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

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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 dihydrodiphenylenediamine) (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^{10} 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 influence 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 (MWNs) sheets and long, aligned and high volume fraction of MWNs were realized in the composites. The excellent mechanical, electrical and thermal properties of MWNs, 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...
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 (see 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. Thermogravometric analysis (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 MWNT 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.
The high molecular weight makes it difficult to penetrate nano-structures; however, the spray winding method provides a unique way to disperse the matrix using the layer-by-layer spray method. The polyimide, in this way, can be integrated with each layer of carbon nanotubes, ensuring the good infiltration between MWNTs and matrix.

3.2. Mechanical properties

The typical stress–strain curves of MWNT/BPDA–PDA polyimide composite (black square) and the pure BPDA–PDA polyimide (red circle) are shown in Fig. 5. The pure BPDA–PDA polyimide had tensile strength of 227.7 ± 25.3 MPa and elastic modulus of 4.04 ± 0.72 GPa. The elongation was around 20%. When aligned MWNTs acted as the reinforcement, significant enhancement of modulus was observed from the slopes of two curves. The elastic modulus of MWNT/polyimide composite was 53.73 ± 3.29 GPa, almost 12 times larger than that of pure polyimide. For a traditional carbon nanotube composite, due to the discontinuous MWNTs structure and low volume fraction, it can only increase the modulus by <50% [27–29]. The strength was improved by 300% over that of the pure polyimide, while the ductility (strain to failure) decreased from 20% to 1–2%. In this high volume carbon nanotube composite, MWNTs was the main constitute while polyimide acted as the adhesive, so the ductility was mostly determined by carbon nanotube assembly. The bonded network was harder to deform under tension, so the ductility decreased.

The fracture surface image was taken after the tensile test, as shown in Fig. 6. The composite was observed to be compact due to the hot pressing and spray winding processes. No excess matrix stayed on the surfaces of the composite samples, which could be easy to happen in low carbon nanotube volume composite. The MWNTs were uniformly dispersed due to the layer-by-layer winding. The standing ends of carbon nanotubes indicated that pull-out happened between MWNTs and polyimide during the tensile test.

3.3. Electrical property

The alignment of MWNTs provides a more effective path for electron transfer along the length of the composite, so it greatly enhances the electrical conductivity of the unidirectional carbon nanotube composite. Since polyimide is an insulator, it can reflect directly how much the electrical conductivity is improved by adding aligned MWNTs. The advantage of aligned structure of MWNTs largely benefit to the electrical conductivity along the longitudinal direction, therefore, only the longitudinal electrical conductivity was measured and shown in Table 1. By adding aligned carbon nanotubes in composite, the electrical conductivity increased by 10^{18} times. From the previous studies, the electrical conductivity of MWNT/polyimide composite were within 10 S/cm [30–32], and higher values cannot be achieved due to the randomly dispersion and low volume fraction of the MWNTs. By using spray-winding method, the electrical conductivity were dramatically improved and had potential to be enhanced further by applying pre-treatment, such as pre-stretch mentioned in Ref. [14].

3.4. Thermal properties

The polyimide is well-known as a type of high temperature resistance polymer; therefore, the MWNT/BPDA–PDA polyimide composite has the potential to be used in high temperature applications. Thermal gravimetric analysis was conducted to verify the high temperature resistance of the composite. As shown in Fig. 7,
The TGA and DTG curves reveal how MWNT/BPDA–PDA polyimide behaves from room temperature to 900 °C. The composite did not decompose until 400 °C. After a slow decomposition, the composite lost only 18% weight at 900 °C, indicating the excellent thermal stability of MWNT/BPDA–PDA polyimide composite under extremely high temperature conditions.

Heat transport in carbon nanotube based polymer composite is determined by phonon transport. The in-plane thermal diffusivity of unidirectional MWNTs composite was measured by a scanning laser heating analyzer. Its thermal conductivity $\kappa$ (W/(mK)) can be calculated by,

$$\kappa = \alpha \rho \frac{C_p}{3}$$

where $\alpha$ is the in-plane thermal diffusivity (m$^2$/s), $\rho$ is the composite density (kg/m$^3$) and $C_p$ is the specific heat capacity (J/(kgK)).

The amplitude decay and the phase shift were adopted to eliminate the effects of heat loss. Fig. 8 is a typical curve of thermal diffusivity measurement of MWNT/BPDA–PDA polyimide composite. The black and red curves represent amplitude decay and phase shift, respectively. $\alpha_a$ and $\alpha_p$ were obtained from those two curves, and the optimized thermal diffusivity are calculated by,

$$\alpha = \sqrt{\alpha_a - \alpha_p}$$

The thermal conductivity of pure BPDA/PDA polyimide film and unidirectional carbon nanotube/polyimide composite are given in Table 1. By adding the aligned MWNTs, the thermal conductivity is improved by 681 times. The thermal conductivity of the composite (18.4 W/mK) is higher than unidirectional carbon fiber reinforced composite (4.5 W/mK) [33] and carbon nanotube composite with high volume fraction (0.4–1.3 W/mK) [34]. This is an expression of phonon transfer in the length direction of MWNTs.

### 4. Conclusions

The spray-winding was used in this study to fabricate unidirectional MWNT/BPDA–PDA polyimide composites with long MWNTs length, high volume fraction and good alignment. The composite exhibited good mechanical and electrical properties with the highest strength of 691 MPa and electrical conductivity of 183.3 S/cm. The high temperature resistance of this composite was also proved to be excellent with only 18% weight loss under 900 °C. And the thermal conductivity reached to 18.4 W/mK, which was beyond what can be achieved in previous studies. Therefore, the spray winding method was suitable to produce high volume fraction composite with high performances. Furthermore, this work is the first attempt to use BPDA–PDA polyimide as matrix in unidirectional carbon nanotube composites. The excellent properties of the unidirectional MWNT/BPDA–PDA polyimide composites make them promising materials for use as lightweight multifunctional material in aerospace applications.

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