SYNERGISTIC FLAME RETARDANT EFFECT OF ATTAPULGITE ON PP/APP/PER COMPERSITES

XQ Su, J Tao *, YW Yi, YH Cui, Q Wang
College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing, PR China.
*Corresponding author(taojie@nuaa.edu.cn)

Keywords: flame retardant; PP; Attapulgite; IFR; Thermal stability

1 Introduction
Polypropylene are widely used in many applications owing to its excellent mechanical properties and low cost. However, polypropylene is highly flammable at room temperature. Halogenated organic compounds are broadly used as effective flame retardants for most polymeric materials [1]. But the release of halogen acids, metal halides and some high toxic products during combustion causes serious environmental problems and human hazards [2]. Thus, low toxic environmental friendly flame retardants have attracted more and more interest from both scientists and engineers in recent years. Among them, intumescent flame retardants (IFR) are efficient in reducing the flammability of polypropylene (PP). In general, a typical intumescent flame retardant (IFR) system mainly consists of three components, namely an acid source, a carbonization agent and a blowing agent [3,4]. The association of an ammonium polyphosphate (APP) and the pentaerythritol (PER) has been shown to be an efficient fire-retardant (FR) intumescent system for polyolefinic materials. Moreover, synergistic agents such as montmorillonite [5], zeolite [6], zinc borate [7] and other inorganic fillers [8] have been used in IFR (APP/PER) system to gain the more effective flame retardancy. Clay is reported to enhance the flame retardancy which makes it the first selected candidate for a potential flame retardant [9-11]. In this work, supported attapulgite (ATP) as a synergistic agent was used to improve flame retardancy of APP/PER mixture in PP matrix. Fourier transformed infrared spectroscopy (FTIR) was used to identify the composition of the pyrolytic char at about 600°C, which can explain how this synergistic effect happened. The flame retardant properties and thermal stability of the materials were evaluated by UL-94 standard, LOI, and TGA, and a analysis for the mechanism of char formation was studied.

2 Experimental

2.1 materials
The polypropylene (PP) with the trade name of 140-2 used was supplied by Wuhe plastics Co., Ltd (nanjing, China). Ammonium polyphosphate (APP) was supplied by Zhenjiang Xingxing Flame-retardant Co., Ltd ( Zhenjiang ,China). Pentaerythritol (PER, AR grade) was bought from Lingfeng chemical reagent Co., Ltd, (Shanghai, China). Attapulgite(ATP) was purchased from Nanjing mining Co., Ltd (Nanjing, China). The maleic anhydride-graft-polypropylene copolymer (denoted as PP-g-MAH) was provided by Huada science and technology development Co., Ltd(Nanjing, China).

2.2 Preparation of PP composites
PP composites were prepared using the CM reciprocating single-screw extruder (CM-30). Their compositions are listed in Table 1. The resulting compounds were subsequently dried in a oven and were further injection molded into bars with an injection molding machine (HTF86X1) for fire properties characterizations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (wt%)</th>
<th>IFR (wt%)</th>
<th>ATP (wt%)</th>
<th>PP-g-MA (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP/ATP</td>
<td>74</td>
<td>26</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>PP/IFR</td>
<td>74</td>
<td>26</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>

Note ( IFR: APP/PER= 3/1, by weight)
2.3 Characterization and testing

The limited oxygen index (LOI) was measured on a HC-2 oxygen index meter (Jiangning, China) with sheet dimensions of 130×6.5×3mm, according to GB 2406 standard. The vertical burning test was carried out on a CFZ-3-type instrument (Jiangning Analysis Instrument Company, China) according to the UL 94 test standard. The specimens used were of dimensions 130×13×3mm. Thermogravimetric analysis (TGA) was carried out under nitrogen at a heating rate of 10 ℃/min by means of a Pyris 1 TGA thermal analyzer. The samples of intumescent char were taken after burning the PP composites in a crucible at 600 ℃ under air, and the char composition was pelletized with KBr and characterized by FTIR spectrometer (NEXUS 670). The char surface was observed by means of scanning electron microscopy (SEM, JEOL JSM-700F).

3 Results

3.1 Fire retardant properties

The effect of ATP on the flame retardancy of the PP/IFR composites is shown in Table 2. The results indicate that, whatever containing ATP or APP/PER (IFR), the PP composites do not possess good flame retardancy even at 26wt% additive level. The ATP used in FR intumescent systems leads to a synergistic effect on the fire-proofing performances. Therefore compare with PP/ATP or PP/IFR composites, PP/IFR/ATP composites have a bigger LOI value at the same additive loading with V-0 of UL 94 ratings.

Table 2. The LOI values UL 94 testing results of flame retarded PP composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>LOI</th>
<th>UL-94 rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PP</td>
<td>18</td>
<td>No rating</td>
</tr>
<tr>
<td>PP/ATP</td>
<td>22</td>
<td>No rating</td>
</tr>
<tr>
<td>PP/IFR</td>
<td>30</td>
<td>No rating</td>
</tr>
<tr>
<td>PP/IFR/ATP</td>
<td>32</td>
<td>V-0</td>
</tr>
</tbody>
</table>

3.2 Thermal stability

Fig. 1 shows the TG curves of PP/ATP, PP/IFR and PP/IFR/ATP in nitrogen atmosphere. The data of char residue and onset and final decomposition temperatures are summarized in Table 3. For PP/ATP, a one-step decomposition was found at 350-500 ℃ under nitrogen. PP/ATP started to decompose at 384 ℃. A larger residue shows an enhanced thermal stability due to the barrier properties of clay layers. For IFR samples (PP/IFR and PP/IFR/ATP), a two step degradation (260-320 ℃ and 370-520 ℃, respectively) was found. The onset temperature of the first degradation decreased to a lower temperature compared with that of PP/ATP. The first step degradation was caused by the decomposition of IFR and release of gaseous products \[^{[12,13]}\]. The breakdown of carbonaceous char led to the second step degradation. The earlier degradation step was nearly absent which might be attributed to the integration of initial decomposition of fire retardants and PP that had similar T\(_{\text{onset}}\).\[^{[9,14,15]}\]

Fig.1 TGA curves for PP/IFR, PP/ATP and PP/IFR/ATP at a heating rate of 10 ℃/min in N\(_2\).

A significant change in thermal stability was found for PP/IFR/ATP. When ATP was introduced into the IFR flame retarded PP systems, the value of T\(_{\text{max}}\) was almost 6 ℃ higher than that of PP/IFR composites, indicating a thermal enhancing effect on flame retarded PP.

Table 3. TGA thermograms of PP and its flame retarded composites in N\(_2\) at 10 ℃/min

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(_{\text{onset}}) (℃)</th>
<th>T(_{\text{max}}) (℃)</th>
<th>Residue at 600 ℃ (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/ATP</td>
<td>384</td>
<td>441.9</td>
<td>21.4</td>
</tr>
<tr>
<td>PP/IFR</td>
<td>325</td>
<td>465.7</td>
<td>13.1</td>
</tr>
<tr>
<td>PP/IFR/ATP</td>
<td>329</td>
<td>471.8</td>
<td>13.6</td>
</tr>
</tbody>
</table>
The final char for PP/IFR/ATP composites has the value of 13.6%, which is higher than that of PP/IFR composites. The above results suggest that the synergistic effect does exist between ATP and IFR. The appearance of ATP can promote the composite to form a more thermally stable barrier to prevent heat and gas transformation, can significantly enhance the thermal stability of flame retarded PP systems and the char formation. And it is further evidenced by the FTIR results to be discussed in Section 3.3.

### 3.3 Characterization of char residue

To further analyze how the ATP affects the formation of intumescent char, FTIR spectroscopy was used to analyze the char composition of PP/IFR, PP/ATP, and PP/IFR/ATP composites. The FTIR spectrum of the intumescent residual char for all PP composites is given in Fig. 2. For PP/ATP composites, the absorption at 1036 cm\(^{-1}\) and 1647 cm\(^{-1}\) are ascribed to vibration of Si–O and C=C stretching, respectively \([16,17]\). It shows that the char residue has almost no hydrocarbon absorption and contains a great amount of layered silicates.

As for PP/IFR composites, the broad peak at 2705 to 2500 cm\(^{-1}\) and the peak at 1159 cm\(^{-1}\) were attributed to the stretching vibration of P–OH\(^{[5,18-20]}\) and P=O groups \([5,21]\) respectively. The bands at 1005 cm\(^{-1}\) are attributed to stretching vibration of P-O-P \([22]\). The peak at 1636 cm\(^{-1}\) also present the absorption of C=C stretching of aromatized chars. It indicates that PP-IFR systems without ATP can form a good char structure, which can effectively protect the PP matrix below the char layer during combustion. For PP/IFR/ATP composites, we can see that the characteristic absorption peak at 1185 cm\(^{-1}\) related to P=O double bond stretching became apparent and moves gradually to a higher wave number(from 1160 cm\(^{-1}\) to 1185 cm\(^{-1}\)), when compared with those of the PP/IFR composites. The reason might be that the appearance of ATP can impel the esterification of the system and then promote the char formation. It has been reported that the complex crystallographic structure and habit of clay minerals result in some catalytic active sites. The active sites can catalyze the formation of a protective coat-like char on the nanocomposite. Moreover, the active sites can catalyze the dehydrogenation and crosslinking of polymer chains. Accordingly, the thermal-oxidative stability is improved\([23]\).

It can clearly be noted that the addition of ATP into the intumescent PP does not modify the degradation process of PP/IFR. The residue is mainly composed of polyphosphoric acid and aromatic species, and a magnesium orthophosphate and/or silico-phosphate is suspected to be formed, which may stabilize the char structure\([24]\).

From foregoing investigations, it can be noted that a structure with a relatively strong charred layer is important \([25]\) to minimize the heat transfer and provide good protection for the substrate. In order to elucidate how the formation of intumescent char affects the combustion of the flame retarded PP composites, the char morphologies left after pyrolyse in a muffle at 600°C for 30min were examined by taking photographs with a digital camera and the microstructures of the residues were investigated with SEM.

Fig. 4 are digital photos of residues of PP/IFR and PP/IFR/ATP respectively. For PP/IFR, a char layer with many flaws in the surface was formed. As for PP/IFR/ATP, the surfaces of both char residues were continuous and compact and no cracks were observed.

Fig.5 shows different morphologies of the chars for PP/IFR and PP/IFR/ATP. Compare with PP/IFR, PP/IFR/ATP showed a denser and more compact char layer. Thus the barrier effect of ATP together with the intumescent shield of IFR prompt more integrate char’s formation and the thermal stability is increased accordingly.
Conclusions

In summary, we have found that the combination of ATP with IFR system based on APP and PER exhibited an evident synergistic effect in the flame retardancy of PP. The LOI value of PP/IFR systems increased from 30 to 32 and raised UL-94 rating from no rating to V0 via adding ATP. FTIR spectra of the residue chars indicated final char were almost polyphosphoric acid, ATP could impel the esterification but it could not change the degradation process. Macro and micro images further explained that ATP helped form a more integrated char structure. The active sites on ATP could catalyze the dehydrogenation, and charring of the composites. The more dense and compact protective coat-like char should be responsible for the delay of thermal-oxidative degradation of PP composites.
Acknowledgments

The authors gratefully acknowledge Ford URP Project (Preparation and properties of thermoplastics modified by nanomaterials for injection molded auto parts) and “Peak of six major human resources plan” of Jiangsu province (Preparation of halogen-free FR PP with high impact grade and low smell for cars) for financial supports.

References


