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Characterization of medium-temperature phase change materials for solar thermal energy storage using temperature history method

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ABSTRACT

In this work, thermal properties of five phase change materials (PCMs) with medium phase change temperature including mannitol, sebacic acid (SA), SA/expanded graphite (EG) composite, $LiNO_3$-KCl eutectic salt and $LiNO_3$-KCl/EG composite, were characterized using temperature history (T-history) method with improved accuracy. The studies on mannitol showed that although the T-history method could yield a supercooling degree which was lower than that from differential scanning calorimetry (DSC) determination, the severe supercooling and great latent heat loss during mannitol's solidification were still the problems which hindered the use of this material. As for the rest materials, slight or no supercooling phenomena were observed and the obtained phase change temperatures were well matched to literature data. The latent heat measurements of these four materials proved a proportional relationship between the PCM/EG composite's latent heat and PCM's mass fraction. However, the latent heat values determined by T-history were higher than the DSC results. Therefore, repeated studies were still required to further evaluate the latent heat storage densities of these materials. The results in this work could play key roles in design, simulation and modification of latent thermal energy storage (LTES) systems based on these medium-temperature PCMs for solar heat applications.

1. Introduction

Utilization of solar heat is an important measure to deal with worldwide fossil fuel shortage problem and reduce greenhouse gas emission. Its importance lies in the solar heat can substitute for fossil fuels to offer the possibility of building heating [1], cooking [2] and large-scale electricity generation [3]. However, until now, massive utilization of the solar heat still faces some barriers due to the intermittent nature of solar radiation. In some solar heat application facilities, sustained solar heat demand still cannot be met during off-sunshine hours [4]. Therefore, to ensure a desired level of solar heat supply and then promote the utilization efficiency of the solar heat, feasible and effective measures should be taken.

Latent thermal energy storage (LTES) is an attractive technology in recent years for its colossal future to serve the requisite of renewable energy use [5,6]. With the assistance of phase change materials (PCMs), a LTES system can allow a huge amount of the solar heat to be stored at a nearly constant temperature during sunshine hours, and then acts as the heat source when solar heat supply stops. Given that, the LTES system can be used to address the limitations of the solar heat [7].

To date, the LTES system has become indispensable parts in many solar heat application plants [8]. Since the PCM is the core of the LTES system, studying the thermal properties of the PCMs becomes a very essential issue. Commonly, thermal characterizations of the PCMs are performed with differential scanning calorimetry (DSC) [9,10]. This method is one of the most powerful thermal property analysis techniques due to it can provide the PCM's phase change temperature, phase change latent heat and specific heat capacity in a short time through simple procedures. Nevertheless, the heating or cooling rate adopted by DSC test usually is higher than the rate found in practical situation, easily leading to some deviations of the results from the intrinsic properties of the bulk PCMs such as an increase in the supercooling degree or an upward or downward shift in the phase change temperature interval. The sample mass for the DSC test is very small (5–50 mg). Even a slight error in the process of sample weighing may result in significant changes in the measurement results of phase change latent heat and specific heat capacity. Moreover, in order to improve the thermal conductivities of some PCMs and help them to retain their shapes when the PCMs melt, PCM composites formed by combining the PCMs with some matrixes are developed [11]. These composites are

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known for heterogeneity and their thermal behaviors presented by small samples are very different from that demonstrated by the corresponding bulk materials in the practical LTES systems. Thus, the reliability and repeatability of the DSC results of the PCM composites can hardly be achieved.

Besides the DSC, temperature history (T-history) method is another available technique for thermal analysis of the PCMs. This method is based on recording the temperature vs. time curves of the PCM and a reference under natural convection condition and can permit the sample mass above 10 g [12]. Since Zhang et al. [13] first proposed the T-history method in 1999, the potential of this method to overcome the drawbacks of the DSC test and meet the researchers' needs has been widely recognized. Many works about modification of the T-history method and using this method to characterize various types of the PCMs can be found in recent publications. For instance, Marín et al. [14] modified the data processing approach for the T-history method and provided the temperature dependent thermophysical properties of paraffin. Hong et al. [15] and Rady et al. [16] pointed out the limits of the solid and liquid phases of the PCM in T-history curves in new ways and obtained the thermal properties of paraffin and paraffin/ceramic granular composites with improved accuracy. In the works of Stanislava et al. [17] and Hanson et al. [18], in order to have an accurate knowledge of the thermal characteristics of the PCMs and help to select appropriate PCMs for solar energy applications, the T-history method was used to investigate several different classes of the PCMs including paraffin waxes, salt hydrates and mixtures of fatty acids. Polyols, which were another class of the PCMs, were also added to the T-history investigation list in the work of Gunasekara et al. [19,20].

Although previous T-history studies have provided a lot of valuable information for achieving optimal design and modeling of the LTES systems, almost all the PCMs being investigated in those works belong to a low-temperature PCM group in which the PCMs experience phase changes at temperatures lower than 120 °C. As for the PCMs with melting points above 120 °C, their working temperature range is obviously much wider than that of the low-temperature PCMs, leading to the heat storage performances of the corresponding LTES systems more sensitive to the their specific heat capacities and phase change temperature intervals. In addition, with the promotion of PCM composite fabrication technology, more medium and high-temperature PCM composites with improved properties are developed. These materials differ in sample size and shape and their thermal characteristics as bulk materials can hardly be revealed when they are sealed into small containers during the DSC experiments. Therefore, more special attentions are urgently needed to be paid to their accurate thermal characterization so as to facilitate their use in the LTES systems.

In this work, we focused on characterization of the medium-temperature PCMs (PCMs with phase change temperature between 120 and 300 °C) by using the T-history method. Medium-temperature PCMs are also of great interests in recent years due to they can store a large amount of the solar heat to generate processing steam for applications in food processing, paper production and in textile industry [21,22]. To cover most types of the medium-temperature PCMs and demonstrate more thermal features of them, five PCMs including pure PCMs and PCM composites representing three material classes (sugar alcohols, fatty acids and inorganic salts) were chosen in this work. The supercooling behaviors of these materials and the relations of the thermal properties between the PCMs and their composite materials were discussed in details based on the T-history analysis. The obtained results were compared with the literature findings and could offer more effective design and development process of the LTES systems integrated with these selected materials.

2. Materials and methods

2.1. Materials

The PCMs with phase change points at medium temperatures between 120 and 300 °C mainly comprise three classes: sugar alcohols, fatty acids and inorganic salts. Here, we selected mannitol, sebacic acid (SA) and $LiNO_3$-KCl eutectic to represent these three classes, respectively. Considering many medium-temperature PCM composites with desirable thermal performance have been developed and studied, we also take two PCM composites including SA/expanded graphite (EG) composite and $LiNO_3$-KCl/EG composite for example. All the materials being investigated in this work were selected based on two criteria. First, they should possess high phase change enthalpy to make sure high heat storage density of the PCM-based LTES system. Secondly, good thermal and chemical stability and good compatibility with many container materials were needed to enable the long-term use of these materials. Mannitol and SA were directly purchased from commercial manufactures while 50 wt% $LiNO_3$-50 wt% KCl eutectic salt, SA/15 wt % EG composite and $LiNO_3$-KCl/20 wt% EG composite were prepared in laboratory. The detailed descriptions of the preparation method for SA/15 wt% EG composite can be found in Ref. [23] and the methods for 50 wt% $LiNO_3$-50 wt% KCl eutectic salt and $LiNO_3$-KCl/20 wt% EG composite are presented in Ref. [24]. The thermophysical properties of all the selected materials obtained from previous researches are summarized in Table 1.

2.2. Experimental procedure

The T-history experiments in this work were conducted by the original method presented by Zhang et al. [13] with some procedural modifications. Initially, the tubes filled with about 10–20 g PCM and reference material, respectively, were heated to a uniform temperature T_o (higher than the melting point of the PCM). Then, the tubes were suddenly moved to a motionless air chamber and cooled down (shown in Fig. 1). The temperature inside the chamber was assumed to be the ambient temperature and monitored by a T-type thermocouple. The temperatures of the PCM and reference material were measured at the same time by using the other two thermocouples, respectively. The accuracy of the temperature measurement was within ± 0.1 °C and that of the measurement of the sample mass was within ± 0.001 g. Because the phase change temperatures of the PCMs selected in this work were in medium temperature range and some PCMs might have corrosion behaviors [34], silicone oil was chosen as the reference material and the tubes used in this study were made of stainless steel 304 L. To ensure that the temperature distribution inside the tubes was uniform and the lumped capacity assumption (Biot number < 0.1) could be applied, the dimensions of the tubes were set as 10 mm (interior diameter) × 250 mm (length) and the thickness of the tube was 1 mm.

2.3. Mathematical calculation

The temperature vs. time curves recorded during the T-history experiments can be used to determine the phase change temperature, specific heat capacity, degree of supercooling and latent heat of the PCMs. The mathematical method employed in this work to analyze the data obtained from the T-history experiments was based on Marín's theory [14]. Hong's modification steps [15] to rule out the effects of the sensible heat on the value of the phase change latent heat were also taken into account.

Fig. 2(a) shows the temperature variation of the silicone oil during cooling from T_o toward the ambient temperature in the motionless air chamber. The heat released from the testing tube during a very small temperature interval ($\Delta T_i = T_i - T_{i+1}$) can be calculated by