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The effects of graphene on the flammability and fire behavior of intumescent flame retardant polypropylene composites at different flame scenarios

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This work explores the feasibility of using graphene as an effective synergist for intumescent flame retardant (IFR). The flammability test and fire behavior under different fire scenarios are investigated. The incorporation of graphene results in different responses of IFR/polypropylene (PP) composites to small fire tests and burning under forced-flaming condition. The addition of graphene weakens the reaction of flame retardant PP to small flame. Lower loading of graphene is observed to improve the swelling of char, resulting in better insulation of the char and decrease in heat and smoke release. The further increase of graphene leads to the worsened fire safety. Flame retardant mechanism and model are proposed on the basis of the analyses of thermal decomposition products and process, and melt viscosity change. This works provides a solution to comprehensively assess the synergistic or antagonistic effect of graphene, and will be beneficial to developing its flame retardant mechanism.

1. Introduction

Polypropylene (PP) is one of the widely used polyolefins with broad applications. However, its intrinsic inflammability and serious melt dripping during combustion greatly limit its applications. Therefore, it is of great significance to improve its flame retardancy. Due to environment and health concerns, halogenated flame retardants are being phased out. Halogen-free flame retardant, especially intumescent flame retardants (IFRs) have been attracting considerable attention in the development of high performance PP composites, due to their outstanding advantages, such as low yield of smoke and toxic gases, and halogen-free feature [1]. Generally, IFR formulations contain three ingredients, namely acid source, carbonization agent and blowing agent. Intumescent char layer is produced via the dehydration and charring of carbonization agents under the catalysis of acid source, and the released gases from blowing agents trigger the expansion of the forming char [2]. Thus, the prominent flame retardant mechanism of IFR is the formation of swollen multicellular charred layer on the surface, creating a physical protective barrier.

The application of nanotechnology in polymer flame retardant field is acknowledged as a revolutionary strategy. Flame retardancy of polymer can be significantly enhanced by the addition of a small amount of nanofiller. Graphene, a nanomaterial firstly isolated by a micromechanical cleavage approach in 2004, integrates the excellent physical properties. Low loading of graphene results in the obvious enhancements on thermal stability, mechanical properties, thermal and electrical conductivity of the resultant polymer composites [3,4]. Furthermore, graphene has been employed as a promising flame retardant nanofiller for polymers, including charring and non-charring materials. Dittrich et al. reported that the well-exfoliated graphene exhibits pronounced effect on the burning behavior of PP [5]. The reduction of peak heat release rate (PHRR) is as high as 74%, when 5.0 wt% graphene is added to PP matrix. However, the conventional flammability results, such as UL-

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94 rating and limiting oxygen index (LOI), are hardly enhanced. The action mode of graphene for enhancing flame retardancy of PP is generally acknowledged that the barrier effect of carbon nanomaterial residue leads to the limitation of heat and mass transfer between gas and condensed phases [5–7]. Taking into consideration the similar flame retardant mechanisms of graphene and IFR, the combination of them seems to be a meaningful topic.

Nanomaterials have also been used as adjuvants for conventional IFRs, and they can influence the performance via physical or chemical modes. Expansion, strength and cohesion of the char and melt viscosity of polymer can be modified by the added nanomaterials [8,9]. Furthermore, barrier performance of the char can be reinforced, and the thermal conductivity and diffusivity can also be changed [10]. In addition, some nanomaterials have been proven to stabilize and improve char yield by their chemical effects. Aluminosilicophosphate species formed by the reactions between clay and ammonium polyphosphate (APP) can stabilize the P-O-C bonds and improve their high temperature stability [11]. As a new two-dimensional (2D) nanomaterial, graphene has raised high expectations as a synergist for conventional flame retardants. The research group of Bernhard Schartel has carried out a serial of investigations on the influence of graphene on the reaction to small flame and fire behavior of flame retardant PP [12–15]. The results indicated that the incorporation of graphene can further reduce the PHRR value of flame retardant PP. The synergistic or antagonistic effect of graphene on the reaction to small flame tests depends on the action modes of flame retardants and the viscosity changes by the added graphene [13,14]. For example, the graphene has a negative influence on the LOI value and UL-94 rating of halogenated flame retardant PP composites [12,13,15]. Furthermore, the achievement of synergism between IFR and graphene has rarely reported, although the reduction in PHRR for polymer nanocomposites. Huang et al. claimed that the addition of 2 wt% reduced graphene oxide (RGO) just slightly increases the LOI value of IFR/PP (29.2%) to 30.6% and the UL-94 rating is not enhanced [16]. This enhancement in LOI is not remarkable as compared with other 2D nanomaterials, such as clay [17]. To date, systematic study on the effects of graphene on the combustion, expansion behavior, char structure and decomposition process of IFR is lack.

The aim of this work is to comprehensively investigate the possibility of graphene as an effective synergist for IFR. The IFR consists of APP and charring-foaming agent (CFA), which plays the role of both carbonization and blowing agents [18]. RGO nanosheets were incorporated in APP/CFA/PP flame retardant system and its effects on the flammability and combustion heat release of flame retardant PP composites were investigated. Flame retardant mechanisms are proposed on the basis of the analyses of thermal decomposition and combustion products in the gas and condensed phases. Fire behavior of the samples under different flame scenarios is compared. This study will provide a novel understanding of the synergistic or antagonistic effects of graphene on the flame retardancy of IFR/PP composites.

2. Experimental section

2.1. Materials

APP (n > 1500) was obtained from Cangshan Hongchuang Flame Retardant Co., Ltd. The CFA was a macromolecular triazine derivative containing hydroxyethylamino, triazine rings and ethylenediamino groups, and it was synthesized in our laboratory according to the previous work [18]. Isotactic PP homopolymer was supplied by Sinopec Yangzi Petrochemical Co., Ltd. Graphite oxide and RGO were prepared according to the methods described in our previous studies [19,20]. Briefly, graphite oxide was prepared from graphite powder by pressurized oxidation strategy and graphene oxide (GO) was reduced by hydrazine and ammonium hydroxide. The RGO obtained was dried by freezing-thawing-drying approach.

2.2. Preparation of flame retardant PP composites

PP, APP and CFA were dried in an 80 °C oven overnight before use. Flame retardant PP composites were prepared by direct melt mixing method. APP and CFA were pre-mixed in a plastic cup. PP and flame retardants were melt-mixed in a twin-roller mill for 10 min. PP was melted and then the mixed flame retardants were fed into the mill. The temperature and roller speed of the mill were maintained at 185 °C and 80 rpm, respectively. Detailed formulations of flame retardant PP composites were listed in Table 1. PP composites with different loading of flame retardant and ratio of APP to CFA were prepared.

2.3. Preparation of flame retardant PP/graphene nanocomposites

The optimum ratio of APP to CFA was 4:1, according to the results of LOI and UL-94. The loading of RGO was kept at 0.5, 1.0 and 2.0 wt%, and the total content of RGO and IFR was maintained at 25 wt%. Flame retardant PP nanocomposites containing RGO were prepared by master batch-based melt mixing method. PP master batch containing 40 wt% RGO was prepared by the approach

Table 1
Formulations of flame retardant PP composites and flammability results.

Sample	Composition (wt%)				LOI	UL-94	
	PP	APP	CFA	Graphene	(%)	Dripping	Rating
PP	100	–	–	–	17.0	Y	NR
PP1	75	25	–	–	20.5	Y	NR
PP2	75	20.85	4.15	–	33.0	N	V-0
PP3	75	20	5	–	34.0	N	V-0
PP4	75	18.75	6.25	–	32.0	N	V-0
PP5	75	16.67	8.33	–	32.0	N	V-0
PP6	75	12.5	12.5	–	29.5	N	V-0
PP7	75	8.33	16.67	–	25.0	Y	V-2
PP8	75	–	25.0	–	22.0	Y	NR
PP9	77	18.4	4.6	–	31.0	N	V-0
PP10	80	16	4	–	28.0	N	V-1
PI-0.5	75	19.6	4.9	0.5	32.0	N	V-0
PI-1.0	75	19.2	4.8	1.0	28.0	N	V-0
PI-2.0	75	18.4	4.6	2.0	25.0	Y	V-2

NR: No rating; N: No; Y: Yes. PI is denoted as PP3.