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Silica-coated poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing organic phase change materials

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ABSTRACT

Macroporous sorbents differing in size were prepared by the 2,2′-azobis(isobutyronitrile) (AIBN)-initiated suspension radical polymerization of glycidyl methacrylate and ethylene dimethacrylate in the presence of an inert porogen. The microspheres were loaded with paraffin and cetyl alcohol phase change materials (PCMs) and coated with silica by sol-gel method using trimethoxy(methyl)silane hydrolysate. The energy storing capacity of the PCM-containing composite particles was monitored by differential scanning calorimetry. Accelerated thermal cycling tests were carried out to determine the thermal reliability of the microencapsulated PCMs. Paraffin and cetyl alcohol content in the microcapsules was 42.9 wt.% and 48.9 wt.%, respectively. The microcomposites with higher PCM content showed correspondingly higher latent heat storage capacity (melting and solidification enthalpies were 96.1 J/g and 94.5 J/g, respectively). However, there was low enthalpy change observed after 1000 thermal cycles of cetyl alcohol-containing capsules, which indicated that PCM leakage from the microspheres was minimal.

1. Introduction

Thermal energy storage has received increasing attention during the past decades due to the importance of energy saving. Latent heat storage is one of the most efficient ways of thermal energy storing. The main benefits of latent heat storage compared with that of sensible heat are the much higher storage density accompanying with a smaller temperature difference between storing and releasing heat. Phase change materials (PCMs) are used for latent heat storage. Most promising applications of PCMs are waste heat recovery, solar heating, building energy conservation and air-conditioning systems. Most of the organic PCMs are non-corrosive and chemically inert (stable), recyclable and compatible with numerous building materials. They have desirable cohesion, a high latent heat per unit weight, low vapour pressure, no supercooling, and offer congruent melting and self-nucleation. They have disadvantages such as low thermal conductivities, flammability and high changes in volume during phase change. In order to overcome these problems, their microencapsulation can be an efficient tool. Microencapsulation is the entrapment of PCMs in natural or synthetic polymer capsules. The advantages of the microencapsulated PCMs are their protection against the environmental effects, the enhancement of specific heat-transfer area, and the elimination of the volume change of the PCM during phase change by providing void space [1].

Most frequently applied microencapsulation techniques of organic PCMs are simple coacervation, in situ polymerization of, e.g., methacrylates [1,2], other acrylic polymers [3] or melamine–formaldehyde [4]. Emulsion methods/phase separation [5,6] and interfacial coacervation and crosslinking [7] can be also efficient to prepare PCM-containing capsules of core-shell structure.

Organic/inorganic composite form-stable phase change materials combine the advantages of the inorganic and the organic components [8,9]. The inorganic supporting material provides structural strength and prevents the leakage of the organic PCM component. Several preparation methods of the organic/inorganic composite form-stable phase change materials were described. The most important ones are absorption [8,10], solution intercalation

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Nomenclature

AIBN	2,2′-Azobis(isobutyronitrile)
D_v	Volume mean diameter
DSC	Differential scanning calorimetry
EDMA	Ethylene dimethacrylate
GMA	Glycidyl methacrylate
M_w	Molecular weight
PCM	Phase change material
P(GMA-EDMA)	Poly(glycidyl methacrylate-ethylene dimethacrylate) beads
P(GMA-EDMA)-CA-Me-SiO_2	Silica covered poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing cetyl alcohol
P(GMA-EDMA)-P-Me-SiO_2	Silica covered poly(glycidyl methacrylate-ethylene dimethacrylate) beads containing paraffin
PVA	Poly(vinyl alcohol)
PVP	Poly(*N*-vinyl-2-pyrrolidone)
S_{BET}	Specific surface area
TMMS	Trimethoxy(methyl)silane
V_p	Pore volume

[11] and sol–gel method [12,13]. Among them, the main benefit of the sol–gel method is the simplicity and low cost.

In the present work, the form-stabilization of PCM was achieved by imbedding cetyl alcohol or paraffin in porous poly(glycidyl methacrylate-ethylene dimethacrylate) P(GMA-EDMA) beads, and the leakage of PCM was prevented by a silica shell prepared by sol-gel method. The carrier beads synthesized from this copolymer by suspension radical polymerization have not been used as support for PCMs so far. However, Chen et al. [14] covalently bound poly(glycidyl methacrylate) (PGMA) to poly(ethylene glycol) PCM through the ring-opening crosslinking reaction of oxirane groups in PGMA and end-carboxyl groups of poly(ethylene glycol).

The main benefits of our prepared form-stable composite is that the porous organic beads provide shape-stable environment for the PCMs, and due to the capillary forces they are able to keep the latent heat storing material even in the liquid phase, while the inorganic silica shell inhibits the leakage that would definitely occur during long term application.

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA; Aldrich; St. Louis, MO, USA) and ethylene dimethacrylate (EDMA; Ugilor S.A., France) were distilled before use under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN; recrystallized from ethanol), [(2-hydroxypropyl)methyl]cellulose (Methocel 90 HG), (2-hydroxyethyl)cellulose, poly(*N*-vinyl-2-pyrrolidone) K 90 (PVP; $M_w = 360{,}00$) and cetyl alcohol (CA) were obtained from Fluka (Buchs, Switzerland), poly(vinyl alcohol) (PVA; Polyviol W 25/140; $M_w = 80{,}000$) was from Wacker (Germany). Trimethoxy(methyl)silane (TMMS) and Tween 20 were from Sigma-Aldrich and paraffin (P), melting-solidification range 53–55 °C, from Paramo (Pardubice, Czech Republic). Other chemicals and solvents were purchased from Lachner (Neratovice, Czech Republic).

2.2. Synthesis of macroporous beads

Macroporous sorbents were prepared in a 10-l reactor equipped with anchor-type stirrer by the AIBN-initiated suspension radical polymerization of GMA and EDMA using an inert porogen [15]. Aqueous 0.2 wt.% PVP, 0.2 wt.% hydroxyethyl cellulose and 0.006 wt.% PVA solution (6 l) formed the continuous phase, while the dispersed phase consisted of GMA (480 g), EDMA (320 g), AIBN (4 g) and porogen. The porogen was composed of the mixture of toluene (885 g) and 1,2-dichloroethane (315 g) or that of cyclohexanol (1180 g) and dodecan-1-ol (20 g). While the polymerization employing the first mixture was used for production of large beads ($\sim$700 μm), the reaction using the second porogens yielded small beads ($\sim$150 μm) due to different stirring. The reaction mixture was stirred at 90 rpm (large beads) or 150 rpm (small beads) and heated to 75 °C for 6 h. The resulting beads were washed with water, toluene and methanol to remove porogens, unreacted compounds, and other soluble admixtures.

2.3. Loading of phase change materials in the beads and formation of silica shell

It is advantage that macroporous P(GMA-EDMA) beads are hydrophobic, which enables their wetting with PCM; as a result, the pores are well-filled with cetyl alcohol or paraffin avoiding thus need of vacuum degassing. Briefly, macroporous beads (2 g) were dispersed in molten cetyl alcohol (5 g) or paraffin (5 g) which were loaded at 65–100 °C. The PCM-loaded particles were separated by centrifugation using a stainless sieve to remove free cetyl alcohol or paraffin and again dispersed in aqueous 0.1 wt.% Methocel 90 HG solution (20 ml) at 70 °C in 50 ml reaction vessel under stirring with an anchor-type stirrer (500 rpm).

The silica shell was formed around the beads to keep PCM inside and to prevent particle aggregation at elevated temperatures. TMMS (1.36 g; 10 mmol) was thus hydrolyzed in 0.01 M HCl (0.54 g; 30 mmol) at room temperature to yield $SiMe(OR)_3$ hydrolysate. The volume of the mixture was adjusted to 5 ml by adding distilled water. The TMMS hydrolysate (1 ml) was added to the poly(glycidyl methacrylate-ethylene dimethacrylate)-phase change beads (P(GMA-EDMA)-PCM), the suspension was stirred at 70 °C for 3.5 h and the product eight times washed in 0.01 wt.% Tween 20 (100 ml each). Finally, the poly(glycidyl methacrylate-ethylene dimethacrylate)-phase change material-methyl silica particles (P(GMA-EDMA)-PCM-Me-SiO_2) were dried in air. The preparation of beads and the loading of PCMs as well as the formation of silica shell are drawn in Fig. 1.

2.4. Characterization methods

Carl Zeiss optical microscope (Germany) was used for the imaging of the particles. The size distribution of the beads was measured by Mastersizer 2000 (Malvern Instruments, Malvern, UK) applying laser diffraction method.

The specific surface area (S_{BET}) of the microspheres was determined by nitrogen adsorption (77 K) using a Gemini VII 2390 Analyzer (Micromeritics; Norcross, GA, USA). Pore volume was determined from cyclohexane or 1-chlorododecane regain using centrifugation method [16]. The PCM content of the beads was calculated after weighing 100 mg of the beads, and extracting the PCM 3 times from the microcapsules by each 5 ml *n*-hexane.

The thermal properties of the microcapsules compared to the neat PCMs were determined by a Setaram μDSC3evo differential scanning microcalorimeter. The samples (10.2 mg cetyl alcohol, 12.8 mg paraffin, 17.6 mg of each of the microencapsulated PCM) were weighed into 100 μl aluminium crucibles, and ethylene glycol as a heat transferring medium was added, which covered the