Intumescent Flame Retardants based on Graphene Oxide

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Abstract

In recent years, the use of highly heat-resistant graphene and graphene derivatives for flame retardant polymer materials to enhance the fire rating of materials has become a hot research topic. In this paper, the research on the flame retardancy of polymers by graphene, modified graphene, and graphene synergistic flame retardants is comprehensively described.

Keywords

Flame Retardant; Graphene; Modified; Synergistic Flame Retardant.

1. Introduction

The development of nanotechnology in flame retardancy of polymers is widely considered as a revolutionary research. Properly dispersed nanomaterials can contribute significantly to the properties of polymers such as thermal stability and flame retardancy[1]. Among them, graphene has attracted great attention since 2004 for its excellent thermal conductivity, electrical properties and mechanical properties. [2,4] As an important carbon material, graphene can be used as a flame retardant to improve the flame retardant properties of polymers due to its high stability, strong barrier, large surface adsorption and other properties that can effectively reduce the heat and mass transfer in the combustion process of materials. In the 21st century, many governments and institutions have issued banning orders on a variety of halogen-containing flame retardants and proposed that flame retardants should meet the requirements of environmentally friendly, non-toxic, non-leaching and halogen-free, etc. Graphene or modified graphene occupies a position in the big family of flame retardants as an environmentally friendly flame retardant, and this paper reviews the progress of graphene and modified graphene in flame retardant polymers in recent years.

2. Flame Retardant Properties of Graphene Alone

Graphene was mixed with polymers to study its flame retardant properties. The main methods for preparing graphene reported in the related literature are micromechanical splitting, epitaxial growth, chemical vapor deposition and reduction of graphene oxide. The main methods for mixing with polymers are in situ emulsification, melt blending, casting fusion dense refining, molding, etc.

Hu Jing [5] et al. prepared graphene oxide (GO) from expandable graphite by Hummers method and blended it with aqueous polyurethane (WPU) by in situ emulsification, and the dispersion stability of G0 in the matrix was good. The addition of only a trace amount of GO made the composite system much more flame retardant, which could significantly increase the amount of decomposed residual carbon of the polymer, and its maximum smoke emission factor was

reduced from 360 kW/㎡ of WPU to 200 kW/㎡, which was about 40% lower, and the smoke suppression effect was obvious.

Cai [4] et al. obtained functionalized graphene flakes (FGNS) by chemical exfoliation in hexa(4-carboxyphenoxy)phosphonitrile (HCPCP) solution added to thermoplastic polyurethane (TPU) to determine their flame retardant properties. Due to the low defects on the surface of graphene, the structure is more stable and the barrier property is stronger.

Weibin Gao [6] et al. prepared GO by redox method, and poly(methyl methacrylate) (PMMA)/GO and poly(methyl methacrylate) (PMMA)/GO samples were prepared by casting, melting and dense refining, and molding methods. The results showed that the thermal stability of the materials could be improved with the addition of only a small amount of GO.

Ma Junzhi [7] et al. prepared GO/viscose staple fiber composites using a melt blending method. It was found that the LOI of the composites was 29.1% with the addition of 2% GO, which was slightly higher than the LOI of viscose fibers. The GO/polyurethane foam composites were prepared by Zhang Jiahui et al. using a one-step process. The best flame retardant effect of 19.1% (0.9% increase) was achieved with the addition of 1% GO. The LOI increased to 19.4% when the amount of GO was increased to 2%-3%, and the flame retardant effect was not obvious.

According to the above literature, it can be seen that when a small amount of graphene or its derivatives are monodispersed in the polymer matrix, it can effectively improve the heat resistance, flame retardancy and mechanical properties of the polymer[8], but as a nanomaterial, graphene particle size is small and prone to agglomeration, strong interactions between graphite layers, graphite layers are easily stacked, and poor compatibility with the polymer cannot give full play to its excellent flame retardancy.

3. Flame Retardant Properties of Modified Graphene

At present, GO is mainly prepared by Hummer[9] method and modified Hummer[10] method. The GO prepared by this method has a large number of oxidized functional groups, and the removal of functional groups on the GO surface can be done by reduction, etc. The functionalized graphene can also be prepared by modifying the GO surface, which can enhance the flame retardant properties of graphene while reducing the surface polarity of GO and improving its compatibility with polymer materials.

Gao[11]et al. prepared modified graphene oxide (MGO) from graphene oxide, boric acid and 3-aminopropyltriethoxysilane in aqueous ethanol solution by ultrasonic stirring, and characterized its structure by Fourier transform infrared, X-ray diffraction and elemental analysis. Subsequently, MGO was incorporated into epoxy resin (EP) as a synergist together with ammonium polyphosphate (APP) to improve the mechanical properties and flame retardant properties of epoxy resin. The flame retardant properties of EP/APP/MGO nanocomposites were investigated using the limiting oxygen index (LOI) test, UL-94 test and cone calorimetry test (CCT). By adding 15% wt% of flame retardant, the LOI value of EP/APP/MGO nanocomposites reached 28.8% and the UL 94 test reached V-0 level. The experimental results show that MGO can significantly improve the flame retardant properties of EP/APP/MGO nanocomposites due to the dense structure of residual carbon. Meanwhile, MGO can also improve the mechanical properties of EP. The reaction process is shown in Fig 1.

Ye [12] et al. Surface modification of graphene oxide (GO) with 9,10-dichloro-9-oxa-10-phospha-phenanthrene-10 oxide (DOPO) and preparation of flame-retardant epoxy resin (EP) composites. The modified graphene oxide (DOPO-GO) was characterized by Fourier infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and thermal weight loss analysis (TGA). Cone calorimeter and scanning electron microscope (SEM) were used to study the flame-retardant properties, residual carbon microstructure, etc. of the EP composites. The results showed that

DOPO successfully modified the surface of GO, and the residual carbon rate of EP composites increased by 1.8% compared with that of pure EP when DOPO-GO was added at 3%, thus achieving certain flame-retardant effect. Cone calorimeter test and microstructure observation of residual carbon showed that the peak heat release rate of EP composites decreased with the increase of DOPO-GO addition, and DOPO-GO generated PO‧ which can capture the reactive radicals H‧ and OH‧ released from the polymer after combustion, and achieve the effect of interrupting the chain reaction. At the same time, after adding DOPO-GO, the carbon layer of the composite material is dense after combustion, which plays the role of delaying the combustion of epoxy matrix.
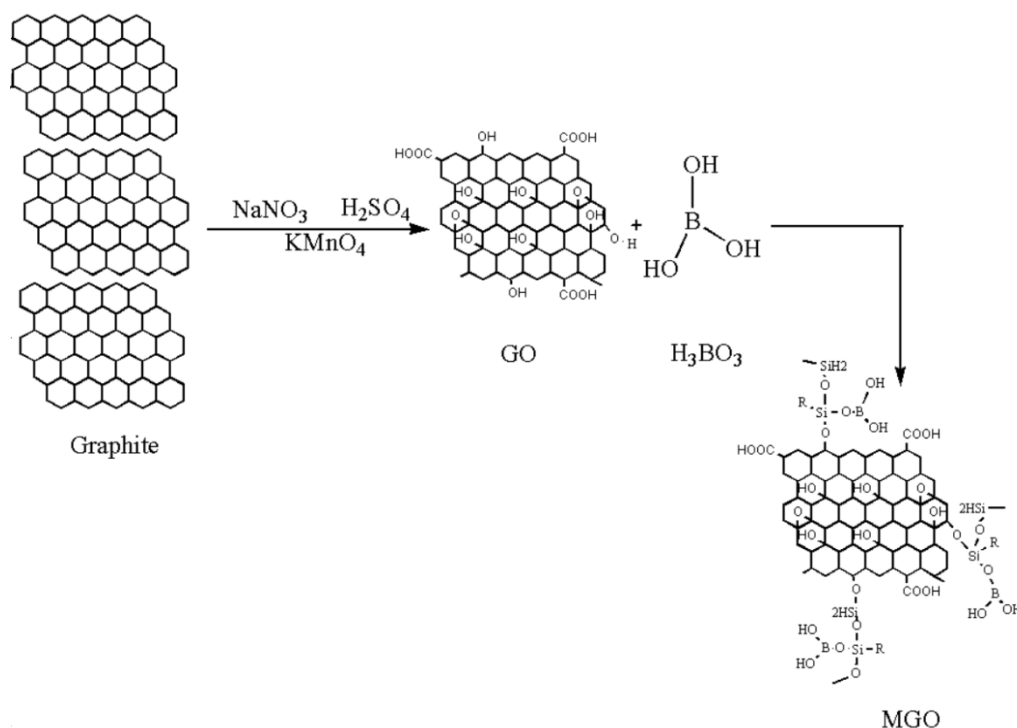

Fig 1. Schematic diagram of the route for synthesizing MGO

Graphene oxide (GO) was modified using phosphite in a study by Long[13] et al. The phosphite modifier was coated on the graphene oxide nanoflakes. The chemical structures were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction. The polypropylene (PP) composites were prepared by melt compounding method and functionalized graphene oxide (FGO) was thermally reduced in situ during the preparation. The thermal stability, mechanical properties and flame properties of the composites as well as the morphology of the carbon layer were investigated by thermogravimetric analysis, tensile, impact and scanning electron microscopy, respectively.SEM and TEM results showed that the FGO nanosheets were uniformly distributed in the polymer matrix with intercalated and exfoliated microstructure. Compared with graphene oxide and pure polypropylene, FGO/PP nanocomposites have higher thermal stability and flame retardant properties. The introduction of -P=O in the thermal decomposition process to improve the flame effect increased the yield of residual carbon. The reaction process is shown in Fig 2.
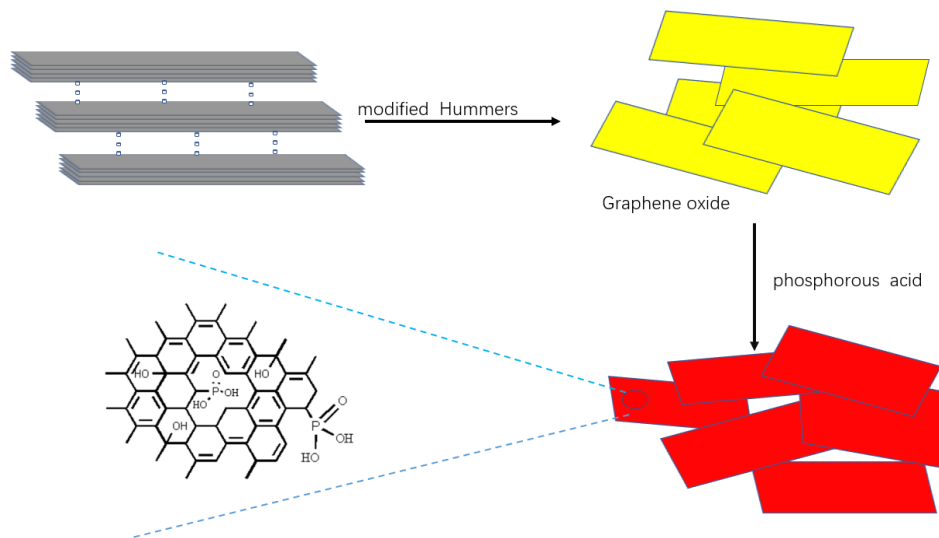
Fig 2. FGO preparation process

Jiao Yu[14] et al. covalently grafted polyetheramines onto the surface of graphene oxide via an epoxy-ammonia reaction while achieving the reduction of graphene oxide. The reduced graphene materials grafted with polyetheramines were characterized by infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, X-ray diffraction analysis (XRD), and transmission electron microscopy (TEM). The results showed that the polyetheramines not only successfully grafted onto the reduced graphene oxide surface, but also reduced the graphene oxide to some extent. Further, the polyetheramine grafted reduced graphene oxide was added to epoxy resin to prepare functionalized graphene/epoxy resin nanocomplexes. Thermogravimetric analysis (TGA) and limiting oxygen index (LOI) tests showed that when polyetheramine grafted reduced graphene was added at 10 wt%, the residual carbon rate (700°C) and LOI of the complexes were increased by 137% and 30%, respectively, indicating that polyetheramine grafted reduced graphene significantly improved the flame retardant properties of the epoxy resin, which is an excellent flame retardant with potential application value. The reaction process is shown in Fig 3.
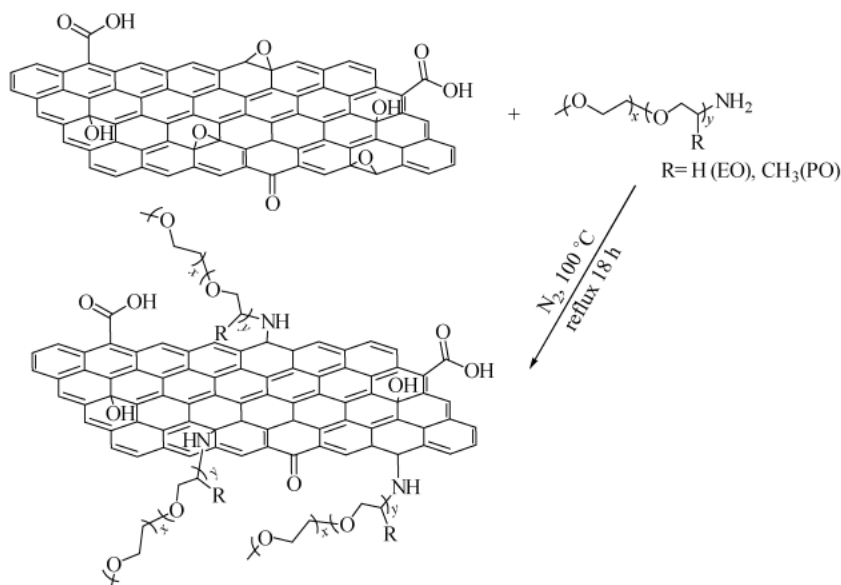

Fig 3. Schematic diagram of the synthesis route of functionalized and reduced graphene oxide

Jing[15] et al. prepared high-performance flame retardant poly(lactic acid) (PLA) composites using bio-based polyphosphonate (BPPT) and polyethyleneimine modified graphene oxide (M-GO) as flame retardants with a total of only 3%. When the BPPT content in the polymer matrix was 2.4 wt% and the M-GO content was 0.6 wt%, the prepared PLA composites could achieve UL-94 V-0 class with an LOI value of 36.0. The analysis of residual coke and pyrolysis products showed that the combined mechanism of gas phase and condensation contributed to the good flame retardant properties. In addition, the tensile toughness of PLA was improved. The PLA composites containing 2.1% wt% BPPT and 0.9% wt% M-GO had an elongation at break of 13.1% and a tensile strength of 39.1 MPa.

Qiang Ma[16] et al. prepared amphiphilic random polymers P(GMA-co-NVC) by free radical polymerization using glycidyl methacrylate (GMA) and N-vinylcarbazole (NVC) as copolymer monomers, which were used for the non-covalent modification of graphene. Epoxy resin composites with different contents of P(GMA-co-NVC)/RGO were prepared using P(GMA-co-NVC)-modified graphene (P(GMA-co-NVC)/RGO) as fillers, and the effects of the addition of polymer-modified graphene on the mechanical properties, electrical properties, thermal stability and glass transition temperature of the epoxy resin were investigated. The results showed that P(GMA-co-NVC) adsorbed on the graphene surface through the π-π interaction between the carbazole group and graphene, which effectively prevented the agglomeration of graphene and improved its dispersion in the epoxy resin. In addition, the epoxy group on P(GMA-co-NVC) has good compatibility with the epoxy resin matrix and can also participate in the curing reaction of the epoxy resin to enhance the interfacial force between them, so that P(GMA-co-NVC) is like a bridge, relying on the force formed at both ends to firmly connect graphene and the resin matrix together, making it an organic whole and significantly improving the The mechanical properties of the epoxy resin are significantly improved. When the addition amount of modified graphene reaches 0.35%, the composite material has the best overall performance, and the tensile strength and elongation at break are 41% and 82% higher than those of pure epoxy resin, respectively. At the same time, the thermal conductivity of the composites was also improved substantially.

Wang[17] et al. prepared a novel flame retardant by grafting synthetic polyphosphoramidite (PPA) onto the surface of graphene nanosheets (GNSs) and combined it with an epoxy resin matrix to improve the flame retardant properties. The chemical structures and morphologies of the precursors and target products were determined by NMR hydrogen spectroscopy, Fourier transform infrared spectroscopy and atomic force microscopy. The tensile results showed that the mechanical strength and modulus of the composites were higher than those of pure EP and PPA/EP due to the excellent reinforcement of graphene. the reaction process is shown in Fig 4.

Fig 4. Preparation process of PPA-g-GNS

Therefore, the modified graphene has a more abundant flame retardant element and thus its flame retardant property is improved, and the expected flame retardant effect can be achieved by adding a smaller amount of modified graphene. The newly grafted flame retardant elements can further strengthen the carbon layer of graphene, which can improve the oxidation resistance of the carbon layer. Moreover, the modified graphene generally has better solubility in solvents, which is more favorable for the preparation of polymer/modified graphene composites.

4. Add Flame Retardant Synergistic Flame Retardant

Yuan et al [18] blended three substances, ammonium polyphosphate (APP), macromolecular triazine derivatives (CFA) and rGO, with PP. It was found that when rGO was blended with intumescent flame retardant system, 2% rGO was added to PP / APP / CFA to obtain PI-20 material, and the UL94 grade increased from V-0 to V-2, and the better char formation of APP and CFA made PH0.5 and PH-1.0 contain higher residual char rate after combustion compared with PI-2.0, and have good smoke suppression.

Zhang[19] et al. synthesized composites of graphene oxide (GO) and kaolinite nanotubes (HNT) and prepared a series of cyanate (CE) resin composites. The effects of GHNT on the heat resistance, flame retardancy and smoke suppression properties of the composites were investigated. The composites containing 5.0 wt % GHNT/CE not only had 15.18 °C higher initial degradation temperature, but also had 54.6% or 37.9% lower peak exothermic rate or maximum smoke density than the CE resins. These results clearly indicate that GHNT is not a simple combination of graphene oxide and HNT; rather, it shows a significant positive synergistic effect in simultaneously improving the flame retardancy and heat resistance of CE resins. The improvement of its flame retardancy can be attributed to the cohesive phase mechanism, including the enhancement of coke yield, formation of dense coke layer and scavenging of free radicals. The reaction process is shown in Fig 5.
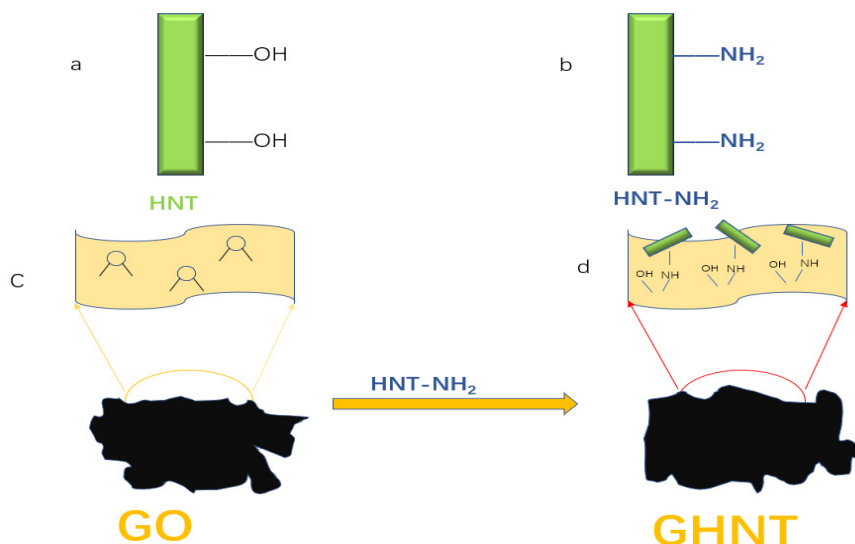

Fig 5. The process of making GHNT

Meng Xiangfei et al [20] co-operated APP, pentaerythritol and nano-graphite flakes to flame retard PS. The results showed that the LO1 of the composite could reach 36% when the amount of intumescent flame retardant (IFR) composed of pentaerythritol and APP was 245% and the amount of nano-graphite flakes was 0.5%. If only IFR is added, the LOI of the composite can reach 36% only when its dosage is 30%. It fully indicates that IFR and graphene have good synergistic flame retardant effect.

A halogen-free intumescent flame retardant ethylene vinyl acetate copolymer (EVA/IFR) system containing organic montmorillonite (OMMT) and graphene nanosheets (GNSs) with a well-dispersed structure and enhanced thermal oxidation resistance at high temperatures was prepared. The results showed that the residual carbon yielded by thermogravimetric analysis increased to 12.7 wt% at 700°C. The EVA / IFR composites containing both OMMT and GNS exhibited the best flame retardancy with a minimum peak exothermic rate value of 529.58 kW /m^{-2} , and a maximum ultimate oxygen index value of 24.8%. The excellent flame retardancy was attributed to the formation of an intact and dense protective carbon layer. In addition, the combination of OMMT and GNSs in EVA/IFR systems can eliminate the degradation of mechanical properties due to the incorporation of IFR, allowing them to maintain a high volume resistivity[21].

Zhang [22] et al. prepared a new flame retardant (ZB / RGO) blended with zinc borate (4ZnO-B_2O_3 -H_2O) and RGO. When 7.71% of RG0 was added to polyvinyl chloride (PVC), it could play a synergistic role in flame retardant performance and smoke suppression performance, and the ultimate oxygen index of PVC / ZB / RGO / MH composite could reach 29.5%, which was higher than 24% of pure PVC, and the HRR, PHRR, SPR, maximum smoke yield (PSPR), TSP and weight loss (MAL) of the material were reduced. In particular, the values of PHRR, TSP and MAL were reduced by 35%, 34% and 15%, respectively, indicating that in addition to the synergistic effect between ZB and MH, the addition of RGO effectively improved the flame retardant effect of the cohesive phase.

In summary, the compounding of graphene with traditional flame retardants can produce a synergistic flame retardant effect on polymeric materials.

5. Conclusion

When a small amount of graphene or its derivatives are monodispersed in a polymer matrix, they can effectively improve the heat resistance, mechanical properties and flame retardant properties of the polymer. Due to the strong interaction between graphite layers, the graphite layers are easily stacked and cannot fully exploit their excellent properties. Therefore, organic modification of graphene is necessary. GO, as an important derivative of graphene, is favorable for organic modification of graphene because its surface contains a large number of reactive groups, such as hydroxyl, carboxyl and epoxy groups. With the continuous development of high-performance flame retardant materials, a single flame retardant material can no longer meet the demand due to its own defects. In order to improve the fire resistance of materials, the synergistic flame retardant system has become a research hotspot for polymeric flame retardants. For further research directions Combining other excellent properties of graphene with the properties of polymers for obtaining flame retardant polymer materials with special functionalities Further enriching the functionalities and applications of flame retardant polymers.

Acknowledgments

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