Preparation and characterizations of HDPE–EVA alloy/OMT nanocomposites/paraffin compounds as a shape stabilized phase change thermal energy storage material

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Abstract

A kind of shape stabilized phase change nanocomposites materials (PCNM) based on high density polyethylene (HDPE)/ethylene-vinyl acetate (EVA) alloy, organophilic montmorillonite (OMT), paraffin and intumescent flame retardant (IFR) are prepared using twin-screw extruder technique. The structures of the HDPE–EVA alloy/OMT nanocomposites are evidenced by the X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that an ordered intercalated nanomorphology of the HDPE–EVA alloy/OMT nanocomposites is formed. Then the structures of the shape stabilized PCNM are characterized by scanning electron microscopy (SEM). The HDPE–EVA alloy/OMT nanocomposites act as the supporting material and form the three-dimensional network structure. The paraffin acts as a phase change material and disperses in the three-dimensional network structure. Its latent heat is given by differential scanning calorimeter (DSC) method. The SEM and DSC results show that the additives of IFR have little effect on the network structure and the latent heat of shape stabilized PCNM, respectively. The thermal stability properties are characterized by thermogravimetric analysis (TGA). The TGA analysis results indicate that the flame retardant shape stabilized PCNM produce a larger amount of char residue at 800 °C than that of shape stabilized PCNM, although the onset of weight loss of the flame retardant shape stabilized PCNM occur at a lower temperature. The formed multicellular char residue contributes to the improvement of thermal stability performance. The probable combustion mechanisms are also discussed in this paper.
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Keywords: Phase change nanocomposites materials (PCNM); Organophilic montmorillonite (OMT); Thermal stability; Latent heat; Flame retardant mechanism

1. Introduction

Energy needs for a wide variety of applications are depended on time and some energy resources. Therefore 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 to release 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 phase change material (PCM), which represent a rational alternative to traditional PCM. The traditional PCMs have several defects, one of which is that to store and to release the latent heat of the PCM, special

latent storage device or elements such as shell-and-tube PCM heat exchanger or many cans to encapsulate the PCM will have to be involved, it causes the increase not only in heat resistance but also in the associated cost, to develop heat exchanger in which the heat transfer medium can contact PCMs directly, it is important to investigate form-stable PCMs [1–8]. Among the various kinds of PCMs of interest, paraffin have been found to exhibit many desirable characteristics, such as high latent heat, negligible supercooling, low vapor pressure in the melt, chemically inert and stable, self-nucleating, etc. Zhang et al., Xiao et al. and Sari et al. study the latent heat, the thermal storage and thermal conductivity of PCM using paraffin as a phase change material [3,4,6–8].

At the same time, much attention has been paid to polymer nanocomposites, especially polymer-layered silicate nanocomposites, which represent a rational alternative to conventional filled polymers. Because by employing minimal addition lev-

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els, nanoclays enhance mechanical, thermal, dimensional and barrier performance properties significantly [9–11]. However, due to chemical characteristics of the macromolecule (HDPE and EVA) and paraffin, the shape stabilized PCMs are easily flammable and therefore the improvement of thermal and flammability properties becomes very important. Much literature [11–17] have reported that intumescent flame retardant (IFR) is efficient in polyolefin and widely used as environmental, halogen-free additives. These additives systems consist of a precursor of carbonization catalyst such as ammonium polyphosate (APP) and a carbonization agent such as polyol(pentaerythritol, PER) and a blowing agent (melamine phosphate, MPP). The IFR, while burning, gives a swollen multicellular char, which protects the underlying material from the action of the fire. The mechanism of this fire retardant is assumed that the char acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing pyrolysis of the materials to volatile combustible products. Up to now, the flammability and thermal properties studies of the shape stabilized PCMs are relatively rare, and thus confine their application in many domains, especially in buildings. So, the aim of this study is in order to improve the flammability and thermal properties of the shape stabilized PCMs with flame retardant in combination with layered silicate clays. The clay commonly used for the produce of nanocomposites is montmorillonite (MMT), which consists of two-dimensional layers where two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either alumina or magnesia. The appropriate basal spacing is in favor of the organic modified and the intercalation of polymer, which has been used for fabrication of nanocomposites. The IFR (APP and PER) is chosen for the system of the shape stabilized PCNM. The incorporation of the OMT loadings lead to the thermal stability and flammability properties improvements of the shape stabilized PCNM.

2. Experimental

2.1. Materials

The HDPE and EVA (containing 18 wt% vinyl acetate) were supplied as pellets by Daqing Petrochemical Company, ChinaPetroleum and Beijing Petrochemical, respectively. The paraffin was available commercially with melting temperature $T_m = 56$–$60\,^\circ$C and latent heat 167.03 J/g. The ammonium polyphosphate (APP, white power, average particle size: 92% < 10 μm) and pentaerythritol (PER, white power, average particle size: 92% < 10 μm) were provided by Keyan Company. The organophilic montmorillonite (OMT) was prepared by the researchers of our laboratory.

2.2. The preparation of organophilic montmorillonite (OMT)

Organophilic montmorillonite (OMT) was prepared by cation exchange of natural counterions with ammonium cationic surfactant according to the method of Kawasumi et al. [18]. The alkyl quaternary ammonium salts used were hexadecyl trimethyl

Table 1
Samples identification and compositions

Samples	Compositions
PCNM1	Paraffin 60% + HDPE–EVA 40%
PCNM2	Paraffin 60% + HDPE–EVA 20% + APP-PER 20%
PCNM3	Paraffin 60% + HDPE–EVA 18% + OMT 2% + APP-PER 20%
PCNM4	Paraffin 60% + HDPE–EVA 15% + OMT 5% + APP-PER 20%

ammomum bromide (C16). The OMT was dried under vacuum at 80 °C for several hours before use.

2.3. Synthesis of the HDPE–EVA/OMT nanocomposites and the corresponding shape stabilized PCNM

The HDPE, EVA and desired amounts of OMT were premixed in high-speed blender, and then extruded at 180 °C using a twin-screw extruder (TE-35, KeYa, China). The ratio of HDPE–EVA was fixed as 75/25 by weight. The OMT proportion relative to the polymer matrix (HDPE and EVA) is 2/18 and 5/15 by weight, respectively. The extruded strands were palletized, dried at 80 °C and yielded finally the HDPE–EVA/OMT nanocomposites.

Then, the shape stabilized PCNM with the aforementionedly prepared HDPE–EVA/OMT nanocomposites, paraffin and intumescent flame retardant (IFR) were premixed and prepared by using a twin-screw extruder. The ratio of APP/PER was fixed as 1:1 by weight. The samples are identified in Table 1. The temperature range of the twin-screw extruder was 120–170 °C and screw rotation speed was 450 rpm, thus the shape stabilized PCNM specimens were obtained.

2.4. Characterization

X-ray diffraction (XRD) experiments were performed directly on the samples using a Japan Rigaku D/max-rA X diffraction meter (30 kV, 10 mA) with Cu ($\lambda = 1.54$ Å) irradiation at a rate of 20/min in the range of 1.5–10°. Transmission electron microscopy (TEM) images were obtained on a Jeol JEM-100SX transmission electron microscope with an acceleration voltage of 100 kV. The HDPE–EVA/OMT nanocomposites specimens were cut at room temperature using an ultramicrotome (Ultracut-1, UK) with a diamond knife from an epoxy block with the films of the nanocomposite embedded.

Scanning electron microscopy (SEM) observations were performed for the shape stabilized PCNM. The shape stabilized PCNM specimens were fractured in liquid nitrogen and the fracture surfaces were gold coated before SEM investigation. At the same time, the char residue of PCNM2, PCNM3 and PCNM4 obtained through burning in a muffle furnace for 2 min under 800 °C was also studied using SEM. SEM images were obtained on a Philips XL30ESEM microscopy.

The thermal stability properties of the shape stabilized PCNM were characterized by Thermogravimetric analysis (TGA) using NETZSCH STA409C Thermal Analyzer. In each case, the about 10 mg specimens were heated from 20 to 800 °C using a linear heating rate of 10 °C/min under N_2 atmosphere.
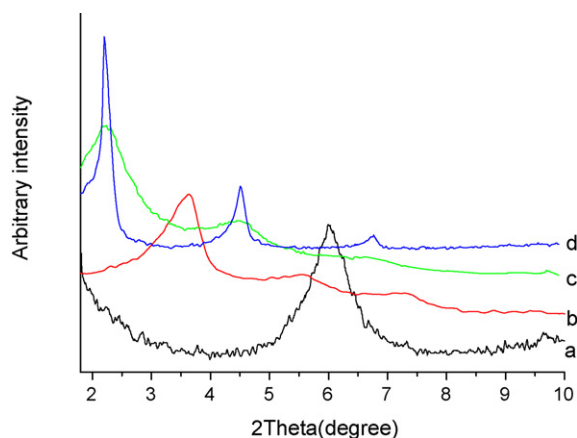
Fig. 1. XRD patterns of (a) MMT, (b) OMT, (c) HDPE–EVA/OMT (5 wt%) nanocomposites and (d) PCNM4.

Fig. 2. TEM micrographs of HDPE–EVA/OMT (5 wt%) nanocomposite.

Differential scanning calorimeter (DSC) was carried out in a nitrogen atmosphere by means of Perkin-Elmer Diamond DSC thermal analyzer from 20 to 200 °C at a heating rate of 10 °C/min, flow rate was 20 ml/min, precision on calorimeter and temperature measurements are ±2.0% and ±2.0 °C, respectively. Indium was used as a reference for temperature calibration. Samples were measured in a sealed aluminum pan with a mass of about 5.0 mg. The latent heat was calculated as the total area under the peaks of solid–solid and solid–liquid transitions of the paraffin in the shape stabilized PCNM by thermal analysis software.

3. Results and discussion

3.1. Dispersibility of HDPE–EVA/OMT nanocomposites and the corresponding shape stabilized PCNM

Fig. 1 shows the XRD patterns of (a) MMT, (b) OMT, (c) HDPE–EVA/OMT (5 wt%) nanocomposites and (d) PCNM4. The peaks correspond to the (0 0 1) plane reflection of the clays. The average basal spacing of MMT increases from 1.5 to 2.4 nm when the original MMT was modified by C16. The increased spacing suggests the chains of C16 intercalate into the gallery of MMT and expand it. The HDPE–EVA/OMT nanocomposites (Fig. 1c) and PCNM4 (Fig. 1d) show the intercalated morphology is characterized by the interlayer spacing derived from the $d_{0 0 1}$ peak of montmorillonite and is increased from 2.4 nm for OMT (Fig. 1b) to 3.8 nm. The 1.4 nm gallery height increase compared with that of OMT indicates an intercalated nano-structure has been formed. The TEM microscopy of HDPE–EVA/OMT (5 wt%) nanocomposites is demonstrated in Fig. 2. Uniform and ordered dispersion of the individual clay layers and the tactoids throughout the HDPE–EVA blend are observed. This is because the vinyl acetate (VA) groups in the EVA chains promote the interaction with clay layers by penetration of the EVA chains into the clay galleries, meanwhile, HDPE is compatible with EVA in the amorphous region, which leads to a good dispersion of the clay in the matrix [19].

The morphology of the shape stabilized PCNM is investigated by SEM. Fig. 3 shows the shape stabilized PCNM images.
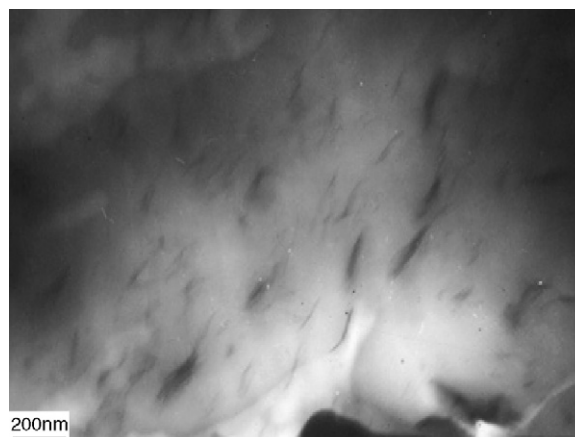
SEM studies show that the HDPE–EVA alloy can enwrap commendably the paraffin and flame retardant, and form compact network structure (Fig. 3(a) and (b)). The flame retardant are well dispersed in the HDPE–EVA alloy and the paraffin. The additive of OMT cause the coalescent more compact among the HDPE–EVA alloy, paraffin and flame retardant (PCNM3 and PCNM4, Fig. 3c and d). The reasons may be that the paraffin partly intercalates into the clay galleries and the OMT itself is also a kind of supporting material [20].

3.2. Thermal degradation stability of HDPE–EVA alloy/paraffin hybrid and the shape stabilized PCNM

The thermal stability property of the shape stabilized PCNM is discussed and compared with that of HDPE–EVA alloy/paraffin hybrid (PCNM1). The TGA curves and DTGA curves are shown in Fig. 4a and b, respectively. The TGA data corresponding to the 5 wt% loss temperature ($T_{-5 \, wt\%}$), the maximum temperature of mass loss (T_1 and T_2) obtained from the DTGA curves and the weight loss (Δm_1 and Δm_2) during different degradation stages for HDPE–EVA alloy/paraffin hybrid and the shape stabilized PCNM are listed in Table 2. During thermal degradation, the TGA curves display a two-stage degradation process. The deacylation reactions of the EVA and the paraffin chains degrade first and then the HDPE chains and the backbone of the EVA degrade in the following step. The first step is roughly from 200 to 450 °C, corresponding to the degradation of the ethylene-vinyl acetate (EVA), intumescent flame retardant (IFR), paraffin molecular chain and surfactant molecule hexadecyl trimethyl ammonium bromide (C16). The $T_{-5 \, wt\%}$ degradation temperature and the maximum loss temperature (T_1) of the shape stabilized PCNM are lower than that of the PCNM1. This is partly caused by the degradation of the flame retardant and surfactant molecule, which occurs in the lower temperature. The earlier mass loss is attributed to the Lewis or Bronsted acid sites on the clay layers generated at 200 °C according to the Hofmann degradation mechanism for OMT, which has a catalyst effect on the deacylation of EVA [21]. The second step is about from 450 to 500 °C, it may be assigned to the degradation of the HDPE and the backbone of the EVA which formed
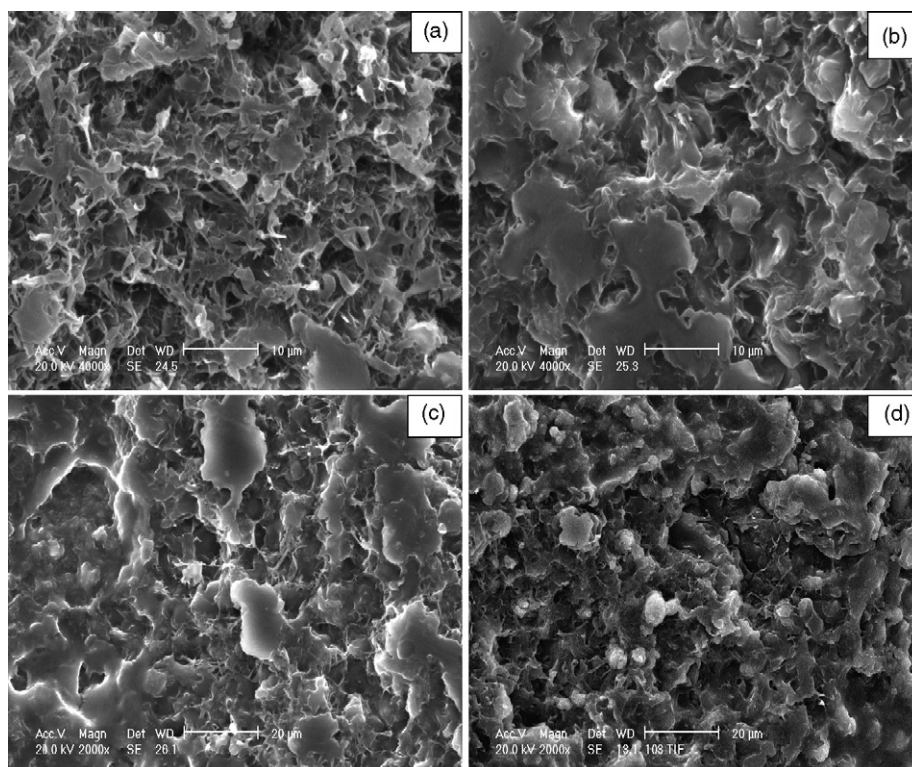
Fig. 3. SEM images of the shape stabilized PCNM: (a) PCNM1, (b) PCNM2, (c) PCNM3 and (d) PCNM4.
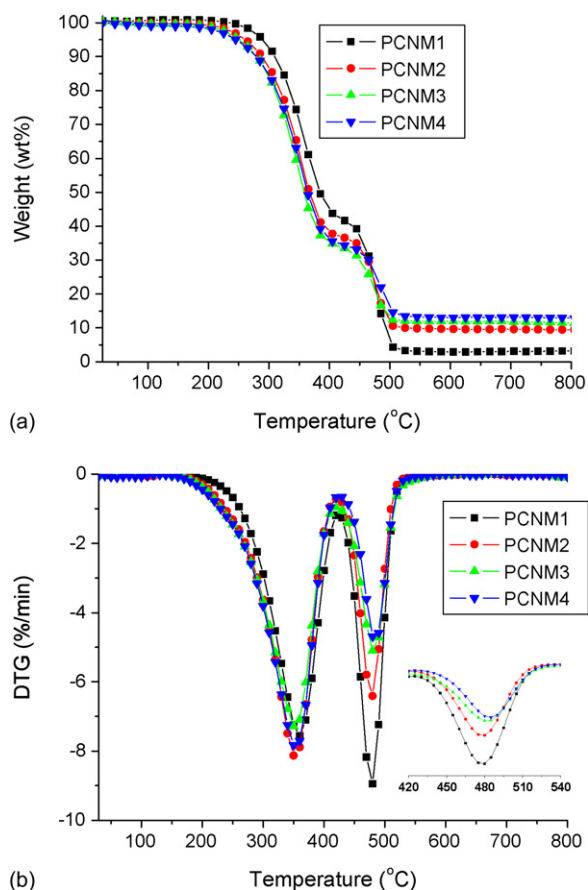

(a)

(b)

Fig. 4. The TGA curves (a) and DTGA curves (b) of the shape stabilized PCNM.

in the first step. As seen in Table 2, the maximum temperature of mass loss (T_2) and the weight loss (Δm_2) of the shape stabilized PCNM are higher than those of the PCNM1. In comparison with Δm_2 of the PCNM1, there are 31.1%, 43.5% and 49.3% decrease in weight loss for the PCNM2, PCNM3 and PCNM4, respectively. The char residue, which is obtained through the decrease of weight loss, improves the thermal stability of the shape stabilized PCNM.

Although the onset of weight loss of the shape stabilized PCNM occurs at a lower temperature than that of HDPE–EVA alloy/paraffin hybrid, the shape stabilized PCNM give a larger char residue at 800 °C. The char residue amount increases order of stability: PCNM4 > PCNM3 > PCNM2 > PCNM1. The char residue amount of the PCNM3 and PCNM4 with OMT is higher than that of PCNM2, probably because that the OMT is more advantageous to form high-performance carbonaceous-silicate char layer building up on the surface, which insulates the underlying material and slows the escape of the volatile products generated during thermal degradation. The results may explain the enhancement of thermal stability of the shape stabilized PCNM compared with HDPE–EVA alloy/paraffin hybrid.

3.3. The probable combustion mechanism for the shape stabilized PCNM

The formed multicellular char residue, which obtained through burning in a muffle furnace under 800 °C is investigated by SEM. The char residue structure of PCNM2, PCNM3 and PCNM4 are shown in Fig. 5. The SEM images indicate that the char residue structure of PCNM4 (Fig. 5c) is tighter and

Table 2
TGA data of the HDPE–EVA alloy/paraffin hybrid and the shape stabilized PCNM

Sample	$T_{-5\,wt\%}$ (°C)	T_1 (°C)	Δm_1	T_2 (°C)	Δm_2	Char residue (800 °C)
PCNM1	289.9	359.4	58.92	478.0	37.74	3.23
PCNM2	261.8	353.0	63.15	478.4	26.01	9.44
PCNM3	250.7	352.7	65.41	482.1	21.33	11.43
PCNM4	246.6	353.6	66.54	484.3	19.15	12.93

denser than any other char residue (Fig. 5a and b). The results are in accordance with the increase order of thermal stability in Fig. 4. Moreover, high magnification SEM shows that the microstructure of the char residue of PCNM4 (Fig. 5f) is more homogeneous than that of PCNM3 (Fig. 5e) with many pores on surface and PCNM2 (Fig. 5d) with loose surface. The compact char residue increases the "trapping" of the decomposition products in the char and as a consequence, reduces the evolved, small, flammable molecules and decreases the toxicity of the combus-

tion products. At the same time, the nanocomposites can lead to the formation of ceramic-like material on the samples surface, which protects the material throughout combustion, limit the transfer of flammable molecules to the gas phase, the transfer of heat from the flame to the condensed phase and oxygen diffusion in the condensed phase [22].

The results of char residue morphology analysis show that there is an enhancement of flame retardant in the shape stabilized PCNM. In intumescent flame retardant systems, APP is used as
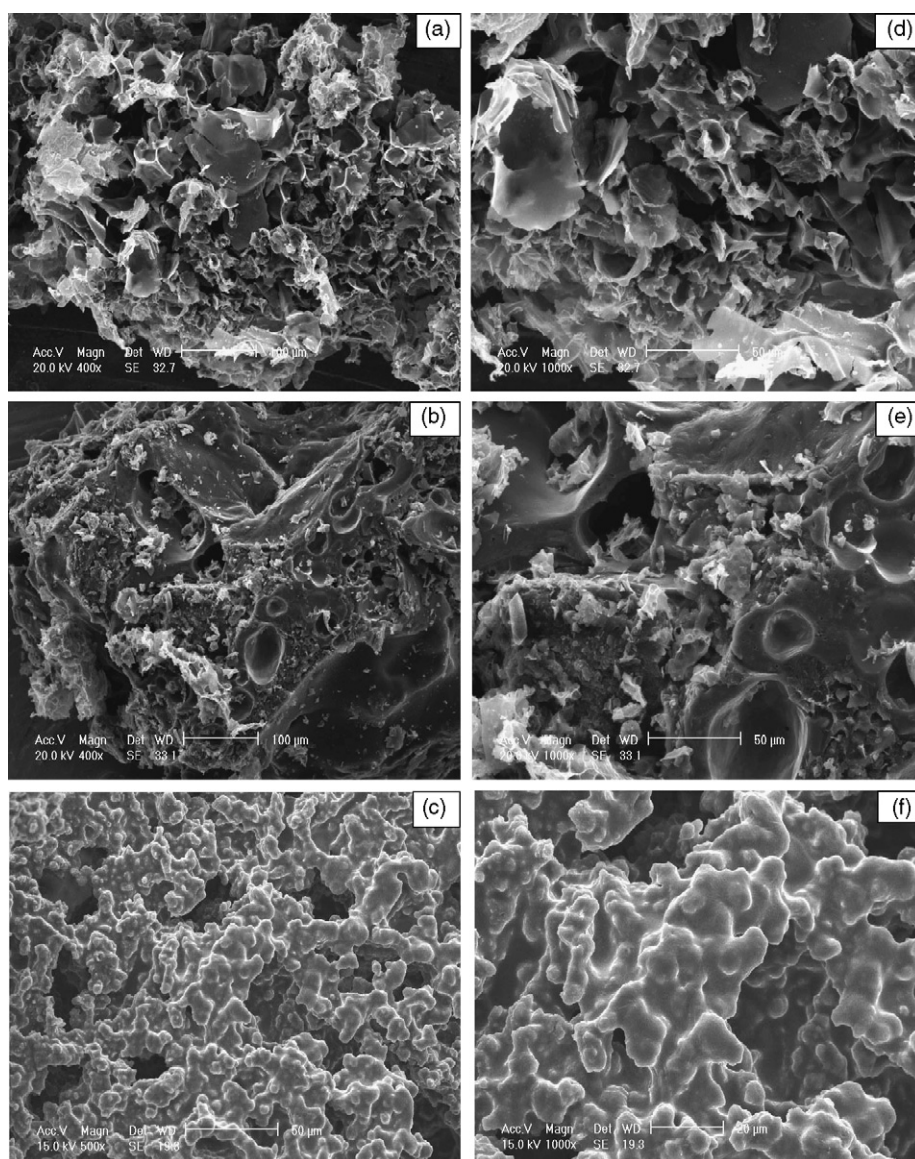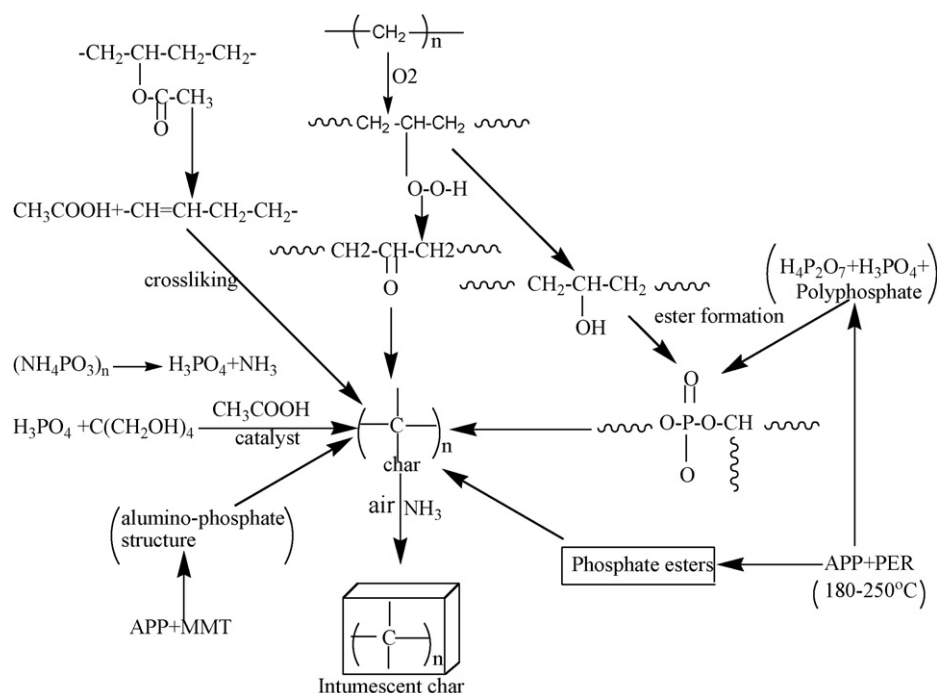

Fig. 5. SEM images of char residue at low magnification (a) PCNM2, (b) PCNM3, (c) PCNM4 and high magnification (d) PCNM2, (e) PCNM3 and (f) PCNM4.

Scheme 1. Chemical reactions in the shape stabilized PCNM intumescent formulations.

the acid source, while heating, polyphosphoric acid is formed which is used an acid catalyst for organic reactions. It takes part in the dehydration of the carbonific compounds to yield the carbonaceous and phosphocarbonaceous residue, which acts as a physical protective barrier. And during the heating process, APP decomposes to yield gaseous product (NH_3), which volatilizes and makes the mixture of the carbonaceous residue and phosphocarbonaceous materials to swell leading to the formation of the intumescent char residue [13,14].

The whole combustion process of the shape stabilized PCNM may be explained by two reasons. First, the acidity reinforcement is caused by the functionalized co-monomers (EVA). The thermal degradation of the acetate functions leads to the formation of carboxylic acid species, which may act as an acid catalyst for organic reactions in the condensed phase process. At the same time, evolution of acetic acid may be accompanied by crosslinking of the unsaturated carbon–carbon of residual polymer, leading to an increase in the viscosity of the charred protective layer and thus to its reinforcement [23]. Secondly, the OMT plays a positive role for the improved fire properties. APP reacts with MMT to form an aluminophosphate structure and a ceramic-like structure. These aluminophosphate species may thermally stabilize and produce good fire performance [11,22,24]. Meanwhile, the catalytic role of the layered silicates derives from the Hoffman reaction of C16 [25]. The decomposition of the C16 leaves a strong acid catalytic site that may further favor the oxidative dehydrogenation-crosslinking charring process and increase the char yield in charring processes [26]. Moreover, during combustion, an ablative reassembling of the silicate layers may occur and create a physical protective barrier on the surface of the material. The physical process of layers reassembling would act as a protective barrier in addition to the intumescent shield and can limit the oxygen diffusion to the sub-

strate or give a less disturbing low volatilization rate [11,17]. The scheme of the combustion mechanism for the shape stabilized PCNM intumescent formulations is shown in Scheme 1.

3.4. Latent heat of the HDPE–EVA alloy/paraffin hybrid and the shape stabilized PCNM

The typical thermograms of the paraffin, HDPE and the corresponding shape stabilized PCNM are presented in Fig. 6. It can be seen that the paraffin has two peaks of phase change. The first minor peak at the left about $42\,°C$ corresponds to the solid–solid phase transition of the paraffin and the second sharp or main peak corresponding to $58\,°C$ represents the solid–liquid phase change of the paraffin. At the same time, the molten peak of HDPE is also presented, corresponding to around $127\,°C$. Fig. 6 indicates that the phase change peaks of the paraffin are still existence in shape stabilized PCNM. This is because the paraffin is a homologous compound of HDPE, there is no chemical reaction between the paraffin and HDPE in the preparation of the shape stabilized PCNM. However, the phase change peaks of the paraffin are weaker than the pure paraffin, probably because the three-dimensional network structure partly confines the molecule heat movement of the paraffin in the phase change temperature range. The phase transition peak of the HDPE is ahead of schedule comparing with pure HDPE. The main reasons have two aspects: firstly, the HDPE and EVA, OMT form alloy nanocomposites; secondly, the HDPE and paraffin form polymer alloy in the shape stabilized PCNM, thereby reducing the melting temperature of HDPE [27].

In Table 3, some results obtained by the DSC measurement are given. From the table, the latent heat of the PCNM1 is lower than those of the other shape stabilized PCNM, may be that the three-dimensional network structure is more intense and molec-
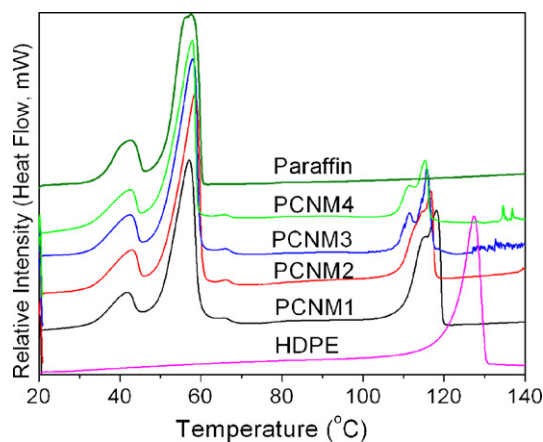
Fig. 6. The DSC curves of the paraffin, HDPE the corresponding shape stabilized PCNM.

ular heat movement of the paraffin is confined more successive with a higher content of HDPE and EVA in the PCNM1. However, the latent heat values of the other shape stabilized PCNM are not markedly different. There is mainly the following several reasons which restrict each other. On the one hand, the amount of the HDPE and EVA reduction, cause the latent heat of the paraffin to increase in the shape stabilized PCNM; on the other hand, the OMT content is increased, result in the more paraffin molecular intercalate into the interlayer of the OMT and reduce the release of the latent heat of the paraffin; Thirdly, the flame retardant has absorption effect on paraffin, thus constrict partly the molecular heat movement of paraffin. When the additive amount of flame retardant is the same (20 wt%), the latent heat of the shape stabilized PCNM decreases firstly and then increases slightly. This is because the restricting effect of the clay layers is predominant with a low OMT fraction. But with increasing OMT loading and decreasing the polymer supporting material, the network structure packing of paraffin reduces slightly and becomes dominant so that the latent heat of the shape stabilized PCNM decreases. In summary, there are two opposing functions effecting on the latent heat of the shape stabilized PCNM, one is the lower HDPE and EVA amount which should improve the latent heat value, and the other is the OMT interlay confinement and the flame retardant absorption effect which would decrease the release of the latent heat of the paraffin. Therefore two opposing functions have little effect on the latent heat of the shape stabilized PCNM.

In addition, it is observed that liquid leakage does not occur while the shape stabilized PCNM is performing the phase change from solid to liquid, owing to the fact that the paraffin is dispersed in the formed three-dimensional network structure of the HDPE–EVA/OMT nanocomposites. The similar results are investigated in other literatures [5–8,27,28].

4. Conclusion

Shape stabilized phase change nanocomposites materials (PCNM) based on HDPE–EVA alloy, OMT, paraffin and IFR are prepared using twin-screw extruder technique. The investigations of XRD and TEM show that an ordered intercalated nanomorphology of the HDPE–EVA alloy/OMT nanocomposite is formed. The SEM images indicate that the HDPE–EVA alloy/OMT nanocomposites act as the supporting material and form the three-dimensional network structure. The paraffin acts as a phase change material and disperses in the three-dimensional network structure. The SEM and DSC results show that the IFR additives hardly have any effect on the network structure and the latent heat of the shape stabilized PCNM, respectively. Two opposing functions effect the latent heat of the shape stabilized PCNM, one is the lower HDPE and EVA amount which should improve the latent heat value, and the other is the OMT interlay confinement and the flame retardant absorption effect which would decrease the release of the latent heat of the paraffin. The TGA analysis results indicate that the flame retardant shape stabilized PCNM produce a larger amount of char residue at $800\,^{\circ}C$ than that of the shape stabilized PCNM, although the onset of weight loss of the flame retardant shape stabilized PCNM occurs at a lower temperature. The multicellular char residue formed contributes to the improvement of thermal degradation performance. The probable combustion mechanisms explain the improvements in thermal performance.

Acknowledgements

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Table 3
Latent heat of the shape stabilized PCNM

Samples	Latent heat (J/g)
PCNM1	76.70
PCNM2	90.55
PCNM3	88.15
PCNM4	91.84

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