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Three dimensional orientation angle distribution counting and calculation for the mechanical properties of aligned carbon nanotube/epoxy composites

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ABSTRACT

This paper presents effects of carbon nanotube (CNT) orientation angle distribution on elastic moduli of aligned CNT/epoxy composites that were fabricated with various volume fractions using hot-melt prepreg method. Tensile testing was conducted to evaluate the composites' mechanical properties. The composites' Young's moduli increased with increasing CNT volume fraction. Scanning electron microscopy (SEM) revealed CNT orientation angle distribution data for the surface and through-thickness planes. The standard deviation of CNT orientation angle distribution was about 30° for the surface, and 22.5° for the through-thickness plane. The effective Young's modulus of CNT was estimated using the equivalent inclusion theory (Eshelby/Mori–Tanaka theory) incorporating a three-dimensional CNT orientation distribution function. The CNT Young's modulus was approximately 800 GPa, which agrees with reported theoretical and experimental values.

1. Introduction

Numerous studies of the mechanical properties of composites, including interlaminar reinforcement properties using carbon nanotubes (CNTs) or vapor grown carbon fibers (VGCFs) have been conducted over the last decade because of CNTs' extremely high strength and elastic modulus [1–14]. However, the mechanical properties of the CNT/ polymer composites are much lower than the theoretically predicted values [1–7]. Insufficient mechanical properties of CNT/polymer composites result from the random orientation, inadequate dispersion such as agglomerations of CNTs, low volume fraction, low aspect ratio of CNTs and weak CNT/ matrix interfacial strength [1,15].

To control the CNT orientations in composites, Thorstenson and Chou proposed "microtome cutting method" [15]. Using this technique, the CNT alignment can be controlled. The standard deviation of the orientation angle distribution was within 15° for arbitrary aligned direction. Nevertheless, applying this method to actual engineering products is difficult for three reasons; the sample becomes smaller, the system requires specific facilities, which makes costs prohibitively high.

Application of CNT bucky paper as a stiffener and increase of the CNT volume fraction in composites have been attempted [9]. In fact, CNT/polymer composites with high CNT volume fraction (>10 vol.%) were produced using bucky papers. Randomly oriented CNT sheets for the surface direction were obtained using this method. Nevertheless, the problem for the orientation angle of CNTs remains unresolved.

Recently, the application of vertically grown multi-walled CNT (MWNT) has been attempted to achieve high CNT volume fractions, high aspect ratios and better orientation in the CNTs/polymer composites. Several technologies used to produce vertically grown multi-walled CNT (MWNT) have been established in recent years [16–18]. For example, Bradford et al. produced highly oriented CNT sheets and CNT/ epoxy composites by pushing down the CNT-array in the diagonal direction [18]. They reported that CNT/epoxy composites exhibit high tensile strength of 402 MPa and Young's modulus of 22.3 GPa by adding a 32% weight fraction of CNT, which values are about 8.5 times and 6 times higher than those of pure epoxy. This method has been demonstrated for the reproduction of high elastic modulus and strength with higher

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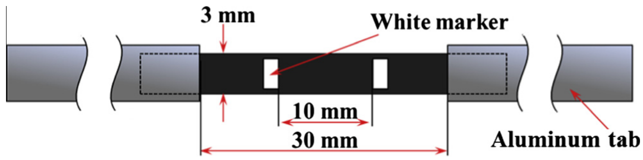

Fig. 1. Geometry and dimension of tensile test specimen (thickness: about 30 μm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

volume fraction than that of existing CNT composites. Thermal and electrical properties of CNT papers were also evaluated by another group [19]. However, the size of the produced CNT sheets is restricted by the size of the substrate used for CNT production.

Zhang et al. proposed a better method to produce aligned CNT sheets from CNT forests in 2005. Horizontally aligned CNT sheets were obtained easily by drawing CNTs horizontally from a vertically grown CNT forest [20,21]. This method might be applicable for mass production of large lots. Cheng and Fan have reported similar studies related to aligned CNT sheet composite [22–24]. For example, they reported 16.5 wt.% CNT/epoxy composites, tensile strength of 230 MPa, and elastic modulus of 20.4 GPa.

For the effective production of aligned CNT sheets from CNT forests, it is necessary to grow a CNT forest with high efficiency. Inoue et al. proposed an efficient technique to grow a multi-walled CNT forest of high quality using iron chloride as a catalyst precursor [25]. They can grow CNTs to a length of several millimeters in only 20 min using thermal chemical vapor deposition (CVD) [26].

Manufacture and evaluate the mechanical properties of aligned CNT sheet/ epoxy composites has been conducted, of which CNT forests were produced by Inoue et al. [27,28]. Stable production of CNT/ epoxy composites with easy control of the volume fraction of CNT became possible by application of hot-melt method using the uncured resin film as a matrix. This manufacturing process is surprisingly easy, producing high-quality CNT/ epoxy composites. The highest mechanical properties of our composites to date are the tensile strength of 239 MPa and Young's modulus of 89.6 GPa achieved by adding 32.8% weight fraction of CNT [28]. These values are 4.4 times and 37.6 times higher than the tensile strength and Young's modulus of epoxy polymer. Generally, mechanical properties of dispersed type CNT (10–20 vol.%)/polymer composites increases at most around several tens of percent [6,7], which implies that the aligned CNT sheet/epoxy composites are extremely effective for the improvement of composites' mechanical properties. However, the estimated Young's moduli of CNTs from the tensile testing are 230–380 GPa, which value is lower than the actual Young's modulus of CNTs (500–1500 GPa) reported from application of theoretical and experimental methods [28–36].

These mismatches are thought to result from the CNT orientation distribution and interfacial shear strength between CNT and polymer. For the quantitative evaluation of interfacial shear strength for MWNT/PEEK and the MWNT/epoxy composite, so-called "nano-pullout testing" using a nano-pullout machine was previously conducted [37]. The average interfacial shear strength (IFSS) between MWNT and epoxy was about 20 MPa, which is smaller than that of ordinary CFRP composites (in the range of 25–90 MPa [38–41]). However, alignment effects of CNTs in the polymer for mechanical properties of composites remain ambiguous.

This study specifically addressed the orientation angle of CNT in the composites. The production method of aligned CNT sheet composites strongly affects their mechanical properties. For instance, Wang et al. produced a 60 wt.% aligned CNT by stretching from randomly dispersed CNT "buckypaper", and fabricated aligned CNT/ bismaleimide (BMI) composites. The tensile strength and Young's moduli are, respectively, 2.1 GPa, and 169 GPa [23]. In contrast, Wang et al. produced 60 wt.% aligned CNTs by stretching from aligned CNT sheet. The CNT/bismaleimide (BMI) composite showed strength of 3.8 GPa, and Young's modulus of 239 GPa [24], which suggests that the CNT orientation in the composites influences their mechanical properties. However, no report has described a study undertaken for the quantitative evaluation of orientation angles of CNTs, assessing the actual reinforcement effects of CNT/epoxy composites.

Previous study specifically addressed the two-dimensional alignment angle of CNTs by evaluating the surface alignment, of which the Young's modulus of CNT was about 680 GPa [28]. However evaluation of the alignment of the thickness direction is yet to be conducted.

The primary objective of this study is to evaluate the quantitative effects of the orientation distribution of CNTs in the composites. Composites with a higher volume fraction of CNTs were fabricated and mechanical properties were evaluated. The quantitative evaluation for orientation angle distribution of CNT was expanded for three dimensions. Orientations for the surface

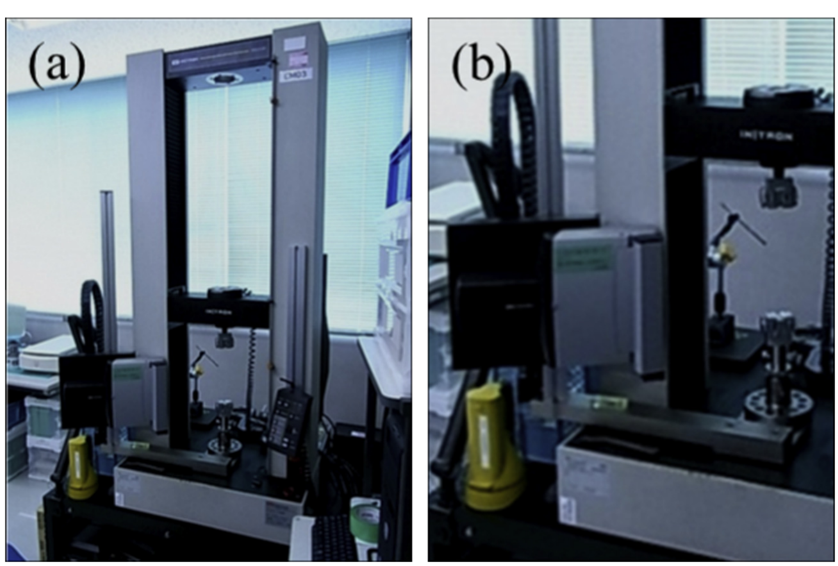

Fig. 2. (a) Electrical material testing machine (5966R) and (b) video extensometer (AVE). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)