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Enhanced thermal conductivity and satisfactory flame retardancy of epoxy/alumina composites by combination with graphene nanoplatelets and magnesium hydroxide

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ABSTRACT

Thermally conductive epoxy composites with eco-friendly flame retardancy are prepared by using spherical alumina (Al_2O_3), magnesium hydroxide and graphene nanoplatelets (GNPs) as thermally conductive fillers. Highly filled alumina particles do not seriously increase the viscosity of the epoxy monomer due to their spherical shape and smooth surface and thus the compounding keeps a good processibility; The incorporation of small amounts of layered GNPs efficiently increases the thermal conductivity of epoxy/Al_2O_3 composites because of the synergistic effect between layered GNPs and spherical Al_2O_3 on forming a thermally conductive network within epoxy matrix. Interestingly, the addition of a small amount of eco-friendly magnesium hydroxide endows the thermally conductive epoxy composites with a satisfactory flame retardancy. The epoxy composite with 68% Al_2O_3, 7% modified GNPs (m-GNPs) and 5% magnesium hydroxide is determined as the optimum composition with a high thermal conductivity of 2.2 W/(mK), 11 times of that of neat epoxy. Its satisfactory flame retardancy is confirmed by the high limiting oxygen index of 39% and UL-94 rating of V-0 with no dripping. The compact, dense and uniform char layers derived from well-dispersed m-GNPs act as efficient barrier layers and contribute to the flame retardant properties of the epoxy composites.

1. Introduction

Thermally conductive polymer composites have attracted tremendous attention recently due to their heat dissipation performance in highly integrated electronic devices such as high-power laser, high brightness light-emitting diode, and solar cells [1–7]. The increasing miniaturization of electronic device components poses higher requirements for heat dissipation, fire safety and electrical insulating, it is thus imperative to develop polymer composites with high thermal conductivity and satisfactory flame retardancy [8–15]. Although conventionally used thermal fillers, including metals (Cu, Ni, Ag, etc.), metal oxides (Al_2O_3, MgO, ZnO, etc.), ceramics (AlN, SiC, etc.) and carbon materials (carbon black, graphite, etc.), are cost-effective, high loading of more than 50 wt% is usually required to endow polymers with satisfactory thermal conductivities, which makes resultant polymer composites difficult to be processed.

Hybrid fillers with different shapes and sizes are commonly used to improve the thermal conductivity of polymers by facilitating the formation of a compact and efficient heat transfer network [16–25]. Yan et al. [26] used a small amount of one-dimensional carbon fibers to enhance through-plane and in-plane thermal conductivities of phenol formaldehyde resin (PF)/graphite composites. By replacing 10 wt% of graphite with carbon fibers, the through-plane and in-plane thermal conductivities of the PF composite were as high as 8.6 and 31.5 W/(mK), respectively. Yuan et al. [27] combined tetrapod-shaped zinc oxide (T-ZnO) whiskers and boron nitride (BN) flakes to improve thermal conductivity of PF. The in-plane thermal conductivity of the PF composite was as high as 1.96 W/(mK) with 30 wt% BN and 30 wt% T-ZnO, 6.8 times higher than that of neat PF and 71.9% higher than that of the PF composite with 60 wt% BN. Due to its stereo structure with four needles, T-ZnO played an important role in bridging the BN flakes in through-plane and in-plane directions, thus facilitated

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the formation of an efficient conductance network within PF matrix. Because of the layered structure and high thermal conductivity [28,29], 1 wt% of graphene nanoplatelets (GNPs) apparently increased the thermal conductivity of epoxy/carbon nanotube composites [30]. By filling with 12 wt% GNPs and 71.7 wt% silicon carbide, their epoxy composite exhibited an excellent thermal conductivity, 26.1 times higher than that of neat epoxy [24]. Mortazavi et al. [31] developed a combined multiscale modeling method, which confirmed that flake size was the main factor affecting the thermal conductivity of graphene and BN laminates. Nevertheless, it is still a challenge to achieve high thermal conductivity for polymer composites with electrically insulating and ease of processing.

Additionally, thermally conductive polymer composites are usually required to be flame retardant due to their high temperature environment in practical applications [32–36]. Although conventional flame retardants, including organohalogen, organophosphorus, organonitrogen, are widely used to improve the flame retardancy of polymer composites [37,38], most of them are not eco-friendly and large quantities are commonly required to achieve satisfactory flame retardant performances [39,40]. Rabczuk et al. [41,42] developed a model which was capable of handling dislocation and crack propagation in the three-dimensional space at an atomistic level. Therefore, it is imperative to develop novel approaches to endow polymers with both high thermal conductivity and satisfactory flame retardancy.

In the present work, a multi-components and multi-dimensional fillers system is adopted to improve both thermal conductivity and flame retardancy of epoxy resin. Spherical Al_2O_3 particles with smooth surface and different sizes are chosen as the main thermally conductive fillers. Small amounts of layered GNPs are used to facilitate the formation of a three-dimensional thermal conductance network of epoxy/Al_2O_3 composites due to their layered structure and high thermal conductivity. As an eco-friendly inorganic flame retardant, $Mg(OH)_2$ is incorporated to enhance flame retardancy of the thermally conductive epoxy composites. Flammability performances of the composites are evaluated with cone calorimeter, limiting oxygen index (LOI) and UL-94 vertical burning measurements. The resultant epoxy composites are investigated in terms of thermal and electrical conductivities, flame retardancy, and mechanical properties.

2. Experimental

2.1. Materials

Spherical Al_2O_3 particles with mean sizes of 5 and 40 μm were purchased from Shanghai Bestry Performance Materials (China). GNPs with a mean size of ~40 μm and a thickness of ~100 nm were provided by Xiamen Knano Co. Ltd. (China). $Mg(OH)_2$ powders were bought from Haolong Chemicals (China). Bisphenol-A liquid epoxy monomer was provided by Changshu Jiafa Chemicals (China). The curing agent of methyl hexahydrophthalic anhydride (MHHPA) was supplied by Jiaxing Dongfang Chemicals (China) and the curing accelerator of 2,4,6-tris(dimethylaminomethyl)phenol (DMP30) was provided by Changzhou Shanfeng Chemicals (China).

2.2. Surface modification of GNPs

GNPs were modified by the silane coupling agent with terminal epoxide groups (A187) using ethanol as the solvent, where the coupling agent was kept as 10 wt% of GNPs. After the mixture of GNPs and ethanol solution of the silane coupling agent was stirred with a high speed magnetic stirrer at 60 °C for 30 min, it was further mixed with an IKA T25 homogenizer (Germany) for 1 h, filtrated, washed with ethanol, and dried at 110 °C for 1 h in a vacuum oven.

2.3. Preparation of thermally conductive epoxy composites

Epoxy composites were prepared by solution compounding, casting and curing. Bisphenol-A liquid epoxy monomer was first mixed with Al_2O_3 of 40 and 5 μm (w/w 7:3), GNPs and the accelerator. The resultant mixture was vigorously stirred for 1 h to form a uniform suspension. After adding the curing agent of MHHPA, the mixture was further stirred for 1 h and then degassed in the vacuum oven for 1 h to avoid the formation of bubbles. Finally, the mixture was poured into molds and kept at 120 °C for 3 h for curing. In addition, 5 wt% Al_2O_3 was replaced with $Mg(OH)_2$ to prepare thermally conductive composites with a satisfactory flame retardancy.

2.4. Characterization

GNPs, Al_2O_3 and their epoxy composites were observed with a JEM-7401F field emission scanning electron microscope (SEM, Japan). Viscosities of epoxy composites before curing were measured with a Malvern Bohlin Gemini HR nano rheometer (UK) in a steady flow state with shear rates of 1–100 s^{-1}. Through-plane thermal conductivities of the epoxy composites with a diameter of 60 mm and a thickness of 5 mm were measured with an ECO HC-110 thermal meter (Japan). UL-94 vertical burning tests and LOI measurements were conducted to investigate flame retardant performances of epoxy composites. Combustion experiments of the epoxy composites with dimensions of 100 × 100 × 3 mm^3 were carried out with a FTT cone calorimeter (UK) at a heat flux of 35 kW/m^2 according to the ISO 5660 standard.

3. Results and discussion

3.1. Dispersion of Al_2O_3 and GNPs in epoxy composites

The combination of fillers with different dimensions and shapes usually facilitates the construction of highly efficient pathways for thermal conductance in polymer matrices. Fig. 1 shows a schematic illustrating the advantage of using inorganic fillers with different

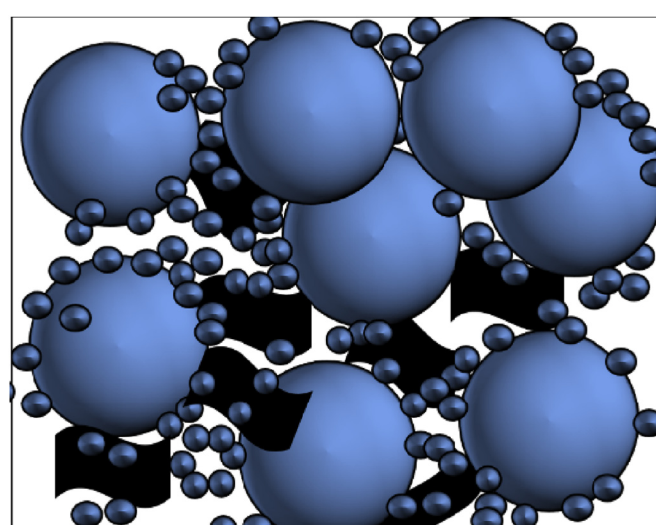

Fig. 1. Schematic showing the advantage of using fillers with different sizes and shapes.