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Composite phase change materials prepared by encapsuling paraffin in PVC macrocapsules

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ABSTRACT

A novel phase change material capsules with SiO_2 in their surface was prepared by absorbing paraffin into PVC hollow capsules and by the polycondensation reaction of TEOS in different conditions. X-ray photoelectron spectroscopy (XPS) analysis and scanning electronic microscope (SEM) were used to determine chemical composition and microstructure of the composite capsules, respectively. Enthalpy capacity and thermal stability of the composite capsules are systematically characterized by using differential scanning calorimeter (DSC), thermogravimetric analyzer (TGA) and thermocycling tests. The composite has high heat capacity with good stability and absence of supercooling phenomena.

1. Introduction

With the growing energy issues, energy saving and environmental protection has become a topic of widespread concern. Phase change materials (PCMs) due to their own advantages play increasingly important roles in green energy and environmentally friendly materials research [1–3]. Energy storage not only reduces the mismatch between supply and demand, but also improves the performance and reliability of energy systems and plays an important role in conserving energy [4,5]. How to storage the energy in suitable forms is still a big challenge.

Many methods have been searched for encapsulation of PCMs. These encapsulation methods can be divided into two main categories: micro-encapsuled PCMs [6–8] and PCMs within space mesh or porous structure [9,10]. Since 1953, the first patent [11] was filed which worked with oil-filled microcapsules. A multitude of research on microcapsules grew increasingly. Zhang et al. [12] synthesized a microencapsulated phase change materials based on n-octadecane core and silica shell through interfacial polycondensation. Luz et al. [13] carried out microencapsulation of polyrotaxanes (PRS) paraffin wax by means of suspension-like homo-polymerization of methyl methacrylate (MMA) and by the copolymerization of this monomer with methyl acrylate (MA) and methacrylic acid (MAA). Jin et al. [14] synthesized capsules containing paraffin as phase change core by the absorption and polymerization of urea–formaldehyde prepolymer onto the core in the presence of hydrolyzed styrene-maleic anhydride copolymer as emulsifier in aqueous phase. Py et al. [10] presented a new supported phase change material made of paraffin impregnated by capillary forces in a compressed expansed natural graphite matrix. Ye et al. [15] prepared a novel form-stable phase change material–polyethylene–paraffin compound (PPC), which is a compound consisting of a paraffin as a dispersed phase change material and a high density polyethylene as a supporting material. However, micro-encapsuled PCMs due to proportion of the shell/core and their small particle sizes, which results in their low PCM concentrations and low phase change enthalpy. While the second category, where the PCM captured within space mesh or porous structure by infusing a porous bulk material into a PCM in the liquid state to disperse PCMs into higher melting-point materials acting as supporting materials. This method has defects that prone to leak. Therefore, macrocapsules with thin and dense shell would be a promising material to encapsulate large amount of phase change matters to form composite with high phase change enthalpy and low, and even no leaking.

In this article, we presented a novel composite PCM with paraffin being absorbed into PVC hollow capsule prepared by phase inversion method. The composite PCM by this approach has a high phase change enthalpy and good encapsulation, which solve the above problem to a large extent. A detailed investigation on phase behavior of the PCMs capsules was performed to well understand phase change stability by thermocycling tests. Thermal stability and

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Table 1
Weight loss of the different composite PCMs after stay at 70 °C for different times.

Sample		1 h	2 h	3 h	4 h	5 h	6 h	7 h	8 h
Paraffin:TEOS = 2	a	17.53%	21.65%	21.65%	24.74%	27.84%	29.90%	31.96%	35.05%
	b	14.89%	20.21%	22.34%	25.53%	28.72%	30.85%	34.04%	37.23%
Paraffin:TEOS = 4	a	8.57%	11.43%	14.29%	16.19%	17.14%	19.05%	20.00%	21.90%
	b	12.39%	15.04%	16.81%	17.70%	19.47%	21.24%	22.12%	23.89%
Paraffin:TEOS = 6	a	16.59%	22.21%	24.53%	28.42%	33.18%	35.49%	38.53%	40.84%
	b	7.67%	12.38%	16.26%	19.33%	22.40%	24.75%	27.72%	31.60%
Uncoated		19.51%	23.33%	27.12%	32.22%	34.36%	38.04%	40.18%	42.20%

a, the hydrolysis of TEOS under acidic condition.
b, the hydrolysis of TEOS under alkaline condition.

enthalpy capacity are systematically characterized by differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA).

2. Experimental

2.1. Materials

Polyvinyl chloride (PVC) was obtained from Tianjin Motimo Co. Ltd., dried in an oven before use. Nickel chloride ($NiCl_2{\cdot}6H_2O$) and hydrochloric acid (HCl) were obtained from Tianjin Chemical Reagent Factory. Sodium borohydride ($NaBH_4$), tetraethyl orthosilicate (TEOS) and N,N-dimethyl formamide (DMF) were all purchased from Tianjin Kermel Chemical reagent Co. Ltd. Solid slice paraffin with melting point 49–53 °C was obtained from instrument Co. Ltd. (Shanghai Yi Yang). Ammonia ($NH_3{\cdot}H_2O$) was obtain from Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd.

2.2. Preparation of composite PCMs

PVC hollow capsules were prepared by phase inversion as previous work [16]. 2 g PVC and 0.1 g $NiCl_2{\cdot}6H_2O$ were added to 20 ml DMF with constant stirring for 12 h at room temperature. After mixing uniformly, the obtained homogeneous polymer solution was dripped into coagulating bath composed of the alkaline solution of sodium borohydride using a syringe with a 1.4 mm-diameter needle equipped with a syringe pump. During the process, the $NaBH_4$ reacted with water catalyzed by NiB and hydrogen gas was produced. The hydrogen gas went out the capsules and took the mass to go to the surface of the capsules, thus the capsules obtained was extremely hollow.

Under 70 °C and 0.08 MPa vacuum conditions, mixtures of TEOS and molten paraffin were absorbed into the PVC hollow capsule (the ratio of TEOS to paraffin from 0, 1/6, 1/4 to 1/2). TEOS was hydrolyzed under acidic or alkaline conditions at 60 °C when adding the capsules into water bath with magnetic stirring for 12 h. The composite PCM was finally obtained.

2.3. Characterization of the composite PCMs

The morphology and microstructure of the composite PCMs were observed by using a scanning electronic microscope (SEM, Quanta 200, FEI Company) operating at a 10 kV acceleration voltage. The thermal properties of the composite PCMs, such as phase change temperature and latent heat, were investigated by using a differential scanning calorimeter (DSC, DSC6220, Seiko Instruments Inc.) under a nitrogen atmosphere from room temperature to 120 °C for two cycles with a heating and cooling rate of 5 °C/min. The thermal stabilities of the composite PCMs were determined by thermocycling tests which referred to the weight loss of composite PCMs every one hour in an oven at 70 °C (also done at varied temperatures at 50, 60, 70 and 80 °C for 4 h) and the thermogravimetric analysis (TGA) using a TG/DTA6300 thermogravimetric analyzer (Seiko Instruments Inc.) at a heating rate of 5 °C/min under a nitrogen atmosphere from room temperature to 400 °C.

3. Results and discussion

3.1. Thermocycling stability of composite PCMs with thermocycling tests

Thermocycling stability plays an important role in thermal cyclic utilization of PCMs, which determines their working durability and availability. The weight loss of the different composite PCMs with thermocycling tests was shown in Table 1. From Table 1, after 8 h thermocycling, the weight loss of composite PCMs was less than 41%, meanwhile, the weight loss of coated composite PCMs with SiO_2 was less than the uncoated ones. It was indicated that coated SiO_2 at surface of the composite PCMs had in some degree hindered the leaking of paraffin even at high temperature of 70 °C, which is much higher than the melting temperature of paraffin (round 52 °C). As shown in Table 1, with the different radio of the paraffin/TEOS, the weight loss rate and the residual percentage of the paraffin in capsules represented different. It was found that the residual percentages of the paraffin in capsules by thermocycling tests were affected by the weight ratio of paraffin/TEOS and the pH of reaction solution. It was discovered that the samples synthesized with smaller weight ratio of paraffin/TEOS show higher residual percentages, because less amount of paraffin was infused out the hollow capsules encapsulated by greater amount of silica material. In particular, the samples synthesized with the paraffin/TEOS weight ratio of 4/1 achieved the smaller weight loss and higher residual percentages. On the other hand, samples were synthesized with the same weight ratio of paraffin/TEOS, the paraffin capsules obtained under alkaline condition had higher residual percentages than that under acidic condition and the uncoated. This indicated that SiO_2 had good encapsulation of composite PCMs under alkaline condition. From Table 2, the weight loss of the compsite PCMs

Table 2
weight loss of the different compsite PCMs stay at different temperatures for 4 h.

Sample	48 °C	53 °C	60 °C	70 °C	80 °C
Paraffin:TEOS = 4:1 pH = 2	0.71%	20.93%	25.18%	31.37%	47.83%
Paraffin:TEOS = 4:1 pH = 10	0.58%	16.73%	19.15%	24.64%	46.10%
Uncoated	1.52%	14.05%	44.84%	46.31%	57.40%