Energy Conversion and Management 76 (2013) 101–108

Contents lists available at SciVerse ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Preparation of shape-stabilized co-crystallized poly (ethylene glycol) composites as thermal energy storage materials

Yong Qian [a], Ping Wei [a,*], Pingkai Jiang [a], Zhi Li [a], Yonggang Yan [a], Kejian Ji [b], Weihua Deng [b]

[a] School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China
[b] Shandong Non-Metallic Materials Institute, Jinan 250031, People's Republic of China

ARTICLE INFO

Article history:
Received 21 May 2013
Accepted 11 July 2013

Keywords:
Poly (ethylene glycol)
Sol–gel
Cocrystallization
Thermal energy storage

ABSTRACT

Shape-stabilized co-crystallized poly (ethylene glycol) (PEG) composites were prepared by sol–gel process. Tetraethoxysilane was utilized as supporting matrix precursor. The crystallization property as well as thermal energy storage properties of PEG was influenced by silica network. The combination of PEG 2k and PEG 10k with suitable ratio (3:1 by weight) led to synergistically increased fusion enthalpy attributed to cocrystallization effect. Furthermore, halogen-free flame retarded PEG composites were obtained using diammonium phosphate as flame retardant. With suitable composition, the latent heat value of flame retarded PEG composite was 96.7 kJ/kg accompanied with good thermal stability and improved flame retardancy properties. Fourier transform infrared spectrum (FT-IR), X-ray diffraction (XRD), polarized optical microscope (POM) and scanning electron microscope (SEM) were used to characterize the structure of PEG composites. Thermal stability properties of PEG composites were investigated by thermogravimetric analyzer (TGA). Char residue obtained from muffle furnace of PEG composites was analyzed by SEM and FT-IR. Flame retardancy properties of PEG composites were estimated by pyrolysis combustion flow calorimeter. Results showed that it was potential for shape-stabilized halogen-free flame retarded PEG composite to be applied in thermal energy storage field.

1. Introduction

Due to severe shortage problems of petrochemical energy in the next coming decade, novel energy solutions have been focused from academe and industry in order to better balance the pressure from society, economy and environment. New energy and relevant technologies have been provided to try to make alternative proposals, such as shale gas [1], fuel cell [2,3], wind power [4], tidal power [5] as well as solar energy [6,7]. Among these promising solutions, using latent heat phase change materials (PCMs) is a kind of cost-effective method to provide high-efficient temperature or energy-controlling devices that can be utilized in intelligent house [8], photovoltaic system [9], and solar heating equipments [10].

PCMs can be separated into two series: inorganic and organic type. Inorganic PCMs, such as hydrated salts, have advantages like large latent heat value and cheap cost but the energy storage properties can be reduced by supercooling and phase-separation [11]. Compared with inorganic type, organic PCMs (such as aliphatic hydrocarbon [12], high-chain fatty acid esters [13,14], poly (ethylene glycol) (PEG) [15], paraffin [16] and carboxylic acid [17]) have little or no supercooling behavior accompanied with suitable phase change temperature and large fusion heat. Organic PCMs have tendency to be used as energy storage materials once the leakage problem has been solved.

PEG is semi-crystallization material that once it forms shape-stabilized PCM composites, un-crystallized region of PEG may be increased because of the crystallization inhibition effect originated from supporting matrix, thus leading to decreased energy storage properties of composites. In other words, energy storage properties of PEG composite can be improved when un-crystallized area of PEG is transformed into crystallization state. When different PEG materials are combined together, molecule chain from one PEG could enter the unit lattice from the other PEG, achieving interpenetration to make co-crystals [18]. After that, the overall crystallization region is increased, thus leading to improved fusion heat value. This may provide a novel method to develop form-stable phase change materials. However, to the best of our knowledge, there is little reference reporting the increased energy storage properties of PCM composites are originated from cocrystallization effect.

In this article, shape-stabilized PEG composites were prepared by sol–gel process using tetraethoxysilane as supporting matrix precursor. Water-soluble diammonium phosphate was added as halogen-free flame retardant during sol–gel process. The structure of PEG composite was characterized by FT-IR, XRD, POM and SEM. Thermal stability and energy storage properties of PEG composites

---

* Corresponding author. Tel.: +86 021 34202509; fax: +86 021 54741297.
E-mail address: pingwei@sjtu.edu.cn (P. Wei).

0196-8904/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.enconman.2013.07.014

were estimated by TGA and DSC, respectively. Pyrolysis combustion flow calorimeter was utilized to investigate the improved flame retardancy of PEG composite.

2. Experimental

2.1. Materials

Two poly (ethylene glycol) (PEG 2k and PEG 10k) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as the matrix of phase change materials. Tetraethoxysilane (TEOS), absolute ethanol, diammonium phosphate (DAP) and aqueous ammonia (25 wt%) were provided by Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of PEG composites

The ingredients are shown in Table 1. PEG and 20 g of deionized water with or without DAP were added into a Teflon bottle equipped with a magnetic apparatus, stirring for 0.5 h at 25 °C. Then, TEOS combined with 3 g of absolute ethanol was added into the Teflon bottle drop by drop, stirring for another 0.5 h. After that, 1 ml of aqueous ammonia was injected into the mixture and the whole system stirred for 3 h. At last, the system was poured into a flask, dried at 70 °C in a vacuum oven until the weight of product remained constant.

2.3. Characterization

Differential scanning calorimetry (DSC) was carried out using TA Q2000 at heating/cooling rate of 10 °C/min from 20 °C to 80 °C in nitrogen atmosphere.

Fourier transform infrared spectrum (FT-IR) was obtained with Perkin Elmer Paragon 1000 instrument. Potassium bromide (KBr) was used for tabletting.

X-ray diffraction (XRD) was recorded with Rigaku D/Max 2000 X-ray diffractometer with a Cu Kα tube and Ni filter (λ = 0.1542 nm).

Polarized optical microscope (POM; LEICA DM LP, Germany) was utilized to analyze the crystallization property of PEG composites.

Scanning electron microscope (SEM) micrographs were obtained using S-2150 (Hitachi Corp., Japan) at 20 kV. All the tested samples were firstly coated with a conductive gold layer using Ion Sputter Coater (Shanghai Institute of Electron Optics).

Table 1
Ingredients of PEG composites.

Sample	PEG 2k (g)	PEG 10k (g)	TEOS (g)	DAP (g)
1	Pure			
2		Pure		
3	1.0		2.5	
4		1.0	2.5	
5	0.25	0.75	2.5	
6	0.33	0.67	2.5	
7	0.67	0.33	2.5	
8	0.75	0.25	2.5	
9	0.75	0.25	3.5	
10	0.75	0.25	3.0	
11	0.75	0.25	2.0	
12	0.75	0.25	1.5	
13	0.75	0.25	1.0	
14	0.75	0.25	2.5	0.3
15	0.75	0.25	2.5	0.5
16	0.75	0.25	2.5	0.7

Thermogravimetric analysis (TGA) was conducted on TA Q5000IR thermogravimetric analyzer at a heating rate of 10 °C/min from 50 °C to 600 °C in nitrogen atmosphere.

Flame retardancy properties of PEG composites were investigated using pyrolysis combustion flow calorimeter (GOVMARK MCC-2).

3. Results and discussion

3.1. Thermal energy storage analysis

Samples in Table 1 could be separated into four groups to make the discussion more clearly: samples 1–4 were attributed to pure PEG and composite with one type PEG; samples 5–8 were used to investigate the influence of different ratio between PEG 2k and PEG 10k on the energy storage property of composite; samples 8–13 were utilized to estimate the effect of TEOS loading on the energy storage property of composite; samples 14–16 were focused on the influence of flame retardant DAP.

For shape-stabilized PEG composites containing a single type (PEG 2k or PEG 10k, see Table 2), they showed relative low melting latent heat value. Different ratio (1/3, 1/2, 2/1 and 3/1 by weight) between PEG2k and PEG10k was applied to make shape-stabilized composites (samples 5–8). It showed that sample 8 had largest fusion heat (108.6 kJ/kg) among the four samples. And also, the enthalpy value of sample 8 was higher than that of samples 3 and 4 by 56.3% and 128.6%, respectively, showing PEG 2k and PEG 10k had synergism in improving the thermal energy storage properties. Further, the weight ratio (3/1 = PEG2k/PEG10k) was settled and the loading of TEOS was altered. The fusion enthalpy of samples 8–13 changed obviously with the variation of TEOS. When the loading of TEOS was higher (samples 9 and 10) or less (samples 11–13), the latent heat values were decreased significantly. Sample 8 also had the largest fusion heat among the six samples. There might be synergism in the case of suitable TEOS loading and PEG component. It indicated that sample 8 had the suitable ingredient to give PEG composite with large latent heat value for thermal energy storage application.

The theoretical fusion enthalpy is calculated as: $\Delta H_{THE} = a\Delta H_{PEG1} + b\Delta H_{PEG2}$, in which formula, the components are supposed to have no interaction. The two numbers (a and b) represent the weight portion of PEG1 and PEG2. For sample 8, the experimental latent heat value was higher than theoretical value (64.0 kJ/kg) by 69.7%. The latent heat value of sample 6 was

Table 2
Latent heat of PEG composites during the melting and solidifying processes.

	Melting process (solid–liquid change)		Solidifying process (liquid–solid change)	
	Peak (°C)	ΔH (kJ/kg)	Peak (°C)	ΔH (kJ/kg)
Sample 1	51.7/57.8	180.6	40.1	170.3
Sample 2	62.4	170.9	38.9	168.6
Sample 3	49.3	69.5	22.7	73.8
Sample 4	48.0	47.5	20.6	51.6
Sample 5	48.5	46.2	21.8	53.6
Sample 6	56.3/60.0	82.2	35.9	81.7
Sample 7	46.7	53.8	20.4	55.8
Sample 8	56.5/59.2	108.6	35.2	106.6
Sample 9	50.6/59.2	72.5	27.4	75.5
Sample 10	47.0	54.4	18.7	57.3
Sample 11	51.9	89.3	27.0	83.2
Sample 12	53.5/57.9	95.0	34.4	92.2
Sample 13	52.1	95.2	30.5	91.8
Sample 14	49.7	52.5	29.0	49.6
Sample 15	59.9	96.7	45.2	94.8
Sample 16	56.5	60.6	40.2	57.4