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A novel medium-temperature form-stable phase change material based on dicarboxylic acid eutectic mixture/expanded graphite composites

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ABSTRACT

Low stability, reliability, and corrosion are considerable challenges to widespread application of succinic acid (SA) as phase change material (PCM). Here, we present a novel medium-temperature form-stable phase change material (FSPCM) aiming to eliminate these obstacles. In this study, FSPCM was fabricated by adsorbing eutectics of adipic acid (AA) and SA into expanded graphite (EG). The molar ratio of AA and SA in eutectics was determined to be 7:3, and the optimal mass ratio of EG in FSPCM is ca. 0.1. The composite was characterized by diffraction scanning calorimetry, scanning electron microscopy, Fourier transform infrared spectrometer, X-ray diffractometer, and thermal gravimetric analyzer. The results showed that the FSPCM melts at ca. 135 °C with latent heat storage of 206 J/g. No notable change of thermal behavior in FSPCM was observed after experienced 100 accelerated cycle test. Compared to SA, both the stability and reliability were promoted in FSPCM. Besides, the leakage of dicarboxylic acid was prevented, thus the corrosion was alleviated.

It is envisioned that the as-prepared FSPCM have considerable potential in medium-temperature latent heat storage.

1. Introduction

It is both environmentally and economically vital for storing thermal energy. Therefore, bridging the time gap between the energy demand and thermal energy supply has come under heated discussion among researchers in the field of thermal energy storage (Haillot et al., 2011). As one of most efficient ways to resolve the gap between energy demand and provision, latent heat storage possesses many superiorities, such as high energy storage density, small temperature difference between storing and releasing heat (Zhao and Zhang, 2011). Accordingly, latent heat storage have attracted wide spread interests and extensively research, especially for low temperature application, up to 100 °C (Agyenim et al., 2010; Delgado et al., 2012; Kenisarin and Mahkamov, 2007; Kenisarin, 2014; Kenisarin and Kenisarina, 2012; Oró et al., 2012; Pielichowska and Pielichowski, 2014; Sharma et al., 2009; Zalba et al., 2003). However, studies concerning the topics of latent heat storage for solar cooker (Chandel and Agarwal, 2017; Joshi and Jani, 2015), solar desalination application (Sarwar and Mansoor, 2016), solar power generation (Xu et al., 2015), and process heat sector (Haillot et al., 2011), which temperature regime is generally above 120 °C are comparatively insufficient. Therefore, exploring novel medium-temperature (120–150 °C) PCMs is of great significance.

Favorable characters of dicarboxylic acid such as proper melting temperature, large heat storage capacity, small extent of super cooling during phase change process, moderate price make it a potential candidate PCMs for medium temperature latent heat storage. However, dicarboxylic acid as PCMs have not drew much attraction. Especially, only a few reports focus on PCMs based on dicarboxylic acid (Seki et al., 2015; Wang et al., 2014). To the best of our knowledge, the issue of PCMs based on SA still remains to be a relatively unexplored research area.

To meet the actual demands in practical applications, the large-scale utilization of SA as PCMs is possible only if taking comprehensive factors such as heat storage capacity, cost, operating temperature, stability, corrosion and thermal conductivity into consideration. In the case of SA, the heat storage capacity is high, the cost is quite low. However, it tends to unsteady when temperature exceed the melting temperature (T_m), since temperature difference between onset of weight loss and T_m is merely about 10 °C. What's more, the operating temperature is high for medium-temperature heat storage. Besides, there are also other shortcomings such as corrosion to container, which may obstruct

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its application in practice. Therefore, SA cannot be used directly as PCMs.

Eutectic mixture is a composition of two or more components, in which each of them melts and freezes at the same temperature, and the mixture with lowest melting temperature and best thermal reliability among the mixtures, is termed as the eutectics. Correspondingly, the melting temperature of the eutectics as the congruent melting point (Cao et al., 2015). We are wondering if it is possible to promote thermal stability of SA, meanwhile regulating phase transition temperature into medium-temperature applied range (120–150 °C) by preparation of eutectic binary mixture with AA.

To mitigate corrosion organic acid exerted on corresponding container, and remedy other undesirable properties of PCMs, several supporting materials was employed to promote its feasibility, include carboxyl methyl cellulose (CMC) (Cao et al., 2015), diatomite (Tang et al., 2015), EG (Fang et al., 2010b; Wang et al., 2014; Xia et al., 2010; Zhang and Fang, 2006; Zhang et al., 2012), silicon dioxide (Fang et al., 2010a), organosilicon (Zhu et al., 2015), graphene oxide (Li et al., 2013), activated carbon (Khadiran et al., 2015), Urea and formaldehyde (Fang et al., 2009), agar, Arabic gum and gelatin (Bayés-García et al., 2010), segmented copolymer (Kenisarin and Kenisarina, 2012). In the case of EG, organic PCMs can be incorporated into the porous network of EG by capillary force and surface tension, thus he leakage of melted organic PCMs from the composites can be prevented and the corrosion can be alleviated.

Herein, FSPCMs was developed based on both dicarboxylic acid eutectics and EG aiming to modulate phase transition temperature, enhance thermal stability, and reliability. Mixtures of SA and AA with various molar ratios were prepared to determine the eutectic point. EG was employed to alleviate the corrosion of composites by dint of multiple pores (Fang et al., 2010a). Both the thermal behavior of AA-SA binary eutectic mixture (EM) and the final FSPCM were investigated and discussed.

2. Experimental methods

2.1. Materials

AA with a purity of 99% and SA with a purity of 99.5% obtained from Aladdin Industrial Corporation were used as received. The expandable graphite with expandable volume of 300 ml/g, was obtained from Qingdao YanHai Graphite Co., Ltd., China.

2.2. Preparation

2.2.1. Preparation of EG

EG was prepared by microwave method (Zhang et al., 2012). Typically, the expandable graphite was dried in an oven at 110 °C for 24 h, to remove the possible adsorbed water. To obtain EG, the sample was irradiated in a domestic microwave oven (Galanz-G80F23N3P-ZS) with overall power of 800 W. In this experiment, sample irradiated for 1 min yields the maximum volume, and the worm-like structure in EG was not destructed (Fig. 4(d)). Thus, the optimal irradiation time for EG fabrication is 1 min.

2.2.2. Preparation of EM

To obtain EM and verify rationality of empirical formula-Schrader equation applied in eutectics theoretical calculation, series of binary mixtures of AA and SA with various molar ratios were fabricated by melt-blending method (shown in Fig. 1). Typically, certain weight of AA and SA was placed in a flask and mixed with magnetic stir bar. After that, the temperature was elevated to 185 °C and kept for 10 min in oil bath under stirring. Then the mixture was quenched to room temperature, milled and conserved. To obtain the eutectics in AA/SA binary system, thermal events were recorded by DSC (diffraction scanning calorimetry), and further analysis was presented in Section 4.1.2.

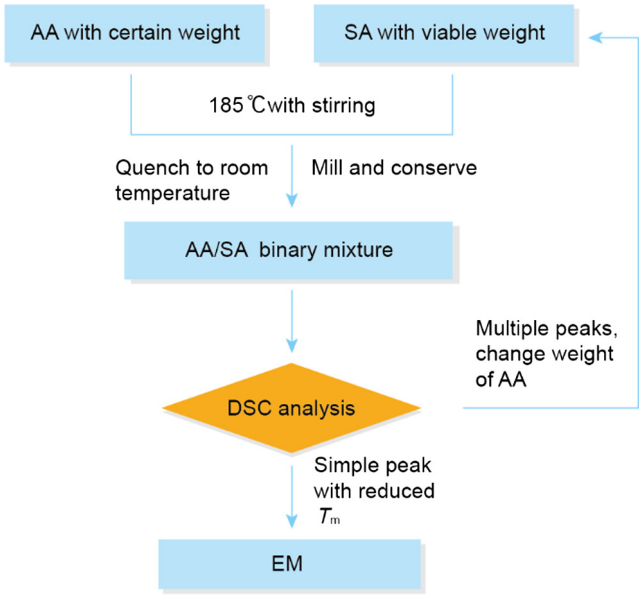

Fig. 1. Preparation of EM.

2.2.3. Preparation of FSPCM

To prepare FSPCM composite, EM/EG composite materials with different EG mass ratios was prepared by melt-blending method (shown in Fig. 2).

Typically, certain weight of EM and EG were introduced into flask through a conical funnel one after another. Then, the columnar EG was dispersed with glass rod to cover EM powder below. Afterwards, the flask was set in oil bath. The temperature was elevated to 139 °C and kept until EG was saturated. After that, all samples were cooled to temperature and conserved for further characterization.

Considering EG was just used as scaffold for EM, the mass fraction of EG should be small, to increase latent heat capacity of composite material. However, in composite material with too small fraction of EG, leakage of EM will be present after it is melt. Leaching test was performed with a filter paper trace method (Wang et al., 2014). Briefly, composite material was placed on a piece of filter paper in an oven at the temperature of 139 °C (above melting temperature of EM) for 30 min. Then the sample was quenched to room temperature and removed from the filter paper. Since trace on filter paper is clue of EM leakage and overloaded EG, the filter paper was carefully examined to found out if any evident trace presented on it. The optimal mass ratio of EG was crude estimated to be above 0.05. According to previous research, the optimal mass ratio of EG in composite PCMs is usually within 0.2. Thus, only composite samples with mass ratio of EG as 0.05, 0.1, and 0.15 were served for further morphological analysis (Section 4.2).

The optimal mass ratio of EG in composite materials was about 0.1. Hence the EM/EG composite material with EG mass ratio of 0.1 was adopted and compressed into a cylinder mold with a tablet press under pressure of 10 kg/cm^2. The final FSPCMs density was calculated to be 1.03 g/cm^3.