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Aligning carbon nanotubes using bulk acoustic waves to reinforce polymer composites

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ABSTRACT

Bulk acoustic waves (BAWs) are used to align multi-walled carbon nanotubes (MWCNTs) in polymer composite materials. MWCNTs are first dispersed in the liquid state of a thermoset resin and aligned using standing BAWs. Cross-linking of the resin fixates the aligned MWCNTs in the polymer matrix material. We have quantified the alignment obtained with this method on the macro, micro, and nanoscale, and it is found to be similar to other alignment techniques such as stretching, slicing, and wet spinning. The elastic modulus and ultimate tensile strength of composite material specimens with aligned MWCNTs, fabricated using this technique, are evaluated and compared with specimens consisting of randomly oriented MWCNTs and resin material without MWCNTs. Different MWCNT loading rates are considered. The elastic modulus of composite material specimens with only 0.15 weight percent aligned MWCNTs is observed to be 44% higher than specimens with randomly oriented MWCNTs, and 51% higher than specimens without MWCNTs. However, further increasing the MWCNT loading rate does not significantly increase the elastic modulus and ultimate tensile strength, likely because of insufficient dispersion of MWCNTs in the thermoset matrix material.

1. Introduction

Carbon nanotubes (CNTs) exhibit extraordinary mechanical properties [1,2]. Attempting to implement CNTs as nanoscale reinforcement in composite materials or fibers is an active research area [3–12]. Several parameters are critical when manufacturing composite materials with CNT reinforcement, such as dispersion of the CNTs in the polymer matrix [13,14], bonding between the CNTs and the matrix material [15–18], and alignment of the CNTs in the direction of the applied external loading [19,20]. In this paper, we focus on the alignment of the CNTs in the polymer matrix.

A variety of techniques to align CNTs have been documented in the literature, including methods based on stretching [21], magnetic [22–25] or electrostatic forces [26], slicing [27], liquid crystals [28], shear flow [29], and surface acoustic waves [30]. Fibers reinforced with aligned CNTs have been produced using wet spinning [31], melt spinning [32–34], and direct spinning [35]. These fibers must be further processed into a bulk composite material. While these are effective methods to align CNTs, scalability for use as a manufacturing technique of macroscale specimens is often the limiting factor.

This paper attempts to address this limitation and presents a novel technique, based on bulk acoustic waves (BAWs), to align CNTs in a polymer matrix. BAWs have previously been used to manipulate microscale particles [36–39], cells [40,41], and nanoparticles [42]. Here, multi-walled carbon nanotubes (MWCNTs) are dispersed in the liquid state of a thermoset resin and subsequently aligned and organized into parallel lines by means of BAWs. The obtained pattern of MWCNTs is fixated by cross-linking the resin, which yields a polymer composite material reinforced with aligned MWCNTs. The alignment is experimentally quantified on the macro, micro, and nanoscale. The elastic modulus and ultimate tensile strength of the composite material specimens with aligned MWCNTs are measured in the direction of the MWCNT alignment, and compared against composite material specimens consisting of randomly oriented MWCNTs and pure resin material without MWCNTs. Different MWCNT loading rates are considered.

2. Experimental methods

2.1. Apparatus

Fig. 1 shows a schematic of the experimental apparatus. A dog-bone shaped reservoir is machined from high density polyethylene, which displays low adhesion to the polymer matrix material [43]. The reservoir is mounted on a glass base. Two parallel lead zirconate titanate (PZT-5) plates are embedded in recess slots in the side walls of the reservoir, and oppose each other over the entire 18 mm gauge length. The dog-bone specimen is 68 mm long,

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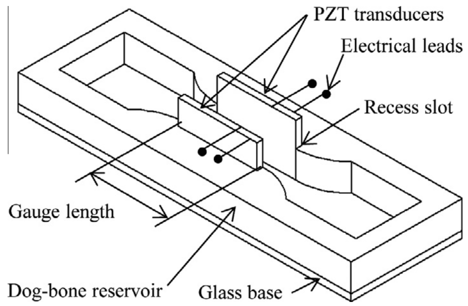

Fig. 1. Schematic of the experimental apparatus to manufacture dog-bone composite material specimens, with aligned MWCNTs in the gauge length.

5 mm thick, and 7.5 mm wide in the gauge section (measured between the PZT plates). These dimensions are chosen to resemble an ASTM D638 Type V plastic specimen. The PZT material (18×12 mm) has a center frequency of 1.5 MHz. The PZT transducers create BAWs in the reservoir to align the MWCNTs in the gauge section of the dog-bone specimen.

2.2. Aligning CNTs using bulk acoustic waves

The pressure P of a one-dimensional BAW is represented as [44]:

$$P(x,t) = P_a \cos(\omega t - kx) + P_a \cos(\omega t + kx) \quad (1)$$

where P_a is the pressure amplitude, $k = 2\pi/\lambda$ is the wave number, λ is the wave length, ω is the angular frequency, t is the time, and x is the distance from the transducer. The acoustic radiation force F associated with the pressure wave, acting on a cylinder, has been shown to be of the following form [44–47].

$$\frac{F}{L} = \{[(1-\beta)/(1+\beta)]/2 + 1\}\upsilon\omega\left(\frac{P_a^2}{\rho_0 c^3}\right)\sin(2kx) \quad (2)$$

where L is the length of the cylinder. The amplitude of the radiation force is a function of the pressure wave amplitude P_a, the volume of the cylinder per unit length υ, the density of the medium ρ_0, the density of the cylinder ρ_1, $\beta = \rho_0/\rho_1$, the sound speed c of the medium, and the angular frequency ω. Fig. 2 illustrates the normalized magnitude of a pressure wave (dashed line) and the corresponding acoustic radiation force (solid line) as a function of the distance from the PZT transducer, nondimensionalized with the wave length λ of the BAW. The location of the nodes and antinodes is indicated, and the horizontal bold arrows denote the direction in which the MWCNTs are driven; a positive radiation force induces a displacement along the positive x-axis and vice versa [42].

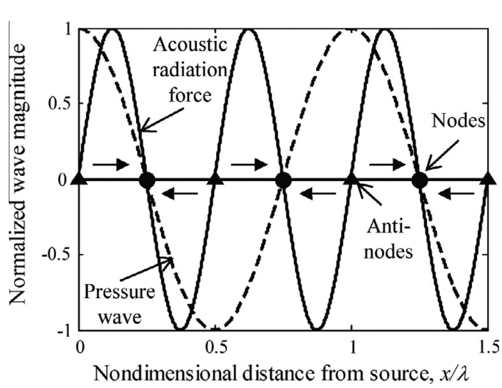

Fig. 2. Node and antinode locations of a pressure wave and the corresponding acoustic radiation force (see Eqs. (1) and (2)) with arrows showing the direction in which MWCNTs are driven.

Fig. 3 shows the manufacturing process to create polymer composite material specimens with aligned MWCNTs. Virgin MWCNTs with a diameter of 50–80 nm and length of 10–20 µm are added to part A of a two-part, low-viscosity, fast curing thermoset resin (Smooth-Cast 300 thermoset, Smooth-On Inc.) (Fig. 3(a)), and dispersed by means of bath sonication (Fig. 3(b)). Part B of the resin is then added (Fig. 3(c)) prior to transferring the mixture to the dog-bone shaped reservoir (Fig. 3(d)). The sound speed of the thermoset resin c is 1353 m/s at room temperature (20 °C) and is determined with a pulse echo time-of-flight measurement [48]. The viscosity of the liquid resin at room temperature is 0.008 Pa s, and it is noted that the viscosity of the polymer increases with increasing MWCNT loading. A standing BAW is created between the two opposing PZT transducers at a frequency close to their resonance frequency, to maximize the amplitude of the pressure wave and, correspondingly, the magnitude of the acoustic radiation force (see Eq. (2)). This force aligns the MWCNTs and drives them to the nodes of the standing BAW (Fig. 3(e)), when it exceeds the drag force acting on the MWCNTs [38]. The PZT transducers are energized by a function generator (Tektronix, AFG 3102), amplified by a 45 dB 50 W RF power amplifier (electronic navigation industries, 440LA). By controlling the location of the nodes of the standing BAW, which depends on the wave length or frequency of the wave and the sound speed in the polymer matrix material, one can control the locations where the MWCNTs assemble and align. Cross-linking of the mixture starts immediately following the addition of part B of the resin. The sample is extracted from the reservoir upon completion of the cross-linking process (Fig. 3(f)).

Fig. 4(a) depicts a typical dog-bone specimen with one weight percent (wt%) aligned MWCNTs, fabricated using BAWs with a frequency of 1.477 MHz. Fig. 4(b) shows a detail of the gauge section with parallel lines of aligned and clustered MWCNTs. The surface of the specimen is locally polished to reveal the alignment of the MWCNTs. Details of the nanoscale alignment of the MWCNTs are shown in Section 3. The spacing between two lines of aligned MWCNTs is 458 µm, which is expected based on the sound speed of the resin matrix material (in liquid state), and the occurrence of two nodes per wave length as shown in Fig. 2. Dog-bone specimens with randomly oriented MWCNTs are fabricated using the same process as outlined in Fig. 3, with the exception of the step in which the MWCNTs are aligned.

3. Results and discussion

3.1. Quantifying MWCNT alignment

The orientation factor H [49] quantifies the alignment of the MWCNTs, and is based on the average angle ϕ between the axis of the MWCNTs and the composite axis. The composite axis is defined as the axis in which alignment is desired, and in which the external load will be applied. Perfect alignment results in $H = 1$ ($\phi = 0°$). If all fiber axes are oriented orthogonal to the composite axis ($\phi = 90°$), $H = -0.5$, and for randomly oriented fibers ($\phi = 45°$), $H = 0.25$. This method has previously been used to quantify fiber alignment in nanostructured polymer composite materials e.g. [50–52], and H is computed as:

$$H = \frac{1}{2}(3\cos^2\phi - 1) \quad (3)$$

To quantify the macroscale alignment of clusters of MWCNTs in the composite material specimen, a 6.7 by 5.0 mm section of the specimen is photographed through a trinocular stereo zoom microscope (AmScope MT500). The grayscale digital image is binarized