LOW-TEMPERATURE MANUFACTURING OF CARBON NANOTUBE-GRAFTED GLASS FIBERS AND COMPOSITES THEREOF

Ga-Young Kim[1], Geunsung Lee[1], Woong-Ryeol Yu[1]

[1] Department of Material Science and Engineering and Research Institute of Advanced Materials (RIAM), Seoul National University, 1 Gwanak-ro, Gwanak-gu, 151-744, Seoul, Korea
(* E-mail: woongryu@snu.ac.kr)

Keywords: glass fibers, carbon nanotube, chemical vapor deposition, mechanical properties

Abstract
Glass fibers are widely used as a reinforcing material in composites due to their excellent strength and insulating properties. Many researchers have sought to improve the mechanical properties and interfacial shear strength of glass fiber-reinforced composites. One means of doing this is to graft carbon nanotubes (CNTs) onto glass fibers by chemical vapor deposition (CVD). CNT-grafted glass fibers improve the interfacial shear stress and electrical conductivity of their composites. However, the growth of CNTs by CVD requires relatively high temperatures that can result in thermal degradation of the glass fibers, resulting in poor mechanical properties.
In this study, a low-temperature, floating catalyst-based CNT grafting process was investigated using a bimetallic catalyst. The catalyst was decomposed in the first section of the furnace at high temperature, while the carbon source and glass fibers were housed in a separate section of the furnace that was maintained at a lower temperature. The mechanical properties, and particularly the tensile properties, of the resulting CNT-grafted glass fibers were evaluated.

1. Introduction

Due to their excellent strength and insulating properties, glass fibers are widely used in a variety of engineering applications, especially as a reinforcing material in composites. Glass fiber-reinforced polymer composites (GFRPs) are used in the aerospace and automotive industries and in industrial construction due to their high strength and stiffness, good fatigue performance, and low cost. However, it is difficult to develop GFRPs with both good mechanical properties and electrical conductivity.

Carbon nanotube (CNT)-coated fibers have been studied for use in electrically conductive fiber-reinforced composites and have demonstrated improved interfacial properties in such materials [1, 2]. Several techniques can be used to coat CNTs onto glass fibers, including electrophoretic deposition, spray coating, dip coating, and chemical vapor deposition (CVD). CNT-grafted glass fibers by CVD were reported to improve the interfacial shear stress and electrical conductivity of their composites [3]. A serious problem, however, is the thermal degradation of glass fibers under the conditions used for CNT deposition [4]. CNTs are commonly grown by CVD at temperatures above 500oC. At such temperatures, glass fibers can be thermally degraded, resulting in significantly lower tensile strength and stiffness.

This report details a low-temperature CNT grafting process using floating catalyst-based CVD (FCVD) with a bimetallic catalyst [5]. Floating catalyst-based CVD is expected to enable continuous grafting of CNTs on the surface of glass fibers. Here, homogeneous CNT growth on glass fibers was realized by FCVD using bimetallic catalyst precursors to lower the process temperature. The resulting CNT-grafted glass fibers were evaluated for their mechanical properties.

2. Experimental

2.1 Materials

Glass fibers (Chongqing Polycomp International Corp.) were used as a substrate. Nickelocene ($Ni(C_5H_5)_2$, Sigma-Aldrich) and ferrocene ($Fe(C_5H_5)_2$, Sigma-Aldrich) were used as bimetallic catalyst precursors and toluene (99.5%, Sigma-Aldrich) as a carbon source.

2.2 Fabrication of CNT-grafted glass fibers by FCVD

FCVD is a one-step process used to graft CNTs onto a substrate without any further substrate modification and results in uniform CNT growth through a continuous process. A bimetallic catalyst, composed of a mixture of nickelocene and ferrocene at a weight percent ratio of 2:1, was prepared in toluene. These metallocene catalyst precursors have similar melting points, 171℃ and 173℃, respectively, and a decomposition temperature around 400℃ [6,7]. The procedure was conducted in a mixed atmosphere of argon and hydrogen at flow rates of 600 sccm and 200 sccm, respectively. During FCVD, a mixture of metallocene catalyst precursors and carbon source was sublimated in the first zone of the furnace and carried to the second zone by the carrier gas. Decomposition of the carbon source and catalysts, and growth of CNTs on the glass fiber substrate, occurred simultaneously.

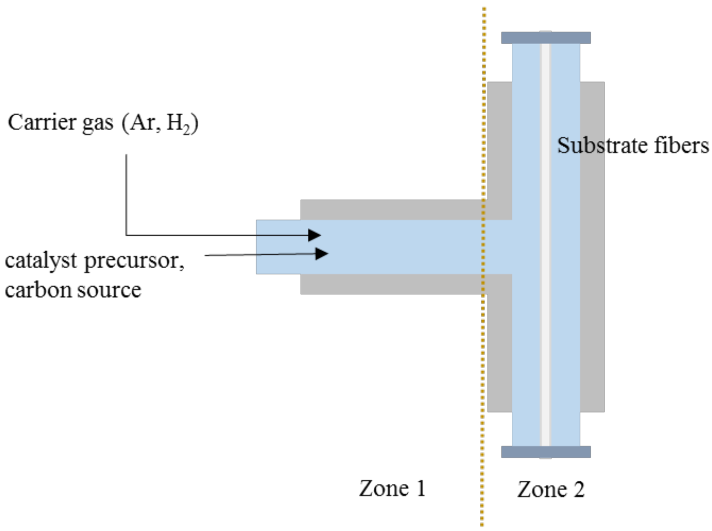

Figure 1. Schematic of the FCVD process.

2.3 Mechanical testing

Single fiber tensile tests were carried out with a universal testing machine (RB 302 ML, R&B Inc., Korea) with a load cell (Dacell, Korea) of 100 g to determine the tensile properties of the glass fibers (20 mm gage length and 1 mm/min strain ratio).

3. Results and Discussion

3.1 Morphologies of CNT grafted glass fiber

Figures 2 and 3 show the morphology of CNT-grafted glass fibers as observed by field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Analysis of these micrographs shows that uniform growth of multi-walled CNTs was attained on the glass fibers.

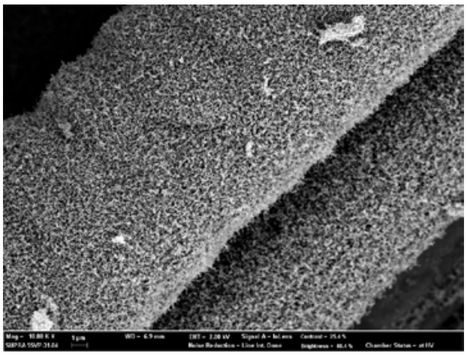

Figure 2. SEM microgragh of CNT grafted glass fibers.

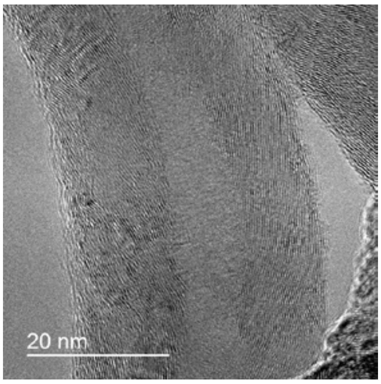

Figure 3. TEM microgragh of CNTs gown on the surface of a glass fiber.

However, degradation of the mechanical properties of CNT-grafted glass fibers was also observed. Note that only heat-treated glass fibers were evaluated for their tensile properties. The data in Figure 4 indicate that thermal degradation occurred at 500℃ as CVD progressed.

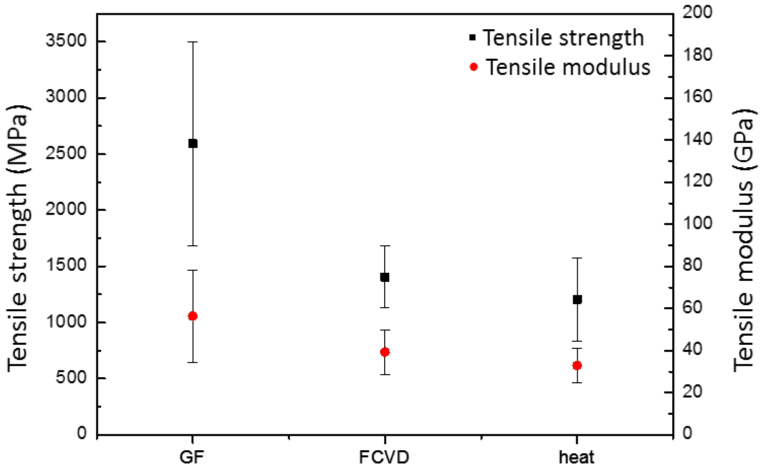

Figure 4. Tensile strength and modulus of as-received glass fibers, CNT grafted glass fibers, only heat-treated glass fibers without CVD.

Glass fibers were subjected to additional heat treatments without CVD to identify the temperature at which the glass begins to degrade. The data in Figure 5 show that thermal degradation of the glass fibers begins between 370℃ and 400℃.

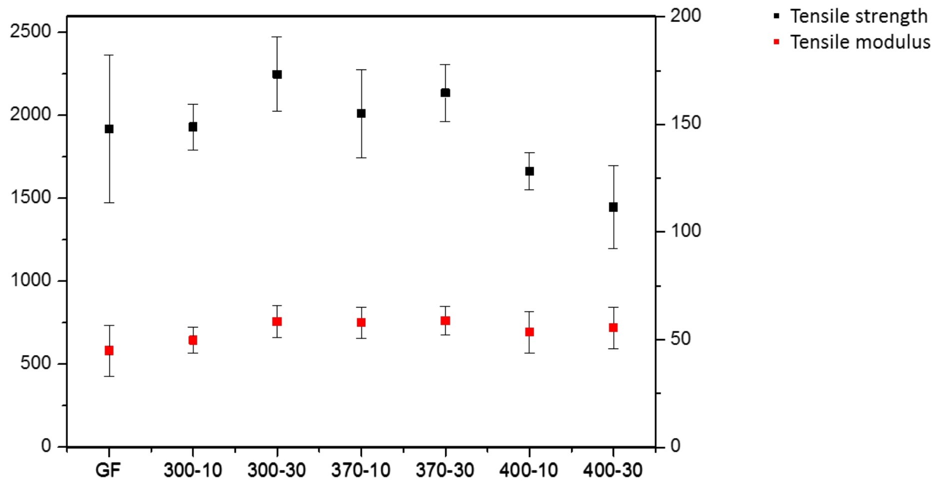

Figure 5. Tensile strength and modulus of glass fibers as a function of heat-treatment temperature.

Ideally, CNT-grafted glass fibers should be synthesized at temperatures below the thermal degradation temperature of the glass fibers. However, the degradation of bimetallic catalysts requires temperatures around 400℃. This conflict requires that CVD temperatures must be lowered to fabricate CNT-grafted glass fibers without degrading their mechanical properties.

4. Conclusions

CNT-grafted glass fibers were synthesized by FCVD, a process that enables continuous production. The glass fibers underwent significant thermal degradation above 400℃, the required temperature for the decomposition of bimetallic catalysts. Using a multi-chamber furnace, and adjusting furnace temperatures such that the bimetallic catalysts are decomposed in the first chamber while the glass fibers are housed in a second chamber held below 370℃ effectively prevents thermally induced fiber degradation. Further experimental results and analyses will be presented at the conference.

Acknowledgments

This work was supported by the National Research Foun-dation of Korea (NRF) grant funded by the Korea government(MSIT)(No. NRF- 2015R1A5A1037627).

References

[1] E.T. Thostenson, W.Z. Li, D.Z. Wang, Z.F. Ren, and T.W. Chou. Carbon nanotube/carbon fiber hybrid multiscale composites. *Journal of Applied physics.* 91.9; 6034-6037. 2002.

[2] H. Qian, A. Bismarck, E.S. Greenhalgh, G. Klinka, and M.S.P. Shaffer. Hierarchical composites reinforced with carbon nanotube grafted fibers: the potential assessed at the single fiber level. *Chemistry of Materials* 20.5; 1862-1869. 2008.

[3] D. He, B. Fan, H. Zhao, X. Lu, M. Yang, Y. Liu, and J. Bai. Design of Electrically Conductives Structural Composites by Modulating Aligned CVD-Grown Carbon Nanotube Length on Glass Fibers. ACS applied materials & interfaces, 9.3; 2948-2958. 2017.

[4] S. Feih, K. Manatpon, Z. Mathys, A. G. Gibson, and A. P. Mouritz. Strength degradation of glass fibers at high temperatures. Journal of Materials Science, 44.2; 392-400, 2009.

[5] G. Lee, J. Youk, J. Lee, I. Sul, and W.R. Yu. Low-temperature grafting of carbon nanotubes on carbon fibers using a bimetallic floating catalyst. *Diamond & Related Materials.* 68; 118-126. 2016

[6] L. Brissonneau, R. Sahnoun, C. Mijoule, and C. Vahlas. Investigation of nickelocene decomposition during chemical vapor deposition of nickel. *Journal of The Electrochemical Society*, 147; 1443 1448. 2000.

[7] M. Bernhauer, M. Braun, and K.J. Hüttinger. Kinetics of mesophase formation in a stirred tank reactor and properties of the products—V. Catalysis by ferrocene. *Carbon*, 32;1073-1085. 1994