



A new flame retardance strategy for shape stabilized phase change materials by surface coating



Ling Xu, Jianping Wang, Rui Yang*

Key Laboratory of Advanced Materials (MOE), Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

A new flame retardance strategy for shape stabilized phase change materials (SSPCMs) by surface coating was proposed. The coating was composed of acrylic resin, expandable graphite (EG) and/or red phosphorous (RP). The flame retardant effects of surface coatings on SSPCMs were evaluated by limiting oxygen index (LOI) determination, vertical burning test, cone calorimeter test, field emission scanning electron microscopy (FESEM) and thermogravimetric analysis-Fourier transfer infrared spectrometry (TGA-FTIR). The results showed that surface coated SSPCMs exhibited very good flame retardance, with the LOI values increasing to 35.9 vol% and 36.9 vol%, respectively, from 18.7 vol%. And UL-94 V0 level was achieved at the vertical burning test. In contrast, the same loading of EG and/or RP contributed little to flame retardance of SSPCMs when they were melt-blended into the bulk. The cone calorimeter test revealed that peak heat release rates (PHRR) of surface coated SSPCMs decreased by 60%, and the burning processes prolonged significantly. The flame retardant mechanism of surface coating was investigated using TGA-FTIR. The results showed that EG played a crucial role. When samples were exposed to flame, EG expanded and absorbed evaporated paraffin and heat at the same time so that the combustibles and temperature were decreased. Keywords: Shape stabilized phase change material (SSPCM), Flame retardant property, Surface coating, Expandable graphite (EG), Red phosphorus (RP)

1. Introduction

Phase change materials (PCMs) can absorb or release heat in a temperature range to control the temperature fluctuations, and largely improve energy efficiency. This character promotes them to be a good alternative in thermal management applications [1–4]. Among PCMs [5], paraffins, denoted as C_nH_{2n+2} , are the most extensively studied owing to the versatile phase change temperatures, high latent heat, excellent thermal stability, little or no super-cooling effect as well as relative low cost. However, leakage and inflammability of paraffin will cause the potential fire safety risks during storage, transportation and usage, and restrict its further commercial applications.

Preparation of shape stabilized phase change materials (SSPCMs) by melt-blending of polymers (supporting matrices) and paraffin (thermal storage material) is a most convenient and effective method to solve the leakage problem [6–14]. For example, Wang et al. [11] applied high-density polyethylene (HDPE) and an elastomer (styrene-butadiene-styrene block copolymer (SBS), styrene-isoprene-styrene block copolymer (SIS) or ethylene-propylene-diene copolymer (EPDM)) as the matrix, and observed that paraffin was encapsulated well due to excellent absorption ability of elastomers, with only 8–10% mass loss after 100 cycles.

Introducing flame retardant additives into SSPCMs is a most widely used method to improve the flame retardancy of SSPCMs [12–28]. Cai et al. [13] proposed that $Mg(OH)_2$, microencapsulated red phosphorus and organic montmorillonite (OMMT) contributed to form compact and homogeneous char residue and thus improve the thermal property and flammability of SSPCMs. They also demonstrated that the peak heat release rate (PHRR) and the mass loss rate (MLR) of HDPE/paraffin/OMMT decreased markedly due to an aluminophosphate and ceramic like structure formed by the reaction between OMMT and intumescent flame retardant (IFR), which strengthened the trapping of gaseous combustibles [16]. Mochane et al. [25] studied the effect of expanded graphite, diammonium phosphate (DAP) and Cloisite 15 A clay on the flame retardant properties of ethylene vinyl acetate (EVA)/wax phase change materials. The results revealed that expanded graphite/Cloisite 15 A clay was more efficient than expanded graphite and expanded graphite/DAP. The PHRR reduced to 397 kW/m^2 from 836 kW/m^2 and the time to PHRR prolonged to 465 s from 300 s. This was ascribed to the dense char layer which formed a more effective barrier against penetration of oxygen and heat, and release of flammable volatiles. Zhang et al. [19] explored the synergistic effect of iron and intumescent flame retardant (ammonium polyphosphate (APP)/pentaerythritol (PER)/melamine (MA)) on the improved flame resistance of SSPCM.

* Corresponding author.

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Table 1
Compositions of flame retardant coatings.

Coating	Composition
A	Acrylic resin: acetone: EG = 10: 20: 10
B	Acrylic resin: acetone: EG: red phosphorus = 10: 20: 5: 5

Table 2
LOI values of different SSPCM formulations.

Formulation	LOI/vol%
PCM/OMMT	18.7
PCM/OMMT-A	35.9
PCM/OMMT-B	36.9
PCM/OMMT/EG	17.5
PCM/OMMT/EG/RP	19.2

Iron could promote the generation of ammonia and water (gaseous phase flame retardant) from APP and MA, and then APP acted with the formed Fe^{n+} to enhance the barrier property of the char layer (condensed phase flame retardant). The effect of other metals such as Mg, Al and Zn was also investigated to confirm this mechanism [22]. The flame retardant efficiency of expanded graphite and IFR (APP/PER/MA) was demonstrated by Zhang et al. [21] through the incorporation of expanded graphite and IFR into HDPE/paraffin composites. The results suggested that expanded graphite formed the first char layer at the beginning, and then the synergistic effect between EG and intumescent char layer began to work. Since inhibition of the layers functioned, the PHRR significantly decreased from 1133.83 kW/m² to 430.36 kW/m², despite the shortened ignition time.

The present researches mainly focused on paraffins with phase change temperatures of 40–65 °C. For SSPCMs applied in energy-saving buildings, paraffins with phase change temperatures of 20–30 °C are most concerned. These paraffins have low boiling points and turn to combustibles at low temperatures before most flame retardants act. But, few work was reported in literatures [12,24,28]. Li et al. [12] added a novel triazine char forming agent (CFA) and APP into the eutectic mixed paraffin/PP(30/70) system. The results indicated that 30 wt% APP/CFA enhanced the charring ability and self-extinguishing was observed. The CONE data further confirmed that the peak heat release

Table 3
Vertical burning results of different SSPCM formulations.

Formulation	Classification	Dripping	Comment
PCM/OMMT	NC	No	Burned very fast and the flames spread to the tong.
PCM/OMMT-A	V0	No	EG expanded once exposed to fire and the strips extinguished within 10 s after ignited.
PCM/OMMT-B	V0	No	Similar to PCM/OMMT-A.
PCM/OMMT/EG	NC	No	Burned fast and the strips expanded due to the expansion of EG in the bulk and the flames spread to the tong finally.
PCM/OMMT/EG/RP	NC	No	Similar to PCM/OMMT/EG, but the expansion of the strips was a little weaker.

NC: not classified.

Table 4
Data recorded at cone calorimeter tests for SSPCMs.

Formulation	PHRR (kW/m ²)	Average HRR (kW/m ² s ⁻¹)	t _{PHRR} (s)	t _{flame out} (s)	Peak concentration of CO ₂ (%)	t _{CO₂ peak} (s)
PCM/OMMT	1035.2	241.8	145	200	2.07	244
PCM/OMMT-A	419.4	160.9	460	700	0.70	600
PCM/OMMT-B	454.1	141.5	385	600	0.71	469
PCM/OMMT/EG	434.08	205.6	170	400	0.72	352
PCM/OMMT/EG/RP	378.7	169.6	155	400	0.55	284

rate (PHRR), total heat release (THR) and smoke produce rate (SPR) of PCM decreased obviously. Sittisart et al. [24] investigated the effect of different flame retardants such as Mg(OH)₂, Al(OH)₃, expanded graphite, APP, PER and treated MMT on the properties of HDPE/paraffin (RT21), and showed that the formulations containing IFR (e.g. APP/PER/MMT, APP/MMT) were better candidates to improve the fire retardancy. Wang et al. [28] added OMMT/EG/tert-butyl hydroperoxide (TBHP, cross-linking agent) into HDPE/SBS/paraffin system, and achieved good flame resistant property, with the PHRR decreased by up to 72.7% and less CO₂ and CO yields.

In order to achieve improved flame retardant property, large loading (generally 20–40 wt%) of flame retardants were added. This would weaken the heat storage capacity of SSPCMs significantly. But even with so many flame retardants, SSPCMs may be still flammable, although with less heat release and less CO/CO₂ emission. In this paper, a new flame retardance strategy by surface coating was proposed. In contrast to conventional flame retardance strategy by adding large amount of various flame retardants, this new surface coating strategy is quite easy to carry out and can achieve better flame retardancy with much less flame retardants. At optimal concentration, UL 94 V0 level was achieved.

2. Experimental

2.1. Materials

High-density polyethylene (HDPE) was purchased from Beijing Eastern Petrochemical Co., Ltd. (Beijing, China). Styrene-butadiene-styrene star copolymer with S/B ratio of 3/7 (SBS, T161B), was supplied by Dushanzi Petrochemical Co., Ltd. (Xinjiang, China). Paraffin, with phase change temperature of 30 °C and latent heat of 132.7 J/g, was obtained from Shijiazhuang Zhongdejienergy Phase Change Material Company. Organic montmorillonite (OMMT, NB901), expandable graphite (EG, expansion ratio 100–400 ml/g), and red phosphorus (RP) were provided by Zhejiang Huate Chemical Co., Ltd., Qingdao Nansuhongda Graphite Products Co., Ltd., and Tianjin Fuchen Chemical Reagents Factory, respectively. Acrylic resin (FB9788) and acetone were from Shanghai Weathercock Chemical Science Co., Ltd. and Modern Oriental (Beijing) Technology Development Co., Ltd., respectively.

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