiber surfaces and improve the weak catalyst-carbon interaction.



(a) AR (×15,000) (b) HT (×15,000)

Figure 3. FE-SEM images of as-received and heat-treated carbon fiber surfaces.

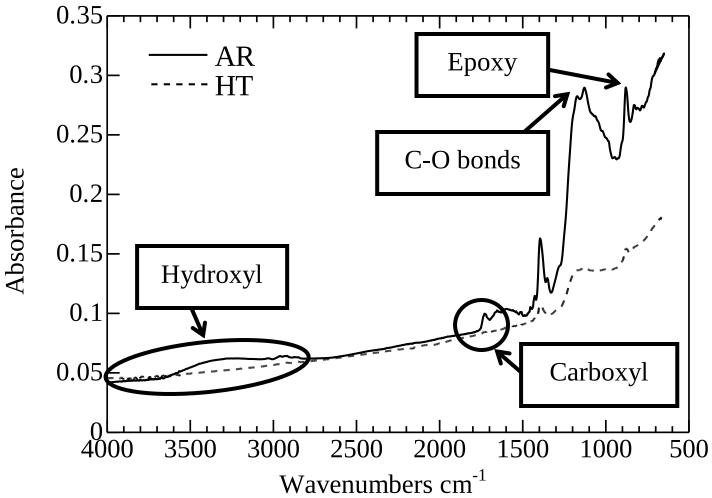
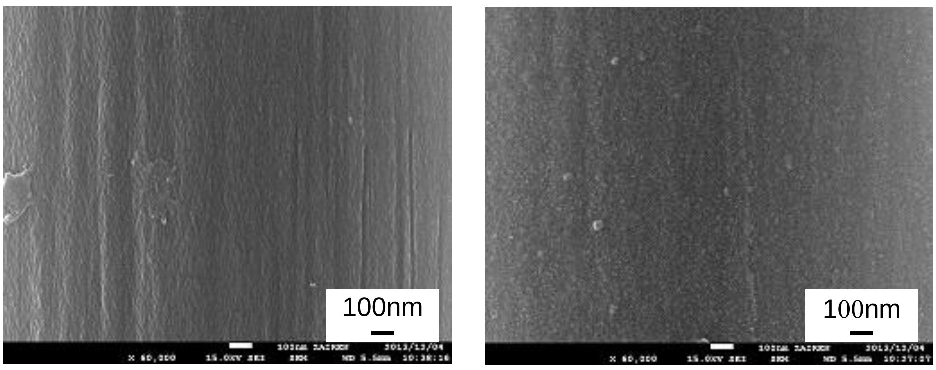


Figure 4. FT-IR spectra of carbon fibers.



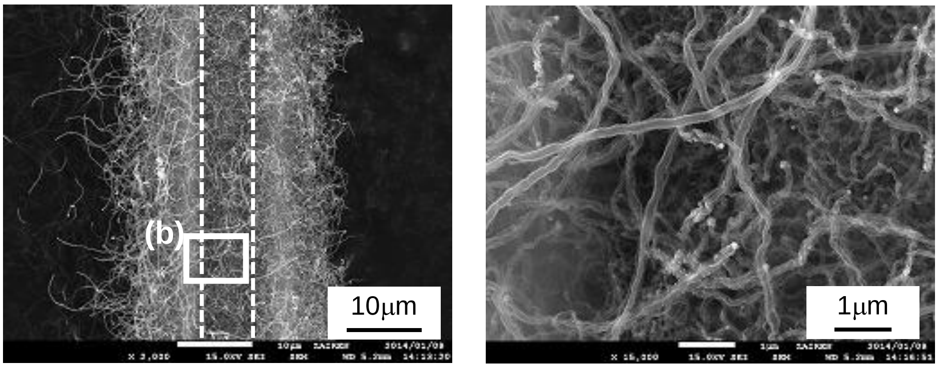
(a) Ni (×60,000) (b) AT (×60,000)

Figure 5. FE-SEM images of Ni-deposited and annealed carbon fiber surfaces.

Surface morphologies of Ni and AT were also observed (Figure 5). Ni deposition leaves film-like coating with rough surface onto the fiber, shown in Figure5 (a). The tendency can slightly be seen that the rough surface of Ni film become granular after the anneal treatment, which is shown in Figure 5 (b), but basically the appearance is almost unchanged before and after the annealing step.

3.2 Observation of CNT-grafted carbon fiber

Figure 6 shows the thick growth of CNTs onto the carbon fiber surface. It is obvious that the functional groups and annealed Ni films described above contribute to the CNT synthesis. Particularly, Ni film might have effectively worked as a catalyst, and that made it possible for CNTs to grow thick and long in a short time. CNTs synthesized using Ni film as a catalyst are so fine and long that they may develop a better anchor effect on fiber surface, and that will lead to better interfacial adhesion.



(a) CNTG (×2,000) (b) CNTG (×15,000)

Figure. 6 FE-SEM images of CNT-grafted carbon fiber surfaces.

3.3 Tensile properties of CNT-grafted carbon fiber

Figure 7 shows Weibull distributions of fiber strength. Figure 5 demonstrates the tendency of improvement in the distributions of tensile strength with the progression of the preparation step and CNT grafting process. The distributions of tensile strength are related to shape parameter *m* showed in Table 2. Scale parameter σ_0, Young's modulus *E*, and tensile strain ε % in Table 2 tell us the beneficial result that carbon fibers remain almost undamaged through thermal, Ni deposition, and CVD process.

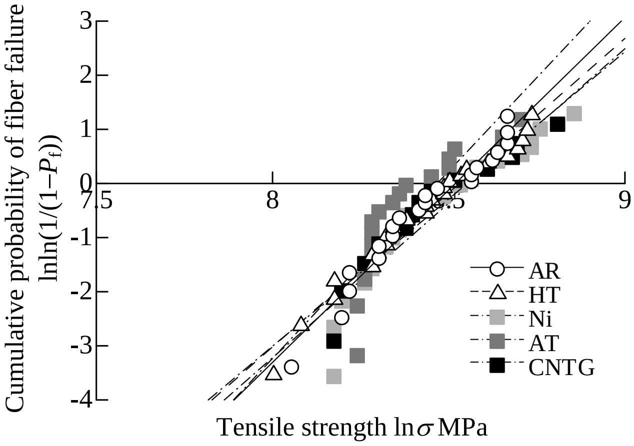


Figure 7. Weibull distributions of fiber strength.

Table 2. Results of fiber tensile tests.

	Number of specimens	Shape parameter m	Scale parameter σ_0 MPa	Young's modulus E GPa	Tensile strain ε %
AR	21	6.37	5008	221 (20.7)	2.09 (0.37)
HT	24	5.70	5063	220 (24.6)	2.11 (0.40)
Ni	25	5.71	5239	219 (17.7)	2.38 (0.35)
AT	17	6.92	4757	205 (20.2)	2.19 (0.26)
CNTG	13	5.44	5180	216 (15.8)	2.15 (0.49)

Values in ( ) indicate the standard deviation.

Hu et al. [1] has reported that the fracture load of CNT-grafted carbon fibers decreased by 35% compared with as-received ones after several preparations and CNT grafting process. The major difference of our CNT grafting method from the ones of Hu and other researchers [1-3,5-7] is the Ni deposited film as the catalyst. Iron compounds such as Ferrocene ($C_{10}H_{10}Fe$) or iron nitrate ($Fe(NO_3)_3$), which are often used as the catalyst for grafting CNTs, are well known for dissolving into carbon fibers and forming fine fractures onto surfaces, which is called nanopit, while Ni film doesn't have such bad influence. Therefore, the CNT grafting process taking advantage of the Ni film is superior to the conventional one using iron compounds as the catalyst.

3.4 The influence of CNT-grafting on interfacial shear strength

The effect of CNTs on the interfacial properties was also investigated by single fiber fragmentation test. As shown in Table 3, fiber break points n_{fb} indicates 205% increase and critical length L_c has shortened by 66% after grafting CNTs. The increase of n_{fb} and the decrease of L_c demonstrate the enhancement of interfacial adhesion and the prevention of debonding. Consequently, the interfacial shear strength τ_{IFSS} of CNT-grafted fibers shows the significant increase compared with that of As-received ones by 224%. Images shown in Figure 9 indicate not only the significant decrease of interfacial debonding in length, but the formation of CNT layers with impregnated resin around the fiber.

Table 3. Results of fiber fragmentation tests.

	Number of Specimens n	Number of fiber break points n_{fb}	Critical length L_c μm	Tensile strength of fibers at L_c σ_{fb} MPa	Interfacial shear strength τ_{IFSS} MPa
AR	6	21 (0.98)	826 (39.0)	4804 (34.6)	20.4 (1.06)
CNTG	3	64 (3.46)	277 (14.3)	5219 (49.2)	66.0 (4.16)

Values in ( ) indicate the standard deviation.

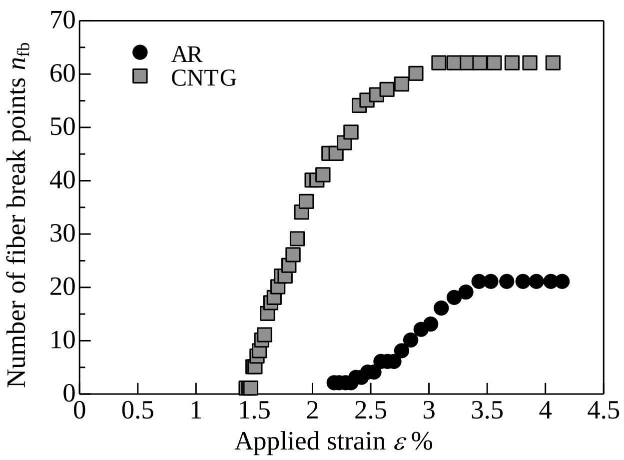
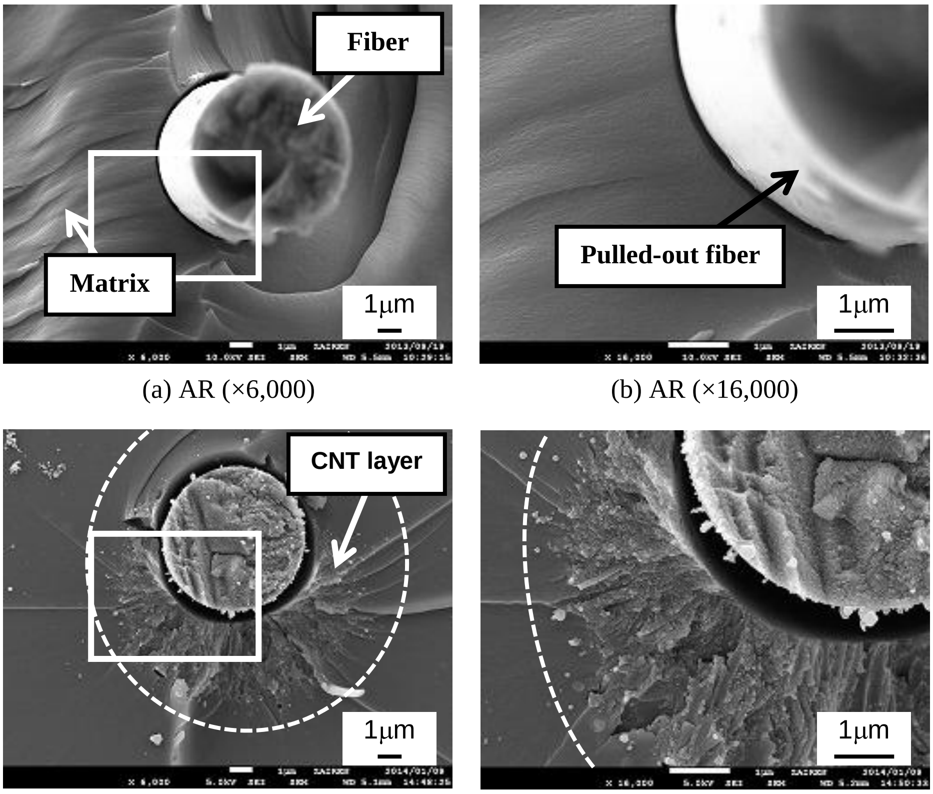


Figure 8. Number of fiber break points against applied strain.



(a) AR (×6,000) (b) AR (×16,000)

(c) CNTG (×6,000) (d) CNTG (×16,000)

Figure 9. FE-SEM images of embedded carbon fiber neighborhoods in SFC cross-sections.

3.5 Interlaminar shear strength of multiscale FRP

We conducted a three point bending test for short beam specimens. From the test results shown in Table 4 and Figure 10. Maximum load FM to hierarchical CFRP shows the increase by 38% compared with as-received one. Accordingly, inter-laminar shear strength τ_{ILSS} demonstrates 32% improvement. Fine and long CNTs on each fiber surfaces, which is synthesized using Ni film as the catalyst, has developed the good anchor effect between each layer, and that has led to the improvement of interlayer adhesion.

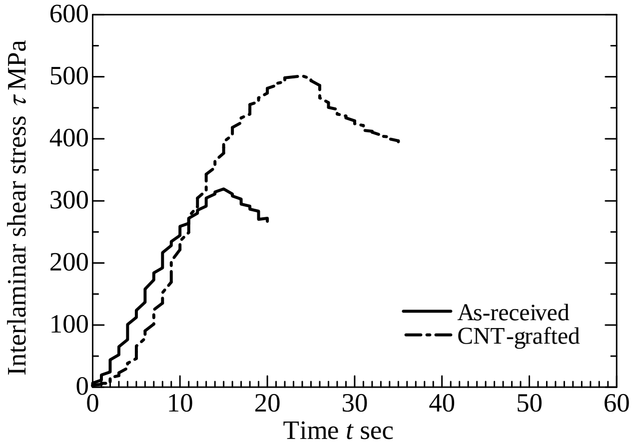


Figure 10. Interlaminar shear stress-time curves.

Table 4. Interlaminar shear strengths by short beam.

	Number of specimens *n*	Maximum load F_M N	Interlaminar shear strength τ_{ILSS} MPa
AR	3	4147 (902)	333 (74.2)
CNTG	3	5720 (693)	441 (52.2)

Values in ( ) indicate the standard deviation.

4. Conclusion

In this study, CNTs were grafted onto carbon fibers using Ni deposited film as the catalyst, and their interfacial properties were evaluated for the purpose of figure out the significant effect of CNTs introduced at the fiber/resin interface in CFRP laminates. The following are the concluding remarks from the experiments. CNTs were grafted onto carbon fiber surfaces without any significant degradation of tensile properties. That might be because of Ni film which effectively worked as a catalyst without dissolving into carbon fibers like iron compounds do. CNT-grafted fibers also showed the remarkable interfacial and interlaminar properties. Interfacial shear strength of CNT-grafted fibers, experimentally obtained from the fiber fragmentation test, indicated 224% improvement compared with as-received ones. Furthermore, hierarchical CFRP laminate was fabricated and intelaminar shear strength by short beam specimen was studied. As a result, interlaminar shear strength has increased by 32%. Those beneficial results derive from an anchor effect of CNTs introduced to the fiber/resin interfaces. Since fine and long CNTs synthesized from Ni film develop the good anchor effect, the enhancement of interfacial adhesion and the prevention of debonding may lead to the improvement in stress transferring efficiency. Considering those remarkable improvement of the interfacial property, CNT-grafted carbon fibers will be recognized as the useful reinforcement material for CFRP in practical use.

References

[1] Hu Zhi-hui, Dong Shao-ming, Hu Jian-bao, Wang Zhen, Lu Bo, Yang Jin-shan, Li Qing-gang, Wu Bin, Gao Le, Zhang Xiang-yu, "Synthesis of carbon nanotubes on carbon fibers by modified chemical vapor deposition", *New Carbon Materials*, 27, 352-361,2012.

[2] S. Rahmanian, A.R. Suraya, R. Zahari, E.S. Zainudin, "Synthesis of vertically aligned carbon nanotubes on carbon fiber," *Applied Surface Science* 271, 424-428, 2013.

[3] Kimi Kimiyoshi Naito, Jenn-Ming Yang, Yuta Inoue, Hiroshi Fukuda, "The effect of surface modification with carbon nanotubes upon the tensile strength and Weibull mudulus of carbon fibers," *Journal of Materials Science*, 47, 8044-8051, 2012.

[4] Kyoung Ju Kim, Jina Kim, Woong-Ryeol Yu, Ji Ho Youk, Jinyong Lee, "Improved tensile strength of carbon fibers undergoing catalytic growth of carbon nanotubes on their surface," *Carbon*, 54, 258-267, 2013.

[5] Peng Lv, Yi-yu Feng, Peng Zhang, Hui-min Chen, Naiqin Zhao, Wei Feng, "Increasing the interfacial strength in carbon fiber/epoxy composites by controlling the orientation and length of carbon nanotubes grow on the fibers", *Carbon*, 49, 4665-4673, 2011.

[6] Lin Yang, Xiaodong He, Lei Mei, Liyong Tong, Rongguo Wanga, Yibin Li, "Interfacial shear behavior of 3D composites reinforced with CNT-grafted carbon fibers", *Composites: Part A*, 43, 1410-1418, 2012.

[7] S. Rahmanian, K.S. Thean, A.R. Suraya, M.A. Shazed, M.A. Mohd Salleh, H.M. Yusoff, "Carbon and glass hierarchical fibers: Influence of carbon nanotubes on tensile, flexural and impact properties of short fiber reinforced composites", *Material and Design*, 43, 10-16, 2013.