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Enhancement in thermal property and mechanical property of phase change microcapsule with modified carbon nanotube

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HIGHLIGHTS

• Carbon nanotubes was grafted and used to enhance the thermal conductivities of the microcapsules.

• The average particle size of the prepared MicroPCMs/CNTs-SA is 0.1 μm.

• The thermal conductivity of MicroPCMs/CNTs-SA with 4% of CNTs increased by 79.2% compared with MicroPCMs.

• MicroPCMs/CNTs-SA has better durability and thermal stability compared to the original MicroPCMs.

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ABSTRACT

Carbon nanotubes grafted with stearyl alcohol (CNTs-SA) was used in synthesizing phase change microcapsules (MicroPCMs) in order to enhance the thermal conductivities of the microcapsules. Urea–formaldehyde resin (UFR) was used as wall material. Scanning Electron Microscope (SEM), laser particle size analyzer, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimeter (DSC) are employed to characterize the prepared MicroPCMs containing the grafted CNTs (MicroPCMs/CNTs-SA). The results indicated that CNTs improved the performance of microcapsules. The average particle diameter of MicroPCMs/CNTs-SA is much smaller than that of MicroPCMs. There was no chemical reaction among paraffin, CNTs and UFR. The phase change temperature and latent heat of MicroPCMs/CNTs-SA was 26.2 °C and 47.7 J/g, respectively. The thermal conductivity of MicroPCMs/CNTs-SA with 4% of CNTs increased by 79.2% compared with MicroPCMs. The initial decomposition temperature of Micro-PCMs/CNTs-SA is 38 °C higher than that of MicroPCMs. After 100 heating and cooling cycles, Micro-PCMs/CNTs-SA still has good durability and thermal stability.

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1. Introduction

Research on microencapsulated phase change materials (PCMs) began in the 1970s. PCMs are encapsulated by natural or synthetic macromolecular to form spherical particles with diameter from 1 to 1000 μ m [1]. Phase change occurs within microcapsules and heat are absorbed or released. Consequently, the purpose of adjusting temperature or storing thermal energy was achieved [2]. Microencapsulation can not only solve the volume change in solid–liquid phase transition, but also prevent PCMs from being exposed to the external environment [3].

Phase change microcapsules (MicroPCMs) have drawn greater attention than traditional PCMs. Ahmet Sari used methyl meth-

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http://dx.doi.org/10.1016/j.apenergy.2014.04.029 0306-2619/© 2014 Elsevier Ltd. All rights reserved. acrylate as wall material to prepare microcapsules with latent heat of 86.4 J/g and coating rate of 43% [4]. Zhang found that microcapsules using styrene maleic anhydride copolymer (SMA) as emulsifier exhibited good phase change characteristics, high encapsulation efficiency and excellent stability [5]. Wei used melamine-formaldehyde resin as wall material to prepare microcapsules through in situ polymerization. The microcapsules had an average diameter of 2.2 µm, the latent heat of 144 J/g and the encapsulation efficiency of 59% [6]. Ma et al. [7] prepared a series of MicroPCMs with butyl stearate and paraffin as a binary core material and poly(methyl methacrylateco-divinylbenzene) copolymer as shell material. The binary core material content in MicroPCMs was in the range between 50% and 85%. The MicroPCMs decomposed above 200 °C. Li et al. [8] fabricated a series of MicroPCMs with polyurethane shell. The fusion heat of polyurethane MicroPCMs was less than 60 J/g.







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Paraffin is a promising phase change material due to its large latent heat, little supercooling, property stability, non-corrosiveness and low price. The leakage problem during phase change process can be solved by microencapsulation method. However, paraffin has low thermal conductivity and microencapsulation hinders heat transfer from paraffin to the outer of wall material of microcapsules. As a result, the thermal conductivity of MicroPCMs is very low and the applications are limited. In order to improve the thermal conductivity of PCMs, metals and carbon materials have been used. Wang et al. [9] used mechanical method to shorten carbon nanotubes (CNTs) for improving dispersion of CNTs in epoxy. The result suggested that the thermal conductivity of shortened CNTs/epoxy composites increased by 40% in comparison with epoxy resin. Cui et al. [10] studied PCMs filled with carbon nanofibers (CNFs) and CNTs. The experimental results show that the thermal conductivity of PCMs increased with loading content of CNFs or CNTs. Mills et al. [11] found that the thermal conductivity of paraffin wax was increased by two orders of magnitude by impregnating porous graphite matrices with paraffin. Xiao et al. [12] found that the thermal conductivity of paraffin/copper foam composite is nearly 15 times larger than that of pure paraffin. Oya et al. [13] developed new PCMs using graphite and nickel particles as highly thermal conductive fillers. The effective thermal conductivity became two orders of magnitude larger than that of the original PCMs. The study of Vitorino et al. [14] showed that the gelled graphite suspensions had enhanced the thermal conductivity of phase change materials. However, little work has been focused on improving heat transfer of MicroPCMs with carbon materials.

CNTs have light weight and high thermal conductivity (about 6000 W/m K for single walled nanotubes [15] and about 3000 W/ m K for multi-walled nanotubes [16]). This characteristic is beneficial to enhance the heat transfer performance of PCMs in heat storage application [17]. This study aims to prepare MicroPCMs with excellent thermal property, mechanical property and long-term behavior. The CNTs were modified to improve the dispersity and therefore improve properties of the original MicroPCMs. The influence of CNTs on morphology and properties of MicroPCMs was investigated by comparing the property differences between MicroPCMs and MicroPCMs/CNTs-SA.

2. Experiments

2.1. Materials

Paraffin was provided by Rubitherm PCM Co., Ltd., China, The phase change temperature and latent heat of paraffin is 28.1 °C and 206.1 J/g, respectively. CNTs (multi-wall carbon nanotubes) were supplied by Beijing Dk Nano technology Co., Ltd. The purity



 $2000 \times$

(a) MicroPCMs



50000× 50000× (b) MicroPCMs/CNTs-SA

Fig. 1. SEM micrographs of (a) MicroPCMs (2000×, 10,000×) and (b) MicroPCMs/CNTs-SA (50,000×, 50,000×).

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