Composites Science and Technology 88 (2013) 48–56

Contents lists available at ScienceDirect

Composites Science and Technology

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

Nanoscopic observations for evaluating the failure process of aligned multi-walled carbon nanotube/epoxy composites

Terumasa Tsuda [a,*], Toshio Ogasawara [b], Sook-young Moon [b], Kengo Nakamoto [c], Nobuo Takeda [a], Yoshinobu Shimamura [d], Yoku Inoue [d]

[a] Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa-shi, Chiba 277-8561, Japan
[b] Advanced Composites Technology Center, Japan Aerospace Exploration Agency (JAXA), 6-13-1, Osawa, Mitaka-shi, Tokyo 181-0015, Japan
[c] Graduate School of Mechanical Engineering, Aoyama-Gakuin University, 5-10-1 Fuchinobe, Chuo-ku, Sagamihara-shi, Kanagawa 252-5258, Japan
[d] Faculty of Engineering, Shizuoka University, 3-5-1, Johoku, Naka-ku, Hamamatsu-shi, Shizuoka 423-8561, Japan

ARTICLE INFO

Article history:
Received 8 April 2013
Received in revised form 12 August 2013
Accepted 24 August 2013
Available online 7 September 2013

Keywords:
A. Carbon nanotubes
A. Nanocomposites
D. Transmission electron microscopy (TEM)
B. Debonding

ABSTRACT

This study examined the nanoscopic damage progression of aligned multi-walled carbon nanotubes (CNT)/epoxy composites under tensile loading using transmission electron microscopy (TEM). Aligned CNT/epoxy composite films (30 μm thickness) were processed using a forest-drawn aligned CNT sheet and hot-melt prepreg method. Four film specimens, respectively subjected to tensile stress of 0 MPa, 45 MPa, 95 MPa and 110 MPa, were prepared. After tensile loading, each specimen was machined until the thickness became about 100 nm using a focused ion beam milling machine (FIB) for TEM observations. Damage of three kinds, i.e. CNT break derived from the disordered CNT structures around metallic catalyst, sword-in-sheath type CNT break, and several patterns of interfacial debonding, was observed clearly. The broken CNTs and interfacial debonding per unit area were counted from TEM photographs. Results show that broken CNTs and interface debonding increased considerably at 95–110 MPa, which suggests multiple fracture of CNT under tensile loading. The CNT length at the failure stress (110 MPa) was approximately 45 μm. Estimated values from the strength of CNTs resemble those from macroscopic stress–strain behavior.

1. Background

Since the first discovery of carbon nanotubes (CNTs) by Iijima [1], single-walled carbon nanotubes (SWNTs), and multi-walled carbon nanotubes (MWNTs) have been widely known to show high elastic modulus and high strength [2–9]. Therefore, CNTs are anticipated for use as ideal fillers for polymers to enhance their mechanical properties. Nevertheless, numerous studies for the first stage of R&D of CNT application to polymer reinforcement performed for the last two decades have failed to demonstrate their excellent mechanical, electrical, and thermal reinforcement capabilities for polymers [10–13]. The actual mechanical properties of CNT/polymer composites are generally inferior to those of theoretical predicted properties, mainly because of poor dispersion, low volume fraction, random orientation, and weak interfacial strength between CNTs and polymers [14–16].

As described above, CNT orientation is one important factor in enhancing the mechanical properties of CNT/polymer composites. Several efforts at fabricating CNT/polymer composites with unidirectional alignment of CNTs have been conducted, such as the use of buckypaper, shear pressing from vertically aligned CNTs (VA-CNTs), and “domino-pushing” [17–23]. These results show a higher elastic modulus and strength attributable to the highly aligned nature of CNTs with high volume fraction. However, these methods are not practical because of the poor efficiency of producing aligned CNTs. For example, regarding the shear pressing method conducted by Bradford et al. [22], the specimen size is restricted because of the small substrate used to produce VA-CNTs.

For marked improvement of mechanical properties of CNT/polymer composites, an epoch-making processing method to fabricate unidirectionally aligned CNT was proposed in 2005. Horizontally aligned CNT sheets drawn from a vertically aligned CNT array were produced by Zhang et al. [24]. This method is especially anticipated for fabricating practical sizes of aligned CNTs/polymer composites because the CNT sheet size is easy to handle. Moreover, using the aligned CNT sheets, the aligned CNT/polymer composites with higher volume fraction can be fabricated easily. Several studies examining aligned CNT sheets/polymer composites have been conducted. Cheng et al. fabricated aligned CNT sheets/epoxy composites by resin transfer molding [25,26]. The weight fraction of

* Corresponding author. Tel./fax: +81 04 7136 4026.
E-mail address: tsuda@smart.k.u-tokyo.ac.jp (T. Tsuda).

0266-3538/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.compscitech.2013.08.034

CNT composite was 16.5 wt%. The mechanical properties showed high tensile strength of 231 MPa, and high Young's modulus of 20.4 GPa. Furthermore, they produced 60 wt% aligned CNT/bismaleimide (BMI) composites that had 2.1 GPa strength and 169 GPa of elastic modulus that stretched randomly dispersed CNT sheet [27]. Another group has reported 3.8 GPa strength and 293 GPa of elastic modulus that stretched aligned CNT sheet, which is the highest strength and elastic modulus reported to date [28]. Several researchers have also reported other properties, such as mechanical stiffness and electrical properties of aligned CNT/polymer matrix composites [29,30].

The authors examined the mechanical properties of the aligned CNT/epoxy composites processed using hot-melt technique [31]. The prepreg method presents several advantages compared with ordinary composite molding methods such as resin infusion and resin transfer molding. A prepreg is easy to handle and enables complex structures or components production. Furthermore, aligned CNT/epoxy prepregs are applicable to press molding because CNTs are not continuous fibers. The resultant composites showed the maximum elastic modulus and ultimate tensile strength (UTS) of a 21.4 vol.% CNT/epoxy composite of 50.6 GPa and 183 MPa.

Aligned CNT/polymer composites exhibit far superior mechanical properties than conventional randomly oriented CNT composites do. Nevertheless, the mechanical properties remain inferior to those of theoretical predictions. To improve mechanical properties further, understanding the nanoscopic damage progression is indispensable. A few experiments and theoretical calculations related to CNT fracture processes have been conducted. For example, Yamamoto et al. reported the possibility of internal fracture process of MWNTs [32]. They investigated the failure mechanism of the MWNTs during crack opening at the fracture surface of MWNT/alumina composite through single nanotube pullout tests and transmission electron microscope (TEM) observations. Their research revealed the sword-in-sheath fracture of MWNTs after pullout of MWNT and tensile testing. Based on these results, they schematically modeled the sword-in-sheath fracture of MWNTs. Our previous reports [31] also described sword-in-sheath fractures of CNTs at the fracture surface of CNT/epoxy composites after tensile testing.

Other researchers have attempted to produce theoretical models of fracture process of CNTs or CNT-reinforced composites. Huang et al. [33] simulated the fracture process of SWNTs by molecular dynamics with an applied general CA algorithm. Results showed that an initial vacancy with Stone–Wales defects occurs first at the initial vacancy sites, implying that the initial vacancy engenders the earlier advent of plastic deformation. Furthermore, critical fracture strain becomes lower than that of perfect SWCNTs, indicating that the initial vacancy causes considerable damage in CNTs. Niaki et al. [34] also simulated the fracture process of graphene sheet and SWNTs using a similar approach and reported that dynamic fracture stresses were, respectively, determined approximately 115 GPa and 122 GPa for different sizes of graphene sheet and armchair CNTs. A multiscale mechanics method used to study the deformation and fracture of CNTs embedded in a composite was presented by Shi et al. [35], who reported that the critical strain of defect nucleation of a CNT is sensitive to its chiral angle, but not to its diameter and that the constraint effect of matrix makes the CNTs easier to fracture. They also simulated the effect of some other factors such as the waviness of CNTs, the CNT–matrix interface adhesion, and the distributed residual stresses in composites. They concluded that these factors might influence the CNT fracture behaviors. However, because of the extremely small size of the CNT, direct observation of nanoscopic damage progress such as interfacial debonding, matrix cracking, and multiple fractures of CNTs in matrix under tensile loading has not been reported.

The objective of this study is to examine the nanoscopic damage progression of aligned multi-walled carbon nanotubes (MWNTs)/epoxy composites under tensile loading. Aligned CNT/epoxy composite specimens, which were processed using forest-drawn aligned CNT sheet and hot-melt prepreg method, were subjected to tensile loading. Thin samples (100 nm thick) were prepared for transmission electron microscope (TEM) observations using a focused ion beam (FIB) method. Using TEM, nanoscopic damage at each tensile stress was observed in detail.

2. Experiments

2.1. Processing of aligned CNT sheets

Inoue et al. established a simple and efficient synthesis method for producing vertically aligned long MWCNTs using iron chloride powders as precursor of a catalyst [36]. The MWCNTs with length exceeding 1 mm were grown on a bare SiO_2 substrate using conventional thermal chemical vapor deposition (CVD) with single gas flow (acetylene) for 20 min. In addition to such a high growth rate, well-aligned MWCNT sheets are produced easily from the MWCNT forest by pulling it out [31]. The CNT sheets have a high volume fraction without a great amount of entanglement, which are ideal properties for use in reinforcement of the composites. Respectively, their diameters and lengths are 40–70 nm and about 1 mm.

2.2. Processing of CNT/epoxy composites

The procedure used to produce CNT/epoxy prepreg is presented in Fig. 1(a). The B-stage un-cured epoxy resin with release paper was obtained from a commercial prepreg company. The epoxy resin consists of bisphenol-A type epoxy, novolac type epoxy, and an aromatic diamine curing agent. The areal weight of epoxy resin film is controlled as 30 g/m^2, with thickness of approximately 25 μm. A stacked CNT sheet was put on a PTFE sheet. Then it was covered with epoxy resin film with a release paper. Epoxy resin was impregnated into the CNT sheet at 90 °C for 3 min between steel plates of a hot press. After peeling off a prepreg sheet from the release paper, the prepreg sheet was cured at 130 °C for 1.5 h between steel plates in an oven, yielding a film specimen. A steel plate was put on a stacked prepreg sheet during curing. The pressure was approximately 2.0 MPa. Details of procedures used for CNT sheet and composite fabrication have been reported elsewhere [31,37].

The composites' microstructure was observed using a scanning electron microscope (FE–SEM, S-4700; Hitachi Ltd., Japan). The CNT weight fraction was ascertained using a thermogravimetric analyzer (TGA, TGA-6300; SII, Japan). Method of determining volume fraction of CNTs is reported elsewhere [31]. An SEM image of CNT/epoxy composite was depicted in Fig. 1(b). The CNT volume fraction, as evaluated using TGA is about 8%. The composite thickness was about 30 μm.

2.3. Tensile loading, sample preparation, and TEM observations

To prepare the fracture process observation specimen, tensile tests were conducted on a screw-driven mechanical testing machine (Model 5966R; Instron Corp., USA) under a constant displacement rate of 0.2 mm/min at room temperature. Geometry and dimensions of tensile test specimen are presented in Fig. 2. The longitudinal strain was measured using a non-contacting video extensometer (AVE; Instron Corp., USA). Specimens were subjected