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Melamine resin/graphite nanoflakes hybrids and its vacuum-assisted prepared epoxy composites with anisotropic thermal conductivity and improved flame retardancy

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ABSTRACT

Melamine resin/graphite nanoflakes hybrids (MGNH) were synthesized by *in situ* polymerization. The SEM and TEM demonstrate that melamine resin was self-deposited on the surface of the flakes. MGNH is uniform sheeted hybrids which exhibits excellent dispersiveness. MGNH/epoxy composite (MGNH/EP) is prepared via vacuum-assisted method. The special prepared method endows MGNH/EP with interesting anisotropic thermal conductivity. The coefficient of thermal conductivity of the composite in normal direction is 0.4024 W m^{-1} K^{-1}, while that of MGNH/EP in horizontal direction is 1.5596 W m^{-1} K^{-1}. The optical microscope image of the composite suggests that the nanoflake is arranged as a parallel conduction medium, it is demonstrated that direct flake-flake conduction can form heat-transfer passages, which contributes to the higher thermal conductivity of the composite in horizontal direction. Also, MGNH/EP shows excellent flame retardant properties, evidenced by the dramatically reduced peak heat release rate and 51% of total heat release values compared with neat EP obtained from a micro-combustion calorimeter. The reduced fire hazard can mainly attributed to the synergistic effects of melamine resin and graphite nanoflakes.

1. Introduction

Improving the thermal conductivity and flame retardant of polymer materials has been recognized as a key to dramatically increase their wide applications [1–6]. Substantial property improvements can be achieved using various carbon-based materials, such as graphene oxide, thermally expanded or graphene, graphite flakes etc [4,7–10]. Carbon-based materials show great promise as nanofiller in polymer composites due to its high physical aspect ratio, excellent thermal, electrical conductivities and its potential fire retardant properties [3,11–15].

Graphite nanoflakes (GNH) possessed large surface area, high thermal conductivity and has a high aspect ratio and it is low cost. Recently, the use of graphite nanoflakes as a thermally conductive additive in polymer nanocomposites tends to be intense [16–18]. In addition, expanded graphite or carbon nanotubes have been used to impart the flame retardant properties to polymers [3]. Similarly, as carbon-based materials, GNH is expected to reduce fire hazards of polymers due to its unique carbon sheet structure.

Epoxy resin exhibits unique properties advantageous properties with respect to: ease of processing, low cost and excellent mechanical properties, bring in its application metal matrix composites, modern electronic/electrical insulation, and electric encapsulates areas [19,20]. Modern electronic and LED device has a high requirement for efficient thermal management and fire safety due to their rapidly increasing power densities and the continued miniaturization [21–24].

In this study, in order to prepared anisotropic thermal conductive and flame retarded epoxy composite, firstly, melamine resin/graphite nanoflakes hybrids (MGNH) were synthesized by *in situ* polymerization, then, MGNH/epoxy composite (MGNH/EP) is prepared via vacuum-assisted method. The special prepared method is expected to endow MGNH/EP with anisotropic thermal conductivity. MGNH is characterized by fourier transform infrared (FTIR), scanning electron microscopy (SEM), transmission electron

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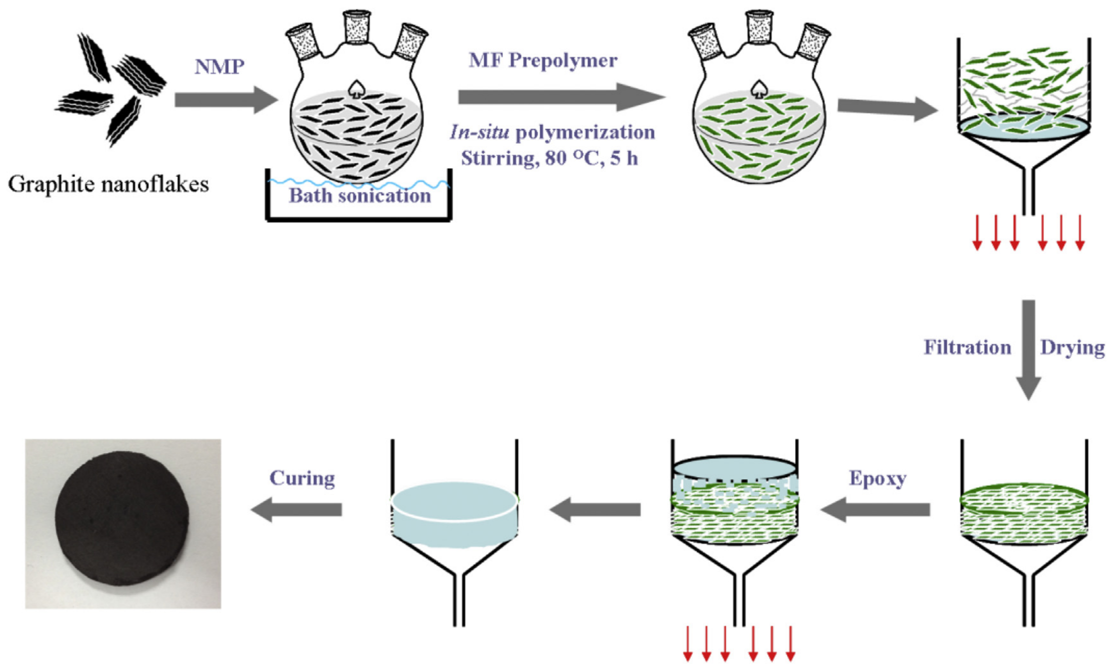

Scheme 1. Schematic diagram of the preparation of MGNH and its epoxy composite.

microscope (TEM) and X-ray diffraction (XRD). The epoxy composite is prepared via vacuum-assistance. The thermal conductivity is observed in two directions. The combustion property of the composite is evaluated using a microscale combustion calorimeter (MCC). The fire retardant mechanism is studied.

2. Experimental

2.1. Materials

The epoxy used in this work is the common bisphenol A-type epoxy resin (EP) supplied by Laboratory Text & Industrial Measurement Intrusments. The cured agent is methylhexahydrophthalic anhydride (MHHPA), which is obtained from Xiya reagent Research Center. N,N-dimethylbenzylamine was provided by Aladdin Chemistry Co., LtD. Melamine (AR) and formaldehyde (37%) was obtained from Tianjing Kemiou Chemical Reagent Co.Ltd., Graphite nanoflake (GNH) was purchased from Suzhouhengqiu Technological Co., Ltd.

2.2. Synthesis of MGNH

Preparation of melamine-formaldehyde (MF) prepolymer: Melamine (10.0 g) was mixed with 50.0 ml distilled water in a flask. Formaldehyde (17.9 ml, 37%) was dropped into the suspension. The reaction process was undergoing at 80 °C for 30 min with mechanical stirring after the PH was adjusted to 8–9 with sodium carbonate solution. The resultant product was MF prepolymer.

Preparation of MGNH via *in-situ* polymerization: GR was dispersed in N-methyl-2-pyrrolidone (NMP) by sonication for 30 min. After that, half of the prepared MF prepolymer was poured into the flask. The mixture was stirred at 80 °C for 5 h. Subsequently, the resultant suspension of the product was obtained.

2.3. Preparation of EP composite (MGNH/EP) via vacuum assistance

The MGNH resultant suspension was filtered and dried. The EP and the harder MHHPA was mixed at a certain stoichiometric ratio, following the removal of the bubbles. After that, the mixture was added into the funnel which contains the dried MGNH. The EP compound was vacuumed until the resin can sustainable flow out from funnel. Thus, the flowed EP can fill the space in the MGNH layers. Finally, the composite was cured at 100 °C for 2.5 h, 150 °C for 3 h. The prepared diagram was shown in Scheme 1.

2.4. Characterization

Fourier transform infrared spectra (FTIR) were carried out using bruker TENSOR 27 FTIR spectrophotometer Scanning electron microscopy (SEM) was performed on Hitachi S3400N scanning electron microscope. Energy Dispersive Spectroscopy (EDS) result of sample was recorded X-ray energy dispersive spectroscope (EDS, Bruker). Transmission electron microscope (TEM) was performed on a JEM-1230 transmission electron microscope. Thermogravimetric analyses (TGA) of samples was performed on a NETZSCH TG 209F3 instrument from 30 to 800 °C at a heat rate of 10 °C min^{-1}. The thermal conductivities of the composites were measured by using a laser flash system at room temperature (TA DXF-500). The microscale combustion calorimeter (MCC) tests were conducted on a MCC-2 (GOVMARK) microscale combustion calorimeter at a heating rate of 1 °C/s.

3. Results and discussion

3.1. FTIR, SEM and TEM characterization of MGNH

The MF resin was prepared and investigated by FTIR. The spectra of MF, GNH and MGNH are shown in Fig. 1. The typical bands of MF are located at 3350, 1635, 1513, 1330, 1191 and 1120, which can be assigned to the absorption of N–H stretch, bending vibration of N–H of primary amine, stretching vibration of C=N and the stretching vibration of symmetric C–O–C– of $-CH_2-O-CH_2-$ between melamine groups [25]. Raw GNH shows no typical absorption, while MGNH presents the same characteristic absorption