Microencapsulation of phase change materials with carbon nanotubes reinforced shell for enhancement of thermal conductivity

Weiwei Cui1,2, Yongpeng Xia1,2, Huanzhi Zhang1,2*, Fen Xu1,2, Yongjin Zou1,2,3*, Cuili Xiang1,2, Hailiang Chu1,2, Shujun Qiu1,2 and Lixian Sun1,2,4*

1 School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China,
2 Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, China.

E-mail:3* zhanghuanzhi@guet.edu.cn, 4* sunlx@guet.edu.cn

Abstract. Novel microencapsulated phase change materials (micro-PCMs) were synthesized via in-situ polymerization with modified carbon nanotubes(CNTs) reinforced melamine-formaldehyde resin as shell material and CNTs reinforced n-octadecane as PCMs core. DSC results confirm that the micro-PCMs possess good phase change behavior and excellent thermal cycling stability. Melting enthalpy of the micro-PCMs can achieve 133.1 J/g and has slight changes after 20 times of thermal cyclings. And the incorporation of CNTs supplies the micro-PCMs with fast thermal response rate which increases the crystallization temperature of the micro-PCMs. Moreover, the thermal conductivity of the micro-PCMs has been significantly enhanced by introducing CNTs into their shell and core materials. And the thermal conductivity of micro-PCMs with 1.67 wt.% CNTs can increase by 25%. These results exhibit that the obtained micro-PCMs have a good prospect in thermal energy storage applications.

Keywords: phase change materials, microencapsulation, thermal conductivity, carbon nanotubes reinforced shell

1. Introduction

Energy is well recognized to be a significant role in the rapid development of worldwide economics [1]. However, conventional fossil energy sources are limited and non-renewable. Thus, their increasing consumption inevitably results in the shortages of energy resources [2]. Nowadays, the well-designed thermal energy storage unit is an important system for reducing dependency on the fossil fuels, which is mainly attributed to the rational use of thermal energy by “peak shaving” [3, 4]. Phase change materials (PCMs) are recognized as potential candidates for thermal energy storage units due to their very high density of latent heat [5, 6]. PCMs are materials which can absorb or release large amount of heat during phase transformation process within a unit change of temperature [7, 8]. Therefore, they have opened a prospective application in various fields and have been widely used as thermal energy storage materials. However, practical application of PCMs in thermal systems is not easy to manipulate because of their poor chemical stability, erosion and super-cooling problems [9]. Microencapsulation is a commonly used technique to overcome the inherent shortcomings of PCMs.
by which a core material can be protected by a shell. Consequently, it makes PCMs easy to be manipulated in commercial refrigeration, solar heating systems, textile and buildings [10]. Microencapsulated PCMs (Micro-PCMs) not only have high heat transfer rates and good durability, but also reduce interactions of PCMs with the external environment [11]. Generally, Micro-PCMs exhibit a well-defined core-shell structure via self-assembly to protect interior specific functional materials from leakage [12]. As a result, their chemical and thermal stability, thermal response rate and compatibility are depended on the shell structure, so the selection of shell materials is very crucial to the application of Micro-PCMs [13]. Traditionally, the shell materials of micro-PCMs consist of polymer such as melamine–formaldehyde (MF) resin, urea–formaldehyde (UF) resin, polymethyl methacrylate (PMMA), styrene–butadiene- styrene (SBS) copolymer and polystyrene (PS) [14,15]. Although these micro-PCMs with polymer shell materials have good performance, there are still some defects such as poor thermal stability, low thermal conductivity [16]. Moreover, the inherent thermal conductivity of PCMs is quite low. Accordingly, in order to improve comprehensively thermal properties and mechanical properties for micro-PCMs, many researchers rely on high thermal conductive fillers mixing with PCMs such as metal nanowires and carbon nano-particles [17]. Nevertheless, poor compatibility between organic PCMs and these inorganic nano-fillers always induces low thermal stability and durability for thermal energy storage systems. In this case, the extremely high interface area between the fillers (nanoparticles or nanofibres) and the polymer shell or core materials may solve these problems and confer the micro-PCMs excellent comprehensive properties.

Carbon nanotubes (CNTs) are a kind of beneficial nano-reinforcement materials with low density, high aspect ratios, extraordinary mechanical properties and distinguished intrinsic thermal conductivity (~10³ W/(m·K)) due to their unique structure [18,19]. Furthermore, the high interface of CNTs makes them susceptible to bonding with different materials and contributes to the enhancement of properties for composites [20]. Hence, CNTs have stimulated significant interest in the nano-reinforcement material world, especially in the field of polymer-based composites. And the composites impregnated with CNTs exhibit significantly higher thermal conductivity than that of pure polymers [21]. Moreover, some researchers have filled CNTs into pure PCMs to achieve high thermal conductivity [22-25]. Nevertheless, there are little reports on the micro-PCMs with CNTs reinforced shell materials and PCMs core at the same time.

Therefore, in this paper, novel micro-PCMs with CNTs reinforced shell and core materials are synthesized via in-situ polymerization. In order to improve the thermal conductivity of traditional micro-PCMs, amount of CNTs are mixed with PCMs core and as well modified CNTs are pre-polymerized with melamine–formaldehyde pre-polymers forming shell materials, respectively. Furthermore, the influence of CNTs on the properties of micro-PCMs is also investigated. It can be found that the obtained novel micro-PCMs exhibit excellent comprehensive properties which have a potential prospect as thermal energy storage materials.

2. Experimental

2.1. Materials

Carbon nanotubes (CNTs) (purity of 95%, Shenzhen Nanotech Port Co., Ltd) were used to reinforce micro-PCMs. n-Octadecane (Analytical reagent, purity of 90%, Alfa Aesar) was used as the phase change material (PCM). Formaldehyde aqueous solution (Analytical reagent, purity of 37%, Xilong Chemical Co., Ltd) and Melamine (Analytical reagent, Sinopharm Chemical Reagent Co., Ltd) were used to prepare the shell materials of micro-PCMs. Citric acid monohydrate (Analytical reagent, purity of 99.5%, Xilong Chemical Co., Ltd) and triethanolamine (Analytical reagent, purity of 98%, Xilong Chemical Co., Ltd) were used to control pH value. The sodium salt of styrene–maleic anhydride copolymer (SMA) (19% of aqueous solution, Shanghai Leather Chemical Plant) was used as an emulsifier. Distilled water was used as a solvent. All materials are used as obtained without further purification.
2.2. Sample preparation

2.2.1. Modification of Carbon nanotubes. In order to enhance the compatibility and bonding energy between CNTs and the polymer shell of micro-PCMs, the purchased CNTs were modified by using concentrated acid to receive hydrophilic property which makes sure the reaction and bonding between CNTs and shell materials. And the synthetic process is presented as follows: 1.2 g CNTs and 50 ml of concentrated sulfuric acid (98 wt%) were mixed in a 250 ml three-neck flask with magnetic stirring for 15 min at room temperature. Then, the mixed solution was ultrasonicated for 1 hour. After that, 50 ml of concentrated nitric acid (65 wt%) was added into the solution and stirred for 15 min. Next, the mixed solution reacted at 140 °C in an oil thermostat bath with refluxing for 2 hours. Finally, the resulting suspension was cooled and washed with distilled water for several times until the solution became neutral. And then the product was dried at room temperature.

2.2.2. Preparation of novel CNTs reinforced micro-PCMs. Modified CNTs are subjected to ultrasonication in a 100 ml stand-up flask for 10 min to obtain a homogeneous solution. Then, 3 g melamine was added and ultrasonicated for another 10 min. Subsequently, 6 ml formaldehyde aqueous solution and 10 ml distilled water were added. And the mixture was reacted at 70 °C with stirring until it changed into transparent solution getting the CNTs reinforced shell pre-polymer.

Novel CNTs reinforced Micro-PCMs were synthesized via in-situ polymerization. First, 9 g n-octadecane and 50 mg CNTs were mixed homogeneously by ultrasonication for 15 min in a 250 ml three-neck flask. Then, 5 g SMA and 150 ml distilled water were adding into the mixture. And the mixed solution was emulsified at 50 °C with a stirring rate of 1200 rpm for 2 hours. Next, the CNTs reinforced shell pre-polymer was slowly added into the emulsion. Then, pH value of the mixed solution was adjusted to 4-5 by citric acid monohydrate. After that, the polymerization was conducted for 6 hours at 70 °C with a stirring rate of 600 rpm. At last, pH value of the mixture was adjusted to 8-9 by triethanolamine to terminate the reaction. The product was washed with 60 °C distilled water for several times till the solution became neutral and then dried at room temperature. Series of novel micro-PCMs were prepared with modified CNTs content ranging from 0.22 wt% to 1.67 wt%. These samples are summarized in table 1.

Table 1. The constituent of the CNTs reinforced micro-PCMs.

| Microcapsule name | Core materials | Shell materials | The amount of CNTs for core materials | The amount of modified CNTs for shell materials |
|-------------------|----------------|-----------------|--------------------------------------|-----------------------------------------------|
| Sample 1          | n-octadecane   | MF resin        | 0                                    | 0                                             |
| Sample 2          | n-octadecane   | MF resin        | 50 mg                                | 0                                             |
| Sample 3          | n-octadecane   | MF resin        | 50 mg                                | 20 mg                                         |
| Sample 4          | n-octadecane   | MF resin        | 50 mg                                | 50 mg                                         |
| Sample 5          | n-octadecane   | MF resin        | 50 mg                                | 100 mg                                        |
| Sample 6          | n-octadecane   | MF resin        | 50 mg                                | 150 mg                                        |

2.3. Characterization techniques

Morphologies of the obtained samples were observed by using scanning electron microscopy (SEM) (FEI, Quanta 450 FEG). Fourier transform infrared (FTIR) (Thermo Fisher Scientific, Nicolet 6700) spectra was used to survey the chemical structures of the samples with wavenumber range between 500 cm⁻¹ and 4000 cm⁻¹ by KBr sampling method. X-ray diffraction (XRD) (Bruker, D8 Advance) is used to detect the crystallization properties of the obtained micro-PCMs with copper Ka radiation in the 2θ range of 10-90°. Differential scanning calorimeter (DSC) (Setaram, Sensys) is used to measure the thermal storage properties of the samples in the range of -30–50 °C under a nitrogen atmosphere. DSC analysis was carried out with the sample mass of 5–10 mg. Thermal conductivity analysis (TCA)
(Setaram. TCI) was used to measure the thermal conductivity of the obtained micro-PCMs at room temperature. Reported results demonstrated the average value of three measurements for each sample to ensure the repeatability.

3. Results and discussion

3.1. Synthetic mechanism of the CNTs reinforced micro-PCMs
In order to enhance the thermal conductivity and mechanical properties of micro-PCMs, CNTs and the modified CNTs are filled into the PCMs core and shell materials, respectively. The high interface area of CNTs makes sure the strong bonding energy among CNTs, core and shell materials of micro-PCMs. And high thermal conductivity and good mechanical properties of CNTs may provide excellent comprehensive thermal properties for the obtained CNTs reinforced micro-PCMs. The corresponding synthetic mechanism of the CNTs reinforced micro-PCMs (as seen from figure 1) is illustrated as follows: first, the mixture of n-octadecane and CNTs is emulsified into homogeneous micellar solution. The added CNTs can improve the thermal conductivity and thermal stability of core materials due to their good lipophilicity. Then, the modified CNTs which possess hydrophilic groups through covalent modification are reacted with melamine and formaldehyde by hydrogen bond forming into CNTs reinforced shell pre-polymers. Subsequently, the pre-polymers are dropped into the micellar solution and adsorbed around the micellar liquids by the hydrogen bond of different hydrophilic groups between pre-polymers and micelles. And the resulted polymers after reaction are deposited gradually onto the surface of the micellar liquids forming the shell materials of micro-PCMs. Consequently, CNTs and modified CNTs are successfully filled into the core and shell materials of micro-PCMs. As a result, CNTs reinforced micro-PCMs are successfully synthesized.

Figure 1. Schematic formation of CNTs reinforced micro-PCMs.

3.2. Morphology of the CNTs reinforced micro-PCMs
The micrographs of the obtained micro-PCMs detected by SEM are shown in figure 2. It is obvious that the synthesized micro-PCMs have a regular spherical structure with fairly uniform morphology in
each case. And the diameter of the microcapsules is about 5 μm. This phenomenon indicates that the addition of modified CNTs has no effect on the formation of micro-PCMs and the hydrophilic groups of modified CNTs are successfully combined with the shell materials during the polymerization process. It also demonstrates that modified CNTs are homogeneously dispersed into the polymer chains, instead of being placed on the surface of the microcapsule. As a result, the surfaces of the obtained micro-PCMs are smooth and compact. Nevertheless, there are some particles accumulating on the surface of spherical micro-PCMs. It is attributed to the fact that some polymers are not forming into the micro-PCMs shell and sticking to the surface of micro-PCMs. These results mean that series of micro-PCMs doped with different content of modified CNTs are successfully synthesized. Furthermore, the maximum addition amount of the modified CNTs is 150 mg to synthesize the reinforced micro-PCMs as known from the preparation process.

Figure 2. SEM images of the CNTs reinforced micro-PCMs: A-Sample 1, B-Sample 2, C-Sample 3, D-Sample 4, E-Sample 5, F-Sample 6.

3.3. Chemical structure of the CNTs reinforced micro-PCMs

FTIR spectra are performed to investigate the chemical compositions of modified CNTs, micro-PCMs without CNTs and the CNTs reinforced micro-PCMs. The corresponding spectra are presented in figure 3. It is distinct that there is a wide peak at approximately 3400 cm⁻¹ in the spectrum of modified CNTs, which is corresponding to the absorption of O–H and –COOH. As seen from the spectrum of micro-PCMs without CNTs, the strong peaks at 2922 cm⁻¹ and 2852 cm⁻¹ are associated with the asymmetric and symmetric stretching vibration of aliphatic C–H. The wide absorption peaks at approximately 3400 cm⁻¹ are attributed to the stretching vibrations of O–H and N–H in MF resin. Furthermore, the peak at approximately 1015 cm⁻¹ is resulted from the stretching vibration of C–OH. It is clear that all the characterized peaks of modified CNTs and micro-PCMs without CNTs are appearing on the spectra of the obtained micro-PCMs with different content of modified CNTs. This result further indicates that the CNTs reinforced micro-PCMs are successfully synthesized.

Figure 3. FT-IR spectra of the modified CNTs and the CNTs reinforced micro-PCMs.

Figure 4. XRD patterns of CNTs, modified CNTs and the CNTs reinforced micro-PCMs.
3.4. Crystallization properties of the CNTs reinforced micro-PCMs

The crystallinity of CNTs, modified CNTs, micro-PCMs without CNTs and the CNTs reinforced micro-PCMs are determined by XRD. And the influence of CNTs and modified CNTs on crystallization features of micro-PCMs is also investigated. The received XRD patterns are shown in figure 4. A diffraction peak for CNTs and modified CNTs can be remarkably observed at the 2θ value of 26°, which is well corresponding to (002) plane of CNTs. It is clearly observed that micro-PCMs without CNTs reveal series of diffraction peaks at approximately 2θ of 19.4°, 19.9°, 23.5° and 24.8°, which can be indexed as (011), (012), (101) and (102) reflections of n-octadecane, respectively. These diffraction peaks also appear on the XRD patterns of CNTs reinforced micro-PCMs with different modified CNTs content, indicating that crystallization structure of micro-PCMs almost have no change after adding CNTs. It demonstrates that the incorporation of CNTs and modified CNTs does not affect the crystallization structure of micro-PCMs and they are just uniformly dispersed in the core and shell materials by interaction between molecules. As a result, the novel CNTs reinforced micro-PCMs are successfully synthesized and they keep a good crystallization structure which may ensure them excellent phase change behaviors.

3.5. Thermal storage properties of the CNTs reinforced micro-PCMs

Figure 5 shows the DSC curves of micro-PCMs without CNTs and the CNTs reinforced micro-PCMs, and the date calculated from DSC curves are summarized in table 2. For the CNTs reinforced micro-PCMs, the phase change characteristics during phase process are quite similar to those of micro-PCMs without CNTs because of the fact that there is no significant influence of CNTs additional content on the formation of microcapsules. It is clearly seen that there is a single peak in the melting process for the micro-PCMs, while there are two phase change peaks in the cooling thermograms. Some researchers pointed out that n-alkane probably exist several stable phases and partially ordered phases [26]. The minor peak and the mainly wide peak in figure 5 are corresponding to the solid–solid phase transition (the order–disorder transitions in PCMs) and solid–liquid phase change (the melting-cooling process of PCMs), respectively. In this case, the temperature of the solid–solid transition is lower than that of the solid–liquid one [27]. These results imply that the CNTs reinforced micro-PCMs maintain a good phase change behavior. Furthermore, the melting peaks of the CNTs reinforced micro-PCMs shift to a lower temperature with the increasing of CNTs content, and their crystallization peaks move to a higher temperature correspondingly. It suggests that the addition of CNTs improves the thermal conductivity of the obtained micro-PCMs which supplies a quickly thermal response rate to the ambient temperature.

![Figure 5. DSC curves of the obtained micro-PCMs.](image-url)
sample 3 is the highest among all the samples. And the melting latent heat decrease slightly with the increase of the CNTs meaning that the addition content of the CNTs has little influence on the phase change behavior of the obtained micro-PCMs. That is to say, the CNTs reinforced micro-PCMs possess a quite good thermal energy-storage property.

### Table 2. DSC data of the CNTs reinforced micro-PCMs.

| Sample name | Solidifying | Melting |
|-------------|-------------|---------|
|              | Temperature (°C) | Latent heat (J/g) | Temperature (°C) | Latent heat (J/g) |
| Sample 1    | 13.13       | -131.93  | 32.85       | 116.89          |
| Sample 2    | 15.73       | -132.08  | 31.34       | 118.54          |
| Sample 3    | 17.28       | -133.11  | 32.13       | 121.22          |
| Sample 4    | 16.01       | -132.40  | 31.49       | 120.10          |
| Sample 5    | 14.60       | -130.04  | 31.25       | 120.44          |
| Sample 6    | 15.89       | -131.92  | 31.73       | 122.71          |

#### 3.6. Thermal durability of the CNTs reinforced micro-PCMs

The change in thermal properties of the CNTs reinforced micro-PCMs is also evaluated by using sample 3 tested for 20 times of DSC thermal cycles and is shown in figure 6. Melting and crystallization temperatures of the sample 3 almost keep the same till the 20th thermal cycling. Meanwhile, the peak areas of melting and crystallization process change slightly after 20 times of thermal cycling, suggesting that there is no significant change in latent heats for the sample after 20 thermal cyclings. Based on these results, it is notable that the CNTs reinforced micro-PCMs exhibit high thermal reliability in its phase change process. The phase change temperatures and latent heats can keep almost constant in each heating-cooling cycle. It implies that the synthesized samples can maintain repetitious phase change behavior, meaning that the samples perform a good thermal durability in heat storage capacity.

![Figure 6. DSC curves of the CNTs reinforced micro-PCMs for 20 times of thermal cycles.](image)

#### 3.7. Different heating rates test of the CNTs reinforced micro-PCMs

The DSC curves are performed as well to investigate the phase change behavior and thermal energy-storage property of the micro-PCMs without CNTs and the CNTs reinforced micro-PCMs at different heating rates of 5 K/min, 10 K/min, 15 K/min and 20 K/min. The phase transformation behaviors and the phase change characteristic parameters are plotted in figure 7 and table 3, respectively. The sample exhibits comparatively high enthalpy which almost is unchanged during both heating and cooling phase change process at different heating rates. It is also notable that the crystallization peaks of the samples shift to a lower temperature with the increasing heating rate, and the melting peaks move to a higher temperature. This phenomenon is ascribed to the truth that a faster scanning rate can cause more serious super-cooling for a phase change system [28]. However, the crystallization temperatures
of the CNTs reinforced micro-PCMs are higher than those of the micro-PCMs without CNTs. This result indicates that the thermal response rate of the CNTs reinforced micro-PCMs is faster than that of the pure micro-PCMs. Such a feature is attributed to the highly thermal conductive CNTs which provide a superior thermal response rate for the CNTs reinforced micro-PCMs.

![Figure 7](image1.png)

**Figure 7.** DSC curves of the CNTs reinforced micro-PCMs tested at different heating rates.

| Heating rate | Solidifying Temperature (°C) | Melting Temperature (°C) |
|--------------|-------------------------------|--------------------------|
|              | Sample 1                      | Sample 3                 | Sample 1        | Sample 3        |
| 5 K/min      | 14.65                         | 16.37                    | 30.21           | 32.51           |
| 10 K/min     | 8.99                          | 11.07                    | 36.73           | 36.83           |
| 15 K/min     | 6.82                          | 7.07                     | 38.47           | 40.76           |
| 20 K/min     | -2.59                         | -1.89                    | 46.41           | 48.22           |

**Table 3.** DSC data of the CNTs reinforced micro-PCMs at different heating rates.

3.8. **Thermal conductivity of the CNTs reinforced micro-PCMs**

![Figure 8](image2.png)

**Figure 8.** Thermal conductivity of the CNTs reinforced micro-PCMs.

To further evaluate the thermal energy storage and thermo-regulating capacity of PCMs, thermal conductivity is considered as an important contributing factor, as it may delay or promote the thermal response to the storage and release of latent heat. The thermal conductivity of each sample is shown in figure 8. The effect of different mass fractions of modified CNTs on the thermal conductivity of micro-PCMs is also provided. The thermal conductivities of sample1-6 are 0.092, 0.093, 0.095, 0.097, 0.104 and 0.115 W/(m·K) at room temperature, respectively. It is evident that thermal conductivity of the samples show a linear increase with the increment of modified CNTs in shell materials, owing to the internal high thermal conductivity of CNTs. Compared to the sample 1, the thermal conductivity of sample 6 performs a remarkable improvement (25%). These phenomena suggest that CNTs and the modified CNTs are excellently combined with n-octadecane and shell materials, respectively. And they are dispersed uniformly in the core and shell materials. Therefore, the CNTs can perfectly improve the thermal conductivity of the obtained micro-PCMs.
4. Conclusions
Novel micro-PCMs with good phase change behavior and high thermal conductivity are successfully synthesized through in-situ polymerization with modified CNTs reinforced melamine-formaldehyde resin as shell material and CNTs reinforced n-octadecane as PCMs core. The comprehensive performance of the CNTs reinforced micro-PCMs is determined by SEM, FT-IR, XRD, DSC, TGA and TCA. SEM results confirm that the samples are successfully prepared with smooth and compact spherical surface. FTIR spectra and XRD patterns reveal that the incorporation of CNTs and modified CNTs are just uniformly dispersed in the core and shell materials by interaction between molecules. On the basis of the DSC data, all of the samples present good phase change behavior and thermal cycling stability. The TCA implies that thermal conductivity of the samples shows a linear increase with the increment of CNTs mass fractions, owing to the internal high thermal conductivity of the CNTs. As a result, the CNTs reinforced micro-PCMs have excellent phase-change latent heat and high thermal conductivity, which provide a good prospect in thermal energy storage applications.

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