High latent heat stearic acid impregnated in expanded graphite

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ABSTRACT

The drawbacks of the relatively high phase change temperatures, fluid leakage, and low thermal conductivity of organic phase change materials limit their applications. Expanded graphite used in this study played two roles, one was shape-stabilized container, and another was a heat transfer intensifier. Stearic acid was impregnated into expanded graphite to form the shape stabilized organic-inorganic phase change composites with a high latent heat, minute supercooling, and no fluid leakage. The results showed that the melting and solidifying enthalpies were reached up to about 168 J/g and 163 J/g, and the phase change temperature is about 53.00 °C. The supercooling of the samples was diminished to 0.35 °C. The optimum mixing mass ratio of the stearic acid and expanded graphite for preparing the samples was about 19:1. The samples exhibited a good thermal stability and thermal conductivity.

1. Introduction

Phase change materials (PCMs) are eye-catching in recent years for the energy crisis [1,2]. PCMs can be applied in many practical fields, such as building energy conservation, heat pumps, smart textiles, waste heat recovery, solar heating systems, and air-conditioning systems [3–7]. There are two main groups in a general view, that is, inorganic and organic PCMs [8–10]. Inorganic PCMs, such as salt hydrates, have been widely studied, which melting temperatures are normally in the area 15 °C–117 °C, and volume-related melting enthalpies are larger than those of organic PCMs. But salt hydrate PCMs have some intrinsic disadvantages: (1) Salt hydrates may decompose and yield other hydrates or dehydrated salts after some thermal runs, and leading to the heat storage capacities decrease. (2) Biggish supercooling [11]. Organic PCMs have more merits than inorganic PCMs, such as no phase segregation, less supercooling effect, non-corrosive nature, and high mass-related thermal storage density in their phase change processes [12–15]. Stearic acid is one of the most attention getting organic PCMs in recent years for its high phase change enthalpy (about 170 J/g) [16,17]. But the stearic acid inherits not only the above merits of organic PCMs, but also the weakness, the leakage during its phase change process.

Many methods have been tried to avoid the leakage. And in them, the most effective and easy way is to impregnate organic PCMs in porous materials [3,17–20]. For example, Cheng's group impregnated paraffin into expanded graphite to form shape stable PCMs [3]. Lin's group sealed stearic acid with expanded vermiculite to avoid the stearic acid leakage [17]. The leakage was relatively well overcome by impregnating organic PCMs in most porous materials. But when we deliberated the latent heat of the most composite PCMs, and to take the stearic acid impregnated materials as examples, found that the latent heats of the stearic acid composite PCMs are normally lower, about 55 J/g–97 J/g, compared with pure stearic acid [21]. But this runs counter to the high latent heat purpose. To pursue a relatively high density latent heat of stearic acid impregnated composite materials, normally accepted idea is improving the stearic acid impregnation rate in porous materials and seeking adequate porous materials to impregnate stearic acid.

To seek suitable materials to impregnate stearic acid, some good works were done, for example, Fang et al. reported to use the expanded graphite as the stearic acid impregnated material, and the corresponding impregnation rate and the latent heat are 83.00 wt% and 155.50 J/g, respectively [21]. The latent heat was impressively improved to use expanded graphite as a stearic acid impregnated material. But there still exists a relatively large room to improve the impregnation rate of expanded graphite to stearic acid according to other related studies, for example, the most loaded amounts of tetradecanol, *n*-octadecane and paraffin in expanded graphite are 93.00 wt%, 90.00 wt.% and 92.00 wt.%, respectively [14,22,23]. In addition, some other problems, like the supercooling phenomenon after stearic acid

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impregnated in expanded graphite, heat recycle life, and so on, need to be studied in detail.

The focus is to synthesize stearic acid-expanded graphite composite PCMs with high latent heat with a minute supercooling by impregnating the stearic acid into the expanded graphite.

2. Experimental section

2.1. Materials

Stearic acid (analytically pure) and expanded graphite was purchased from Xilong Chemical Engineering Co., Ltd in China and Qingdao Jin Ri Lai Graphite Co., Ltd in China, respectively. The average diameter, expansion ratio, and BET surface area of the expanded graphite are 0.18 mm, 300.00 ml/g, and 100.00 m²/g, respectively.

2.2. Sample preparation

The samples were prepared by physical absorption, and detailed as follows [24]. Firstly, the stearic acid and expanded graphite in mass ratio area 4.00–19.00 were mechanically mixed for about 15 min. Secondly, the mixture was ultrasonically dispersed at 70 °C for 1 h. Thirdly, the mixture was automatically cooled to 20 °C in air. The as-synthesized samples were named as EG-SA80, EG-SA90, and EG-SA95, corresponding to the weight percentages (80.00 ± 0.02) wt.%, (90.00 ± 0.03) wt.%, and (95.00 ± 0.05) wt.% of the stearic acid in the samples.

In preparation of the full load samples of the stearic acid impregnated in the expanded graphite, excessive stearic acid was used, and the weight ratio of the stearic acid and expanded graphite was designed as 200.00 after some preliminary experiments. The preparation process was the same, but a little difference in removing the unabsorbed stearic acid. In removing the unabsorbed stearic acid, an 80-mesh sieve was used to sieve the samples at about 60.00 °C. The reason to use this temperature is that the stearic acid would be melted at 60.00 °C, a little higher compared with the stearic acid phase change temperature. This full load sample was named as EG-SA99. Every sample was repeatedly prepared for three times.

2.3. Characterization

To test the impregnating performance, the samples (1.00 g) were placed on an 80-mesh sieve and maintained the temperature at 70.00 °C for 48 h by a drying oven. The impregnating performance of the samples was evaluated by the leakage mass percentage of the stearic acid and calculated by Formula (1). The temperature 70.00 °C was chosen is because the stearic acid would be liquefied, but not gasified, at this temperature [16,17], and the stearic acid outside of the expanded graphite pores could be screened out.

$$E = \frac{m - m_0}{m_0} \times 100(\%) \tag{1}$$

where E (wt%) is the leakage mass percentage of the stearic acid, m_0 (mg) and m (mg) are the sample mass before and after being sieved.

To check the leakage, the form stability, and indirectly check the degree of the stearic acid impregnated in the interlayers of the expanded graphite of the samples after some thermal cycles, a test was carried out as follow. The flat cylinder samples with a diameter 29.72 mm, and a height 8.19 mm were isostatic pressed under a pressure 1 Mpa for 15 s by a tablet press (FY-15, Tianjing Sichuang technology development co. LTD. China). The masses and sizes of the cylinder samples were measured, and the digital photos were taken before and after each thermal cycle. The thermal cycles processed 5 times (25 °C–60 °C) and maintaining at 60 °C for 2 h in a drying cabinet. All the data were measured for 6 times. The results derived in average, and the uncertainty was obtained by the standard deviation of the data

Table 1
Impregnation rate of stearic acid obtained from TGA and impregnation performance test.

Sample	T_{INT}^{*} (°C)	T_{FIN}^{*} (°C)	W_{EG}^{**} (wt.%)	$\eta_{TGA}^{\dagger}$ (wt.%)	$\eta_{E}^{\dagger}$ (wt.%)
Stearic acid	189.10 ± 0.03	235.40 ± 0.02	–	–	–
EG-SA99	216.50 ± 0.09	262.20 ± 0.07	1.11	98.89	99.50 ± 0.08
EG-SA95	201.40 ± 0.04	258.90 ± 0.04	5.78	94.22	95.00 ± 0.05
EG-SA90	206.00 ± 0.03	260.40 ± 0.03	4.32	95.68	90.00 ± 0.03
EG-SA80	195.80 ± 0.03	239.40 ± 0.03	13.56	86.44	80.00 ± 0.02

* Extrapolated initial and terminate decomposition temperature of the samples obtained from TGA.

** Remaining weight percentage of the samples at the temperature ≥ 350 °C obtained from TGA.

† Impregnation rate of the stearic acid in the samples derived from the TGA curves and the Impregnation performance test.
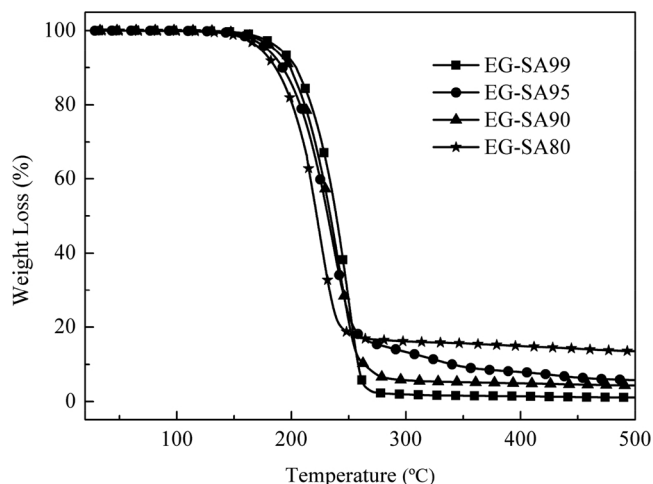

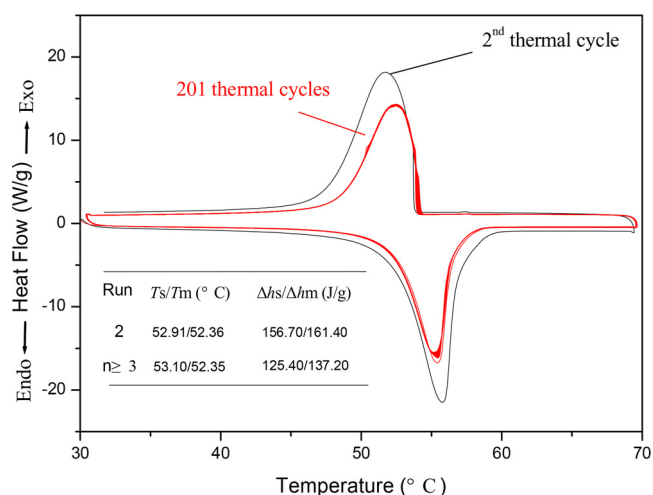**Fig. 1.** TGA curves of EG-SA99–EG-SA80.

Fig. 2. DSC curves of EG-SA95 in 2nd and 201 thermal cycles (Exo: exothermicity, and Endo: endothermicity).

arithmetic mean value.

The surface morphology of the samples was observed by a scanning electron microscopy (SEM, JSM-7001F) with an acceleration voltage of 20 KV. The thermal stability of the samples was tested by a thermogravimetric analyzer (TGA, Q5000) in the temperature area 20.00 °C–500.00 °C and nitrogen atmosphere. The ramping rate was