Investigation of thermal property and flame retardancy of ABS/montmorillonite nanocomposites

X. J. He¹, L. J. Wang*¹, X. L. Xie² and K. Zhang¹

Acrylonitrile–butadiene–styrene (ABS)/montmorillonite (MMT) nanocomposite was prepared by melt blending of ABS and organomodified montmorillonite (OMMT). X-ray diffraction, TEM and Fourier transform infrared spectra were used to characterise the morphology and structure of the nanocomposites. Thermal stability and flame retardancy of the nanocomposites were studied by thermogravimetric analysis, cone calorimetry, limit oxygen index and UL94 test. The basal spacing of sodium MMT was found to increase from 1·46 to 2·69 nm after modification by cetyltrimethyl ammonium bromide, and ~3·3 nm after melt blending with ABS. Transmission electron microscope observation showed that organo-MMT was intercalated and exfoliated in ABS. The results by cone calorimetry analysis indicated that the reduction of the peak heat release rate of ABS/OMMT nanocomposites (with 5% OMMT loading) and ABS/OMMT/triphenyl phosphate (TPP) nanocomposites (with 4% OMMT and 10% TPP loading) was 47·3 and 57·3% respectively, while the total heat released decreased by about 10 and 17% and the mass loss rate decreased by about 41 and 53% respectively, as compared with pristine ABS. Limit oxygen index value of ABS/OMMT and ABS/OMMT/TPP nanocomposites increased to 22·8 and 28% from 18% of pristine ABS respectively. The vertical burning test (UL-94V) results revealed that the nanocomposites could achieve V-0 grade.

Keywords: Fire retardancy, Acrylonitrile–butadiene–styrene, Montmorillonite, Nanocomposite

Introduction

Polymer/layer silicate nanocomposites have received much interest over the past decades because of their outstanding properties and potential applications, such as enhanced physical–mechanical properties and flame retardancy. Currently, many researchers are involved in the nanocomposites of polymers and 2:1 clay mineral such as montmorillonite (MMT). There are four principal methods for producing polymer/layered silicate nanocomposites: in situ template synthesis, intercalation of polymer or pre-polymer from solution, in situ intercalative polymerisation and melt intercalation.¹ These methods can achieve molecular level incorporation of the layered silicate into the polymer matrix by addition of the modified silicate during the polymerisation (in situ method),²,³ template synthesis,⁴ polymer melt⁵ or intercalation of polymer.⁶

Intercalation and exfoliation are used to describe two general classes of the morphology of the additives in the nanocomposites. Intercalated structures are well ordered multilayered structures where the extended polymer chains are inserted into the gallery space between the individual silicate layers, while the exfoliated structures are obtained when the individual silicate layers are no longer close enough to interact with the adjacent layers.⁷ These two types of morphology can be conveniently monitored by X-ray diffraction (XRD). With face-to-face aggregation of clay platelets, the basal spacing is very similar to that of ‘as received’ clay powder. With intercalation of organic compounds in the clay gallery, an increase in the basal spacing can be detected by XRD. When completely exfoliated, the clay diffraction peaks disappear because the crystallographic order is lost.⁸ Polymer/clay nanocomposites often exhibit properties superior to conventional composites, including strength, stiffness, thermal and oxidative stability, barrier properties and flame retardancy as well.⁹ These polymer/clay nanocomposites have many potential applications due to the outstanding properties.¹⁰⁻¹³

Acrylonitrile–butadiene–styrene (ABS) has outstanding impact strength and is widely used in many engineering applications as automobile, wiring, spin, building, etc. Nevertheless, flammability of this material restricts its
application. Owen and Harper\textsuperscript{14} reported that Sb\textsubscript{2}O\textsubscript{3}, together with four commercially available brominated materials (octabromodiphenyl oxide, 1,2-bistribromophenoxy ethane, tetrabromobisphenol A and polydibromostyrene), was respectively added into ABS polymer matrix for the flame retardancy studies. They found that the addition of Sb\textsubscript{2}O\textsubscript{3} and brominated materials can significantly increase limit oxygen index (LOI) of the composites. However, the presence of halogen in the fillers is problematic because the flame retardants containing halogen are hazard to environment. In this context, the main purpose of this research is to prepare ABS/MMT nanocomposites by melt blending method and investigate the flame retardancy and thermal properties of the halogen-free nanocomposites.

**Experimental**

**Materials**

The sodium montmorillonite (NaMMT) clay with a cationic exchange capacity of 90 meq/100 g was supplied by the Zhejiang Fenghong Clay Chemical Co., Ltd. Cetyltrimethyl ammonium bromide (CTAB) was purchased from Tianjin Kernel Chemical Reagent Co., Ltd.

Acrylonitrile-butadiene-styrene (GP22) was purchased from BASF Chemical Company. The grafted ABS and toughening agent were purchased from Shenyang Syketong Co., Ltd. Triphenyl phosphate (TPP), a conventional flame retardant was respectively added into ABS polymer matrix for the preparation of organo-MMT. The nanocomposites were prepared in a tightly intermeshing corotating twin screw extruder with screw diameter of 27 mm and L/D ratio of 36. At first, the pristine ABS was mixed with OMMT and TPP on a high speed mixer according to the formula shown in Table 1 and the mixture was put into the extruder. Then the extruded master batch strands were water cooled as they emerged from the extruder die and granulated. The processing conditions are shown as follows. The temperature in the extruder barrel was 170°C at the feed region and 200°C at the die section; the screw speed was 12 rev min\textsuperscript{-1}, the feedrate was 5 kg h\textsuperscript{-1}. In the second step, the nanocomposites samples were made by injection moulding for the burning tests. The additives of grafted ABS and toughening agent were used for improving the compatibility between polymer matrix and the fillers and enhancing the impact strength.

**Characterisation**

Power XRD data were collected on a PANalytical X’pert PRO powder diffractometer, using Cu K\textsubscript{α} radiation (\(\lambda = 1.5405 \text{ Å}\)) at 40 kV and 40 mA. Scans were taken at 20\textdegree = 20\textdegree to 70\textdegree at 2\textdegree min\textsuperscript{-1}. Polymer composite samples were pressed into 20\times 15\times 1 mm plaques by compression moulding. Fourier transform infrared spectra spectroscopic analyses were carried out on a Nicolet 560 Fourier transform infrared spectrometer using the KBr method. The spectra were recorded between 400 and 4000 cm\textsuperscript{-1}. Transmission electron microscope H-600 was employed to observe microstructure at an accelerating voltage of 75 kV. Thermogravimetric analysis (TGA) was performed on a Netzsch STA-449 instrument at 12–14 mg scale under a flowing nitrogen atmosphere at a ramp rate of 20°C min\textsuperscript{-1}. Cone calorimetry was performed on a FTT cone-2 according to ASTM M1356 at an incident flux of 50 kW m\textsuperscript{-2}, in which the exhaust flow was set at 20 L s\textsuperscript{-1} and all the samples were burn in triple. Cone samples (~30 g) were prepared by compression moulding into 100\times 100\times 3 mm square plaques. Limit oxygen index measurements were carried out on an Atsfaar high temperature oxygen indexer according to ISO4589-1-1996. Vertical burning tests were performed on a DMS horizontal–vertical flame chamber testing instrument.

**Results and discussion**

**Organomodified MMT**

Figure 1 shows XRD patterns of NaMMT (Fig. 1a) and OMMT (Fig. 1b). The basal spacing of NaMMT and OMMT is 1.46 and 2.69 nm respectively, which indicates that the CTAB has been intercalated into the interlayer of NaMMT. The basal spacing of OMMT is

![X-ray diffraction patterns of NaMMT and OMMT](image)

**Table 1 Formulations of nanocomposites**

<table>
<thead>
<tr>
<th>Samples</th>
<th>ABS, wt-%</th>
<th>Grafted ABS, wt-%</th>
<th>Toughening agent, wt-%</th>
<th>OMMT, wt-%</th>
<th>TPP, wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>87</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>ABS2</td>
<td>85</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>ABS3</td>
<td>83</td>
<td>5</td>
<td>5</td>
<td>7</td>
<td>0</td>
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<tr>
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<td>5</td>
<td>5</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
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<td>76</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>ABS6</td>
<td>75</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>10</td>
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</table>
slightly larger than that reported by Zhang et al.\textsuperscript{15} The chain length of CTAB simulated by ChemDraw software was 2.29 nm. The basal spacing of OMMT and the chain length of CTAB manifest that CATB have inclined monolayer arrangement in the interlayer of MMT and the inclined angle of CTAB in the interlayer is \( \sim 54^\circ \) to the layer of NaMMT (Fig. 2).

The Fourier transform infrared spectrum of OMMT (Fig. 3) consists of two types of vibrations: one corresponding to the intercalated organic ions and the other to the pristine NaMMT. The sample shows broad intense bands centred at 3625 and 3440 cm\(^{-1}\), due to the OH stretching of layer hydroxyl groups and interlayer water molecules. The bands of NaMMT are clearly seen at 466, 523, 1038 and 1641 cm\(^{-1}\) corresponding to Si–O–Si deformation, Si–O–Al, Si–O stretching and stretching bands of O–H respectively (Fig. 3a). Organomodified MMT shows additional bands at 2924 and 2852 cm\(^{-1}\) due to the CH\(_2\) asymmetric and symmetric stretching as a result of the incorporation of organic modifiers into the clay layers (Fig. 3b).

Thermogravimetric analysis curves of NaMMT and OMMT are illustrated in Fig. 4. The first weight loss stage of NaMMT with weight loss of 15%, up to 148\,°C, originates from the loss of physical adsorption and interlayer water. The second stage with weight loss of 4%, up to 610\,°C, is due to the conversion of hydroxyl groups of silica layer into oxide groups (Fig. 4a). The weight loss of OMMT, up to 260 and 375\,°C, is due to the decomposition of CTAB in the interlayer. The total weight loss of two stages is \( \sim 25\% \) (Fig. 4b).

Nanocomposites of ABS/OMMT and ABS/OMMT/TPP

X-ray diffraction patterns of ABS/OMMT nanocomposites made by melt blending are illustrated in Fig. 5. The basal spacing of OMMT is 2.69 nm. After melt blending with ABS, the change of the basal spacing of OMMT in the nanocomposites is observed. The basal spacing of OMMT in all the nanocomposites is \( \sim 3.3\) nm. In comparison with that of OMMT, the intercalation of ABS increases the interlayer distance, leading to a shift of the diffraction peak towards lower angle. The increase in basal spacing may be due to the intercalation of polymer chain segments into the interlayer region of OMMT, which is induced by a strong shear during melt blending.

Transmission electron microscope is an important tool to evaluate the dispersion of OMMT in the polymers, which can provide a picture of the morphology of nanocomposites. Both lower magnification...
image, to show the global dispersion of OMMT in ABS, and higher magnification image, to evaluate the registry of the layer, were obtained. A fair degree of delamination of OMMT in ABS/OMMT nanocomposites can be observed (Fig. 6a and b). It is reasonable to describe these materials as exfoliated. The single OMMT layers, evidence for exfoliation, are present in abundance throughout the polymer matrix. There is no significant orientation of these platelets. However, with an increase in the OMMT amount in the nanocomposites, intercalated layers co-exist with large agglomerated OMMT, which suggests that the OMMT has a poorer dispersion in polymer matrix (Fig. 6c and d). Besides, the addition of TPP is unable to affect dispersion of OMMT in the nanocomposites (Fig. 6e and f). Meanwhile, there exist exfoliated nanoscale sheets and intercalated structure in all the nanocomposites.

Thermogravimetric analysis traces of ABS/OMMT and ABS/OMMT/TPP nanocomposites are given in Figs. 7 and 8. Table 2 summarises the characteristic data of TGA of all the samples. The data reported include onset temperature of degradation, as measured by temperature at which 10% of the sample is lost, $T_{0.1}$, the temperature at which 50% mass is lost, the midpoint...
temperature $T_{0.5}$, and the fraction of the non-volatile residue remaining at 600°C, labelled as char. The presence of OMMT in the composites leads to changes in thermal decomposition behaviour of the pristine polymer. For the sample ABS1, at 3% OMMT loading, the onset temperature and midpoint temperature of degradation are higher than those of the pure ABS. The char yields after combustion at 600°C in nitrogen atmosphere are nearly zero for the pure ABS as they are completely converted into gaseous products. The amount of non-volatile residue, 4–6%, for the ABS/OMMT and ABS/OMMT/TPP composites is attributed to the MMT residues. The residues of the composites are not significantly higher than the theoretically calculated value, but their blackish colour may indicate the presence of some carbonaceous materials. In addition, the residues amount of the nanocomposites without TPP is lower. This means that TPP is able to enhance thermal stability of matrix ABS, which is a synergistic result of the flame retardant.

**Fire retardancy of nanocomposite**

Cone calorimeter has been widely used to evaluate fire performance of polymers. The parameters that offered by cone calorimeter include heat release rate (HRR), peak value of HRR (PHRR), time to ignition $T_{ig}$, and the average mass loss rate (AMLR). The parameter that has been given the greatest attention in fire retardancy is PHRR, which gives information about the size of the fire and can be viewed as the ‘driving’ of the fire and is considered to be one of the most important parameters in assessing potential behaviour in real fire. 17,18

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{0.5}$, °C</th>
<th>$T_{0.9}$, °C</th>
<th>Char, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>420</td>
<td>426</td>
<td>0-6</td>
</tr>
<tr>
<td>ABS1</td>
<td>424</td>
<td>430</td>
<td>2-9</td>
</tr>
<tr>
<td>ABS2</td>
<td>427</td>
<td>431</td>
<td>4-0</td>
</tr>
<tr>
<td>ABS3</td>
<td>429</td>
<td>431</td>
<td>4-6</td>
</tr>
<tr>
<td>ABS4</td>
<td>428</td>
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</tr>
<tr>
<td>ABS5</td>
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<td>432</td>
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</tr>
<tr>
<td>ABS6</td>
<td>428</td>
<td>432</td>
<td>8-3</td>
</tr>
</tbody>
</table>

**Table 2 Thermogravimetric analysis data of ABS and its nanocomposites**

The cone calorimetric data of ABS and its nanocomposites obtained at a heat flux of 50 kW m⁻² are shown in Table 3 and Fig. 9. Compared with pristine ABS, PHRRs of ABS2 containing 3% OMMT and ABS4 containing 4% OMMT and 10% TPP decrease from 972 kW m⁻² of pristine ABS to 512 and 415 kW m⁻², and the reduction rate is 47-3 and 57-3% respectively. The total heat release of the nanocomposites is reduced to 178 MJ m⁻² ABS2 and 163 MJ m⁻² ABS4 from 196 MJ m⁻² ABS, with the reduction rate of 10 and 17% respectively. These results may be caused by the barrier effect of intercalated and exfoliated OMMT layers and endothermic reaction of OMMT layers’ decomposition. The AMLR reduced from 0-32 g s⁻¹ m⁻² pristine ABS to 0-19 g s⁻¹ m⁻² ABS2 and 0-15 g s⁻¹ m⁻² ABS4, which means that the amount of volatile combustible gases produced by polymer matrix significantly decreases. In addition, $T_{ig}$ for both the pristine ABS and ABS nanocomposites is 60 s, which has not yet been changed.

The LOI values of the nanocomposites are shown in Fig. 10. For pristine ABS, its LOI is 18-0 and the addition of small amount of OMMT leads to a significant change in the LOI value. The LOI values of ABS1, ABS2, ABS3, ABS4, ABS5 and ABS6 increase to 21-8, 22-8, 22-5, 26-0, 28-0 and 27-0 respectively. The LOI value of the nanocomposites may be related to dispersion of OMMT in the polymer matrix. With a rise in OMMT loading, dispersion of OMMT changes from exfoliation to intercalation and agglomeration. It is clear that both exfoliated and intercalated structures can significantly increase LOI value of the nanocomposites as a result of the gas barrier effect of OMMT layers.

**Table 3 Cone calorimetric data of ABS and its nanocomposites**
which is accordant with the above TGA results. However, with increasing OMMT loading in the composites, the agglomerated OMMT in the polymer matrix cannot keep up the increase in LOI value. UL94 test was carried out in terms of vertical burning tests. The pristine ABS cannot pass the test specification. When the OMMT and TPP had been added into ABS, the results obtained from the tests indicate that these materials could achieve V-0 grade (Table 4). Compared with the pristine ABS, the flame retardancy of the nanocomposites is significantly improved. The reasons are summarised as follows:

(i) the addition of OMMT lowers the HRR of the nanocomposites
(ii) the addition of OMMT and TPP improve thermal stability of the nanocomposites
(iii) TPP prevents decomposition of the polymer matrix
(iv) both exfoliated and intercalated structures of OMMT layers act as gas barrier.

Conclusions

The basal spacing of OMMT increased from 1.46 nm of pristine MMT to 2.69 nm. The ABS/OMMT and ABS/OMMT/TPP nanocomposites were prepared by melt blending ABS with OMMT. The char residue was increased by 4-6% for ABS/OMMT and 8-3% for ABS/OMMT/TPP nanocomposites at 600°C. The reduction rates of the peak HRR of ABS/OMMT nanocomposites (containing 5% OMMT) and ABS/OMMT/TPP nanocomposites (containing 4% OMMT and 10% TPP) were 47-3 and 57-3% respectively. The total released heat decreased by about 10 and 17%, while the mass loss rate decreased by about 41 and 53% respectively, as compared with the pristine ABS. The LOI values of ABS/OMMT and ABS/OMMT/TPP nanocomposites increased to 22-8 and 28% from 18% pristine ABS. Vertical burning tests (UL-94V) indicated that the nanocomposites could achieve V-0 grade. The LOI value and UL-94 result of ABS/OMMT/TPP are very close to those of ABS containing Sb2O3 and brominated materials. Taking into account the environmental impact, fire retardant ABS/OMMT nanocomposites are more promising for future applications.

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References