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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.

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

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%

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.