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Multi-functional interface tailoring for enhancing thermal conductivity, flame retardancy and dynamic mechanical property of epoxy/Al_2O_3 composites

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ABSTRACT

Interfacial tailoring is always the key to preparing high-performance polymer-based thermal conductive composites (PTCs). Herein, we reported a multi-functional interface tailoring approach to simultaneously improve the thermal conductivity, flame retardancy, thermal and mechanical properties of PTCs, by forming a core-shell structured graphene oxide coating Al_2O_3 hybrid (Al_2O_3@HGO). Simultaneously a flame retardant bridging agent was introduced to improve the coating amount and flame retardant efficiency of the hybrid. The morphology analysis revealed the significant reinforcement of interfacial interaction of Al_2O_3 in epoxy (EP) by HGO coating. As a result, such the interfacial tailoring induced both the significant decrease in interfacial thermal resistance and the formation of additional thermal conductive paths by the graphene coating layer, resulting in the significant improvement in thermal conductivity of EP/Al_2O_3@HGO composites. The flame retardant parameters, peak heat release rate, total heat release and total smoke production, showed a 49.3%, 40.9% and 71.2% reduction, respectively, comparing to neat EP, which was ascribed to the strong interface with GO coating layer and the flame retardant bridging agent catalyzed charring to form an intact and compact char protective layer with Al_2O_3. Moreover, the strong interfacial interaction also restricted the segment movement, increasing the storage modulus and T_g.

1. Introduction

Polymer-based thermal conductive composites (PTCs) have been widely used to address the thermal problems induced by the high-degree miniaturization and integration of electronic components in modern electronics, due to their light density and low cost, high sealing and secure processing [1,2]. Since polymer matrices with low intrinsic thermal conductivity (K_c) (0.1–0.5 W/mK), incorporating high thermal-conductive fillers, such as metal [3] and ceramic [4] particles, carbon fillers [4] and their hybrids [5], has been regarded as a prerequisite for realizing the thermal management of composites. Unfortunately, the high interfacial thermal resistance, caused by phonon acoustic mismatch at fillers/matrix interfaces usually results in the very low experimental K_c values comparing to the theoretical values [6]. Besides, the additional properties in PTCs including flame retardancy, thermal and mechanical properties, are also relying heavily on their fillers/matrix interfacial property. Therefore, exploring an appropriate approach to tailoring interfacial properties for realizing the simultaneous improvement in K_c, flame retardancy, thermal and mechanical properties is still a significant challenge for preparing high-performance PTCs.

Notably, nonequilibrium molecular dynamics (MD) simulations have demonstrated that suitable organic chain grafting for thermal-conductive fillers have a significant enhancement in their interfacial thermal transport in polymer matrix [7], which also has been

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confirmed by experimental data [8,9]. Our previous study [6] demonstrated that introducing less stiff silica intermediated coated layer on the surface of thermal-conductive filler has the ability to weak the modulus mismatch of fillers and matrix, further analogous metal (Ag [10]) or ceramic (Al_2O_3 [11]) intermediate nanolayers with high intrinsic thermal conductivity have been also adopted in the recent researches. However, complicated process and low-yield production severely restrict their application for the commercial PTCs due to the massive filler loading. Recently, an amphiphilic graphene oxide (GO) consisting of aliphatic six-member regions and aromatic regions with nonoxidised benzene rings [12] has been used to improve the interfacial properties of particles in matrix by a simple electrostatic strategy [13,14]. Such GO coating layers not only can reduce the interface thermal resistance [15], but also connect together to form extra thermally conductive paths in PTCs [16]. In view of the easy bulk production of GO, this simple coating strategy is regarded as a promising interfacial tailoring approach for mass producing high-performance PTCs.

The fire hazards of PTCs used in electronic devices, originating from high energy dissipation and heat transfer, are very significant but often ignored. GO and its derivatives as promising flame retardant additives for polymers without damaging the mechanical and thermal properties, while minimizing environmental impact have drawn the considerable attention of scientists [17–20]. Functionalizing GO with phosphorus and/or nitrogen compounds has found it to be more efficient than pure GO in improving flame retardant efficiency [17,21]. Thereby, there comes an intriguing question: can GO coating strategy realize the construction of desired interfacial properties to simtaneously improve the flame retardancy as well as thermal and mechanical properties of PTCs? Herein, it can be realized by an ingenious multi-functional interface tailoring strategy: thermal-conductive Al_2O_3 coated with GO layers using a high stability flame retardant of hexachlorocyclotriphosphazene (HCCP) as bridging agent [22], to form a core-shell structured hybrid (Al_2O_3@HGO) was designed to improve the interfacial property between Al_2O_3 and epoxy resin. In the presence of HCCP molecule not only maximum reinforces the coating amount of GO, further reinforcing the interfacial interaction between matrix and Al_2O_3, but also improves the flame retardant efficiency of GO coating layer. Besides, the GO coating layer can be further reduced during matrix curing process to form additional thermally conductive paths as shown in Fig. S1. Therefore, the final epoxy-based composites show a simultaneous improvement in thermal conductivity, flame retardancy, thermal and mechanical properties.

2. Experimental

2.1. Materials

Spherical aluminum oxide (s-Al_2O_3, ZF-KQ05) powders with a mean diameter of 5 μm were purchased by Zhanfan Trading Co., Ltd (China). GO sheets were synthesized from natural graphite by using Hummers' method based on our previous work [23]. Epoxy (EP) monomers of diglycidyl ether of bisphenol-F (DGEBF, YDF-170) were supplied by KUKDO Chemical Co., Ltd (China). The curing agent of 2-ethyl-4-methylimidazole (EMI-2,4, AR), and HCCP (97%) were supported by Aladdin Industrial Corporation (USA). Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), triethylamine (TEA), chloroform and ethanol were provided from Sinopharm Chemical Reagent Co., Ltd (China). THF, DMF, TEA, and chloroform were purified by distillation to remove water. Other reagents were used as-received without further purification.

2.2. Synthesis of GO-HCCP (HGO)

Briefly, as shown in Fig. 1a, GO sheets (1 g) and TEA (20 mL) were ultrasonically dispersed into 250 mL distilled THF for 1 h. Then HCCP (5 g) dissolved in THF (50 mL) was dropwise added into the GO solution for more than 1 h with an ice bath, magnetic stirring and argon shielding. After that, the system was reacted at room temperature with drastic stirring for 12 h. The resultant solid products were filtered firstly, then dissolved into 500 mL chloroform to remove the triethylamine hydrochloride. The finally products (GO-HCCP or HGO) were obtained by filtration and drying in a vacuum oven at 60 °C for 12 h.

2.3. Preparation of Al_2O_3@HGO hybrid

Al_2O_3 (10 g) powders were dispersed into 100 mL DMF with vigorous stirring as shown in Fig. 1b. A certain amount of HGO (1:50, 1:40, 1:30, 1:20 relative to Al_2O_3) was ultrasonic-dispersed into 200 mL DMF for 1 h. The HGO solution was then injected into the Al_2O_3 system with vigorous stirring. Afterwards, the mixture system was heated to 70 °C with continuous stirring and argon shielding for 8 h. The resultant solid products were collected by standing and washing in ethanol at least 3 times, and drying in vacuum oven at 80 °C for 12 h. For the sample of 1:20, the product was collected by filtration. The obtained powders (Al_2O_3@HGO) have an apparent color change from white to brown (Fig. 1b).

2.4. Fabrication of EP/Al_2O_3@HGO composites

EP/Al_2O_3@HGO composites were fabricated using the following procedure. Typically, stoichiometric Al_2O_3@HGO powders, EP monomers and 6 wt% (relative to EP resin) curing agent EMI-2,4 were blended and degassed by using a planetary stirrer with a blending procedure (3 min at 1800 rpm) and a degassing procedure (1 min at 2200 rpm) at room temperature. This process was repeated at least 3 times to ensure the uniform dispersion. The obtained mixtures were poured into a mold and cured according to programmed-temperatures of 60 °C for 2 h, 100 °C for 2 h and 150 °C for 5 h.

2.5. Characterizations

Bruker Equinox 55 Fourier transform infrared spectrometer (FTIR) was used in transmission-mode to check the chemical structure of GO-HCCP and Al_2O_3@HGO. The morphologies of Al_2O_3@HGO and its composites were observed by using FEI Nova NanoSEM450 field emission scanning electron microscope (FE-SEM) under an acceleration voltage of 15 kV and Tecnai G2 20 S-TWIN transmission electron microscopy (TEM) under an acceleration voltage of 200 kV. Synchronizing with SEM measurements, Oxford Inca X-max energy disperse X-ray spectrometer (EDX) was carried out to analyze the component of Al_2O_3@HGO. K_c value of composites was detected by using a KEM QTM-500 Quick Thermal Conductivity Meter according to ASTM C1113 90 standard. Combustion behaviors were assessed by using cone calorimeter (CC, Fire Testing Technology) according to ISO 5660-1:2002. Samples for CC tests ($100 \times 100 \times 3\ mm^3$) were wrapped with aluminum foil and irradiated horizontally under a heat flux of $35\ kW/m^2$. Dynamic mechanical analysis (DMA Q800, TA) was conducted in single cantilever mode from 30 to 180 °C at a linear heating rate of 3 °C/min.