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Influence of clay dispersion on flame retardancy of ABS/PA6/APP blends

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ABSTRACT

Influence of dispersion of clay in acrylonitrile–butadiene–styrene/nylon-6 (ABS/PA6) blends on flame retardancy was investigated. The results of FTIR spectra and transmission electron microscopy (TEM) showed that ammonium polyphosphate (APP) and clay were exclusively dispersed in the PA6 phase. Clay modified with poly (styrene-*co*-maleic anhydride) (SMA) was selective localization at the interface of blends. Introduction of clay and modified clay to blends caused the dispersion of clay not only in PA6 phase, but also at the interface. The flame retardancy was evaluated by limiting oxygen index (LOI), vertical flammability test, and cone calorimeter tests. For the blends with dispersed PA6 phase, the dispersion of clay only in PA6 phase or at interface had negative effect on flame retardant property. Morphology of residue char characterized by scanning electron microscope (SEM) showed that the inhibition of clay platelets on the expansion of residue char should be responsible for the deterioration of flame retardant properties. When clay dispersed both in PA6 phase and at the interface, the reinforcement of clay platelets on residue char caused the formation of compact and continuous superficial char, resulting in significant improvement of flame retardancy. In blends with continuous PA6 phase, introducing clay to blends caused the formation of compact and continuous superficial char thus improved the flame retardancy no matter where the clay dispersed in blends. The characterization of energy dispersive spectrometry (EDS) revealed that the morphology of char was determined by the dispersion of clay platelets in residue char.

1. Introduction

Polymer/clay nanocomposites attract great research interest owing to the modification of polymer properties in an exceptional manner with the use of very low filler loadings usually less than 5 wt%. The addition of clay brings about a large enhancement of thermal stability and fire retardant properties of polymer matrix. The reduced flammability of polymer/clay nanocomposites is generally attributed to the formation of a physical barrier layer on the sample surface, which effectively shields the underlying polymer against external heat exposure and impedes diffusion of volatiles across itself during thermal degradation and combustion [1–3]. Nanodispersion of clay in polymer matrix is a key factor in improving fire retardant properties. Poorly dispersed clays in the polymer matrix would not significantly improve flame retardancy since the material lacks the formation of an effective barrier layer during combustion. Nanomorphology of clay (exfoliation, intercalation and presence of tactoids) does not play any significant role to obtain the better flame retardant properties if nanodispersion of clay is achieved [4,5].

Addition of clay alone in polymers mainly decreases the peak heat release rate (PHRR) as one of the flame retardant property in cone calorimeter study. When flame retardancy is evaluated using LOI and UL 94 test, some results showed that clay do not show any enhancement in improving flame retardant properties [6–8]. Therefore, clay should be employed in synergistic combinations with other traditional flame retardants (FR) to achieve better flame retardant properties.

Intumescent flame retardant (IFR) has attracted considerable attention from those interested in the development of flame retardation in polymers not only because they are more environmentally friendly than traditional, halogen-containing, flame retardants but also as they have high flame retardant efficiency. On heating, intumescent flame retardant additives form a foamed

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cellular charred layer on the surface of the product, which decelerates heat and mass transfer between the gaseous and condensed phases [9–11]. In recent years, replacement of a certain portion of IFR by clay has been employed to enhance flame retardancy owing to the strong synergy arising in strengthening of chars through the reinforcement by clay layers. Synergism has been found between IFR and clay nanocomposites including polypropylene (PP), ethylene vinyl acetate (EVA), Acrylonitrile–butadiene–styrene (ABS), Epoxy, etc. [12–19].

Achieving nanodispersion of clay in the polymer flame retarded nanocomposites is critical in obtaining significant synergies [20–22]. Hussain et al. [22] showed that the addition of clay to an epoxy and phosphinate system resulted in PHRR and total released heat values that were higher than the system without the organoclay. Although the reason for this flame-retardancy antagonism was unclear, the lack of uniform clay dispersion may have been responsible. Moreover, Fang et al. [17] found that the distribution of clay between polymer matrix and IFR is a key factor in obtaining significant synergies. They investigated the effect of organically modified clay (DK4) on the combustion behaviour of PS containing an intumescent flame retardant, poly (4, 4-diaminodi phenylmethane spirocyclic pentaerythritol bisphosphonate) (PDSPB). Being Compared to the dispersion of DK4 in PS, the dispersion of DK4 in PDSPB is more favourable to the improvement of flame retardant properties. However, for flame retardant polypropylene (PP) which consists of PP, brominated epoxy resin-antimony oxide (BER-AO) and clay, the flame retardancy of composites with dispersion of clay in PP is better than that of composites with dispersion of clay in BER-AO [23].

In the case of immiscible polymer blends, clay tended to segregate into one of the phases or at the interface, causing that the effect of the dispersion of clay on synergy between FR and clay is more complex [24]. For blends with clay dispersed in one of the phases, the morphology of blends was a key factor in improving the flammability. In blends of PS/PA6 in which clay and APP dispersed in PA6 phase, Lu [25,26] found that a better flammability was observed when a co-continuous morphology was formed. Entezam [27] found that the clay was mainly localized in PET phase of PP/PET blends. A higher efficiency of flame retardancy of the clays was observed for the PET-rich blend, as compared to the PP-rich blends. Pack [24,28] investigated the effect of clay localized at the interface on the flame retardancy of PS/PMMA and PC/SAN blends. The results showed that the effect of clay on the improvement of the flame retardancy in polymer blends is more efficient than in respective homopolymers due to the dispersion of clay at the interface of polymer blends. Lu [29] investigated the effect of the localization of clay at the interface of PS/PA6 blends on their flame retardancy. For blends with a dispersed PA6 phase, the dispersion of clay in blends has an insignificant effect on the flame retardancy. However, in blends with a continuous PA6 phase, the flame retardancy of blends with clay dispersed at the interface was better than that of blends with clay dispersed in PA6 phase.

As far as we know, a comparative study of flame retardancy for the blends with dispersion of clay in one of the phases, at interface, in one of the phases and interface has not been reported. Blends of PA6 and ABS are of commercial interest for the potential to obtain materials with superior properties [30]. The flammability of ABS/PA6 has greatly limited its more broad applications in various fields. Therefore, in this paper, the association of clay and APP as flame retardants was used for improving the fire resistance of ABS/PA6 blends. The spontaneous dispersion of clay in ABS/PA6 blends was employed to control the clay in one of the phases. The method that poly (styrene-*co*-maleic anhydride) (SMA), the compatibilizer of ABS and PA6, was first reacted with clay and then blended with ABS/PA6 was employed to control clay at the interface. As a result, three kinds of distribution of clay in ABS/PA6 blends should be prepared: clay was dispersed in one of the phases, dispersed at interface, dispersed in one of the phases and at interface. The influence of the distribution of clay in ABS/PA6 blends with different morphologies on the flame retardancy was studied.

2. Experimental

2.1. *Materials*

The materials used in this study were acrylonitrile–butadiene–styrene (0215A, MI = 20 g/10 min, $d = 1.05$ g/cm^3) supplied by Jilin petrochemical Co., Ltd and polyamide-6 (PA6) (33500, relative viscosity of 3.50, d = 1.14 g/cm^3), supplied by Xinhui Meida-DSM Nylon Chips Co., Ltd. Ammonium polyphosphate [$(NH_4PO_3)_n$, n = 1500, purity level >90%] was supplied by Zhejiang Longyou Gede Chemical Factory (China). The compatibilizer employed in this study was SMA (MPC1501, Shanghai SUNNY New Technology Development Co., Ltd.). The amount of maleic anhydride in SMA was 18 wt%. The organically modified clay (purity level >95%), coded as DK2, was supplied by Zhejiang Fenghong Clay Products, which was ion-exchanged with dioctadecyl dimethyl ammonium chloride.

2.2. *Preparation of composites*

Based on the condition of the reaction between hydroxyl group at clay surface and maleic anhydride in the SMA, the SMA/clay composites were prepared as follows: SMA and clay with the proportion of 20/80 (w/w) were dissolved in dimethylbenzene and then reacted at 120 °C for 24 h. The reactant was deposited with acetone at room temperature and then dried in a vacuum oven at 90 °C for 24 h to remove the solvent.

PA6, clay and APP were dried before blending at 85 °C for 12 h to remove any moisture. The composites were prepared by passing them through a co-rotating twin screw extruder with a barrel length to diameter ratio of 28 at a barrel diameter of 34 mm; the temperatures from hopper to die were 180, 225, 225, and 230 °C. The screw-speed and throughput were 300 rpm and 10 kg/h, respectively. The composites were dried at 85 °C for 12 h and injection moulded into sheets of suitable thickness in an injection-moulding machine with a hydraulic injection pressure of 50 MPa. The injection and mould temperatures were 230 and 30 °C, respectively; the injection and cooling times were 5 and 20 s respectively. The different blends prepared are listed in Table 1.

2.3. *Measurement and characterization*

The LOI value was measured using a JF-3 instrument (Chengde, China) on sheets measuring 120 × 6 × 3 mm according to the

Table 1
Formulation of blends.

Sample code	ABS	PA6	APP	Clay	SMA/clay	SMA
PA24	56	24	20	0	0	
PA56	24	56	20	0	0	
PA24-clay	56	24	20	5	0	
PA56-clay	24	56	20	5	0	
PA24-(SMA/clay)	24	56	20	0	5	
PA56-(SMA/clay)	56	24	20	0	5	
PA24-SMA/clay–clay	56	24	20	3	2	
PA56-SMA/clay–clay	24	56	20	3	2	
PA24-SMA	56	24	20			1
PA56-SMA	24	56	20			1

SMA/clay ratio is 20/80 (w/w).