Materials and Design 87 (2015) 600–605

Contents lists available at ScienceDirect

Materials and Design

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

Advanced multifunctional properties of aligned carbon nanotube-epoxy thin film composites

Peng Liu, Adriel Lam, Zeng Fan, Thang Q. Tran, Hai M. Duong *

Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, EA-07-05, Singapore 117575, Singapore

ARTICLE INFO

Article history:
Received 29 May 2015
Received in revised form 3 August 2015
Accepted 16 August 2015
Available online 22 August 2015

Keywords:
Carbon nanotubes
Composites
Floating catalyst chemical vapor deposition
Resin transfer molding
Mechanical properties
Electrical properties

ABSTRACT

Carbon nanotube (CNT)/epoxy composite films were successfully developed by a combination of layer-by-layer and vacuum-assisted resin transfer molding methods using directly chemical vapor deposition (CVD)-spun CNT plies. CNT fractions in the composite films were found to be dramatically enhanced as the number of CNT plies increased. The as-prepared CNT/epoxy composite films with 24.4 wt.% CNTs exhibited ~10 and ~5 times enhancements in their strength and Young's modulus, respectively, and high toughness of up to 6.39×10^3 kJ/m^3. Electrical conductivity reached 252.8 S/cm for the 20-ply CNT/epoxy films, which was 20 times higher over those of the CNT/epoxy composites obtained by conventional dispersion methods. This work proposed a route to fabricate high-CNT-fraction CNT/epoxy composites on a large scale. The high toughness of these CNT/epoxy composite films also makes them promising candidates as protective materials.

1. Introduction

Carbon nanotubes (CNTs), with remarkable multifunctional properties, such as high strength and Young's modulus of 100 GPa and 1 TPa [1–3], respectively, ultrahigh electrical conductivity of 3×10^4 S/cm [4,5] and outstanding thermal conductivity of 2000–3500 W/m·K [6,7], have attracted great attention over past few decades. CNTs have been regarded as promising reinforcements for developing high-performance multifunctional composites. However, due to the low volume fraction, poor dispersion and random orientation of the CNTs in matrices, most resultant CNT-based composites can only receive limited enhancements and exhibit properties much lower than expected [8,9]. To overcome these challenges, various CNT preforms, such as buckypapers [10], CNT arrays [11–13] and CNT yarns [14], have been developed to pre-arrange the CNTs in a pre-forming structure before preparing composites.

One traditional approach is to extract CNT films from CNT suspensions via solvent evaporation or vacuum-assisted filtration [15,16]. As surfactants and sonication are commonly involved to achieve a good dispersion of CNTs, the CNTs dispersed would usually suffer from inevitable damages or shortenings during this process, and the CNT orientation is also uncontrollable. Towards taking full advantages of the anisotropic properties of individual CNTs, a number of studies focused on the developments of aligned CNT architectures and aligned CNT polymer composites. Many previous works have shown that the well-aligned CNTs could facilitate higher CNT packing densities and yield greater property enhancements in the composites than their tangled configurations [11–13,17–22]. So far, most aligned CNT preforms are fabricated from the CNT arrays [11–13] or dry-drawn CNT films from aligned CNT arrays [23]. Wardle et al. [11] reported the densification of CNT arrays reaching a high CNT volume fraction of up to ~20%, which nearly approached the theoretical limit of the intertube spacing in CNT arrays. Jiang et al. [24] reported a dry-drawing method to produce CNT sheets by directly pulling out the CNTs from CNT arrays. These as-prepared CNT sheets were further applied to fabricate CNT/epoxy composites which demonstrated improvements of 716% and 160% respectively in their Young's modulus and strength compared with pure epoxy [25]. Although these array-based methods provide a higher CNT content in the composites, a scaled-up fabrication is still restrained by the low production and the limited size of the CNT arrays [26].

Recently, continuous and large-scaled CNT sheets have been successfully synthesized via a floating catalytic chemical vapor deposition (FC-CVD) method [27,28]. In this process, aligned CNT sheets with controlled thickness and dimensions can be directly collected from the self-assembled CNT aerogels in the CVD furnace. Song et al. [29] reported CVD-grown CNT films with lateral dimensions of several tens of square centimeters, which exhibited Young's moduli of up to 700 GPa. By a similar approach, Ma et al. [30] produced strong and highly conducting films, which possessed strength of 360 MPa and electrical conductivity of over 2000 S/cm. Feng et al. [31] reported a one-step fabrication of double-walled CNT films and further enhanced their electrical conductivity to approximately 8000 S/cm. Such direct CVD-grown

* Corresponding author.
E-mail address: mpedhm@nus.edu.sg (H.M. Duong).

http://dx.doi.org/10.1016/j.matdes.2015.08.068
0264-1275/

method, therefore, not only provides an effective way to fabricate CNT films on a large scale, but also favors the fabrication of unidirectional CNT-based composites in a mass production.

Resin transfer molding (RTM) is a very common and cost-effective method to fabricate composites in industries, in which the liquid resins are first injected to the preforms and then cured to be solid [25,32,33]. Given its capability of making composites with large sizes and complex shapes, RTM is expected to be appropriate for preparing large-scaled CNT/epoxy composites using the CVD-grown CNT films. For the as-prepared CNT/epoxy composite films, understanding the effects of CNT-ply numbers on their multifunctional properties can also provide a basis for the optimization of their properties.

In this work, we report a simple yet controllable strategy to fabricate large-scaled CNT/epoxy composite films. The multi-plied CNT films were prepared by uniaxially stacking 1, 5, 10 and 20 CNT plies, which were continuously collected from CNT aerogels via FC-CVD. The CNT/epoxy composite films with high CNT volume fractions were readily obtained through a following vacuum–assisted resin transfer molding (VA-RTM) process. Multifunctional properties of these as-prepared CNT/epoxy films were characterized as a function of the numbers of their CNT plies. This work reports a novel approach to prepare high-volume-fraction CNT-based composites, and also seeks to identify the factors limiting their mechanical performance.

2. Experimental section

2.1. Materials

Ferrocene, thiophene and ethanol were purchased from Sigma-Aldrich Company Ltd. Methane, hydrogen and helium were purchased from Chem-Gas Pte Ltd. Epicote 1004 epoxy resin and Epicote 1004 hardener were obtained from Polymer Technologies. All the chemicals above were used as received.

2.2. Fabrication of CNT films

CNT films were synthesized via a FC-CVD method [34]. A mixture of methane (CH_4), hydrogen (H_2), ferrocene and thiophene was injected into a heated reactor at 1200 °C under nitrogen (N_2) environment. CNT aerogels were continuously formed at the heating region, blown out by the carrier gas and winded on a roller to form the CNT films, as shown in Fig. 1(a). In this work, an as-rolled CNT film from a 10-min continuous collection was defined as 1 CNT ply. Multiple CNT plies (containing 5, 10 and 20 individual CNT plies) were then stacked in the same CNT direction to form the CNT preforms, as shown in Fig. 1(b).

2.3. Fabrication of CNT/epoxy composite films

To fabricate the CNT/epoxy composite films, the as-prepared CNT films above were first placed in a self-made RTM mold, and then the epoxy resin was allowed to pass through the CNT films under vacuum. As recommended by the manufacturer, the mix ratio of Epicote 1004 and Epicote 1004 hardener was in a weight ratio of 5:2, while the curing condition was at the room temperature for 24 h. In order to minimize the air bubbles in the composite films, loads of ~20 kg were placed on the top of the molds during curing. CNT/epoxy composite films were eventually obtained by carefully releasing the samples from the RTM mold, as the process illustrated in Fig. 1(c)–(d). In order to investigate the effects of CNT-ply numbers, CNT/epoxy films with 1, 5, 10 and 20 CNT plies were prepared.

2.4. Characterization

Tensile tests were conducted along the CNT direction on an Instron 5500 tensile tester. Gauge length and crosshead speed were set to 15 mm and 1.5 mm/min, respectively. Thickness of the films was measured by a micrometer. Mechanical properties of these films were finally obtained by testing at least three samples at ambient conditions.

Theoretically, effective mechanical properties of the CNT films could be calculated from a modified rule of mixtures (ROM) [9,25] as below:

$$E_c = \eta_0 \cdot \eta_L \cdot V_f \cdot E_f + (1-V_f) \cdot E_m \quad (1)$$

$$\sigma_c = \eta_0 \cdot \eta_L \cdot V_f \cdot \sigma_f + (1-V_f) \cdot \sigma_m \quad (2)$$

where E_c, E_m and E_f and σ_c, σ_m and σ_f are Young's modulus and strength of composite, epoxy and CNTs, respectively. η_L and η_0 are introduced as length efficient factor and CNT orientation factor respectively, both of which could be set to be 1 for aligned CNTs with a high aspect ratio.

After the tensile tests, fracture surfaces of the composite films were coated with gold and subjected to field emission scanning electron microscope (FE-SEM, Model S-4300, Hitachi, Japan) to investigate their

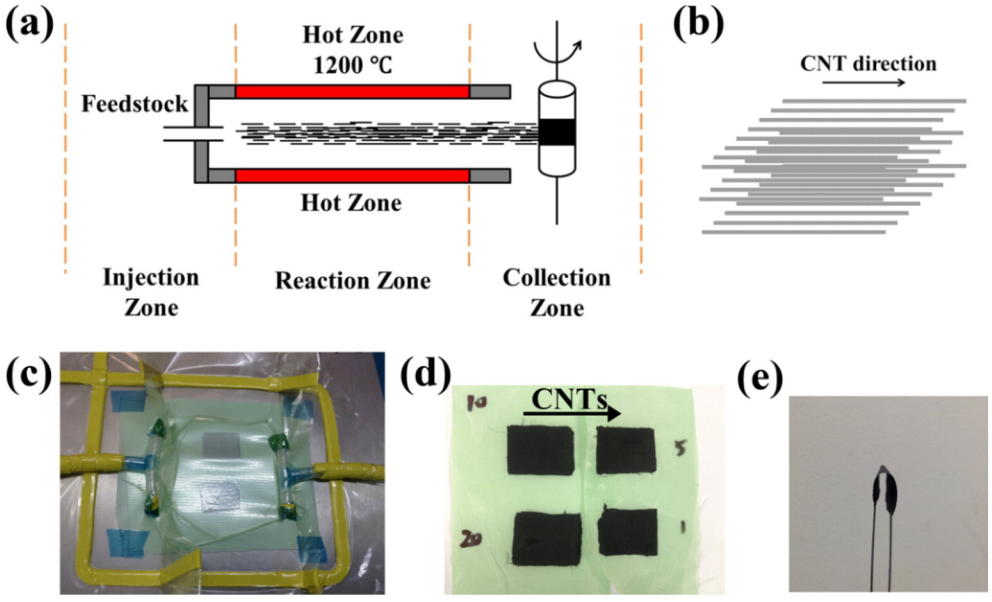

Fig. 1. Fabrication process of the CNT/epoxy films. (a) Schematic illustration of the fabrication of CNT plies by a FC-CVD method. (b) Schematic illustration of the arrangement of CNT plies. (c) Experimental set-up of the RTM process for preparing CNT/epoxy films. (d) As-prepared CNT/epoxy films with 1, 5, 10 and 20 CNT plies. (e) A flexible CNT/epoxy film bent by tweezers.