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Improved thermal properties of stearyl alcohol/high density polyethylene/expanded graphite composite phase change materials for building thermal energy storage

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ABSTRACT

Form–stable phase change materials (FSPCM) with high thermal energy storage capacity and thermal conductivity were manufactured by adding expanded graphite (EG) into stearyl alcohol (SAL) and high density polyethylene (HDPE) mixtures. In the composites, HDPE was used to prevent SAL leakage, and EG was not only a supporting material just like HDPE but also a thermal conductivity promoter. The influences of EG on the thermal properties of the SAL/HDPE phase change materials were investigated with a series of measuring means. Several lines of evidence showed that SAL and HDPE were mixed uniformly and EG was evenly dispersed in the SAL/HDPE composites. Approximately constant melting temperatures of FSPCM at around 57 °C and high latent heat of at least 200 kJ/kg were presented by the differential scanning calorimeter (DSC). It was found that the leakage rate of the SAL phase change materials decreased obviously when EG was added into the FSPCM. Furthermore, the thermal conductivity of FSPCM with 3% EG could increase up to 0.6698 W (m K)⁻¹ while thermal conductivity of FSPCM without EG was only 0.1966 W (m K)⁻¹. Finally, the FSPCM with EG could provide considerable thermal energy storage capacity and high thermal conductivity for latent heat storage.

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1. Introduction

Thermal storage system is an alternative solution to the energy crisis and the carbon emissions pressure [1]. The thermal energy can be redistributed on the basis of the energy requirement for improving energy utilization efficiency and thermal management in the thermal storage system [2]. The most common application is in building system by storing thermal energy in the daytime and releasing thermal energy in the nighttime [3,4]. In general, phase change materials (PCM) which play an important role on energy storage are mixed with concrete for building application [5,6]. PCM is often used to storage and release latent heat considering the outstanding properties of high phase change latent heat and even work space temperature [7,8]. Sensible heat and reversible thermochemical reaction are also the manner of thermal energy storage but the latent heat energy storage based on PCM is the priority research field in the recent decades [9].

PCM is usually classified as organic and inorganic materials and several authors have made a comparison of the advantages and disadvantages of the two materials. The organic PCM benefit

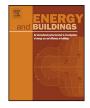
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http://dx.doi.org/10.1016/j.enbuild.2017.08.005 0378-7788/© 2017 Elsevier B.V. All rights reserved. from non-corrosives, low subcooling, chemical and thermal stability while the inorganic PCM have greater phase change enthalpy [10,11]. In consideration of the practical application, the organic PCM are better for latent heat energy storage because the inorganic PCM have serious disadvantages of phase separation and lack of thermal stability. Stearyl alcohol (SAL) with high phase change enthalpy above 200 kJ/kg is a representative organic PCM and would be employed in this work [12,13].

The main disadvantage of PCM is the leakage of the energy storage media, which is one of the primary research direction. The utilizations of micro-encapsulated phase change materials (MEPCM) and form-stable phase change materials (FSPCM) can solve the leakage problem [14-17]. For their shape, the MEPCM look like powder while the FSPCM are blocked, which determine their different applications in the thermal storage system. The FSPCM are prepared by absorbing the traditional PCM onto or into the supporting materials, which can keep the shape of the FSPCM and prevent the leakage of the PCM at the operating temperature. The common supporting materials including polypyrrole [18], diatomite [19,20], bentonite [21], expanded perlite [22,23], attapulgite [24], high density polyethylene (HDPE) [25,26], expanded vermiculite and perlite [27], eudragit [16]. As the base phase change material is fatty acid alcohol in this study, HDPE is preferred as the supporting material because it possesses the feature of acid and alcohol resis-







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4	2

Samples	HDPE (g)	SAL(g)	EG (g)	Mass fraction of SAL (%)	Mass fraction of EG (%)
HPCM1	12.50	37.50	0	75	0
HPCM2	10.00	40.00	0	80	0
НРСМ3	7.50	42.50	0	85	0
CPCM1	12.00	37.50	0.5	75	1
CPCM2	9.50	40.00	0.5	80	1
CPCM3	7.00	42.50	0.5	85	1
CPCM4	6.50	42.50	1	85	2
CPCM5	6.00	42.50	1.5	85	3

 Table 1

 The compositions of the SAL/HDPE/EG composites.

tance. Sari [25] prepared the paraffin/HDPE composites as FSPCM and presented the determination of their thermal properties. The result showed that the maximum mass fraction of paraffin in the PCM composites without leakage was as high as 77%. In this work, stearyl alcohol would be absorbed into HDPE, which is not reported in previous literatures.

Under certain circumstance, quick energy storage and release are necessary for short-time work period. The low thermal conductivity of organic PCM will limit the practical application. Adding extremely high thermal conductivity materials into PCM is popular solution to this defect. The effects of several nano-additives on the thermal conductivity of PCM were investigated in our previous works [28–30]. The thermal conductivity of myristic-stearic binary eutectics was increased by 63.6% when the mass fraction of the additive carbon nanotubes was 15%. And while the nano-additives were nano-Al₂O₃, nano-graphite and grapheme nanoplatelets, the values of the thermal conductivity enhancement are 95% (12% nano-Al₂O₃), 121% (12% nano-graphite) and 151% (4% graphene nanoplatelets) respectively. According to the data, it was obvious that the effect of grapheme was significantly greater than other nano-additives. It resulted from the flaky shape with broad surface and high specific surface of the graphene nanoplatelets, and meanwhile a layer structure was developed in the composites. However, the nano-additives are too expensive to be employed in the practical application. Expanded graphite (EG) is an ideal additive to replace the graphene nanoplatelets as EG also have the characteristics of flaky shape with broad surface and high thermal conductivity. Of course, there are many reports on the FSPCM modified by EG and many researchers have achieved satisfactory experimental results. The development of layer structure can also help absorbing the PCM and reducing the leakage. However, few reports took the thermal conductivity enhancement and leakage prevention of EG into consideration together.

Hence, the focus of this work would be the effects of EG on the thermal conductivity and leakage rate in the SAL/HDPE/EG composites. In the composites, HDPE acted as a supporting material and SAL was used to store thermal energy. In order to increase the phase change enthalpy, the mass fraction of the supporting material should be as low as possible. If EG can help HDPE preventing the leakage of the SAL, the phase change enthalpy of FSPCM further improves. The thermal conductivity of FSPCM was investigated with different mass fraction of EG. The thermal properties, chemical stability and microstructure of the FSPCM were also presented respectively in this work. From the result, the FSPCM modified by EG with high phase change enthalpy and thermal conductivity have promising practical application in the thermal storage system.

2. Experimental

2.1. Materials

SAL ($C_{18}H_{38}O$, octadecanol, Chemically Pure), was supplied by Jiangsu Huakang Chemical Reagent Company and was used to store latent heat. HDPE (melt flow index: 20g/10min, density:

 0.953 g/cm^3 , Vicat softening temperature: $126 \,^{\circ}\text{C}$) was provided by Dongguan Huangjiang Co., Ltd and acted as supporting materials for preventing the leakage of the SAL. EG (expansion ratio: $200-400 \,\text{ml/g}$, fixed carbon: >90%) was obtained from the Qingdao Graphite Co., Ltd.

2.2. Preparation of the SAL/HDPE/EG composite

In order to investigate the effects of EG on the thermal conductivity and leakage rate in the composites, the SAL/HDPE/EG composites were prepared with different compounding ratios. Table 1 listed the detailed proportions of the composites. Firstly, for the SAL/HDPE composites, the HDPE was melted at around 180 °C and the SAL was melted in water bath at 70 °C. Then, the SAL was added into melted HDPE and the composites were adequately mixed by a twin-screw agitator with the speed of 1500 rpm for 30 min at 180 °C. For the SAL/HDPE/EG composites, before the melted SAL was added into the HDPE. The EG and SAL was mixed in water bath at 70 °C by a magnetic stirrer with the speed of 1500 rpm for 30 min. Other steps were the same as the synthesis of the SAL/HDPE composites. HPCM1-HPCM3 and CPCM1-CPCM3 are the comparative groups to reveal the influence of EG on the leakage rate of the FSPCM. HPCM3 and CPCM3-CPCM5 are used to reveal the relationship between the mass fraction of EG and not only the leakage rate but also the thermal conductivities of the FSPCM.

2.3. Characterization techniques

The microstructure and morphology of the samples were displayed by a scanning electron microscope (SEM, S-3400NII, Hitachi Inc., Japan). A fourier transformation infrared spectroscope (FT-IR, Nicolet Nexus 870, spectra range: 400–4000 cm⁻¹, resolution: 2 cm⁻¹, operating temperature: 40 °C) was used to determine the chemical structure analysis of the FSPCM. An X-ray diffractometer (XRD, D/MAX–Ultima III, scanning rate: 5° (2 θ) min⁻¹, operating voltage: 40 kV, operating current: 40 mA, operating temperature: 20°C, Japan) was employed to indicate the crystalloid phase and crystallinity of the FSPCM. Thermal properties including phase change enthalpy and phase change temperature were measured by differential scanning calorimeter (DSC, Perkin-Elmer, temperature accuracy: ± 0.2 °C, enthalpy accuracy: $\pm 5\%$, heating/cooling rate: 10°C/min,), which was vital for PCM. The operating temperature range of DSC was 30°C to 140°C because the phase change temperatures of SAL and HDPE were about 58°C and 120 °C [12,25]. The thermal reliability and decomposition temperature were investigated by a thermogravimetric analyzer (TGA, Perkin-Elmer, heating/cooling rate: 20°C/min) and the operating temperature range was 25 °C to 700 °C. The heat cycle test was conducted to measure the leakage rate of the FPCM and the cycle test involved 300 times melting and solidifying processes for approximately 30 h. The lowest and greatest work temperature is 30 °C and 80 °C. After thermal cycling, the weight of dried samples would be compared with that of the original samples for calculating the leakage rate.

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