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Experimental study on effective thermal conductivity of microcapsules based phase change composites

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ABSTRACT

As for thermal energy storage (TES) with phase change materials (PCM), thermal conductivity is a crucial property for heat storage/release rates and energy storage efficiency. In this study, a sort of new microcapsules based phase change composites (PCC) with carbon network to enhance the thermal conductivity and thermal stability was developed. The effective thermal conductivities of the as-prepared PCC were investigated by experiments and theoretical models. The influencing factors of PCC thermal conductivity were analyzed systematically. The morphology of PCC with carbon network structure was detected by energy dispersive spectroscopy using a scanning electron microscope. The experimental thermal conductivities were measured by the transient plane source method, while the theoretical ones were calculated by effective medium theory (ETM). Additionally, an effective theoretical model was proposed and modified to predict the thermal conductivity of such kind of composites with different mass fractions of expanded graphite (EG). As a result, obvious denser carbon network structure of PCC was further confirmed with 24 wt.% EG, the corresponding thermal conductivity was increased by as much as 24 times of the pristine paraffin. The predictions of modified Agari-Uno model were in good agreement with the experiments. Negligible change in thermal conductivity of the PCC was proved after 500 heating and cooling cycles. Hence, the enhancement on thermal properties of PCC can be promising for further applications in TES system.

1. Introduction

Advanced thermal energy storage (TES) systems are required urgently, whereas the deteriorating energy crisis and along with environmental problems [1,2]. For such efficient systems, long-term serving durability, high heat exchange rate and large heat capacity are essential [3]. To satisfy the requirements of numerous thermal applications, utilizing phase change materials (PCM) for latent heat thermal storage (LHTES) is a promising route and also under active investigations [4,5]. In this way, TES is typically based on the energy storage or release during a phase transition of PCM at a constant temperature range [6,7]. PCM has shown potential to be applied in building energy conservation [8], battery thermal management [9], industrial exhaust heat recovery [10] and solar heat utilization [11].

However, one of the main defects of TES systems is the low heat transfer rate, which is derived from the inherent low conductivity of traditional PCM materials [12–14]. Higher heat transfer rate results in more total thermal energy within a unit time, thus energy storage efficiency can be enhanced by improving thermal conductivity in this way. Moreover, pure PCM still suffer from leakage during the solid-liquid phase transition [15,16], which results in some negative effects, such as gradual failure of energy storage, environment pollution, security potential danger, and then greatly limit its practical thermal applications [17].

In order to avoid the leakage of PCM from their own location and also increase the heat transfer areas, microencapsulation technique has received extensive attentions in recent years [18]. Microencapsulated phase change materials (MEPCM) can hold the PCM core within a tiny container shell and protect it from the surrounding materials [19]. The conventional MEPCM with organic polymer shells have been widely studied, which possess good thermal stability but poor in thermal conductivity [20], such as urea formaldehyde resin [21], melamine formaldehyde resin [22], poly (methyl methacrylate) [23] and polystyrene [24]. Whereupon, MEPCM with inorganic shells were further investigated to improve thermal conductivity, for instance, calcium carbonate [25], silicon dioxide [26], titanium dioxide [27] and germanium dioxide [28]. In spite of the greater enhancement on

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Nomenclature

C_1	porosity correction factor
K_{exp}	experimental thermal conductivity, W/m·K
$^*K_{exp}$	experimental thermal conductivity after 500 heating and cooling cycles test, W/m·K
K_{eff}	effective thermal conductivity, W/m·K
K_1	effective thermal conductivity of continuous phase, W/m·K
K_2	effective thermal conductivity of dispersed phase, W/m·K
Φ_{EG}	volume fraction of EG,%
Φ_M	volume fraction of MEPCM,%
ω_{EG}	mass fraction of EG,%
ω_M	mass fraction of MEPCM,%
ρ_{app}	packing density of PCC, kg/m^3
ρ_t	theoretical density of PCC, kg/m^3
ρ_{air}	theoretical density of air, kg/m^3
ε	porosity of porous matrix
V_{af}	porosity of MEPCM/EG composites
V_f	percolating threshold value

thermal conductivity by MEPCM with inorganic shells, it's still inadequate for meeting the targets of most TES systems.

To further accelerate heat transfer rate and improve its thermal stability as well, the exploration of phase change composites (PCC) that consisted of MEPCM and high thermal conductivity fillers is needed. Several researches has been proposed that the thermal conductivity of PCC can be remarkablely increased by blending organic shell MEPCM with high thermal conductivity fillers, including expanded graphite (EG) [29], carbon fibers [30], carbon nanotubes [31] and graphene [32]. Each study has presented a significantly enhancement on the thermal conductivity of PCC, owing to the inherent high conductivity, low density and large specific surface area of the high thermal conductivity additives [33]. Hereinto, forming a carbon network structure is a more efficient way to improve thermal conductivity of PCC, since it can maintain the continuity of heat conduction through the constructed heat conduction channels. Generally, the formation of network structure depends on the connection state of fillers. Of the utmost importance, the amount of fillers in PCC is called percolating threshold value when the thermal conductivity be significantly increased at first time [34]. Likewise, the maximum increasing rate point of thermal conductivity can be reached when a specific content of fillers is used on the basis of above situation. To date, scarcely any studies deeply investigated the percolating threshold value and maximum increasing rate point of thermal conductivity of forming a carbon network in MEPCM based PCC especially with inorganic shells. As a consequence, it's crucial to form a more effective network structure to achieve the percolating threshold and maximum increasing rate point of thermal conductivity with less filler content.

In view of the above review, this paper attempts to solve the two challenges simultaneously. The lightweight of microcapsules based phase change composites with carbon network were developed to enhance the thermal conductivity and thermal stability. The effective theoretical model was put forward to predict the thermal conductivity of such kind of composites and save the experimental costs as well. The influencing factors of PCC thermal conductivity were analyzed by both experimental and theoretical methods. The relationship between effective thermal conductivity of PCC and high conductive carbon network structure was further investigated.

2. Experimental details and characterization

2.1. Materials

Paraffin (RT42) (ZDJN PCMS Co., Ltd., China) was selected as core PCM material, as it has a phase change temperature (T_m) of 48 °C and with a latent heat (ΔH_m) of 233 J g^{-1}, but a thermal conductivity of 0.369 W m^{-1} K^{-1}. Calcium carbonate ($CaCO_3$) was used as shell material and prepared by precipitation reaction of Calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3).

Expanded graphite (EG) (mesh 80, Qingdao Graphite Co. Ltd., China) was acted as the high thermal conductivity filler. The EG thermal conductivity in the vertical direction was 49.120 W m^{-1} K^{-1} when the packing density of 400 kg m^{-3}.

2.2. Preparation of the PCC

Fig. 1 demonstrates the procedures to prepare the PCC. The detailed process was described in our previous study [35]. Firstly, oily paraffin was added into the aqueous solution containing SDBS as the surfactant to obtain a stable oil-in-water emulsion. Secondly, a $CaCl_2$ aqueous solution was added dropwise into the above emulsion system. The Ca^{2+} could be assembled on the surface of paraffin micelle through the charge interaction between Ca^{2+} and SO_3^{2-} of the surfactant. Then, the $CaCO_3$ shell was formed through the precipitation reaction between Ca^{2+} and CO_3^{2-} with addition of the Na_2CO_3 solution. At this stage, the MEPCM with paraffin core and calcium carbonate shell was synthesized by self-assembly method. Ultimately, the as-prepared MEPCM was mixed with EG externally according to the proportion. The above mixture was compressed by 10 KN, cut and polished into sheets (Φ 40 mm).

2.3. Characterization

The morphologies of MEPCM and PCC were observed by scanning electron microscope (SEM, JEOL JSM-7400F). The phase change properties were clarified by differential scanning calorimeter (DSC, TA Q20), the samples were heated to 80 °C and cooled to 10 °C with a rate of 10 °C/min under nitrogen atmosphere. The experimental thermal conductivities (K_{exp}) of PCC were tested through thermal conductivity meter (Sweden Hot Disk) by transient plane source method. The PCC specimens were carefully polished with #2000 emery paper to reduce the thermal contact resistance. The uncertainty of thermal conductivity measurements was found to be in the range of ±5%. The elemental composition and distribution of the PCC were detected by energy dispersive X-ray spectrometers (EDS, Oxford Inca Energy-350) with the view of a SEM.

3. Results and discussion

3.1. Morphology and microstructure

Fig. 2 demonstrates the SEM images of the (a) MEPCM and (b) PCC contains 20 wt.% EG. The intact spindle microcapsules are uniformly dispersed and surrounded by EG network. The MEPCM with length about 1–6 μm can be observed in Fig. 2a. The high aspect ratios of MEPCM tends to lie within a plane perpendicular to the