Applied Energy 138 (2015) 661–674

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Development of bifunctional microencapsulated phase change materials with crystalline titanium dioxide shell for latent-heat storage and photocatalytic effectiveness

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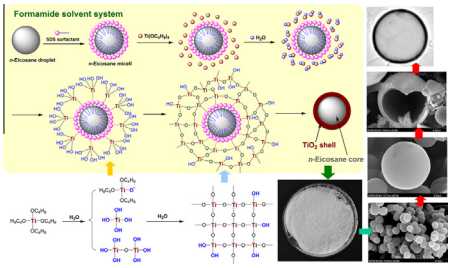
HIGHLIGHTS

- We designed and synthesized a sort of bifunctional PCMs-based microcapsules.
- These microcapsules have an *n*-eicosane core and a crystalline TiO_2 shell.
- Such a crystalline TiO_2 shell exhibited a good photocatalytic activity.
- The microcapsules showed good performance in energy storage and sterilization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 May 2014
Received in revised form 26 October 2014
Accepted 1 November 2014
Available online 20 November 2014

Keywords:
Microencapsulated *n*-eicosane
Crystalline TiO_2 shell
Microstructure
Phase-change characteristics
Photocatalytic activity

ABSTRACT

A sort of novel bifunctional microencapsulated phase change material (PCM) was designed by encapsulating *n*-eicosane into a crystalline titanium dioxide (TiO_2) shell and, then, was successfully synthesized through *in-situ* polycondensation in the sol–gel process using tetrabutyl titanate as a titania precursor. The resultant microcapsule samples were characterized by *Fourier*-transform infrared spectroscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy to determine their chemical compositions and structures. Furthermore, the crystallinity of the TiO_2 shell was verified by powder X-ray diffraction patterns. It was confirmed that the fluorinions could induce the phase transition from the amorphous TiO_2 to the brookite-form crystals during the sol–gel process, thus resulting in a crystalline TiO_2 shell for the microencapsulated *n*-eicosane. The scanning and transmission electron microscopy investigations indicated that all of the resultant microcapsules presented a perfect spherical shape with a uniform particle size of 1.5–2 μm, and they also exhibited a well-defined core–shell structure as well as a smooth and compact shell. The crystalline TiO_2 shell made the resultant microcapsules a photocatalytic activity, and therefore, these microcapsules demonstrated a good photocatalytic effect for the chemical degradation and an antimicrobial function for some of the *Gram*-negative bacteria. Most of all, all of the microencapsulated *n*-eicosane samples indicated good phase-change performance and high thermal reliability for latent-heat storage and release, and moreover, they achieved a high encapsulation efficiency and a high thermal-storage capability. The bifunctional microencapsulated *n*-eicosane synthesized in this study will be a potential candidate for the applications of waste heat recovery and treatment, intelligent textiles or fabrics for the warmth underwear and medical protective clothing, preservation and sterilization of foods, and solar energy storage and recovery, etc.

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http://dx.doi.org/10.1016/j.apenergy.2014.11.006
0306-2619/

1. Introduction

Phase change materials (PCMs) are a type of renewed energy materials through melting and solidification at an almost constant temperature. They are able to store and release tremendous amount of latent heat energy when undergoing phase changes. Owing to the prompt growth of the consumption of fossil energy sources, the shortage of fossil fuels and the increase in greenhouse gas emission have caused serious environmental problems, and now, the frequent occurrence of haze in many Chinese large cities is a typical case due to such environmental disasters. Therefore, the development of new energy storage materials has been attracting great attention in both academic and industrial communities. PCMs are considered as a good candidate with highly efficient utilization of energy to reduce the dependence of traditional fossil energy sources [1,2]. In recent years, PCMs have opened a prospective application in the recovery and utilization of solar and industrial waste energy and have been widely used for thermal conservation and insulation in buildings, thermal comfort and thermal regulation for intelligent fibers and textiles, commercial refrigeration, transportation packaging for temperature-sensitive products, cooling of electronic chips and devices, etc. [3]. The organic paraffin waxes, fatty alcohols, fatty acids, neopentyl glycol, and eutectic mixtures, and some inorganic substances like salt hydrates are the most usually used PCMs, which have high phase-change enthalpies in the range of 150–240 J/g [4]. However, the application of PCMs in traditional manners has several disadvantages like the necessity of using special latent heat devices or heat exchange surface, which may increase the associated cost and thermal resistant between the PCMs and the environment. Moreover, the flowing PCMs are difficult to be handled when the phase change occurs from solid to liquid. The salt hydrates are floating when combined with other materials such as building materials and textile materials and may sweat out at the surface or wash out in the moist climate. Their crystal water content may change due to the variety of humidity [5]. The paraffin waxes in the molten state easily diffuse throughout the other materials, and they may also evaporate into the ambient air and, accordingly, increase the volatile organic content of the air [6]. Therefore, the application of PCMs without encapsulation is generally not recommended [5]. In order to solve the problems rising in the application of bulk PCMs, a packaging technology is demanded to make PCMs a form-stable feature either in liquid or in solid states and be isolated from the surrounding materials [7].

Encapsulation of PCMs into inert materials is the most potential and actually useful method for the preparation of the form-stable PCMs. This method can engulf small solid or liquid particles with a solid wall and thus will prevent the leakage of PCMs from their location, reduce the interference toward phase-change behaviors from the outside environment, increase the heat-transfer area, and make liquid PCMs easy to be handled when the phase change occurs [8]. The traditional microencapsulated PCMs were fabricated by using polymeric wall materials such as melamine–formaldehyde resin [9], urea–formaldehyde resin [10], polyurethane [11], polystyrene, styrene–butadiene-styrene copolymer [12], or polymethyl methacrylate (PMMA) through *in-situ* polymerization or interfacial polymerization in an emulsion system [13,14], and generally, these reported PCM microcapsules exhibited a well-defined core–shell structure. However, there are several defects such as flammability, poor thermal and chemical stabilities, and low thermal conductivity for these microencapsulated PCMs due to the polymeric shells [15,16]. Furthermore, there is a requirement of fast heat transfer for PCMs to give a prompt response during the heat energy storage and thermal regulation processes. Recently, a new trend for the encapsulation technology of PCMs is to employ inorganic materials as shells for the enhancement of thermal conductivity and mechanical strength of microencapsulated PCMs. There is no doubt that, compared to polymeric materials, the inorganic ones generally have a better rigidity and higher mechanical strength, and therefore, the inorganic microcapsule shells not only improve the thermal transfer performance of a PCM system but also increase the durability and working reliability of microencapsulated PCMs [17,18]. There are a few publications concerning the inorganic silica as a wall material for encapsulation of PCMs. Wang et al. [19] first reported the encapsulation method of PCMs into silica through the *in-situ* polycondensation in an oil-in-water emulsion and also discussed the formation mechanism. Chang et al. [20] studied the synthetic technology of microencapsulated *n*-octadecane PCMs with PMMA network-silica hybrid shell via the sol–gel process. Jin et al. [21] developed a one-step synthetic technique for the microencapsulated PCMs with the silica wall under a surfactant- or dispersant-free condition. Li et al. [22] also reported the preparation of the form-stable paraffin/silica phase-change composites through *in-situ* emulsion interfacial polycondensation of tetraethyl orthosilicate and found that these phase-change composites achieved a very high heat-storage capability. We also reported the synthesis of silica-microencapsulated PCMs using sodium silicate as a low-cost silica precursor and found that these microcapsules exhibited a well-defined core–shell structure and a uniform particle size under the moderately acidic condition [23]. The latest literature survey indicated that aluminum hydroxide, calcium carbonate, and titanium dioxide (TiO_2) could also be employed as inorganic wall materials for the encapsulation of PCMs [24–27]. Nevertheless, the aforementioned inorganic encapsulation technologies toward PCMs are unexceptionally developed to serve the solo function of latent heat storage.

Considering the functional diversity of inorganic materials, it will be possible to impart dual-function to PCMs-based microcapsules when a functional inorganic shell is fabricated onto the PCM core. In our previous work, we have successfully developed the bifunctional microcapsules based on a PCM core and an inorganic Fe_3O_4/SiO_2 hybrid shell for thermal energy storage and magnetic effectiveness, respectively. [28] In the current study, we design a new type of novel bifunctional microencapsulated PCMs with a crystalline TiO_2 shell. The resultant microencapsulated PCMs not only have a capability of latent-heat storage but also achieve the specified photocatalytic function derived from the crystalline TiO_2 shell. Fang et al. [27] have reported the synthesis of microencapsulated PCMs with a TiO_2 shell, and however, the formed TiO_2 shell is amorphous and inert without any physicochemical functions as a result of the hydrothermal synthesis of organic titanium source. By now, there have no other references reporting the synthesis of microencapsulated PCMs with the crystalline TiO_2 shell. Evidently, the formation of the crystalline TiO_2 shell is a considerable difficulty when we attempt to synthesize the microencapsulated PCMs via a conventional hydrothermal method. As a great originality of this work, we designed a nonaqueous oil-in-water (O/W) emulsion templating system to fabricate the TiO_2 shell surrounding the PCM core in the sol–gel process. Meanwhile, the fluorinions were incorporated into this templating system to induce the formation of crystalline TiO_2. In this case, the formed microcapsules not only have a perfect core–shell structure but also achieve the crystalline TiO_2 shell with photocatalytic effectiveness. Such a sort of bifunctional microencapsulated PCMs will offer the tremendous potential to fulfill the dual-function of heat-energy storage and photocatalytic effectiveness for the application of warmth underwear and medical protective clothing. The goal of this work is to develop a feasible technology for the encapsulation of PCMs with the crystalline TiO_2 shell, to discover the effect of crystallinity of TiO_2 wall material on the photocatalytic activity, and to