



Fabrication and characterization of microcapsulated phase change materials with an additional function of thermochromic performance



Hao Wang^{a,b}, Jie Luo^a, Yanyang Yang^{a,b}, Liang Zhao^{a,b}, Guolin Song^{a,*}, Guoyi Tang^{a,b,*}

^a Institute of Advanced Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

^b Key Laboratory of Advanced Materials, School of Materials Science and Engineering, Tsinghua University, Haidian District, Beijing 100084, China

ARTICLE INFO

Article history:

Received 5 August 2016

Received in revised form 3 October 2016

Accepted 9 October 2016

Available online 27 October 2016

Keywords:

Phase change materials

Microcapsules

Dual functionalized features

Energy storage

ABSTRACT

In this study, a new type of microencapsulated phase change materials (microPCMs) with an additional function of thermochromic performance was designed and synthesized successfully. Thermochromic pigments were firstly assembled on the interface of *n*-octadecane droplets in oil/water emulsion. And then a thermochromic pigment/PMMA shell was fabricated through suspension-like polymerization. The microstructures and chemical compositions of the resultant microcapsules were investigated by scanning electronic microscope (SEM) and Fourier transformation infrared spectroscopy (FT-IR). SEM images display that these microcapsules presented a spherical shape and well-defined core-shell structure. According to DSC and TGA examinations, these dual functionalized microPCMs exhibited excellent thermal energy storage-release performance, high thermal storage capability (higher than 97%), and good thermal stability. In addition, these microPCMs successfully achieved thermochromic function as their temperature exceeded the target temperature. The dual functionalized microcapsules developed in this work showed great potential in applications for solar energy storage, thermo-sensors, food and medicine package and intelligent textiles or fabrics, etc.

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1. Introduction

Thermal energy storage with phase change materials (PCMs) is one of the most efficient methods for latent heat storage since they can store and release great amounts of energy when undergoing phase change (Jamekhorshid et al., 2014; Zhou et al., 2012). Nowadays, PCMs have attracted a great deal of attention in different applications such as heat storage fibers (Sarier and Onder, 2012), regulation of building temperature (Bastani et al., 2014; Ye et al., 2014), solar heating systems and heat recovery (Noro et al., 2014; Yuan et al., 2015). However, they share several disadvantageous features while employing PCMs in traditional manner like easily evaporating at high temperatures, inflammability and low thermal conductivity for organic PCMs, phase separation, super-cooling and ease of corrosion for inorganic PCMs (Zhao and Zhang, 2011). The pristine PCMs call for a holder to keep their shape of solid or liquid phase and make them isolated from the surrounding as phase change occurs (Khadiran et al., 2015; Zhang et al., 2016).

Microencapsulation of PCMs is regarded as a considerably feasible solution, which can prevent leakage of the melted PCMs during the phase change process, reduce PCMs reactivity with the outside environment, enlarge heat transfer area and increase the heat transfer rate (Hyun et al., 2014). In addition, it can also enhance the thermal and mechanical stability of the PCMs. Microencapsulated phase change materials (microPCMs) are PCMs as core materials which are encapsulated in polymer, inorganic or hybrid shells. Since organic materials can offer good sealing tightness and structural flexibility, microPCMs with polymer shells are widely studied and applied. As reviewed from the literature, there are a multitude of techniques for the microencapsulation of PCMs with different polymer shells, such as interfacial polycondensation (Su et al., 2007), suspension polycondensation (Yang et al., 2015), in situ polycondensation (Aydin, 2013) and complex coacervation (Deveci and Basal, 2009). Meanwhile, the polymeric shell materials for microPCMs can be formulated by a wide variety of materials including melamine-formaldehyde resin (Zhang and Wang, 2009), polyurea-formaldehyde resin (Sarier and Onder, 2007), polystyrene (Sánchez et al., 2007), PMMA (poly(methylmethacrylate)) (Ma et al., 2012) and even biodegradable polymers like gelatin (Özonur et al., 2006). Nowadays, most publications were mainly focused on how to improve the heat conductivity, flame resistance and mechanical strength of the microPCMs, but these microPCMs

* Corresponding authors at: Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China.

E-mail addresses: song.guolin@sz.tsinghua.edu.cn (G. Song), tanggy@tsinghua.edu.cn (G. Tang).

almost exhibit a single function for the latent-heat storage. Less attention has been given to functionalize the microPCMs with novel features to expand their applications scopes, especially for the microPCMs with organic shell. Recently, some researchers have successfully fabricated the microPCMs with inorganic shell, and the resultant microcapsules present intriguing features such as fluorescent, magnetic, and bactericidal due to the functional diversity of the inorganic materials (Chai et al., 2015; Wang et al., 2016). Zhang et al. (2015) reported the preparation of zirconium oxide/*n*-eicosane microPCMs with fluorescent characteristics. Jiang et al. (2014) synthesized magnetic microcapsules with a Fe₃O₄/SiO₂ hybrid shell for dual-functional phase change materials. Nevertheless, microPCMs with inorganic shells commonly present poorer endurance during the practical applications compared to those with organic wall, because inorganic material are hardly to withstand the thermal stress resulting from volume change during repetitive phase change process due to the lack of flexibility (Yin et al., 2014). The integration of another functional component into polymer shell may be a feasible way to solve the problem mentioned above because of the sealing tightness and structural flexibility of organic materials. Therefore, in this work, the functionalization of the microPCMs is designed to realize by the in-situ incorporation of functional component with polymer shell during the synthesis process.

Thermochromic pigment is a intriguing organic compound, which can respond thermally to the surrounding environment, and in particular, its color could change reversibly from dark to light as temperature alters and vice versa (Karlessi et al., 2009). Such a compound has been widely applied in the field of stealth technology, anti-counterfeiting and intelligent textiles or fabrics, etc (Granqvist et al., 2009). In the present work, thermochromic pigments were developed to incorporate with the microPCMs to achieve the thermochromic function besides the latent heat storage. These dual functionalized microcapsules can be a great potential candidate for early warning and protection in various emerging applications of solar cells, thermo-sensors, architectural coatings, food and medicine package and some exothermic reactions, in addition to traditional thermal energy storage.

Our previous studies have reported the successful fabrication of the microPCMs with PMMA shell in the oil-in-water (O/W) emulsion by the suspension-like polymerization method, and the resultant microcapsules displays high thermal storage capability, high thermal reliability and good thermal stability (Qiu et al., 2012). In the work described here, PMMA is selected as the shell material to encapsulate PCMs via the similar synthesis process. As is well known, particles at the micro- or nano- scales are prone to aggregate in the liquid phase and it is considerably significant to perform the surface modification of thermochromic pigments in order to promote them even distribution on the PMMA shell. Therefore, organoalkoxysilane is firstly grafted on thermochromatic pigments to adjust the surface affinity to improve their orientation at the interface of oil and water phases. Meanwhile, the kind of organoalkoxysilane used in this work has the —C=C group, which tends to participate in the polymerization reaction of MMA monomer, resulting in the adherence of thermochromatic pigments with the PMMA shell. The objective of the work is dedicated to fabricate the functional microPCMs with an additional function of thermochromatic and to investigate the chemical compositions, surface morphology, phase change property, color-change behavior and thermal stability of the microcapsules in details. This novel microcapsule structure with thermochromic pigments embedded onto PMMA shells prepared successfully in this work presented both of thermochromic and latent-heat storage features. Furthermore, this study could also provide a feasible way to fabricate functional microPCMs with the polymer shell through the introduction of characteristic inorganic component such as ZrO₂, TiO₂, Fe₃O₄, etc.

2. Materials and methods

2.1. Materials

Chemical grade *n*-octadecane was supplied by Tianjin Chemical Reagents Co., Ltd. (Tianjin, China). Thermochromic pigments were purchased from Qianbian Pigment Co., Ltd. (Shenzhen, China). γ -methacryloxypropyltrimethoxysilane (MPTMS, 98 wt.%) was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetic acid (HAC, 99 wt.%) and Methylmethacrylate (MMA, 99 wt.%) were obtained from Tianjin Damao Chemistry Reagent Co., Ltd. (Tianjin, China). Sodium salt of styrene-maleic anhydride copolymer (TA) was bought from Shanghai Leather Chemical Works. (Shanghai, China). Pentaerythritol tetraacrylate (PETRA, 80 wt.%) was offered by Nanjing Shoulashou Co., Ltd. (Nanjing, China). Azobisisobutyronitrile (AIBN, 98 wt.%) was supplied by Shanghai Jingchun Chemical Co., Ltd. (Shanghai, China). Other reagents are analytical grade and used as received.

2.2. Modification of thermochromic pigments

Thermochromic pigments were modified by MPTMS. The specific experimental process is as follows: at first, ethanol aqueous solution was prepared to ethanol concentration of 90 wt.%. The pH value of the ethanol solution was adjusted to 5 via dropping acetic acid into ethanol solution at room temperature. Then, 3 wt.% MPTMS was dissolved to ethanol solution with mechanically stirring for 4 h at 50 °C in water bath. Afterwards thermochromic pigments were added into the mixture, dispersed using ultrasound for 15 min in ultrasonic bath, and reacted at 50 °C for 1 h. The modified thermochromic pigments were washed with water and ethanol respectively. And then they were dried at 50 °C for 4 h.

2.3. Preparation of thermochromic microPCMs

The thermochromic microPCMs (TC-microPCMs) were fabricated through following procedures: (i) 7 g TA was dissolved in 100 g deionized water, and aqueous phase was obtained; (ii) a dose of modified thermochromic pigments were ultrasonically dispersed in the solution of 8 g *n*-octadecane and 7 g MMA for 15 min to obtain a homogenous oil phase at 40 °C; (iii) the oil phase was emulsified to the aqueous phase with a mechanically stirring speed of 1000 rpm for 15 min at 40 °C to form a stable oil-in-water emulsion; (iv) 0.3 g AIBN and 3 g PETRA were added into the emulsion, then heated the emulsion to 60 °C to start suspension-like polymerization under a stirring speed of 400 rpm for 6 h; (v) the resultant TC-microPCMs were centrifugated and washed with de-ionized water at 40 °C for three times, and finally dried in an oven at 45 °C for 8 h.

For comparison, microPCMs without thermochromic pigments were prepared. The recipes employed for the fabrication of microPCMs are presented in Table 1.

2.4. Characterization

The morphology of emulsion was characterized using HIROX digital microscope KH-7700. The particle sizes were estimated by laser scattering particle size distribution analyzer (LA950V2, HORIBA). Fourier transform infrared spectroscopy (FT-IR) was performed to characterize the chemical structure of the samples using a spectrophotometer (Vertex 70, Bruker, Germany) in the range 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. The surface morphologies of the samples were observed using a field emission scanning electron microscope (FESEM, S4800, HITACHI). The thermal properties

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