



Synergistic flame retardancy effect of graphene nanosheets and traditional retardants on epoxy resin



Shan Liu ^{a,b,c}, Zhengping Fang ^{a,c}, Hongqiang Yan ^a, Venkata S. Chevali ^b, Hao Wang ^{b,*}

^aLaboratory of Polymer Materials and Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China

^bCentre for Future Materials, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

^cKey Laboratory of Macromolecular Synthesis and Functionalization, Institute of Polymer Composites, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

Novel non-toxic halogen-free flame retardants are replacing traditional flame retardants in polymer and polymer matrix composite structures. In this study, graphene nanosheet (GNS) is investigated in combination with traditional layered double hydroxide (LDH), layered rare-earth hydroxide (LRH), and phosphorus-based flame retardant (DOPO) to enhance the flame retardancy of epoxy resin. A synergistic flame retardancy effect is achieved in GNS/LDH and GNS/DOPO systems where combined GNS and LDH increased the viscosity of the epoxy melt, and limited the flame propagation through inhibition of dripping. The limiting oxygen index of epoxy increased from 15.9 to 23.6 with addition of 0.5 wt.% each of GNS and LDH. With the addition of 2.5 wt.% of both GNS and LDH, the total heat release of epoxy resin also reduced from 33.4 MJ/m² to 24.6 MJ/m². The synergistic effect of GNS and DOPO adopted a different mechanism. The addition of 2.5 wt.% of GNS and DOPO reduced the peak heat release rate from 1194 kW/m² to 396 kW/m², and the total heat release rate from 72.5 MJ/m² to 48.1 MJ/m². The synergistic mechanisms of the flame retardants were closely analyzed and correlated with the flame retardant properties.

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1. Introduction

Flame retardancy of epoxy resin (ER) [1] is critical for commercial utilization in aerospace and defense, automotive, electrical industry in addition to mechanical stiffness and toughness, solvent and chemical resistance, and adhesion. Flame resistance and retardancy albeit remain major selection and screening criteria for epoxy resins [2,3]. Today, halogen-based flame retardants are most prevalent for use in industrial applications of ER, however, they release corrosive and toxic chemicals during combustion [1]. Therefore, the development of halogen-free flame retardants has attracted increasing attention for addressing environmental and health concerns. Two common halogen-free flame retardants for epoxy resins are layered double hydroxides (LDH) and phosphorus-based 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). However, they are unsatisfactory because they require levels of loading and show low efficiency in flame retardancy, necessitating the need to find new strategies to overcome this challenge [1–4].

LDH is a class of 2 dimensional nano-structured anionic clays, whose structure is based on brucite (Mg(OH)₂)-like layers. Today, LDH can be easily synthesized on a large scale in the industry [5,6]. LDH contributes to the flame retardancy of the polymeric matrix through producing a refractory oxide residue on the surface of the material, and releasing aqueous vapor and carbon dioxide during polymer decomposition. The endothermic nature of these processes and the dilution of combustible gases of pyrolysis delay the ignition time, and hence reduce the heat release during polymer combustion. However, high levels of LDH loading are required to achieve this flame retardancy effect [5–8].

Layered rare-earth hydroxides (LRH) are composed of alternating positively-charged hydroxo-cation layers and charge-compensating anion layers [9–11]. The basic structure of LRH is similar to LDH, leading to a similar performance and hence emerging as a promising class of flame retardants. Furthermore, LRH are typical anion-exchangeable lamellar compounds possessing a general formula RE₂(OH)₅X·nH₂O, where RE = rare-earths and X = interlayer organic or inorganic anions [12–16]. A large capacity and high affinity for ion-exchange reactions with a wide range of organic anions in their interlayer space makes LRH a class of layered solids used as a host for active molecules [12,13]. With distinctive electronic, optical, magnetic, and catalytic properties of

* Corresponding author.

E-mail address: hao.wang@usq.edu.au (H. Wang).

the rare-earth elements, LRHs not only exhibit anion exchange properties, but also bear a catalytic property and chemical intercalation capability [14,15]. LRHs are extensively used for thermoplastic polymers; however, the effect of these class of flame retardants for thermosetting resins such as ER is relatively unknown.

DOPO is a class of phosphorus-based intumescent flame retardants that possess exceptional thermal stability, oxidation resistance, and water resistance characteristics [17–24]. However, DOPOs with high phosphorus content can decrease the cross-link density of the resin, causing decrease in the mechanical properties upon curing, and reducing the effectiveness of fire retardancy because of elutriation [22,25–27]. DOPO is known as an effective flame retardant, however, if a combination of DOPO with other flame retardants will result in enhanced flame retardancy is unknown.

Nano-sized fillers and additives have drawn great interest due to their potential to improve the flame retardancy of resins at low weight fractions (<5 wt.%) [1–4,28–30]. Graphene nanosheet (GNS) is emerging as an outstanding nano-sized filler exhibiting enhanced mechanical and chemical properties in many resins. GNS can also be utilized as a flame retardant because of its unique thermal stability and large surface area.

The standalone flame retardancy of traditional flame retardants (such as LDH and DOPO) on ERs exhibit a lack of overall effectiveness. To the knowledge of the authors, the flame retardancy effect of GNS in ER and ER-based composites is not studied systematically. Moreover, the combined effect of GNS and traditional flame retardants is rarely investigated, particularly if a synergistic effect during combustion exists between the GNS and traditional flame retardants. The main objective and aim of this study is provide a comparison of GNS, LDH, LRH, and DOPO as flame retardant vis-à-vis their flame retardancy effects and mechanisms. An additional objective of this study is to investigate the effectiveness of LRHs, which are used for thermoplastics, as flame retardants in thermosetting ER. The (a) individual flame retardancy effect of GNS, LDH, and DOPO on ER and (b) the combined effect of GNS and LDH, and of GNS and DOPO on ER are systematically investigated. The underlying flame retardant mechanisms were analyzed and discussed.

2. Experimental

2.1. Materials

Epoxy resin (JY-256, 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 TX, USA) was used as the curing agent. GNS (JCGNP-1, density = 2.25 g/cm³, >99.5% purity) was obtained from Jcnano Technology Ltd., China. Al(NO₃)₃·9H₂O and Mg(NO₃)₂·6H₂O (analytical pure) was supplied by Sinopharm Group, China. Yb(NO₃)₃·5H₂O and Gd(NO₃)₃·6H₂O were obtained from Aladdin Reagent Co., Ltd., Shanghai, China. KOH (analytical grade) were obtained from Shanghai Chemical Reagents Co. Ltd., China. DOPO (>99% purity) was supplied by Qingdao Lianmei Chemical Co. Ltd., China.

2.2. Preparation of LDH, LRH, ER, and ER composites

The LDH was prepared by a conventional co-precipitation method as described by Liu et al. [5]. Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O solutions were slowly added into decarbonated water to keep pH = 10.0. The prepared solution was heated to 100 °C under stirring for 12 h, then kept at 95 °C for another 12 h. After filtering, washing and freeze-drying, the final products were Mg/Al-LDH.

The LRH was synthesized using a hydrothermal reaction. An appropriate amount of KOH solution was added to Gd(NO₃)₃·6H₂O solution until a pH of 7.0 was reached. A careful adjustment around pH ≈ 6.7–7.2 was required for the formation of the layered hydroxide structure, since reactions at a higher pH range produced a considerable amount of RE(OH)₃ as impurity and a low percentage yield of product was recovered at a pH lower than 6.7. The resultant colloidal suspension from the hydrothermal reaction was transferred into a Teflon lined stainless-steel autoclave after being constantly stirred for 30 min. The autoclave was sealed and put in an electric oven preheated to 130 °C. After 24 h, the autoclave was left to cool naturally to room temperature, and the hydrothermal product was collected by filtration, washed with distilled water, and dried at 60 °C for 24 h. Yb₂(OH)₅NO₃·nH₂O and (Gd_{1-x}Y_bX)₂(OH)₅NO₃·nH₂O ($x = 0-1$) were synthesized using a process similar to that used to produce Gd₂(OH)₅NO₃·nH₂O. These three LRHs, (1) Gd₂(OH)₅NO₃·nH₂O, (2) Yb₂(OH)₅NO₃·nH₂O and (3) (Gd_{1-x}Y_bX)₂(OH)₅NO₃·nH₂O ($x = 0-1$) were designated as R1, R2, and R3 respectively for brevity.

ER composites were produced by solution blending method. An appropriate content of GNS and LDH (or DOPO) was dispersed in acetone and dimethyl formamide (DMF) respectively with ice bath, ultrasonicated, and stirred for 1.5 h. After the epoxy monomer was added, this solution was ultrasonicated for an additional 1.5 h. Acetone and DMF were removed by placing the solution into an oil bath at 70 °C and 160 °C respectively, then transferred to a vacuum chamber at 70 °C or 160 °C for 1 h to remove the residual acetone or DMF. The mixture was cooled to room temperature, and the curing agent was added with simultaneous stirring for 30 min. The mixture was placed in a vacuum chamber to degas for 1 h, and then carefully poured into silicone rubber molds using an injector, pre-cured at 50 °C for 5 h, and post-cured at 110 °C for 2 h to obtain ER composites. The obtained samples were designated as ER/GNS x /LDH (or DOPO) y (mass ratio of ER/GNS/LDH (or DOPO) = 100/ x/y). The weight ratio of LDH (R1, R2, R3) in ER/R1, ER/R2, ER/R3 was fixed as 100:1.

ER was prepared by the same procedure as ER/GNS, as a control. The epoxy monomer was added in acetone with stirring, the solution was placed into an oil bath at 70 °C for about 5 h, transferred to a vacuum chamber at 70 °C for 1 h to remove the residual acetone. The mixture was cooled to room temperature, and then curing agent was added with stirring for 30 min. A curing process identical to ER composite processing was used for the ER as well.

2.3. Characterization

X-ray diffraction (XRD) was conducted using a Rigaku X-ray generator (Cu K_α radiation) in the reflection mode at room temperature to determine the interlayer spacing of GNS, LDH, LRH, and their composites. A Hitachi S-4800 (Hitachi, Japan) scanning electron microscope (SEM) was used to observe the micro-scale morphology of composites. The samples were coated with a gold layer about 10 nm to improve the conductivity of the surface. Transmission electron microscopy (TEM) images were obtained to observe the microstructure of LRH on a JEM-1200EX electron microscope (JEM, Japan) with an accelerating voltage of 120 kV. Thermo-gravimetric analysis (TG) was carried out using a TGA 209 F1 thermal analyzer (NETZSCH, Germany) to determine the thermal properties of ER composites. Samples were heated to 700 °C at a heating rate of 20 °C/min, and each specimen was examined in triplicate. The accuracy for the temperature and mass measurements were ±1 °C and ±0.1 wt.%. Limiting oxygen index (LOI) was measured by HC-2 Oxygen Index instrument (Jiangning Analyser Instrument, China) according to the international standard ISO 4589 [31]. Micro combustion calorimetry (MCC) was performed on a Govmark MCC-2 Microscale Combustion Calorimeter.

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