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Scalable manufacturing of carbon nanotubes on continuous carbon fibers surface from chemical vapor deposition

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ABSTRACT

A novel process has been successfully developed to grow carbon nanotubes (CNTs) on continuously moving carbon fibers (CF) surface by a unique open-ended chemical vapor deposition (CVD) furnace. Systematic researches were carried out under various deposition temperatures, velocities of continuous carbon fibers and catalyst concentrations. The morphologies and structures of CNTs were investigated by field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM), which indicated clearly that carbon fibers with uniformly distributed CNTs were achieved, with the optimum parameters of 650 °C deposition temperature and 6 cm min^{-1} velocity of continuous carbon fibers and 0.05 M catalyst concentration, respectively. By means of the single fiber push-out tests, the interfacial shear strength (IFSS) of carbon fibers growing CNTs was increased significantly by 84.4% compared to the desized carbon fibers. Furthermore, the results of single fiber tensile test verified that there is scarcely any degradation in the mechanical properties of carbon fibers after the growth of CNTs with the optimum parameters. This study provides a new and original vision for scalable manufacturing of CNTs on continuous moving substrate, when compared to the traditional batch process.

1. Introduction

Carbon fiber reinforced polymer composites (CFRP) have been widely used in the application of aerospace, automobile manufacturing and leisure sports due to its excellent performance of high specific strength, high specific modulus, low density and corrosion resistance [1–3]. However, the interlaminar mechanical and electrical performance of CFRP are relatively low in virtue of the weak interaction between carbon fibers and resin matrix [4,5]. Therefore, the modification of carbon fibers is quite necessary to increase the CFRP interfacial bonding strength. Carbon nanotubes (CNTs) as a new carbon material can be used as a promising composite reinforcement owing to its unique mechanical properties, electrical properties, thermal properties [6–8]. But the entanglement, aggregation and float phenomenon [9] will be appeared when CNTs are applied to reinforcement, which seriously hinders its wide application. Preparation of CF/CNTs multi-scale reinforcement has become one of the most effective means to enhance the interlaminar mechanical and electrical performance of CFRP when it combined with the resin matrix, which can not only give play to their outstanding performance, but also modify carbon fibers surface and solve the poor dispersion of CNTs [10].

In addition to chemical grafting [11] and electrophoretic deposition [12], catalytic chemical vapor deposition (CVD) [13–15] is the most promising approach to design CF/CNTs multi-scale reinforcement. Several researches have been reported CNTs grown on substrate by CVD method. Qian et al. [16] used CVD to grow the pure and nitrogen-doped MWCNTs on silica fiber and found that MWCNTs were attached to the fiber surface by catalyst pitting between the catalyst and substrate. De Greef et al. [17] studied the influence of CVD parameters on the mechanical properties of carbon fibers and found the large catalyst particles etching on carbon fibers surface when CNTs direct grown on carbon fibers. Lv et al. [18] also revealed the interfacial strength in CFRP could be

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enhanced by growing CNTs on carbon fibers through the catalyst etched into carbon fibers surface.

However, all the studies discussed above are confronting the same challenge that they can't meet the demand of huge market. It can only be carried out in batch processing [19] where CNTs were synthesized on the stationary substrate inside CVD furnace. What's more, to our knowledge, few of continuous CVD manufacturing studies have been emerged in the open literature [20,21]. Consequently, the scalable CVD manufacturing technique was strong required to yield CNTs on the moving substrate.

In this paper, a novel process to synthesize CF/CNTs multi-scale reinforcements is creatively presented by growing CNTs on continuous carbon fibers surface through a unique open-ended CVD furnace. The influences of process parameters including CVD temperature, the velocity of continuous carbon fibers and catalyst concentration on morphologies, microstructures and properties of the multi-scale reinforcement have been investigated in detail. This continuous fabrication technology is potential for the application of composites in the future if it could be like carbonization process of manufacturing carbon fibers on the large-scale.

2. Experimental

2.1. Materials

Carbon fibers (T-700-12K) with special properties in Table 1 were purchased from Japan Toray Company. Ammonium biphosphate ($NH_4H_2PO_4$) was purchased from Tianjin Guangfu Technology Development Co. Ltd. Ethanol and cobaltous nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. N_2 (99.99%), H_2 (99.99%) and C_2H_2 (99.99%) were purchased from Jinan Gas Company. E-51 epoxy resin was produced by Wuxi resin factory of lanxin new materials. T403 curing agent was produced by Huntsman Corp in the United States. Deionized water was made from our own laboratory.

2.2. Continuous CVD furnace system

The experimental manufacturing system is shown in Fig. 1a. CNTs were synthesized on the continuously moving carbon fibers surface by a unique open-ended CVD furnace which consists of volume flow controllers and roll-to-roll systems driven by motors. The diameter of the quartz tube is 10 cm, and the length of the heated zone is 60 cm. At the both ends of CVD furnace, a gas sealing device is provided to ensure the process atmosphere in the furnace is not affected by outside. What's more, it's also equipped with an air suction device to purge the exhaust gas produced during the experiment. Before CNTs were grown on carbon fibers, N_2 was used to purge the inside of reactor, and would be kept open throughout the whole experiment performed. Fig. 1b shows the temperature profiles along the furnace heated zone.

2.3. Growth of CNTs on continuous carbon fibers surface

The sizing agents of carbon fibers were removed by heat treatment with N_2 at 450 °C for 1 h. Afterwards, carbon fibers were pulled into electrolyte solution with the content of 5 wt% $NH_4H_2PO_4$ solution experienced 0.4 A electrochemical treatment intensity for 80 s with electrochemical anodic oxidation (EAO). Carbon fibers were cleaned with deionized water for 10min and dried at 120 °C for 10 min to dislodge residual electrolytes. The catalyst solution of $Co(NO_3)_2{\cdot}6H_2O$ in ethanol with concentrations ranging from 0.03 to 0.15 M. After immersion for 10 min, carbon fibers were taken out and drized in oven at 80 °C for 10 min as well.

Subsequently, CVD furnace was flushed with N_2 (0.5 L min^{-1}) for 5min by displacing trapped air from it to furnish an inert atmosphere which contains oxygen content less than 500 ppm as detected by an oxygen analyzer. N_2 was maintained introduced under the same flow rate throughout the process until system was cooled to room temperature. Then the furnace was heated to 450 °C by PID controller in N_2 atmosphere, H_2 (0.5 L min^{-1}) will be delivered to the internal furnace. Simultaneously, carbon fibers loaded with catalyst coating were pulled through the furnace by the motor systems. After reduction reaction lasted for 5 min by adjusting the running velocity of carbon fibers, H_2 was cut off and the temperature of furnace was raised to the deposition temperature varied from 600 to 750 °C, respectively. A reactant mixture of H_2/C_2H_2 (0.5/0.5 L min^{-1}) was introduced and the direction of carbon fibers will be reversed with the aim of synthetizing directly CNTs on the surface of continuous carbon fibers, which was moved with

Table 1
Physical properties of T-700-12K carbon fibers.

Carbon fibers	Tensile strength (σ_f, GPa)	Tensile modulus (E_f, GPa)	Failure strain (ε_f, %)	Density (g cm^{-3})
T-700-12K	4.9	230	2.1	1.8

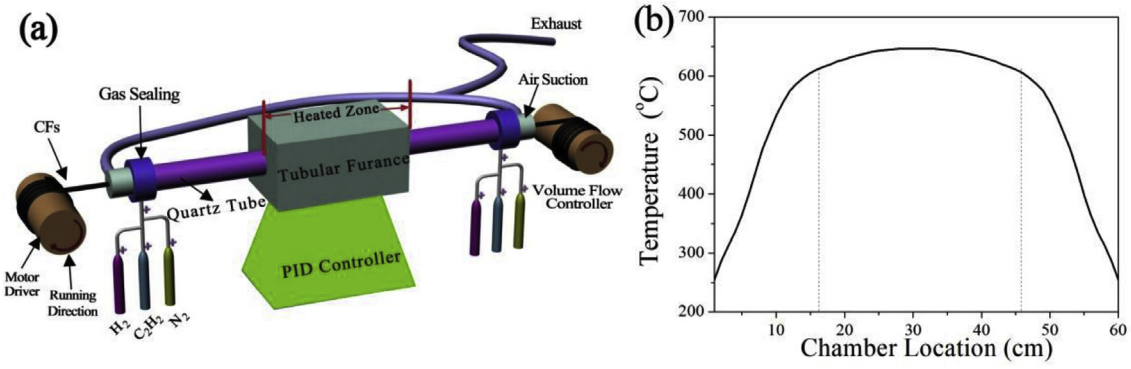

Fig. 1. Scalable manufacturing of CNTs on continuous carbon fibers surface: a) device of the unique CVD system, b) temperature profile along the center of the furnace heated zone (650 °C).