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Material Properties

A comparative study on the effect of carbon fillers on electrical and thermal conductivity of a cyanate ester resin

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ABSTRACT

Carbon fillers including multi-walled carbon nanotubes (MWCNTs), carbon black (CB) and graphite were introduced in a cyanate ester (CE) resin, respectively. The effects of the fillers on the electrical and thermal conductivity of the resin were measured and analyzed based on the microscopic observations. MWCNTs, CB and graphite exhibited percolation threshold at 0.1 wt%, 0.5 wt% and 10 wt%, respectively. The maximal electrical conductivity of the composites was 1.08 S/cm, 9.94×10^{-3} S/cm and 1.70×10^{-5} S/cm. MWCNTs showed the best enhancement on the electrical conductivity. The thermal behavior of the composites was analyzed by calorimetry method. Incorporation of MWCNTs, CB and graphite increased the thermal conductivity of CE resin by 90%, 15% and 92%, respectively. Theoretical models were introduced to correlate the thermal conductivity of the CE/MWCNTs composite. The interfacial thermal resistance between CE resin and MWCNTs was 8×10^{-8} m^2K/W and the straightness ratio was 0.2. The MWCNTs were seriously entangled and agglomerated. Simulation results revealed that thermal conductivity of the CE/MWCNTs composites can be substantially elevated by increasing the straightness ratio and/or filler content of MWCNTs.

1. Introduction

Development of polymer composites with carbon fillers has become an attractive topic in tailoring the electrical and thermal properties of the insulating or low conductive polymer matrix [1–6]. Compared with traditional fillers, carbon fillers possess high surface to volume ratio and aspect ratio. They are significantly effective for enhancing the performance of polymer at low incorporation, owing to their superior conductivity, unique structure, excellent physicochemical stability and thermal stability [7–11]. However, improvements on the dispersion of carbon fillers and their interactions with polymers are the main challenges that limit the performance promotion of the composites [12–14]. Optimizing network structure and distribution of fillers is necessary to form a conductive path in matrix [14–17].

Recently, there is an increasing demand for high-performance thermosetting resins in industry [18]. The thermosets/carbon fillers composites show good performance as anti-static materials, conductive coating, electric heating devices, bipolar plate, etc. [17,19–21]. In order to extend their applications, thermosets/carbon fillers composites have been developed with improved electrical and thermal properties. Florian et al. [8] prepared epoxy composites by adding CNTs and CB. The percolation threshold was observed at low filler concentrations. The thermal conductivity was slightly increased. Similar result was obtained by investigating the conductivity of epoxy/MWCNTs composites in Vahedi's [22] research. An et al. [19] investigated the electric heating behavior of epoxy/graphene composites. The electrical resistance of composites varied dramatically with increasing the graphene content. The composite showed rapid temperature response and good stability. Effects of graphite on the properties of epoxy resins were also studied. However, the improvement of thermal conductivity was always much smaller than the corresponding improvement in mechanical properties [23,24]. The increase in the electrical conductivity was not notable [25].

Cyanate ester resin is one of the most important high performance thermosets that provide excellent mechanical properties and chemical resistance [26]. CE resins have been widely utilized in aerospace and defense industries. Compared with other thermosets, CE resins are more attractive with low moisture absorption, inherent flame retardancy, excellent mechanical strength, good

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surface finish and dimensional stability [27–30]. The glass transition temperature of CE resin used in this study is over 400 °C. CE resins have been widely proposed as replacements for epoxy resins in high temperature applications [31]. However, the electrical and thermal properties of CE resins are not satisfactory. The investigations on these properties of CE resins are inadequate [32,33]. The low thermal conductivity of CE resins induces considerable accumulations of thermal energy, which could affect its mechanical properties for long term usage at elevated temperature. Therefore, the improvement on the thermal conductivity becomes quite important. For a successfully enhanced CE resin composite, an effective conductive network is essential. It can be actualized based on a good dispersion of the carbon fillers in matrix, but the dispersion has been challenging due to the high viscosity and high curing temperature of CE resins. Moreover, each type of carbon filler has its unique structure including dimension and aspect ratio. The effects of the filler structure on the electrical and thermal properties of CE resins are still unclear. In our previous work [27,34], a CE resin, PT-30, composites were prepared by incorporation of carbon fillers. The processing and curing dynamics of the composites were studied. The dispersion and network formation of the fillers in CE matrix were sufficiently discussed. Based on this knowledge, in this study, the influences of different types of carbon fillers on the electrical and thermal conductivity of PT-30 are analyzed. We attempt to compare the enhancement effects of these fillers, and suggest appropriate applications of the CE resin composites, in order to guide the further development of the CE composites.

2. Experimental

2.1. Materials

Cyanate ester resin, Primaset PT-30 was purchased from LONZA Ltd. The molecular structure of CE resin is shown in Fig. 1. Ultrafine carbon black powder with particle size about 40 nm was supplied by Cobalt, Belgium. Purified multi-walled carbon nanotubes (MWCNTs) were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Science. The MWCNTs (purity > 95%) had a length of approximately 50 μm and diameter of 8–15 nm. The density was about 2.1 g/cm^{-3}. Ultrafine grade graphite with particle size 4–7 μm was received from Qingdao Kropfmühl Graphite Company, China.

2.2. Preparation of PT-30 composites

The carbon fillers MWCNTs, CB and graphite were fully dried and dispersed in the PT-30 matrix by strong mechanical stirring for 2 h at 100 °C, respectively. The stirring speed was 1000 rpm. The composites were produced at the same processing conditions, by varying filler content up to 10 wt% for each type of carbon filler. The mixtures were then placed in a vacuum oven (800 mbar) for 1 day to remove residual moisture. The mixtures was poured into a mould and cured for 2 h at 220 °C and post-cued for 1 h at 290 °C.

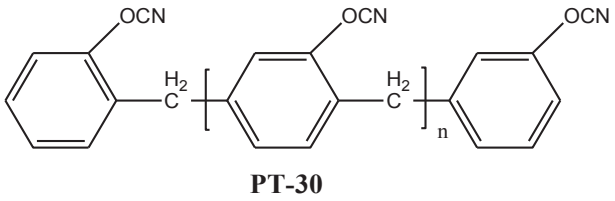

Fig. 1. Molecular structure of PT-30 resin.

2.3. Characterization

A Field-Emission Gun Scanning Electron Microscopy (FEGSEM) (LEO 1530VP instrument) was used to observe the morphology of fracture surface of the composites. Before the observation, the samples were freeze-fractured in liquid nitrogen and coated with gold by a sputter coater for 60s. Electrical conductivity of composites was measured using a Keithley Semiconductor Characterization System 4200-SCS. A direct voltage, V, was loaded on the specimen, and the current, I, was obtained. The electrical conductivity, σ, can be calculated by the following equation:

$$\sigma = \frac{L}{S} \times \frac{I}{V} \quad (1)$$

where L is the length of the cuboid sample, S is the cross-sectional area. Before measurements, Silver paste was deposited on the top and bottom sides of each specimen, in order to get steady values when they were contacted with the probes. At least three specimens were tested for the electrical conductivity to obtain an average value for each composite. A standard model of TA instruments differential scanning calorimetry (DSC) 2920 Calorimetry was utilized to evaluate the thermal conductivity [35]. Fig. 2 illustrated the setup of DSC test for thermal conductivity. Pure indium (melting temperature: 156.7 °C) was the calibration substance. The tests were run from 100 to 180 °C at a heating rate of 10 °C min^{-1}. The thermal conductivity value was obtained from calculation based on the following equation:

$$\lambda = \frac{H}{S} \times \frac{\phi}{\Delta T} \quad (2)$$

where λ is the thermal conductivity, H is the height of the sample, S is the cross-sectional area, and $\frac{\phi}{\Delta T}$ is the slope of the melting curve of indium, which was obtained from the DSC plot. At least three specimens were tested for the thermal conductivity to obtain an average value for each composite.

3. Results and discussion

The incorporation of carbon fillers into the PT-30 induced an electrical conduction, by forming a conductive pathway. The lowest filler concentration, which is known as percolation threshold, is necessary to achieve conductivity, $\sigma \geq 10^{-8}$ S/cm. The percolation theory states the critical amount of fillers required for the transition of composites from insulating to conductive. The electrical conductivity of the PT-30 composites was measured and plotted in Fig. 3. It can be found that the percolation threshold of PT-30/MWCNTs composite occurred at very low filler content, which was 0.1 wt%. The MWCNTs showed excellent improvement on the electrical conductivity of PT-30, owing to their high aspect ratio. In contrast, 2 wt% CB was required to achieve a similar conductivity. The percolation threshold of PT-30/CB composite was 0.5 wt%.

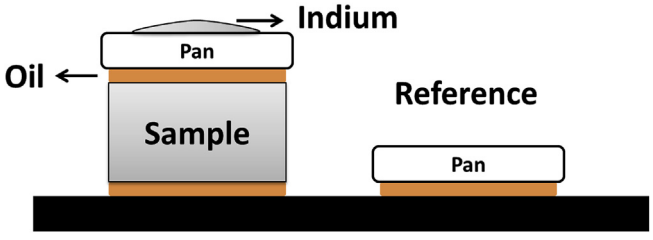

Fig. 2. The setup of DSC test for thermal conductivity.