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Highly mechanical strength and thermally conductive bismaleimide–triazine composites reinforced by Al_2O_3@polyimide hybrid fiber

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ABSTRACT

Bismaleimide–triazine (BT) resins have received a great deal of attention in microelectronics due to its excellent thermal stability and good retention of mechanical properties. Thereafter, developing BT based composites with high mechanical strength, thermal conductivity and dielectric property simultaneously are highly desirable. In this study, one hybrid fiber of Al_2O_3 nanoparticle (200 nm) supported on polyimide fiber (Al_2O_3@PI) with core–shell structure was introduced into BT resin to prepare promising Al_2O_3@PI–BT composite. The results indicated that the resultant composites possessed high Young's modulus of 4.06 GPa, low dielectric constant (3.38–3.50, 100 kHz) and dielectric loss (0.0102–0.0107, 100 kHz). The Al_2O_3@PI hybrid film was also conductive to improve thermal stability ($T_{d5\%}$ up to 371 °C), in-plane thermal conductivity (increased by 295% compared to that of the pure BT resin). Furthermore, the Al_2O_3@PI–BT composite were employed to fabricate a printed circuit substrate, on which a frequency "flasher" circuit and electrical components worked well.

1. Introduction

Nowadays, bismaleimide–triazine (BT) resins become widely used in the microelectronics, such as semiconductors encapsulates, electric motor and circuit boards due to its excellent thermal stability, reliable electrical properties and good retention of mechanical properties at elevated temperatures, especially in hot/wet environment [1,2]. With the semiconductor device toward higher density connection and miniaturization in the electronics industry, the dissipation of unwanted heat generated in electronic components has attracted much attention [3]. However, pure BT resin materials are inherently poor thermal conductors with low mechanical properties. Meanwhile, a great deal of attention has been paid on developing BT resin-based composites with high thermal conductivity and mechanical strength [4–7]. As reported in our previous work, the polyethyleneglycol (PEG) was used to construct a flexible bridge at interface between the glass fiber and BT resin to improve mechanical strength [8]. As a result, the elongation, tensile stress and toughness of the composites were increased by 67.1%, 17.9% and 78.2%, respectively, compared with those of unmodified one. Furthermore, we developed a core–shell structure multiwalled carbon nanotubes (MWCNTs) encapsulated with an insulating silicon oxide (SiO_2) layer which was used to reinforce BT resin as well [2]. And the stress strength and Young's modulus of the composite were 87.4 MPa and 3.18 GPa, respectively. To improve integrity of signal and reliability of device, high thermal conductive materials with electrically insulation are much more significant. Thus, a number of inorganic fillers, such as silicon carbide (SiC) [9,10], silicon nitride (Si_3N_4) [11,12], boron nitride (BN) [13–15], aluminum nitride (AlN) [16,17] and alumina (Al_2O_3) [18,19] have been used as thermal conductive fillers embedded in a polymer matrix. Therefore, developing BT based composites with high mechanical strength and thermal conductivity simultaneously are highly desirable.

Thereinto, Al_2O_3 nanofiber with special structure prepared by calcination was reported for reinforcing the thermal conductivity of resin [20]. It was reported that the advantage of the branched nanofiber was high aspect ratio and facile interconnection with each other to increase the probability of formation of phonon

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paths, leading to the high thermal conductivity of the nanocomposite. But the mechanical properties of composites modified by alumina nanofiber did not mention. Another researcher reported a novel method that the AlN particle modified with polyimide (PI) was used for electronic encapsulation, which exhibited excellent thermal and dielectric properties [21]. However, a high volume fraction of thermally conductive fillers, generally >60 vol%, is necessary to build the thermal conductive network in polymer matrix [22], which may consequentially disserve the mechanical property of composite. Hence, endowing high thermal conductivity and excellent mechanical property into one composite is a challenge.

As mentioned above, a novel hybrid film with core–shell structure of Al_2O_3 nanoparticles (NPs) adhere to PI fiber (Al_2O_3@PI) had been successfully developed by facile coaxial electrospinning in our recent work, which shows superior in plane thermal conductivity of 9.66 W m^{-1} K^{-1} and higher elastic modulus (2.11 GPa) [23]. This core–shell structure is conducive to attain high aspect ratio of Al_2O_3 NPs and improve the interconnection of each other, which is the key to form the thermal conductivity network in matrix. Furthermore, the core component of PI fiber provides flexible and excellent mechanical properties of composites. Thereafter, Al_2O_3@PI hybrid films are used to reinforce BT resin in this work to yield BT-based composites with high mechanical strength and thermal conductivity simultaneously. The mechanical properties, dielectric properties, thermal stability and thermal conductivity were investigated comprehensively. Furthermore, the composites have been successfully applied to fabricate a frequency flash circuit with parallel light emitting diode (LED) lamps and which works well.

2. Experimental

2.1. Materials

Pyromellitic dianhydride (PMDA), 4,4′-oxidianiline (ODA) and N,N-dimethylacetamide (DMAc) were commercially obtained from China National Medicine Co. Polyvinylpyrrolidone (PVP) was supplied by Aladdin. The Al_2O_3 NPs with an average diameter of 200 nm were supplied by Denki Kagaku Kogyo Kabushiki Kaisha, Japan. 2,2′-Bis (4-cyanatophenyl) propane (BCE, Heijang Kinlyuan Pharmaceutical Co., Ltd, China), 4,4′-bismaleimidodiphenylme thane (BMI, Honghu Bismaleimide Resin Factory, China) and 2,2′-diallyl bisphenol A (DBA, Wuxi Resin Factory, China) were used as starting materials to prepare the BT resin.

2.2. Preparation of Al_2O_3@PI–BT composite

The Al_2O_3@PI hybrid fiber film was prepared by coaxial electrospinning as reported previously [23]. The modified BT resin was prepared by a melt method, mixed by stirring at 130 °C for 30 min to form transparent, amber-colored liquid, and cooled to room temperature. 40 wt% BT resins were dissolved in methyl ethyl ketone to form a homogeneous solution. The Al_2O_3@PI hybrid fiber was attached to a copper foil to ensure that the film remains flat to minimize thickness variations. Following that, the resin solution prepared above was coated on the film with appropriate weight. The composites were dried at 100 °C for 1 h to evaporate the solvent for preparing prepreg. Two sheets of prepreg with 90° orientation were laminated between sheets of copper foil under a pressure of 5 kgf cm^{-2} at 150 °C for 1 h, resulting in Al_2O_3@PI–BT composite, as shown in Fig. S2. Then the composite was cured at 150, 180, 220 °C for 1 h, respectively. The weight fraction of hybrid fiber for different composite laminates was the same as 20 wt% but with different contents of Al_2O_3 nanoparticles containing 5.34 wt%, 8.44 wt%, 11.86 wt% and 14.95 wt% which were used for further research.

2.3. Characterization

The cross-section images of the composite sample were examined using Scanning electron microscope (Nova NanoSEM 450, FEI) combined with an energy dispersive spectrometer (X-Max50, Oxford Instruments) with 5 or 10 kV accelerating voltage. The thermal stabilities of the composites were analyzed using thermal gravity analysis (TGA) which was made on a TA SDT Q600 thermo-gravimetric analyzer. The microbalance has a precision of ±0.1 mg. Samples of about 10 mg were placed into 70 μL alumina pans. The samples were heated from 30 to 800 °C under an air flow of 100 mL min^{-1}. Dynamical mechanical analysis (DMA) tests were carried out using a dynamic mechanical analyzer (TAQ800), in tensile mode at a fixed frequency of 1 Hz and amplitude of 10 μm. The specimen dimensions were 50 × 5 × 0.3 mm^3. Measurements were performed from 30 to 350 °C at a heating rate of 3 °C min^{-1}. Static uniaxial in-plane tensile tests were conducted with a dynamic mechanical analyzer (DMA Q800, TA Instruments). The samples were cut with a razor into rectangular strips of approximately 5 × 15 mm^2 for mechanical testing. All tensile tests were conducted in controlled force rate mode with a preload of 0.001 N and a force ramp rate of 1.0 N min^{-1} at room temperature. The thermal diffusivity of the composites was investigated at 25 °C through xenon flash equipment (LFA467, Germany) according to ASTM E1461. The diameter of sample used for laser flash method was 1 in. and a thickness of 250 ± 5 μm with the mirror-like polished surface. Differential scanning calorimetry (DSC) with sapphire reference was used to measure the specific heat capacity (C_p) with a heating rate of 5 °C min^{-1} under nitrogen. The density of composites was measured by the Archimedean buoyancy method using an electronic analytical balance (FA2104J, China) at room temperature. The dielectric and electrical properties were measured with an impedance analyzer (Agilent 4991A) in the frequency range of 10^3–10^7 Hz at room temperature. A frequency "flasher" circuit was fabricated by bonding discrete electronic components to the Al_2O_3@PI–BT composite (30 × 30 mm^2) to demonstrate its potential application in printed circuit substrates. FLIR-T355 infrared camera was used to take picture for the temperature field of substrate at room temperature (23 °C) with relative humidity of 58%.

3. Results and discussion

3.1. Preparation and microstructure of Al_2O_3@PI–BT composite

Without a doubt, decorating one material with high thermal conductivity and mechanical strength through architecture design is significant. As reported previously, Al_2O_3@PI hybrid film with Al_2O_3 nanoparticles were located on the shell layer of the fiber uniformly by coaxial electrospinning. And more Al_2O_3 nanoparticles were exposed after imidization (Fig. S1). Therefore, the as-prepared hybrid fiber with core–shell structure was introduced into BT matrix which would increase the thermal conductivity of composite by tightly Al_2O_3 nanoparticles as well as improve the mechanical strength by PI fiber and Al_2O_3 nanoparticles simultaneously. The preparation of Al_2O_3@PI–BT composite was schematic illustrated as shown in Fig. 1. Firstly, a solution of 40 wt% BT resins in methyl ethyl ketone was dropped into the Al_2O_3@PI hybrid fiber film and the solution can be completely adsorbed by the hybrid film attributing to the porous structure and large specific surface area. Then the composites were dried at 100 °C for 30 min to evaporate the solvent. Secondly, two sheets of prepreg were laminated