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Magnesium hydroxide sulfate hydrate whisker flame retardant polyethylene/montmorillonite nanocomposites

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Flame retardant maleated polyethylene/magnesium hydroxide sulfate hydrate whisker (MAPE/MHSH) composites containing organo-modified montmorillonite (OMT) were prepared by direct melt intercalation. Their morphology, combustion behaviour and thermal stability were carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM), cone calorimetry and thermogravimetric analyses (TGA). The exfoliation of silicate layers within MAPE has been verified by XRD and TEM images. Cone calorimetry results indicated that a synergistic flame retardant effect on reducing heat release rate (HRR) occurred when MHSH and OMT were both present in nanocomposite. The reduction in HRR improved as the mass fraction of OMT was increased from 2 to 10 wt%, but there was little improvement above 5 wt% OMT loading level. TGA profiles of the nanocomposites revealed that the thermodegradation stability of the nanocomposites decreased as the OMT fraction increased from 2 to 10 wt%.

1. Introduction

Polyethylene (PE) is one of the most important polyolefins, but the fact that it is inherently flammable and emits smoke and poisonous gases while burning has restricted the range of its practical applications. Therefore, improving its flame retardancy has become very important. Halogen-free flame retardant polymeric materials filled with inorganic fillers, typically magnesium hydroxide (MH) and aluminum trihydrate (ATH) have been achieved in many investigations. However, the high loading (>50% by weight) required for adequate flame retardancy often lead to a marked deterioration in mechanical properties of the materials [1–3]. Recently, interest in using inorganic whisker as flame retardants has been increased due to they not only improve flame retardancy of the filled polymers but also enhance their mechanical properties. This is because the whiskers are short, fiber-shaped single crystals with high tensile strength owing to their nearly perfect microstructure [4].

In our previous study, it has been found that magnesium hydroxide sulfate hydrate whisker (MHSH) significantly improves the flammability properties of the filled polyethylene, and red phosphorous is an effective synergist in improving flammability properties of the PE/MHSH composites [5]. As far as we are aware, remarkable improved flammability properties have been achieved by the formation of exfoliated and/or intercalated layered silicates in host polymer, evident that the heat release rate (HRR) during combustion in a cone calorimetry study has been dramatically reduced [6–8]. However, to our knowledge, no work has been done on

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the influence of silicates on whisker flame retardant polymeric materials.

It is known that it is difficult to fabricate polyolefin-based nanocomposites and maleic anhydride grafted polyolefin is often introduced to promote the interaction between polyolefin chains and silicate layers [9, 10]. For simplicity, in this paper, the maleated polyethylene is used as a model polymeric matrix to investigate the effect of the combination of MHSH and organo-montmorillonite (OMT) used as flame-retardant additives on morphology, flammability properties and thermal stability of the material.

2. Experimental section

2.1. Materials

The maleated polyethylene (MAPE) with approximate 1.0 wt% maleic anhydride was supplied by Haier Kehua, China. Organophilic montmorillonite (OMT), which has been ion-exchanged with hexanecyl trimethyammounium bromide was kindly provided by Keyan Chemistry Co. Magnesium hydroxide sulfate hydrate whisker (MHSH) with a size of diameter <1 μm and length >10 μm was also provided by Keyan Chemistry Co. The scanning electron micrograph of the MHSH is shown in Fig. 1.

2.2. Preparation

MAPE (dried) and desired additives, MHSH and OMT, were premixed then blended by a two-roll mill (XK-160, JiangShu, China) at 165°C for 10 min. The resulting mixtures were then compression molded at 165°C into sheets (1- and 3-mm thickness) under a pressure of 10 MPa for 15 min. The formulations used in this paper are listed in Table I.

2.3. Characterization

X-ray diffraction (XRD) patterns were performed on the 1 mm thick compression moulded films with a Japen Rigaku D/Max-Ra rotating anode X-ray diffractometer equipped with a Cu Kα tube and Ni filter ($\lambda = 0.1542$ nm). Transmission electron microscopy (TEM) images were obtained on a Jeol JEM-100SX transmission electron microscope with the acceleration voltage of 100 kV. The nanocomposite specimen was cut at room temperature using an ultramicrotome (Ultracut-1, UK) with a diamond knife from an epoxy block with the films of the nanocomposite embedded. Morphology observation of MHSH whiskers was performed on DXS-10 scanning electron microscope (SEM).

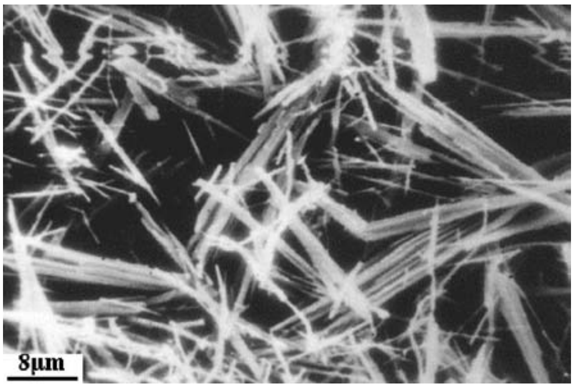

Figure 1 SEM image of the MHSH whiskers.

TABLE I Formulations and fire parameters for MAPE/MHSH composites with different contents of OMT at the same levels of 40 wt% additives

Sample	Additives MHSH/OMT (wt%)	t_{ign} (sec)	Peak HRR ($kW \cdot m^{-2}$)	Mean MLR ($g \cdot s^{-1}$)
PE0	pure	34	1864	0.465
PE1	40/0	42	507	0.093
PE2	38/2	45	375	0.080
PE3	35/5	52	307	0.058
PE4	30/10	44	302	0.055

The cone calorimeter experiments were evaluated using a Redcroft Cone Calorimeter following the procedure defined in ISO 5660, on 3 mm thick 100×100 mm^2 plaques. The cone data obtained are reproducible to within $\pm 10\%$ when measured at a heat flux of 50 $kW \cdot m^{-2}$.

Thermogravimetric analyses (TGA) were conducted with a Netzsch STA 409C thermoanalyzer instrument. The 10 mg specimens were heated from 25 to 700°C using a linear heating rate of $10°C \cdot min^{-1}$. All runs were performed in nitrogen atmosphere at a flow rate of $50\ ml \cdot min^{-1}$.

3. Results and discussion

3.1. Structure of MAPE/MHSH/OMT nanocomposites

Fig. 2 shows the XRD patterns of MAPE/MHSH composites with different OMT contents at the same 40 wt% loading levels. The disappearance of the d_{001} reflection peak derived from the interlayer spacing of montmorillonite in PE2-4 samples (Fig. 2B–D), suggests that the silicate layers had lost their reciprocal order, and almost complete exfoliation of clay had taken place.

The morphologies of the selected PE3 sample with 35 wt% MHSH and 5 wt% OMT elucidated by TEM at different resolutions are shown in Fig. 3. Fig. 3A demonstrated that the whiskers homogeneously dispersed throughout MAPE matrix, with noticeable suffering in morphology caused by the shear strength on the extrusion process. Fig. 3B shows the TEM image of PE3 at higher resolution, where most of the silicates exhibited single exfoliated layer are well-dispersed within matrix. It is consistent with the absence of d_{001} peak in XRD studies and confirms that an exfoliated nanostructure has been obtained.

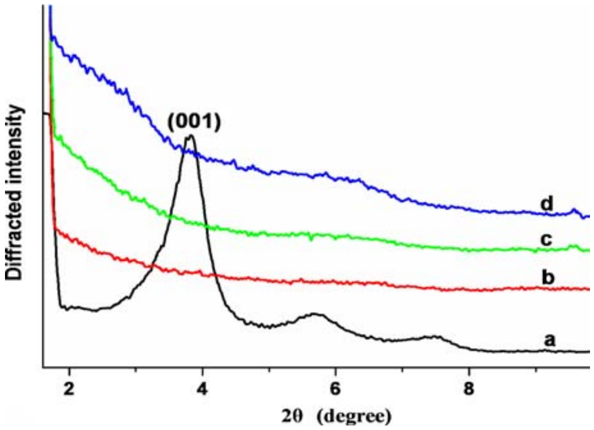

Figure 2 XRD patterns of (a) OMT, (b) PE2, (c) PE3, and (d) PE4.

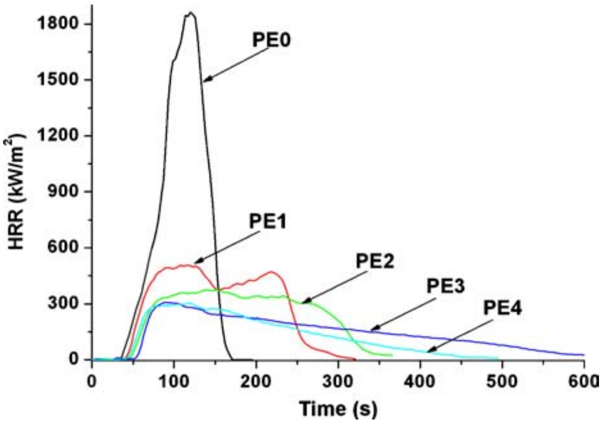

Figure 4 The HRR curves for MAPE/MHSH composites with different contents of OMT at the same levels of 40 wt% additives.

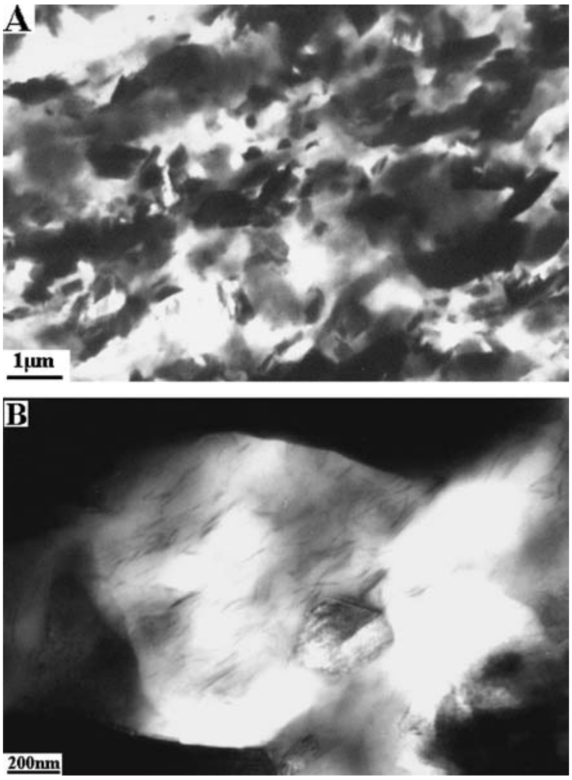

Figure 3 TEM images of PE3 sample at different resolutions.

3.2. Flammability properties

Measurement with a cone calorimetry is one of the most effective bench-scale methods for studying the change in flammability properties of materials. Heat release rate (HRR), in particular peak HRR has been found to be the most important parameter to evaluate fire safety [11].

The comparison of the HRR behavior of MHSH partially replaced by OMT at the same 40 wt% loading levels is shown in Fig. 4. The corresponding cone data are listed in Table I. Neat MAPE was ignited in 34 sec and showed a very sharp HRR curve at the time range of 30–170 sec with a maximum of 1864 kW $\cdot$ m^{-2} at 120 sec. An addition of 40 wt% MHSH sample (PE1) decreased the peak HRR by 73%; increased the time to ignition (t_{ign}) up to 42 sec and prolonged the combustion progress when compared with MAPE. It is clear that two separated HRR peaks appeared in PE1. The first peak is assigned to the development of the protective charred shield formed from the degradation products of MHSH after ignition up to 80 sec. This shield reduced the HRR and a plateau is reached in which the HRR is suppressed (80–160 sec). The second peak may be due to the destructure of the shield, which results in the increased rate of the volatiles feed into flame area.

When OMT is present, combustion of the nanocomposites (PE2-4) shows different HRR features with that of PE1. That is all those samples exhibited a further reduction in HRR and prolonged combustion process; the t_{ign} was slightly retarded above 42 sec and the 5 wt% OMT contained sample (PE3) had achieved the maximum of 52 sec. In the case of PE2 containing 2 wt% OMT, a steady HRR flat ($80 < t < 280$ sec) during burning without the apparent second HRR peak is observed, which suggests that incorporating OMT into the MAPE/MHSH system stabilizes the charred shield. As for PE3 and PE4 samples, the HRR rises initially then decreases gradually till the material is consumed up over 500 sec. The primary parameter which is responsible for a lower HRR of material is the mass loss rate (MLR) during combustion. The data listed in Table I confirm that the mean MLR of the OMT contained nanocomposites have the lower values than that of the PE1, and the PE3 exhibits the lowest value. These results indicate that the charred residues containing silicate layers are more efficient in preventing the transportation of the volatilization, which is beneficial with regard to the improvement in flammability properties. The reduction in HRR improves as the mass fraction of OMT is raised from 2 to 10 wt%, while there is little improvement above 5 wt% OMT loading level.

The cone experiments demonstrate that a synergistic effect on reducing HRR occurred when OMT and MHSH are both present. It is evidence that the improvement in flame retardancy for polymer-layered silicate

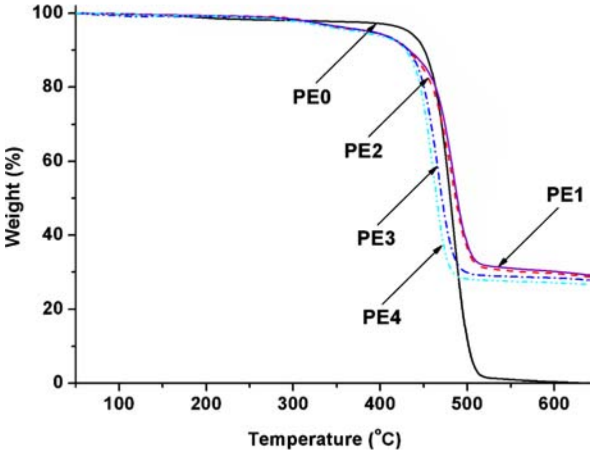

Figure 5 The TGA curves for MAPE/MHSH composites with different contents of OMT at the same levels of 40 wt% additives.

nanocomposites is due to the homogeneous multilayered carbonaceous-silicate char formed in the condensed phase [12–14]. Moreover, in the recent report, it is found that the transportation of clay particles pushed by numerous rising bubbles of degradation polymer products has a key role in the flame retardant mechanism of polyamide/clay nanocomposites [15]. The possibility of the effect of water vapor released from MHSH on the transportation of the layers is therefore considered. In the investigation here, the mechanism of the flame-retardant synergy may be that the water vapor is favorable to accelerate the transportation of silicate layers during the molten matrix to accumulate over the substrate. The carbonaceous-silicate char not only acts as a protective shield in addition to the physical barrier formed form the MHSH, but also provide a mechanical reinforcement of the barrier and make it more resistant to ablation. This shield insulates the heat transfer and prevents the diffusion of the oxygen and the volatile products efficiently, which leads to the reduction in HRR significantly.

3.3. Thermodegradation stability

Fig. 5 illustrates the TGA curves of MAPE, MAPE/MHSH composite and MAPE/MHSH/OMT nanocomposites. The MAPE mainly shows the thermal degradation of PE since the amount of maleic anhydride in MAPE is very small. When MAPE is filled with MHSH alone, the degradation starts earlier than pure MAPE and proceeds in two steps. The earlier mass loss in the temperature range form 260 to 360°C is attributed to the dehydration of crystal waters from MHSH [5]. The weight loss rate increases rapidly with increasing degradation temperature above 360°C. However, the degradation of MAPE is efficiently retarded by MHSH over 460°C. This is because the temperature range of the further dehydration from the anhydrous magnesium oxysulfate whisker is very close to that of the polyethylene, therefore, the rate of weight loss is retarded [16]. When MHSH-whisker is partially replaced by OMT at the same loading levels, the nanocomposites do not show any improvement, and the thermal degradation stability decreases with the increasing fraction of OMT. This can be explained that the thermal degradation of OMT take place with the Hofmann mechanism leaving an acid proton on the surface of the clay in the place of the ammonium cation, which is an efficient catalyst of the thermal degradation for MAPE with unsaturated functional groups.

4. Conclusion

Exfoliated nanocomposites were obtained by blending MAPE, OMT and MHSH whisker using melt intercalation technique. A synergistic flame retardant effect was observed when OMT and MHSH were both present in the nanocomposites during cone experiments. The synergistic mechanism is mainly due to the water released from MHSH accelerates the transportation of silicate layers to accumulate over the substrate. This carbonaceous-silicate materials not only collaborated with the physical barrier generated from MHSH but also stabilized the barrier structure, which resulted in the heat and mass transfer were inhibited efficiently. However, thermodegradation stability of the nanocomposites decreased as the fraction of OMT increased from 2 to 10 wt%.

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