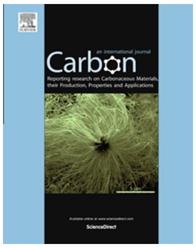
Available at www.sciencedirect.com

ScienceDirect

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



Effect of polymer infiltration on structure and properties of carbon nanotube yarns

Yeonsu Jung, Taehoon Kim *, Chong Rae Park *

Carbon Nanomaterials Design Laboratory, Global Research Laboratory, Research Institute of Advanced Materials, and Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Republic of Korea

ARTICLE INFO

Article history:
Received 23 October 2014
Accepted 19 February 2015
Available online 26 February 2015

ABSTRACT

Polymer-infiltrated carbon nanotube yarns (CNTYs) were prepared to enhance the mechanical and electrical properties of CNTYs through physical interactions. This work additionally explored the role of the polymer in altering the structures of the CNTYs. The reticulate structures of the CNTYs produced through aerogel methods were infiltrated with a dilute (0.05 wt%) solution of polystyrene (PS), polyacrylonitrile (PAN), or polyvinyl alcohol (PVA), and the structures were characterized. The performances of the CNTYs were closely related to the junction strength and the bundle size in the reticulate CNTYs. Among the three polymers examined, infiltration of PVA—the polymer with the poorest affinity toward CNTs—yielded the greatest improvement in the mechanical and electrical properties of the CNTY. The CNTY deformation properties at each stage of the stress–strain curves could be explained based on the effects of the polymer infiltration on the structure and properties of the CNTY. The results indicated that the specific stiffness, specific strength, toughness, and electrical conductivity are significantly influenced by the molecular-level coupling between the polymer, the CNTs, and the internal structure of the CNTY.

1. Introduction

Carbon nanotubes (CNTs) and CNT yarns (CNTYs) have drawn considerable attention due to their excellent mechanical and electrical properties and their potential utility [1–3]. CNTYs with a high electrical conductivity and strength are thought to require void-free and defect-free materials with a high degree of CNT alignment; however, CNTYs produced through a variety of methods have exhibited significantly poorer mechanical and electrical properties [2,4–9] than individual CNTs, which exhibit moduli as high as 1 TPa, strengths as high as 50 GPa [10,11], and electrical conductivities on the order of $10^6\ \mathrm{S\,m^{-1}}$ [3,12,13]. Over the last decade, several papers have described the manufacture and improvement of CNTY properties through nanostructural control, including the number of walls, diameters, and lengths of the CNTs [14,15], as well as microstructural control, including the twist angle and CNT alignment along the yarn axis [1,9,16]. Long and highly aligned CNTs tend to produce high-performance CNTYs [1,17]. Despite the variety of structural approaches tested thus far, raw CNTYs still show poor properties due to the interfacial slippage among bundles or CNTs [7,8]. Recent studies have modified the CNT surfaces using chemical reactions to introduce covalent or hydrogen bonds, which are stronger than the van der Waals interactions, in an effort to enhance the interfacial strength [18–20]. The functional groups introduced onto the CNT surfaces are essential for inducing bonding sites [21], and they provide a powerful

---

* *Corresponding authors:* Fax: +82 2 885 1748.
E-mail addresses: dawnair7@snu.ac.kr (T. Kim), crpark@snu.ac.kr (C.R. Park).

http://dx.doi.org/10.1016/j.carbon.2015.02.065
0008-6223/

approach to improving the interfacial strength; however, functionalization necessarily introduces defects. The conversion of sp^2 into sp^3 carbon atoms on the CNT surfaces decreases the inherent mechanical and electrical properties of the CNTs [12,13]. Additionally, it is difficult to attach functional groups uniformly onto the CNT surfaces because additional procedures, such as re-dispersing closely packed CNTs for chemical reactions after CNTY formation, are required.

Physical interactions may potentially ameliorate interfacial slippage. One such method of enhancing the physical interactions involves polymer infiltration. This method does not require the re-dispersion of CNTs or chemical modification. The amount of additive infiltrated into the CNTY may be easily controlled. Polymer infiltration, therefore, provides a simple and promising method of fabricating high-performance CNTYs without destroying the unique CNT structures or properties. Only a few polymers, including epoxy [22,23] or PVA [2,14,22,24–26], are effective in improving the CNTY load transfer efficiency, although it has not previously been understood how these polymers act in the CNTY/polymer composite materials.

The architectures of CNTs are important not only in CNT/polymer composite materials, but also in CNTYs. Raw CNTY or CNTY/polymer materials deformed differently under tensile stress, depending on the CNT architecture, which influenced the load delivery efficiency and provided very different properties [1,6,14,22,27,28]. Although the CNTs present in the CNTYs were linked to one another through weak van der Waals interactions, the total interaction energy depended strongly on the CNT bundle structure, including the contact area. Closely packed CNT bundles tended to show better mechanical properties [9,25,26]. Solvent densification provides one approach to improving both the mechanical and electrical properties of the CNTYs by reducing the number and size of the pores in the CNTYs, thereby changing the bundle structure without incorporating supporting materials [9,25]. The structure of a CNT is of crucial importance to determining both the mechanical properties and the electrical properties of a CNTY and a CNTY/polymer composite material [1,16,22]. For these reasons, conventional composite theory, which has focused mainly on the interfacial strength between the matrix and the CNTs without considering the CNT architectures, has not been able to explain CNTY strengthening via polymer infiltration [22,29,30].

In this work, we explored the effects of polymer infiltration into CNTYs and measured the structural and property changes that took place throughout the process. A variety of polymers with different Hansen affinity parameters (HAPs) toward CNTs were infiltrated into the CNTYs in an effort to characterize the effects of the interactions between the CNTs and the polymer. The structural changes that took place during the process and the properties of the polymer-infiltrated CNTY were strongly related to the interactions determined by the HAP. The mechanical and electrical properties were simultaneously improved by polymer infiltration into the CNTY. The deformations of the CNTYs could be predicted based on the relationship between the properties and the structures of the polymers infiltrated into the CNTYs.

2. Experimental

2.1. *Spinning the CNTYs*

Continuous CNTYs were prepared using aerogel spinning methods involving chemical vapor deposition (CVD) in a vertical furnace at 1200 °C [29,30]. The carrier gas and reactants, hydrogen, ferrocene, thiophene, and methane, were supplied at the top of furnace, and the CNT assemblies were transformed into the yarn through a water bath at the bottom of the furnace. Adsorbed water was removed by heating at 100 °C in a vacuum dry oven.

2.2. *Solvent and polymer infiltration into the CNTY*

The solvent- and polymer-infiltrated CNTYs were obtained by passing the CNTY through a second bath, as shown in Fig. 1a, at room temperature. One-third of the winder was submerged in the second bath filled with the solvent or polymer solution. The CNTY was soaked in the second bath solution for an hour to prepare the fully solvent- or polymer-absorbed CNTYs to eliminate the kinetic effect because the polymer infiltration into CNTYs is a kinetic limited process. The CNTY was then dried in a vacuum oven at 100 °C for more than 6 h. The densification and polymer infiltration agents dimethyl sulfoxide (DMSO), PS (MW 280000, Sigma Aldrich), PAN (MW 150000, Sigma Aldrich), and PVA (MW 130000, Sigma Aldrich) were purchased and used as received. The polymer infiltration bath was prepared using polymer solutions (0.05–1.0 wt%). The polymers were dissolved in the solvents (PS in dimethylformamide (DMF), PAN and PVA in DMSO) at 80 °C.

2.3. *Characterization of the CNTYs*

The linear densities (tex, g km^{-1}) of the raw and polymer-infiltrated CNTYs were measured by weighing 50 m of each sample. Thermal gravimetric analysis (TGA, SDT-Q600, TA Instruments) was used to measure the purity of the CNTs, between room temperature and 950 °C in an air atmosphere. The number of walls and diameters of the synthesized CNTs were analyzed using TEM methods (JEM-2100F, JEOL). The crystallinity, alignment of CNTs along the yarn axis, and chemical characteristics of the CNTs were evaluated using X-ray photoelectron spectroscopy (XPS) (AXIS-His, KRATOS) and polarized Raman spectroscopy using a 532 nm laser (RAMANplus, Nanophoton) integrated with a tensile stage (TST350, Linkam). The surface morphologies and internal structures of the CNTY were measured before and after cutting with a focused ion beam (FIB) (Helios 650, FEI) using SEM methods (JSM-6700F, JEOL). The mechanical and electrical properties were measured using a 10 mm length of CNTY at a strain rate of 3 mm min^{-1} on an INSTRON 5543 instrument equipped with a 50 N load cell and a Keithley 2634B unit.

3. Results and discussion

The CNTYs were fabricated continuously without a substrate using the floating catalyst CVD method [31,32] in which a first water bath and a winder were placed below the vertical