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Reversible thermochromic microencapsulated phase change materials for thermal energy storage application in thermal protective clothing

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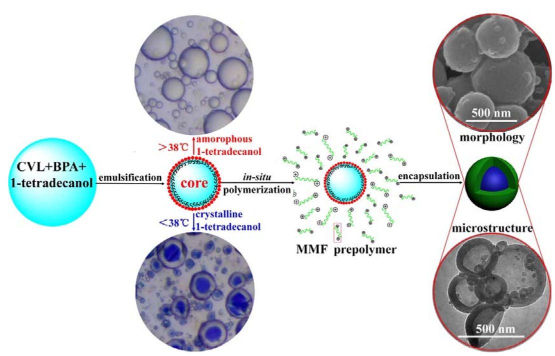
HIGHLIGHTS

- Reversible thermochromic microencapsulated phase change materials (TC-MPCMs) were designed and fabricated successfully.
- The thermochromic function provided a visual evidence of energy storage or release performance in real time.
- TC-MPCMs expressed higher than 99% thermal storage capability and excellent cyclic durability performance.
- TC-MPCMs showed great potential applications in thermal protective clothing and other thermal regulation fields.

GRAPHICAL ABSTRACT

Reversible thermochromic microencapsulated phase change materials for thermal energy storage.



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ABSTRACT

In this study, a series of reversible thermochromic microencapsulated phase change materials (TC-MPCMs), exhibiting excellent latent heat storage-release performance, were designed and fabricated successfully. The characterization and microstructure regulation of TC-MPCMs were conducted systematically as well. The core of TC-MPCMs was comprised of crystal violet lactone employed as thermochromic colorant, bisphenol A employed as developer and 1-tetradecanol employed as co-solvent, respectively. These influencing factors of encapsulation process such as the amount of emulsifier, stirring rate, feeding weight of core/shell ratio, acid resistance and thermal cyclic durability were carried out to clarify the effect of various experimental conditions. The surface morphology, shell thickness and core–shell structure of TC-MPCMs were characterized via optical microscope (OM), thermal field emission scanning electronic microscope (TFE-SEM), transmission electron microscope (TEM), respectively. From different scanning calorimetry (DSC) analysis, the performance of temperature of fusion and crystallization and enthalpy of TC-MPCMs under various conditions were measured as well. The results of thermogravimetric (TG) analysis illustrated the influence on thermal stability of TC-MPCMs. In addition, Lab color space obtained by colorimeter is certainly intuitive to observe the colorimetric characteristics of TC-MPCMs as well. More importantly, the reversible thermochromic property associated with phase state of the 1-tetradecanol could also provide a visual evidence of energy storage or release performance of the TC-MPCMs. Furthermore, The TC-MPCMs exhibited excellent stability even after 100th thermal cycling test without any obvious performance degradation, including the morphology, phase change properties and thermal stability. In the end, the fire fighter protective clothing containing TC-MPCMs was designed and fabricated, which could

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provide adequate thermal protection in the various fire environments. Thus, TC-MPCMs developed in this work showed great potential applications in thermal protective clothing and other thermal regulation fields.

1. Introduction

Thermal energy storage through phase change materials (PCMs) [1–4] can absorb, store and release large amounts of latent thermal energy during the process of physical state change without changing its temperature, which is attracting increasing attention to enhance the energy utilization efficiency and thermal regulation [5–7]. A considerable research related on microencapsulated PCMs (MicroPCMs) [3,8–10] possessing excellent capacity of latent thermal energy storage [3,11] have been intensively investigated during recent decades. MicroPCMs have gained a considerable development in fundamental researches such as solar-thermal conversion systems [12], thermal energy storage [13,14] and so on [15–18]. In addition, great progress in the fields such as encapsulated autonomic healing materials [19,20], drug delivery [21], photochromic materials [22,23] and reversibly thermochromic materials [24] have made as well.

The study related on MicroPCMs with a novel thermochromic function is considered as a promising research topic, which is attracting comprehensive and significant commercial interest [25,26]. The applications of reversible thermochromic microcapsules are being extensively applied such fields as inks [27], coatings of smart materials [28], cements, textiles [29], luminescent thermosensors [30] and color indicators [31]. Recently, luminescent dye or leuco dye based thermochromic (TC) systems [32] was selected as the core materials to fabricate thermochromic microcapsule which was sensitive to temperature [33]. Crystal violet lactone (CVL) consisted of the DMAP and MGL segments, is considered as a kind of common leuco dye used as the color former. Bisphenol A used as the color developer is a kind of weak acid, and 1-tetradecanol is used an organic solvent. Reversible thermochromic systems consists of electron donor (Crystal violet lactone, CVL), electron acceptor (Bisphenol A) and organic solvent (1-tetradecanol). The system shows color when electron donor and electron acceptor react, and acceptance and giving electron reversibly change with temperature. When the temperature is higher than the melting point of 1-tetradecanol, the color developer combined with protons, and the leuco dye favors the colorless, ring-closed state. When the temperature is lower the melting point of 1-tetradecanol, Bisphenol A release protons and gain electron, forming a complex with CVL that favors the colored ring-open, where molecular rearrange and conjugate double bond through, which show the color. Thus, the above three-component organic thermochromic materials [34,35], which could become blue colored under the crystallization temperature of 1-tetradecanol and turn colorless above melting point, were selected as the core materials of reversible thermochromic microcapsules.

There are various encapsulation techniques available to synthesize microcapsules or nanocapsules, e.g. *in-situ* polymerization [36], spray drying [8], sol-gel [37], interfacial poly-condensation, complex coacervation, suspension polymerization and emulsion polymerization. And *in-situ* polymerization is adopted widely because of its simple, cheap, eco-friendly and technically feasible fabrication. Owing to low price, simple fabrication, good seal tightness and endurance, fire resistance, acid and alkaline resistance, the melamine–formaldehyde resin capsule has been successfully commercialized for decades [38,39]. The residual formaldehyde is actually considered as the main drawback that affects its application, however, the residual level of formaldehyde could be reduced to meet the requirements of formaldehyde in clothing and other textiles by heat treatment or addition of ammonium chloride and urea [40,41]. By contrast, there is no residual formaldehyde problem involved in capsules with vinylic shell such as acrylic-based polymer and styrene-based polymer [38,39], however, certain vinylic monomers would inevitably remain in the resultant shell due to the insufficient reaction in free radical polymerization during encapsulation process (reaction temperature of emulsion system is usually lower than 100 °C under 1 atm). In addition, some solid nanoparticles self-polymerized from vinylic monomers dissolved in aqueous phase, always make it difficult to obtain the microcapsule powder product.

In this study, we discussed systematically the encapsulation, characterization and application of TC-MPCMs. The objectives of this work were to investigate the effects of different experimental conditions, i.e. dosage of surfactant, stirring rates and various core/shell ratios, on surface morphology, diameter and diameter distribution of TC-MPCMs. The influence on the melting and crystallization properties, thermal properties, as well as chromogenic properties of TC-MPCMs was discussed via optical microscope, field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), different scanning calorimetry (DSC), thermogravimetric (TG) and Colorimeter. Furthermore, the thermal cyclic durability of TC-MPCMs was carried out via heating and cooling microscope stage, and the fire fighter protective clothing with TC-MPCMs was also fabrication and investigated. The TC-MPCMs developed by this work showed excellent latent thermal energy storage-release performance, reversible thermochromic property and stability would offer tremendous potential applications in thermal energy storage especially thermal protective clothing.

2. Experimental section

2.1. Materials

Three-component thermochromic mixtures cores are generally consist of a leuco dye used as an electron donor, a phenolic color developer used as an electron donor, and a high-melting organic solvent. Crystal violet lactone (6-dimethylamino-3,3-bis[p-(dimethylamino) phenyl] pahtalide, CVL, 96%, Guangzhou Qiao Xuan Chemical Co., LTD) was employed as color former, bisphenol A (2,2-bis(4-hydroxyphenyl) propane, BPA, Aladdin Industrial Corporation) was used as developer and 1-tetradecanol (AR, 99%, TianJin Guangfu Fine Chemical Research Institute) was selected as the co-solvent. The methylated melamine-formaldehyde (MMF) prepolymer solid contents of 73.0% were purchased from Tianjin Aonisite Chemical Trade Co., Ltd, and were used to synthesize the capsule shells. SMA (sodium styrene-maleic anhydride copolymer, 19 wt% aqueous solution, Shanghai Leather Chemical Workers) was employed as emulsifier. Both citric acid and sodium hydroxide were supplied by Tianjin Chemical Regents, Inc. and employed as pH regulators. All chemicals were obtained commercially and used without further purification.

2.2. Fabrication of TC-MPCMs

Emulsion preparation: 0.31 g crystal violet lactone, 0.94 g bisphenol A and 18.75 g 1-tetradecanol were dissolved at 200 °C thermostatic oil bath and kept 1–2 min, then the obtained transparent and uniform oil phase was employed as core materials of capsules. The homogeneous oil solution, different dosages of SMA and 170 mL of distilled water were emulsified mechanically under 50 °C with a stirring rate of 7000 rpm for 15 min. During the process of emulsification, droplets of homogeneous oil solution were wrapped by colloid particles evenly with carboxyl groups because of negative charge, which played an important role to stabilize O/W emulsion and size of capsules. Then the pH value of the emulsion was adjusted 5.5 approximately with 20.0 wt