



Effect of graphene nanosheets on morphology, thermal stability and flame retardancy of epoxy resin



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ABSTRACT

Effect of graphene nanosheets (GNS) on morphology, thermal stability and flame retardancy of epoxy resin (ER) was investigated. GNS was partially exfoliated, large and flat graphene flakes exists in ER/GNS nanocomposites. GNS changed the decomposition pathway of ER at high temperature, enhanced the thermal stability and promoted the formation of char residue. The compactness of both the surface and the bottom char residues were significantly improved with the addition of GNS. Furthermore, GNS can effectively decrease melt flow and inhibit the flammable drips of ER during combustion. Incorporation of 3 wt% of GNS increased the LOI value of ER from 15.7 to 21.0 and reduced the total heat release from 33.37 to 28.20 kJ/m². The peak heat release rate presented earlier increase and later decrease trend with the increase of GNS content due to the competition between the effect of thermal conductivity and barrier property of GNS.

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1. Introduction

Epoxy resin (ER) is one of the most important thermoset polymers, owing to its outstanding mechanical stiffness and toughness, good solvent and chemical resistance, and superior adhesion. However, flammability has restricted their applications. Extensive research has been developed to improve the flame retardant performance of ER. Traditionally, ER can be endowed flame retardancy by the incorporation of halogen-containing flame retardants, which are extremely effective [1]. However, the utilization of these halogenated flame retardants will generate toxic, corrosive gases and endocrine-disrupting chemicals during combustion, which is harmful to the environments and human health.

Among the established halogen-free flame retardants, nanocomposites are competitive because they can improve the flame retardancy and the mechanical properties simultaneously [1–3]. Carbon nanotubes (CNT) have been extensively studied to improve the flame retardancy of polymers for many years. Nevertheless, its high manufacturing costs, high viscosity caused by the “bird’s nest” structure of the entangled tubes, and high anisotropic functionality limit its application [4].

Graphene, a single-atom-thick two-dimensional carbon layer, has triggered considerable interest in developing a variety of novel composites due to its high surface area, electrical conductivity, high flexibility, and mechanical strength and exhibits great promise for potential applications in the fields of nanoelectronics, sensors, batteries, super-capacitors, hydrogen storage, and nanocomposites [4–7]. Graphene nanosheets (GNS) is not a single (individual) graphene sheet but comprises multiple graphene sheets that are stacked together.

Compared to CNT, GNS is a new class of filler with exceptional functions. It is an ideal candidate to replace CNT for the following reasons: its abundance in nature, which means low cost; its extremely high specific surface area, which carries higher levels of transferring stress across interface and provides higher reinforcement than CNT; its isotropic electrical/thermal conductivities on the graphene plane; its low viscosity when compounded with polymers and its non-toxicity [4–7].

Recently, a lot of attention from researchers has been given to graphene/polymer composites. Yavari F reported the synthesis and fatigue characterization of fiberglass/epoxy composites with GNS infiltrated into ER as well as directly spray-coated onto the glass microfibers. The graphene network toughens the fiberglass/epoxy-matrix interface and prevents the delamination/buckling of the glass microfibers under compressive stress [8]. Rafiee MA compared the mechanical properties of ER nanocomposites with GNS, single-walled CNTs, and multi-walled CNTs at the same nanofiller weight fraction. The results indicate that graphene platelets

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significantly out-perform CNTs additives [9]. Guo YQ investigated the flame retardant properties of graphene, graphite oxide and functionalized graphite oxides in epoxy composites, graphene composites perform better than graphite oxide composites [10]. Zaman I synthesized two types of epoxy/GNSs nanocomposites with different interfacial strength. The interface modification enhanced the glass transition temperature of neat epoxy. Toughening mechanisms are attributed to the voiding, microcracking and breakage of GNS, while matrix may not consume as much fracture energy as functionalized GNS do [4]. Kim KS synthesized 4-aminobenzoyl-functionalized graphite (AB-graphite). The physical properties of the resulting ER/AB-graphite composites were improved because of the efficient load transfer between the additive and epoxy matrix through covalent links [11].

So far the research works on ER/GNS composites largely focused on the mechanical properties and thermal conductivity [8,9,12–16], the flame retardant property has not been studied systematically. The interaction between GNS and ER matrix and the morphology of ER/GNS is not clear. The mechanism of ER/GNS during combustion is still unknown. This paper aims to evaluate the influence of GNS on the morphology, thermal stability and flame retardancy of ER/GNS composites.

2. Experimental

2.1. Materials

Epoxy resin (JY-256, density 1.13–1.15 g/cm³, epoxy value 0.54–0.56 mol/100 g) was obtained from Jiafa Chemical Co., Ltd., Changshu, China. Poly(propylene glycol)bis(2-aminopropyl) ether (Jeffamine D230, Huntsman Co., Houston Texas, America.) were used as curing agents. Graphene nanosheets (JCGNP-1) with an average density of 2.25 g/cm³ and a purity of >99.5% was obtained from Jcnano Technology Co., Ltd., Nanjing, China. The area ratio of D band to G band (I_D/I_G) of the Raman spectrum is only 0.36, indicating that GNS is of high quality with relatively few defects. Before compounding, the GNS was ultrasonicated in ice bath for 1.5 h so as to ease its dispersion in the matrix.

2.2. Preparation of ER/GNS composites

GNS was dispersed in acetone (100 mL of acetone to 0.01 g of GNS) with ice bath ultrasonic treatment and stirred for 1.5 h. Then the epoxy monomer was added to the mixture and sonicated for another 1.5 h. To remove the acetone, the solution was put into 70 °C oil bath and stirred for 5 h, then transferred to a vacuum chamber at 70 °C for 1 h to remove the residual acetone. Subsequently, the mixture was cooled to 25 °C then curing agent was added with stirring for 0.5 h. The mixture was degassed for 1 h, then carefully poured into silicone rubber moulds with injector, precured at 50 °C for 5 h, and postcured at 110 °C for 2 h to obtain the ER/GNS samples. The pure ER was prepared by the same procedure for comparison.

2.3. Characterization

Raman measurements were carried out using a HR800 Micro-Raman Spectrometer (Horiba Jobin Yvon, France) at 457.9 nm laser in an ambient atmosphere at room temperature. X-ray diffraction (XRD) test was conducted by using a Rigaku X-ray generator (Cu K α radiation) in the reflection mode at room temperature. A Hitachi S-4800 (Hitachi, Japan) scanning electron microscope (SEM) was used to observe the micro-morphology of composites. The samples were coated with a gold layer about 10 nm to improve the conductivity of the surface. Transmission electron micrograph

(TEM) images were obtained on a JEM-1200EX electron microscope (JEM, Japan) with an accelerating voltage of 120 kV. Thermogravimetric analysis/infrared spectrometry (TG-IR) was carried out using a TGA 209 F1 thermal analyzer (Netzsch, Germany) interfaced to a Thermo Nicolet iS10 FTIR spectrophotometer (Nicolet, USA). Samples were heated to 700 °C at a heating rate of 20 °C/min. Limiting oxygen index (LOI) was measured by HC-2 Oxygen Index Instrument (Jiangning Analyser Instrument, China). Micro combustion calorimetry (MCC) was performed on a Govmark MCC-2 Microscale Combustion Calorimeter. Samples were heated to 700 °C at a heating rate of 1 °C/s. Each test was repeated three times.

3. Results and discussion

3.1. Structure and morphology

XRD patterns of GNS and the ER/GNS composites are shown in Fig. 1. The sharp diffraction peak of 2 θ at 26.5° in GNS features an interlayer spacing of 0.34 nm. In ER/GNS composites, the diffraction peak of GNS does not shift at all regardless of the amount of GNS addition. This implies that the restacking and agglomeration of the GNS still exists in ER/GNS composites. The peak intensity at 26.5° of ER/GNS composites increased with the increase of GNS content.

To determine the dispersion of GNS, TEM analysis was carried out in Fig. 2. Under low magnification, some small clusters of GNS are observed. The clusters are found consisting of a lot of GNS which contain a few partly exfoliated graphene layers, some large and flat graphene flakes can be seen under high magnification. This indicates that ER/GNS composites are nanocomposites.

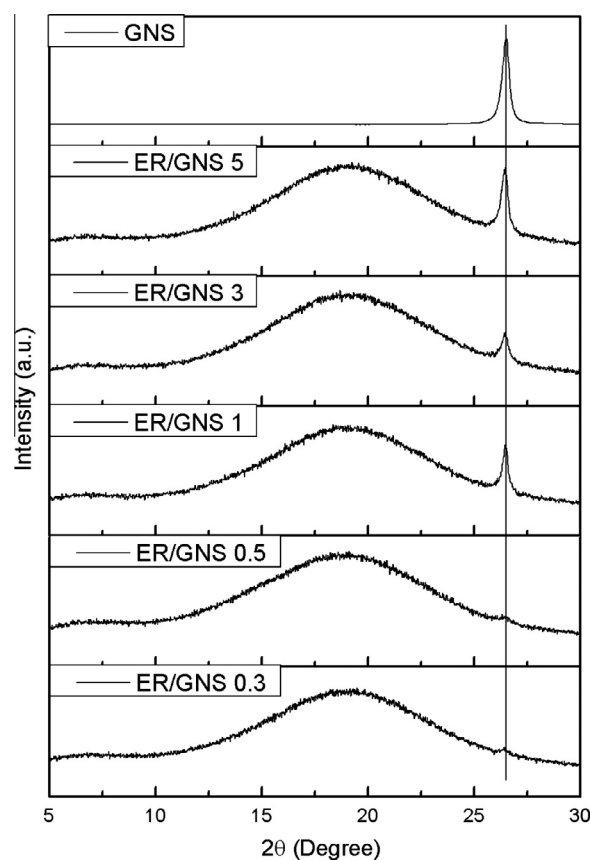


Fig. 1. XRD patterns of GNS and ER/GNS composites.

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