DEVELOPMENT OF UNTWISTED CARBON NANOTUBE YARN WITH HIGH STRENGTH BY HEAT TREATMENT

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Abstract
Carbon nanotube (CNT) is increasingly applied as a reinforcement of polymer matrix composite because of extremely high mechanical properties. Among several forms of CNT reinforcement, CNT yarn can be a next-generation reinforcement which enables the use of CNTs in the macro-scale. In this study, untwisted CNT yarns were fabricated by the dry spinning method using a die and graphitized in order to develop CNT yarns with high strength and stiffness. Impure materials and defective structures on MWCNTs were removed after graphitization treatment. G/D ratio was improved more than 10 times. Stress transfer between constituent MWCNTs of CNT yarns became more effectively by removing impure materials. Consequently, macroscopic mechanical properties of CNT yarns were improved by the graphitization treatment in addition to improvement of MWCNT itself.

1. Introduction

Carbon nanotubes (CNTs) have been applied as a reinforcement material in polymer matrix composites because of excellent mechanical properties. Dispersion in matrix resin has been studied as the main methods of introducing CNTs to PMCs. It is difficult to achieve high CNT content and homogeneous dispersion mainly owing to the agglomeration of the nano-scale material.

Jiang et al. developed a method for fabricating CNT yarns from vertically aligned multi-walled CNT (MWCNT) arrays [1]. Such CNT yarns are expected to be a next-generation reinforcement fiber that will enable the extremely excellent mechanical properties of CNTs to be exploited on the macro-scale, and make it possible to fabricate CNT composites which have high CNT content and orientation. As MWCNTs which constitute CNT yarns are unified by Van der Waals' forces, it is possible to improve mechanical properties of CNT yarns by densification. There are various methods to strengthen CNT yarns, such as densification treatment using acetone or polymer solution [2] and compression molding using a die [3]. However, mechanical properties of CNT yarns are still much lower than that of MWCNT itself, and strength property expected as a reinforcement fiber have not been achieved.

There are some impure materials and defective structures such as amorphous carbon and five-membered ring structure on CNTs synthesized by chemical vapor deposition. They can decrease strength of CNT yarns, whereas it is possible to increase mechanical properties of CNT yarns by removing them. Graphitization treatment is well known as an effective method to remove impure materials and defects on carbon materials. Graphitized CNTs tend to have excellent mechanical and

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electrical properties. On the other hand, it is unclear whether graphitization is effective to improve mechanical properties of CNT yarns which are aggregation of CNTs.

In this study, untwisted CNT yarns were fabricated and graphitized in order to develop CNT yarns with high strength and stiffness. Untwisted CNT yarns were fabricated by the dry spinning method using a die. Mechanical properties of graphitized CNT yarns were evaluated by single fiber tensile test, and the effect of graphitization on mechanical properties of CNT yarns were revealed.

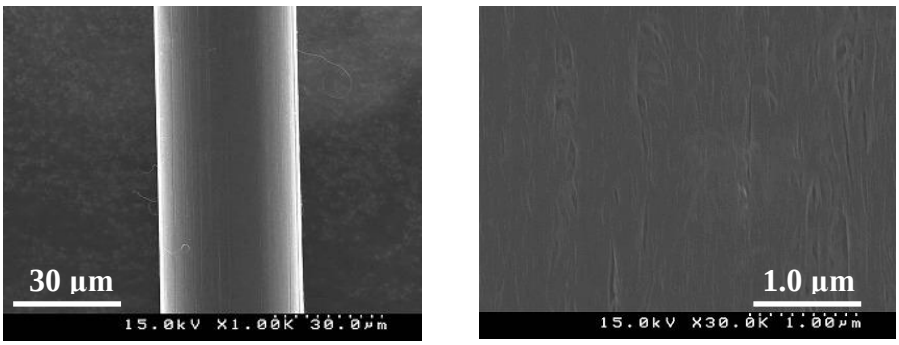
2. Materials

2.1. Vertically aligned multi walled carbon nanotube

Vertically aligned multi walled CNTs (MWCNTs) were synthesized by a chemical vapor deposition (CVD) method at atmospheric pressure. Iron particles deposited on the Si wafer substrate by electron beam evaporation were used as the catalyst, and acetylene (C_2H_2) gas was used as the carbon source. From observations using a field emission-scanning electron microscopy (FE-SEM) and a transmission electron microscopy (TEM), MWCNTs used in this study were found to be approximately 492 μm long and 10.9 nm in outer diameter, 5.61 nm in inner diameter, and with a wall number of about 7.

2.2. Untwisted carbon nanotube yarn

Untwisted CNT yarns were fabricated using a dry spinning method by passing CNT sheets through a ceramics die. CNT sheets were drawn continuously from vertically aligned MWCNT arrays. In this study, two kinds of CNT yarns with different densities (AR22.5 and AR30) were fabricated by changing width of the CNT sheet from the CNT array. Table 1 shows diameter and density of the fabricated CNT yarn, and Fig. 1 shows side view of the untwisted CNT yarn observed using FE-SEM. Constituent CNT bundles in the untwisted CNT yarns tend to have higher orientation to longer direction of the CNT yarn compared with general twisted CNT yarns.



(a) Overview (b) Magnified view

Figure 1. Side view of untwisted CNT yarn.

Table 1. Diameter and density of untwisted CNT yarns.

Specimen	Diameter (μm)	Linear density (tex)	Density (g/cm^3)
AR22.5	36.2	0.83	0.80
AR30	36.5	1.05	1.04

3. Testing methods

3.1. Graphitization treatment

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CNTs synthesized by CVD method tend to include some impure materials and defective structures such as amorphous carbon and five-membered ring structure. They can degrade mechanical properties of CNTs. G/D ratio of MWCNTs used in this study was measured 1.2 by Raman spectroscopic analysis, and it was shown that crystallinity of the MWCNT was relatively low and there were some defective structures. Therefore, untwisted CNT yarns were graphitized after the fabrication in order to improve the mechanical properties by removing the defects. Graphitization treatment was conducted using a high temperature furnace at 2800℃ for 1 hour under argon gas atmosphere. CNT yarns were fixed on a carbon felt and placed in a cylindrical carbon crucible.

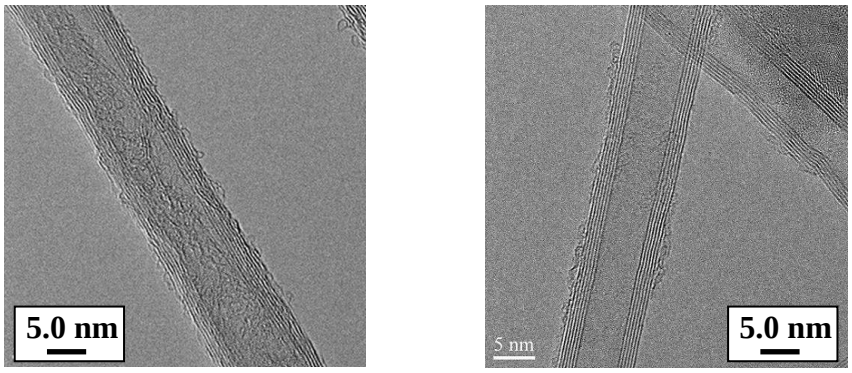
3.2. Single fiber tensile test

Single fiber tensile tests were conducted to evaluate the mechanical properties of the CNT yarn, using a universal testing machine. The specimens for measurement were prepared by fixing a length of CNT yarn on a protective sheet with an adhesive. Then, the gauge length was set to 5 mm and the tensile test was conducted under a test speed of 0.20 mm/min.

4. Results and Discussions

4.1. Morphological changes in CNT yarns by graphitization

Figure 2 shows morphological changes in MWCNTs by the graphitization treatment observed using FE-TEM. There were some amorphous carbons on the surface of MWCNTs before the graphitization treatment, and the typical hollow structure of CNTs was unclear. Walls composing the MWCNT were disorganized. On the other hand, most of the impure materials on MWCNTs were removed after the graphitization treatment and the hollow structure was observed clearly. Furthermore, constituent walls were arranged parallel. It was confirmed that impure materials and defective structures on each constituent MWCNT could be removed by graphitization treatment of the CNT yarn. There was not significant change by graphitization in diameter of MWCNTs and the number of walls.



(a) Untreated MWCNT (b) Graphitized MWCNT
Figure 2. Morphological change in MWCNT by graphitization treatment.

Diameter and density of CNT yarns became smaller after the graphitization (Table 2). AR22.5 showed 28%, 8% decrease in linear density and apparent density, whereas AR 30 showed 17%, 12% decrease. These reductions were result from heat decomposition of impure materials. Figure 3 shows Raman spectrum of untwisted CNT yarns. As a result of the graphitization treatment, G band derived from crystallinity of CNT significantly increased, and D band derived from defect structure decreased. G/D ratio was improved more than 10 times by graphitization and reached 14.3 (in G22.5) and 14.4 (in

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G30) respectively. Defective structures in untreated CNT yarns were removed and crystallization was promoted by the graphitization treatment.

Table 2. Diameter and density of graphitized CNT yarns.

Specimen	Diameter (μm)	Linear density (tex)	Density (g/cm^3)
G22.5	32.5	0.60	0.74
G30	35.6	0.87	0.91

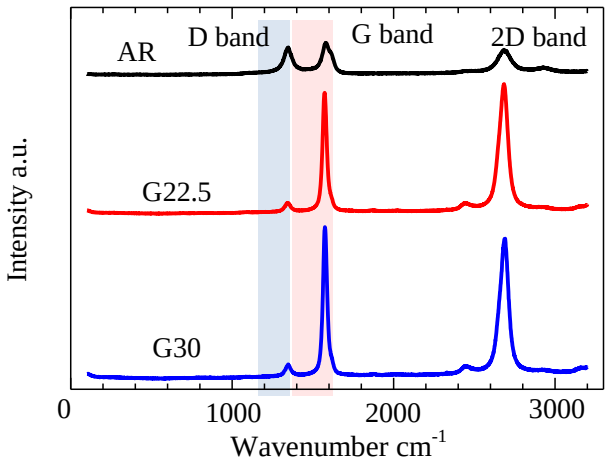

Figure 3. Raman spectrum of untwisted CNT yarns.

4.2. Mechanical properties of graphitized CNT yarns

Figure 4 and Table 3 shows stress-strain curves and mechanical properties of CNT yarns obtained by the single fiber tensile tests.

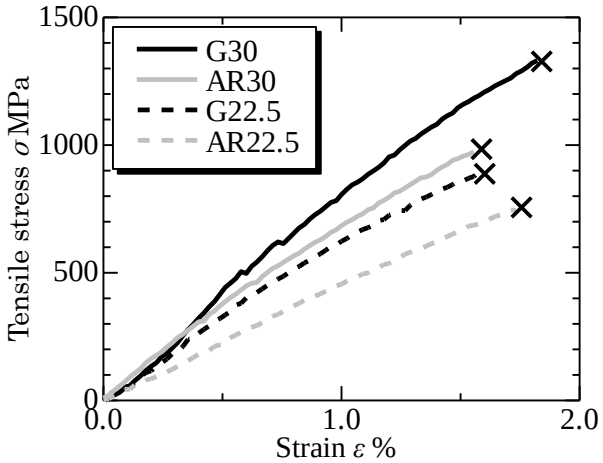

Figure 4. Stress strain curves of untreated and graphitized CNT yarns.

Table 3. Mechanical properties of untreated and graphitized CNT yarns.

Specimen	Strength (MPa)	Fracture strain (%)	Young's modulus (GPa)
AR22.5	823	1.77	59.8
G22.5	981	1.65	74.7
AR30	988	1.79	73.4
G30	1335	2.23	89.8

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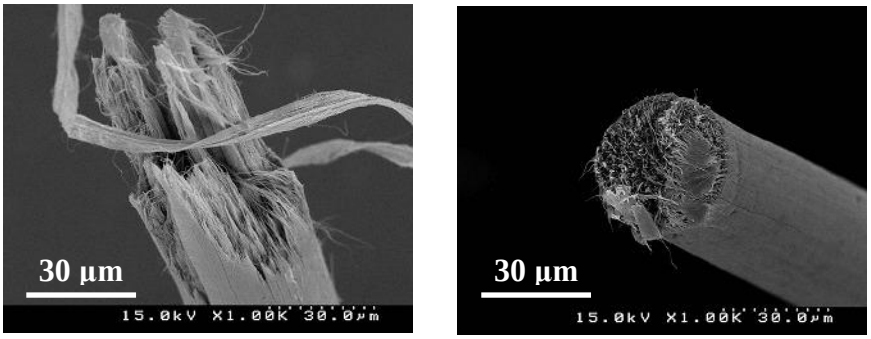

(a) Untreated CNT yarn (b) Graphitized CNT yarn

Figure 5. Changes in fracture surfaces of CNT yarns by graphitization treatment.

Mechanical properties of untwisted CNT yarns were improved after graphitization. Strength and Young's modulus of CNT yarns were increased by 19%, 25% in G22.5, by 35%, 22% in G30 respectively. Strengthening of CNT yarns was due to the crystallization of constituent MWCNTs in addition to the apparent improvement of mechanical properties by decrease in yarn diameter. Fracture surface of untreated CNT yarn were across a large area and CNT bundles were pulled out (Fig. 5). On the other hand, fracture areas of graphitized CNT yarns were small and it was possible that constituent MWCNTs were broken (Fig. 5). Stress transfer between constituent MWCNTs became more effectively by removing impure materials. It led to transfer loading until pure MWCNTs with high strength broke. As a result, macroscopic mechanical properties of CNT yarns were improved by the graphitization treatment in addition to improvement of MWCNT itself.

5. Conclusions

In this study, untwisted CNT yarns were fabricated by the dry spinning method using a die and graphitized in order to develop CNT yarns with high strength and stiffness. Impure materials on MWCNTs were removed and constituent walls of MWCNTs were arranged parallel after graphitization treatment. G/D ratio was improved more than 10 times and reached about 14. Defective structures in untreated CNT yarns were removed and crystallization was promoted by the graphitization treatment. Stress transfer between constituent MWCNTs of CNT yarns became more effectively by removing impure materials. Consequently, macroscopic mechanical properties of CNT yarns were improved by the graphitization treatment in addition to improvement of MWCNT itself.

Acknowledgments

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