

## Research paper

# Combination effects of graphene and layered double hydroxides on intumescent flame-retardant poly(methyl methacrylate) nanocomposites



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## ABSTRACT

A novel intumescent flame-retardant poly(methyl methacrylate) (PMMA) nanocomposite has been prepared via in situ polymerization by incorporating intumescent flame retardants (IFRs), graphene and layered double hydroxides (LDHs). Results from X-ray diffraction (XRD) and transmission electron microscopy (TEM) indicate that a fine dispersion of IFR particles, intercalated LDHs and exfoliated graphene is achieved in the PMMA matrix. Thermal and flammability properties of PMMA nanocomposite were investigated using thermogravimetry, cone calorimetry, limiting oxygen index (LOI) and vertical burning (UL-94). The use of IFRs in combination with graphene and LDHs in the PMMA matrix improves greatly the thermal stability and flame retardant properties of the nanocomposites. The PMMA/IFR/RGO/LDH nanocomposites, filled with 10 wt.% IFRs, 1 wt.% graphene and 5 wt.% LDHs, achieve the LOI value of 28.2% and UL-94 V1 grade. Compared with neat PMMA, the PHRR of PMMA/IFRs/RGO/LDHs is reduced by about 45%, while the mechanical properties of PMMA/IFR/RGO/LDH nanocomposites exhibit almost no deterioration. The results from scanning electronic microscopy (SEM) confirm that the compact and dense intumescent char enhanced with LDHs and graphene nanosheets is formed for the PMMA/IFR/RGO/LDH nanocomposites during combustion, which inhibits the transmission of heat and mass when exposed to flame or heat source, and thus improves the flame retardant properties of the nanocomposites.

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## 1. Introduction

Poly(methyl methacrylate) (PMMA) is a typical amorphous polymer and has been widely used in a wide range of fields with several desirable properties such as good flexibility, high strength, and excellent dimension stability. However, PMMA is very flammable and thus reducing its flammability is becoming imperative, especially in those fields where a flame retardancy property of materials is demanded. Incorporating a flame retardant into the polymer matrix is one of the most efficient methods of improving the flame retardancy of PMMA. For environmental concerns, intumescent flame retardant (IFR) is considered as a promising halogen-free flame retardant additive owing to their advantages of low toxicity, low smoke, low corrosion, and relatively high flame retarding efficiency. Typically, an IFR system consists of three basic components: an acid source, a carbonization agent, and a blowing agent. However, actual developments have been aimed at the synthesis of a single compound which provides all the functions required for intumescence (Almeras et al., 2004; Chen and Wang, 2010; Ma et al., 2007; Peng et al., 2008; Wang et al., 2004).

Layered double hydroxides (LDHs) are commonly used nanofillers for improving the flammability of polymers due to its excellent fire retardant effect and environmental friend. A lot of articles have been published on the flammability of polymer/LDH nanocomposites (Costache et al., 2006; Du et al., 2007; Hussein et al., 2002; Pereira et al., 2009; Qiu et al., 2006; Zhang et al., 2007; Zhao et al., 2008). The combination effect between IFRs and nanoparticles (e.g. nanoclay, LDHs or carbon nanotubes) in fire performance has also been already reported recently (Chen et al., 2009; Huang et al., 2011a,b; Ma et al., 2008a,b; Tang et al., 2004; Ye et al., 2008, 2009). For IFR/LDH filled polymer system, LDHs absorb the heat and send out H<sub>2</sub>O, CO<sub>2</sub> when burned, which lowers temperature of substrate and enhances foam char structure. Porous thermal-decomposed products of LDHs with large specific surface area give smoke suppression effects by absorbing the smoke and gases produced in the course of combustion (Wang et al., 2005). In recent years, much attention has been attracted in using graphene for making polymeric nanocomposites due to their excellent properties (Kim et al., 2010a,b; Liang et al., 2009; Rafiee et al., 2009; Salavagione et al., 2009; Stankovich et al., 2006; Zhao et al., 2010a,b) and, among these, enhanced fire retardancy of the polymers is one of the most important (Higginbotham et al., 2009; Wang et al., 2011). Previous researches of the flame retardant properties of graphene-based polymeric nanocomposites mainly demonstrate a significant decrease in the heat release rate, a change in the char structure, and a decrease in time to ignition during combustion in a cone calorimeter (Guo et al., 2011; Huang

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et al., 2012; Song et al., 2012). During combustion, the barrier effect of the graphene nanosheets added into IFR/LDH filled polymer system could further slow down heat and mass transfer between the gas and condensed phase and prevent the under-lying polymeric substrate from further attack by heat flux in flame. To our best knowledge, however, a few reports about the combination of graphene and LDHs for reducing the flammability of intumescent flame-retardant polymers have been published since the discovery of graphene.

In this paper, intumescent flame-retardant PMMA (IFR–PMMA) nanocomposites were prepared by in-situ polymerization by incorporating IFRs, graphene and LDHs. The thermal property and flammability of PMMA nanocomposites were investigated by thermogravimetric analysis (TGA), cone calorimeter and burning tests. The residual chars after combustion were also examined by scanning electronic microscopy (SEM). It is anticipated that the combination of IFRs, graphene and LDHs could improve thermal stability and flame retardancy of PMMA nanocomposites.

## 2. Experimental

### 2.1. Materials

Graphite colloidal F-1 (~4 μm) was purchased from Qingdao BCSM Co. Ltd. (Qingdao, China). Magnesium aluminum-layered double hydroxide (LDH) carbonate with the formula of  $\text{Al}_2\text{Mg}_6\text{CO}_3 \cdot 16(\text{OH}) \cdot 4(\text{H}_2\text{O})$  was provided by Shaoyang Heaven Assistant Chemical Industry Co. Ltd. (Hunan, China). The organics-modified layered double hydroxides (O-LDHs) were prepared by the rehydration process of calcined MgAl-LDH with sodium dodecyl sulfate (SDS). Methyl methacrylate (MMA) and benzoyl peroxide (BPO) were purchased by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Neopentyl glycol, phosphoryl trichloride and ethylenediamine were supplied by Shanghai Chemical Reagent Co. (Shanghai, China). 1,2-Bis(5,5-dimethyl-1,3,2-dioxaphosphacyclohexane phosphoryl amide) ethane (BPEA) was prepared according to the published procedure (Li and Ou, 2001).

### 2.2. Preparation of the composites

Graphene oxide (GO) was prepared by the modified Hummer's method, and reduced graphene oxide (RGO) is obtained by chemical reduction of GO using hydrazine according to the literature (Kovtyukhova et al., 1999; Xu and Gao, 2010). For composite fabrication, a dispersion of 1 g of RGO, 5 g of O-LDHs and 10 g of BPEA in 84 g of methyl methacrylate containing 0.6 wt.% of BPO was sonicated for 3 h. Then, the dispersed solution was stirred mechanically at 90 °C until a critical viscosity that corresponds to a prepolymerization of the monomer was reached. The viscous mixture was then inserted into a mold and kept at 50 °C for 48 h to complete the polymerization process. Finally, the PMMA/IFR/RGO/LDH composites were kept for 6 h at 120 °C to be sure that the entire prepolymer fraction has been converted. The formulations of various PMMA composites prepared by in situ free radical bulk polymerization are summarized in Table 1.

**Table 1**  
Formulations for various PMMA composites.

Sample code	Proportions (g)			
	PMMA	RGO	O-LDHs	BPEA
PMMA	100	0	0	0
PMMA/RGO	99	1	0	0
PMMA/LDHs	95	0	5	0
PMMA/RGO/LDHs	94	1	5	0
PMMA/IFRs	90	0	0	10
PMMA/IFRs/RGO	89	1	0	10
PMMA/IFRs/LDHs	85	0	5	10
PMMA/IFRs/RGO/LDHs	84	1	5	10

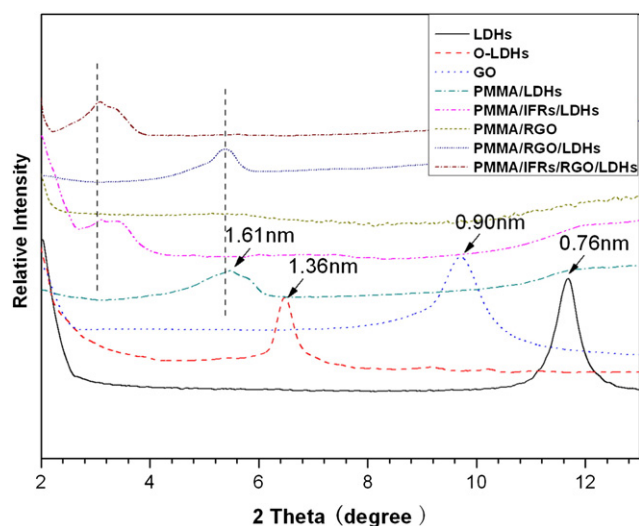
### 2.3. Characterization methods

X-ray diffraction patterns were obtained in Bruker AXS D8 Advance diffractometer using a Cu-K $\alpha$  radiation generator. The diffraction patterns were collected using scanning rate of 0.6°/min. Transmission electron microscopy (TEM) samples were cut using a diamond knife and RMC MTXL ultramicrotome. The ultrathin sections were then placed on 400 mesh copper grids and photographed using JEM-1230 transmission electron microscope. Tensile tests were carried out using a mechanical strength tester (model AGS-J) from Shimadzu Inc. The samples were cut into strips according to ASTM D638. Tests were performed at room temperature with a cross-head speed of 5 mm/min. Five measurements were conducted for each sample, and the results were averaged to obtain mean value. Thermogravimetric analysis (TGA) was carried out on a Q600SDT thermogravimetric analyzer. Sample weight is the range of 12–15 mg, respectively. All samples of TGA were measured from 30 °C to 600 °C at a heating rate of 10 °C/min with a continuous nitrogen flow. The flame retardant PMMA nanocomposites were tested using cone calorimeter (ISQ 5660) with heat flux of 35 kW/m<sup>2</sup> using a cone radiator. All samples with the dimensions of 10 cm × 10 cm × 3 mm plates were wrapped in aluminum foil, and then put in a box with the same dimension in the horizontal direction. The cone data reported here was an average of three replicated measurements. The limiting oxygen index (LOI) was measured with sheet dimensions of 120 × 6.5 × 3 mm<sup>3</sup> according to ASTM-D-2863, and UL-94 rating was determined according to the UL-94 (ASTM D 3801) standard. Char residue was examined by scanning electron microscopy (SEM) using Hitachi S-4800(II) scanning electron microscope.

## 3. Results and discussion

### 3.1. Morphology of composites

Fig. 1 shows the X-ray diffraction (XRD) patterns of LDHs, O-LDHs, GO and PMMA composites. The (003) reflection of LDHs indicates a basal spacing of 0.77 nm. The O-LDH sample shows a basal spacing of 1.36 nm. The increased spacing indicates that the surfactant SDS has intercalated LDHs by ion-exchange. PMMA/LDH shows a basal spacing of 1.61 nm, suggesting that some polymer chains have intercalated LDHs via in situ polymerization. Similar results for the state of LDH dispersion were obtained for other nanocomposites prepared by melt intercalation, which showed that LDHs modified with SDS were not delaminated in the polymer matrix (Qiu et al., 2006; Zhang et al., 2007). The PMMA/IFR/LDH sample shows a basal spacing of 2.67–2.84 nm (20:



**Fig. 1.** X-ray diffraction patterns of LDHs, O-LDHs, GO and PMMA composites.

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