Enhanced flame-retardant property of epoxy composites filled with solvent-free and liquid-like graphene organic hybrid material decorated by zinc hydroxystannate boxes

Peipei Li [a], Yaping Zheng [a,*], Mengzhi Li [a], Wendi Fan [a], Ting Shi [a], Yudeng Wang [a], Aibo Zhang [a], Junsheng Wang [b]

[a] *School of Natural and Applied Science, Northwestern Polytechnical University, Xi'an 710072, PR China*
[b] *Tianjin Fire Research Institute of the Ministry of Public Security, Tianjin 300383, PR China*

A B S T R A C T

A polyether amine (M2070) was covalently grafted onto the surface of graphene nanosheets (GNS) decorated by zinc hydroxystannate boxes (ZHS) to obtain an organic hybrid material (GNS-ZHS-M2070) with solvent-free and liquid-like behavior. It was subsequently incorporated into epoxy resin (EP) to investigate the flame-retardant property. The GNS-ZHS-M2070, which was a homogeneous sticky fluid at room temperature without any solvent, could stably disperse in a broad spectrum of solvents. Most importantly, the GNS-ZHS-M2070/EP composites possessed superior flame-retardant performance, such as the lowest peak heat release rate and fire growth rate index values. Furthermore, it had been demonstrated that the superior flame-retardant performance of GNS-ZHS-M2070/EP should be ascribed to the excellent processability and good compatibility of GNS-ZHS-M2070 derived from the unique flowability and soft organic shell. All of these advantages along with the solvent-free nature of GNS-ZHS-M2070 provided a green, efficient and environment-friendly way to fabricate high flame-retardant performance composite materials.

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1. Introduction

Epoxy resin (EP) is one of the most widely used thermosetting materials in the fields of adhesive, coating, electronic/electrical insulation and composites, owing to its high thermal stability, good mechanical performance, simple processability and excellent chemical property [1–5]. However, it is a pity that the high flammability and large yield of smoke during combustion greatly limit its further applications [6]. Thus it is necessary to improve the fire-retardant performance in practical applications. Generally, the incorporation of flame-retardant nanofillers such as layered silicates [7], layered double hydroxides [8], multiwalled carbon nanotubes (MWCNTs) [9] and graphene [10], can efficiently improve the fire resistance of EP. However, there are two critical problems emerging in the conventional particle-filled polymer materials, where the nanofillers play a role in the enhancement of the fire resistance of epoxy resins. The first one is that the flame-retardant nanofillers are easy to agglomerate and hard to disperse uniformly in the polymer matrix, which makes them difficult to process and even deteriorate the flame-retardant performance of their composites [11]. The other one is that the solution processing technique usually need expensive organic solvents and complex post-treatment, which easily induces defects and also hampers the performance of composites [12]. Therefore, developing a green, efficient and environment-friendly approach to achieve the homogeneous dispersion of flame-retardant nanofillers in EP without sacrificing their processability and flame-retardant property is of great value in polymer science.

Recently, researchers had focused on the surface modification of additive-type fire retardants to improve their compatibility with polymer matrix, such as PPA-g-GNS, which was generally solid-like without any solvent and didn't undergo a microscopic solid-to-liquid transition below 150 °C [10]. Furthermore, the possessing technique was still the solution processing method, which could cause serious pollution to the environment. Fortunately, the solvent-free liquid-like nanofluids, which comprise an inorganic core and an organic outer organic shell, can efficiently solve those problems. This approach can not only make the flame-retardant nanofillers disperse well in polymer matrix, but also enhance the processability of composites. Although many works had been

reported in the field of liquid-like graphene nanofluids, those materials were nanoscale ionic materials [13–15]. To the best our knowledge, there is not yet literature so far that reports the solvent-free and liquid-like graphene organic hybrid material through a covalent bond. Moreover, the solvent-free and liquid-like organic hybrid material had been reported that it had a potential application in carbon dioxide uptake [13,16,17] and could be used as a kind of plasticizers with the effect of toughening and reinforcement of its composites at the same time [2,11]. But the effect of the solvent-free and liquid-like organic hybrid material on the flame-retardant property is still not investigated in the open literature.

It is well known that the combination of two or more components often presents a synergistic effect and offers an excellent flame resistance to polymer. For example, MWCNTs and Ni_2O_3 [18], graphene and ZnS [19], graphene and SnO_2 [6], etc. Thus the zinc hydroxystannate (ZHS) and graphene are chosen to synthesis the graphene organic hybrid material (GNS-ZHS-M2070) with solvent-free and liquid-like behavior to investigate its influence on flame-retardant property of its resulting epoxy composites.

Herein, the GNS-ZHS-M2070 was first synthesized through a covalent bond and subsequently incorporated into epoxy matrix to enhance the flame-retardant property of its epoxy composites. It had been demonstrated that the enhanced flame-retardant property should be ascribed to the excellent processability and good compatibility of GNS-ZHS-M2070 derived from unique flowability and the soft organic shell. Last but not least, a complementary analysis on the possible flame-retardant mechanism of this epoxy composites was also investigated and discussed in this paper.

2. Experimental section

2.1. Materials

Graphite powder (<20 μm) was purchased from Xiamen Knano-Tech Port Co. Ltd. Zinc sulfate heptahydrate ($ZnSO_4·7H_2O$) and sodium stannate trihydrate ($Na_2SnO_3·3H_2O$) were from Aladdin. γ-(2,3-epoxyproxy) propytrimethoxysilane (KH560, AR, 98%) was from Chengdu Ai Keda Chemical Technology Co. Ltd. JEFFAMINE polyether amine (M2070, 98%) was bought from Suzhou Long Branch Industrial Co. Ltd. Methyl tetrahydrophthalic anhydride (METHPA) was from Guang Zhou Weibo Chemistry Co. Ltd. 2,4, 6-tri(dimethylaminomethyl) phenol (DMP-30) was bought from Aladdin Chemistry Co. Ltd. Epoxy resin (CYD-128) was purchased from Yueyang Petrochemical Co. Ltd. The other chemicals and reagents were used as received without further purification. Deionized water was generated with a Milli-Qintegral pure and ultrapure water purification system.

2.2. Synthetic procedures

To obtain the GNS-ZHS-M2070/EP composites, the detailed synthetic procedures are illustrated in Fig. 1, where the synthetic pathway of graphene nanosheets decorated by ZHS (GNS-ZHS), GNS-ZHS-M2070 and the final epoxy composites (GNS-ZHS-M2070/EP) are clearly shown.

2.2.1. Preparation of the GNS-ZHS

Briefly, GO was synthesized by oxidizing natural graphite powder according to the modified Hummers method [20]. Then it was exfoliated in water to form a GO suspension (1 mg mL^{-1}). Subsequently, 10 mmol $ZnSO_4·7H_2O$ was added into the brown GO suspension, and the solution was stirred at room temperature

until $ZnSO_4·7H_2O$ was dissolved completely. After that, an appropriate $Na_2SnO_3·3H_2O$ was added into solution, making the molar ratio of [Zn]/[Sn] = 1:1. After completing the above steps, the mixed solution was under continuous magnetic stirring for 5 h. Then the black precipitates were collected by centrifugation, washed with deionized water for several times to remove residual ions in the product and dried under reduced pressure.

2.2.2. Synthesis of the GNS-ZHS-M2070

Typically, 3 wt% M2070 in ethanol was prepared and a molar equivalence of KH560 was added. Then the polyether-silane solution was stirred at 45 °C for 12 h to ensure react completely. Subsequently, the GNS-ZHS hybrid suspension prepared in ethanol and water, was added dropwise into polyether-silane solution and the resulting mixture was stirred for 5 h and dialyzed (MWCO 3.5 k) for 24 h to remove excess polyether-silane. Finally, the GNS-ZHS-M2070 was obtained by removing water under vacuum at 35 °C [2].

2.2.3. Preparation of GNS-ZHS-M2070/EP composites

In general, the preparation of GNS-ZHS-M2070/EP composites could be illustrated below: 2.2 g GNS-ZHS-M2070 was dispersed in 60 g CYD-128 and 48 g METHPA. Next, the resulting mixture was sonicated for 45 min at 60 °C to obtain a black suspension. Next 0.6 g DMP-30 was added in the black suspension and stirred for 5 min. The mixture was heated in a vacuum oven at 60 °C to remove any residual bubble. Then the sample was cured at 90 °C for 90 min, followed by 100 °C for 30 min, 110 °C for 30 min, 120 °C for 30 min and 140 °C for 90 min [2]. For comparison, GNS-ZHS-M2070/EP and GNS-ZHS/EP with other contents were also prepared using similar processing procedures.

2.3. Characterization

X-ray diffraction (XRD) analysis was carried out on a Scintag D/MAX-3C using Cu Kα radiation (λ = 1.54056 Å). Transmission electron microscope (TEM) images were obtained with an FEI Tecnai G2 F20 microscope. The structure of the sample was investigated by Fourier transform-infrared (FTIR) spectrometer analysis (WQF-310, Beijing Second Optical Instruments Factory) with KBr pellets. Rheological measurements were tested at 35 °C on an AR G2 using a cone and plate geometry with a 40 mm diameter plate and 2° cone angle. Thermo gravimetric analysis (TGA) measurements were taken with heating rate of 10 °C min^{-1} in air by using TGA Q50 TA instrument. Glass transition temperatures (T_g) were obtained by using differential scanning calorimetry (DSC) with heating rate of 10 °C min^{-1} in N_2 atmosphere.

Limited oxygen index (LOI) tests were performed according to ASTM D2863-2012. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions $130 * 6.5 * 3.5$ mm^3. Vertical (UL 94V) burning tests were also conducted to investigate the flammability property of composites on the test bars ($130 * 12.7 * 3.5$ mm^3) according to ASTM D3801. The flammability of the sample was also characterized by a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. Each specimen with the dimensions of $100 * 100 * 3.5$ mm^3 was exposed to 35 kW m^{-2} heat flux. Scanning electron microscope (SEM) pictures were observed with an FEI Nova Nano SEM 230. The sample was previously coated with a conductive layer of gold.