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Facile method of fabricating microencapsulated phase change materials with compact bonding polymer–silica hybrid shell using TEOS/MPS

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ABSTRACT

A facile method was developed for encapsulating paraffin wax with St-DVB-SiO_2 organic − inorganic hybrid shells through the combination of suspension emulsion polymerization and hydrolysis and condensation reaction. In this work, the influence of TEOS/MPS mass ratios on the morphology, particle size distribution (PSD), content of core materials, latent heat storage capacity, thermal conductivity and stability of these microcapsules has been studied. SEM and PSD analysis showed that the fabricated microcapsules had a bowl-like shape with concaves on the shell. Moreover, SEM and TGA results jointly illustrated that the higher amount of MPS incorporated into the experimental process, the more SiO_2 particles bonded on the shell of microcapsules. DSC measurements revealed that the microcapsules had a melting temperature range of 44.36–55.03 °C and latent heat storage capacities of 38.90–95.67 J/g. It was suggested that microencapsulated paraffin wax with St-DVB-SiO_2 hybrid shells has been synthesized successfully.

1. Introduction

Microencapsulated phase change materials(MePCMs) have been extensively studied because of their potential applications in thermal energy storage and management [1,2], latent functionally thermal fluids (LFTF) [3–6], energy-saving building [7], solar thermal energy storage [8,9], thermal-regulating textiles [10] and heat transfer [11,12]. During the past years, great efforts have been made to synthesize new shell materials, which played an important role in packing phase change materials (PCMs), mainly affecting the morphology, shell mechanical strength, heat capacity and thermal stability of the microcapsules. Generally, melamine–formaldehyde (MF) [13,14], poly(methylmethacrylate) (PMMA) [15,16] and polystyrene(St) [17], were adopted as the traditional organic polymeric shell materials. It was revealed that polymer shells could offer structural flexibility and more compatibility with the polymer matrix. However, there are some defects existing for the polymeric shells, such as flammability, poor thermal and chemical stabilities, low thermal conductivity and release of poisonous gases. Thus, some attempts have been taken to encapsulate PCM into inorganic shells, such as silica [18], zirconia [19], TiO_2 [20,21], graphene [22], graphite [23], Al_2O_3 [24] and some double-layered shells like silver/silica [25]. Although inorganic materials are usually nonflammable, free of poisonous gases release, more thermally stable and conductive, there are some limits existing such as brittleness and poor endurance.

Recently, organic-inorganic hybrid shell materials emerge as a fascinating class of microcapsule shells by integrating both the physical and chemical properties of organic polymer materials and inorganic shells [22,26]. For environmental consideration, incorporating silica into polymer shells was popular, due to the properties of nontoxic, readily available, structurally stable and well-defined surface. These hybrid materials display some significant features, such as structural flexibility, less flammable, thermally stable and conductive. An illustrative example is the uniform morphology of particles, enhanced conductivity and stability of poly(methacrylic acid)(PMAA)-SiO_2 hybrid microspheres first prepared by Li et al. [27]. The development of new strategies for the synthesis of organic-inorganic hybrid shell materials is of great importance. Chang et al. [28] studied the encapsulation of *n*-octadecane as PCM with PMMA-silica hybrid shell, based on the suspension polymerization process. Yin et al. [29] reported microencapsulated PCMs with covalently bonded polymer-silica hybrid shell via Pickering emulsion polymerization. However, these synthesis procedures are somewhat complicated, due to the synthesis and modification of SiO_2 before the fabrication of microcapsules. Recently, organosilica, prepared through co-hydrolysis and co-condensation of various alkyl silane precursors, provided a quite straightforward and facile way to synthesize hybrid shell materials [30–33].

Inspired by the preparation processes of organosilica shells, a

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similar approach of fabricating silica in the polymer shells was created, which would provide reactive −C=C group to compactly bond the polymer shell and silica particles. Furthermore, this synthesis process was designed to eliminate the procedure of treating silica particles surface using methacryloxypropyltrimethoxy silane (MPS) before, and offer more compact connection between polymer shell and SiO_2 particles. Here we reported a convenient procedure for fabricating microcapsules of paraffin wax with St-DVB-SiO_2 hybrid shells, based on suspension-like polymerization. To the best of our knowledge, preparing St-DVB-SiO_2 shells with suspension-like polymerization and hydrolysis and condensation reaction of tetraethyl orthosilicate (TEOS) and MPS has not been investigated. Morphologies, thermal and phase change properties of the MePCMs with different weight ratios of TEOS/MPS were also investigated systematically, aimed to control the amounts of SiO_2 bonded in the polymer shells.

2. Experimental

2.1. Materials

Paraffin wax (model $58^{\#}$) used as a core material, was kindly supplied by Beijing Yan Shan Petrochemical Co., Ltd. China. TEOS, MPS and St with a purity of 98 wt% were purchased from Xi Long Chemical Co., Ltd., China. 2,2-azobisisobutyronitrile (AIBN) (98 wt%) was obtained from Tianjin Fu Chen Chemical Reagents Company, China. DVB was supplied by Energy Chemical (Technology) Shanghai Co., Ltd., China. Polyvinylpyrrolidone (PVP) (K88–96, Mw130000), was purchased from Aladdin Reagent Chemical Co., Ltd., China. Anhydrous ethanol was commercially supplied by Beijing Tong Guang Fine Chemical Co., Ltd., China. $NH_3{\cdot}H_2O$ (25 wt%) was purchased from Beijing North Chemical Co., Ltd., China. All chemicals were of analytical reagent (AR) quality and used without further purification.

2.2. Preparation of MePCMs

Paraffin wax was used as a core material. TEOS and MPS were employed as precursors to produce organosilica, AIBN and $NH_3{\cdot}H_2O$ were used as initiator, PVP was selected as a dispersant. St was used as organic monomer and DVB was used as the cross-linking agent. Anhydrous ethanol was used as a solvent and ancillary detergent. The preparation was carried out in a 1000 mL three-neck round bottomed flask equipped with a mechanical agitator and thermostated in a water bath. PVP (1.8 g) was dissolved in a mixed solution of distilled water (281.6 mL) and anhydrous ethanol (220 mL), to form the continuous phase. An organic solution (Table 1) of paraffin wax, TEOS, MPS, St, DVB and AIBN was mixed as the discontinuous phase. Then the discontinuous phase was added into the continuous phase, under vigorous agitation (1500 rpm) for 10 min, before adding 18 g $NH_3{\cdot}H_2O$. The mixture was further emulsified with a high shearing emulsifier (FM200A, FLUKO, Shanghai) at the rate of 7000 rpm for 10 min at 60 °C, to form a stable emulsion. The polymerization process was continued with stirring (1000 rpm) at 80 °C for 5 h. Afterwards, the obtained suspension was filtrated and washed exhaustively with hot water and ethanol (60 °C), and dried in an oven at 50 °C for 24 h.

In order to study the effects of reaction conditions on the shell materials of MePCMs, solid polymer particles without paraffin wax were prepared under the conditions identical to those of MePCMs. The reaction conditions and recipes are listed in Table 1.

2.3. Characterizations of MePCMs

Fourier transformed infrared spectroscopy (FT-IR) was used to investigate the chemical structures of paraffin wax, MePCMs and polymer particles at room temperature. The spectrum was collected in the wave number range of 350–4000 cm^{-1} on a TENSOR 27 Bruke spectral instrument with KBr pellets before analysis.

The crystal structures of the samples were characterized by X-ray diffraction (XRD, BrukerD8 Advance diffractometer) using CuKα radiation of $\lambda = 0.154$ nm with continuous scanning mode at a rate of 5°/min in the 2θ ranging from 5° to 50°, and the operation conditions were 40 kV and 50 mA. XRD analysis was conducted with the room temperature of 25 °C.

Scanning electron microscope (SEM) was used to study the morphology, particle size and surface elemental analysis of MePCMs on a Quanta-2000 scanning electron microscope and energy-dispersive X-ray spectroscopy (EDS) with an accelerating voltage of 5 kV. Samples were coated with a layer of gold before observation to ensure a good conductivity of the samples. Image-Pro Plus software was used here to calculate the particle size of the MePCMs.

Thermal gravimetric analyzer (TGA) was used to determine the thermal stabilities of paraffin wax, MePCMs and polymer particles, carried out on a TG-DTA 6200 LAB SYS thermal gravimetric analyzer in a nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 600 °C.

Differential scanning calorimeter (DSC) was used to measure the phase change properties of paraffin wax, MePCMs and polymer particles, in the range of 30–75 °C at a heating or cooling rate of 10 °C/min in a nitrogen atmosphere. The content of paraffin wax (Core%) within the MePCMs was calculated by Eq. (1).

$$\text{Core\%} = \frac{\Delta H_{\text{Microcapsule}}}{\Delta H_{\text{Parrafin wax}}} \times 100 \tag{1}$$

Where $\Delta H_{\text{Microcapsule}}$ and $\Delta H_{\text{Paraffinwax}}$ are the measured melting enthalpy of MePCMs and PCM, respectively.

Thermal conductivity was measured by Heat flow method (EKO, HC-074-200), according to GB/T 10295. Accelerated thermal cycling test (500 melting/freezing processes) was conducted using a programmable high-low temperature test chamber.

Table 1

DSC analysis data and encapsulation parameters of paraffin, St-DVB and microcapsule samples synthesized at different weight ratios of silane precursors[a].

Samples	Silane precursors		Crystallization process			Melting process			ΔT_s[b] (°C)	Core%[c] (%)	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)
	TEOS (g)	MPS (g)	$T_{m,1}$ (°C)	$T_{m,2}$ (°C)	ΔH_m (J/g)	$T_{c,1}$ (°C)	$T_{c,2}$ (°C)	ΔH_c (J/g)			
Paraffin	–	–	45.61	62.60	166.02	39.9	55.93	143.23	6.67	–	–
St-DVB	–	–	–	–	–	–	–	–	–	–	–
St-DVB-paraffin	0	0	45.20	61.32	91.52	40.10	55.03	92.98	6.29	64.92	0.3845
S1	50	0	45.72	61.13	107.64	39.96	54.85	95.67	6.28	66.79	0.3872
S2	40	10	45.30	60.01	77.28	40.35	54.50	78.27	5.51	54.65	0.4024
S3	30	20	45.63	60.91	58.70	44.36	48.51	52.40	16.55	36.58	0.4421
S4	25	25	46.08	60.87	49.46	44.39	49.06	45.60	16.48	31.84	0.4371
S5	0	50	46.18	61.32	53.35	42.43	55.03	38.90	6.29	27.16	0.3989

[a] S1–S5: paraffin wax,30.0 g; St, 26.6 g; DVB, 3.4 g; AIBN, 0.7 g.

[b] $\Delta T_s = T_{c,2}\text{-}T_m$.

[c] Core% calculated using ΔH_c.