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Preparation and thermal properties of exfoliated graphite/erythritol/mannitol eutectic composite as form-stable phase change material for thermal energy storage

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ABSTRACT

The *m*-Erythritol (erythritol, ME)/D-mannitol (mannitol, DM) binary system was investigated by differential scanning calorimetry (DSC), and the phase diagram was then obtained. It was found that the eutectic composition was at the mole fraction of erythritol $x_{ME} = 0.87$. The latent heat of fusion ($\Delta_m H$) of the eutectic mixture was 322.8 J/g with a peak melting temperature ($T_{p,\ m}$) of 114.4 °C. A cyclic DSC experiment revealed that the $\Delta_m H$ of the eutectic mixture slightly decreased, and the $T_{p,\ m}$ remained stable over 50 DSC cycles. Exfoliated graphite (EG) was then applied to absorb the eutectic mixture to obtain the EG/eutectic composite form-stable phase change material (PCM) and enhance its thermal conductivity. Good form stability could be obtained when the loading of EG in the EG/eutectic composite reached 2.0 wt%. The thermal conductivity of the eutectic mixture was greatly enhanced by EG. When the loading of EG was 10.0 wt%, the thermal conductivity increased by 408% compared to that of the eutectic mixture. Additionally, severe supercooling of the eutectic mixture was also greatly alleviated by EG. The best result was obtained when 3.0 wt% EG was added, for which the degree of supercooling (ΔT) was 62.6 °C and the heat of crystallization ($\Delta_{cr} H$) was 185.7 J/g. X-ray diffraction (XRD) experiments revealed that the eutectic mixture was simply a physical mixture of erythritol and mannitol. Thermal gravimetry (TG) investigations showed that the eutectic mixture and the EG/eutectic composite form-stable PCM exhibited good thermal stability for its applications.

1. Introduction

The development and utilization of renewable energy has drawn great attention across the world in recent decades. Solar energy is one of the most promising renewable energies, as it is inexhaustible and environmentally friendly. Efficient and inexpensive energy storage systems are indispensable for the application of solar energy, however, since solar irradiation varies daily and seasonally [1]. Phase change materials (PCMs) are latent heat energy storage materials that can absorb, store and release heat energy by changing their phases and exhibit the advantages of high storage density in a small temperature range [2]. As a result, latent heat energy storage systems in which PCMs are applied as thermal energy storage materials show great advantages in solar energy thermal applications [3,4].

PCMs can be divided into organic and inorganic PCMs that possess different advantages and disadvantages [5]. Among the organic PCMs, sugar alcohols exhibit very high phase change thermal energy storage capacity (enthalpy of melting, $\Delta_m H$) [6]. Their phase change temperature is suitable for applications in fields such as solar absorption cooling [7,8] and waste heat recovery [9]. *m*-Erythritol (erythritol, ME) and D-mannitol (mannitol, DM), melted at ~118 °C and ~166 °C with the $\Delta_m H$ of ~340 J/g and ~310 J/g, respectively [10,11], are two important sugar alcohols. They have been regarded as promising solid-liquid PCMs, as they are environmentally friendly, non-corrosive, non-flammable, and can be mass-produced with relatively low degradation when used repeatedly [12–17]. The stability of erythritol during long-term phase change cycles has been investigated and proved to be outstanding [15], while the stability of mannitol is affected by some parameters such as the amount of oxygen with which it comes into contact [6]. Unfortunately, most sugar alcohols, including erythritol

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and mannitol, exhibit ultra-high supercooling and low thermal conductivity, which would hinder their applications [18,19].

By mixing two or more pure PCMs together, it is possible to obtain a eutectic mixture that melts at a lower temperature than the original pure PCMs. So far, forming eutectic mixtures has been an important method for obtaining new PCMs with the desired phase change temperature [20]. Recently, some eutectic mixtures of sugar alcohols have been reported. A eutectic mixture of galactitol and mannitol, which exhibited a melting temperature (T_m) of 153 °C and a very high $\Delta_m H$ of 292 J/g at the eutectic composition of 30:70 M ratio of galactitol and mannitol, has been investigated as a valuable PCM [21]. Adonitol-erythritol, arabitol-erythritol, xylitol-erythritol and arabitol-xylitol eutectic mixtures have also been reported, and their eutectic compositions were identified [11,22]. Other reported sugar alcohol eutectic mixture PCMs include erythritol–xylitol, erythritol–sorbitol and xylitol–sorbitol [23]. A mixture of erythritol and mannitol has also been reported [24,25]; however, their phase diagram and the eutectic composition were not presented. The phase diagram and the eutectic composition are crucial for eutectic mixtures to be applied as PCMs since the mixture would melt conjugately only at the eutectic composition. Off-eutectic compositions would eventually lead to phase inhomogeneity, resulting in a temperature range of phase transition and thereby reducing the efficiency for energy storage [20].

Like the original pure solid-liquid PCMs, the obtained eutectic mixture is also made up of solid-liquid PCMs. It would benefit their application if the solid-liquid PCMs are transferred to form-stable PCMs [26–28]. Exfoliated graphite (also called expanded graphite, EG) is an excellent supporting material for form-stable PCMs due to its high thermal conductivity, porosity and specific surface area [29–31]. Form-stable PCMs with EG as a supporting material always exhibit high thermal conductivity and high $\Delta_m H$ [32]. Additionally, the high specific surface area of EG is beneficial for suppressing the supercooling of the PCMs [12].

In the present work, the phase diagram of the erythritol and mannitol binary mixture was investigated by differential scanning calorimetry (DSC), and the eutectic composition was obtained. Then, the long-term thermal energy storage properties of the eutectic mixture were studied by cyclic DSC. Afterwards, form-stable PCMs, in which the eutectic mixture and EG were applied as PCM and supporting material, respectively, were prepared. Their properties were then investigated, and the results are reported here.

2. Experiment

2.1. Materials

Erythritol, mannitol and all other reagents were of analytical grade, obtained commercially and used as received without further purification. Exfoliated graphite was prepared according to a reported chemical oxidation technique using flake graphite [32,33].

2.2. Preparation of erythritol-mannitol binary mixture

Erythritol, mannitol and a certain amount of ethanol were mixed in a mortar. The mixture was ground until the ethanol was almost evaporated. The procedure was repeated twice. The mixtures were then dried in an oven at 50 °C for 4 h to obtain erythritol-mannitol binary mixtures. Nine mixtures, in which the mole fraction of erythritol (x_{ME}) varied from 0.1 to 0.9 with an interval of 0.1, were prepared.

2.3. Preparation of EG/eutectic composites

After the erythritol-mannitol eutectic composition was obtained, the eutectic mixture was melted at approximately 120 °C. Then, 1.0, 1.5, 2.0, 3.0, 5.0 and 10.0 wt% of EG were added. The mixtures were stirred for 20 min and then cooled to room temperature to obtain the EG/eutectic composites.

2.4. Characterization

The thermal energy storage properties of the samples were measured by DSC (TA, Q2000) coupled with a refrigerating cooling system 90 (RCS 90, TA) under a constant flow of dry nitrogen with the flow rate of 50 mL/min. To obtain the phase diagram of the erythritol-mannitol binary system and find the eutectic point accurately, the DSC experiments of the pure compounds and their mixture were carried out at the heating rate of 2 °C/min, while the cyclic DSC experiments of the eutectic mixture and the DSC experiments of the EG/eutectic composites were carried out with heating and cooling rates of 10 °C/min. Prior to the DSC experiments, the instrument was calibrated using indium (99.999%) as the standard material. The thermal stability of the samples was characterized by means of thermogravimetry (TG)/differential thermal analysis (DTA) on a thermogravimetric analyzer (NETZSCH STA 409 PG/PC) from room temperature to 500 °C with the heating rate of 10 °C/min using N_2 as carrier gas. The analyzer was calibrated using $CaC_2O_4{\cdot}H_2O$ (99.9%) prior to the experiment. The thermal conductivity of the samples at room temperature was measured by means of the steady-state heat flow method using a thermal conductivity tester (DRX-II-RW, Xiangtan Huafeng Instrument Manufacturing Co., Ltd, China). Before the measurement, the samples were ground and pressed under 16 MPa to obtain discs ($\Phi = 30$ mm). The hot plate of the tester was set at 35 °C, and the cold plate was cooled by 15 °C water. A disc was mounted between the two plates. The thermal conductivity of the disc was measured when the temperature of the two plates remained stable for more than 1 h. X-ray diffraction (XRD) experiments were performed on a Rigaku D/max-gb X-ray diffractometer with a monochromatic detector. Copper Ka radiation with a power setting of 30 kV and 30 mA and a scanning rate of 5 °/min was used. The EG/eutectic composites were pressed under 16 MPa to obtain discs, and then the discs were heated at 140 °C for 2 h to examine the form-stability.

3. Thermodynamic modeling

The phase diagram of the erythritol-mannitol binary system was also calculated based on the following equations [22]:

$$x_A = \exp\left[\left(\frac{\Delta_m H_A}{RT_{mA}}\right)\left(\frac{T - T_{mA}}{T}\right)\right] \tag{1}$$

$$x_B = \exp\left[\left(\frac{\Delta_m H_B}{RT_{mB}}\right)\left(\frac{T - T_{mB}}{T}\right)\right] \tag{2}$$

$$x_A + x_B = 1 \Longrightarrow \exp\left[\left(\frac{\Delta_m H_A}{RT_{mA}}\right)\left(\frac{T - T_{mA}}{T}\right)\right] + \exp\left[\left(\frac{\Delta_m H_B}{RT_{mB}}\right)\left(\frac{T - T_{mB}}{T}\right)\right] = 1 \tag{3}$$

where x_i (i = A and B) represents the mole fraction of i-compound in the liquid phase. $\Delta_m H_i$ and T_{mi} are the $\Delta_m H$ and the T_m of the pure compound, respectively. T is the temperature of the system, and R is the ideal gas constant.

The eutectic temperature (T_E) was first determined by using Eq. (3), and the corresponding eutectic composition was calculated by using either Eq. (1) or Eq. (2) with $T = T_E$. These two equations were then used to determine the liquidus temperature at compositions below and above the eutectic composition

4. Results and discussion

4.1. DSC curves and phase diagram of the erythritol-mannitol binary system

Fig. 1 shows the heating DSC curves of erythritol, mannitol and the erythritol-mannitol binary mixtures. Only one endothermic peak was