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Mechanical, electrical and thermal properties of aligned carbon nanotube/polyimide composites

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ABSTRACT

Carbon nanotubes (CNTs) have high strength and modulus, large aspect ratio, and good electrical and thermal conductivities, which make them attractive for fabricating composite. The poly(biphenyl dianhydride-*p*-phenylenediamine) (BPDA/PDA) polyimide has good mechanical and thermal performances and is herein used as matrix in unidirectional carbon nanotube composites for the first time. The strength and modulus of the composite increase by 2.73 and 12 times over pure BPDA–PDA polyimide, while its electrical conductivity reaches to 183 S/cm, which is 10^{18} times over pure polyimide. The composite has excellent high temperature resistance, and its thermal conductivity is beyond what has been achieved in previous studies. The improved properties of the composites are due to the long CNT length, high level of CNT alignment, high CNT volume fraction and good CNT dispersion in polyimide matrix. The composite is promising for applications that require high strength, lightweight, or high electrical and thermal conductivities.

1. Introduction

Since its discovery [1], carbon nanotube (CNT) is regarded as one of the potential reinforcements for next-generation multi-functional composites [2–10]. It has been a challenge to incorporate high volume fraction of long and aligned CNTs into polymer matrix to make high performance composites. Recently, our group reported a spray winding method that can apply polymer while the CNT ribbons were wound onto a rotating mandrel. This method was verified to be effective to produce CNT composites with high volume fraction and excellent mechanical, electrical and thermal properties [11–16].

Poly(biphenyl dianhydride-*p*-phenylenediamine) (BPDA–PDA) is a rigid-rod-like polyimide that is a candidate for a variety of applications due to its useful properties such as high mechanical property, chemical resistance, excellent thermal stability, and moisture resistance [17–22]. However, as a matrix in nanocomposite, the applicability of BPDA–PDA has not been well studied yet. The rigid molecule structure and high molecular weight of BPDA–PDA polyimide lead to high viscosity, so it is a challenge to use it as a matrix in CNT based composites. Little work has been done on BPDA–PDA/CNT composite. Naebe et al. made BPDA–PDA/CNT composite by dispersing CNTs into polyamic acid solution, and obtained more than two folds increase in tensile strength and improved the thermal stability of the composites [18]. However, the tensile strength was only around 140 MPa and no electrical property was studied. Therefore, it will be of scientific and practical importance to develop BPDA–PDA/CNT composite with multi-functional properties.

In addition, it has been found that the polymer matrix is highly affected by nano-sized reinforcements where the dimension, dispersion state and the interaction of the reinforcements play significant roles [18,23,24]. Understanding how aligned carbon nanotubes influences poly(biphenyl dianhydride-*p*-phenylenediamine) and how the composite performs are critical for composite application and design.

In this work, we apply the spray winding method to fabricate the unidirectional carbon nanotube reinforced BPDA–PDA polyimide composites. Our results showed that polyimide was well infiltrated in multi-walled carbon nanotubes (MWNTs) sheets and long, aligned and high volume fraction of MWNTs were realized in the composites. The excellent mechanical, electrical and thermal properties of MWNTs, and the high thermal resistance of polyimide were maintained in the composites.

2. Experimental

2.1. Fabrication of MWNT/BPDA–PDA composite

The MWNT array was grown on a silicon wafer with sputtered iron catalyst by chemical vapor deposition (CVD)[25]. The MWNTs

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were about 700 μm height, 5–6 walled and around 10 nm in diameter. The MWNT arrays were highly drawable and self-aligned. The MWNTs sheets were firstly pulled out from a MWNT array at a speed of 18 mm/s and wound onto a rotating cylindrical polytetrafluoroethylene (PTFE) spool. The polyimide precursor, polyamic acid, was supplied by UBE America Inc. with a molecular weight of 14,000 and concentration of 20 wt%. In order to decrease the viscosity, the polyamic acid was diluted by N-methyl-2-pyrrolidone (NMP) to 0.1 wt%. The N-methyl-2-pyrrolidone was used as the original solvent in polyimide production, and proved to have good compatibility with BPDA–PDA polyimide. During the winding process, the polyimide precursor was sprayed onto the MWNTs sheets layer by layer (seen Fig. 1). The composite prepreg was 10–20 μm after 1 h of winding, and was then hot-pressed in a vacuum oven at 120 °C for 2 h. The curing process followed a stepwise heating program from 120 °C to 450 °C, as shown in Fig. 2. The composite after hot-pressing became compact and the thickness was reduced to (7–15) ± 1 μm.

2.2. Composite characterization and testing

Tensile properties were tested at room temperature using a Shimadzu EZ-S tensile testing machine with a crosshead speed of 0.5 mm/min and gauge length of 6 mm. The sample width was measured using a calibrated scale bar in an optical microscope (30×). The sample thickness was measured using a micrometer. At least five specimens were tested for each MWNT composite. Scanning electron microscope (SEM) analysis of the MWNTs network and composite fracture surface was carried out on the JEOL 6400F microscope with an acceleration voltage of 5 kV. The electrical conductivity of the composites was measured using a 4-probe Agilent 34410A 6.5 digit multimeter. Thermogravametric analysis

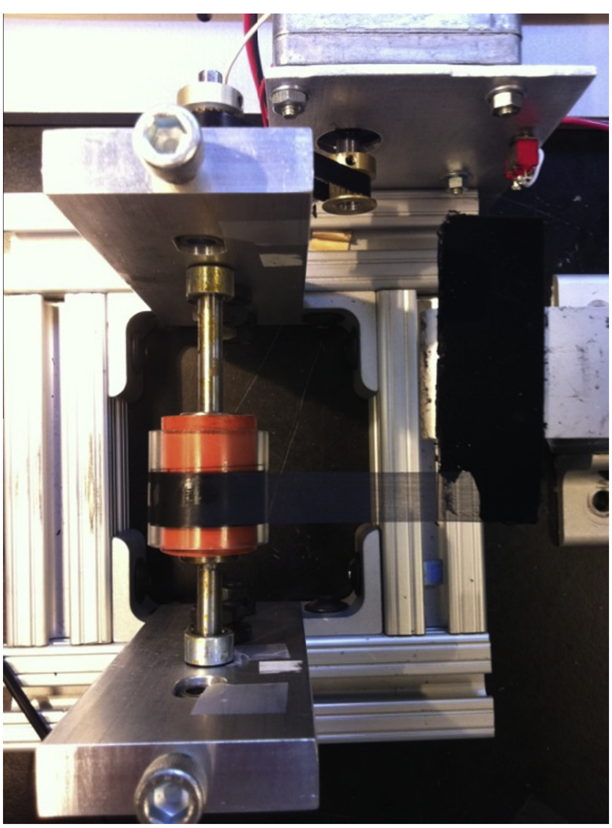

Fig. 1. Fabrication of a unidirectional MWNT composite using spray winding method.

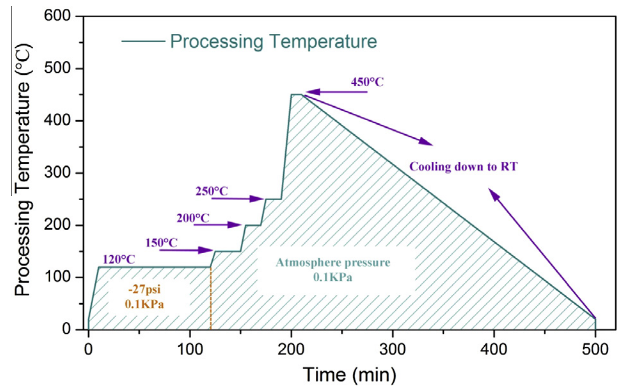

Fig. 2. The stepwise heating program of BPDA–PDA polyimide curing.

(TGA) was conducted in a Perkin Elmer Pyris 1 machine in nitrogen (99.999%) with a heating rate of 10 °C/min. The in-plane thermal diffusivity of the MWNT composites was measured by a Laser PIT device (Ulvac-Riko, Inc.) at room temperature and in a vacuum of less than 0.01 Pa.

3. Results and discussion

3.1. Morphology of MWNTs sheet

Fig. 3 is the macroscopic image of a unidirectional MWNTs reinforced polyimide composite. The size of the sample is 94 mm × 12.7 mm. Fig. 4 is an SEM image of the as-drawn MWNTs sheet, in which most of the MWNTs are aligned and parallel to each other. The image was taken after the composite sample was heated in TGA to make sure the polyimide was decomposed. Due to the Van der Waals' forces, the carbon nanotubes can be connected continuously. When the polymer matrix was sprayed while the MWNTs sheets were wound onto the spool, the high level of alignment of MWNTs was preserved. And the winding step further compacted the MWNT assembly due to the normal forces. This spray winding method is effective to make high volume fraction carbon nanotube composites since the matrix concentration can be controlled to very low by dilution. The BPDA–PDA polyimide is a type of semi-crystalline polyimide with a rigid backbone

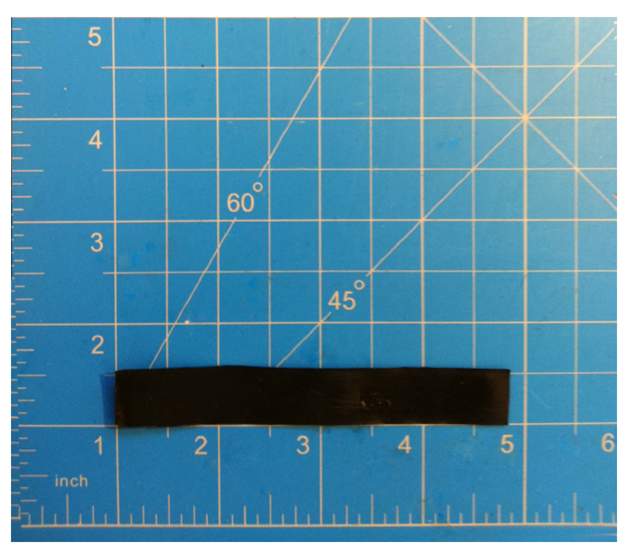

Fig. 3. Macroscopic image of a unidirectional carbon nanotube reinforced polyimide composite made via spray winding method.