

## Effect of zinc oxide on properties of phenolic foams/halogen-free flame retardant system

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**ABSTRACT:** A halogen-free flame retardant system consisting of ammonium polyphosphate (APP) as an acid source, blowing agent, pentaerythritol (PER) as a carbonific agent and zinc oxide (ZnO) as a synergistic agent, was used in this work to enhance flame retardancy of phenolic foams. ZnO was incorporated into flame retardant formulation at different concentrations to investigate the flammability of flame retardant composite phenolic foams (FRCPFs). The synergistic effects of ZnO on FRCPFs were evaluated by limited oxygen index (LOI), thermogravimetric analysis (TGA), cone calorimeter tests, and images of residues. Results showed that the flame retardant significantly increased the LOI of FRCPFs. Compared with PF, heat release rate (HRR), total heat release (THR), effective heat of combustion (EHC), production or yield of carbon monoxide (COP or COY) and Oxygen consumption (O<sub>2</sub>C) of FRCPFs all remarkably decreased. However specific extinction area (SEA) and total smoke release (TSR) significantly increased, which agreed with the gas-phase flame retardancy mechanism of the flame retardant system. The results indicated that FRCPFs have excellent fire-retardant performance and less smoke release. And the bending and compression strength were decreased gradually with the increase of ZnO. The comprehensive properties of FRCPFs were better when the amount of ZnO was 1~1.5%. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42730.

**KEYWORDS:** composites; degradation; flame retardance; foams; properties and characterization

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### INTRODUCTION

In the last decades, the research and application of the foam plastics were mainly focused on polystyrene, polypropylene, polyethylene, polyurethane and polyvinyl chloride foam.<sup>1–3</sup> However, the poor flame-retarding performance had led to generate abundant smoke, toxic and corrosive gases, which could cause secondary disasters and environmental pollution, as well as the lower survival of human beings.<sup>4</sup> Most recently, the frequent occurrence of the fires in Chinese high-rise building that caused substantial damage and casualties, have promoted the great demand for new environmentally friendly fire-retarding foam plastics.

Phenolic foams (PFs), as one of excellent retardant materials that characterized with low thermal conductivity, excellent fire resistant performance, low water absorption, and low generation of toxic gas during combustion, have been widely applied in the fields of agriculture, horticulture, thermal insulation, and sound insulation.<sup>5–8</sup> However, the intrinsic friability of PFs have severely restricted their applications.<sup>9</sup> In generally, the friability of PFs was reduced by the introduction of toughening agents, however, the flame retardancy of PFs will deteriorate at the same time.<sup>10</sup>

In order to further enhance the flame retardancy of PFs, various flame retardants were introduced into the PFs. Halogen-free flame retardants (HFFRs) [such as ammonium polyphosphate (APP)] that characterized with relatively low degradation temperature, dual mechanistic action (gas and condensed phases) and environmental concerns have been receiving considerable attention.<sup>11–13</sup> However, compared with bromine-containing flame retardants, HFFRs also has some flaws such as low flame-retarding efficiency.<sup>14,15</sup> Hence, the combination of HFFRs and intumescent flame retardant (IFR) was used as flame retardant in polymer.<sup>16–20</sup> In addition, synergistic agents such as some transitional metal oxides and metal compounds have been used in PFs, which have been evidenced in many reports.<sup>21–26</sup> It's important to point out that the flame retardancy of PFs is a system process including flame retardants, char forming agents, synergistic agents etc.

As a transition metal element, zinc was believed to catalyze dehydration and oxidation reactions of the IFR system, and zinc oxide (ZnO) was thought to be acted in condensed phase which can increase the charred residues and thus increase the flame retardancy of the IFR system composite materials.<sup>27,28</sup> Herein,

**Table I.** The Composition of the Samples

| Sample No. | HSRPRs (%) | Surfactant <sup>a</sup> (%) | Curing agent <sup>b</sup> (%) | Blowing agent <sup>c</sup> (%) | APP (%) | PER (%) | ZnO (%) |   |     |   |   |   |   |
|------------|------------|-----------------------------|-------------------------------|--------------------------------|---------|---------|---------|---|-----|---|---|---|---|
| PF         | 100        | 12                          | 10                            | 5                              | 0       | 0       | 0       | 0 | 0   | 0 | 0 | 0 | 0 |
| PF-1       | 80         | 12                          | 10                            | 5                              | 15      | 5       | 0       | 0 | 0   | 0 | 0 | 0 | 0 |
| PF-2       | 80         | 12                          | 10                            | 5                              | 15      | 5       | 0.5     | 0 | 0   | 0 | 0 | 0 | 0 |
| PF-3       | 80         | 12                          | 10                            | 5                              | 15      | 5       | 0       | 1 | 0   | 0 | 0 | 0 | 0 |
| PF-4       | 80         | 12                          | 10                            | 5                              | 15      | 5       | 0       | 0 | 1.5 | 0 | 0 | 0 | 0 |
| PF-5       | 80         | 12                          | 10                            | 5                              | 15      | 5       | 0       | 0 | 0   | 0 | 3 | 0 | 0 |
| PF-6       | 80         | 12                          | 10                            | 5                              | 15      | 5       | 0       | 0 | 0   | 0 | 0 | 5 | 0 |

<sup>a</sup>Surfactants: Polysorbate-80.

<sup>b</sup>Composite curing agents: hydrochloric acid/phosphoric acid/p-toluene sulfonic acid/water = 8/4/6/3.

<sup>c</sup>Blowing agents: petroleum ether.

in this work the effect of ZnO using as synergist on the flammability of PFs, as well as on halogen-free flame retardant system, was investigated by limiting oxygen index (LOI), thermogravimetric analyzer (TGA), and cone calorimeter method.<sup>29–32</sup>

## MATERIALS AND EXPERIMENTAL

### Materials

Phenol (>99%), formaldehyde (37 wt % aqueous solution), CaO, hydrochloric acid (36%), phosphoric acid, NaOH were obtained from Nanjing Chemical Reagent, Ltd and used as received. Paraformaldehyde ( $\geq 95\%$ ) and pentaerythritol were purchased from Shanghai Lingfeng chemical Reagent, Polysorbate-80, petroleum ether, p-toluenesulfonic acid, polyethyleneglycol-200 were purchased from Sinopharm group chemicals Reagent Co.; APP was purchased from Shifang Taifeng chemical Co.; zinc oxide (ZnO) was obtained from Xilong chemical Co.

### Synthesis of High-Solid Resol Phenolic Resins (HSRPRs)

Phenol (4.3 mol) and formaldehyde (1.4 mol) were charged into a 1000 mL four-necked round bottom flask fitted with stirrer and condenser. And a calculated amount of CaO (0.015 mol) was dropped slowly into the vessel within 30–40 min under continuously stirring at 85°C. The first part of paraformaldehyde (1.8 mol) and NaOH aqueous solution (50%, 0.3 mol) was then added into the reactor and stirred at 85°C for 50–70 min. Then the second part of paraformaldehyde (1.8 mol) and NaOH aqueous solution (50%, 0.3 mol) was added and stirred at 85°C for 50–70 min. Finally the third part of NaOH aqueous solution (50%, 0.15 mol) and polyethyleneglycol-200 (0.2 mol) was added to the reactor and the reaction was performed temperature at 75°C for 15–20 min. The HSRPRs was obtained after cooled down to 40–50°C. The solid content of HSRPRs was about 85 wt % calculated by oven-dry measurement.

### Preparation of PFs

Surfactants (Polysorbate-80), composite curing agents (hydrochloric acid/ phosphoric acid/ p-toluenesulfonic acid/ water = 8/4/6/3), flame retardant (APP), char forming agents (PER), and synergist (ZnO), and blowing agents (petroleum ether) were added into HSRPRs and rapidly mixed well before poured into the mold. The composition of the samples was shown in Table I. The PFs were obtained after bubbling at 70°C for 40 min.

### Limiting Oxygen Index (LOI)

LOI test was carried out with JF-3 oxygen index meter (LOI analysis instrument company, Jiangning County, China) according to ISO 4589-1-2000. The samples used for the test were 100×10×10 mm<sup>3</sup>.

### Thermogravimetric Analyzer (TGA)

TGA curves were recorded on NETZSCH (Germany) STA 409 thermogravimetric apparatus to study the thermal stability and degradation of HSRPRs. Each sample was placed on a balance located in the furnace with the temperature range from 35°C to 900°C at heating rate of 15°C/min in flowing nitrogen atmosphere (20 mL/min). The thermograms of weight loss versus temperature were obtained to show the different degradation processes.

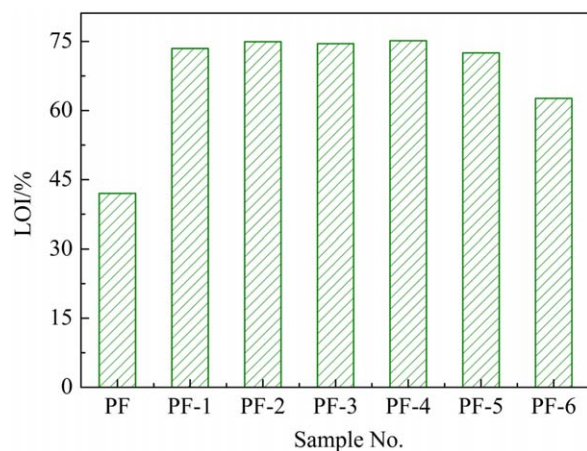
### Cone Calorimeter Tests

A cone calorimeter (Fire Testing Technology, East Grinstead, UK) was employed to evaluate the efficiency of the fire retardant, as specified using the ASTM E 1354 and ISO 5660 method. Each specimen (100 × 100 × 10 mm) was wrapped in an aluminum foil and exposed horizontally to 50kW/m<sup>2</sup> external heat flux, and the duration of the test was 290 s.

## RESULTS AND DISCUSSION

### LOI of PF and Flame Retardant Composite Phenolic Foams (FRCPFs)

LOI is defined as the minimum fraction of oxygen-nitrogen mixture that is sufficient to sustain combustion of the specimen after ignition under specified conditions, and could be used as an indicator to evaluate flame retardancy of a polymer. The higher LOI value, the more difficulty when the material was burned. Generally, LOI values for flammable material, combustible material and flame retardant are defined as less than 22%, between 22% and 27%, and above 27%, respectively.<sup>32</sup> As shown in Figure 1, LOI of PF and FRCPFs (PF-1, PF-2, PF-3, PF-4, PF-5, and PF-6) are all above 42%, indicating that PF and FRCPFs are flame retardant material. It was reported that carbon and nitrogen atoms of FRCPFs decomposed under high temperature and generate N<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub> and some others, which could not only dilute the concentration of combustible gas and oxygen in the combustion zone, but also have an overriding blanket effect.<sup>33</sup> When PFs decomposed at high temperature, a variety of cross-linked material could be formed, such as

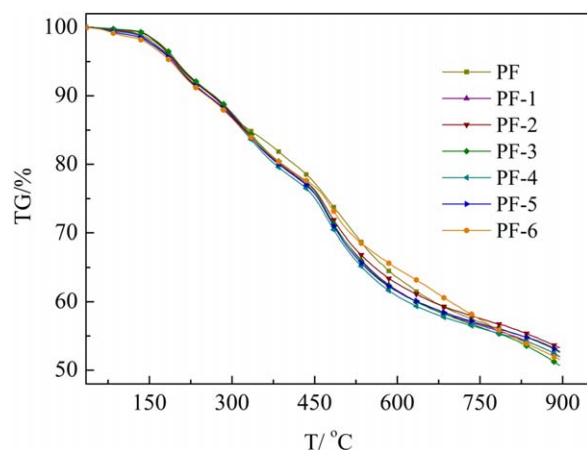


**Figure 1.** LOI of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

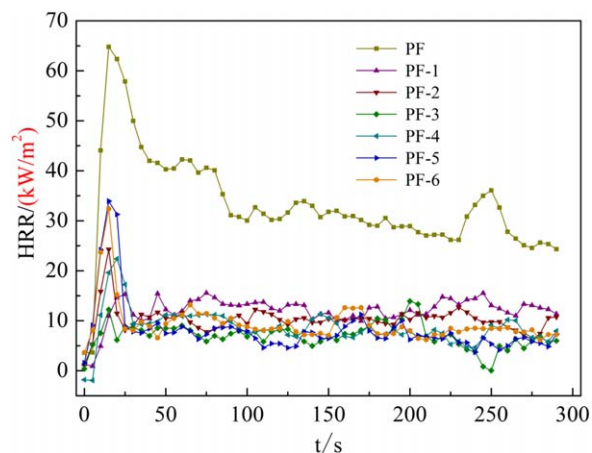
the high ratio of carbonization. In general, some relationships existed between the carbonization ratio of fire-retardant plastics and the flame resistance (such as LOI). The higher ratio of carbonization, the better the flame resistance.<sup>34</sup> Besides, we could see that LOI value of sample increased slightly, when mass fraction of ZnO was less than 1.5%. However LOI value decreased, when mass fraction of ZnO was equal to or more than 3%. The reason may be attributed to the reaction occurred between ZnO and APP, and the formation of bridge bonds between APP during the combustion process. A small amount of bridge bonds could increase the stability of the APP, and reduce the volatilization of phosphorus during pyrolysis.<sup>35</sup> Therefore flame retardancy of samples increased slightly. When the dosage of ZnO was more, a large amount of bridge bonds were formed, which led to APP's hardening and lost reaction activity,<sup>36</sup> as well as the decrease of LOI value of samples. Nonetheless the FRCPFs have a high LOI value (62.6–75.1%) in contrast to PF, and exhibited excellent fire-retardant performance while using the flame retardant.

#### TGA of PF and FRCPFs

The initial decomposition temperatures ( $T_i$ ), a parameter to evaluate the thermal stability of polymers, could be obtained



**Figure 2.** TGA curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



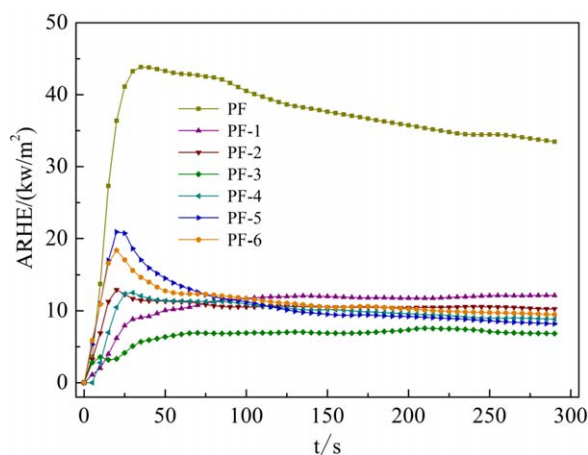
**Figure 3.** HRR curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

from the TGA curves located at the intersection between the starting mass line and the maximum gradient tangent. The polymer with higher  $T_i$  was considered more thermally stable.<sup>37,38</sup> TGA curves of PF and FRCPFs were shown in Figure 2,  $T_i$  values of PF and FRCPFs (PF, PF-1, PF-2, PF-3, PF-4, PF-5 and PF-6) were 152.0°C, 138.8°C, 149.2°C, 150.6°C, 146.4°C, 147.2°C and 143.7°C respectively. And the residues (900°C) of PF and FRCPFs were 54.26%, 51.87%, 53.16%, 50.5%, 51.79%, 52.55%, and 51.42%, respectively. These results showed that compared with other FRCPFs, PF-3 had higher thermal stability, which reflected by  $T_i$  values; while PF-2 had thermal stability at high temperature, which reflected by the loss of mass.

#### Heat Release Rate (HRR) of PF and FRCPFs

HRR was determined by the measurement of the concentration of oxygen that consume during the combustion, which was one of the most important parameters in determining the hazard from a fire.<sup>39</sup> The larger HRR was, the faster thermal cracking of the polymer material surface, thereby the more volatile combustibles generated, which accelerated the spread of flame and the greater risk of polymer materials in the fire. Therefore, Reducing HRR was conducive to control the size of the fire and flame spread, and reduce the emission of smoke, toxic and corrosive gas.<sup>40</sup>

HRR curves of PF and FRCPFs were shown in Figure 3. Compared with PF, HRR of FRCPFs decreased dramatically. HRR of PF reached to the Peak value (64.81 kW/m<sup>2</sup>) when combustion time was about 15s. And then HRR gradually decreased with the extension of combustion time. HRR of FRCPFs (PF-1, PF-2, PF-3, PF-4, PF-5, and PF-6) reached to the Peak value (15.29 kW/m<sup>2</sup>, 24.27 kW/m<sup>2</sup>, 12.25 kW/m<sup>2</sup>, 22.39 kW/m<sup>2</sup>, 33.92 kW/m<sup>2</sup>, and 32.41 kW/m<sup>2</sup>) when combustion time was 25s, 15s, 15s, 20s, 15s and 15s respectively. And mean HRR data of foams were shown in Table III. Compared with the PF, the foam's HRR significantly reduced when APP and PER were added. And the foams' HRR was found slightly decrease after adding ZnO (synergist). Especially, PF-3 was observed to have the lowest HRR and ARHE from above research (Figure 4). The result showed that synergistic flame retardant effect existed among ZnO, APP and PER. The reason was that ZnO had a large surface area and low



**Figure 4.** ARHE curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

density, tending to migrate near the regressing sample surface without sinking through the polymer melt layer during the burning process. The accumulated ZnO consequently formed a charred layer by collaborating with APP/PER, which acted as a heat insulation barrier. This charred layer prevented heat transfer and transportation of degraded products between melting polymer and surface, thus reducing the HRR and ARHE. Meanwhile the more content of ZnO was not the better, there was a suitable quantity,<sup>41</sup> the results of HRR and ARHE showed that the properties of the composite foam was better when the amount of ZnO was 1%.

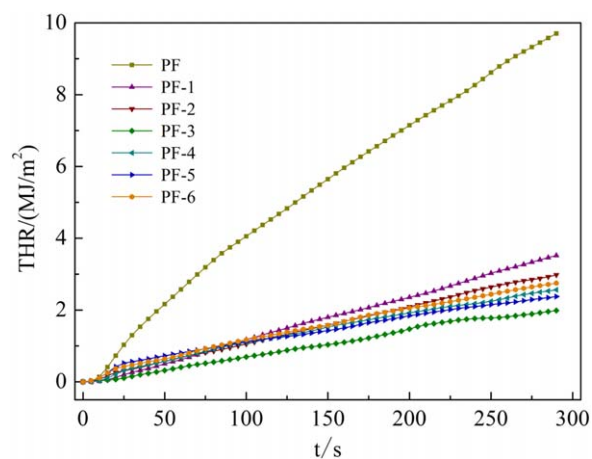
#### Total Heat Release (THR) of PF and FRCPFs

THR was defined as the amount of heat released per unit area of a material from the beginning to the end of the combustion under specified test conditions. Generally, the bigger THR, the greater heat release when polymer burned, namely the greater risk of material in the fire. THR was one of the fundamental properties of fire and almost always be taken into account in the assessment of the material combustibility and flame retardancy. Thus, THR has more objectives, comprehensive guidance on fire research with HRR.<sup>42</sup>

Figure 5 presents THR for all samples. The slope of THR curve could be assumed as representative of fire spread.<sup>43</sup> From Figure 5, THR of the sample containing flame retardant was lower than the sample without flame retardant. With the addition of flame retardant, the THR decreased significantly. Especially THR of PF-3 was the lowest one among all the samples in the time between 0 to 290 s. It indicated that the flame spread of PF-3 was the comparatively lowest among all the samples. During the combustion process, condense and compact char residue was formed due to the existence of ZnO,<sup>44,45</sup> which can isolate heat from the outside and combustible gases from the inside, this structure of char was good enough to stop flame spread. It also suggested that the property of FRCPFs was better when the amount of ZnO was 1%.

#### Specific Extinction Area (SEA) of PF and FRCPFs

The main fire hazard is the smoke arose from the incomplete combustion. SEA is another very valuable parameter, which is

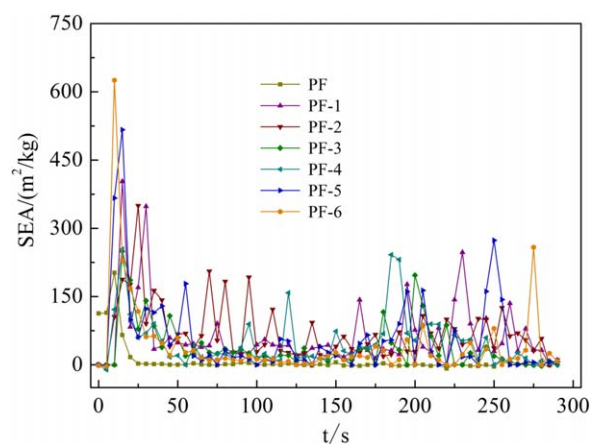


**Figure 5.** THR curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

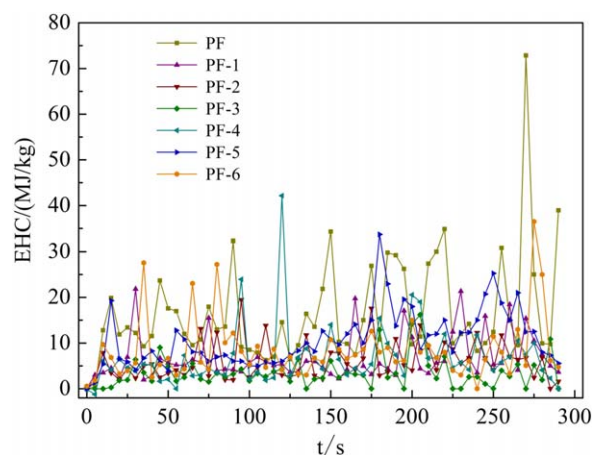
characterized by the smoke obscuration.<sup>46</sup> The reduction of light transmission is measured by a laser beam through the exhaust duct and used to evaluate the contribution of the thermal degradation products from polymeric materials to smoke. Higher SEA means that the smoke amount produced from volatiles is higher during burning process.<sup>47</sup> SEA values of the all samples were summarized in Figure 6. All of the flame retarded systems had similar smoke emission trends. Flame retardation normally increased the SEA of polymeric materials since flammability was suppressed and some combustible components were changed into soot and/or smoke in an incomplete combustion manner.<sup>48</sup>

#### EHC of PF and FRCPFs and Flame Retarded Mechanism Analysis

Effective heat of combustion (EHC) was defined as the amount of combustion heat released per unit mass by volatile combustible component foamed by thermal decomposition during the combustion process of materials. The release of flame retarded materials during the combustion leads to the formation of original fuel and stop burning. Therefore EHC could be used to evaluate the amount of the effective burning component of



**Figure 6.** SEA curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



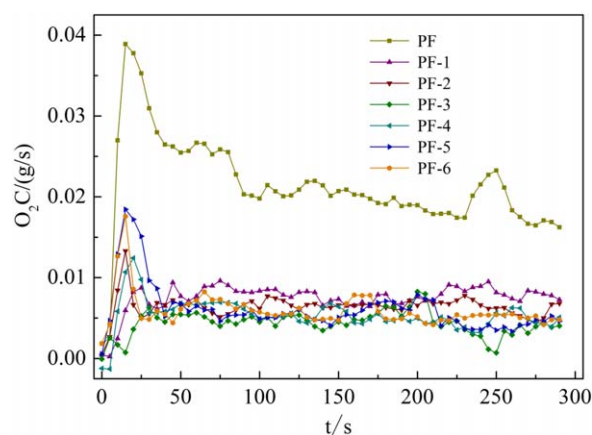
**Figure 7.** EHC curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

material in the gas phase. A higher EHC means the more completely combustion of volatiles.<sup>47</sup> Moreover EHC together with HRR and SEA could help to analyze the flame retardant mechanism. As shown in Figure 7. EHC values of the flame retarded samples were significantly decreased. It also could be seen that EHC of PF-3 was the lowest one among all the samples. This might be attributed to incomplete combustion of volatiles, as compared with PF. However, due to incomplete combustion, THR was rather small to the lever that couldn't cause any significant fire danger and hazard in reality (Figure 5).

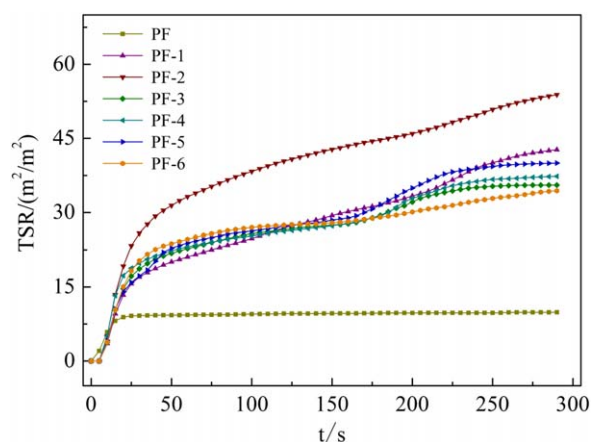
In the evaluation of FRCPFs, the significant reduction of EHC and HRR, plus the remarkable increase of SEA, suggested that the flame retardant take effect in the gas phase and resulting in incomplete combustion, which agreed with the gas-phase flame retardant mechanism.<sup>49</sup>

#### Oxygen Consumption of PF and FRCPFs

Oxygen consumption ( $O_2C$ ) was defined as the amount of oxygen consumed per unit time by a material during the combustion under specified test conditions. Generally, the lower  $O_2C$  is indicative of the more incomplete combustion of material, and



**Figure 8.**  $O_2C$  curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** TSR curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

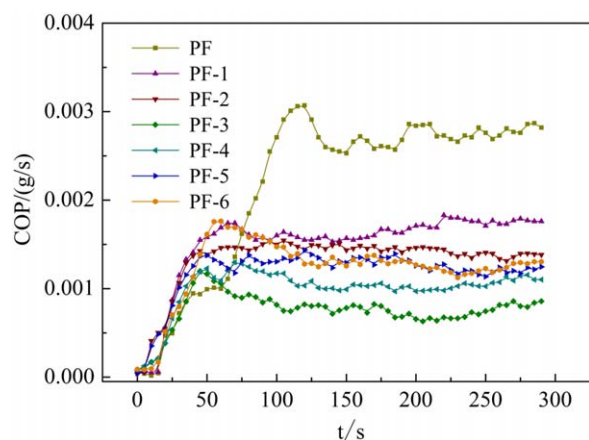
the lower heat release. The  $O_2C$  and total oxygen consumption (TOC) of the all samples were showed in Figure 8 and Table III.  $O_2C$  and TOC of FRCPFs had similar trends, and obviously reduced. The reason was that ZnO had a large surface area and low density, tending to migrate near the regressing sample surface and increase the stability of the carbon layer. On the other hand, when ZnO was added, the cross-linking reaction between resin and phosphorus was promoted and produced high strength carbon layer, which slowed down the pyrolysis rate of combustible gas.<sup>22</sup> In addition, the  $O_2C$  and TOC of the samples also obviously reduced. But at the condition of the content of ZnO was too much or little, the quality of cross-linking carbon layer could not reach the best state. So the use of ZnO should design in a suitable amount. As shown in Figure 8 and Table III,  $O_2C$  and TOC of PF-3 was the lowest one among all the samples. The results showed that there had good effect on decreased the  $O_2C$  and TOC of composite foams when the amount of ZnO was 1%.

#### Total Smoke Release (TSR) of PF and FRCPFs

TSR of all samples was shown in Figure 9 and Table III. We could see that TSR mean value of PF was  $10 \text{ m}^2/\text{m}^2$  in the absence of flame retardant. However, TSR of PF-1 increased to  $42.7 \text{ m}^2/\text{m}^2$  after adding APP/PER, and when co-synergist S (A&P) was applied, TSR of PF-2, 3, 4, 5, 6 were  $44.7 \text{ m}^2/\text{m}^2$ ,  $35.5 \text{ m}^2/\text{m}^2$ ,  $31.4 \text{ m}^2/\text{m}^2$ ,  $40.0 \text{ m}^2/\text{m}^2$  and  $38.5 \text{ m}^2/\text{m}^2$  respectively. Compared with PF, TSR of FRCPFs obviously increased. The reason could be explained that nonflammable gases released by flame retardant could isolate the combustible gases from flame zone and retard flame spread, therefore more smoke was released due to the incomplete combustion of volatiles. It could conclude that S (A&P) presented negative effect on reducing the smoke release of PFs.<sup>50</sup>

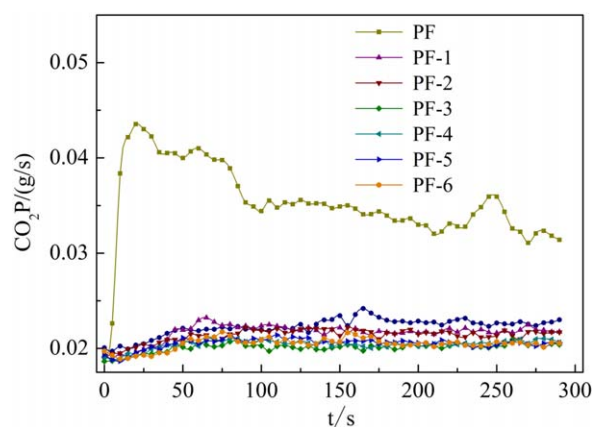
#### Production of CO (COP, $CO_2P$ ) and Yield of $CO_2$ (COY, $CO_2Y$ ) of PF and FRCPFs

HRR, THR, EHC, and SEA are important parameters for evaluating flame retardancy and flammability of polymeric materials. Another important parameter is the emission of toxic gases which helps the understanding of the fire hazard related to



**Figure 10.** COP curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

materials. The toxicity of gaseous products from the combustion of materials is the emission of CO accompanied by CO<sub>2</sub>.<sup>51</sup> The production of CO and CO<sub>2</sub> for all samples was shown in Figures 10 and 11. Compared with PF, FRCPFs generated lower level of CO and CO<sub>2</sub>. Especially, the CO and CO<sub>2</sub> production of PF-3 and PF-4 were lower than others'. The yield of CO and CO<sub>2</sub> for all samples was listed in Table II. The mean yield of CO and CO<sub>2</sub> for the sample containing flame retardant was lower than the sample without flame retardant. With the addition of flame retardant, the mean yield of CO and CO<sub>2</sub> decreased significantly. The reason was that cross-linking reaction between resin and phosphorus was promoted when ZnO was added and produced high strength carbon layer, which slowed down the pyrolysis rate of combustible gas.<sup>22</sup> Therefore the mean and maximum yield of CO and CO<sub>2</sub> decreased significantly. But the excess or less content of ZnO could not generate the apt cross-linking carbon layer. As a result, suitable amount of ZnO should deliberately design. From Figures (10 and 11) and Table II, it could be seen that the mean and peak yield of CO and CO<sub>2</sub> of PF-3 was the relatively lower one among all the samples in the time between 0 to 290 s. The results showed that there had good effect on suppressing the release of toxic gas in



**Figure 11.** CO<sub>2</sub>P curves of PF and FRCPFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** COY and CO<sub>2</sub>Y of PF and FRCPFs During the Entire Test Period

| Sample no. | COY (kg·kg <sup>-1</sup> ) |       | CO <sub>2</sub> Y (kg·kg <sup>-1</sup> ) |       |
|------------|----------------------------|-------|--|-------|
|            | Mean                       | Peak  | Mean                                     | Peak  |
| PF         | 0.16                       | 1.09  | 2.02                                     | 10.21 |
| PF-1       | 0.075                      | 0.328 | 1.10                                     | 4.44  |
| PF-2       | 0.065                      | 0.339 | 1.05                                     | 4.89  |
| PF-3       | 0.057                      | 0.500 | 1.02                                     | 8.46  |
| PF-4       | 0.052                      | 0.549 | 1.11                                     | 10.91 |
| PF-5       | 0.041                      | 0.155 | 1.05                                     | 3.72  |
| PF-6       | 0.070                      | 1.62  | 1.16                                     | 24.92 |

the combustion of composite phenolic foam when the amount of ZnO was 1%.

### Pictures of Char Residues

Figure 12 presents images of residues of all samples. It could be seen that abundant coherent and dense char was formed after the addition of flame retardant. The difference in char structure could be used to explain the combustion phenomenon of the flame retardant samples. The formation of the efficient char could prevent the heat transfer between the flame zone and the burning substrate, and thus protecting the underlying materials from further burning and retarding the pyrolysis of polymers. However, the residues' surface of PF-1, PF-2, and PF-6 appeared obvious cracks, especially for PF-6, which affect negatively on flame retardancy of polymers. It can be explained that cross-linking reaction between resin and phosphorus was accelerated when ZnO was added, and produced high strength carbon layer. But the speed of cross-linking reaction was accelerated when ZnO content was more than 3%, the viscosity of system increased and did not match with foaming rate, which caused the failure of the formation of carbon layer. The different char residues also contributed to the flame retarding performance. In comparison, the residues' surface of PF-4 was more homogeneous. For the above reasons, PF-4 was better flame retardant system for PFs than others.

Based on the figures illustrated above and the statistics data shown in Table III, there are obvious differences on the combustion parameters. By comprehensively comparing various performances, the properties of FRCPFs were better when the amount of ZnO was 1–1.5%.

### Mechanical Properties of Phenolic Foam

FRCPFs were low density rigid foams, whether the stress resulted from compression could be effectively dispersed had a great direct effect on the compression strength.<sup>52</sup> Foam with good toughness had better capacity of bubble deformation, which could effectively dispersed stress into the bubbles, while it would be the opposite with poor toughness.<sup>53</sup> Table IV showed the mechanical properties of all the foams. It could be seen that the compression and bending strength were reduced gradually with the increase of the synergist. The reason was that the original cell structure of foam was broken by flame retardant, so the cell structure got irregular and distribution became uniform making the ratio of closed cell much lower. Therefore, it could

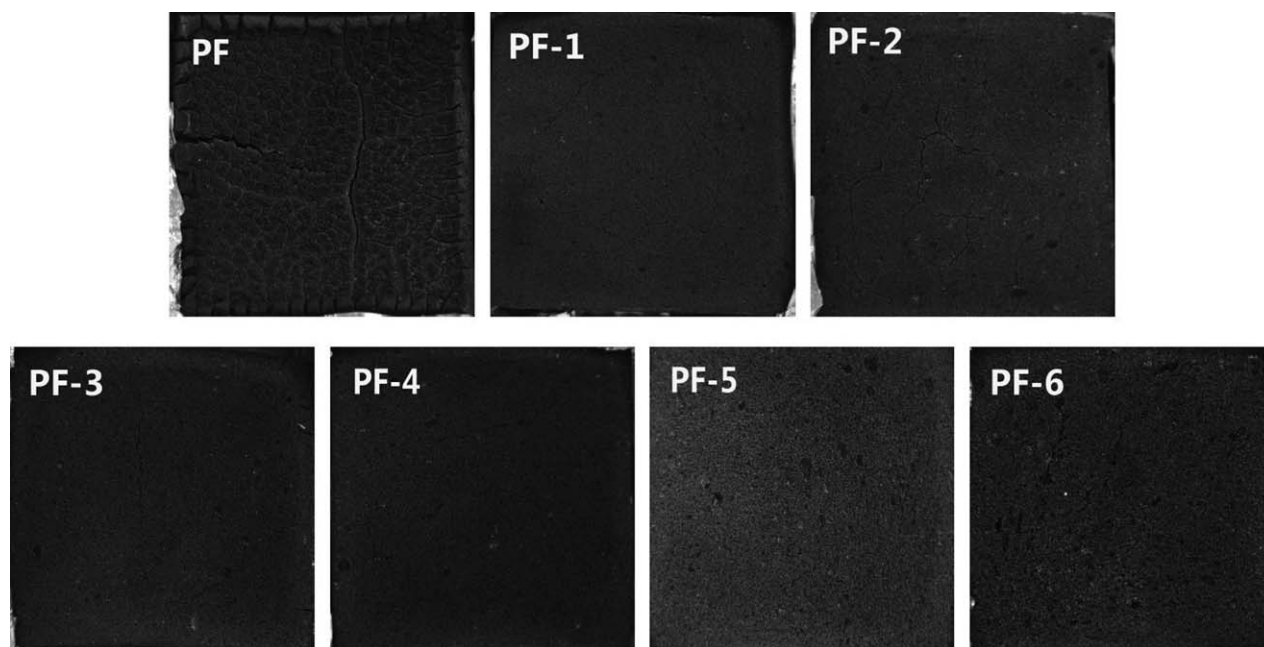


Figure 12. Pictures of residues after the cone calorimeter tests.

Table III. The Average Data (0~290 s) From Cone Calorimeter of PFs

| Sample no. | HRR (kW·m <sup>-2</sup> ) | THR (MJ·m <sup>-2</sup> ) | EHC (MJ·kg <sup>-1</sup> ) | SEA (m <sup>2</sup> ·kg <sup>-1</sup> ) | TOC (g) | TSR (m <sup>2</sup> ·m <sup>-2</sup> ) | AHRE (kW·m) |
|------------|---------------------------|---------------------------|----------------------------|---|---------|--|-------------|
| PF         | 30.4                      | 13.7                      | 15.96                      | 7.95                                    | 8.90    | 10.0                                   | 43.8        |
| PF-1       | 12.1                      | 3.50                      | 5.45                       | 66.0                                    | 2.20    | 42.7                                   | 12.1        |
| PF-2       | 10.39                     | 3.0                       | 4.51                       | 66.94                                   | 1.9     | 44.7                                   | 11.2        |
| PF-3       | 6.84                      | 2.0                       | 3.01                       | 53.73                                   | 1.3     | 35.5                                   | 7.6         |
| PF-4       | 7.25                      | 2.1                       | 3.79                       | 56.38                                   | 1.3     | 31.4                                   | 14.6        |
| PF-5       | 8.91                      | 2.4                       | 4.11                       | 69.15                                   | 1.4     | 40.0                                   | 20.9        |
| PF-6       | 9.41                      | 2.7                       | 4.71                       | 66.27                                   | 1.7     | 38.5                                   | 20.5        |

only afford smaller load force, the compression and bending strength were both decreased. But the compression strength of PF-6 was also meeting the requirement of GB/T 20974-2007 (Rigid phenolic foam for thermal insulation).

Table IV. Mechanical Properties of the Foams

| Sample no       | Bending strength (KPa) | Compression strength (Kpa) | Density (kg/m <sup>3</sup> ) |
|-----------------|------------------------|----------------------------|------------------------------|
| PF              | 400.5                  | 256.3                      | 52.75                        |
| PF-1            | 334.3                  | 226.1                      | 51.44                        |
| PF-2            | 290.0                  | 190.0                      | 48.13                        |
| PF-3            | 239.4                  | 180.9                      | 49.07                        |
| PF-4            | 243.3                  | 179.8                      | 52.88                        |
| PF-5            | 238.5                  | 174.5                      | 50.04                        |
| PF-6            | 216.2                  | 168.8                      | 52.35                        |
| GB/T 20974-2007 | -                      | ≥100                       | ≤60.00                       |

## CONCLUSIONS

The retardant additives including eco-friendly halogen-free flame retardants APP, PER, and synergist (ZnO) were added in HSRPRs to fabricate the FRCPFs. The effects of synergist content on the performance and properties of FRCPFs were investigated. It was found that LOI of FRCPFs significantly increased and reached to around 75.1%. HRR, AHRE, THR, EHC, O<sub>2</sub>C, TOC and emission of toxic gases (COP and COY) remarkably decreased, while SEA and TSR were significantly increased. The flame retardant system was proved to agree with the gas-phase flame retardant mechanism. The results showed that FRCPFs had excellent flame retardancy, although it has a minor negative effect on reducing the smoke release. With the increase of the Zinc Oxide, the bending and compression strength were decreased gradually. The properties of the composite foam were better when the amount of ZnO was 1–1.5%.

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