Materials Letters 156 (2015) 17–20

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

# Effect of oxygen plasma treatment on the mechanical properties of carbon nanotube fibers

Ok-Kyung Park [a], Woo Young Kim [a,b], Seung Min Kim [a], Nam-Ho You [a], Youngjin Jeong [c], Hun Su Lee [a,*], Bon-Cheol Ku [a,d,**]

[a] Carbon Composite Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92, Chudong-ro, Bondong-eup, Wanju-gun, Jeollabuk-do 565-905, Republic of Korea
[b] Department of Carbon Fusion Engineering, Jeonju University, 45 Baengma-gil, Wansan-gu, Jeonju, Jeollabuk-do 560-759, Republic of Korea
[c] Department of Organic Materials and Fiber Engineering, Soongsil University, 369 Sangdo-ro, Dongjak-Gu, Seoul 156-743, Republic of Korea
[d] University of Science and Technology, Gajeong-ro, Yuseong-gu, Daejeon 305-350, Republic of Korea

ARTICLE INFO

*Article history:*
Received 28 March 2015
Accepted 27 April 2015
Available online 7 May 2015

*Keywords:*
Carbon nanotube fibers
Plasma treatment
Mechanical properties
Hydrogen bonding

ABSTRACT

The effect of atmospheric-pressure plasma treatment on the mechanical properties of carbon nanotube (CNT) fibers was investigated. When the CNT fibers were irradiated with RF atmospheric-pressure plasma, it was confirmed that functional groups such as hydroxyl or carboxylic acid groups were generated on the surface of the CNT fibers. The mechanical properties of CNT fibers were improved as a result of the plasma treatment because the functional groups on individual CNTs were able to induce hydrogen bonds between them. After plasma treatment with gas flow of argon (10 lpm) and oxygen (100 sccm), the tensile strength of the pure CNT fiber increased by approximately 40%, from 0.62 N/tex to 0.86 N/tex, and the modulus increased by approximately 20%, from 27.9 N/tex to 32.9 N/tex.


## 1. Introduction

The unique structure of carbon nanotubes (CNTs) has received considerable interest due to their potential mechanical, electrical, and thermal properties [1–4]. These potential properties make CNTs promising candidates for the development of a new generation of high-performance fibers.

A CNT fiber is a macro-scale structure consisting of longitudinally aligned CNTs. Recently, the fabrication of lightweight and strong CNT fibers has attracted significant research attention all over the world [5,6]. Since CNT fiber is an assembly of individual CNTs, it has the potential to be as highly strong and electrically and thermally conductive as individual CNTs but with much lower density than carbon fiber; however, the properties of CNT fibers are not even close to the theoretical properties of individual CNTs, indicating that overall performance of CNT fiber is not governed by intrinsic properties of CNTs but interactions between the CNTs that compose CNT fiber. Especially, mechanical properties of CNT fibers are limited by the weak interfacial interactions between individual CNTs. These weak interfacial interactions lead to low slip resistance between adjacent CNTs, which significantly lowers the effective mechanical performance of the microscopic constituents. Thus, a significant amount of research in recent years has focused on improving the interfacial interaction between individual CNTs [7–10]. Among the methods to improve interfacial forces between CNTs, plasma treatment is not only a very effective and easily scalable process but also an ecologically benign method in that it produces no liquid chemical waste. In addition, atmospheric-pressure plasma can treat materials in a continuous manner, which can significantly enhance productivity in the industry. When plasma is discharged with oxygen-containing gas, oxygen gas is dissociated to become oxygen atoms or ions in order to generate oxygen-containing radicals. As a result, oxygen functional groups can be generated on the defect site of the surface of CNTs. In this study, we take advantage of a simple and fast atmospheric-pressure plasma post-treatment method to enhance the interfacial interaction of CNTs. This is likely to induce attractive interfacial interactions by forming hydrogen bonding between CNTs, thereby improving the mechanical properties of CNT fibers.

## 2. Experimental details

The CNT fibers were synthesized by floating catalyst chemical vapor deposition. The details of the procedures are reported elsewhere [11]. The precursor solution used for the CNT synthesis was a mixture of acetone (98.0 wt%), ferrocene (0.2 wt%), thiophene (0.8 wt%), and polysorbate-20 (1.0 wt%). The prepared solution was injected at a rate

* Corresponding author.
** Corresponding author at: Carbon Composite Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92, Chudong-ro, Bondong-eup, Wanju-gun, Jeollabuk-do 565-905, Republic of Korea. Tel.: +82 63 219 8132; fax: +82 63 219 8139.
*E-mail addresses:* a123@kist.re.kr (H. Su Lee), cnt@kist.re.kr (B.-C. Ku).

http://dx.doi.org/10.1016/j.matlet.2015.04.141
0167-577X/

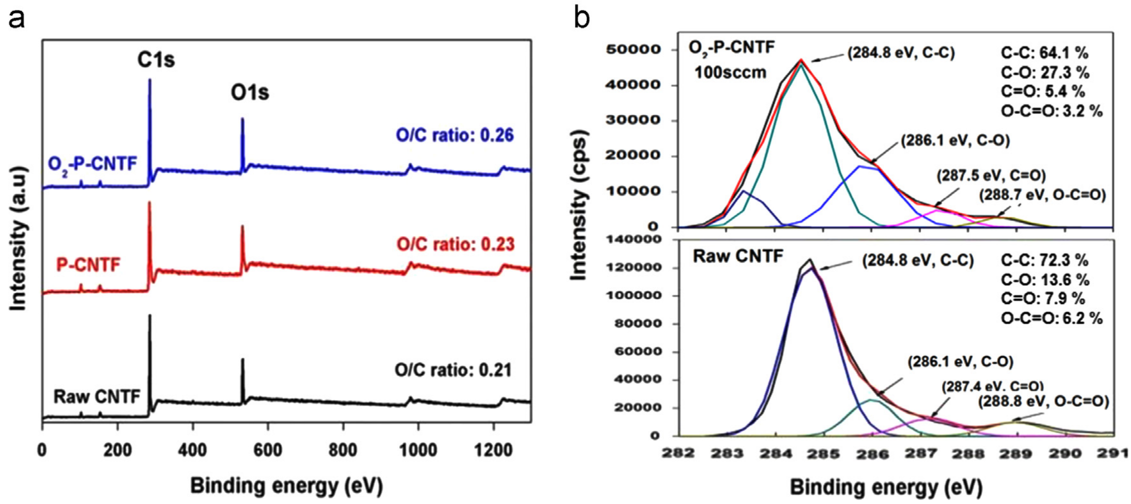


**Fig. 1.** (a) XPS survey spectra of raw CNTF, P-CNTF and $O_2$-P-CNTF 100sccm and C1s XPS of raw CNTF and $O_2$-P-CNTF 100 sccm (b).

of 10 mL/h with a hydrogen gas flow rate of 1000 sccm into a vertical reactor heated to 1200 °C. The residual catalyst content in a synthesized CNT fiber was below 18 wt%.

The plasma system used for the CNT fiber treatment was an atmospheric-pressure RF plasma source with an electrode size of 200 mm × 20 mm. A 13.56 MHz power supply for the discharge was connected to the electrode via matching network to discharge plasma with 300 W with minimized power reflection. Argon gas of 10 lpm was released for the plasma discharge, and oxygen was added with 0, 50, 100, 150 or 200 sccm to optimize the generation of the functional groups and surface damage. The plasma treatment time was set to 5 min, and CNT fibers were placed 4 mm apart from the electrode in order to avoid damage from direct contact with plasma.

## 3. Results and discussions

The chemical groups on the CNT fibers induced by atmospheric-pressure plasma treatment were investigated using XPS as described in Fig. 1. When the CNT fibers were treated with the plasma with 100 sccm of oxygen and 10 lpm of argon ($O_2$-P-CNTF), the atomic ratio between oxygen and carbon (O/C ratio) increased from 0.21 to 0.26 compared to that of raw CNT fiber. XPS C1s spectrum of raw CNTF and $O_2$-P-CNTF are shown in Fig. 1(b). After oxygen plasma treatment, the percentage of C–O bond in the CNTF increased from 13.6 to 27.3%. This is indicative of the relative amount of oxygen that was incorporated into the surface of CNT fiber by the oxygen plasma treatment.

As can be seen from Fig. 2, the O/C ratio increases with an increase in the flow rate of oxygen by 50 sccm; however, more oxygen flow for the discharge does not increase the content of oxygen incorporated into the CNT fiber. We speculate that this resulted from the decrease of plasma density with oxygen level increase or from the etching of CNT rather than functional group generation.

The influence of the functional groups, generated by the plasma treatment, on the mechanical properties of the CNT fibers is investigated by measuring typical stress–strain curves as shown in Fig. 3(a). In the case of 10 lpm argon-only plasma, the tensile strength of the fiber slightly increased by 15%; however, when 100 sccm of oxygen flow is added to the argon, the tensile strength and tensile modulus of the fiber further increased by 40% and 20% each after just 5 min of atmospheric-pressure plasma treatment.

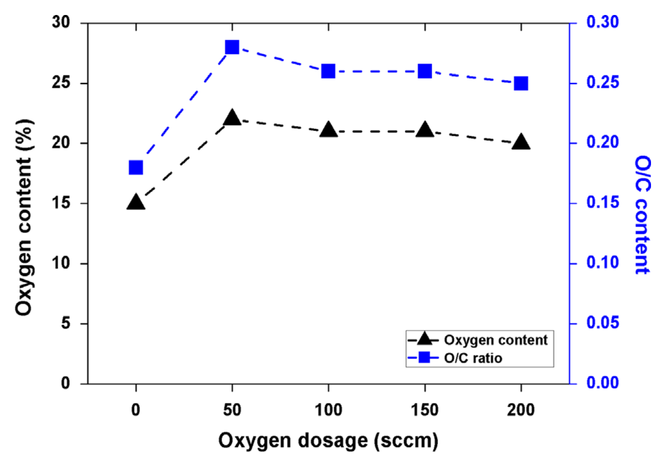


**Fig. 2.** Oxygen content and atomic O/C ratio of raw CNT fiber and oxygen plasma treated CNT fiber.

Therefore, it can be concluded that the plasma treatment is an effective method to improve the mechanical properties of the CNT fiber, and the oxygen species plays an important role in the enhancement of the mechanical properties by inducing a hydrogen bond between the hydroxyl moieties of adjacent CNTs. It is suggested that the oxygen plasma treatment produces the oxygen functional groups on the surface of CNTs, which may possibly induce hydrogen bonding between individual CNTs. This, in turn, can induce efficient stress transfer from the CNT to the adjacent CNTs, resulting in an increase in the mechanical properties of the CNT fiber [12].

Fig. 3(b) shows the effect of oxygen flow rate on the mechanical properties of CNT fibers. The mechanical properties of the CNT fibers show maximum values at an oxygen dosage of 100 sccm. This means that as oxygen flow increases, the number density of oxygen-containing functional groups on the surface of CNTs increases, thereby increasing the amount of interfacial bonding between adjacent CNTs and improving the mechanical properties of CNT fibers. However, as the oxygen flow rises above 100 sccm, the mechanical properties deteriorate even further. In order to investigate why excessive oxygen flow beyond 100 sccm degrades the mechanical properties of CNT fibers, Raman spectroscopy analysis was conducted to evaluate the crystallinity and defects