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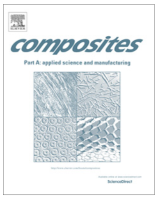

Improving thermal and flame retardant properties of epoxy resin by functionalized graphene containing phosphorous, nitrogen and silicon elements

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A B S T R A C T

As alternative flame-retardant additive for polymers, reduced graphene oxide (RGO) is often limited by its poor interfacial compatibility with matrix. In this work, a new flame retardant, containing phosphorous, nitrogen and silicon elements was used to functionalize RGO. The wrapped flame retardant chains induced the improvement in the dispersion and compatibility of RGO in epoxy (EP) matrix. As a result, the mechanical, thermal and flame retardant properties of EP-based composites were significantly improved by adding flame retardant-functionalized RGO. The peak heat release rate, total heat release and total smoke production reduced by 34%, 14% and 30%, respectively, compared to neat resin. Based the char analyses, the enhancement in flame retardancy is attributed to the outstanding char layers with high strength and thermal stability resulting from the template effect of graphene, the charring effect of phosphorus and nitrogen elements and the enhancing effect of silicon element in grafted flame retardant chains.

1. Introduction

The inherent flammability of polymers, burning rapidly and producing dense smoke and toxic gases, seriously limits the further application for safety consideration. However, the traditional halogenated flame retardants have been prohibited due to its harmful by-productions generated during combustion [1]. The substitutes, halogen-free flame retardants including the phosphorus-containing compounds and metal hydroxides, are seriously restricted because of the deterioration in mechanical and thermal properties of resulting polymers by high-loading level [2,3]. Therefore, it is highly desirable to develop the eco-friendly and chemically stable flame retardant additives.

Recently, incorporating nanoparticles in polymers seems to provide a new and effective approach for weakening its fire hazard, which can figure out the coexistence problem of low flame retardancy, mechanical and thermal properties by its low filler loading [4–7]. Enhancing physical barrier effect by the adding nanoparticles is usually believed to be the main flame retardation mechanism for nanocomposites [1,8]. As a consequent, the nanoparticles with layered structure and high aspect ratio are considered as promising flame retardant additives, such as clay [9], layered double hydroxide (LDH) [10] *etc.* However, for clay or LDH, the close stack of adjacent layers due to the strong ionic bonding, with very small interlayer space (<300 Å), limits their application as nanofiller seriously [4,11]. In comparison to clay or LDH, the two-dimensional (2D) graphene with high aspect ratio, surface area, chemical stability and mechanical and thermal properties has greater potential as flame retardant additives for polymers [12–16]. And there are many previous literatures to reveal the outstanding flame retardant efficiency of graphene for polymers, simultaneously improving the electrical, thermal, mechanical, and gas barrier properties [8,15,17,18]. In spite of the potential of graphene, its weak compatibility with polymer matrices, poor thermal-oxidative stability and low charring capacity seriously restrict severely the flame retardant efficiency, which is still a huge challenge in future [19,20].

One likely solution of functionalizing graphene with organic or inorganic flame retardant can not only improve its compatibility

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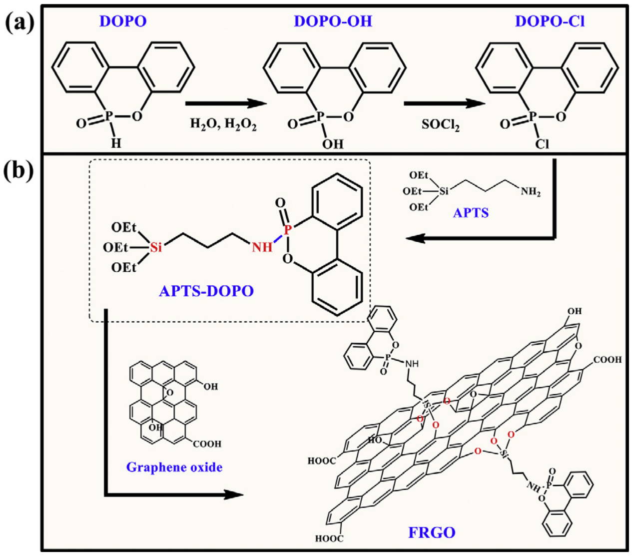
with polymer matrix, but also enhance its charring capacity for polymers, which has drawn great interests and efforts of scientists [21–24]. Among the reported functionalized graphene, phosphorus- and/or nitrogen-containing compounds seem to be an ideal modifier due to their eco-friendly characteristic and strong catalytic carbonization effect during combustion [23,25]. In this regard, Hu and his coworkers utilized a series of phosphorus- and nitrogen-containing flame retardants to modify reduced graphene oxide (RGO), the resultant functionalized RGO is capable of improve the flame retardancy, mechanical and thermal properties of epoxy (EP) [23,26,27]. However, the strength and oxidation resistance of the formed char layer by functionalized RGO with phosphorus-containing compounds are not enough to resist the further burning, which tremendously weakens RGO's physical barrier effect in real fire hazards. To figure out this question, the flame retardants containing organosilicon have been employed by several literatures, they revealed that silicon element played a significant role in the condensed phase as char reinforcer by forming strong Si—O—Si bond during combustion [26,28,29]. By an overall consideration of the above-mentioned reports, the flame-retardant functionalized RGO containing nitrogen, phosphorus and silicon elements is expected a more promising flame retardant additive for EP.



Scheme 1. Illustrations for synthesis routes of (a) DOPO-Cl and (b) FRGO. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives show more excellent thermal stability, water resistance and flame retardancy than the non-cyclized organic phosphate compounds in EP-based materials, because of their stable biphenyl or phenanthrene structure and ultra-thermally stable P—O—C bond [30,31]. In the view of the advantages of DOPO and the positive role of nitrogen, phosphorus and silicon elements for enhancing chars, we herein firstly developed a new DOPO based flame retardant, containing phosphorous, nitrogen and silicon elements, which was further used to functionalize RGO. The influence of obtained functionalized RGO on the thermal and flame retardant properties of EP was investigated and its flame retardation mechanism was proposed based on the char analyses.

2. Experimental

2.1. Materials

Natural Graphite flakes (325 mesh) were purchased from Qingdao Jinrilai Graphite Co., Ltd. (China). Diglycidyl ether of bisphenol-F epoxy (YDF-170) with an epoxide equivalent weight of 160–180 was supported by KUKDO Chemical Co., Ltd (China). 2-ethyl-4-methylimidazole (EMI-2,4) used as curing agent, 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, 97%) and 3-aminopropyltriethoxy- silane (APTS, 99%) were supplied by Aladdin Industrial Corporation (USA). Thionyl chloride ($SOCl_2$), N, N-Dimethylformamide (DMF), acetone, sulfuric acid (98%), potassium permanganate, potassium nitrate, hydrochloric acid (36%), hydrogen peroxide (H_2O_2, 30%), alcohol (95%) and hydrazine hydrate (N_2H_4, 85%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All reagents were used without further purification.

2.2. Synthesis of DOPO based flame retardant

DOPO-Cl is more reactive than DOPO used as flame retardant intermediate. Herein, DOPO-Cl was prepared based on a mild method reported by Lee et al. [32] as shown in Scheme 1a. Briefly, 0.02 mol DOPO compound was heated to 140 °C to entirely melt the DOPO to liquid form. After that, 10 mL deionized water was slowly injected into the system with the temperature at 90–110 °C and magnetic stirring for 30 min. Subsequently, excessive amount of H_2O_2 solution was slowly added into the aqueous solution over 2 h. After continuous stirring for 2 h at 90–110 °C, the system was cooled to room temperature to dissolve out white solid powder, which was 9,10-dihydro-10-hydroxy-9-oxa 10-phosphaphenanthrene 10 oxide (DOPO-OH). The obtained DOPO-OH compound and excessive amount of $SOCl_2$ were heated to 80 °C under reflux over 18 h to complete the acylating chlorination. Then unreacted $SOCl_2$ was removed by reduced pressure distillation so as to obtain a yellowish solid (DOPO-Cl), where in the distilled $SOCl_2$ can be reused. Finally, the resulted DOPO-Cl and excessive amount of APTS with DMF as solvent were heated 80 °C with vigorous stirring and argon shield for 8 h. The resultant mixture was separated by reduced pressure distillation to remove the solvent and unreacted APTS. The final colloidal product (APTS-DOPO) was dried overnight at 80 °C in a vacuum oven.

2.3. Preparation of flame retardant-functionalized graphene (FRGO)

Graphene oxide (GO) was chemically exfoliated from natural graphite using a modified Hummers' method according to our previous work [33]. FRGO was prepared by the reaction between APTS-DOPO and oxygen-containing groups in GO. Typically, the GO sheets (1 g) were dispersed into 500 mL alcohol and APTS-DOPO (2 g) was dissolved in 50 mL alcohol with the assistance of ultrasonication. The APTS-DOPO solution was then added into the GO solution with vigorous stirring at room temperature, and the resultant suspension was subsequently heated to 80 °C with refluxing and argon shield for 24 h, and followed by dropwise adding 2 mL of N_2H_4 to reduce GO for 8 h. The reactant solution was filtered through a 0.8 μm mixed cellulose membrane and washed with alcohol at least 4 times. The obtained product (FRGO) was finally lyophilized to avoid unwanted aggregation. As reference, GO solution was chemically reduced to RGO by N_2H_4.

2.4. Fabrication of EP/graphene composites

EP-based composites containing 1 or 3 wt% RGO and FRGO were fabricated by using the following procedure. Epoxy monomers (YDF-170) with a certain equivalent graphene (RGO or FRGO) were firstly dispersed in acetone and ethanol mixed solution (v/v: 50/50) by sonication 1 h. After which the solvent was removed using a