Effect of flame retardants on flame retardant, mechanical, and thermal properties of sisal fiber/polypropylene composites

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A flame retardant efficiency of flame retardants; ammonium polyphosphate (APP), magnesium hydroxide (Mg(OH)₂), zinc borate (Zb), and combination of APP with Mg(OH)₂ and Zb in sisal fiber/polypropylene (PP) composites was investigated using a horizontal burning test and a vertical burning test. In addition, maleic anhydride grafted polypropylene (MAPP) was used as a compatibilizer to enhance the compatibility between fiber and matrix resulting in improved flame retardancy and thermal stability of the PP composites without deterioration of their mechanical properties. APP and combination of APP with Zb effectively enhanced flame retardancy of the PP composites. No synergistic effect was observed when APP was used in combination with Mg(OH)₂. SEM micrographs of PP composites revealed good distribution of flame retardants in PP matrix and good adhesion between sisal fiber and PP matrix.

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1. Introduction

Natural fiber reinforced polymer composites (NFCs) have received much interest in terms of their industrial applications due to environmental and economical concerns. The advantages of natural fibers are lightweight, high specific strength, low cost, biodegradability, and absence of toxic by-products [1–4]. Among various polymer matrices, polypropylene (PP) has been widely used to produce NFCs because of its low density, low cost, high water resistance, chemical resistance, and ease of processing.

Due to the poor interfacial adhesion between hydrophilic natural fiber and hydrophobic PP matrix, compatibilizers can be added to improve the compatibility between fiber and matrix resulting in the enhancement of the mechanical properties of the composites. Generally, maleic anhydride grafted polypropylene (MAPP) is used as an effective compatibilizer for natural fiber/PP composites [5–8].

Another drawback of NFCs is their high flammability. For some applications such as household goods, it may need to improve this performance. Flammability of NFCs can be reduced by introducing flame retardants into NFCs [9–14]. Since there are environmental concerns about the use of halogenated compounds, halogen free flame retardants become increasing popular. Ammonium polyphosphate (APP) is conventionally used phosphorous flame retardants. They react with the carbonaceous compound to form the char as an insulating protective layer which prevents further flame spread [15]. Magnesium hydroxide (Mg(OH)₂) is widely used metal hydroxide flame retardants. They provide effective flame retarding effects by producing char insulating layer and releasing water at about 360 °C [9]. Boron compounds such as zinc borate (Zb) decompose endothermically and releases water at about 320 °C [15].

The effectiveness of the flame retardants can be improved by the synergistic effect. The combination of APP and Zb in PP leads to an improvement of the fire behavior [15]. The addition of boron compounds enhances the flame retardant properties of intumescent PP composites [16]. Moreover, zinc borate exhibits a synergistic effect on the flame retardancy of PP intumescent composites [17].

The objective of this study was to investigate the uses of APP, Zb, and Mg(OH)₂ as flame retardants and Zb or Mg(OH)₂ as synergists with APP on flame retardancy, thermal, mechanical, and morphological properties of sisal fiber/PP composites.

2. Experimental

2.1. Materials

A commercial grade of isotactic PP (700J) was supplied by Thai Polypropylene Co., Ltd. Maleic anhydride grafted polypropylene (MAPP, Fusabond® P MZ 109D, DuPont) was supplied by Chemical Innovation Co., Ltd. Sisal fiber (Agave sisalana) was purchased from Sisal-Handicraft OTOP Group, Tambon Ban Kao, Amphur Dan Khun Thod, Nakhon Ratchasima, Thailand. Sisal fibers were cut into an approximate length of 2 mm then dried in an oven at 60 °C.

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overnight. Ammonium polyphosphate (APP, Exolit AP 765, Clariant, average diameter of 8 μm) was supplied by Clariant Chemical (Thailand), Co., Ltd. Zinc borate (Zb, Firebrake® ZB, Rio Tinto Mineral, average diameter of 9 μm) was purchased from Global Connections Public Co., Ltd. Magnesium hydroxide (Mg(OH)₂, APYMAG® 40, Nabaltec AG, average diameter of 5 μm) was provided by Behn Meyer Chemical Co., Ltd.

2.2. Composite preparation

The composites were prepared using an internal mixer (Haake Rheomix, 3000p). The rotor speed was 50 rpm, the mixing temperature was 170 °C, and the total mixing time was 13 min. The test specimens were molded by an injection molding machine (Chuan Lih Fa, CLF 80T). Designation and composition of PP composites are listed in Table 1.

2.3. Characterization

2.3.1. Flammability

Flammability of PP and PP composites were studied by a horizontal burning test and a vertical burning test according to ASTM D635 and ASTM D3801, respectively.

For the horizontal burning test, the specimen was held horizontally and a flame was applied to one end of the specimen. The time for the flame to reach from the first reference mark (25 mm from the end) to the second reference mark, which was at 100 mm from the end, was recorded. Then, burning rates of the composites were calculated as follows:

\[ V = \frac{60L}{t} \]  

where \( V \) is the burning rates (mm/min), \( L \) is burned length (mm), and \( t \) is the time of burning (s).

For the vertical burning test, the specimen was held vertically, a flame was applied for 10 s and then removed. The time was recorded. The lowest flame retardancy rating is V-2 (flaming time \( \leq 30 \) s and cotton indicator ignited by flaming particles or drops) and V-0 (no dripping, flaming time reduced (\( \leq 10 \) s) representing a strongly flame retarded material, while V-1 (flaming time \( \leq 30 \) s) is intermediate term between V-0 and V-2. The flammable materials which cannot be classified according to this method are marked with code NC (no classification, complete combustion of the specimen).

Limiting oxygen index (LOI) of PP and PP composites were measured by an in house LOI tester according to ASTM D2863.

2.3.2. Thermal properties

Thermal behaviors of PP and PP composites were examined using a thermogravimetric analyzer (TGA, Mettler Toledo, TGA/DSC 1). Thermal decomposition temperature of each sample was examined under a nitrogen atmosphere, in a temperature range of 30–700 °C and at a heating rate of 20 °C/min.

2.3.3. Mechanical properties

Tensile properties of PP and PP composites were tested by following ASTM D638 using a universal testing machine (UTM, Instron 5565) with a load cell of 5 kN, a crosshead speed of 50 mm/min, and a gauge length of 80 mm.

Unnotched Izod impact test of PP and PP composites were performed according to ASTM D256 using an impact testing machine (Atlas, BPI).

2.3.4. Morphological properties

A scanning electron microscope (SEM, JEOL model JSM6400) was employed to examine morphology of tensile fracture surfaces of PP composites. The specimen was coated with gold before analysis.

3. Results and discussion

3.1. Flammability

Horizontal burning and vertical burning results of PP and PP composites are shown in Table 2. PP/30sisal composite gave the highest burning rate and showed completed combustion (NC). This

![Fig. 1. TGA thermograms of PP and PP composites.](image)

<table>
<thead>
<tr>
<th>Designation</th>
<th>PP (phr)</th>
<th>Sisal fiber (phr)</th>
<th>APP (phr)</th>
<th>Mg(OH)₂ (phr)</th>
<th>Zb (phr)</th>
<th>MAPP (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP/30sisal</td>
<td>100</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>PP/30sisal/40APP</td>
<td>100</td>
<td>30</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>PP/30sisal/40Mg</td>
<td>100</td>
<td>30</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>PP/30sisal/40Zb</td>
<td>100</td>
<td>30</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>PP/30sisal/30APP/10Mg</td>
<td>100</td>
<td>30</td>
<td>30</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>PP/30sisal/30APP/10Zb</td>
<td>100</td>
<td>30</td>
<td>30</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
</tbody>
</table>

Due to the limitation of the LOI instrument, LOI of PP/30sisal composite was lower than 19%.

Table 2

<table>
<thead>
<tr>
<th>Designation</th>
<th>Horizontal burning rate (mm/min)</th>
<th>Vertical burning rating</th>
<th>Limiting oxygen index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>24.60 ± 1.02</td>
<td>NC</td>
<td>20</td>
</tr>
<tr>
<td>PP/30sisal</td>
<td>29.29 ± 0.83</td>
<td>NC</td>
<td>&lt;19*</td>
</tr>
<tr>
<td>PP/30sisal/40APP</td>
<td>No burning</td>
<td>V-0</td>
<td>31</td>
</tr>
<tr>
<td>PP/30sisal/40Mg</td>
<td>16.75 ± 0.07</td>
<td>NC</td>
<td>24</td>
</tr>
<tr>
<td>PP/30sisal/40Zb</td>
<td>27.95 ± 0.25</td>
<td>NC</td>
<td>22</td>
</tr>
<tr>
<td>PP/30sisal/30APP/10Mg</td>
<td>15.02 ± 0.71</td>
<td>NC</td>
<td>24</td>
</tr>
<tr>
<td>PP/30sisal/30APP/10Zb</td>
<td>No burning</td>
<td>V-0</td>
<td>30</td>
</tr>
</tbody>
</table>

* Due to the limitation of the LOI instrument, LOI of PP/30sisal composite was lower than 19%.
indicated that addition of sisal fiber increased flammability of PP composites. On the other hand, adding flame retardants; i.e. APP, Mg(OH)\textsubscript{2}, Zb, APP/Mg(OH)\textsubscript{2}, and APP/Zb, into sisal fiber/PP composites slowed down the burning rate of the PP composite. This suggested that flame retardants improved flame retardancy of the PP composites. Among three types of flame retardants, APP exhibited the most effective improvement of flame retardancy of the PP composites.

In this study, Zb and Mg(OH)\textsubscript{2} were used as synergists with APP in sisal fiber/PP composites. From Table 2, PP/30sisal/30APP/10 Mg composite burned under the horizontal burning test and was classified as NC in the vertical burning test. Mg(OH)\textsubscript{2} exhibited no synergistic effect on the flame retardancy when it used with APP. However, sisal fiber/PP composite containing combination of APP with Zb did not burn under the horizontal test condition and was classified as V-0 in the vertical burning test. Incorporating APP and combination of APP with Zb remarkably enhanced flame retardancy of the PP composites. From the results, PP/30sisal/30APP/10Zb composite gave comparable flame retardancy to PP/30sisal/40APP composite. However, using a combination of 30 phr APP with 10 phr Zb, total cost of the flame retardants can be reduced.

Limiting oxygen index (LOI) measures the minimum oxygen concentration required to support continuous of a sample. Therefore, according to the LOI test, a high flame retardancy material needs high oxygen to burn and presents high LOI. LOI of PP and PP composites are listed in Table 2. PP/30sisal composite had lower LOI than that of PP. This indicated that the adding sisal fiber made the PP more flammable. When flame retardants were incorporated into the PP composites LOI values were increased. This suggested that the flame retardants enhanced the flame retarding properties of the PP composites. PP/30sisal/40APP composite exhibited the highest LOI at 31%. It can be seen that PP/30sisal/30APP/10Zb composite gave LOI at 30% which was close to PP/30sisal/40APP composite. From the results, PP/30sisal/30APP/10Zb composite provided comparable flame retardancy to PP/30sisal/40APP composite. LOI results were in agreement with the burning results.

### 3.2. Thermal properties

TGA thermograms and thermal properties of PP and sisal fiber/PP composites with and without flame retardants are shown in

#### Table 3

<table>
<thead>
<tr>
<th>Designation</th>
<th>T\textsubscript{5%} (°C)</th>
<th>T\textsubscript{50%} (°C)</th>
<th>Char residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>408</td>
<td>458</td>
<td>0</td>
</tr>
<tr>
<td>PP/30sisal</td>
<td>308</td>
<td>461</td>
<td>4.31</td>
</tr>
<tr>
<td>PP/30sisal/40APP</td>
<td>322</td>
<td>474</td>
<td>12.25</td>
</tr>
<tr>
<td>PP/30sisal/40Mg</td>
<td>329</td>
<td>477</td>
<td>21.27</td>
</tr>
<tr>
<td>PP/30sisal/40Zb</td>
<td>320</td>
<td>466</td>
<td>23.60</td>
</tr>
<tr>
<td>PP/30sisal/30APP/10Mg</td>
<td>322</td>
<td>472</td>
<td>18.97</td>
</tr>
<tr>
<td>PP/30sisal/30APP/10Zb</td>
<td>316</td>
<td>472</td>
<td>19.54</td>
</tr>
</tbody>
</table>

#### Table 4

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Impact strength (kJ/m\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>18.67 ± 2.77</td>
<td>1.22 ± 0.44</td>
<td>74.70 ± 1.86</td>
</tr>
<tr>
<td>PP/30sisal</td>
<td>29.05 ± 0.96</td>
<td>2.08 ± 0.09</td>
<td>14.02 ± 0.52</td>
</tr>
<tr>
<td>PP/30sisal/40APP</td>
<td>28.43 ± 1.16</td>
<td>2.31 ± 0.05</td>
<td>10.49 ± 0.31</td>
</tr>
<tr>
<td>PP/30sisal/40Mg</td>
<td>29.92 ± 1.31</td>
<td>2.36 ± 0.11</td>
<td>11.22 ± 0.54</td>
</tr>
<tr>
<td>PP/30sisal/40Zb</td>
<td>32.62 ± 0.53</td>
<td>2.25 ± 0.10</td>
<td>12.96 ± 0.20</td>
</tr>
<tr>
<td>PP/30sisal/30APP/10Mg</td>
<td>28.86 ± 0.70</td>
<td>2.17 ± 0.06</td>
<td>10.72 ± 0.37</td>
</tr>
<tr>
<td>PP/30sisal/30APP/10Zb</td>
<td>28.66 ± 0.70</td>
<td>2.17 ± 0.06</td>
<td>10.72 ± 0.37</td>
</tr>
</tbody>
</table>
Fig. 1 and Table 3, respectively. PP had thermal decomposition temperature at 5% weight loss (T5%) and thermal decomposition temperature at 50% weight loss (T50%) at 408 and 458 °C, respectively with no char residue. The decomposition temperature below 100 °C of the PP/30sisal composite corresponded to the evaporation of moisture. The moisture content about 2% was observed. PP composites gave lower T5% than PP. This was because hemicelluloses in sisal fiber started to decompose at lower temperature when compared with the neat PP [10]. However, the presence of sisal fiber increased T50% of the PP. This may be because lignin, a chemical component in sisal fiber, acted as a char residue, which could increase the thermal decomposition temperature of the PP [11]. From Table 3, T5%, T50%, and char residue observed at 600 °C of the sisal fiber/PP composite significantly increased with addition of flame retardants. The char residue of PP/30sisal composite was 4.31%. When APP, Mg(OH)2, or Zb was added into the composites the char residue was 12.25%, 21.27%, and 23.60%, respectively. This indicated that flame retardants; i.e. APP, Mg(OH)2, Zb remarkable improved thermal stability of sisal fiber/PP composites. Adding Mg(OH)2 resulted in the PP composite having the highest T5%, T50%, and char residue. When compared with PP/30sisal/40APP composite, PP/30sisal/30APP/10Mg composite showed an increase in char residue and no change in T5%, T50%. The char residue of PP/30sisal/30APP/10Mg composite was 18.97%. Bourbigot et al. [18] reported that magnesium phosphate stabilizing phosphorous was formed during the interactions between APP and Mg(OH)2. The combination of APP and Mg(OH)2 provided a physical/thermal barrier protecting the substrate. This barrier was constituted of magnesium phosphate glass and MgO-like ceramic. In a case of PP/30sisal/30APP/10Zb composite, T5% and T50% were slightly lower than that of PP/30sisal/40APP composite. However, the char residue of the composite increased with adding Zb. The char residue of PP/30sisal/30APP/10Zb composite was 19.54%. This may be due to the reaction to produce zinc pyrophosphate which was believed to serve as an efficient intumescent char under high temperature of fire environment [15].

3.3. Mechanical properties

Stress–strain curves of PP and PP composites are displayed in Fig. 2. PP showed ductile behavior. With the addition of sisal fiber or flame retardants into PP, the tensile behavior changed to brittle. A significant decrease in strain was observed. Tensile strength and modulus of PP and PP composites are shown in Fig. 3 and their values are listed in Table 4. Sisal fiber/PP composite exhibited higher tensile strength and modulus than PP as illustrated in Fig. 3. The improvement of tensile strength and modulus of the PP composite were 56% and 71%, respectively. This indicated that sisal fiber is a good reinforcing filler for PP. The addition of APP and Mg(OH)2 showed insignificant effect on tensile strength and modulus of sisal fiber/PP composites but Zb improved tensile strength. This may be because Zb had rougher surface than APP and Mg(OH)2 as shown in
Fig. 5(b)–(d), respectively. Thus, it may promote mechanical interlocking between Zb and PP matrix. From the results, it was interesting to note that the flame retardants did not give the negative impact on the mechanical properties of sisal fiber/PP composites. In general, the incorporation of flame retardants into polymers or polymer composites can cause a reduction of mechanical properties [9,14,19]. Using combination of APP with Mg(OH)2 and APP with Zb exhibited no effect on tensile properties of the composites when compared with those of PP/30sisal/40APP composite.

Impact strength of PP and PP composites are shown in Fig. 4. Adding sisal fiber decreased impact strength of PP by 81%. This was because the fiber disturbed matrix continuity and each fiber and filler was a site of stress concentration, which acted as a micro-crack initiator [20]. The incorporation of flame retardants; i.e. APP, Mg(OH)2, Zb, APP/Mg(OH)2, and APP/Zb slightly reduced impact strength of sisal fiber/PP composites.

3.4. Morphological properties

SEM micrographs of tensile fracture surfaces of PP composites are shown in Fig. 5. The micrographs in Fig. 5(a) showed a good adhesion between sisal fibers and PP matrix. In addition, the micrographs in Fig. 5(b)–(h) revealed good distribution of APP, Mg(OH)2, and Zb in the PP matrix. This indicated that MAPM improved the compatibility between PP and fibers or flame retardants.

4. Conclusions

Incorporating flame retardants; i.e. APP, Mg(OH)2, Zb, APP/Mg(OH)2, and APP/Zb into sisal fiber/PP composites resulted in the improved flame retardancy and thermal stability of the PP composites without deterioration of their mechanical properties. The addition of APP or combination of APP with Zb remarkably enhanced flame retardancy of sisal fiber/PP composites. SEM micrographs of PP composites revealed good distribution of flame retardants in PP matrix and good adhesion between fibers and PP matrix.

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