

# The Dynamic Flammability and Toxicity of Magnesium Hydroxide Filled Intumescent Fire Retardant Polypropylene

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**ABSTRACT:** The flammability properties of an intumescent fire retardant polypropylene added with magnesium hydroxide was discussed in this study. To evaluate the flammability of the material, limit oxygen index, smoke emission, tensile strength, and our exploitation dynamic flammability evaluation system, tests were assessed in experiments. The results showed that the intumescent flame retardant ammonium polyphosphate-filled polypropylene has superior flammability properties but higher carbon oxide (CO) concentration and smoke density. By adding some magnesium hydroxide additives in intumescent fire retarded polypropylene, the smoke density and CO concentration decrease; and the compound also has superior fire properties. It is concluded that intumescent system and magnesium hydroxide additives are effective on improving combustion properties for polypropylene. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 989–995, 1998

**Key words:** intumescent; fire retardant; flammability; toxicity; polypropylene

## INTRODUCTION

Polypropylene (PP) is used in many applications, for example, in cars, furniture, electronic pieces, electric shells, interior decorations, insulation, architectural material, and so on. However, it has a number of fateful defects, including its emission of smoke and poisonous gas while burning. These drawbacks restrict the range of its field of application. Therefore, it should be an important task to reduce the emission of smoke, poisonous gases, and so on.

In tradition, the halogenated organic compounds were well-known fire retardant additives for PP.<sup>1–2</sup> They were generally used in conjunction with antimony trioxide compounds to enhance their fire retardant efficacy (halogen–metal synergistic effect). On burning, they generally evolve

halogen acids and metal halides. However, their proven efficacy as fire retardant is balanced against their known potential effect in increasing the formation of toxic gases and corrosive smokes. It had recently been reported that some currently used brominated aromatic fire retardant may form highly toxic brominated dibenzodioxines and dibenzofurans while burning.<sup>3–4</sup> In the search for halogen-free fire retardant, there is increasing attention on the intumescent and metallic hydroxide fillers.

The intumescent fire retardant, while burning, gives a swollen multicellular char, which protects the underlying material from the action of the fire. This approach was derived from coating for the protection of structures. The coating material is an incorporation of intumescent additives in polymeric material. This method had been used for more than 40 years.<sup>5</sup> The mechanism of fire retardant is assumed that the char acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing pyrolysis of the mate-

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**Table I The Compositions of PP-FR Resins**

|                           | PP  | PMA <sub>00</sub> | PMA <sub>10</sub> | PMA <sub>30</sub> | PMA <sub>50</sub> | PMA <sub>70</sub> |
|---------------------------|-----|-------------------|-------------------|-------------------|-------------------|-------------------|
| PP (phr)                  | 100 | 100               | 100               | 100               | 100               | 100               |
| APP (phr)                 | —   | 23                | 23                | 23                | 23                | 23                |
| PE (phr)                  | —   | 14                | 14                | 14                | 14                | 14                |
| Melamine (phr)            | —   | 13                | 13                | 13                | 13                | 13                |
| Mg(OH) <sub>2</sub> (phr) | —   | —                 | 10                | 30                | 50                | 70                |

rial to volatile combustible products.<sup>6-7</sup> Ammonium polyphosphate (APP) is most used as the acid source in intumescent systems. While heating, its forming polyphosphoric acid is a well-known acid catalyst for organic reactions.

In metallic hydroxide fillers, the magnesium hydroxide [Mg(OH)<sub>2</sub>] is a considerable acid- and halogen-free fire retardant additive for polymers,<sup>8</sup> which has a smoke-suppressing capability. The effectiveness of this widely used fire retardant depends on the following factors.<sup>9-10</sup>

1. The endothermic decomposition release water of hydration from the substrate retards the rate of thermal degradation.
2. The accompanying release of inert gases (water vapor) dilutes the fuel supply present in the gas phase.
3. The relatively higher heat capacity of the fire retardant reduces the thermal energy available to degrade the substrate.
4. The decomposition products may insulate the substrate from the heat source.

Its temperature of decomposition is near 350°C, making certain its incorporation with a wide-range of polymers, including PP.<sup>11</sup>

According to the above analysis, the intumescent additives and Mg(OH)<sub>2</sub> were adopted as the fire retardant for PP in this study. In the experiment, we prefer that the test device should be able to simulate the properties of the burned material in an atmosphere environment. It should also be able to analyze the physical and chemical effects invoked by the burning. However, the older test methods almost invariably supply a qualitative pass-fail output. They are of little use in the

study of the material combustion's mechanism, which is important for the development of fire retardant materials. Therefore we referred to ISO 5660<sup>12</sup> and ASTM-E-1354<sup>13</sup> and developed a combustion evaluation machine, which is named the "dynamic flammability evaluation system".<sup>14</sup> This system can record mass loss rate, heat release rate, toxic gases, and other combustion properties in real time. The heat release rate (HRR) during combustion is generally considered to be one of the most important parameters for characterizing the combustion behavior of organic materials. On the other hand, the limit oxygen index (LOI), smoke emission properties, and mechanical properties are also evaluated in this study by experiment.

## EXPERIMENT

### Materials

The following products were used in the experiment: Isotactic polypropylene (PP, Pro-Fax 366); hydroxide magnesium [Mg(OH)<sub>2</sub>]; Star Brand 100, 90% < 0.85 μm); ammonium polyphosphate (APP, 90% < 0.6 μm); pentarythriol (PE, 90% < 1 μm); melamine (ME, 90% < 0.5 μm).

These fillers are added to PP by mixing in a Brabender at 200°C. Specimens for traditional combustion test (LOI, smoke density) and slabs (100 × 100 mm<sup>2</sup>, 3 mm thick) for burning in the dynamic flammability evaluation system were prepared by hot pressing at 100 kg/cm<sup>2</sup> at 200°C. The various samples made from PP and fire retardant are given in Table I, where parts per hundred parts of resin (phr) is the unit often used

**Table II The Limit Oxygen Index of PP-FR Resins**

|     | PP   | PMA <sub>00</sub> | PMA <sub>10</sub> | PMA <sub>30</sub> | PMA <sub>50</sub> | PMA <sub>70</sub> |
|-----|------|-------------------|-------------------|-------------------|-------------------|-------------------|
| LOI | 17.8 | 34.5              | 25.2              | 28                | 28.8              | 30.2              |

**Table III The Dynamic Flammability Parameters of PP-FR Resins**

| Material          | Heat Flux (kW/m <sup>2</sup> ) | TTI (s) | BP (%) | MLR (g/s) | Maximum HRR (kW/m <sup>2</sup> ) | Average HRR (kW/m <sup>2</sup> ) | THR (MJ/m <sup>2</sup> ) | EHC (MJ/kg) | Flash-Over Index |
|-------------------|--------------------------------|---------|--------|-----------|----------------------------------|----------------------------------|--------------------------|-------------|------------------|
| PP                | 50                             | 24      | 100    | 0.0617    | 687                              | 284                              | 119                      | 45          | 0.0349           |
| PMA <sub>00</sub> | 50                             | 36      | 94.2   | 0.0244    | 115                              | 70.6                             | 67.8                     | 28.8        | 0.313            |
| PMA <sub>10</sub> | 50                             | 36      | 90.8   | 0.0303    | 156                              | 87                               | 63.9                     | 29.1        | 0.231            |
| PMA <sub>30</sub> | 50                             | 43      | 80.4   | 0.0238    | 121                              | 69                               | 58.2                     | 28.4        | 0.355            |
| PMA <sub>50</sub> | 50                             | 43      | 77     | 0.0228    | 121                              | 65.3                             | 54.5                     | 28.6        | 0.355            |
| PMA <sub>70</sub> | 50                             | 44      | 71.3   | 0.0198    | 104                              | 57.5                             | 53.6                     | 28.9        | 0.423            |
| PP                | 25                             | 166     | 100    | 0.0321    | 412                              | 135                              | 105                      | 42.1        | 0.403            |
| PMA <sub>00</sub> | 25                             | 188     | 81.2   | 0.0109    | 65                               | 24.9                             | 46.3                     | 22.9        | 2.892            |
| PMA <sub>10</sub> | 25                             | 196     | 84     | 0.0129    | 79.5                             | 27.8                             | 45.1                     | 21.9        | 2.46             |
| PMA <sub>30</sub> | 25                             | 217     | 74.2   | 0.0138    | 68.8                             | 29.8                             | 39.3                     | 21.6        | 3.15             |
| PMA <sub>50</sub> | 25                             | 220     | 70.9   | 0.0135    | 57.3                             | 27.6                             | 36.4                     | 20.4        | 3.83             |
| PMA <sub>70</sub> | 25                             | 232     | 63.8   | 0.0121    | 54.3                             | 23.1                             | 31.2                     | 19.1        | 4.27             |

in industry.<sup>15</sup> For example, PP 100 phr with fire retardant 30 phr means 100 g PP mixed with 30 g of fire retardant additives.

## Test

### *Dynamic Flammability Evaluation System*

The dynamic flammability evaluation system was operated following the procedure defined in ISO 5660 under heat fluxes of 25 and 50/kW m<sup>2</sup>. This system can measure the flammability properties shown as follows.

- Time to ignition (TTI [s]): The time until the entire surface of the sample burns with a sustained luminous flame.
- Burning percentage (BP): the percentage of the mass lost during burn.
- Mass loss rate (MLR [g/s]): the ratio of the total mass loss over the total burning time.
- Heat release rate (HRR [kW/m<sup>2</sup>]): an instantaneous amount of heat release from material per surface area.
- Effective heat combustion (EHC [kJ/g]): the ratio of the total heat release over the total mass lost.
- Flash-over index (FOI): the ratio of TTI and maximum HRR.
- Carbon oxide (CO) concentration (CO [ppm]): the instantaneous concentration of CO during burning.

### *Limit Oxygen Index*

The minimum oxygen concentration required to sustain burning was measured on a specimen (120 × 6 mm<sup>2</sup>, 3 mm thick) held vertically in a Polymer Laboratory System HFTA II instrument referred to ASTM-D-2863.

### *Smoke Emission Properties*

Smoke evolution properties were determined by using a smoke chamber conforming to National Bureau of Standards specifications in smoldering conditions. This experiment was proceeded on a specimen (75 × 75 mm<sup>2</sup>, 3 mm thick) in a Polymer Laboratory System SN-2400 instrument following ASTM-E-662 specification. Its results are reported in terms of the specific optical density as function of time.

### *Mechanical Properties*

The tensile strength experiment was performed by ASTM D638 Type IV Material Test System (Corp. model MTS 810). The elongation rate was set at 20 mm min.

## RESULT AND DISCUSSION

### *Combustion Properties*

#### *Limit Oxygen Index*

The LOI of PP and fire retarded PP are listed in Table II. It can be seen that the LOI value of pure PP is very low (17.8). It means that PP is

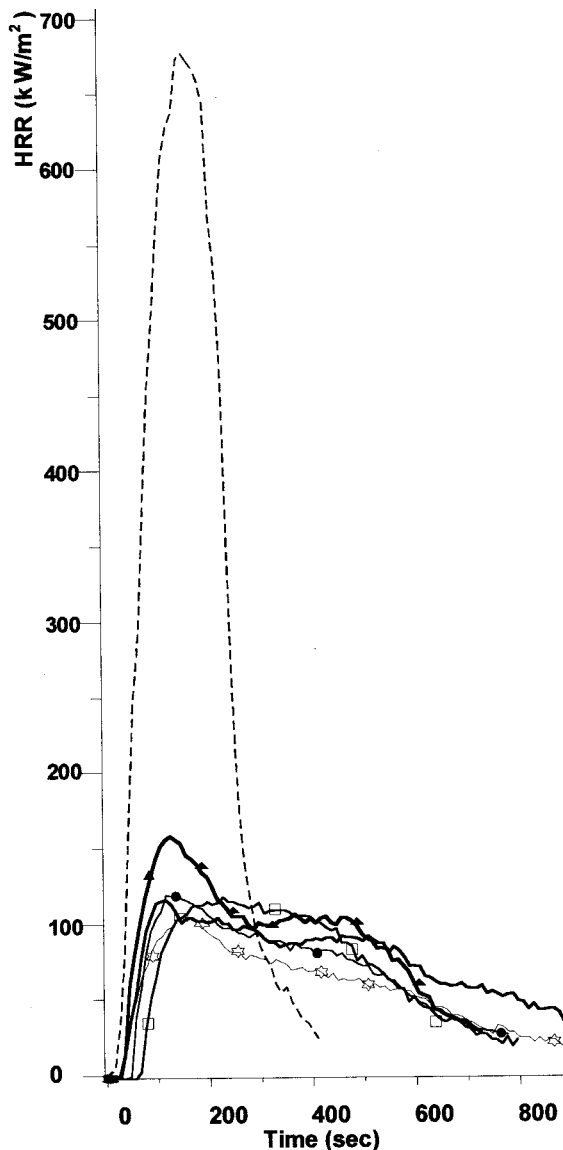
flammable. By adding APP in pure PP, the LOI value of PMA<sub>00</sub> is 34.5 and shows good protection for PP. This is because of the intumescent fire retardant interrupts burning by condensed phase. However, if 10 phr Mg(OH)<sub>2</sub> is added, PMA<sub>10</sub> shows a considerable decrease of the LOI value. It is evident that APP has better efficacy in flame retardancy than Mg(OH)<sub>2</sub>; but if more Mg(OH)<sub>2</sub> is added, the LOI value will raise again.

### Dynamic Flammability

All parameters of dynamic flammability are listed in Table III. Lower BP, MLR, maximum HRR, average HRR, THR, EHC, and higher TTI, flash-over index values indicate less fire hazard. The HRR during combustion is generally considered to be one of the most important parameters for characterizing the combustion behavior of organic materials. In this study, instantaneous HRR is calculated using the oxygen consumption principle.<sup>16</sup> The HRR curves of various samples under heat flux of 50 and 25 kW/m<sup>2</sup> are shown in Figures 1 and 2.

Table III indicates that pure PP has low resistance to combustion. With an addition of intumescent fire retardant, the maximum HRR of PMA<sub>00</sub> under heat flux of 50 kW/m<sup>2</sup> decreases from 687 to 115 kW/m<sup>2</sup>; and the THR and EHC also decrease markedly. It is because, while burning, a foamed multicellular char on the surface of the material makes a thermal insulation and provokes the extinguishment of the flame. It prevents combustible gases from feeding the flame and also separates oxygen from the burning material. When the material absorbs more heat, the carbonaceous char will break, and some heat will be released. The new carbonaceous char will generate immediately, and the phenomenon will occur repetitively. Therefore, the material decomposes in many steps on burning. It can be seen some steps in the heat release curves. Also, it is shown that PMA<sub>10</sub> is getting worse than PMA<sub>00</sub> in HRR. However, some flammability properties are superexcellent in Mg(OH)<sub>2</sub>-filled PP. The combustion properties will be improved if more Mg(OH)<sub>2</sub> is added.

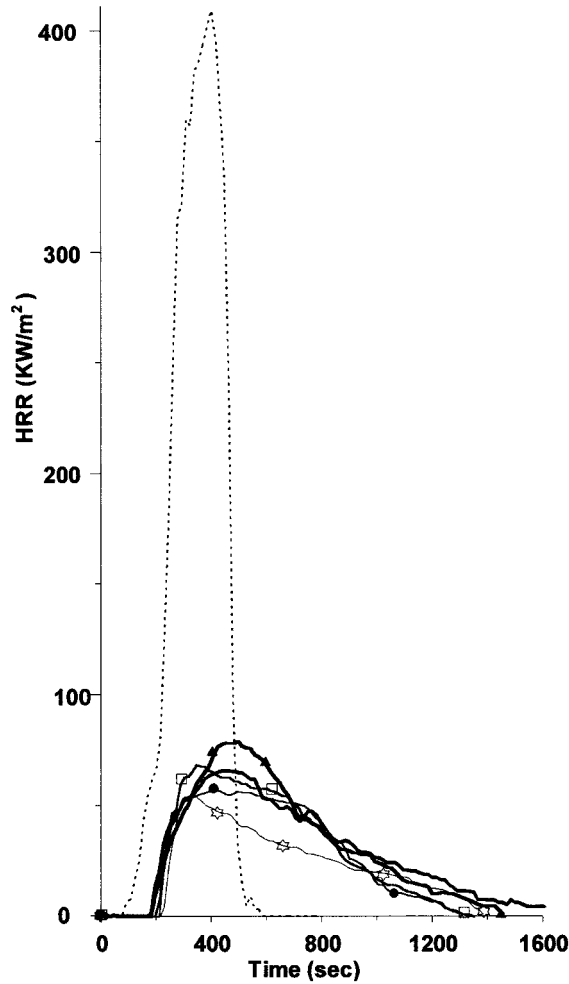
One of the characteristics of the dynamic flammability evaluation system is the measurement of the MLR (mass loss rate) and the BP (burning percentage) during the combustion test, which allows a mechanistic insight in the combustion process. By the addition of intumescent fire retardant in pure polyphosphate, under heat flux 50 kW/m<sup>2</sup>, the BP decreases from 100% (PP) to



**Figure 1** HRR versus time curve for PP-FR resin (50 kW/m<sup>2</sup>): (----) PP, (—) PMA<sub>00</sub>, (▲) PMA<sub>10</sub>, (□) PMA<sub>30</sub>, (●) PMA<sub>50</sub>, and (☆) PMA<sub>70</sub>.

94.2% (PMA<sub>00</sub>); and the MLR also decreases from 0.0617 to 0.0244 g/s. On the other hand, with the increase of the Mg(OH)<sub>2</sub>, the BP will conspicuously decrease; but the MLR will raise and then drop. It is evident that intumescent fire retardant is more effective than the Mg(OH)<sub>2</sub> on retarding material combustion.

FOI (flash-over index) may be the best individual indicator of overall fire hazard. From Table III, the FOI will arise, and the TTI (time to ignition) will be elongated. It is concluded that the



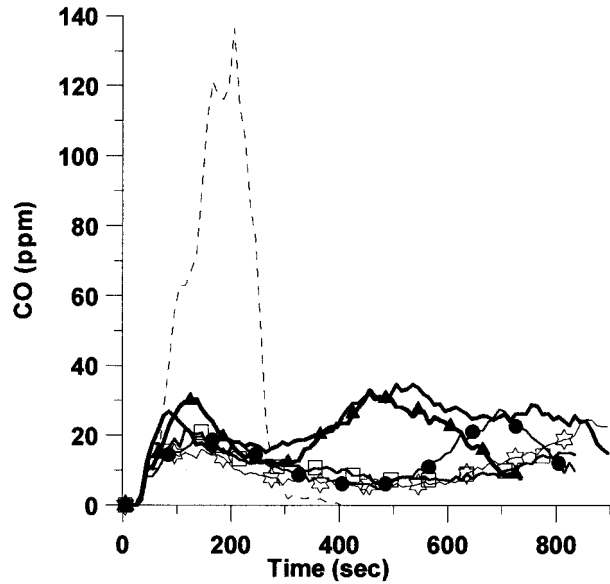
**Figure 2** HRR versus time curve for PP-FR resin ( $25 \text{ kW/m}^2$ ): (----) PP, (—) PMA<sub>00</sub>, (▲) PMA<sub>10</sub>, (□) PMA<sub>30</sub>, (●) PMA<sub>50</sub>, and (☆) PMA<sub>70</sub>.

fire retardant is effective in improving the flammability properties of PP.

**Toxicity**

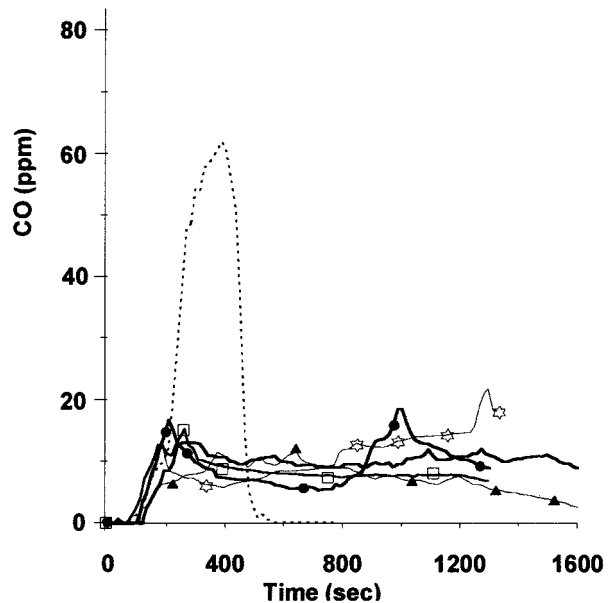
**CO Concentration**

The CO Concentration versus time chart for pure and fire retardant PP is shown in Figure 3 (under a heat flux of  $50 \text{ kW/m}^2$ ) and Figure 4 (under a heat flux of  $25 \text{ kW/m}^2$ ), and Table IV lists the maximum and average values of CO concentration. It is evident that the pure PP has much higher CO concentration than fire retardant PP, and the CO versus time curve of pure PP has a single peak only. With the retardant addition, the CO curve from a single peak increases to many



**Figure 3** CO concentration versus time curve for PP-FR resins ( $50 \text{ kW/m}^2$ ): (----) PP, (—) PMA<sub>00</sub>, (▲) PMA<sub>10</sub>, (□) PMA<sub>30</sub>, (●) PMA<sub>50</sub>, and (☆) PMA<sub>70</sub>.

peaks. Our explanation is the same as heat release mentioned before. When  $\text{Mg}(\text{OH})_2$  is added to the intumescent fire retardant PP, the maximum CO concentration will decrease once, then increase.



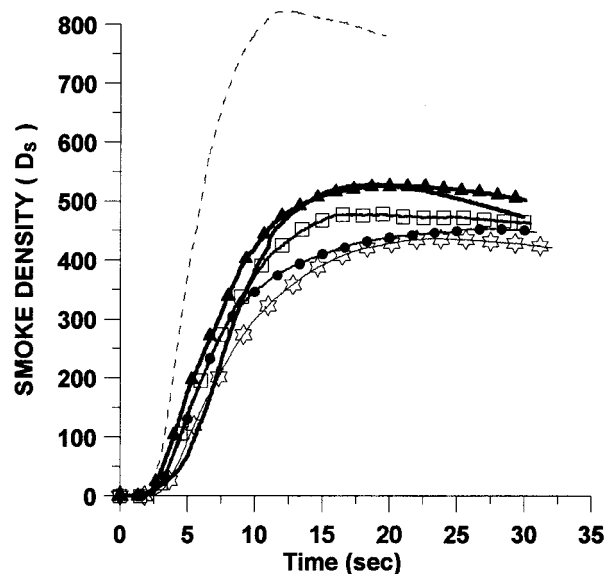
**Figure 4** CO concentration versus time curve for PP-FR resins ( $25 \text{ kW/m}^2$ ): (----) PP, (—) PMA<sub>00</sub>, (▲) PMA<sub>10</sub>, (□) PMA<sub>30</sub>, (●) PMA<sub>50</sub>, and (☆) PMA<sub>70</sub>.

**Table IV The Toxicity and Tensile Strength of PP-FR Resins**

| Material          | Heat Flux (kW/m <sup>2</sup> ) | Maximum CO (ppm) | Average CO (ppm) | Maximum Smoke Density ( $D_m$ ) | Time to $D_s = 16$ (min) | Strength (Pa) |
|-------------------|--------------------------------|------------------|------------------|---------------------------------|--------------------------|---------------|
| PP                | 50                             | 143              | 41.6             | 822                             | 2.13                     | 20.91         |
| PMA <sub>00</sub> | 50                             | 35.2             | 20.4             | 528                             | 2.63                     | 13.98         |
| PMA <sub>10</sub> | 50                             | 33.3             | 19.1             | 526                             | 2.7                      | 13.45         |
| PMA <sub>30</sub> | 50                             | 22.3             | 11.2             | 478                             | 2.86                     | 12.76         |
| PMA <sub>50</sub> | 50                             | 27.6             | 11.6             | 453                             | 2.93                     | 11.50         |
| PMA <sub>70</sub> | 50                             | 25.4             | 10.7             | 436                             | 3.36                     | 10.84         |
| PP                | 25                             | 63.2             | 17.9             | —                               | —                        | —             |
| PMA <sub>00</sub> | 25                             | 14.5             | 9.64             | —                               | —                        | —             |
| PMA <sub>10</sub> | 25                             | 12.3             | 12.3             | —                               | —                        | —             |
| PMA <sub>30</sub> | 25                             | 14.5             | 14.5             | —                               | —                        | —             |
| PMA <sub>50</sub> | 25                             | 19.3             | 19.3             | —                               | —                        | —             |
| PMA <sub>70</sub> | 25                             | 22.1             | 22.1             | —                               | —                        | —             |

### Smoke Emission Properties

The specific optical density of smoke ( $D_s$ ) experiments were done under smoldering test conditions. The results are shown in Figure 5 and Table IV. From these results, it can be seen that PP is a high-smoke polymer (maximum  $D_s = 822$ ). Experiments showed that retardant additives not only reduce the overall level of smoke generated but also delay the onset of detection smoke. It is concluded that increasing the amount of



**Figure 5** Specific optical density of smoke versus time curve for PP/FR resins: (----) PP, (—) PMA<sub>00</sub>, (▲) PMA<sub>10</sub>, (□) PMA<sub>30</sub>, (●) PMA<sub>50</sub>, and (☆) PMA<sub>70</sub>.

Mg(OH)<sub>2</sub> can reduce the overall level of smoke generated. This is because the metallic hydroxide reacts with decomposed hydrocarbon species.

### Mechanical Properties

Table IV lists the results of tensile strength tests. It is evident that adding too much filler to PP will effect its inherent superior mechanical property. If we add 70 phr Mg(OH)<sub>2</sub> to intumescent fire retardant PP (PMA<sub>70</sub>), the tensile strength will decrease approximately 49%, from 20.91 to 10.84 Pa.

### CONCLUSION

It is evident that the intumescent fire retardant PP has superior flammability, especially in LOI and HRR, although it has a high value of CO concentration and smoke density. By adding the amount of Mg(OH)<sub>2</sub> filler in intumescent fire retardant PP, the smoke density and CO concentration decrease, and the TTI is elongated; but if too much Mg(OH)<sub>2</sub> is added to the compound, the tensile strength decreases quickly. It is also an important factor should be considered on material.

Also, it is shown that our exploitation, the dynamic flammability evaluation system, is a very promising and useful tool for mechanistic analysis on the combustion phenomenon of polymer material.

## NOMENCLATURES

|       |   |
|-------|---|
| FR    | fire retardant                            |
| TTI   | time to ignition                          |
| BP    | burning percentage                        |
| MLR   | mass loss rate                            |
| HRR   | heat release rate                         |
| THR   | total heat release rate                   |
| EHC   | effective heat combustion                 |
| FOI   | flash-over index                          |
| LOI   | limit oxygen index                        |
| $D_s$ | specific optical density of smoke         |
| $D_m$ | maximum specific optical density of smoke |

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