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Desirable electrical and mechanical properties of continuous hybrid nano-scale carbon fibers containing highly aligned multi-walled carbon nanotubes

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ABSTRACT

The continuous highly aligned hybrid carbon nanofibers (CNFs) with different content of acid-oxidized multi-walled carbon nanotubes (MWCNTs) were fabricated through electrospinning of polyacrylonitrile (PAN) followed by a series of heat treatments under tensile force. The effects of MWCNTs on the micro-morphology, the degree of orientation and ordered crystalline structure of the resulting nanofibers were analyzed quantitatively by diversified structural characterization techniques. The orientation of PAN molecule chains and the graphitization degree in carbonized nanofibers were distinctly improved through the addition of MWCNTs. The electrical conductivity of the hybrid CNFs with 3 wt% MWCNTs reached 26 S/cm along the fiber direction due to the ordered alignment of MWCNTs and nanofibers. The reinforcing effect of hybrid CNFs in epoxy composites was also revealed. An enhancement of 46.3% in Young's modulus of epoxy composites was manifested by adding 5 wt% hybrid CNFs mentioned above. At the same time, the storage modulus of hybrid CNF/epoxy composites was significantly higher than that of pristine epoxy and CNF/epoxy composites not containing MWCNTs, and the performance gap became greater under the high temperature regions. It is believed that such a continuous hybrid CNF can be used as effective multifunctional reinforcement in polymer matrix composites.

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1. Introduction

The high performance fibers and their resulting composite materials have been applied extensively in many advanced technological fields, such as aerospace, transportation and exploitation of energy resources. Carbon fibers possess the highest specific strength and specific modulus among all commercially available reinforcing fibers. However, the strongest carbon fibers that can be produced today have a tensile strength of only 7.02 GPa (e.g. Toray T1000®), merely 4% of the theoretical value of over 180 GPa [1,2]. All kinds of structural defects are the most crucial barriers to significantly improving the mechanical properties of the carbon fibers. The amount, size, and distribution of structural imperfections have important effects on strength and modulus of the carbon fibers.

The most effective way to minimize the imperfections is to reduce the fiber diameter, as the decreased fiber diameter can greatly reduce the appearance opportunity of the structural defects. The electrospinning process has been recognized as the main method which can be further developed for mass production of continuous nanofibers from various polymers.

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More than 50 different types of polymer-based nanofibers have been successfully produced by using appropriate technological parameters. The continuous nanofibers with amazing characteristics such as a very large surface area to volume ratio (this ratio for a nanofiber can be as large as 10^3 times of a microfiber), flexibility in surface functionalities, and appropriate mechanical performance, have prompted specifically their use as functional filler and reinforcement in composites [3]. Polyacrylonitrile (PAN) with good stability and mechanical properties has been widely used as electrospun nanofibers due to their excellent characteristics, such as spinnability, environmentally benign nature and commercial viability [4]. Furthermore, PAN nanofibers are most commonly used as precursors for producing carbon nanofibers (CNFs), mainly because of its high carbon yield (up to 56%), flexibility for tailoring the structure of the final CNF products and the ease of obtaining stabilized products due to the formation of a ladder structure through nitrile polymerization [5–9]. The resulting CNFs have been used in wide fields including filtration barriers [10], material reinforcements [11], garments, insulators, medical and energy storage devices [12], and so on. However, the continuous nanofibers produced by electrospinning processes are not as strong as desired due to their imperfect microstructure and the un-optimized molecular orientation in the fibers [13]. Moon et al. Prepared CNFs by using electrospun PAN yarns, and the strength of the resulting CNFs was only about 1.0 GPa owing to the existence of pervasive fiber breakage and low fiber alignment as described in the report [14]. Therefore, further structure design and post-processing is necessary for improving the structural perfection and fiber orientation of electrospun nanofibers. There is still a need for the extensive research to develop continuous CNFs with high performance.

The use of nanofillers is a promising way to reinforce nanofibers [15]. Carbon nanotubes (CNTs) possess high electrical conductivity, low mass density, large aspect ratio (typically >1000), whereas predicted data indicate extremely high tensile modulus and strengths [16]. Since the first polymer composites using CNTs as fillers were reported in 1994 by Ajayan et al. [17], there have been many studies on the fabrication of CNT/polymer composites [18]. However, CNT aggregation has been found to dramatically hamper the mechanical properties of prepared composites and the superb properties of CNTs cannot as yet be fully translated into high strength and stiffness of the resulting products. In order to improve the dispersion of CNTs and interface bonding in polymer matrix, it is necessary to carry out surface chemical modification [19,20]. In addition, the content of CNTs added into matrix should be proper to avoid aggregation. Our previous studies showed 320.7% and 204.5% improvement in the tensile strength and modulus of PAN nanofibers by adding 2 wt% grafted multi-walled carbon nanotubes (MWCNTs) [21]. Nevertheless, so far there still is a lack of related reports of hybrid CNFs with good physical and mechanical properties, especially the reinforcing effect of the CNFs in the resulting composites.

In this work, PAN terpolymer nanofibers containing well-aligned acid-oxidized MWCNTs with content of 0–20 wt% were prepared by electrospinning, and followed by a series of heat treatments under tension force to fabricate CNFs. The orientation and crystalline structure of carbonized nanofibers were distinctly improved after moderate addition of MWCNTs. The carbonized hybrid nanofiber membranes with 3 wt% MWCNTs exhibited an anisotropic electrical conductivity, and the conductivity along the fiber direction was up to 26 S/cm, which stood in vivid contrast to previously reported results of CNF papers [22]. In addition, the hybrid CNFs significantly improved the mechanical properties of epoxy resin, and can act as high performance of new reinforcement in advanced composites.

2. Experimental

2.1. Materials

PAN terpolymer (93.0 wt% acrylonitrile, 5.3 wt% methyl acrylate, and 1.7 wt% itaconic acid, with an average molecular weight of 100,000 g mol^{-1} and a density of 1.18 g cm^{-3}) was supplied by Courtaulds Co., Nottingham, UK. N,N'-dimethylformamide (DMF, bp 153 °C), concentrated sulfuric (98%), and nitric acid (70%) were purchased from Beijing Chemicals Co., Beijing, China. MWCNTs (purity, ⩾95%; diameter, 15–20 nm) were supplied by Nanotech Port Co. Ltd., Shenzhen, China, and used as received. The diglycidyl ether of bisphenol A type epoxy resin (Shell EPON 828) was used in this paper. A flexible amine (Jeffamine T403, supplied by BASF, Germany) was used as curing agents.

2.2. Sample preparation

2.2.1. Acid Oxidization of MWCNTs

The as-received MWCNTs were acid-oxidized in a mixture of concentrated H_2SO_4 and HNO_3 (1:1, v/v) by refluxing at 120 °C for 1 h.

2.2.2. Electrospinning

The PAN terpolymer fibers were dried at 80 °C for 2 h prior to use. The MWCNTs were immersed in DMF and sonicated for 10 h in a bath-type sonicator, and then the dried PAN was dissolved in MWCNT-dispersed DMF suspension to prepare a 14 wt% solution (PAN terpolymer/DMF) by ultrasonic mixing. Subsequently, the solution was electrospun at room temperature, with an applied voltage of 18 kV and a distance of 180 mm between the spinneret and the fiber collector. The electrospun nanofibers were collected in the form of a membrane on a 11-cm-diameter aluminum foil-covered rotating drum with a rotation speed of 6.7 m s^{-1}. Hybrid nanofiber membranes with different content of MWCNTs (0 wt%, 1 wt%, 3 wt%, 5 wt%, 8 wt%, 10 wt%, 15 wt% and 20 wt%) were obtained under the same condition.

2.2.3. Hot-stretching and stabilization

In order to improve the degree of orientation of macromolecule chains and reduce the voids in the electrospun nanofibers, the nanofibers were drawn under tension. The electrospun membranes (100 mm in length, 50 mm in width) were peeled from the aluminum foil and multi-step hot-stretched along the nanofiber direction in the air for 5 min at 140 °C. The tensile forces were controlled by the

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