RT100/Expand Graphite Composite Phase Change Material with Excellent Structure

Stability, Photo-thermal Performance and Good Thermal Reliability

Qi Zhang, Huichun Wang, Ziyue Ling, Xiaoming Fang, Zhengguo Zhang^{*}

Key Laboratory of Enhanced Heat Transfer and Energy Conservation, the Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China

^{*}Corresponding author , Tel: 86 20 87112845, Fax: 86 20 87113870,

Email: cezhang@scut.edu.cn

Abstract

The combination of a phase change material (PCM) with expanded graphite (EG) is a simple and effective way to obtain a form-stable composite PCM with relatively high latent heat and enhanced thermal conductivity. In this paper, aiming at developing a high-performance PCM for medium-temperature latent heat storage applications, RT100, a mixture of paraffinic hydrocarbons with a melting point of around 100 °C, has been selected as the PCM to prepare a novel EG-based composite. It is shown that the RT100/EG composite containing 80wt% RT100 is a form-stable PCM. The form-stable RT100/EG composite PCM powders can be compressed into round blocks by dry pressing. All the RT100/EG composite PCM round blocks have much higher thermal conductivity than RT100, and their thermal conductivity linearly increases with the packing density. The thermal conductivity of composite PCM round blocks maintain even in the melting process. Further, the RT100/EG composite PCM shows excellent photo-thermal and direct thermal storage/release performance in simulative condition. Finally, the 200 heating-cooling cycles test along with the structure and thermal property characterizations indicates that the RT100/EG composite PCM has excellent structure stability and good thermal reliability. As a result, the RT100/EG composite PCM with excellent structure stability, good thermal reliability, good formability, enhanced thermal conductivity, excellent photo-thermal performance and good thermal storage/release capacity show great potential for use in medium-temperature thermal energy storage applications.

Keywords: medium-temperature PCM, expanded graphite, RT100, photo-thermal performance, reliability

1. Introduction

Thermal energy storage is an important technology for increasing the utilization efficiency of thermal energy, thus having wide applications in diverse fields, such as solar energy utilization, building energy conservation, industrial waste heat recovery, etc.¹⁻³ Compared with sensible and chemical reaction heat storage techniques, latent heat storage technology using various phase change materials (PCMs) as the working media is particularly attractive due to its advantages of high energy storage density and isothermal nature during the phase change process.⁴ In a latent heat storage system, the used PCM is crucial since its performance characteristics determine the efficiency of the latent heat storage system. The PCMs with large latent heat, high thermal conductivity, and excellent structure stability, and good thermal reliability are highly desirable for latent heat storage applications.

Numerous chemical substances can be used as the PCMs, which are usually classified into two major categories: inorganic and organic compounds.⁵ Most inorganic PCMs have the advantages of large latent heat and low cost. However, they often suffer from some shortcomings like corrosivity, subcooling, and segregation.⁶ Although organic PCMs avoid the above shortcomings inherent in inorganic compounds and possess good stability and relatively high latent heat, they have one major drawback of low thermal conductivity.⁷ To overcome the above disadvantages inherent in the inorganic and organic PCMs, composite PCMs have been prepared by means of encapsulating the PCMs in polymer shells, blending the PCMs with polymers, absorbing the PCMs into porous matrices, etc⁸⁻¹². Among those preparation routes, the combination of PCMs with porous supporting materials has been

proven to be a simple and effective way to obtain form-stable composite PCMs, in which the liquid leakage during the solid-liquid phase change process can be effectively prevented due to the capillary and surface tension forces of the porous matrices^{8,12-23}.

Since our pioneer work¹⁵ in 2006, expanded graphite (EG) has been verified to be the best porous matrix to prepare form-stable composite PCMs, owing to its advantages of large pore volume, low density, and high thermal conductivity^{15,24-32}. As a result, the EG-based composite PCMs possess the advantages of relatively high latent heat and enhanced thermal conductivity,²⁹ which make them widely used in the field of thermal management such as building systems, electron device and solar thermal utilization. Recent years, medium-temperature PCMs like sebacic acid³³ show great potential in the solar thermal utilization and chemical reaction systems, as the medium-temperature PCMs have the advantage of high grade stored energy to improve the effective energy. For instance, the Erythritol was reported to be suitable medium-temperature PCM to efficiently provide heat to LiBr/H₂O solar absorption cooling system³⁴.

In the current work, aiming at developing a high-performance PCM for medium-temperature latent heat storage applications, RT100, a mixture of paraffinic hydrocarbons with a melting point of around 100 °C, has been chosen as the PCM to prepare a novel EG-based composite. The optimal mass fraction of RT100 in the composite has been determined, and the structure and thermal properties of the obtained RT100/EG composite PCM have been characterized. Furthermore, the formability of the RT100/EG composite PCM powders have been investigated by compressing them into several round blocks with different packing densities by dry pressing, followed by the

measurements of their thermal conductivity. In addition, the photo-thermal performance and direct thermal storage/release behavior of the RT100/EG composite PCM were investigated. Finally, the structure stability as well as thermal reliability of the RT100/EG composite PCM has been evaluated by 200 heating-cooling cycles test, and it is found that the RT100/EG composite PCM exhibit excellent structure stability, good thermal reliability, enhanced thermal conductivity, good photo-thermal performance and thermal storage/release behavior, making it very promising for practical applications.

2. Experimental Section

2.1. Materials

RT100 was purchased from Rubitherm Co., Germany. EG was prepared from the expandable graphite powders (expandable volume: 300 mL/g, Qingdao Graphite Co. Ltd., China) by the microwave method.²⁹

2.2. Preparation and characterizations of RT100/EG Composite

The RT100/EG composites containing 80wt% , 85wt%, and 90wt% RT100 were prepared by absorbing different amounts of liquid RT100 into the pores of EG, respectively. To determine the suitable mass fraction of RT100 for its EG-based composite PCM, the liquid leakage test was performed to the three RT100/EG composites containing 80%, 85%, and 90% RT100 as follows. The three samples 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 120 °C (above the melting point of RT100) for 30 min, to make sure that the phase change of RT100 from solid to liquid took 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 were any traces of liquid RT100 left on it, and the masses of the samples were compared before and after the test to further judge if the liquid leakage happened. The composite that the liquid leakage didn't happen to could be considered to be a form-stable PCM, and its mass fraction was considered as the optimal mass fraction of RT100. In addition, the microstructures of EG and the RT100/EG composites containing different mass fractions of RT100 were observed using a scanning electron microscope (SEM, Quanta, FEI, Holland).

Crystalline phases of EG, RT100 and the RT100/EG composite PCM were characterized by an X-ray diffractometer (XRD, D8-ADVANCE, Bruker, German) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Fourier transformation infrared spectra (FT-IR) of RT100 and the RT100/EG composite PCM were measured at room temperature on a spectrometer (Tensor 27, Bruker, Germany). Thermal storage properties of RT100 and the RT100/EG composite PCM were analyzed by a differential scanning calorimeter (DSC, DSC Q20, TA Instruments, URT100) under N₂ atmosphere at a flow rate of 50 mL·min⁻¹. The measuring temperature ranged from 40 °C to 150 °C. The heating/cooling rate was set at 10 °C·min⁻¹. The thermal stability of RT100 and the RT100/EG composite PCM was investigated by the thermogravimetric analysis (TGA) using a thermal analyzer (Q600 SDT, TA, URT100). The measurements were conducted by heating the samples from room temperature to 600 °C at a heating rate of 10 °C / min under air atmosphere with a flow rate of 100 mL/min.

2.3. Fabrication and characterizations of compressed RT100/EG composite PCM

The RT100/EG composite PCM powders containing 80wt% RT100, 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 $100 \text{ kg}\cdot\text{cm}^{-2}$. Based on the volume of the mold 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 mold to fabricate the blocks. Finally, we measured the actual volumes and masses of the formed blocks to calculate their actual packing densities, which were 261.6, 362.7, 460.5, 544.1, 639.9 and $671.7 \text{ kg}\cdot\text{m}^{-3}$.

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, RT100 was melted and poured into the cylindrical mold to fabricate two pieces of casting samples so as to measure the thermal conductivity of RT100. In addition, the thermal conductivity of the compressed RT100/EG composite PCM with density of $671.7 \text{ kg}\cdot\text{m}^{-3}$ at varying temperature was conducted with a muffle furnace to control the temperature.

The photo-thermal conversion performance of RT100 and compressed RT100/EG composite PCM with density of $671.7 \text{ kg}\cdot\text{m}^{-3}$ were conducted under simulated solar irradiation. As shown in Figure 5a, the experimental apparatus consist of photo-thermal conversion system and data collection system. In this experiment, the samples were loaded in a quartzose beaker under the solar simulator (SOLAREGE 700, Perfectlight), the heat storage was carried out when turn the light on. After the temperatures of the samples achieved $\sim 135^\circ\text{C}$, the light was turn off and the samples were immediately cooled at room temperature, which the samples performed the heat release process. The temperature of the

samples during these periods were recorded by thermocouples. An irradiatometer (ST-80C, Photoelectric Instrument Factory of Beijing Normal University) was used to measure and verify the power of the light irradiation from simulated light source.

The direct thermal storage/release performance of RT100 and compressed RT100/EG composite PCM with density of $671.7 \text{ kg} \cdot \text{m}^{-3}$ were conducted in a dryer with temperature of $150 \text{ }^{\circ}\text{C}$. When the samples were placed in the dryer, the direct heat storage was carried out. After the temperatures of the samples achieved $\sim 140 \text{ }^{\circ}\text{C}$, the samples were taken out and immediately cooled at room temperature, which the samples performed the heat release process. The temperature of the samples during these periods were recorded by thermocouples.

2.4. Evaluation of structure stability and thermal reliability of RT100/EG PCM

The structure stability and thermal reliability of the RT100/EG composite PCM containing 80wt% RT100 were studied by placing the sample sealed in a crucible into a high-low temperature chamber to experience 200 heating-cooling cycles, followed by the characterizations by SEM, DSC, and XRD, measured under the same conditions as the as-prepared RT100/EG composite samples were performed.

3. Results and Discussion

3.1. Preparation of form-stable RT100/EG composite PCM

In order to determine the optimal mass percentage of RT100 in its EG-based composite, the liquid leakage test has been conducted on the three RT100/EG composite samples containing 80wt%, 85wt% and 90wt% RT100. The macroscopical size of the composite is about $500 \text{ }\mu\text{m}$ of width and several millimeters of length, as shown in Fig. 1a, c. It can be

observed that the abundant pores of EG have been fully filled with RT100 in the RT100/EG containing 80wt% RT100 (Figure 1a, b), indicating that EG has been probably saturated with RT100. As the mass fraction of RT100 is increased to 85% and 90wt%, some RT100 crystals are found on the surface of EG (Figure 1c-f). It has been found that liquid leakage happened to the sample containing 85wt% and 90wt% RT100, not to that containing 80wt% RT100 in the preparation process. Based on the results from the liquid leakage test and the SEM observations, it can be inferred that the optimal mass percentage of RT100 in its EG-based composite is around 80wt%, at which RT100 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. As a result, the RT100/EG composite containing 80wt% RT100 is a form-stable PCM. It has been reported that the optimal mass percentage of octadecane and paraffin in their EG-based composites are around 90% and 85%^{15,26,29}. It is implied that the optimal mass percentages of the alkanes in their EG-based composite PCMs decrease with the increase in the length of carbon chains.

3.2. Characterization of RT100/EG composite PCM

Figure 2a shows the XRD patterns of RT100, EG and the RT100/EG composite PCM containing 80wt% RT100. It can be seen that EG only has one strong diffraction peak centered at 26.49° with a lattice spacing of $3.3579 \text{ \AA}$ which is attributed to the feature peak (002) of graphite. In the XRD pattern of RT100, there are two strong diffraction peaks located at 21.55° and 23.96° with lattice spacing of 4.1362 and $3.7322 \text{ \AA}$ which should be attributed to the feature peak (110) and (200) of RT100. The RT100/EG composite exhibits three diffraction peaks, which are just the combination of the one from EG and the two ones

from RT100, with a reduction in intensity for all the three peaks, and no new diffraction peak is found in the XRD pattern of the composite. It is revealed that the composite is just the integration of RT100 with EG.

Figure 2b illustrates the FT-IR spectra of RT100 and the RT100/EG composite PCM containing 80wt% RT100. RT100 exhibits four strong absorption peaks, two of which at 2918 and 2849 cm^{-1} represent the stretching vibration of the $-\text{CH}_2$ group, one of which at 1470 cm^{-1} signifies the bending vibration of the $-\text{CH}_2$ group, and one of which at 719 cm^{-1} is ascribed to the swinging vibration of the $-\text{CH}_2$ group. The absorbance peaks in the spectrum of EG at about 3400, 1650, and 1127 cm^{-1} which correspond to the $-\text{OH}$ stretching mode, $-\text{CO}$ vibration mode of the keto form and $-\text{C}-\text{O}$ vibration mode of the enol form. The peaks at 2918 and 2849 cm^{-1} represent the stretching vibration of the $-\text{CH}_2$ group. As shown in Figure 2b, the FT-IR spectrum of the RT100/EG composite is the same as that of RT100. These results confirm that the RT100/EG composite is just the integration of RT100 with EG, and no new substance has generated from the integration. Both the XRD and FT-IR results reveal that no chemical reaction between the RT100 and EG, hence the molecular structure of RT100 is not disrupted by the EG and the stability of RT100 could be maintained. By this simple impregnation method, form stable medium-temperature phase change composites could be made.

3.3. Melting-freezing and thermogravimetric properties of RT100/EG composite PCM

Figure 3a displays the DSC curves of RT100 and the RT100/EG composite PCM containing 80wt% RT100, and their thermal characteristics are listed in Table 1. RT100 exhibits two broad phase change peaks for melting and solidification, and each of them has

two peak temperatures, which is probably due to the fact that RT100 is a mixture of paraffinic hydrocarbons with different carbon atoms. Its phase change temperature is 88.28 °C for melting and 101.85 °C for solidification. RT100 has a large latent heat of more than 200 J·g⁻¹, specifically 233.0 J·g⁻¹ for melting enthalpy and 224.3 J·g⁻¹ for solidification enthalpy on average. As shown in Figure 3a, the melting and solidification points of the RT100/EG composite are 84.62 °C and 105.90 °C, close to those of RT100. The RT100/EG composite possesses an average melting enthalpy of 177.3 J·g⁻¹ and an average solidification enthalpy of 173.3 J·g⁻¹, both of which are slightly lower than the calculated values based on the average latent heat of RT100 and the RT100 mass fraction in the composite. It has been reported that the latent heat values of the EG-based composite PCMs containing paraffin with a melting point of around 60 °C and octadecane with a melting point of around 25 °C are equivalent to the calculated values based on the average latent heat of the corresponding PCMs and their mass fractions in the composite PCMs.^{15,26,29} Since RT100 with a melting point of around 100 °C consists of long-chain alkanes, part of them limited in the narrow zone could not completely melt and crystallize, results in decreasing the melting and solidification enthalpy of this PCM.

Figure 3b illustrates the mass loss curves of RT100 and the RT100/EG composite PCM containing 80wt% RT100. The EG decompose rarely in the temperature range, and the initial decomposition temperature (T_{onset}) of the RT100/EG composite is around 243.2 °C, close to 271.1 °C of RT100. The organic component has totally decomposed and evaporated as the temperature reaches 546 °C. The weight-loss ratio of the RT100/EG composite PCM is about 80%, which is equivalent to the mass fraction of RT100 in the composite.

3.4. Thermal conductivity of formable RT100/EG composite PCMs

The cylindrical compressed RT100/EG composite PCMs were formed by dry pressing

of PCM powders containing 80wt% RT100 in the homemade mould, whose packing densities are 261.6, 362.7, 460.5, 544.1, 639.9 and 671.7 kg·m⁻³, respectively. All the round blocks have smooth surface without any cracks, suggesting that the RT100/EG composite PCM has good formability, as shown in Figure 4a (embedded in the bottom right).

The thermal conductivities of the blocks have been measured by the transient plane source method, an advanced technique evolving from the hot wire method. The thermal conductivity of the RT100 casting sample (as shown in Figure 4a) with the density of 856.4 kg·m⁻³ is measured to be 0.665 W·m⁻¹·K⁻¹. Figure 4a illustrates the thermal conductivity of the RT100/EG round blocks with different packing densities. As the packing density of the blocks is increased from 261.6, 362.7, 460.5, 544.1 and 639.9 to 671.7 kg·m⁻³, their thermal conductivity accordingly increases from 1.707, 2.789, 3.943, 5.035 and 6.040 to 6.792 W·m⁻¹·K⁻¹. The relationship between the packing density (x) and the thermal conductivity (y) of the RT100/EG blocks can be fitted into a linear equation: $y = -1.566 + 0.012x$, indicating an obvious increase in the thermal conductivity with the packing density. The linear equation between the thermal conductivity and the packing density of EG based PCM composite has been demonstrated in our previous work, which is also suitable for other porous encapsulated materials based composites³⁵. Note that all the RT100/EG composite PCM round blocks have much higher thermal conductivity than the RT100 casting sample, owing to the integration of RT100 with EG that has superior thermal conductivity.

To further evaluate the thermal conductivity of the formable composite PCMs, the effect of temperature on the thermal conductivity of formable composite PCMs containing 80wt% RT100 was investigated. As shown in Figure 4b, the thermal conductivity of

composite PCMs containing 80wt% RT100 maintains $\sim 6.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ as the temperature ranges from room temperature to 140°C , implying that the thermal conductivity of the composite PCMs is independent of the temperature. This phenomenon is due to the RT100 is completely encapsulated in the EG, the thermal diffusion behaviour of RT100 in the melting and solidified process has little effect on the thermal conductivity of composite PCMs. Other reports on the thermal conductivities of the carbon materials direct dispersed composite PCMs show that their thermal conductivities decrease rapidly in the solid-liquid phase transition, which limit their thermal management performance. For instance, the thermal conductivity of graphite dispersed composite PCMs (1% of volume fraction) drops from 1.2 to $0.4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ when the composite PCMs melts from solid to liquid phase³⁶. Therefore, the sluggishness of the thermal conductivity of the RT100/EG composite PCMs make it to be very promising for thermal application.

3.5. Photo-thermal performance and direct thermal storage/release behaviour of formable RT100/EG composite PCM

The photo-thermal performance of the formable RT100/EG composite PCM containing 80wt% of RT100 was conducted in the homemade equipment, as shown in Figure 5a. Figure 5b shows the photo-thermal conversion spectra of the RT100 and RT100/EG composite PCM. Compared with the RT100, the temperature of the composite PCM rapidly increased upon solar irradiation. During the heating process, it took 2658 s for RT100 to raise the temperature from room temperature to 110°C but only 666 s for the RT100/EG composite PCM. This behavior is ascribed to the function of EG as an effective photon captor and molecular heater. Simultaneously, the temperature growth platform of the RT100/EG

composite PCM appeared between 80 and 120 °C as the irradiation time increased, illustrates that the phase transition of the RT100/EG composite PCM has occurred upon solar irradiation (as shown in embedded figure in Figure 5b). When the RT100/EG composite PCM absorbed solar radiation, converted the radiation into thermal energy and stored the resulting energy in PCMs. It is indicated that the photo-thermal conversion efficiency of RT100/EG composite PCM could be rapidly improved by EG as encapsulated material. As shown in Figure 5b, the temperature of the RT100/EG composite PCM rapidly decreased after covering the solar irradiation. Both of samples exhibited cool temperature platforms. Thus, a larger amount of heat energy was released by the RT100 and its composite PCM in the form-stable phase change process. During the cooling process, the temperature achieved the room temperature when the time reached 4000 s for RT100, whereas that for the RT100/EG composite PCM is about 800 s. That is ascribed to larger thermal conductivity of the composite to RT100, as shown in Figure 4a. Above results indicate that the RT100/EG composite PCMs with excellent photo-thermal performance show great potential as direct solar light absorber for industrial thermal utilization, such as hot water heater, preheat burner.

In addition, the direct thermal storage/release performances of formable RT100/EG composite PCM containing 80wt% of RT100 were investigated in the range of 30–130 °C, using the constant temperature drying oven method. The temperaturetime curves for melting and freezing process are shown in Figure 5c. There are temperature plateaus during both the heating and cooling processes, which come from the phase transition of the PCM. During the heating process, it takes 556 s for RT100 to raise the temperature from room

temperature to the temperature plateau of 88.3 °C but only 264 s for the formable RT100/EG composite PCM. During the cooling process, the temperature achieved the plateau at about 105 °C when the time reached 986 s for the composite, whereas that for paraffin is about 1246 s. Compared with RT100, the composite reached the temperature plateaus in a shorter time, indicating that the thermal storage/release rates were increased by introducing EG, indicating that the RT100/EG composite PCM has an advantage of efficiently converting heat energy in medium-temperature industrial area.

3.6. Non-leakage of formable RT100/EG composite PCMs

Figure 6 shows the photographs of RT100 and the formable RT100/EG composite PCM containing 80wt% of RT100 heated at 150 °C for different time. As seen from the photographs, the pure RT100 completely melted into liquid after being heated at 150 °C for 20 min. However, the RT100/EG composite PCM kept its form of cylinder during the whole heating process, and no liquid leaked from the sample. The result of the seepage test confirms that the EG provide mechanical strength for the encapsulated composite and prevent the seepage of the melted RT100.

3.7. Thermal reliability of RT100/EG composite PCMs

The thermal reliability of the RT100/EG composite PCM containing 80wt% of the RT100 was investigated by SEM, XRD and DSC measurement on the samples after experiencing 200 heating-cooling cycles. The SEM results show that no liquid exudation happened of the composite PCM after experiencing 200 heating-cooling cycles, as shown in Figure 7a, b, indicating that the RT100/EG composite PCM possesses good form-stability. Figure 7c displays the XRD patterns of the RT100/EG composite PCM before and after

experiencing 200 heating-cooling cycles. It can be seen that the XRD pattern of the RT100/EG composite PCM after experiencing 200 heating-cooling cycles is quite similar to the composite PCM before experiencing the test. The intensity of expanded graphite decrease as the samples cycle 200 heating-cooling processes, it could be attributed to the natural convection of paraffin in the melting process, a part of the liquid paraffin infiltrate the surface of the expanded graphite. The paraffin covered in the surface of the expanded graphite decrease the intensity of graphite. It is indicating the excellent structure stability of the RT100/EG composite PCM. Figure 7d displays the DSC curves of the RT100/EG composite PCM before and after experiencing 200 heating-cooling cycles, and their thermal characteristics are listed in Table 1. It can be seen that the DSC curve of the RT100/EG composite PCM after experiencing 200 heating-cooling cycles is very close to that of the composite PCM before experiencing the test. All above results show that the RT100/EG composite PCMs has a good thermal reliability.

4. Conclusions

RT100 has been selected to prepare a novel EG-based composite by absorbing it into the pores of EG, and the suitable mass fraction of RT100 is determined to be around 80wt%. The RT100/EG composite is just the integration of RT100 with EG, and its melting and solidification temperatures are close to those of RT100. The RT100/EG composite PCM powders can be compressed into round blocks with different packing densities by dry pressing. The form-stable RT100/EG composite PCM can keep its form-stability after dry pressing. All the RT100/EG composite PCM round blocks have much higher thermal conductivity than RT100, and their thermal conductivity linearly increases with the packing

density. Moreover, the thermal conductivity does not decrease in the solid-liquid process. The good formability along with the enhanced thermal conductivity and the form-stability after compression make the RT100/EG composite PCM with excellent structure stability and good thermal reliability very promising for use in latent heat storage systems. In addition, the formable RT100/EG composite PCMs show excellent photo-thermal and direct thermal storage/release performance in simulative experiment, indicating that this new kind of medium-temperature composite PCMs is very promising in the solar thermal utilization and other thermal applications. Finally, the 200 heating-cooling cycles test indicates that the RT100/EG composite PCM containing 80wt% RT100 has excellent structure stability and good thermal reliability. As shown in Figure 7 and Table 1, no obvious changes in melting and solidification points are observed for the RT100/EG composite PCM before and after experiencing the heating-cooling cycling test. The latent heat of the RT100/EG composite PCM after experiencing 200 heating-cooling cycles is $163.6 \text{ J}\cdot\text{g}^{-1}$ for melting and $161.5 \text{ J}\cdot\text{g}^{-1}$ for solidification, which is decreased only by ca. 7.73% and 6.81% as compared to the latent heat of the sample before experiencing the test. All results reveal that the RT100/EG composite PCMs have great potential to be used as medium-temperature phase change materials.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No.U1407132), Guangdong Natural Science Foundation (2014A030312009), and the Joint Project of JST-MOST (2013DFG60080).

References

- (1) Pomianowski, M.; Heiselberg, P.; Zhang, Y. Review of thermal energy storage technologies based on PCM application in buildings. *Energy and Buildings* **2013**, *67*, 56-69.
- (2) Kuravi, S.; Trahan, J.; Goswami, D. Y.; Rahman, M. M.; Stefanakos, E. K. Thermal energy storage technologies and systems for concentrating solar power plants. *Progress in Energy and Combustion Science* **2013**, *39*, 285-319.
- (3) Chan, C.; Ling-Chin, J.; Roskilly, A. Reprint of "A review of chemical heat pumps, thermodynamic cycles and thermal energy storage technologies for low grade heat utilisation". *Applied Thermal Engineering* **2013**, *53*, 160-176.
- (4) Fang, G.; Li, H.; Yang, F.; Liu, X.; Wu, S. Preparation and characterization of nano-encapsulated n-tetradecane as phase change material for thermal energy storage. *Chemical Engineering Journal* **2009**, *153*, 217-221.
- (5) Zhou, D.; Zhao, C. Y.; Tian, Y. Review on thermal energy storage with phase change materials (PCMs) in building applications. *Applied Energy* **2012**, *92*, 593-605.
- (6) Zalba, B.; Marin, J. M.; Cabeza, L. F.; Mehling, H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Appl. Therm. Eng.* **2003**, *23*, 251-283.
- (7) Rathod, M. K.; Banerjee, J. Thermal stability of phase change materials used in latent heat energy storage systems: A review. *Renewable & Sustainable Energy Reviews* **2013**, *18*, 246-258.
- (8) Li, M.; Wu, Z. S. A review of intercalation composite phase change material: Preparation, structure and properties. *Renewable & Sustainable Energy Reviews* **2012**, *16*, 2094-2101.
- (9) Silakhori, M.; Metselaar, H. S. C.; Mahlia, T. M. I.; Fauzi, H.; Baradaran, S.; Naghavi, M. S. Palmitic acid/polypyrrole composites as form-stable phase change materials for thermal energy storage. *Energy Conv. Manag.* **2014**, *80*, 491-497.
- (10) Liang, W. D.; Zhang, G. D.; Sun, H. X.; Zhu, Z. Q.; Li, A. Conjugated microporous polymers/n-carboxylic acids composites as form-stable phase change materials for thermal energy storage. *RSC Adv.* **2013**, *3*, 18022-18027.
- (11) Yang, X.; Yuan, Y.; Zhang, N.; Cao, X.; Liu, C. Preparation and properties of myristic-palmitic-stearic acid/expanded graphite composites as phase change materials for energy storage. *Solar Energy* **2014**, *99*, 259-266.
- (12) Sari, A.; Karaipekli, A. Fatty acid esters-based composite phase change materials for thermal energy storage in buildings. *Applied Thermal Engineering* **2012**, *37*, 208-216.
- (13) Feng, L.; Zheng, J.; Yang, H.; Guo, Y.; Li, W.; Li, X. Preparation and characterization of polyethylene glycol/active carbon composites as shape-stabilized phase change materials. *Solar Energy Materials and Solar Cells* **2011**, *95*, 644-650.
- (14) Xiao, X.; Zhang, P. Morphologies and thermal characterization of paraffin/carbon foam composite phase change material. *Solar Energy Materials and Solar Cells* **2013**, *117*, 451-461.
- (15) Zhang, Z. G.; Fang, X. M. Study on paraffin/expanded graphite composite phase change thermal energy storage material. *Energy Conversion And Management* **2006**, *47*, 303-310.
- (16) Wang, Y.; Zheng, H.; Feng, H. X.; Zhang, D. Y. Effect of preparation methods on the structure and thermal properties of stearic acid/activated montmorillonite phase change materials. *Energy Build.* **2012**, *47*, 467-473.
- (17) Fang, X.; Zhang, Z.; Chen, Z. Study on preparation of montmorillonite-based composite phase change materials and their applications in thermal storage building materials. *Energy Conversion and Management* **2008**, *49*, 718-723.
- (18) Karaipekli, A.; Sari, A. Capric-myristic acid/expanded perlite composite as form-stable phase change

material for latent heat thermal energy storage. *Renewable Energy* **2008**, *33*, 2599-2605.

(19) Karaiepli, A.; Sari, A. Capric-myristic acid/vermiculite composite as form-stable phase change material for thermal energy storage. *Solar Energy* **2009**, *83*, 323-332.

(20) Li, M.; Kao, H.; Wu, Z.; Tan, J. Study on preparation and thermal property of binary fatty acid and the binary fatty acids/diatomite composite phase change materials. *Applied Energy* **2011**, *88*, 1606-1612.

(21) Li, M.; Wu, Z.; Kao, H. Study on preparation, structure and thermal energy storage property of capric-palmitic acid/attapulgit composite phase change materials. *Applied Energy* **2011**, *88*, 3125-3132.

(22) Zhang, J.; Zhang, X.; Wan, Y.; Mei, D.; Zhang, B. Preparation and thermal energy properties of paraffin/halloysite nanotube composite as form-stable phase change material. *Solar Energy* **2012**, *86*, 1142-1148.

(23) Wang, Y.; Xia, T. D.; Feng, H. X.; Zhang, H. Stearic acid/polymethylmethacrylate composite as form-stable phase change materials for latent heat thermal energy storage. *Renewable Energy* **2011**, *36*, 1814-1820.

(24) Wang, C.; Feng, L.; Li, W.; Zheng, J.; Tian, W.; Li, X. Shape-stabilized phase change materials based on polyethylene glycol/porous carbon composite: The influence of the pore structure of the carbon materials. *Solar Energy Materials and Solar Cells* **2012**, *105*, 21-26.

(25) Li, H.; Liu, X.; Fang, G.-Y. Synthesis and characteristics of form-stable n-octadecane/expanded graphite composite phase change materials. *Applied Physics a-Materials Science & Processing* **2010**, *100*, 1143-1148.

(26) Zhang, Z.; Shi, G.; Wang, S.; Fang, X.; Liu, X. Thermal energy storage cement mortar containing n-octadecane/expanded graphite composite phase change material. *Renewable Energy* **2013**, *50*, 670-675.

(27) Py, X.; Olives, R.; Mauran, S. Paraffin/porous-graphite-matrix composite as a high and constant power thermal storage material. *International Journal of Heat and Mass Transfer* **2001**, *44*, 2727-2737.

(28) Xia, L.; Zhang, P.; Wang, R. Z. Preparation and thermal characterization of expanded graphite/paraffin composite phase change material. *Carbon* **2010**, *48*, 2538-2548.

(29) Zhang, Z.; Zhang, N.; Peng, J.; Fang, X.; Gao, X.; Fang, Y. Preparation and thermal energy storage properties of paraffin/expanded graphite composite phase change material. *Applied Energy* **2012**, *91*, 426-431.

(30) Sari, A.; Karaiepli, A. Preparation, thermal properties and thermal reliability of palmitic acid/expanded graphite composite as form-stable PCM for thermal energy storage. *Solar Energy Materials and Solar Cells* **2009**, *93*, 571-576.

(31) Shuping, W.; Peng, Q.; Xiaoming, F.; Zhengguo, Z.; Shuangfeng, W.; Xiaohong, L. A novel sebacic acid/expanded graphite composite phase change material for solar thermal medium-temperature applications. *Solar Energy* **2014**, *99*, 283-290.

(32) Xia, L.; Zhang, P. Thermal property measurement and heat transfer analysis of acetamide and acetamide/expanded graphite composite phase change material for solar heat storage. *Solar Energy Materials and Solar Cells* **2011**, *95*, 2246-2254.

(33) Wang, S.; Qin, P.; Fang, X.; Zhang, Z.; Wang, S.; Liu, X. A novel sebacic acid/expanded graphite composite phase change material for solar thermal medium-temperature applications. *Solar Energy* **2014**, *99*, 283-290.

(34) Agyenim, F.; Eames, P.; Smyth, M. Experimental study on the melting and solidification behaviour of a medium temperature phase change storage material (Erythritol) system augmented with fins to power a LiBr/H₂O absorption cooling system. *Renewable Energy* **2011**, *36*, 108-117.

(35) Ling, Z.; Chen, J.; Xu, T.; Fang, X.; Gao, X.; Zhang, Z. Thermal conductivity of an organic phase change material/expanded graphite composite across the phase change temperature range and a novel thermal

conductivity model. *Energy Conversion and Management*.

(36) Zheng, R.; Gao, J.; Wang, J.; Chen, G. Reversible temperature regulation of electrical and thermal conductivity using liquid–solid phase transitions. *Nature communications* **2011**, 2, 289.

Table 1 Phase change temperatures and latent heat of RT100 and the RT100/EG composite PCM containing 80wt% RT100 before and after 200 heating-cooling cycles.

Sample		Melting point (°C)	Melting enthalpy (J/g)	Solidification point (°C)	Solidification enthalpy (J/g)
RT100		88.28	233.0	101.85	224.3
RT100/EG	Before	84.62	177.3	105.90	173.3
	After	85.74	163.6	106.17	161.5

Figure Captions

Figure 1 SEM images of the RT100/EG composites containing 80wt% (a, b), 85wt% (c, d) and 90wt% (e, f) RT100.

Figure 2 XRD patterns of EG, RT100 and the RT100/EG composite containing 80wt% RT100 (a), FT-IR spectrum of EG, RT100 and the RT100/EG composite containing 80wt% RT100 (b).

Figure 3 DSC curves (a) and Mass loss curves (b) of RT100 and the RT100/EG composite containing 80wt% RT100.

Figure 4 Relationship between the packing density and thermal conductivity of the RT100/EG composite containing 80wt% RT100 (a), the thermal conductivity of the RT100/EG composite with packing density of $671.7 \text{ Kg}\cdot\text{m}^{-3}$ vs temperature.

Figure 5 Schematic of the photo-thermal performance of the RT100/EG composite with packing density of $671.7 \text{ Kg}\cdot\text{m}^{-3}$ (a), the increasing temperature of the RT100/EG composite under solar simulator (b), the thermal storage and release performance of RT100 and RT100/EG composite (c).

Figure 6 The photograph of the RT100 and the RT100/EG composite containing 80wt% RT100 under the same heat source.

Figure 7 SEM images of the RT100/EG composites containing 80wt% of RT100 after experiencing 200 heating-cooling cycles (a, b), DSC curves (c) and XRD patterns (d) of the RT100/EG composite PCM before and after experiencing 200 heating-cooling cycles.

Figure 1, Zhang et al.

Figure 2, Zhang et al.

(a)

(b)

Figure 3, Zhang et al.

(a)

(b)

Figure 4, Zhang et al.

(a)

(b)

Figure 5, Zhang et al.

(c)

Figure 6, Zhang et al.

Figure 7, Zhang et al.

(c)

(d)