

## Enhanced Fire Behavior of Rigid Polyurethane Foam by Intumescent Flame Retardants

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**ABSTRACT:** Using expandable graphite (EG) and ammonium polyphosphate (APP) as flame retardants, we prepared two series of polyisocyanurate–polyurethane (PIR–PUR) foams (i.e., EG foams filled with different amounts of EG alone and APEG foams containing different amounts of expanded EG and APP) and evaluated the effect of the additives on the physical–mechanical property, fire behavior and thermal stability of the foams based on compressive strength test, limiting oxygen index (LOI), cone calorimeter test, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The addition of EG alone or both EG and APP into the foam greatly influences the physical–mechanical property. The compressive strength of APEG foams is closely related to the apparent density. The LOI value showed good improvement in both EG and APEG foams. The addition of APP in APEG foams gave better fire behavior than the EG foams with an obvious decrease in PHRR and increase in residue. In addition, the TGA curves illustrated that APP might be an effective charring agent to promote char formation. The SEM results showed that the incorporation of APP and EG allowed the formation of a cohesive and dense char layer, which inhibited the transfer of heat and combustible gas and increased the thermal stability of PIR–PUR. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 238–246, 2013

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### INTRODUCTION

Rigid polyurethane foam (RPUF) is widely used in thermal insulation, space filling and other applications due to its excellent properties such as closed-cell structure, low thermal conductivity, high compressive strength, and low moisture permeability.<sup>1–4</sup> However, RPUF is highly flammable and susceptible to degradation upon exposure to elevated temperature during fire accident, which constitutes a serious concern and restricts its application.<sup>1</sup> Numerous studies have aimed to improve the fire behavior and thermal stability of RPUF. Halogenated compounds are good flame retardants that are conventionally used as additives in polymers.<sup>1</sup> However, halogen-containing polymers will release excessive toxic gases and smokes during combustion, which can seriously endanger human health.<sup>2–4</sup> As a result, it is imperative to study halogen-free flame retardants for RPUF. Intumescent flame retardant (IFR) has been noted as a good substitute of halogenated flame retardant.<sup>5</sup> The IFR of RPUF release less smoke, have lower toxicity and longer service life, exhibit lower corrosion, and are halogen-free. Common intumescent materials for RPUF are ammonium polyphosphate

(APP) and expandable graphite (EG). APP has a polyphosphate chain structure and a high molecular weight, and its efficacy is due to increased char formation by a condensed phase reaction. On the other hand, EG is a graphite intercalation compound.<sup>6,7</sup> The special layer structure of graphite is treated with sulfuric acid, nitric acid or acetic acid, which are intercalated into the graphite crystal structure.<sup>8,9</sup> The intercalated graphite particle expands under heat (an 100× expansion can occur along the *c*-axis of the crystal structure) and emerges a huge insulating layer, thus providing fire resistance to the polymeric matrix.<sup>10,11</sup> Because the boiling point of graphite is above 3000°C, EG can maintain its integrity in the flame zone and provide better fire protection than many other flame retardants. EG acts mainly in the condensed phase as a smoke suppressant and an insulator.<sup>12</sup> If the expanded carbon layers are too unstable, the EG needs to be combined with other flame retardants to form stable intumescent layers.

Previous studies have indicated that ammonium phosphate (APP) and expandable graphite (EG) may have synergistic flame retarding effect in composite materials.<sup>13,14</sup> Nevertheless, in spite

**Table I.** Formulations of PIR-PUR Foams

| No.                           | Ref   | EG-1  | EG-2  | EG-3  | APEG-1 | APEG-2 | APEG-3 | APEG-4 | APEG-5 | APEG-6 |
|-------------------------------|-------|-------|-------|-------|--------|--------|--------|--------|--------|--------|
| APP wt %                      | 0     | 0     | 0     | 0     | 10%    | 10%    | 10%    | 5%     | 15%    | 20%    |
| Formation EG wt %             | 0     | 5%    | 10%   | 15%   | 5%     | 10%    | 15%    | 15%    | 15%    | 15%    |
| PM-200                        | 280.7 | 281.0 | 281.0 | 281.0 | 280.7  | 280.7  | 280.7  | 280.7  | 280.7  | 280.7  |
| Polyether polyols -4110       | 90.0  | 90.0  | 90.0  | 90.0  | 90.0   | 90.0   | 90.0   | 90.0   | 90.0   | 90.0   |
| Polyether polyols -403        | 10.0  | 10.0  | 10.0  | 10.0  | 10.0   | 10.0   | 10.0   | 10.0   | 10.0   | 10.0   |
| DMCHA                         | 3.0   | 3.0   | 3.0   | 3.0   | 3.0    | 3.0    | 3.0    | 3.0    | 3.0    | 3.0    |
| Triethanolamine               | 5.0   | 5.0   | 5.0   | 5.0   | 5.0    | 5.0    | 5.0    | 5.0    | 5.0    | 5.0    |
| DMP-30                        | 2.0   | 2.0   | 2.0   | 2.0   | 2.0    | 2.0    | 2.0    | 2.0    | 2.0    | 2.0    |
| AK-8805                       | 2.5   | 2.5   | 2.5   | 2.5   | 2.5    | 2.5    | 2.5    | 2.5    | 2.5    | 2.5    |
| Distilled water               | 1.0   | 1.0   | 1.0   | 1.0   | 1.0    | 1.0    | 1.0    | 1.0    | 1.0    | 1.0    |
| APP                           | 0.0   | 0.0   | 0.0   | 0.0   | 47.4   | 50.3   | 53.6   | 25.1   | 86.3   | 124.1  |
| EG                            | 0.0   | 21.3  | 45.0  | 71.2  | 23.7   | 50.3   | 80.5   | 75.4   | 86.3   | 93.1   |
| n-Pentane                     | 9.0   | 10.0  | 10.0  | 10.2  | 8.2    | 8.2    | 8.5    | 8.2    | 8.9    | 9.2    |
| Density (kg m <sup>-3</sup> ) | 38.2  | 33.6  | 34.7  | 37.8  | 45.4   | 66.5   | 59.2   | 56.5   | 60.5   | 82.7   |

of the extensive previous research on the flammability of RPUF, there is few report on the combustion behavior and interaction of APP and EG in PIR-PUR foams. Therefore, in the present work we aim to study the synergy between EG and APP in providing flame retardant effects for PIR-PUR foams, and we also discuss the thermal stability, mechanical properties and morphology of PIR-PUR foams. By carefully studying the thermal decomposition of RPUF, we attempt to address the flammability issue and determine the optimum conditions and formulae to manufacture RPUF with enhanced thermal stability.

## EXPERIMENTAL

### Starting Materials

The systems consist of two components, I and II. Component I is a group of substances containing polyols, surfactant, catalyst, blowing agent, and flame retardant. EG and APP are mixed uniformly in components 1. Component II is polymethylene polyphenylene isocyanate.

Polymethylene polyphenylene isocyanate (PM-200), produced by Yantai WanHua Polyurethane; NCO content 31.3 wt %, viscosity 197 mPa s<sup>-1</sup> (25°C); Polyether 4110: hydroxyl value 475 mg KOH/g, viscosity 3500 mPa s<sup>-1</sup> (25°C); Polyether 403: hydroxyl value 761 mg KOH g<sup>-1</sup>, viscosity 40,000 mPa s<sup>-1</sup> (25°C); *N,N*-dimethylcyclohexylamine (DMCHA) was purchased from Yantai WanHua Polyurethane; 2,4,6-tri(dimethylaminomethyl)phenol (DMP-30) was used as trimerization catalyst for isocyanurate rings; triethanolamine was used as a crosslinking agent for polyurethane; polysiloxane-polyether copolymer AK-8805 was purchased from Yantai WanHua Polyurethane, China; *N*-pentane and water were used as chemical blowing agents; expandable graphite (EG, 100 mesh size) was purchased from Qingdao Huateng Graphite Technology, China; Ammonium polyphosphate was purchased from Yantai WanHua Polyurethane, China.

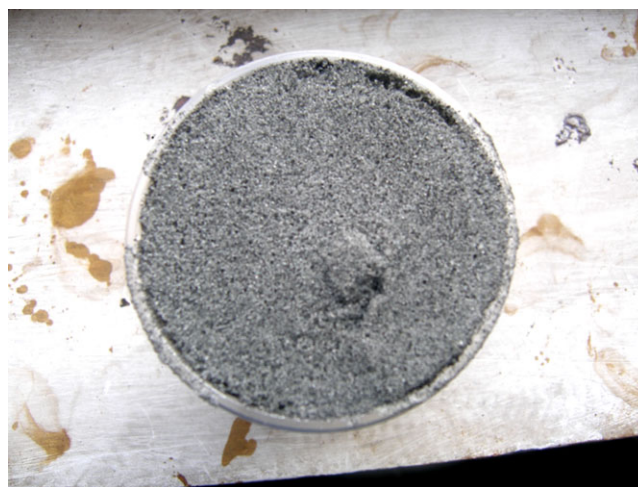
### Preparation of Rigid PUR-PIR Foams

PUR-PIR foams were prepared by a two-step procedure. The foam formulations are listed in Table I. Flame retardants were

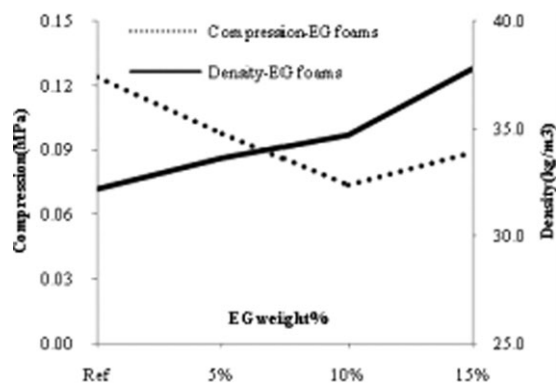
added using different formulae: the first set contained EG only (i.e., 5, 10, 15, 20, and 25 wt %), the second set contained 10% APP and varied amount of EG (i.e., 5, 10, and 15 wt %), and the third set contained 15% EG and varied amount of APP (i.e., 5, 10, and 15 wt %). The foams were prepared by adding component II (isocyanate) into component I (formulated polyol). The components of the formulation were mixed by a high speed stirrer for 20 s at room temperature and poured into a mold (12 cm × 12 cm × 12 cm). The mold was open, and the foam was allowed to rise freely. After preparation, the PUR-PIR foams were kept in an incubator at 70°C for 48 h to drive the polymerization reaction to completion. Finally, the foams were characterized. Figure 1 shows the optical pictures of the foams.

### Test Methods

**Mechanical Characterization.** The physical and mechanical properties were measured by standard test methods. The



**Figure 1.** The optical pictures of the foams. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 2.** Densities and compression strength of the Ref foam and EG foam at different EG content.

apparent density was surveyed according to ISO 845, and the compression strength was determined according to ISO 844 using an electronic universal testing machine.

**Fire Behavior.** Fire behavior was investigated by limited oxygen index (LOI) evaluation according to ISO 4589 using a oxygen index tester (HC-2, Jiang Ning Analytical Instrument Factory, China) and cone calorimeter (FTT0007, Fire Testing Technology, England) test according to ISO 5660. The samples (10 cm × 10 cm × 1 cm) were exposed at 50 kW m<sup>-2</sup> and the data were captured for the first 600 s. The exhaust gas flow rate was 24 L s<sup>-1</sup>. The measured parameters include the heat release rate (HRR, kW m<sup>-2</sup>) and its peak value (PHRR, kW m<sup>-2</sup>), the time of peak heat release rate (TPHRR, s), the total heat evolved (THE, kJ m<sup>-2</sup>), the total smoke released (TSR), the total mass loss (TML, g) and the CO production (g/g sample).

**Morphological Characterization.** The cellular morphologies of the foams in the rising direction were surveyed using a S-3000N scanning electron microscope (SEM, Hitachi, Japan). The material was cut with a razor blade and then sputter-coated with gold before observation.<sup>2,3</sup> Image analysis was performed on the SEM micrographs using Scion Image software (Scion) to obtain the average cell size and cell density. The bulk density of the foams was estimated by directly measuring the weight and volume of the cubic foam samples.<sup>3</sup>

**Thermogravimetric Analysis.** All foams and their related chars were characterized using a STA409C131F instrument (Netzsch, Germany). The heating rate was 10°C min<sup>-1</sup> under a flow of 100 mL min<sup>-1</sup> N<sub>2</sub>. The end temperature was 800°C. The mass loss was continuously recorded as a function of time and temperature. For each test at least five samples were measured to obtain a reproducible result.

## RESULTS AND DISCUSSION

### Physical–Mechanical Characterization

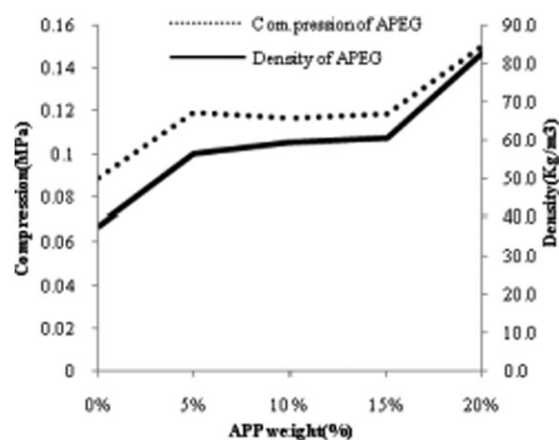
The apparent density is a very important physical property which has great influence on the mechanical properties.<sup>14</sup> Figures 2 and 3 show the apparent densities and compression strength of Ref foam, EG foam and APEG foam. The results show that the flame retardants significantly influence these properties. Higher EG content results in higher density of EG

foams. When APP is used together with 15 wt % EG, the density of the APEG foam also increases with rising APP content (Figure 3). This is because the addition of flame retardants increases the composite (polymer + flame retardants) weight and affects the degree of foaming. As shown in Figure 2, the introduction of EG into the PIR-PUR foam remarkably decreased the compression strength (in the rising direction of foams), and the maximum decrease was observed at 10 wt % EG loading. This decrease may be due to the formation of voids in cell structure and cell collapse, as shown in Figure 4 (EG-1, EG-2). When the EG loading increased from 10 to 15 wt %, the compressive strength increased, which may be due to the increase in apparent density. In the presence of APP, the compression strength of the APEG foam increases with rising APP content (Figure 3). It is obvious that changes in the compressive strength of the foams are closely related to their apparent density.

### Cell Morphology

The cell morphology is an important factor that affects the physical–mechanical properties of the PIR-PUR foam.<sup>15</sup> Figure 4 shows the SEM photographs of the Ref foam and the EG foams. It can be seen that the cell shapes are approximately spherical and polyhedral in both the Ref foam and the EG foams. Compared with the Ref foam, the EG foam containing 5 and 10 wt % EG exhibited obviously enlarged cell size (Figure 5). This is because the EG particles have dimensions similar to that of the cell and are located inside the cell, thus increasing the average cell size of the foam (Figure 6). A higher EG content of 15 wt % causes cell collapse due to excessive coalescence and ruptures of the cell walls (Figure 4, EG-3).

Introducing APP into the EG foams resulted in a significant change in the morphology structure (Figure 7). It can be noted that at low APP content (10 wt %), the average cell size of the APEG-1 foam decreased compared with the EG-1 foam containing 5 wt % EG. This is probably because the average particle size of APP is much smaller than the average cell size of the PIR-PUR foam, and APP can act as uniformity nucleation sites during cell formation, which leads to the formation of a very fine cellular foam structure and reduces cell size. When the EG content was higher (15 wt %), the APEG-3 foam exhibited



**Figure 3.** Densities and compression strength of the APEG foams (15 wt % EG) at different APP content.



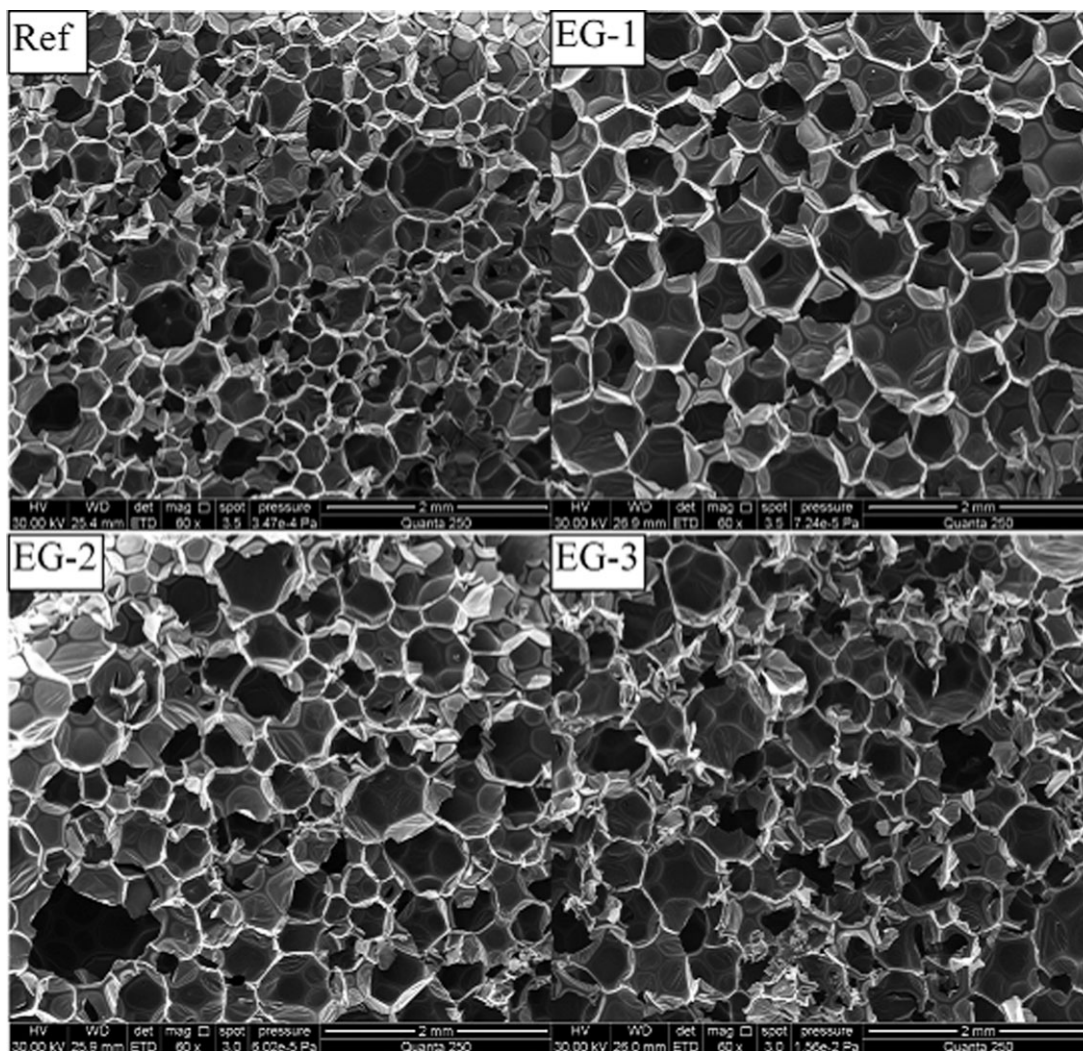


Figure 4. Microphotographs of the Ref foam and EG foams with different EG content.

larger cell size compared with the APEG-1 foam (Figure 8). This is because the increase in EG content causes the combination of small and large cell structures in the PIR-PUR foam. When the APP content reached as high as 20 wt % in APEG-6, the cell size became obviously heterogeneous and showed

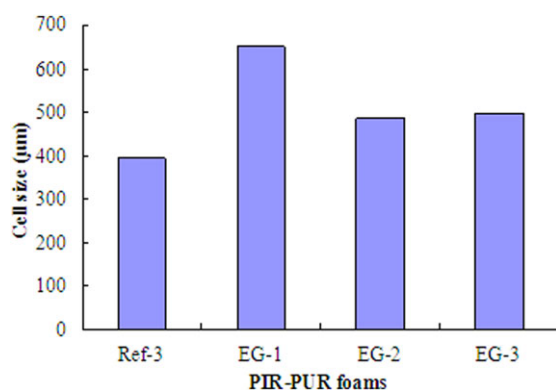


Figure 5. Average cell size of Ref foam and EG foams. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

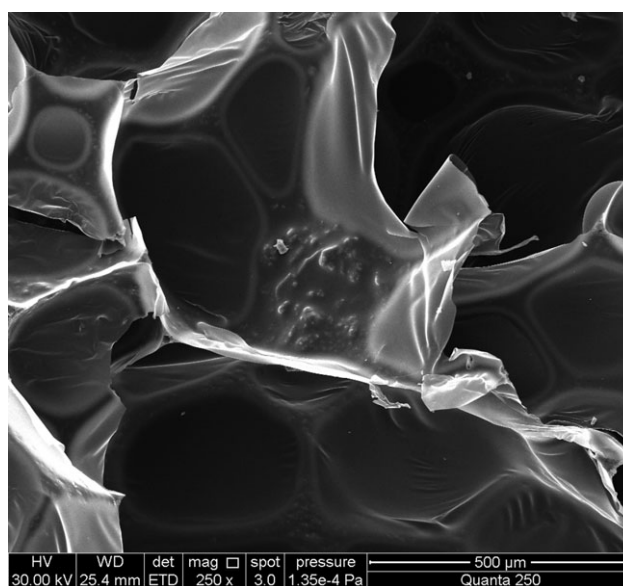
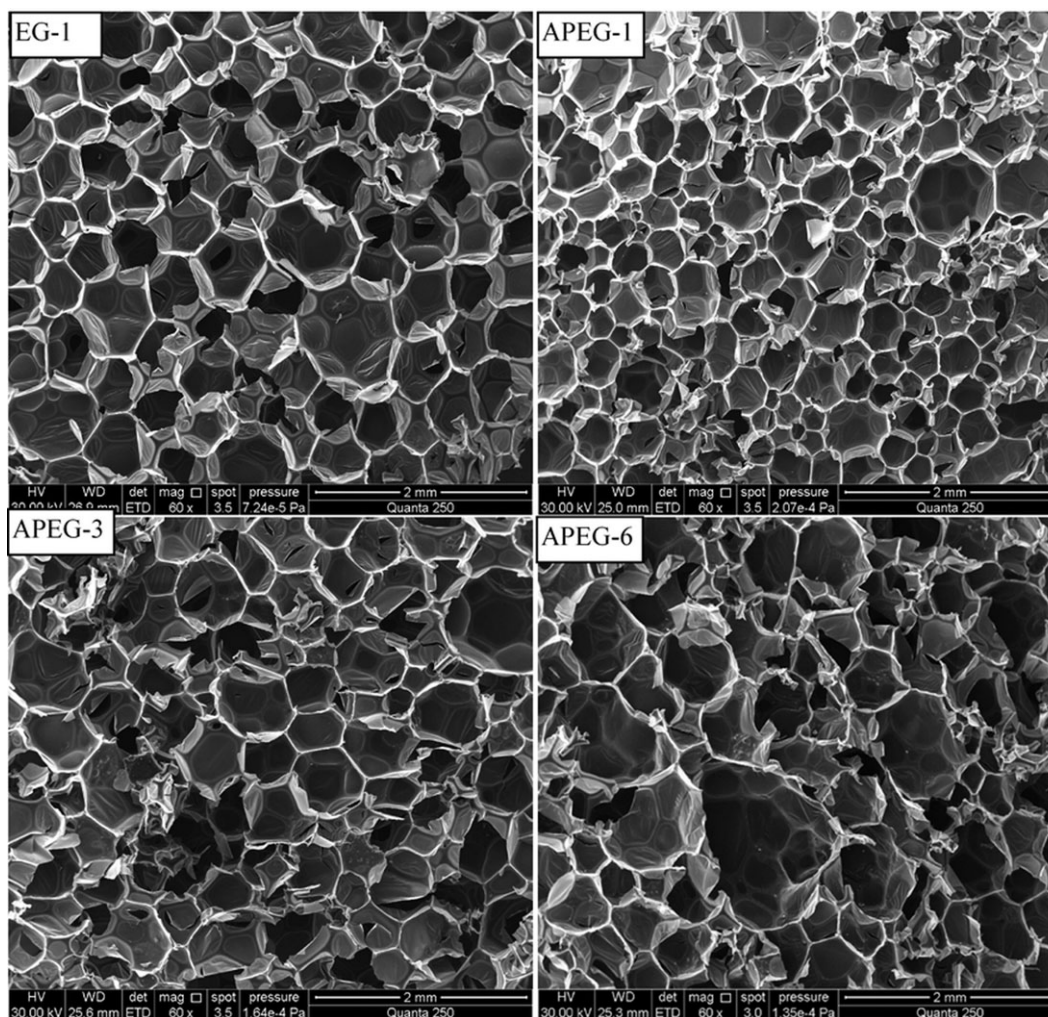
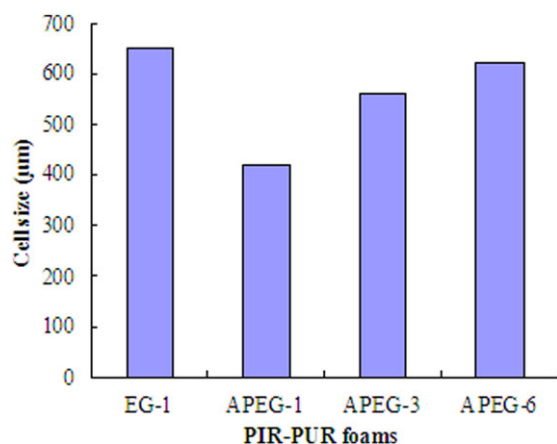


Figure 6. Particle of expandable graphite loading inside the cell.



**Figure 7.** Microphotographs of the Ref foam and APEG foams with different APP content.

bubble collapse, as compared with the APEG-3 foam that had the same level of EG (15 wt %). This result indicates that adding too much flame retardant (20 wt % APP and 15 wt % EG) leads to ruptures of the cell walls.



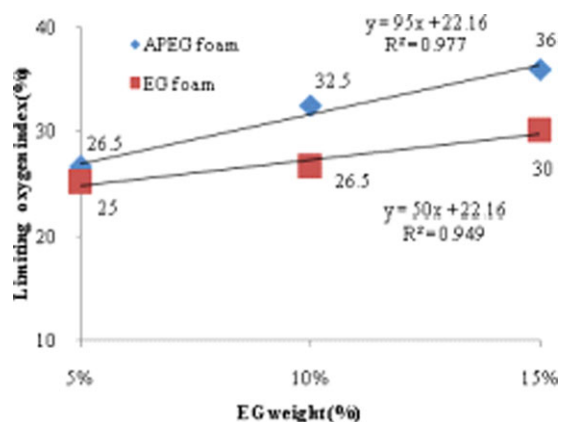
**Figure 8.** Average cell size of APEG foams. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Flame Retardant Behavior

Figure 9 shows the changes in the LOI value of the foam having different amounts of EG. It is clear that the improvement of LOI values for both EG foams and APEG foams is almost linear with increasing EG content (Figure 9). This is due to the thermal expansion of EG that forms a worm-like thermal insulating layer on the foam surface to prevent heat and oxygen transfer.<sup>2,3</sup> By comparing the APEG and EG foams it can be seen that, at the same EG content level, the addition of 10 wt % APP can increase LOI by 3–5% (Figure 9). Notably, in the presence of 15 wt % EG and 10 wt % APP, the LOI value increases to 36, which is presumed to be due to the synergistic effect of EG and APP (LOI on individual 10% APP is only 23). At 10 wt % EG, the introduction of increasing amount of APP also steadily increases the LOI (Figure 10). This result is attributed to the fact that APP both acts in the gas phase and can produce a barrier layer to inhibit combustion.<sup>11</sup> The LOI values at different EG/APP loadings correlate well with the results obtained from cone calorimeter test.

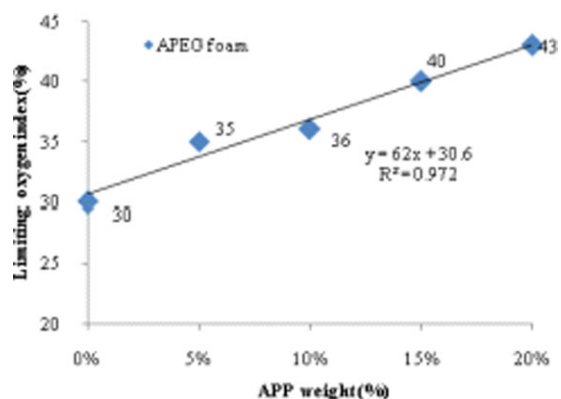
Cone calorimeter provides detailed information about flammability and smoke emission behaviors and has been extensively



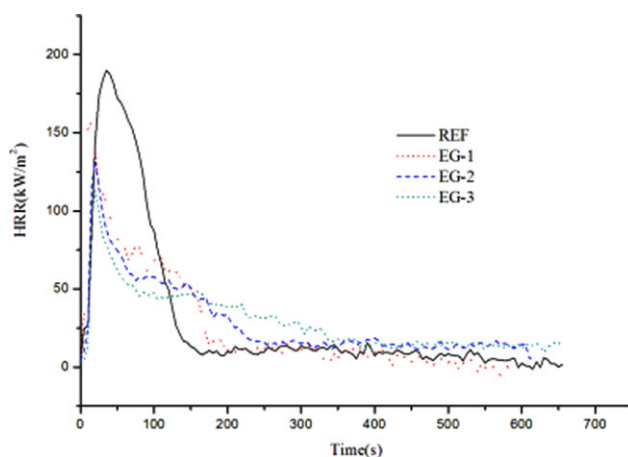


**Figure 9.** Limiting oxygen index of EG foam and APEG foam at different EG content. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

used to evaluate the flame resistance of materials.<sup>12,16</sup> The cone calorimeter is based on the oxygen-consumption principle, which is a small scale test that provides results in good agreement with large scale flame tests.<sup>17</sup> The analysis of the cone calorimetric data as a function of the concentration of the additive provides a very interesting result. Figure 11 shows the heat release rate (HRR) curves of tested foams at a heat input rate of  $50 \text{ kW m}^{-2}$ . It can be seen from Figure 11 that the HRR curves of the investigated samples have a peak (PHRR) at the beginning of the combustion and attenuates afterwards. Compared with the Ref foam, the PHRR of the EG foams is dramatically decreased. The PHRR is  $190.3 \text{ kW m}^{-2}$  for the Ref foam but only  $112.7 \text{ kW m}^{-2}$  for the foam with 15 wt % EG. The PHRR of the EG foam declines as the EG content increases. From Table II, it can be seen that total heat evolved (THE) and the total heat evolved per total mass loss (THE/TML) decreased significantly with increasing EG content. This is because EG thermally expanded and absorbed heat from the system at  $180\text{--}300^\circ\text{C}$ , forming a worm-like protective layer on the material surface.<sup>2,3</sup> This layer acted as a physical protective barrier for heat transfer into the material, resulting in decreased heat release.<sup>2,3</sup> Moreover, when APP is used together with EG, there is a slight



**Figure 10.** Limiting oxygen index of APEG foam at different APP content. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11.** HRR curves of EG-1,-2,-3 foams and Ref foam. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

decrease in PHRR from about  $106.5 \text{ kW m}^{-2}$  at low APP loading (5 wt %) to  $96.4 \text{ kW m}^{-2}$  at 15% APP loading, accompanied by a similar decrease in THE and THE/TML (Figure 12, Table II). In addition, it can be also noted that the PHRR, THE, and THE/TML of the APEG foam are lower than those of the EG foam with the same EG content level. These indicate a cumulative effect between EG and APP on flame inhibition.<sup>18</sup> The synergistic effect may be attributed to the decomposition of APP to yield polyphosphoric acid with strong dehydration during heating, and the polyphosphoric acid promotes the formation of char, which together with EG forms a compact carbonaceous layer with stabilized structure.

The char yields also vary among different foams (Table II). The formation of efficient char can hinder heat transfer between the flame zone and the burning substrate, and thus protect the underlying materials from further burning. It can be noted that residues increase with the increase of EG content. In addition, when APP is used together with EG, the APEG foam has more residue than the EG foam of the same EG content. For APEG foams, more residues were observed at larger APP loading. This indicates that the incorporation of EG and APP can promote the formation of carbonaceous materials in the condensed phase.

The smoke generation is an important hazard parameter in many flame situations. The effect of flame retardants on smoke formation was also measured. Total smoke release (TSR) and the ratio TSR/TML are shown in Table II. It can be noticed that the addition of EG in PIR-PUR foam leads to a remarkable decrease in TSR and TSR/TML. This is because when exposed to fire, EG creates a carbon char with some small porous holes on the surface, which improves the smoke suppressing performance. Furthermore, when APP is used together with EG, the TSR/TML of the APEG foam is lower than that of the EG foam with the same EG content, due to the formation of tight carbon layer.

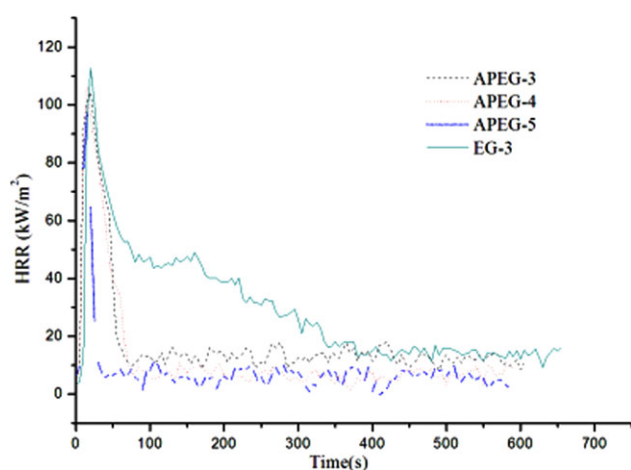
### Thermal Stability

Figures 13 and 14 show the TGA/DTG profiles of the PIR-PUR foams in  $\text{N}_2$  environment. It can be seen that all foams have

**Table II.** Results of Cone Calorimeter Test for PIR-PUR Foams with Different Contents of Flame Retardants

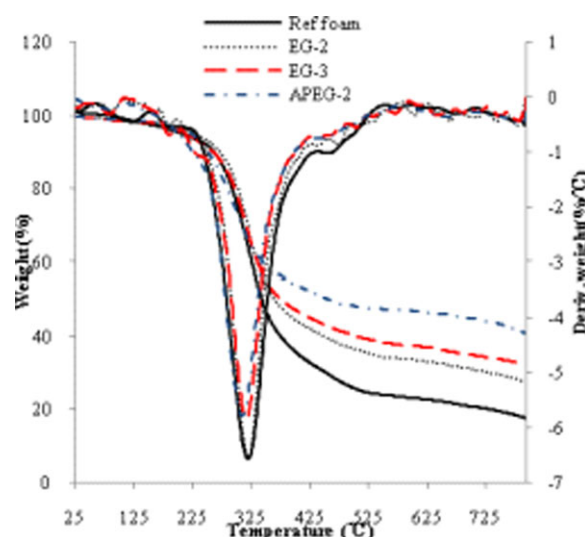
| No.    | Flame-retardants weight (%) | PHRR (kW m <sup>-2</sup> ) | THE (MJ m <sup>-2</sup> ) | TSR   | THE/TML (kJ m <sup>-2</sup> g <sup>-1</sup> ) | TSR/TML (g <sup>-1</sup> ) | Char yield (%) |
|--------|-----------------------------|----------------------------|---------------------------|-------|---|----------------------------|----------------|
| Ref    | 0                           | 190.3                      | 20.0                      | 608.0 | 2.5   | 61.7                       | 16.4           |
| EG-1   | 5%EG                        | 156.8                      | 19.7                      | 374.5 | 2.3   | 43.2                       | 16.6           |
| EG-2   | 10%EG                       | 131.2                      | 17.8                      | 240.7 | 2.1   | 26.5                       | 31.0           |
| EG-3   | 15%EG                       | 112.7                      | 16.6                      | 185.7 | 2.1   | 19.1                       | 38.5           |
| APEG-1 | 10%APP+5%EG                 | 153.0                      | 18.3                      | 434.9 | 2.1   | 49.3                       | 31.6           |
| APEG-2 | 10%APP+10%EG                | 126.7                      | 13.8                      | 269.6 | 1.8   | 34.2                       | 39.4           |
| APEG-3 | 10%APP+15%EG                | 101.3                      | 7.7                       | 226.6 | 1.4   | 30.7                       | 48.2           |
| APEG-4 | 5%APP+15%EG                 | 106.5                      | 8.4                       | 271.7 | 1.6   | 45.8                       | 41.0           |
| APEG-5 | 15%APP+15%EG                | 97.4                       | 4.9                       | 162.5 | 0.8   | 25.4                       | 52.2           |

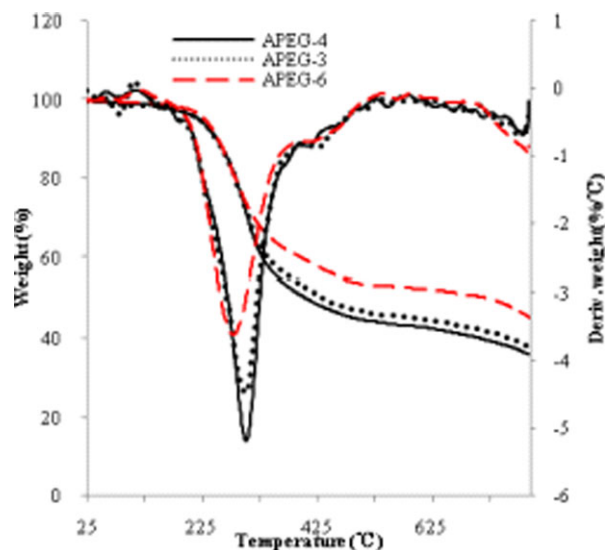
similar thermal stability and only one characteristic temperature region is observed at 180–400°C, which is due to the thermal pyrolysis of the polymer. Font et al. reported similar thermal profiles under N<sub>2</sub> for two regions at ~110°C and ~280°C.<sup>19</sup> However, we do not observe the moisture absorption region at ~110°C in this work, probably because the foams already lost the moisture during polymerization reaction in oven at 70°C for 48 h. Compared with the Ref foam, the EG foams have lower weight loss rate and higher residue at 800°C (Figure 11). At 800°C, the char residue of the Ref foam is only 17.72%, which demonstrates a poor charring ability. However, when EG is added into the PIR-PUR foam, the char residue improved significantly to 27.8% for the EG-2 foam and 32.12% for the EG-3 foam, respectively (Table III). Meanwhile, as shown in Table III, the Ref foam showed very low thermal stability at its onset temperature ( $T_{\text{onset}}$ ) 190°C, as indicated by the 5% weight loss. After addition of EG, the  $T_{\text{onset}}$  is increased to about 230°C for the EG-2 and EG-3 foams, probably because of the formation of worm-like carbon from EG that prevents the weight loss and increases the thermal stability of the foams. The maximum decomposition rates for Ref foam and EG foams are all observed at a temperature of  $T_{\text{max}} \approx 320^\circ\text{C}$ .

**Figure 12.** HRR curves of EG-3, APEG-3, -4, -5 foams. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

When 10 wt % of APP is used together with EG as the flame retardant, the APEG-2 foam showed lower weight loss rate and higher residue compared with the EG-2 foam (Figure 13). The char residue of the EG-2 foam is 27.8%, whereas the residue of the APEG-2 foam is up to 40.88%. The char residue observations are in good agreement with the cone calorimeter test results. There was no significant difference in the  $T_{\text{onset}}$  between APEG-2 foam and EG-2 foam, whereas the  $T_{\text{max}}$  of the APEG-2 foam was about 10°C less compared with the EG-2 foam. This is probably because both APP and EG form a dense carbon layer, which inhibits the further decomposition of the PU matrix, prevents the loss of volatile low molecular mass compounds and reduces  $T_{\text{max}}$ .

To further investigate the thermal stability of the APEG foams containing different levels of APP, the TGA/DTG curves of APEG-3 (10% APP), APEG-4 (5% APP), and APEG-6 (20% APP) are compared in Figure 14. The increase in APP dosage significantly reduced the weight loss rate and improved the quality of residues for APEG foams (Figure 14). From Table III,

**Figure 13.** TGA/DTG thermograms of Ref foam, EG-2 foam, EG-3 foam, and APEG-2 foam. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 14.** TGDG thermograms of APEG-3, APEG-4, APEG-6 foams. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

it can be noted that the residue of APEG-3 foam, APEG-4 foam and APEG-6 foam is 38.09, 36.19, and 45.16%, respectively, which agrees well with the cone calorimeter test results and indicates that APP can assist to form stronger char layer. In addition, the  $T_{onset}$  of APEG-3, APEG-4, and APEG-6 are largely similar, whereas  $T_{max}$  declines with rising APP content. This is because the increased formation of char layer by APP further resists heat and mass transfer, provides good insulation to the underlying combustible polymer, and thus reduces  $T_{max}$ .

#### Morphological Characterization

To survey the morphology of the residual char formed in the LOI tests, we studied the SEM images of the char layer of the Ref foam, EG-3 foam, and APEG-3 foam (Figure 15). There is an obvious difference in the surface of these residues. A lot of big circular holes can be seen on the surface of the Ref foam residual char, which are closely related with its poor flame retardant performance and thermal stability. In the presence of 15 wt % EG, there is a worm-like char layer on the EG-3 foam surface, which corresponds to the higher LOI value and better thermal stability. Furthermore, when 10 wt% APP is used

**Table III.** TG/DTG Result for Ref Foam, EG Foams, and APEG Foams

| No.    | Flame-retardants weight (%) | $T_{onset}$ (°C) | $T_{max}$ (°C) | Residue at 800°C (%) |
|--------|-----------------------------|------------------|----------------|----------------------|
| Ref    | Ref                         | 190              | 319            | 17.72                |
| EG-2   | 10%EG                       | 229              | 320            | 27.80                |
| EG-3   | 15%EG                       | 225              | 316            | 32.12                |
| APEG-2 | 10%APP+10%EG                | 224              | 309            | 40.88                |
| APEG-3 | 10%APP+15%EG                | 223              | 300            | 38.09                |
| APEG-4 | 5%APP+15%EG                 | 223              | 302            | 36.19                |
| APEG-6 | 20%APP+15%EG                | 229              | 280            | 45.16                |

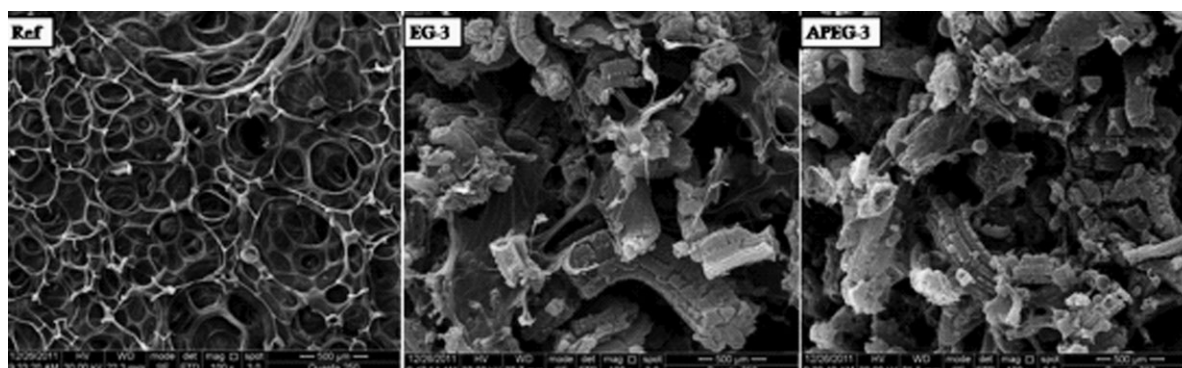
together with 15 wt % EG, a cohesive and dense structure is formed as shown in Figure 13 (APEG-3), which effectively separates the flame and the polymer to preserve the underlying materials and enhance the thermal stability.

#### CONCLUSION

The addition of EG causes a marked decrease in the compressive strength of the PIR-PUR foam, which however can be compensated by the further addition of APP, as the compressive strength increases with increasing APP content in the APEG foams. The fire behavior of the PIR-PUR foams improves at higher EG content, and the addition of APP can further improve the fire behavior and enhance residue formation. Thermo-gravimetric analysis shows that the addition of APP and EG can enhance the thermal stability of the PIR-PUR foam. By studying the morphology of char residues with SEM, we found that the incorporation of APP and EG can form a cohesive and dense char layer, which hindered the transfer of heat flow and combustible gas and improved the thermal stability of PIR-PUR.

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**Figure 15.** SEM images of the charred surface structure of Ref foam, EG-3 foam, and APEG-3 foam.



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