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The effects of modified carbon nanotubes on the thermal properties of erythritol as phase change materials

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ABSTRACT

Three different methods, acid oxidation, mechanochemical process and ball milling, were used to modify multi-walled carbon nanotubes (MWCNTs). The MWCNTs were dispersed into erythritol (Ery) to prepare composite phase change materials (PCMs). The effects of the MWCNTs on the thermal properties of erythritol-based composite PCMs were studied experimentally. FT-IR and XPS spectroscopy show that hydroxyl groups and carboxylic groups were generated on the surface of the MWCNTs after modification. The pretreatment of MWCNTs can improve their dispersibility in erythritol. When the mass fraction of MWCNTs was 1%, the thermal conductivity of Ery was increased obviously from 0.1956 W/(m·K) to 0.9779 W/(m·K). Besides, the MWCNTs could help improve the supercooling and solidification enthalpy of erythritol significantly. When the mass fraction of A-MWCNTs was only 0.5%, the freezing temperature of PCMs increased from 18.8 °C to 58.15 °C and the solidification enthalpy increased 50 J/g. After 10 heating and cooling cycles, the Ery/A-MWCNTs composites show a very good thermal cycling stability.

1. Introduction

Thermal energy is often a secondary product of industrial production processes and is also extensively encountered in nature as solar radiation and geothermal resources. The technology of thermal energy storage (TES) plays a crucial role in the rational use of energy because it can resolve the problem of the energy sources supply and demand. To further improve the energy efficiency of TES, two aspects of research can be conducted. The first aspect is related to software improvement, such as taking advantage of plant measurements and building data-driven predictive models to assist control and optimize energy usage [1,2], and the second is associated with the hardware innovation, such as the latent heat thermal energy storage (LHTES) with phase change materials (PCMs) of large energy storage density at a nearly steady temperature [3,4]. PCM-based TES has been widely applied to building energy management [5], thermal energy storage systems [6], and cold storage systems [7], in an effort to improve the efficiency of thermal energy storage.

Polyalcohols, such as xylitol [8,9], sorbitol [10], and erythritol (Ery) [11–13] are good candidates as PCMs because of their relatively high melting points and high thermal capacities. Erythritol is nontoxic, cheap, easily obtainable and noncorrosive. Its melting point and latent heat is around 119 °C and 340 J/g, respectively. However, the thermal conductivity of erythritol is undesirable for application and the erythritol shows serious undercooling. Therefore, there is a need to improve the thermal conductivity and the serious undercooling.

In order to improve the thermal conductivity of erythritol, lots of efforts have been attempted by scholars, which mainly includes introducing carbon materials, metal oxide fillers [14] and metal [15]. Carbon materials, such as graphene [16], graphite [17,18], carbon nanotubes (CNTs) [19–22], carbon nanofibers (CNF) [23] which show excellent chemical stability, high thermal conductivity and low bulk density, are conducive to the modification of PCMs. Zhang et al. [23] found that the thermal conductivity of PCMs increased by 407.8% with 10% mass fraction of short carbon fibers. However, the loss of enthalpies is 11.3% for composites filled with 10% short carbon fibers. With their low density and good thermal conductivity, CNTs present large potential as additives to improve the thermal conductivity for LHTES. Nevertheless, CNTs tend to aggregate and form clusters owing to high van der Waals force between the tubes. So the solubility in common solvents and interaction between CNTs and other compounds is very limited. It is necessary to improve the dispersion of MWCNTs by modifying the carbon nanotubes [19,24–26]. Wang et al. [24] prepared octanol and oleylamine grafted CNTs to increase successfully the dispersibility of CNTs in palmitic acid. However, there is less research on the undercooling and thermal cycling stability of the PCMs, especially the erythritol/CNTs composites.

In this paper, we prepared MWCNTs composite consisting of

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Nomenclature

TES	thermal energy storage
LHETS	latent heat thermal energy storage
PCMs	phase change materials
Ery	erythritol
CNF	carbon nanofibers
CNTs	carbon nanotubes
MWCNTs	multi-walled carbon nanotubes
O-MWCNTs	original multi-walled carbon nanotubes
B-MWCNTs	the O-MWCNTs after ball milling processing
BB-MWCNTs	the O-MWCNTs after mechanochemical treatment
A-MWCNTs	the O-MWCNTs after acid treatment

erythritol as the matrix and MWCNTs as the additives. The added MWCNTs were modified by three different chemical and/or mechanical methods. The purpose of adding modified carbon nanotubes is not only to increase the thermal conductivity of the PCMs but also to reduce the degree of undercooling and improve the cycling stability of the PCMs. The crystallization and melting behavior of erythritol with modified MWCNTs were investigated. The main objective is to clarify the effects of the modified MWCNTs on the interfacial thermal resistance and the heat transfer in the MWCNTs composites. Furthermore, the thermal cycling stability was also investigated by DSC analysis.

2. Material and methods

2.1. Materials

Both original MWCNTs (O-MWCNTs) and erythritol were supplied by Aladdin Industrial Corporation with a purity of 95% and 99%, respectively. The average diameter and average length of the MWCNTs were 10 nm and 50 μm, respectively. The melting point of the erythritol is 117.6 °C.

2.2. Pretreatment of MWCNTs

Three different methods were used to modify the O-MWCNTs, viz. ball milling method, mechanochemical process and acid oxidation method. Fig. 1 shows the progresses of these methods schematically. In the ball milling method, the O-MWCNTs were directly ball-milled with a weight ratio (20:1) of ball to MWCNTs for 6 h in a planetary milling machine. The MWCNTs after ball milling processing were named as B-MWCNTs. In the mechanochemical reaction method, O-MWCNTs (2 g) were mixed with potassium hydroxide (40 g) and anhydrous ethanol (100 g) at room temperature. Then the mixture was ball-milled for 6 h in a planetary milling machine. The production was diluted by deionized water, then filtered, and washed repeatedly till the washings show no alkalescency. The cleaned and dried MWCNTs obtained from the mechanochemical treatment method were named as BB-MWCNTs. In the acid oxidation method, 2 grams of O-MWCNTs and 60 ml acids mixture were heated and refluxed at 100 °C for 25 min. The acid mixture was consisted of concentrated nitric acid and concentrated sulfuric acid in a volume ratio of 1:3. The MWCNTs after reaction was diluted by deionized water, then filtered, and washed repeatedly till the washings show no acidity. The cleaned samples were collected and freeze-dried for 12 h to remove the attached water. The samples treated by the aforementioned acid oxidation method were named as A-MWCNTs.

2.3. Dispersion experiments

The erythritol/MWCNTs composites were prepared via a melting method. After the erythritol was melted at 125 °C, 0.5, 1, 2, 3, 4 and 5 wt% of MWCNTs were added into the melting erythritol, respectively. They were stirred by a magnetic stirrer at 200 r/min for 10 min and then cooled down to the room temperature. In this way, a series of Erythritol/MWCNTs composite PCMs were obtained.

2.4. Characterization

The surface morphology of all the MWCNTs was examined by JEOL JEM-2100 high resolution transmission electron microscope (HRTEM). Pictures showing the dispersion stability in melting erythritol were recorded using a digital camera (EOS 6D, Canon). Fourier transformation infrared (FT-IR) spectra were obtained using a Spectrum GX-III and the scanning wavenumber was from 400 to 4000 cm^{-1}. X-ray photoelectron spectroscopy was performed on a Thermo ESCALAB 250 XI.

Thermal conductivities (λ) of Ery and Ery/MWCNTs composites were measured by a thermal property analyzer (Hot Disk TPS2500S, Swedish) that is based on the transient plane source method. Thermal conductivity measurements were performed for each sample at elevated temperatures from 50 °C to 130 °C with an increment of 20 °C. Each sample was tested for 3 times, at every tested temperature. Then, the average value was adopted as the experimental results.

The melting point and the latent heat of these samples were measured using a differential scanning calorimeter (Techcomp DSC30). The scanning rate was 5 K/min. All experiments were performed under nitrogen with a flow rate of 50 mL/min. Samples of about 12 mg were weighed by a SHIMADZU AUY120 analytical balance and placed into Al_2O_3 open crucibles. Phase change enthalpies were determined by the integration of the phase transition peaks of the thermograms.

3. Results and discussion

3.1. Structural characterization

The surface morphology of the prepared MWCNTs was examined by TEM analysis and showed in Fig. 2. It is observed that the O-MWCNTs are long and intertwined (Fig. 2A). The average diameter is about 10 nm. The wall of O-MWCNTs is smooth and complete. Fig. 2B and 2C shows that the length of the MWCNTs was shortened greatly. The tube walls of BB-MWCNTs and B-MWCNTs were still smooth and were not damaged by the mechanical treatment. However, there are many obvious broken spots on A-MWCNTs shown in Fig. 2D which were partly circled in red. It showed that the acid treatment has great effects on the MWCNTs and caused the partly destruction of the carbon nanotube

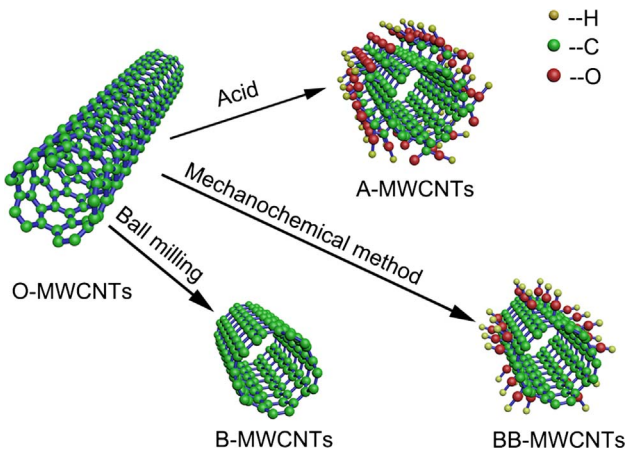

Fig. 1. Process of the ball milling and chemical treatments.