Mechanical properties of CNT-grafted carbon fiber composites

Geunsung Lee[a], Ji-Ho Youk[b], Jinyong Lee[c], Woong-Ryeol Yu[a*]

[a]*Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 151-744, Republic of Korea*
[b]*Department of Advanced Fiber Engineering, Inha University, 253, Yonghyun-dong, Nam-gu, Incheon 02-751, Republic of Korea*
[c]*High Temperature Composite Materials Group, The 4th R&D Institute-4, Agency for Defense Development, Daejeon, 305-600, Republic of Korea*

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Abstract

We prepared hierarchical CNT-grafted carbon fibers (CFs) without their mechanical degradation by chemical vapor deposition (CVD). Ni-Fe bi-metallic catalyst system was used to lower CVD temperature and thus prohibit the diffusion of catalyst particles into the CF, enabling to maintain the mechanical properties of the CFs. Various CNT-grafted CF composites were manufactured using CNT-grafted CFs and their mechanical properties were evaluated, focusing on the effects of CNT-grafted CF on the mechanical properties of the composites.

1. Introduction

Due to their excellent mechanical, electrical and thermal properties, carbon fibers (CFs) have been used in nearly all-engineering fields, promoting vast research to improve their mechanical properties. However, the improvements of the mechanical properties of CFs are now saturated; thereby researchers pursue a new direction for improving the mechanical properties of the CF reinforced composites. On the other hand, carbon nanotubes (CNTs) have been emerged to a new generation reinforcement material, stimulating a considerable amount of research. However, the application of CNTs as reinforcement has brought many problems related with aggregation of CNTs in polymeric matrix and low volume fraction of reinforcement. To solve these problems and also improve the mechanical properties of CF reinforced composites, the hybridization of CNTs and CFs by grafting CNTs on the surface of CFs has been suggested [1, 2, 3]. In this study, we report on low temperature grafting process of CNTs on CFs using bi-metallic catalysts CVD. Here, low temperature processing was extremely important because the degradation of CF properties could be avoided without any pre-treatments. Finally, unidirectional, woven, and 3D braid composites were manufactured using CNT-grafted CFs and their mechanical properties were measured. The effects of CNT-grafted CF on the mechanical properties of the composites were investigated, focusing on the preform structures and the failure mechanism.

2. Experimental

2.1. Grafting process of CNTs on carbon fibers

We chose two types of CVD method to graft CNTs on CF surface. One is floating catalyst chemical vapor deposition (FCVD) method, and another one is thermal CVD. FCVD process is an attractive method for CNT synthesis due to its low cost, simple procedure and high scale-up potential. Many researchers have grafted CNTs onto CF surfaces using FCVD process, undergoing unsuccessful grafting of CNTs on raw CFs surface, presumably because of diffusive nature of catalysts into CF. To prevent inter-diffusion between CF and catalyst particles, barrier layers such as alumina and silica were frequently coated, inducing high cost and low productivity [2]. But in this study, we lowered CVD temperature to 500℃ by introducing Ni-Fe bi-metallic catalysts [4,5] and inter-diffusion between carbon and catalyst particles were inhibited. CNTs were grafted on CF surface using FCVD process with various temperatures to check the effect of temperature on grafting process. Nickelocene and Ferrocene were used as catalysts precursors (1:1 weight ratio) and toluene was used as carbon source.

Although FCVD process has many benefits for continuous production, it is hard to manufacture proper amount of CNT-grafted CFs for macroscale composites in lab scale. Thus we chose thermal CVD method, for which catalysts were introduced by a solution of catalysts precursors. Here, we also used Ni-Fe bi-metallic catalysts, lowering CVD temperature to maintain the mechanical properties of the CF. As a catalyst precursors, we used $FeCl_3 \cdot (H_2O)_6$ and $Ni(NO_3)_2 \cdot (H_2O)_6$ and ethanol as a solvent. First, CFs were soaked in a solution of catalysts precursors for 5 mins and dried at 70℃ for 4 hrs. Detailed conditions of FCVD and thermal CVD processes are listed in Table 1.

Sample	Method	CVD temperature (℃)	Catalysts	Carrier gas ratio (H2 : Ar)	Substrates
Fe-FCVD-R	FCVD	760	Fe only	1:9	Raw CF
Fe-FCVD-O	FCVD	760	Fe only	1:9	Oxidative CF
Bi-FCVD-R	FCVD	500	Fe + Ni	1:9	Raw CF
Bi-FCVD-O	FCVD	500	Fe + Ni	1:9	Oxidative CF
HT-SCVD	Soaking CVD	760	Fe only	1:9	Raw CF
TN-SCVD	Soaking CVD	500	Fe + Ni	1:9	Raw CF
TK-SCVD	Soaking CVD	500	Fe + Ni	1:3	Raw CF

Table 1. Experimental conditions for CNT-grafted CFs.

2.2. Fabrication of the CNT-grafted CF composites

We prepared various forms of CF composites using woven fabric, unidirectional, 3D braided preforms to examine the effects of CNT-grafted CFs on the mechanical properties of the composites. For these composites, CNT-grafted CFs were prepared to have controlled CNT diameter by H_2 ratio in carrier gas by thermal CVD and their composites were manufactured by vacuum assisted resin transfer molding (VARTM) process to minimize voids in the composite. We used epoxy resin (Epofix, Struers) for matrix material.

2.3. Characterizations

The morphologies of CNT-grafted CFs and fractured composites was characterized using scanning electron micro scope (SEM) (JEOL-7100F) and optical microscope. Single fiber tensile tests were carried out to measure the tensile strength of CNT-grafted CFs. The gage length was 20mm and at least 20 tests were conducted. The growth mechanism of CNTs at various temperatures and the deactivation mechanism of catalyst particles were investigated by observing the inside of CNT-grafted CFs using transmission electron microscope (TEM, JEM3100F). For this observation, CNT-grafted CF samples were prepared using focused ion beam (FIB) (Figure 1). The mechanical properties of CNT-grafted CF composites were measured by tensile test using samples with the size of 50mm x 15mm x 1mm.

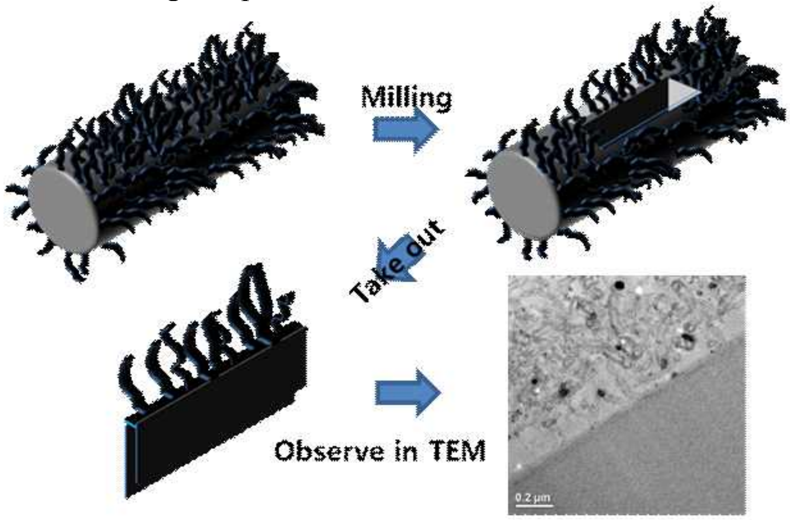
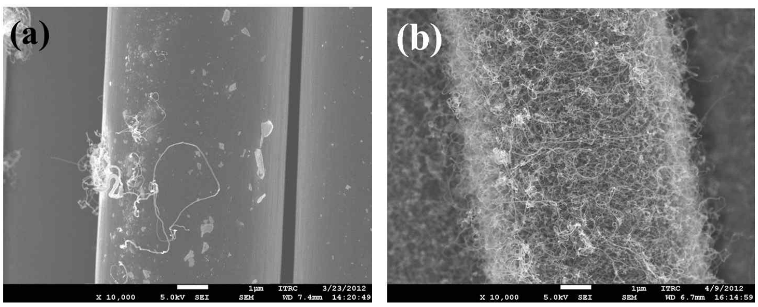


Figure 1. A schematic procedure to prepare samples for observing the internal structure of CNT-grafted CFs.

3. Results & Discussion

3.1. Morphology of CNT-grafted CF

Figure 2 shows the morphologies of CFs after CVD process. By high-temperature CVD using only Fe catalysts, CNTs were uniformly grown on only oxidative CFs (Figure 2 (b)). Note that sparse CNTs were grown on the surface of untreated CFs. This is due to high CVD temperature (e.g., 700 ℃) at which the catalyst nanoparticles were diffused into CFs or deactivated. The oxidation of CFs increased their chemical affinity and surface energy, leading to the uniform growth of CNTs. In contrast, bi-metallic FCVD process shows that CNTs were grown on CF surface regardless of CF surface (see Figure 2 (c) and (d)). For thermal CVD, CNTs were uniformly grown on the surface of CFs regardless their CVD temperature and catalysts because catalysts were introduced on surface before CVD process.



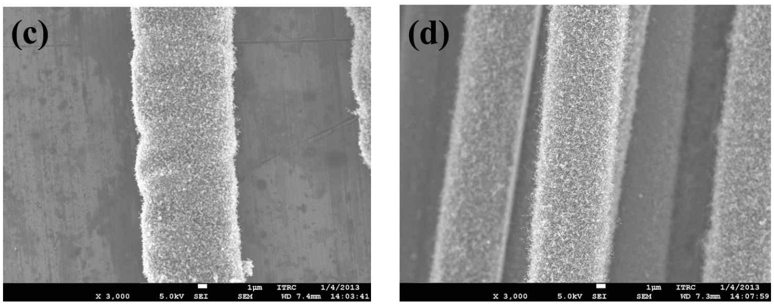


Figure 2. Morphologies of CFs after FCVD process; (a) Fe catalyst only and untreated CF case, (b) Fe catalyst only and treated (oxidized) CFs, (c) bi-metallic catalyst and untreated CFs, (d) bi-metallic catalyst and treated (oxidized) CFs

3.2. Mechanical properties of CNT-grafted CFs

Figure 3 shows the tensile properties of CNT-grafted CFs measured by single fiber tensile test. CNT-grafted CFs prepared using only Fe catalyst underwent severe degradation of their structure and thus mechanical properties while CNT-grafted CFs prepared using bi-metallic FCVD process showed no degradation in the tensile strength. To investigate the reason for the degraded mechanical properties of CFs prepared using only Fe catalyst FCVD, the cross sections of CNT-grafted CFs were observed using TEM. Through the internal structure analysis, we could find out that high-temperature was the main source of the degradation.

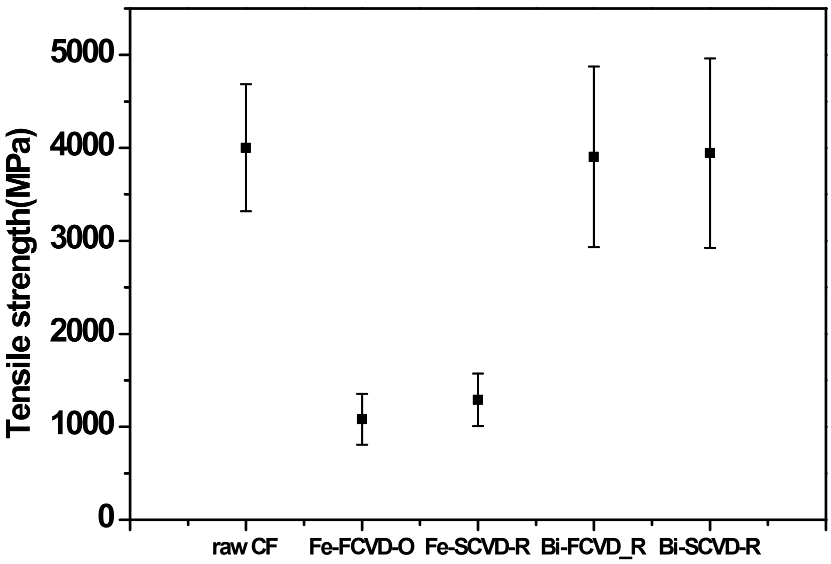


Figure 3. Tensile strength of CNT-grafted CFs measured by single fiber tensile test

3.3. Mechanical properties of the CNT-grafted CF composites

The mechanical properties of the CNT-grafted CF composites were examined by applying a tensile load along with the warp direction. Figure 4 shows the stress-strain curves of 4-layered woven CNT-grafted CF composites. The tensile strength and modulus of the CNT-grafted CF composites were higher than those of the pristine CF composites. In particular, CNT-grafted CF composite prepared by large diameter of CNTs, which was controlled by H_2 ratio in carrier gas, showed better mechanical properties. In contrast, there was no significant difference in the tensile modulus according to the diameter of grafted CNTs. From our previous research, CNT-grafted CF with thick CNTs showed larger IFSS than thin CNT-grafted CF. We tentatively concluded that the effects of CNT-grafted CF on the mechanical properties of the composites came from enhanced interfacial properties of CF. More experiments will be conducted to clarify this fact further, the results of which will be discussed at the Conference.

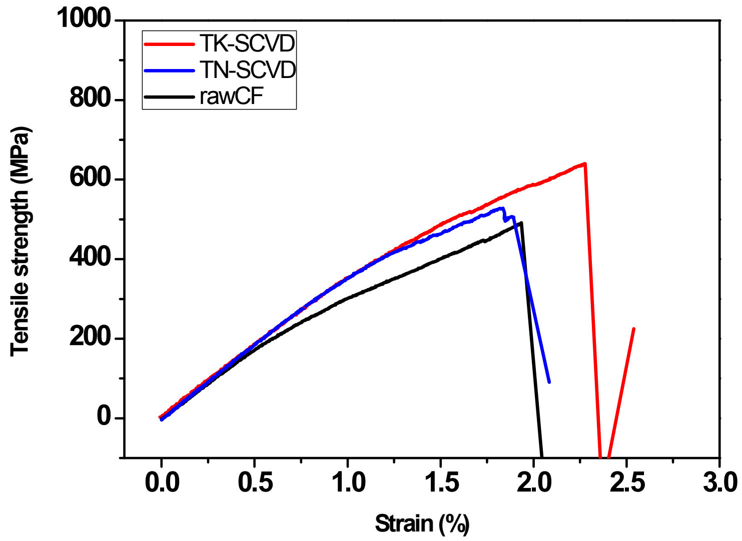


Figure 3. Representative stress-strain curve for CNT-grafted CF composites

3.4. Mechanisms for the improved tensile strength of CNT-grafted CF composites

To understand the mechanism behind the improved tensile strength of the CNT-grafted CF composites, their fractured surfaces were observed by SEM. The pristine CF composite showed individual CFs pulled out from the matrix and a lot of debris from pulled-out CFs, whereas stair-like, clear fractured surfaces were observed in the CNT-grafted CF composites. These results confirmed that IFSS was increased by CNT grafting and thus external loads were more effectively transferred in CNT-grafted CF composites. Furthermore, we can expect that radially grown CNTs may increase the inter-laminar strength of CNT-grafted CF composites. The inter-laminar strength of the composites will be examined further for concrete conclusion.

4. Conclusions

In this study, we demonstrated that CNT-grafted CFs could be manufactured without any mechanical degradation of CFs. This was possible by prohibiting the inter-diffusion between CF and catalysts by lowering CVD temperature using bi-metallic catalysts. Finally, we manufactured CNT-grafted CF composites in macroscale. The tensile properties of 4-layered woven CNT-grafted CF composites were improved more than 30% compared to that of the pristine CF composites.

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