

# Flammability and Thermal Properties of High Density Polyethylene/Paraffin Hybrid as a Form-Stable Phase Change Material

Yibing Cai,<sup>1</sup> Yuan Hu,<sup>1</sup> Lei Song,<sup>1</sup> Yong Tang,<sup>1</sup> Rui Yang,<sup>2</sup> Yinping Zhang,<sup>3</sup> Zuyao Chen,<sup>4</sup> WeiCheng Fan<sup>1</sup>

<sup>1</sup>State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui, People's Republic of China

<sup>2</sup>Department of Chemical Engineering, Tsinghua University, Beijing, People's Republic of China

<sup>3</sup>Department of Building Science, Tsinghua University, Beijing, People's Republic of China

<sup>4</sup>Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, People's Republic of China

Received 20 March 2005; accepted 21 April 2005

DOI 10.1002/app.22065

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this study, form-stable phase change material (PCM)–high density polyethylene (HDPE)/paraffin hybrid with different flame-retardant systems are prepared by using twin-screw extruder technique. This kind of form-stable PCM is made up of paraffin (a dispersed phase change material) and a HDPE (a supporting material). Their structures and flammability properties are characterized by scanning electronic microscope (SEM) and cone calorimetry. Thermal stability is shown by thermogravimetry analysis (TGA) and its latent heat is given by differential scanning calorimeter (DSC) method. SEM results show that the HDPE forms a three-dimensional net structure and the paraffin is

dispersed in it. The peak of heat release rate (HRR) of the flame-retardant form-stable PCM decreases markedly. In TGA curves, although the onset of weight loss of flame-retardant form-stable PCMs occur at a lower temperature than that of form-stable PCM, flame-retardant form-stable PCMs produce a large amount of char residue at 700°C. DSC results show that the addition of flame retardant has little effect on the phase change latent heat of PCM. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1320–1327, 2006

**Key words:** phase change material (PCM); flame retardant; heat release rate; latent heat

## INTRODUCTION

Energy needs for a wide variety of applications depend on time and some energy resources. Therefore, the storage of energy is necessary to meet these energy needs. Among the different methods of thermal energy storage, the latent energy storage is one of the most attractive. It is able to store and release very large quantities of energy per weight of material. In addition, the temperature remains nearly constant during the phase change. Much attention has been paid to form-stable PCM, which represent a rational alternative to traditional PCM.<sup>1–5</sup> Hong and Zhang et al. also investigated PCMs that consist of several kinds of different high density polyethylene (HDPE) and refined paraffin or semirefined paraffin, whose weight percentage is 75%.<sup>5–7</sup> However, form-stable PCMs are

easily combustible, thus restrict the range of its applying fields, especially in the practice of buildings. Little literature has been found on the flame retardant of HDPE/paraffin. Therefore, it should be an important task to study its flame retardation.

Flame retardation is a technology by which the normal degradation or combustion of polymers is altered by addition of certain chemicals. For some polymers, it is necessary to improve their fire performance by incorporating commercially available flame retardant.<sup>8</sup> Generally, intumescent formulation contains three active ingredients: an acid source, such as ammonium polyphosphate (APP); a carbonization compound, such as polyol; and a blowing agent, such as melamine phosphate (MPP). The intumescent flame retardant (IFR) is widely used as environmental, halogen-free additive. Considering the characteristic of HDPE and paraffin, we chose IFR containing pentaerythritol (PER) and MPP, which are typical flame-retardant of polyolefins and compatible with HDPE and paraffin. On heating, intumescent materials form a foamed cellular charred layer on their surface, which limits the transfer of fuel to the gas phase, the transfer of heat from the flame to the condensed phase, and oxygen diffusion in the condensed phase.<sup>9–11</sup> For many poly-

Correspondence to: Y. Hu (yuanhu@ustc.edu.cn).

Contract grant sponsor: China NKBRFSF Project; contract grant number: 2001CB409600.

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50323005 and 50476026.

TABLE I  
Sample Identification and Composition

Samples	Composition (wt %)
PCM1	Paraffin60 + HDPE40
PCM2	Paraffin60 + HDPE20 + MPP10 + PER10
PCM3	Paraffin60 + HDPE15 + MPP15 + PER10
PCM4	Paraffin60 + HDPE15 + MPP10 + PER15
PCM5	Paraffin60 + HDPE15 + TDE19 + AO6
PCM6	Paraffin60 + HDPE15 + MCA25

mers, the traditionally halogenated organic compounds were well-known flame-retardant additives, such as decabromodiphenyl oxide. They were generally used in incorporation with antimony trioxide (AO) to enhance their flame-retardant efficiency (halogen-antimony synergistic effect).<sup>11–13</sup> In the study, the substitute to the most commonly used brominated flame retardant, 1,2-bis(pentabromophenyl) ethan (BPBE), was chosen. The addition of flame retardants, compound BPBE-AO, and melamine cyanurate (MCA) to PCM is also studied.

Consequently, in the present work, form-stable PCM-HDPE/paraffin hybrid with various flame retardants was prepared. The structure and flame-retardant property are investigated using scanning electronic microscope (SEM) and cone calorimetry, respectively. Thermal stability is characterized by thermogravimetry analysis (TGA) and its latent heat is obtained *via* differential scanning calorimeter (DSC) method.

## EXPERIMENTAL

### Materials

The following products were used: HDPE was supplied as pellets by Daqing Petrochemical Company, China Petroleum; paraffin (melting temperature  $T_m = 56–60^\circ\text{C}$  and latent heat 125.27 KJ/kg); pentaerythritol (PER, powder, average size 92%  $<10\ \mu\text{m}$ ); melamine phosphate (MPP, powder, average size 92%  $<10\ \mu\text{m}$ ); the brominated flame retardant, 1,2-bis(pentabromophenyl) ethan (BPBE, with bromine content 82–83 wt %, average particle size  $<5\ \mu\text{m}$ ); the antimony oxide (AO, average particle size  $8\ \mu\text{m}$ ); and melamine cyanurate(MCA, with nitrogen content  $>98\ \text{wt}\%$  and average particle size  $5\ \mu\text{m}$ ) was kindly provided by Ke Yan company. All these flame retardants are commercial products.

### Preparation of form-stable pcms

A twin-screw extruder (TE-35, KeYa, China) was used for the preparation of all samples. The samples are listed in Table I. The temperature range of the twin-screw extruder was  $120–170^\circ\text{C}$  and screw speed was

450 rpm, thus we obtained form-stable PCM and flame-retardant form-stable PCMs.

### Characterization

SEM observations were performed for PCM1, PCM3, and PCM5, and the SEM specimens were cracked in liquid nitrogen, investigate its fracture surfaces. At the same time, the char residue of PCM2 and PCM3 were studied using SEM. SEM images were obtained on a PHILIPS XL30ESEM microscope.

Flammability was characterized by Cone Calorimeter; the signals from the Cone Calorimeter were recorded by a computer system. All samples ( $10 \times 10 \times 0.3\ \text{cm}^3$ ) were examined in a Stanton Redcroft cone calorimeter according to ASTM 1356–90 under a heat flux of  $35\ \text{Kw/m}^2$ . The experiments were repeated three times and the results were reproducible to within  $\pm 10\%$ . The cone calorimeter data reported in this study are the average of three replicated samples.

The thermal properties of form-stable PCMs were characterized by TGA using NETZSCH STA409C Thermal Analyzer under  $\text{N}_2$  atmosphere at the rate of  $10^\circ\text{C}/\text{min}$ . The mass of each sample is about 6–10 mg in TGA. Latent heat of form-stable PCMs were obtained by DSC measurements, which was carried out in a argon atmosphere by means of DT-50 thermal analyzer from 20 to  $500^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$ . Argon flow rate was  $30\ \text{mL}/\text{min}$ , each sample (10 mg) was examined, and precision on calorimeter and temperature measurements were  $\pm 2.0\%$  and  $\pm 2.0^\circ\text{C}$ , respectively.

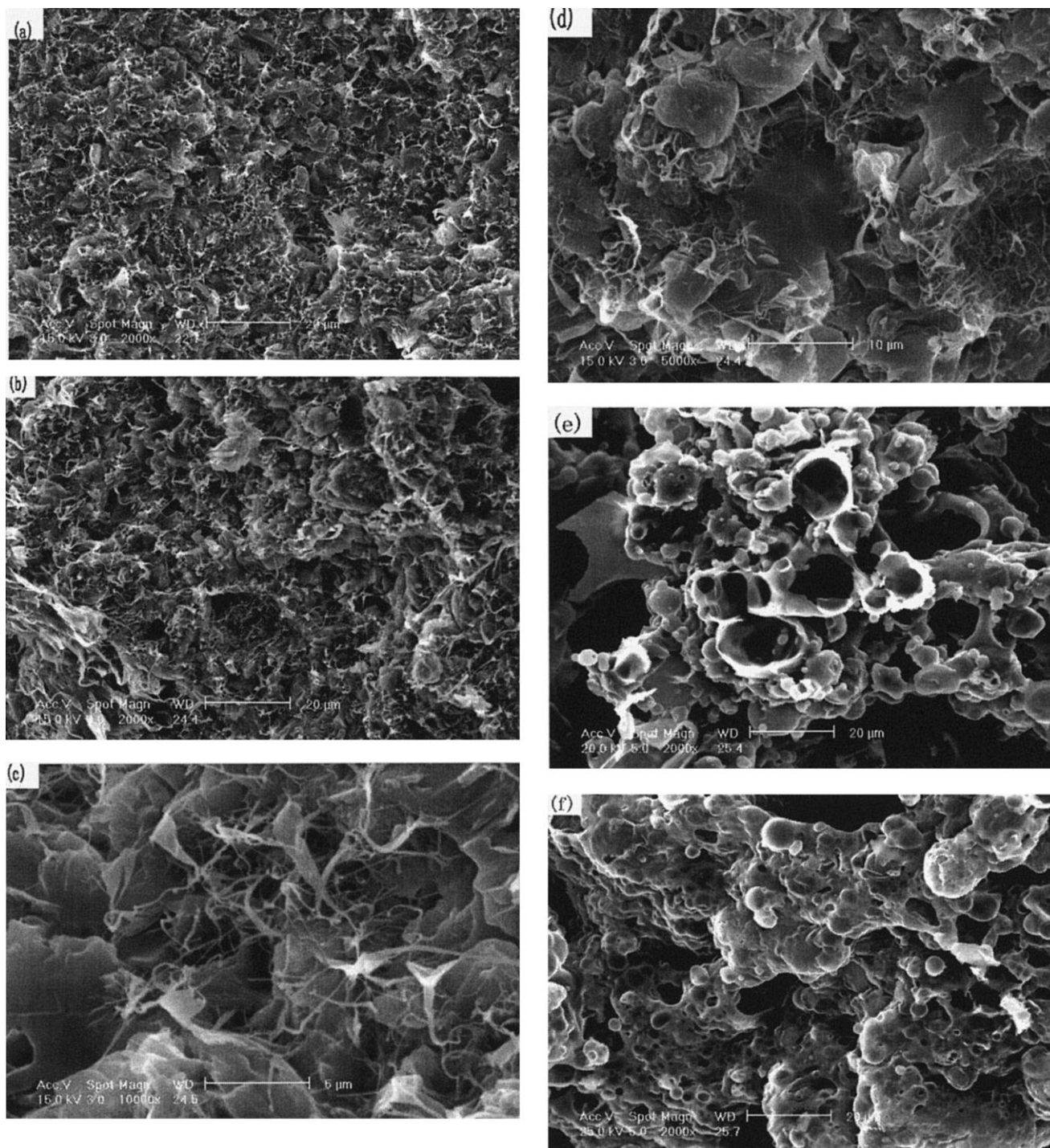
## RESULTS AND DISCUSSION

### Morphology of form-stable pcms

Paraffin is a homologous compound of HDPE and is compatible with HDPE. Form-stable PCMs consist of paraffin (a dispersed PCM) and HDPE (a supporting material). The paraffin disperses in the three-dimensional net structure formed by HDPE, which can be confirmed by SEM. Figures 1(a)–1(d) are the SEM photographs of a form-stable PCM1 and flame-retardant form-stable PCM3 and PCM5. The SEM images also indicate that flame retardant is well dispersed in net structure.

### Flammability properties

Cone calorimeter investigations can be used as a universal approach to ranking and comparing the fire behavior of materials. Therefore, it is not surprising that the cone calorimeter is finding increasing implementation as a characterization tool in the research and development of fire-retarded polymeric materials. All materials burn homogeneously under forced flam-



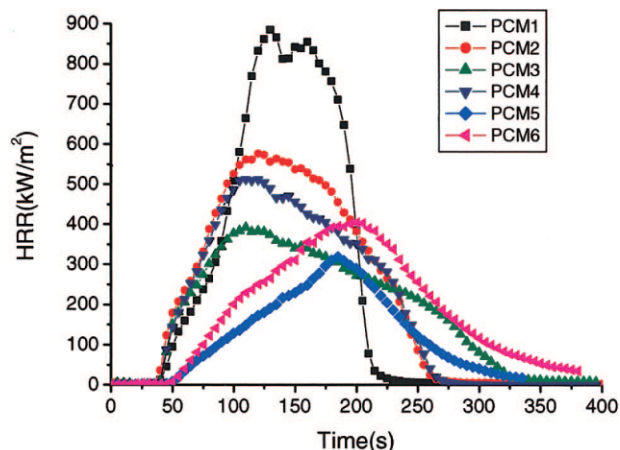
**Figure 1** The SEM photographs of PCM (a) PCM1, (b, c) PCM3, and (d) PCM5; the char residue: (e) PCM2 and (f) PCM3.

ing conditions in the cone calorimeter with stable flame zone above the surface. Hence, an anaerobic pyrolysis of the polymer was expected. At the end of the test, the flame-retardant materials showed minimal flaming along the flame edges, which indicated a delayed burning of the covered materials.<sup>14–17</sup> Cone calorimetry is one of the most effective bench-scale methods for studying the flammability properties of

materials. Heat release rate (HRR), particularly peak HRR, has been found to be the most important parameter to evaluate fire safety.<sup>10,18</sup>

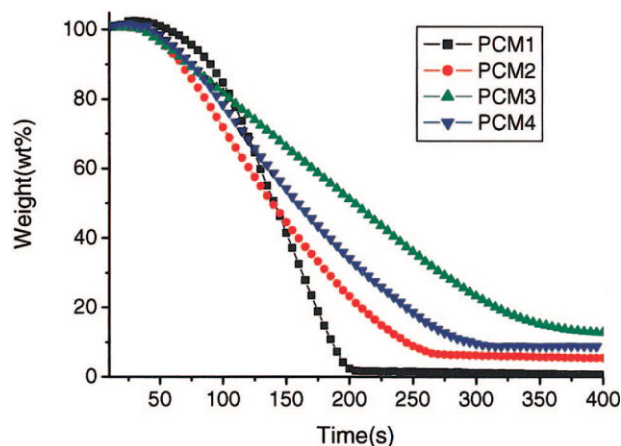
#### Combustion of IFR and PCM

The results of cone calorimeter investigation are a comprehensive characterization of the performance of



**Figure 2** HRR of PCM1, PCM2, PCM3, PCM4, PCM5, and PCM6. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

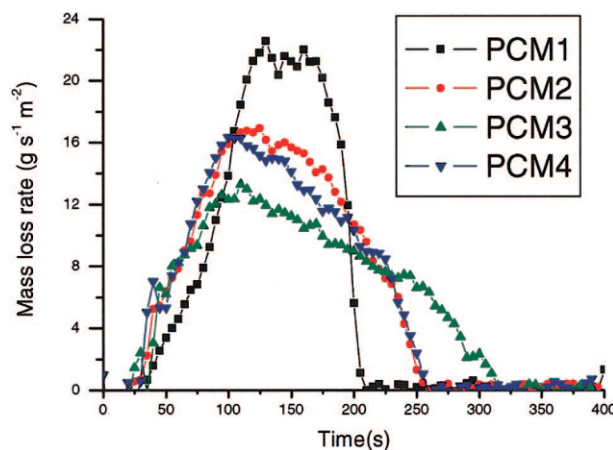
the tested samples in a rather well-defined fire test scenario. Since the cone calorimeter was developed to approximate an ideal performance-based bench scale fire testing method, some of the results even allow an accurate description of the materials' properties, such as the HRR.<sup>14</sup> Figure 2 shows that the HRR of the flame-retardant form-stable PCMs is sharply reduced when compared with that of the form-stable PCM. The peak HRR values of flame-retardant form-stable PCMs are decreased by about 35% (PCM2), 56% (PCM3), and 42% (PCM4) in comparison with the form-stable PCM1. It is because that while burning a formed multicellular char on the surface of the material makes a thermal insulation and provokes the extinguishment of the flame, and also separates oxygen from burning material.<sup>11</sup> The formed multicellular char residue is proved by SEM investigation. The char residue structures of PCM2 and PCM3 are shown in Figures 1(e) and 1(f), respectively. The SEM images indicate that the char residue structure of PCM3 is tighter and denser than that of PCM2. This result is in accordance with the decrease of the peak HRR. It is interesting to note that the HRR of PCM1 has two peaks and the reason for this may be the difference of heat of gasification between HDPE and paraffin. The two peaks correspond to the flammability of paraffin and HDPE, respectively, during the process of combustion. The two-step pyrolysis behavior was pronounced for all PCMs and the phenomenon was also proved by TGA (see Figs. 6 and 7). However, the peak HRR of PCM3 is low compared with PCM4 containing the same mass percent of flame-retardant, but the content of MPP in PCM3 is higher than that in PCM4. The reason may be that in IFR systems,<sup>10,19,20</sup> MPP is used as the acid source, forming polyphosphoric acid as an acid catalyst on heating. The polyphosphoric acid takes part in the dehydration of the carbonific



**Figure 3** Mass loss of PCM1, PCM2, PCM3, and PCM4. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

compounds to yield carbon char, which acts as a physical protective barrier. Figure 3 shows the weight of the char residues. From the Figure 3, we can investigate that the PCM1 has no char residue and the char residue mass of PCM3 is higher than that of PCM4. The more the amount of char residue, the more the HRR decrease is. The mechanism of this fire retardant is as follows: the char acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing pyrolysis of the material to volatile combustible products.<sup>9,11</sup>

The primary parameter that was responsible for a lower HRR of the samples filled with IFR is the mass loss rate (MLR) during combustion, which was significantly reduced compared with those values observed for the form-stable PCM. Figure 4 shows that the MLR decreased in the order of PCM3 > PCM4 > PCM2 > PCM1, this trend is the same as that of the HRR in



**Figure 4** MLR of PCM1, PCM2, PCM3, and PCM4. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

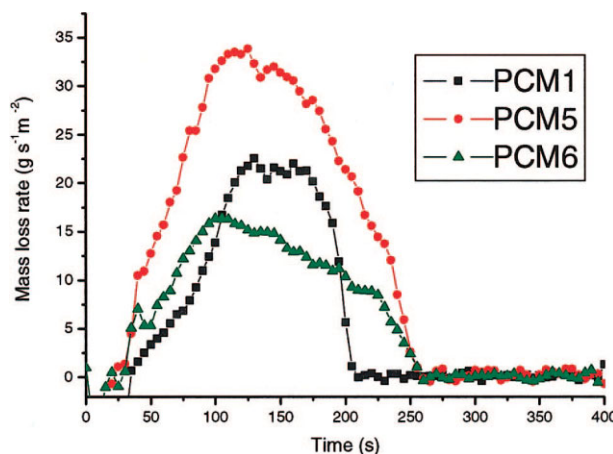
**TABLE II**  
Part Data Recorded in Cone Calorimeter Experiments for All Samples

Sample	THE (MJ/m <sup>2</sup> )	THE/total mass loss (MJ/m <sup>2</sup> )/g	TSR	CO (kg/kg)
PCM1	76.5	3.45	1015.02	0.0172
PCM2	84.1	3.32	1160.99	0.0182
PCM3	70.3	3.08	1312.02	0.0214
PCM4	75.6	3.19	1224.14	0.0199
PCM5	53.2	2.08	2954.46	0.0446
PCM6	87.3	3.46	1176.82	0.0145

the cone calorimeter (Fig. 2). The peak HRR of PCMs with IFR during the complete combustion process was reduced, but the THE (Table II) was not affected in comparison with the form-stable PCM. The formed multicellular char barrier also cancelled out any thermal feedback effect at the end of the burning. The THE/total mass loss (Table II) was reduced slightly for PCMs with IFR in comparison with the form-stable PCM. It was proposed that these minor changes were due to improved ventilation by changing the fuel support rate in the fire in the cone calorimeter. The formed char slows the processes like mixing fuel and air, heating, and igniting, control the rate of burning.<sup>15</sup> The decrease of peak HRR, the SEM images, and the results of the THE/total mass loss all showed the IFR *via* condensed-phase fire-retarded mechanism.

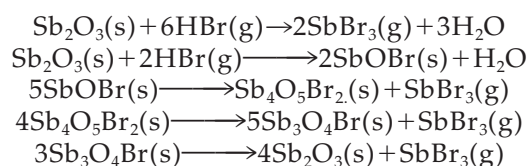
### Combustion of BPBE, AO and PCM, and MCA and PCM

BPBE and AO are one of the substitutes to most commonly used combination of compounds providing a well-known fire-retardant effect. They have effective flame retardancy, high temperature resistance, good processability, and excellent compatibility with polymer matrix. The addition of BPBE and AO to PCM has effect on the combustion test (shown in Figs. 2 and 5). The HRR for PCM5 with BPBE and AO decreases sharper than for PCM1, and the peak HRR value for PCM5 reduces from 884.2 (PCM1) to 319.3 kW/m<sup>2</sup>. There was lower HRR value, as AO was incorporated with BPBE because of synergism. The THE was reduced strongly. The BPBE and AO additive reduced the effective heat of combustion due to radical trapping in the gas phase. Figure 5 shows MLR curves for PCM1 and fire retardant PCM5, and it indicate that the PCM5 has a higher MLR peak compared with that of PCM1. This trend is opposite to the decrease of the peak HRR. Table II summarizes the relevant data of the cone calorimeter measurements. The THE/total mass loss was calculated to assess the influence of the fire retardants on the effective heat of combustion with respect to form-stable PCM. The PCM5 showed a significant decrease in THE/total mass loss (in com-

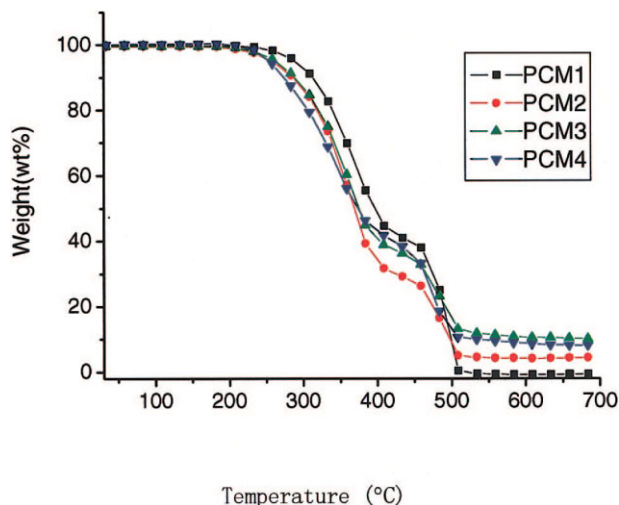


**Figure 5** MLR of PCM1, PCM5, and PCM6. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

parison to PCM1) due to the fire retardancy mechanism in the gas phase.<sup>15</sup> The brominated flame-retardant BPBE takes place during intermolecular elimination reaction and generates hydrogen bromide (HBr) during burning. Then a series of reactions between AO and HBr produce antimony tribromide—a well-known gas phase fire retardant—and various compounds of antimony oxygenbromide, which also decompose into the antimony tribromide in higher temperature zones. The synergistic effect between bromide-antimony in PCM is mainly from the antimony tribromide, which formed a dense white smoke that snuffed the flame by excluding oxygen from the front of the flame. Furthermore, the antimony oxygenbromide can absorb the quantity of heat during the process of decomposition, accordingly retard the degradation temperature and velocity of form-stable PCM. Synergism occurs through a series of reactions, and the basic reaction process is as follows:



Considering the characteristic of PCM during the combustion, another efficient fire retardant MCA is chosen; the well-known mechanism of this additive is that MCA acts as a “carbonization agent” *via* condensed-phase mechanism. MCA facilitates the thermal decomposition of polymer, probably because it interferes with the hydrogen-bonding network of the polymer and exhibits basic catalysis. The HRR peak for PCM6 (see Fig. 2) decreases to 480 kW/m<sup>2</sup>, and the MLR curves (see Fig. 5) for PCM6 and PCM1 have also the same change trend with HRR. The THE of PCM6 was



**Figure 6** The TGA curves of PCM1, PCM2, PCM3, and PCM4. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

increased slightly in comparison to PCM1, but the THE/total mass loss is almost the same between PCM1 and PCM6 (see Table II). This result showed the condensed-phase fire-retarded mechanism of MCA. So, MCA is a kind of well/good flame retardant to PCM.

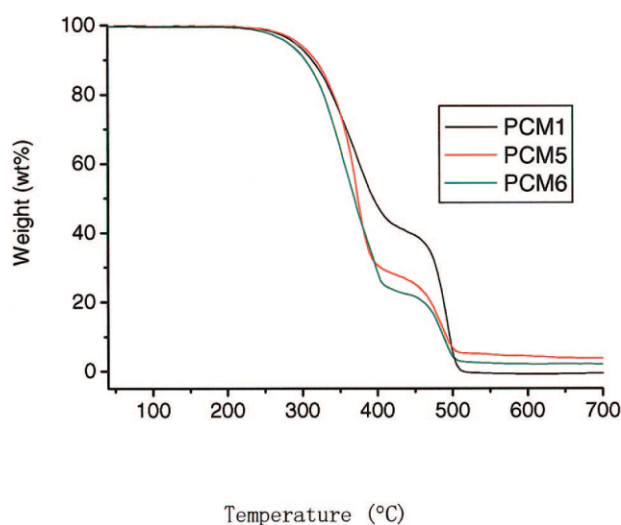
At the same time, Figure 2 shows that HRR of the form-stable PCMs with various flame retardants. It is notable that the decrease of the HRR peak for PCM2 is minimum compared with that of PCM1, because the amount of flame retardant is low. The HRR peak of PCM5 is lower than that of other PCMs when the flame-retardant additive amount is the same. The reason of this may be the gas phase flame retardancy mechanism prevails during the combustion process of PCMs, because the paraffin's low molecule is easily gasified when the PCMs were heated. It is interesting to note that the peak HRR of PCM6 is between PCM3 and PCM4. This may be because IFR yields more carbon char, which acts as a physical protective barrier than MCA, when the acid source reaches certain amount in IFR.

The evaluation of total smoke and CO production is summarized in Table II for the forced flaming and well-ventilated conditions in the cone calorimeter.<sup>15,21</sup> Similar values were detected for all PCMs except PCM5. However, the total smoke production and CO production of PCM5 are significantly higher than other PCMs due to the gas phase action of brominated flame retardant. Although the peak HRR of PCM5 has notable decrease in comparison with other flame-retardant PCMs, the PCM5 with brominated flame retardant has high total smoke production and CO production. Therefore, the brominated flame retardant has a severe surrounding contamination, despite of the high flame-retardant efficiency.

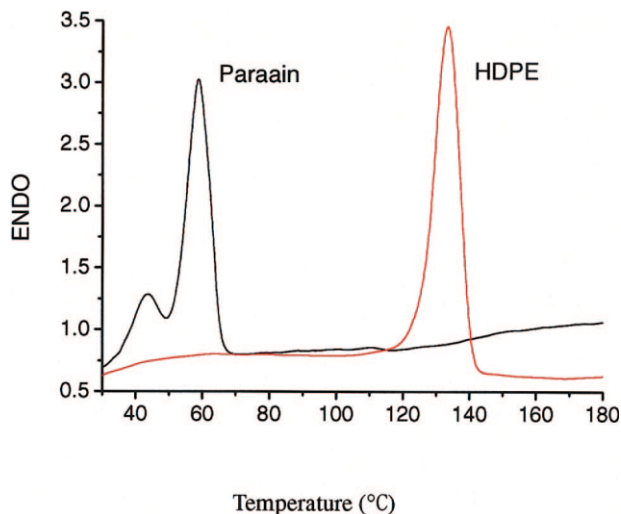
### Thermal degradation of form-stable PCMs

The thermal stability of the flame-retardant form-stable PCMs is discussed and compared with that of form-stable PCM. The TGA curves are shown in Figures 6 and 7. From the TGA curves, we can see that there are two steps in the degradation of PCMs. The first step is roughly from 250 to 450°C, corresponding to the degradation of flame-retardant and paraffin molecular chain, and the second step is about from 450 to 500°C and may be assigned to the degradation of HDPE. Although the onset of weight loss of flame-retardant form-stable PCMs occur at a lower temperature than that of form-stable PCM (partly caused by the degradation of flame-retardant), flame-retardant form-stable PCMs give a larger char residue at 700°C. The char residue amount increases in the order of PCM3 > PCM4 > PCM2. It may be that the content of MPP in PCM3 is higher than that in PCM4. MPP is advantageous for the formation of char layer: high-performance carbonaceous char build up on the surface during thermal degradation and this insulates the underlying material and slows the escape of the volatile products generated during decomposition. When the combination of compounds BPBE, AO, and MCA were added to PCM, the decomposition process is similar to that of PCM with IFR; the char residue amount of PCM5 is higher than that of PCM6. All these results are in agreement with the analysis of cone calorimetry.

In general, all PCMs have the two-step degradation behavior, especially the PCM1 is more pronounced, since PCM1 had the largest HDPE content. PCM1 did not show an additional fire-retardant mechanism. Hence, it must be expected that especially the pyrolysis temperature of PCM1 may be controlled by the decomposition temperature of the material. It becomes likely that the beginning of the burning may be



**Figure 7** The TGA curves of PCM1, PCM5, and PCM6. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

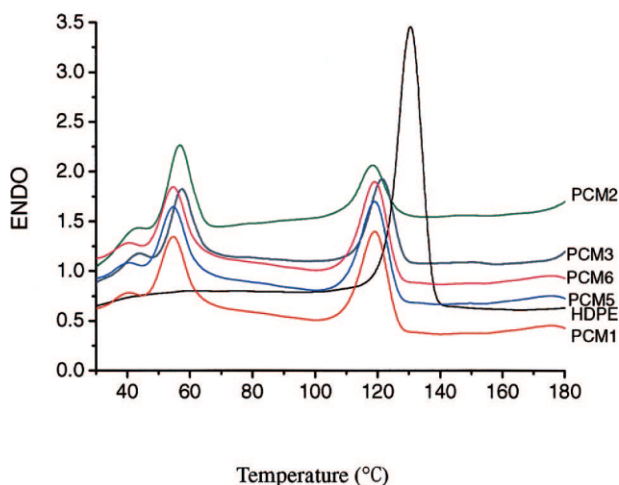


**Figure 8** The DSC curves of paraffin and HDPE. [Color figure can be viewed in the online issue, which is available“ [www.interscience.wiley.com](http://www.interscience.wiley.com).]

influenced more by the paraffin and the end more by the HDPE prolysis.

#### Latent heat of form-stable PCMs

The typical thermograms of paraffin and form-stable PCM are presented in Figures 8 and 9. Figure 8 shows that paraffin has two peaks of phase change, the first phase change peak of paraffin is lesser and corresponds to about 44°C, and the second peak is very high at the near of 58°C. In Figure 9, the molten peak of HDPE is present, corresponding to about 130°C. In form-stable PCM1 and flame-retardant form-stable PCMs, the phase change peaks of paraffin still exist, but the first phase change peak of paraffin is weaker



**Figure 9** The DSC curves of PCM1, PCM2, PCM3, PCM5, PCM6, and the corresponding HDPE. [Color figure can be viewed in the online issue, which is available“ [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE III**  
Latent Heat of Paraffin and PCMs

Samples	Latent heat (kJ/kg)
PCM1	51.42
PCM2	53.92
PCM3	51.02
PCM5	50.30
PCM6	51.26

than the pure paraffin, probably because the three-dimensional net structure partly confines the molecule's heat movement of paraffin in the phase change temperature range. The molten peak of HDPE is ahead of schedule when compared with pure HDPE, because HDPE and paraffin form polymer alloy in PCMs, thereby reduce the melt temperature of HDPE, the third peak (about 120°C) of the thermogram of PCM1 and flame-retardant PCMs stand for the phase transition of the HDPE. Therefore, the paraffin and flame retardants have nearly no much influence on the yield temperature of the HDPE in PCMs compared with the thermogram of the pure HDPE.

Paraffin is a homologous compound of HDPE, and so paraffin can easily mix with HDPE. In the preparation of form-stable PCM and flame-retardant form-stable PCMs, there is no chemical reaction among HDPE, paraffin, and flame retardants. In Table III, some results obtained by DSC measurement are given. From the table, we can see the latent heat of PCM2 is higher than that of PCM1, may be that HDPE formed three-dimensional net structure is more intense and molecular heat movement of paraffin is confined more excessive with a higher content of HDPE in PCM1. However, the latent heat of PCM3, PCM5, and PCM6 is little lower than that of PCM1, possibly there exists two conflict aspect factors influence, on the one hand, the HDPE content of PCM3, PCM5, and PCM6 is lower, the corresponding paraffin molecular heat movement is more active; on the other hand, the flame-retardant content of PCM3, PCM5, and PCM6 is higher, the capability of absorption is heightened, thus constrict partly the latent heat of paraffin. Therefore, the additive of flame retardants has nearly effect on the latent heat of PCMs. In other words, the property of thermal energy storage has not been affected by the additive of flame retardants. The flame-retardant PCMs not only have well thermal energy storage, but also reduce the fire risk of the materials.

#### CONCLUSIONS

Form-stable PCM and flame-retardant form-stable PCMs were prepared by using twin-screw extruder. The morphology of samples was investigated by SEM, the result shows that HDPE formed a three-dimensional net structure and the paraffin was dispersed in it, and the

addition of flame-retardant had no notable effect on the PCM morphology. Flammability properties were characterized by cone calorimetry. The HRR peak values and MLR of flame-retardant form-stable PCMs have distinctly reduced compared with form-stable PCM, and the weight of char residues of flame-retardant form-stable PCMs are markedly higher than that of the form-stable PCM. TGA results showed that the decomposition temperature advanced slightly and the ultima char residue increased in PCMs with flame retardant. Its latent heat is given by DSC method, which showed the latent heat of PCM had not distinct change with the additive of flame retardant. In other words, the property of thermal energy storage has not been affected by the additive of flame retardants. Although halogen containing additives are very effective flame-retardant, they can cause a severe surrounding contamination; consequently, it will be satisfied with the effect of flame retardant in PCM through the additives of IFR or MCA.

## References

1. Inaba, H.; Tu, P. *Heat Mass Tran* 1997, 32, 307.
2. Xavier, P.; Pegis, O.; Sylvain, M. *Heat Mass Tran* 2001, 44, 2727.
3. Xiao, M.; Gong, K. *Energ Convers Manag* 2002, 43, 103.
4. Xiao, M.; Gong, K. *Sol Energ Mater Sol Cell* 2001, 69, 293.
5. Hong, Y.; Xinshi, G. *Sol Energ Mater Sol Cell* 2000, 64, 37.
6. Lin, K.; Zhang, Y. *Energ Build* 2005, 37, 215.
7. Kang, Y.; Jiang, Y.; Zhang, Y. *Energ Build* 2003, 35, 417.
8. Petsom, A.; Roengsumran, S.; Ariyaphattanakul, A. *Polym Degrad Stab* 2003, 80, 17.
9. Dabrowski, F.; Le Bras, M.; Cartier, L.; Bourbigot, S. *J Fire Sci* 2001, 19, 219.
10. Tang, Y.; Hu, Y.; Wang, S. *Polym Int* 2003, 52, 1396.
11. Chiu, S.-H.; Wang, W.-K. *Polymer* 1998, 39, 1951.
12. Hu, Y.; Wang, S. *Macromol Mater Eng* 2003, 288, 272.
13. Yu, L.; Wang, W.; Xiao, W. *Polym Degrad Stab* 2004, 86, 69.
14. Schartel, B.; Bartholmai, M.; Knoll, U. *Polym Degrad Stab* 2005, 88, 540.
15. Braun, U.; Schartel, B. *Macromol Chem Phys* 2004, 205, 2185.
16. Schartel, B.; Braun, U.; Schwarz, U.; Reinemann, S. *Polymer* 2003, 44, 6241.
17. Schartel, B.; Braun, U. *J Fire Sci* 2005, 23, 5.
18. Gilman, J. W. *Appl Clay Sci* 1999, 15, 31.
19. Vandersall, H. L. *J Fire Flamm* 1971, 2, 97.
20. Le Bras, M.; Bourbigot, S. In *Fire Retardancy of Polymers—The Use of Intumescence*, Le Bars, M.; Camind, G.; Bourbigot, S.; Delobell, R. Eds.; The Royal Society of Chemistry: Cambridge, UK, 1998; p 64.
21. Zanetti, M.; Kashiwagi, T.; Falqui, L.; Camino, C. *Chem Mater* 2002, 14, 881.