A Novel Sebacic Acid/Expanded Graphite Composite Phase Change Material for Solar Thermal Medium-Temperature Applications

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Abstract

This paper demonstrates a novel sebacic acid/expanded graphite (SA/EG) composite phase change material for medium-temperature solar heat storage. The optimal mass percentage of SA in the SA/EG composite PCM is determined to be around 85%, at which not only SA exhibits a uniform distribution into the pores of EG but also the liquid leakage can be effectively prevented. The composite PCM with the SA mass percentage of 85% has a phase change temperature of 128 °C with the latent heat as high as ca. 187 J/g. The combination of SA and EG effectively prevents the low extent of subcooling inherent in SA. Compared to SA, the SA/EG composite PCM has the advantages of negligible subcooling as well as better thermal reliability and stability. The SA/EG composite PCM can easily be formed into various shapes by dry pressing, with little loss in thermal properties but a remarkable increase in thermal conductivity. The good thermal properties and formability make the SA/EG composite PCM show great potential in latent heat storage systems.

Keywords: Solar energy utilization; thermal energy storage; phase change material; expanded graphite; sebacic acid

1. Introduction

Solar energy, the most abundant and sustainable natural energy source, has the capacity to play a significant role in replacing conventional fossil fuels to meet the ever-increasing global demand for energy. Among all the routes to harness solar energy including photovoltaic, photothermal and photochemical conversion, solar thermal utilization has always been the major one since ancient times, which can be classified as low- ($< 80\text{ }^{\circ}\text{C}$), medium- ($80 \sim 250\text{ }^{\circ}\text{C}$) and high-temperature ($> 250\text{ }^{\circ}\text{C}$) applications. Compared with low-temperature solar thermal applications mainly including solar water heating that has been well developed and is now being used worldwide (Shukla et al., 2009), medium- and high-temperature applications such as solar drying, cooking, distillation and solar thermal power have lagged behind but show great potential in the future. Owing to the discontinuity and instability inherent in solar energy, thermal energy storage technology that stores intermittent, unstable heat and releases energy when needed, is crucial to improve the utilization efficiency (Sharma et al., 2009), especially in medium- and high-temperature solar thermal applications. Latent heat storage using phase change materials (PCMs) as working media is one of the most efficient methods to store thermal energy due to the advantages of high storage density and isothermal nature during the phase change processes (Fang et al., 2009). Obviously, it is of great significance to develop high-performance phase change materials with the phase change temperature above $80\text{ }^{\circ}\text{C}$ for use in medium- and high- temperature solar heat storage systems.

It is well-known that numerous chemical substances can be used as PCMs, which are usually classified into two major categories: inorganic and organic compounds (Hasnain, 1998; Zalba et al., 2003; Farid et al., 2004; Zhang and Fang, 2006; Kenisarin and Mahkamov, 2007; Zhou et al., 2012). Although most inorganic PCMs have the advantages of large latent heat, relatively high thermal

conductivity and low cost, they often suffer from some shortcomings like corrosivity, subcooling and segregation (Zalba et al., 2003). Organic PCMs not only avoid the above disadvantages inherent in inorganic compounds, but also possess good stability and relatively high latent heat. However, the main drawback of organic PCMs is that their thermal conductivities are always lower than those of the inorganic materials (Rathod et al., 2013). In recent years, the paraffin/expanded graphite (EG) composite phase change material has been studied, and the combination of organic PCMs with inorganic supporting materials to prepare form-stable composite PCMs has been proven to be a simple and effective way to improve the thermal conductivities of organic PCMs as well as to prevent the liquid leakage during the solid-liquid phase change processes (Zhang and Fang, 2006; Kenisarin and Kenisarina, 2012). Except for EG, other carbon materials such as activated carbon (Feng et al., 2011; Chen et al., 2012) and a series of silicate minerals including montmorillonite (Fang et al., 2008; Li et al., 2011; Wang et al., 2012), expanded perlite (Karaiepli and Sarı, 2008; Sarı et al., 2009), vermiculite (Karaiepli and Sarı, 2008), diatomite (Li et al., 2011; Sarı and Karaiepli, 2012), attapulgite (Li et al., 2011) and halloysite nanotube (Zhang et al., 2012) have been used as cheap supporting materials to generate organic/inorganic composite PCMs. Among all these inorganic matrices, EG has been verified to be the best one due to its advantages of large pore volume, low density and good thermal conductivity (Wang et al., 2012). Up to now, several EG-based composite PCMs have been prepared, in which paraffin (Py et al., 2001; Zhang and Fang, 2006; Sarı and Karaiepli, 2007; Xia et al., 2010; Zhang et al., 2012), palmitic acid (Sarı and Karaiepli, 2009), n-octadecane (Li et al., 2010; Zhang et al., 2013) and acetamide (Xia and Zhang, 2011) were used as the organic PCM, and the thermal conductivities of the composite PCMs with different mass fraction of organic substances were measured. However, none of these EG-based

composite PCMs was suitable for the medium- and high- temperature solar heat storage systems since their phase change temperatures were generally lower than 80 °C. In addition, the relationship between packing density of dry pressing and thermal conductivity of the EG-based composite PCMs was not reported in previous studies.

Sebacic acid (SA, C₁₀H₁₈O₄) is a dicarboxylic acid with the structure of (HOOC)(CH₂)₈(COOH), possessing a melting point of ca. 130 °C and latent heat over 200 J/g (Haillot et al., 2011). In the current work, SA was chosen as the organic PCM to prepare the SA/EG composite PCM, aiming at developing a novel high-performance EG-based composite PCM for medium-temperature solar thermal applications. First, the SA/EG composite samples with different mass percentage of SA were prepared by absorbing different amounts of SA into the pores of EG, followed by characterizing their microstructures and crystalline phases. Second, the thermal properties, reliability and stability of the SA/EG composite PCM with the optimal mass ratio of SA were studied, together with those of SA for comparison purpose. Finally, the formability of the SA/EG composite PCM was investigated by compressing the composite powders into round blocks with different packing densities, followed by measuring their thermal conductivities and latent heat.

2. Experimental section

2.1. Preparation and characterization of SA/EG composite PCMs

SA (98%, Analytical Reagent, Tianjing Damo Chemical Reagent Factory, China) was used without further purification. EG was prepared from the graphite powders (expandable volume: 300 mL/g, Qingdao Graphite Co. Ltd., China) by the microwave method (Zhang et al., 2012). The SA/EG composite samples with the SA mass percentage of 80%, 85% and 90% were prepared by absorbing

different amounts of liquid SA into the pores of EG.

The liquid leakage test was carried out as follows. The three SA/EG composite samples containing 80%, 85% and 90% SA were placed on three pieces of filter paper, and then each sample along with the corresponding filter paper were inserted into an oven at a temperature of 150 °C (above the melting point of SA) for 30 min, to make sure the phase change of SA from solid to liquid takes place. After taking out and cooling to room temperature, the samples were removed from the corresponding filter paper. Finally, a careful examination was given to each piece of filter paper to find out if there are any traces of liquid SA left on it. In addition, the masses of the samples were compared before and after the test to further judge if the liquid leakage happened.

The microstructures of EG and the SA/EG composite samples were observed using a scanning electron microscope (SEM, Quanta, FEI, Holland). The crystalline phases of SA, EG and the SA/EG composite PCM with the SA mass percentage of 85% were characterized by an X-ray diffractometer (D8-ADVANCE, Bruker, German) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Fourier transformation infrared (FT-IR) spectra of SA and the SA/EG composite samples were measured at room temperature on a spectrometer (Tensor 27, Bruker, Germany).

The thermal properties of SA and the SA/EG composite samples were analyzed by a differential scanning calorimeter (DSC , DSC Q20, TA Instruments, USA) under N₂ atmosphere at a flow rate of 50 mL/min. The measuring temperature ranged from 80 °C to 160 °C. The heating/cooling rate was set at 2, 5, 8 and 10 °C / min, respectively. The thermal reliability of the SA/EG composite PCM was studied by placing the sample sealed in a crucible into a high-low temperature chamber to experience 3000 heating-cooling cycles, followed by the characterizations by SEM, XRD, FT-IR, and DSC measured under the same conditions as the SA/EG composite samples were measured before the

cycling test. The thermal stability of SA and the SA/EG composite samples were investigated by the thermogravimetric analysis (TGA) using a thermal analyzer (Q600 SDT, TA, USA). The measurements were conducted by heating the samples from room temperature to 600 °C at a heating rate of 10 °C / min under nitrogen atmosphere with a flow rate of 100 mL/min.

2.2. Dry pressing of SA/EG composite PCM powders

The SA/EG composite PCM powders with the SA mass percentage of 85%, whose particle size is mainly distributed in 0.3-0.45 mm (88.6%), were formed into several round blocks by dry pressing with a home-made cylindrical mold (3 cm inside diameter and 1 cm height) under the pressure of 100 kg/cm². The procedures for fabricating the blocks were as follows: First, we selected some densities such as 400, 500, 600, 700, 750 and 800 kg/m³, according to our experiences on measuring the thermal conductivities of the composite PCMs. Based on the volume of the mould we used, we calculated the masses of the composites needed for fabricating the blocks with the selected densities according to the formula $m = \rho \cdot V$. Then, we added the calculated amounts of the composite PCM powders into the mould to produce the blocks. Finally, we measured the actual volumes and masses of the formed blocks to calculate their actual densities, which are 337.5, 471.8, 566.2, 660.6, 714.5 and 768.4 kg/m³. The thermal conductivities of the obtained round blocks with different packing densities were measured using a thermal constants analyzer (Hot Disk TPS 2500S, Hot Disk AB, Sweden). For comparison purpose, SA was melted and poured into a cylindrical mould (5 cm inside diameter and 1.5 cm height) to fabricate two pieces of casting samples so as to measure the thermal conductivity of SA. Moreover, the phase change temperatures and latent heat values of the obtained composite blocks were also measured by DSC, aiming at contrasting the thermal properties of the SA/EG composite PCM before and after dry pressing.

3. Results and discussion

3.1. Structure properties of SA/EG composite

EG is a kind of porous carbon material with a honeycomb network, providing abundant crevice-like and net-like pores for absorbing organic substances (Zhang and Fang, 2006). The EG prepared by the microwave method has a wide pore size distribution, which is mainly composed of mesoporous and macropores (Zhang et al., 2012). According to the previous researches on the paraffin/EG composite PCM (Zhang and Fang, 2006; Zhang et al., 2012), the mass percentage of paraffin in the EG-based composite is usually more than 80 %. In order to determine the optimal mass percentage of SA in the EG-based composite PCM, the liquid leakage test was performed with the three SA/EG composite samples containing 80%, 85% and 90% SA. The result showed that liquid leakage happened to the sample containing 90% SA, not to those containing 80% and 85% SA. Furthermore, the SEM images of the three SA/EG composite samples are displayed in Figure 1. For the composite sample containing 80% SA, there are still a few voids within EG, which can continually absorb liquid PCM, as shown in Figure 1a. As the mass fraction of SA reaches 85%, the abundant pores of EG are fully filled with SA (as shown Figure 1b), indicating that EG has been probably saturated with SA. As the mass percentage of SA in the composite sample is further increased to 90%, a large amount of SA crystals are found on the surface of EG, as shown in Figure 1c. Based on the above results, it can be inferred that the optimal mass percentage of SA in the SA/EG composite is around 85%, at which SA exhibits a uniform distribution into the pores of the EG, and the liquid leakage can be effectively prevented owing to the capillary and surface tension forces of EG (Zhong et al., 2010). The composite sample containing 85% SA is hereinafter called the

SA/EG composite PCM. In addition, the SEM image of the SA/EG composite PCM after experiencing 3000 heating-cooling cycles is displayed in Figure 1d. Compared with the composite PCM (Figure 1b), SA is more uniformly covered on the surfaces of the sheets of EG (Figure 1d) after it has experienced the heating-cooling cycling test. The liquid leakage test also showed that no liquid exudation happened to the SA/EG composite PCM after experiencing 3000 heating-cooling cycles. The above results indicate that the SA/EG composite PCM possesses good form stability.

Figure 2 shows the XRD patterns of SA, EG, and the SA/EG composite PCM before and after experiencing 3000 heating-cooling cycles. EG only has one strong diffraction peak centered at 26.52° , which should be ascribed to the feature peak (002) of graphite. The five strong diffraction peaks of SA are located at 8.1° , 21.5° , 24.1° , 26.5° and 30.1° , respectively. As illustrated in Figure 2, the diffraction peaks of the SA/EG composite PCM are just the combination of the one for EG and the ones for SA with an obviously reduction in the intensity of its strongest peak located at 8.1° , which may be attributed to the confinement of SA within the pores of EG. No new peaks are found in the XRD pattern of the composite PCM, indicating that the composite is just the integration of SA with EG. In addition, no obvious changes in peak position and intensity are found for the SA/EG composite PCM before and after experiencing the heating-cooling cycling test, suggesting good structure stability of the SA/EG composite PCM.

Figure 3 illustrates the FT-IR spectra of SA as well as the SA/EG composite PCM before and after experiencing 3000 heating-cooling cycles. In the FT-IR spectrum of SA, the peak at 1697 cm^{-1} represents the stretching vibration of the C=O group. The peaks at 2937 and 2858 cm^{-1} signify the stretching vibration of the $-\text{CH}_2$ group. The peak at 1421 cm^{-1} is assigned to the bending vibration of the $-\text{CH}_2$ group. The peak at 721 cm^{-1} represents the swinging vibration of the CH_2 group, a feature

of (CH₂)₈. As seen in Figure 3, the absorption peaks of SA at 2937, 2858, 1697, 1421, 1298, 1236, 1184, 929 cm⁻¹ are also presented in the FT-IR spectrum of the composite PCM samples before and after the 3000 heating-cooling cycles test. These results prove again that the composite PCM is just the combination of SA and EG without any chemical interaction between the two components, even after experiencing the heating-cooling cycling test.

3.2. Thermal properties of SA and the SA/EG composite PCM

Figure 4 illustrates the DSC curves of SA (a) and the SA/EG composite PCM (b) measured at different heating/cooling rates. And their corresponding thermal characteristics are summarized in Table 1. For SA, its phase change temperature is ca. 133 °C for melting and ca. 129 °C for solidification, suggesting a subcooling of 4 °C. Moreover, SA has a large latent heat of more than 200 J/g, specifically, 221.5 J/g for melting enthalpy and 214.2 J/g for solidification enthalpy on average. The small difference in latent heat between melting and solidification may originate from the low extent of subcooling inherent in SA. Interestingly, compared with SA, the SA/EG composite PCM exhibits a reduced melting point of around 128.35 °C (Figure 4b). The result suggests the combination of SA and EG with high thermal conductivity enhances the heat transferred within the SA/EG composite PCM during the melting process, thus leading to the reduction in its melting point. The solidification point of the SA/EG composite PCM is ca. 129.02 °C, almost the same as that of SA. As a result, the melting point of the SA/EG composite PCM is almost identical to its solidification point, indicating that negligible subcooling occurs in the composite PCM, as shown in Figure 4b. The SA/EG composite PCM possesses an average melting enthalpy as high as 187.5 J/g, just equivalent to the calculated value based on the average melting enthalpy of SA and the SA mass percentage in the composite. More significantly, the average solidification enthalpy of the composite

PCM is 186.5 J/g, slightly larger than the calculated value of 182.1 J/g. This result may be attributed to the prevention of subcooling in the composite PCM.

Figure 5 shows the DSC curves of the SA/EG composite PCM before and after experiencing 3000 heating-cooling cycles. No obvious difference in the melting temperature is found for the SA/EG composite PCM before and after experiencing the heating-cooling cycling test, while a slight reduction in the solidification temperature from 129.02 °C to 126.14 °C is observed. Moreover, the latent heat of the SA/EG composite PCM after experiencing 3000 heating-cooling cycles is 167.3 J/g for melting and 160.8 J/g for solidification, which is decreased by ca. 8.4 % and 11.6 % compared to the latent heat of the sample before experiencing the test. The results obtained from the 3000 heating-cooling cycling test indicate that the SA/EG composite PCM has good thermal reliability.

Figure 6 illustrates the mass loss curves of SA, the SA/EG composite PCM before and after experiencing 3000 heating-cooling cycles. The initial decomposition temperature (T_{onset}) of SA is 214.0 °C, while that of the composite PCM is 266.5 °C. It is obvious that the integration of SA with EG has the function of increasing the initial decomposition temperature of SA, which can be attributed to the strong adsorption ability of porous EG. Hence, the thermal stability of SA/EG composite PCM is superior to that of SA. In addition, T_{onset} of the composite PCM after experiencing the heating-cooling cycling test is 263.6 °C, similar to that of the sample before the test. A slight decrease in the lost weight is found for the SA/EG composite PCM after experiencing 3000 heating-cooling cycles, which should be ascribed to the evaporation of some volatiles in EG during the heating-cooling cycle test.

3.3. Formability and Thermal conductivity of SA/EG composite PCM

Figure 7a displays the photograph of the round blocks fabricated from the SA/EG composite PCM powders by dry pressing, whose packing densities were calculated to be 377.5, 471.8, 566.2, 660.6, 714.5 and 768.4 kg/m³, respectively. All the round blocks (as shown in Figure 7a) with different packing densities have smooth outer surface without any cracks, suggesting that the SA/EG composite PCM has good formability. The thermal conductivities of the blocks have been measured by the transient plane source method, which is an advanced technique evolving from the hot wire method. The thermal conductivity of the SA casting sample (as shown in Figure 7b) with the density of 1043.2 kg/m³ is measured to be as low as 0.372 W/m·K. Figure 8 illustrates the relationship between the packing density and thermal conductivity of the SA/EG round blocks. As the packing density of the blocks increases from 377.5, 471.8, 566.2, 660.6 and 714.5 to 768.4 kg/m³, their thermal conductivities accordingly increase from 2.395, 3.136, 3.947, 4.344 and 4.814 to 5.353 W/m·K. The relationship between the packing density (x) and the thermal conductivity (y) of the blocks can be fitted into a linear equation: $y = -0.302 + 0.007x$, indicating a gradual increase in the thermal conductivity with the packing density. Note that all the SA/EG composite PCM round blocks have much higher thermal conductivity than SA, owing to the integration of SA with EG that has high thermal conductivity. Based on the DSC measurements, it is found that the phase change temperatures of the SA/EG round blocks with different packing densities are almost identical to that of the SA/EG composite PCM powders before dry pressing. Figure 8 also illustrates the relationship between the melting and solidifying enthalpy with the packing density of the blocks. The melting and solidifying heat values show little change with the packing densities, close to those of the SA/EG composite PCM powders before dry pressing (Table 1). It is revealed that the SA/EG composite

PCM has good stability in thermal properties before and after dry pressing, which makes it promising for use in latent heat storage systems.

4. Conclusions

SA can easily be absorbed into the pores of EG to generate the SA/EG composite PCM. The optimal mass percentage of SA is determined to be around 85%. The composite is just the integration of SA and EG without any chemical interaction. The latent heat of the composite PCM with a phase change temperature of around 128 °C is as high as ca. 187 J/g, just similar to the calculated value based on the mass percentage of SA in the composite. It is shown that the SA/EG composite PCM has the advantages of negligible subcooling as well as better thermal reliability and stability than SA, owing to the high thermal conductivity of EG. In addition, the SA/EG composite PCM exhibits good formability, and its thermal properties show little change before and after dry pressing. The thermal conductivity of the composite PCM is higher than that of SA, indicating a remarkable increase after dry pressing. These excellent properties make the SA/EG composite PCM promising for use in latent heat storage systems.

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Table Captions

Table 1 Phase change temperatures and latent heat values of SA and the SA/EG composite PCM measured at different heating/cooling rates.

Figure Captions

Figure 1 SEM images of the EG (a) and the SA/EG composite samples with different SA mass percentages 80% (b); 85% (c); 90% (d); 85% (e) after 3000 heating-cooling cycles.

Figure 2 XRD patterns of SA, EG and the SA/EG composite PCM before and after experiencing 3000 heating-cooling cycles.

Figure 3 FT-IR spectra of SA and the SA/EG composite PCM before and after experiencing 3000 heating-cooling cycles.

Figure 4 DSC curves of SA (a) and the SA/EG composite PCM (b) measured at different heating/cooling rates.

Figure 5 DSC curves of the SA/EG composite PCM before and after experiencing 3000 heating-cooling cycles.

Figure 6 Mass loss curves of SA, the SA/EG composite PCM before and after experiencing 3000 heating-cooling cycles.

Figure 7 Photographs of the round blocks fabricated from the SA/EG composite PCM powders by dry pressing, whose packing densities were calculated to be 377.5, 471.8, 566.2, 660.6, 714.5 and 768.4 kg/m³ (a), together with that of the SA casting sample (b).

Figure 8 Relationship between the packing density and thermal conductivity as well as latent heat for the round blocks fabricated from the SA/EG composite PCM powders.

Figure 1a

Figure 1b

Figure 1c

Figure 1d

Figure 2

Figure 3

Figure 4a

Figure 4b

Figure 5

Figure 6

Figure 7a

Figure 7b

Figure 8

Table 1

Sample	Heating/cooling Rate (°C /min)	Melting		Solidification	
		T _{phase-change} (°C)	Latent heat (J/g)	T _{phase-change} (°C)	Latent heat (J/g)
SA	2	132.25	221.8	129.29	212.7
	5	132.94	221.1	128.89	212.5
	8	133.28	220.8	128.18	214.0
	10	133.29	222.4	128.89	217.6
SA/EG ₃	2	128.23	187.6	129.66	188.0
	5	128.19	188.4	129.40	186.2
	8	128.28	186.3	129.18	185.5
	10	128.35	187.8	129.02	186.2