Manufacture of carbon-carbon composites using carbon nanotube-grafted carbon fibers and their their properties

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Keywords: carbon nanotube, carbon-carbon composites, carbon fibers, hierarchical structure

Abstract

Hybridization of carbon nanotubes (CNTs) with carbon fibers (CFs) through their direct growth has been suggested as an effective means to upgrade the material properties of CFs because grafted CNTs improve the shear stiffness and the surface roughness of CFs. Such a hybridization method is free from CNT dsispersion problem. For the mass production of CNT-grafted CFs, a continuous process was developed using a bimetallic catalyst and chemical vapor deposition process that did not degrade microstructures and mechanical properties of CFs. The lowering of growth temperature of CNTs was key to manufacture continuously CNT-grafted CFs without any degradation of their mechanical properties. Water vapor-assisted CVD was adopted to accelerate CVD process and T-zone furnace was designed to minimize shade effect. Proper sizing treatment after grafting process Proper sizing process was considered to protect grafted CNTs on CF and increase handling properties. Detail parameters for growth of CNTs are discussed, focusing on the optimal amount and growth speed of CNTs..

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 and stimulated a considerable amount of research. However, the application of CNTs as reinforcement has brought many problems related with aggregation of CNTs in 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]. Carbon-carbon composites are well-suited materials to structural applications at high temperature and where needs high thermal shock resistance. Furthermore, they have more impact resistance than usual ceramic materials. In this study, we report about effects of grafted CNTs on carbon-carbon composites. Unidirectional, woven composites are manufactured using prepared CNT-grafted CFs and their mechanical/thermal/electrical properties are measured and effects of CNT-grafted CF on the properties of the composites are discussed.

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2. Experimental

2.1. Fabrication of CNT-grafted CF

We chose thermal CVD method which introduce catalysts by solution of catalysts precursors since its simplicity and low cost for mass production. In particular, we used Ni-Fe bi-metallic catalysts and lowered CVD temperature to maintain mechanical properties of the CF[4]. We used CF woven fabrics (Entra korea) as substrates. 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. CFs were soaked in solution of catalysts precursors for 5 minutes and dried at 70℃ for 4 hours. After than, thermal CVD process was conducted in the furnace at 500 and Ar:H2 = 9:1 environment for 2 hours.

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Figure 1. Write your figure caption here.

2.2. Fabrication of carbon-carbon composites

Carbon-carbon composites are fabricated through 3-step process. For the first, we fabricated green body composites using vacuum assisted resin transfer molding (VARTM) of phenol-resol resin (KC-4354,Kangnam corporation) and their curing process. After than, green body composites were pyrolized in the furnace with Ar atmosphere. The temperature profile for pyrolysis is detailed at figure 1. Finally, densification process with liquid pitch was conducted at 700 and 1000 bar.

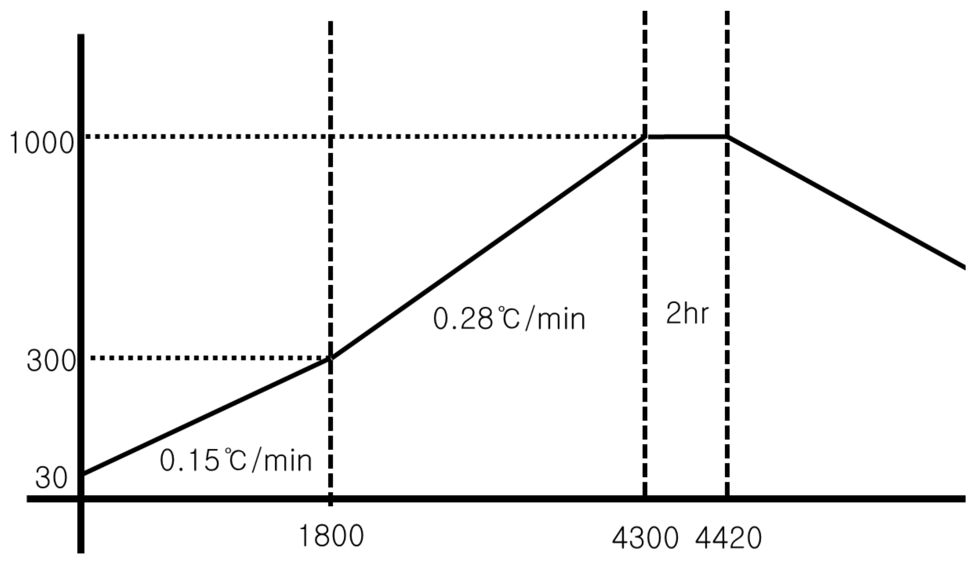

Figure 1. Temperature profile for pyrolysis of carbon-carbon composites

2.3. Characterization

Morphology of CNT-grafted CFs was characterized by field emission scanning electron microscope (FE-SEM, JEOL-7100) and high-resolution transmission electron microscope (HR-TEM,). We characterized mechanical properties of CNT-grafted CF by single fiber tensile test with lab-made

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universal test machine (R&B, Figure). Gage length was 20mm and more than 20 specimens were tested for each samples. Microstructure of CNTs grafted on CF were analyzed by Raman spectroscopy( ).

Density of green body composites, skeletal carbon-carbon composites, densified carbon-carbon composites are measured by Archimedes ---. Mechanical properties of carbon-carbon composites were characterized by 3-point bending test followed by ASTM D790-10. After test, fractured surface of carbon-carbon composites were observed by FE-SEM to observe fracture behavior of composites.

3. Results and Discussion

3.1. CNT-grafted CFs

CNTs were uniformly grafted on CFs as you can see in Figure 2 and had well-developed wall structure (Figure 3). Average diameter of CNTs was 25.7 nm and average wall number of CNTs was 23. From Raman spectroscopy, I_D/I_G ratio for CNTs grafted on CF was obtained as 1.28. Tensile strength of CNT-grafted CFs (3.94 GPa) was little bit higher than that of as-received CFs (3.91 GPa).

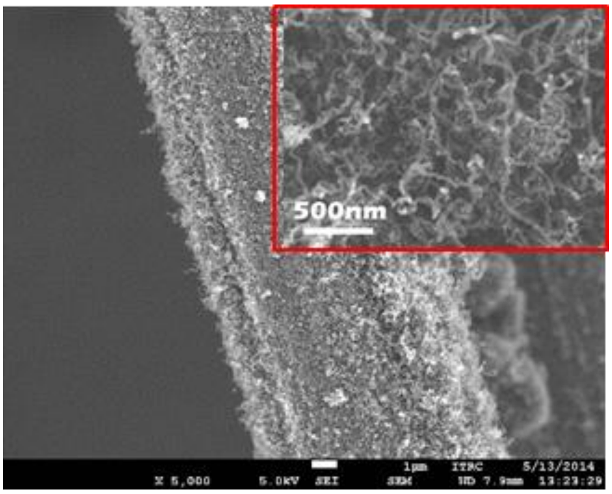

Figure 2. Morphology of CNT-grafted CFs and CNTs grafted on CF

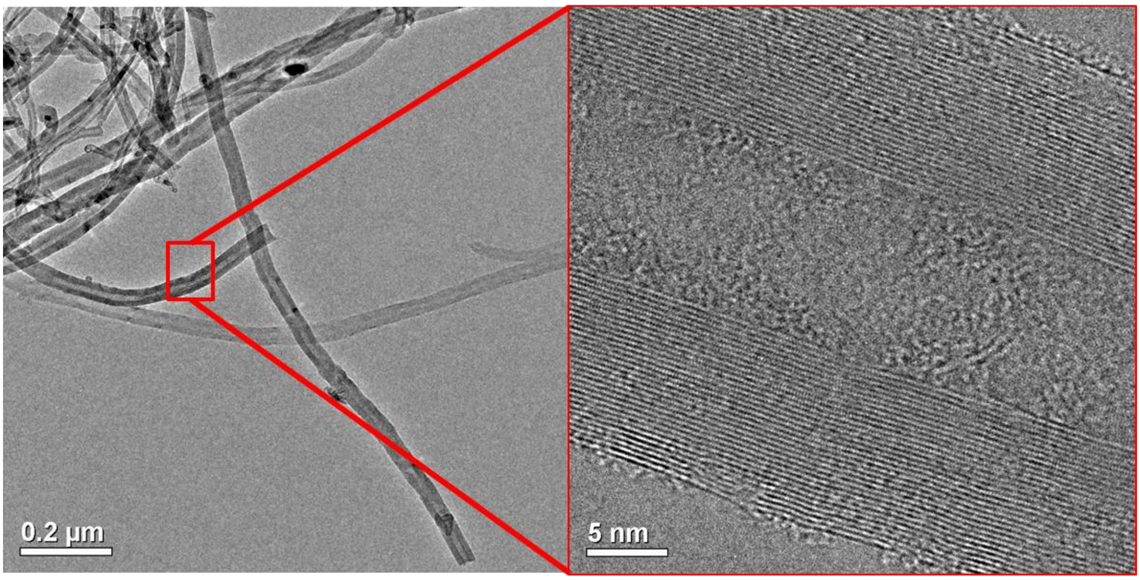

Figure 3. TEM images for CNTs grafted on CF

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3.2. Carbon-carbon composites

Density of composites was varied through fabrication process and fabricated carbon-carbon composites showed different volume fraction because of different thickness. As-received CF composites had 31.3% of fiber volume fraction to axial direction and CNT-grafted CF had 23.5% of fiber volume fraction. Their density was similar to each other (as-received CF: 1.357, CNT-grafted CF: 1.382) . Figure 4 (a) is stress-strain curve for 3-point bending test of carbon-carbon composites. Even as-received CF (rCF) carbon-carbon composites have higher volume fraction, CNT-grafted CF (CNT-gr-CF) carbon-carbon composites showed better mechanical properties. CNT-grafted CF showed 58% higher performance than as-received CF when they compared to mechanical strength calculated by rule of mixture (Figure 4 (b)). To examine the reason for different mechanical strength, we observed fractured surface of carbon-carbon composites. Macroscopically, as-received CF composites showed severe delamination while test but CNT-grafted CF had solid shape after test (Figure 5). In microscopic observation, CNT-grafted CF carbon-carbon composites showed perfect interface between laminar (Figure 6 (b)) and fiber bundles but as-received CF had closed pores between laminar and bundles (Figure 6 (a)). And furthermore, CNT-grafted CF carbon-carbon composites showed larger blocks made by multiple fracture which means higher interfacial shear strength (Figure 6 (c), (d)). We considered that these pores made interlaminar toughness of as-received CF carbon-carbon composites are now investigating reasons for these phenomena.

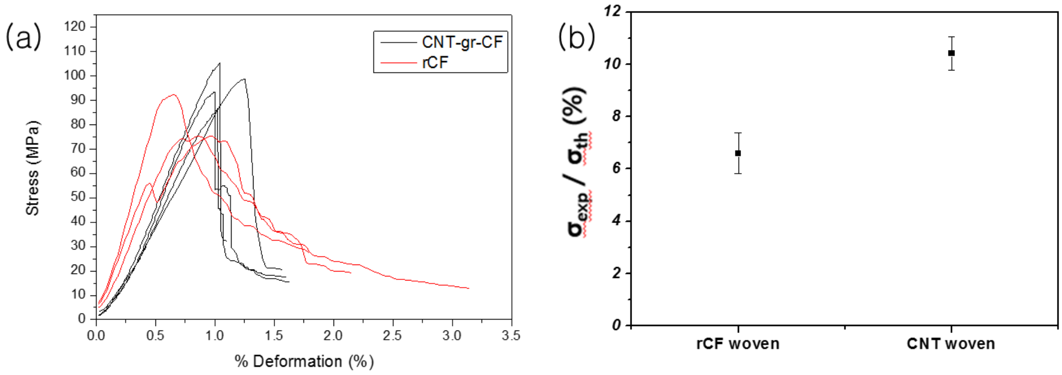

Figure 3. Mechanical properties of carbon-carbon composites (a) stress-strain curve; (b) experimental flexural strength over theoretical strength calculated by rule of mixture.

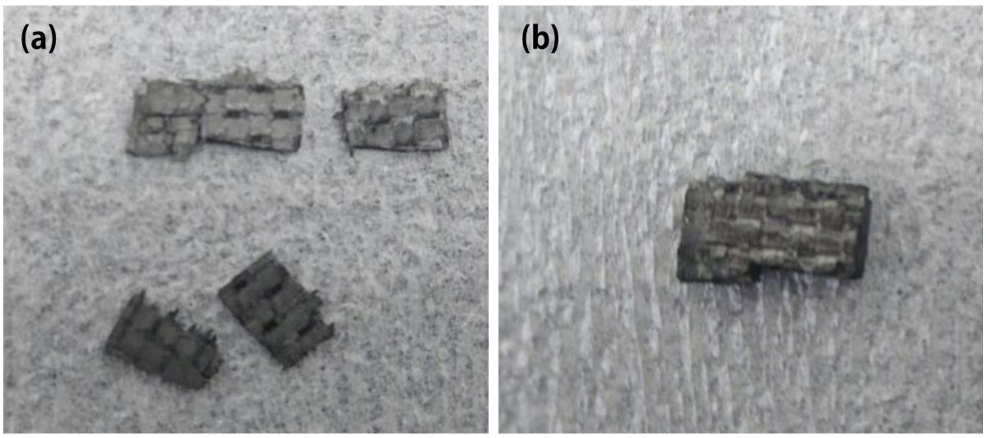

Figure 4. Macroscopic morphology of carbon-carbon composites after 3-point bending test.

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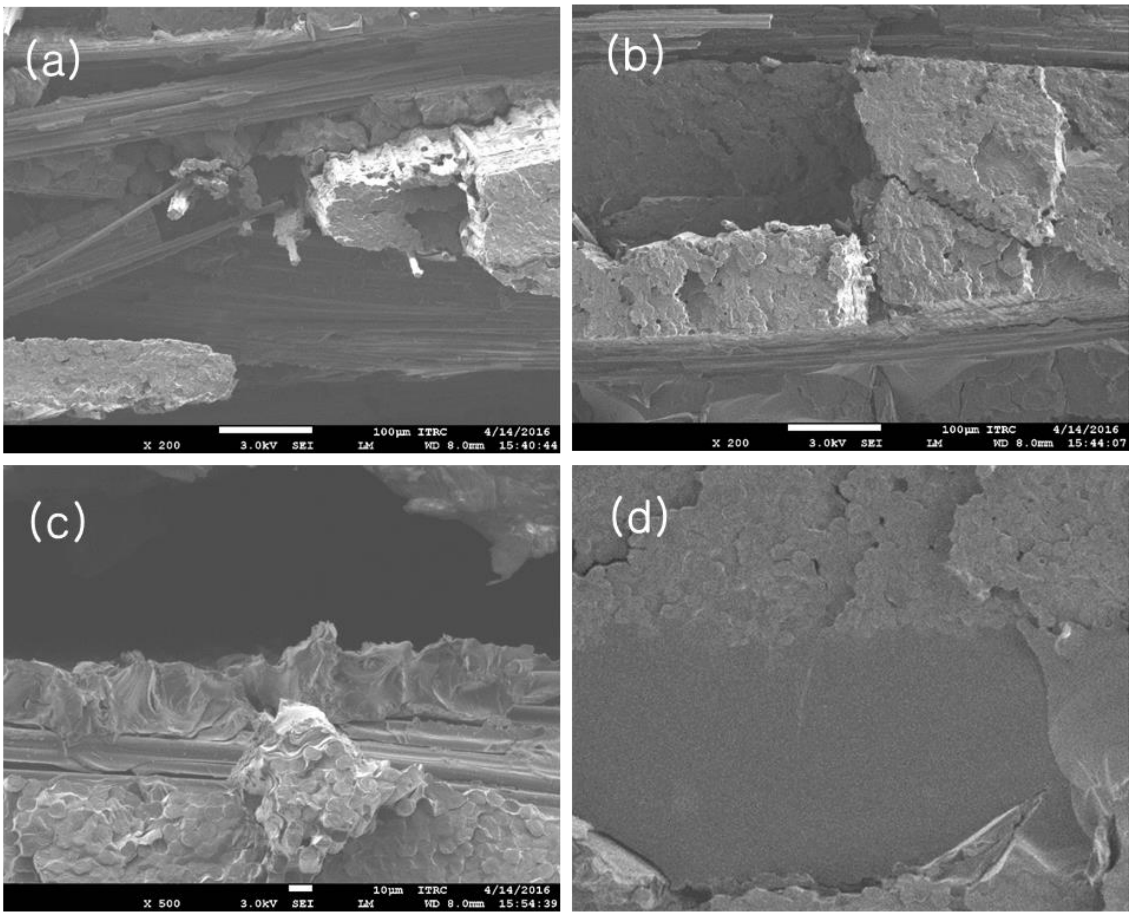

Figure 5. Microscopic morphology of carbon-carbon composties; fiber bundle section for (a) as-received CF carbon-carbon composites and (b) CNT-grafted CF carbon-carbon composites; interlaminar section for (c) as-received CF carbon-carbon composites and (d) CNT-grafted CF carbon-carbon composites

4. Conclusion

We fabricated CNT-grafted CF without degradation of mechanical properties of CF and composed carbon-carbon composites with CNT-grafted CF. Mechanical properties of carbon-carbon composites were investigated by 3-point bending test and CNT-grafted CF showed 58% higher efficiency than that of as-received CF.

Acknowledgments

This work was supported by DAPA and ADD and by the Mid-career Researcher Program through a NRF grant funded by the Korea government (MSIP) (2013R1A2A2A01067717).

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Excerpt from ISBN 978-3-00-053387-7