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Fabrication and performances of microencapsulated paraffin composites with polymethylmethacrylate shell based on ultraviolet irradiation-initiated

Yi Wang [a,b,*], Huan Shi [b], Tian Dong Xia [a], Ting Zhang [b], Hui Xia Feng [b]

[a] State Key Laboratory of Gansu Advanced Non-ferrous Metal Materials, Lanzhou University of Technology, Lanzhou 730050, PR China
[b] College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, PR China

HIGHLIGHTS

- Microencapsulated paraffin with PMMA shell was synthesized via self-assembly.
- Microcapsules with excellent properties can be prepared by UV initiated method.
- The microencapsulation ratio is as high as 66 wt.%.
- Thermal properties are as high as comparable with microcapsules in the literature.

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ABSTRACT

In order to identify the validity of fabricating microencapsulated phase change material by ultraviolet irradiation-initiated method, the paraffin wax/polymethyl methacrylate microcapsules were prepared. The structural characteristics and thermal properties of the microcapsules were also determined by various techniques. The results of differential scanning calorimetry analyses indicate that the melting and freezing temperatures and latent heats of the microcapsules are 55.8 °C, 50.1 °C and 106.9 J g^{-1}, 112.3 J g^{-1}, respectively. Morphology and chemical characteristic analysis indicate that the spherical microcapsules were formed with average diameter of 0.21 μm and maximum microencapsulation ratio of 66 wt.% without leakage of core materials. The results of accelerated thermal cyclic test show that the microcapsules have good thermal reliability and chemical stability although they were subjected 3000 melting/freezing cycles. Based on all these results, it can be concluded that the microencapsulated paraffin composites have good potential for thermal energy storage purposes and ultraviolet irradiation-initiated method is a prominent candidate for preparing microencapsulated PCMs.

1. Introduction

The rapid development of global economy leads to energy demand increase quickly. However, conventional fossil energy sources are limited and their uses are restricted due to the emission of harmful gases which are responsible for climate changes and environmental pollution. Nowadays, thermal energy storage (TES) systems are essential for reducing dependency on fossil fuels and then contributing to a more efficient environmental friendly energy use. Scientists all over the world are in searching of new technologies to develop solar energy storage devices which are as important as developing new sources of energy. Among all ways of energy storage, latent heat thermal energy storage (LHTES) method, in which energy is stored in the form of latent heat in phase change materials (PCMs), is one of the most attractive techniques of storing thermal energy [1,2]. Unlike the sensible heat storage method, this method provides much higher heat storage density and smaller temperature variation between energy storage and release [2–4]. Thus, it plays an important role for LHTES application in many fields, such as spacecraft thermal control and building materials [5], textiles [6], heat transfer [7,8] and etc.

So far, a large number of inorganic and organic compounds have been intensively investigated, such as salt hydrates, paraffins, fatty acids, fatty acid esters and their binary and ternary mixtures. Among the investigated PCMs, paraffins are outstanding for their high energy storage density, excellent stability, and proper thermal characteristics such as little or no supercooling, low vapor pressure and self-nucleating behavior. Unfortunately, paraffin cannot be

* Corresponding author. State Key Laboratory of Gansu Advanced Non-ferrous Metal Materials, Lanzhou University of Technology, Lanzhou 730050, PR China. Tel.: +86 13919809076; fax: +86 931 2973648.
E-mail addresses: wangyi@lut.cn, haoyunwangyi1977@163.com (Y. Wang).

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used directly as phase change material due to its main drawback of liquid migration when phase change occurs, which increases not only the heat resistance but the cost of the LHTES system. Preparing microencapsulated paraffin composites is a potential and practically useful method to solve the above problems [9,10].

Microencapsulated phase change materials (MEPCMs) have many unique advantages such as high cost-effectiveness, favorable shape-stability, no corrosion to the container and can be prepared easily with desirable dimensions. The most significant characteristic is it can be used directly without extra encapsulation because of the PCM has been encapsulated in the resilient and three-dimensional polymer net structure [11]. In addition, thermal conductivity of MEPCMs can increase remarkably by loading carbon fibers, carbon fiber brushes, graphite and etc because of their high thermal conductivity [12,13]. What's more, the micron-scale MEPCMs also can be used as functional slurries to augment heat transfer, improve energy storage ability and offer using flexibility relative to conventional solid–liquid slurry [14]. Many literatures have concentrated on MEPCMs especially polymer-matrix stabilized microcapsules. A literature survey indicates that polystyrene (PS) [15], melamine-formaldehyde (MF) [16], urea-formaldehyde (UF) [17], polyurethane (PU) [18], high density polyethylene (HDPE) [19], styrene–butadiene–styrene (SBS) [20], polymethyl methacrylate (PMMA) [11,21–23], Styrene–ethylene/butylene–styrene (SEBS) [24] and silicon dioxide [25] are usually selected as microcapsule shell materials for the PCMs protection. Among them, PMMA is a thermoplastic, transparent and commercially available acrylic polymer. It has moderate properties, easy handling and processing, high impact strength, relatively good chemical resistance and low cost. From this point of view, PMMA is a versatile material and promising polymer used as shell material for LHTES application.

Several physical and chemical methods have been developed for the production of microcapsules. The common method described in the literature for microencapsulation is interfacial polymerization, emulsion polymerization, suspension polymerization, coacervation and spray drying [5,6,26]. However, using techniques mentioned above to polymerize MMA under thermal initiator is limited to high cost, relatively consuming time and using peroxides.

Ultraviolet (UV) irradiation-initiated polymerization can be easily varied by controlling the light intensity and the exposure time of irradiation. Another advantage of UV initiated polymerization is that the radical flux is independent of temperature, whereas, a certain temperature is necessary for significant decomposition of the initiator in chemical initiation [27,28]. In this regard, the objective of this study is to prepare microencapsulated PCMs which fabricated with PMMA as shell material and paraffin wax as core material by UV photoinitiated dispersion polymerization. Fourier transformation infrared spectroscope (FT-IR), scanning electronic microscope (SEM), differential scanning calorimetry (DSC) were used to determine chemical characteristics, microstructure and thermal performance, respectively. In addition, accelerated thermal cycling test was conducted and FT-IR and DSC were employed to determine chemical and thermal reliability.

2. Experimental

2.1. Materials

Paraffin wax (commercial grade) with a peak temperature (T_p) of 56.3 °C for melting and 50.2 °C for solidification was purchased form Beijing Chemical Co. Ltd. and used as phase change material (core material) without purifying. Methyl methacrylate (MMA, AR) purchased from Tianjin Kermel Chemical Reagent Co. Ltd. was used as shell-forming monomers. MMA was washed several times to remove the polymerization inhibitor and double distilled before use. Polyethylene glycol octyl phenylether (TX-100) and poly(vinyl alcohol) (PVA) were obtained from Shanghai Chemical Reagent Co. Ltd. and used as surfactant and dispersing agent, respectively. Ethylene glycol dimethacrylate (EGDMA) was bought from Shanghai Chuanghe Chemical Reagent Company and used as cross-linking agent. Oil-soluble initiator, 2-hydroxyl-2-methyl-1-phenyl acetone (1173) and deionized water was self-made by our laboratory.

2.2. Preparation of paraffin/PMMA microcapsules

In preparation of the paraffin/PMMA microencapsulated PCMs, dispersion polymerization through UV photoinitiated method was conducted. 4 mL methyl methacrylate monomer, 10.0 g paraffin wax, 0.02 g EGDMA and 0.01 g UV-initiator were assembled as oil phase and 0.02 g PVA, 0.04 g TX-100 dissolved into 100 mL deionized water were defined as aqueous phase. A typical synthesis technology was described as follows: a round bottom flask with aqueous phase was heated above melting point of paraffin wax under nitrogen atmosphere, and then the oil phase was added under the mechanical stirring at the speed of 1000 rpm at the same temperature of 60 °C. The mixture was consequently mixed violently until the O/W emulsion was formed, about 30 min. The mixture was irradiated by UV light of 250 W under room temperature for 30 min and the precipitate was separated form solution by casting water. The particles were washed with warm distilled water (approx. 60 °C) and dried under vacuum at 80°C for 24 h. The washed and dried process was also recognized as leakage test and the composites which did not leak melted PCMs from the microcapsules were defined as form-stable PCMs.

2.3. Characterization of paraffin/PMMA microcapsules

Phase change properties of the paraffin wax and form-stable composites were determined by differential scanning calorimeter (DSC, METZSCH DSC200F3) at the rate of 5 °C per minute for heating and 3 °C per minute for cooling in nitrogen atmosphere. The specimens for DSC analysis with the mass of 5–10 mg were taken from the brittle failure surface of the form-stable PCMs. The extrapolated onset temperature (T_S), peak temperature (T_P) and extrapolated end temperature (T_E) of paraffin wax and microcapsules were obtained by the special software of the DSC. Phase change latent heats were determined by numerical integration of the area under the peaks. In order to prove the compatibility of the components in composites, the microcapsules were characterized by spectroscopy methods. The spectroscopic analysis was performed on a KBr disk in the range of 4000 ~ 400 cm^{-1} by using a Nicolet AVTAR 360 FT-IR. The microcapsules particle size distribution (PSD) from light diffraction was performed using an LA-920 laser particle size analyzer. The detailed process is that 0.5 g microcapsules are dispersed in 5 mL acetone with violent agitation for 2 min and then the mixture was poured into 600 mL water for detecting. The scanning electron microscope (SEM) images of form-stable composites were taken by JSM-6701 model SEM. The specimens were broken and the fractured surfaces were coated with gold before SEM imaging.

2.4. Thermal reliability determination of paraffin/PMMA microcapsules

Accelerated thermal cycling test was conducted to determine heat storage/release performance and thermal reliability using the experimental set-up in Fig. 1. In this experimental set-up, water was circulated throughout the surrounding of test cell to keep the