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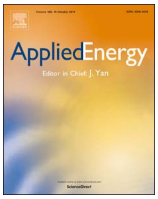

High thermal conductive paraffin/calcium carbonate phase change microcapsules based composites with different carbon network

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HIGHLIGHTS

- A distinct network structure in composite is observed with 10 wt% graphite nanosheets.
- The influences of different carbon fillers on forming network structure are analyzed.
- The thermal properties of composites are improved by the graphite nanosheets network.

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ABSTRACT

Novel microcapsules based phase change composites (PCC) with improved thermal conductivity and thermal stability are developed. Different mass fractions (1%, 5%, 10% and 20%) of flake graphite (FG), expanded graphite (EG) and graphite nanosheets (GNS) acted as heat transfer promoters are employed to enhance thermal properties of PCC. The influences of carbon additives on forming network structure and promoting thermal conductivity are analyzed, the mechanism of heat transfer enhancement is further studied. The results showed that distinct carbon network structure in PCC was observed with 20%, 20%, 10% mass fraction of FG, EG and GNS, respectively. The corresponding thermal conductivity was increased up to 70.0 times of the pristine paraffin when PCC contains 20 wt% GNS. Negligible change in thermal properties of the PCC-GNS was confirmed after 500 times thermal cycling tests. Therefore, such enhancement in thermal properties of PCC can result in an improvement of heat storage efficiency, which will be more suitable for numerous thermal applications.

1. Introduction

Thermal energy storage (TES) technologies have received great attentions for easing the energy crisis. Latent heat, sensible heat and reversible thermochemical reaction are the conventional ways employed for TES. Latent heat storage (LHS) using phase change materials (PCMs) is an effective way to improve energy efficiency, since it has advantages in the large energy storage density and isothermal operation [1–3]. To date, PCMs are widely applied in intelligent building materials, battery thermal management, solar heat utilization and waste heat recovery [4–7]. Moreover, new energy vehicles have been developed rapidly and power battery thermal management (BTW) becomes a key problem need to be solved. Utilization of PCM is one of the best thermal control technologies due to its high latent heat and small temperature changes during a phase change. PCM can absorb/release heat when the battery temperature is too high/low, which helps maintain battery temperature within a safe range. However, PCMs suffer leakage during the melting process and poor heat transfer, which largely restricts their further applications [8–10]. Hence, encapsulation and heat transfer enhancement of PCMs are vital for advanced TES and BTW system.

Nowadays, paraffin has been considered as one of the most promising organic PCMs due to its low cost, excellent phase change properties, good thermal and chemical stability [11–13]. Whereas the leakage during solid-liquid phase change and low thermal conductivity of paraffin are the key problem that need to be solved. It may diffuse throughout the environment when melts into low viscous and mobile liquids, which has security risk and performance degradation due to the flammability of leaked PCM [14]. For this reason, a possible solution is the employment of porous materials as skeleton supporters to retain pristine PCM. In recent years, form-stable phase change composites (FSPCM) with various nano-fillers have been reported to improve thermal stability and thermal conductivity. Mallow et al. [15] used paraffin as PCM and compressed expanded natural graphite as supporting material to prepare a novel FSPCM with high thermal

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conductivity. Fan et al. [16] fabricated a FSPCM by mixing paraffin with graphene nanoplatelets, which were observed to cause greatest relative thermal conductivity enhancement up to 164% at the loading of 5 wt%. Samimi et al. [17] simulated thermal performance of a Li-ion battery cell using paraffin/carbon fibers FSPCM and the average thermal conductivity enhancement is 105% of the pristine PCM. Moreover, Li et al. [18] immersing paraffin/expanded graphite FSPCM in silica gel and Al-honeycomb to prevent the leakage of liquid paraffin from the FSPCM via an encapsulation effect, the results showed high heat-dissipation efficiency for the thermal management of $LiFeO_4$ batteries. Although the employment of FSPCM can effectively resolve the low conductivity issue, leakage after long-term cycling remains a challenge due to its incomplete sealed structure. Another approach is microencapsulation of PCMs with a container which can protect it from the external environment and avoid the leakage [19]. For the past few years, encapsulated paraffin core with organic shells has been widely studied to prevent its seepage and also enlarge the heat transfer area, each study presents good thermal stability but still low thermal conductivity [20–23]. Moreover, a variety of inorganic shells have been tried on the encapsulation of paraffin core to further improve the thermal conductivity, such as silicon dioxide (SiO_2) [24], calcium carbonate ($CaCO_3$) [25], germanium dioxide (ZrO_2) [26], titanium dioxide (TiO_2) [27] and aluminum hydroxide (AlOOH) [28]. In consequence, these microcapsules with inorganic shells have thermal conductivity superior to the organic ones. But it still can't satisfy the practical TES and BTW applications especially for high heat flux density situation.

In view of this, several studies have focused on enhancing thermal conductivities of phase change microcapsules, such as inserting high thermal conductive particles in core or shell [29,30], impregnating microcapsules with high thermal conductive fillers or porous materials in the external. Liu et al. [31] enhanced thermal conductivity through incorporating expanded graphite to the microcapsules with melamine resin shell. Yang et al. [32] focused on improving thermal conductivity by merging modified silicon nitride powders with polymethyl methacrylate microcapsules. Wang et al. [33] strengthened the heat transfer performance by adding reduced graphene oxide in the microcapsules with silica shell. Carbon materials are considered as excellent fillers to enhance thermal conductivity as its high thermal conductivity and low density [34,35]. At the same time, energy density of the microcapsules based phase change composites (PCC) is related to phase change latent heat, which is determined by the containing PCMs of PCC. Paraffin is the only functional constituent of PCC that can store and release thermal energy, while the shell material and high thermal conductive filler are employed to encapsulate and strengthen heat transfer. Therefore, the latent heat of PCC decreases with the increase of high thermal conductive fillers content. Since the addition of fillers will lead to a decrease in unit volume/mass of PCM. It is vital to increase the thermal conductivity more efficiently with less filler content.

It is noteworthy that, the most effective way to improve thermal conductivity of PCC is to form network structure with high thermal conductive fillers [36]. Nomura et al. [37] improved thermal conductivity about 38 times of erythritol by constructing carbon fiber (CF) network structure. Ji et al. [38] embedded ultrathin-graphite foams (UGFs) network structure with erythritol (volume fractions of 0.8–1.2 vol%), the thermal conductivity was increased by up to 18 times and negligible change in the PCM melting temperature or mass specific heat of fusion. In this situation, the heat flow can be transferred continuously thus reducing contact heat resistance, which is beneficial to accelerate heat transfer rate and resulted in improved heat storage efficiency. In conclusion, few studies have deeply investigated the influences of type, size and content of the high thermal conductive fillers on forming effective network structure and thermal conductivity, especially based on the phase change microcapsules with inorganic shells.

In this paper, different mass fractions (1%, 5%, 10% and 20%) of flake graphite (FG), expanded graphite (EG) and graphite nanosheets (GNS) are employed as heat transfer promoters to enhance thermal conductivity of phase change microcapsules with $CaCO_3$ shell. Novel microcapsules based PCC with improved thermal stability, temperature regulatory and thermal conductivity is developed. The influences of carbon additives on forming network structure, thermal conductivity and heat storing/releasing rate of PCC are analyzed, the mechanism of temperature regulatory and heat transfer enhancement are further studied.

2. Materials and methods

2.1. Materials

The microencapsulated phase change materials (MEPCM) are synthesized by paraffin core (RT42) with calcium carbonate shell through self-assembly method, which was reported in our previous study [39]. The paraffin with thermal conductivity of $0.369\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ was provided by ZDJN PCMS Co., Ltd., China. The as-prepared microcapsules has a phase change temperature (T_m) of 48.6 °C and with a latent heat (ΔH_m) of 143.6 J/g, and a thermal conductivity (λ) of $0.814\ \mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$.

Flake graphite (FG), expanded graphite (EG) and graphite nanosheets (GNS) are employed as high thermal conductivity fillers. FG is provided by Qingdao Graphite Co. Ltd., China. Then, EG is obtained by acidizing and microwave treatment of the FG, GNS are prepared by ultrasonic fragmentation on the basis of EG.

2.2. Characterization

The morphologies of carbon materials were detected by scanning electron microscopy (SEM, JEOL JSM-7400F). The experimental thermal conductivities (K_{exp}) of PCC were obtained through thermal conductivity meter (Sweden Hot Disk) by transient plane source method. The phase change enthalpies of PCC were obtained by differential scanning calorimeter (DSC, TA Instruments Q20) with a heating/cooling rate of 10 °C/min under nitrogen atmosphere. Energy dispersive X-ray spectrometers (EDS, Oxford Inca Energy-350) with the view of a SEM were used to analyze the network structures of carbon fillers. In addition, the surface temperature distributions of PCC were presented by thermal imager (FLUKE TiX640).

3. Results and discussion

3.1. Preparation of PCC

The schematic formation process for such microcapsules based phase change composites is illustrated in Fig. 1. Different mass fractions (1%, 5%, 10% and 20%) of FG, EG and GNS are added respectively to enhance the thermal properties of microcapsules. Then, the microcapsules are blended with carbon filler materials in external and compressed into sheets (Fig. 1a).

The SEM images of MEPCM and PCC are demonstrated in Fig. 1b and c. The images show that the spindle microcapsules are intact under proper pressure during preparation, which is due to the elastic protection of carbon materials. There is no chemical reaction between microcapsules and carbon fillers, the PCC integration are mainly attributed to compression and surface tension forces according to our previous work [39]. Furthermore, the proper contents of carbon additives have potential to form an effective network thus improve heat transfer performance and thermal stability of PCC efficiently.

3.2. Microstructure of carbon materials

The microstructures of carbon materials (FG, EG and GNS) are presented in Fig. 2. It can be seen that FG's irregular rough sheet with particle size range from 100 to 500 μm in Fig. 2a and b. It has high