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Microencapsulated phase change materials with composite titania-polyurea (TiO_2-PUA) shell

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HIGHLIGHTS

- A novel approach to synthesize MEPCMs with composite TiO_2-PUA shell at low temperature.
- The MEPCMs have a well-defined core–shell structure with around 73 wt.% of core fraction.
- The composite shell effectively lowers the evaporation and prevents leakage of the core material.
- The MEPCMs show mitigated supercooling, faster thermal response, and high thermal storage capacity.
- TiO_2-PUA MEPCM-modified cement pastes showed distinct latent heat storage capacity.

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ABSTRACT

This paper presents a novel approach to synthesize microencapsulated phase change materials (MEPCMs) with composite titania-polyurea (TiO_2-PUA) shell at low temperature. MEPCM pre-microcapsules with PUA shell were first synthesized through interfacial polymerization in oil-in-water emulsion, followed by deposition of TiO_2 on the surface of pre-microcapsules in solution by means of the liquid phase deposition (LPD) method at low temperature. The two-step synthesis approach results in high yield of microcapsules and the MEPCMs with composite TiO_2-PUA shell integrate advantages of both organic and inorganic shells. Results show that the MEPCMs have a well-defined core–shell structure with around 73 wt.% of core fraction and dense composite TiO_2-PUA shell, which is thermally stable and durable and effectively lowers the evaporation and prevents leakage of the core material even under repeated heating and cooling. The MEPCMs also show mitigated supercooling, faster thermal response, and high thermal storage capacity. TiO_2-PUA MEPCM-modified cement pastes showed distinct latent heat storage capacity.

1. Introduction

Latent heat storage has shown great potential to enhance thermal comfort [1,2] and energy efficiency [3–7]. The main advantage of latent heat storage is the high storage density in small temperature intervals, which can be fulfilled by using phase change materials (PCMs). Studies have reported that building envelopes integrated with PCMs can potentially save 10–30% of the annual cooling and heating loads for buildings in various climate zones in the US [8,9] and even in tropical Singapore [10]. The most widely used PCMs in heat storage are those changing phase from solid to liquid. Encapsulation of PCMs is therefore necessary in many applications to hold the liquid PCM so it does not leak out into the hosting matrix [11]. Encapsulation also prevents PCM to be in contact and react with the surrounding matrix and thus avoiding changes of its composition with time [12]. Other additional benefits of encapsulation include improved compatibility of PCM with the surrounding matrix [13], reduced impact of volume change during phase transformation [14], and enhanced heat transfer to the surrounding matrix due to increased surface to volume ratio of PCM [15].

Microencapsulation is defined as encapsulation of particles with diameter smaller than 1 mm [16]. Microencapsulated PCMs (MEPCMs) are composed of the core PCM and the shell. MEPCMs with organic shell is the most common approach to encapsulate PCMs [17]. Organic shell MEPCMs have been used to fabricate thermo-regulating garment [18] and Micronal® PCM from BASF has been incorporated in building elements to enhance energy efficiency of buildings [19]. It has been

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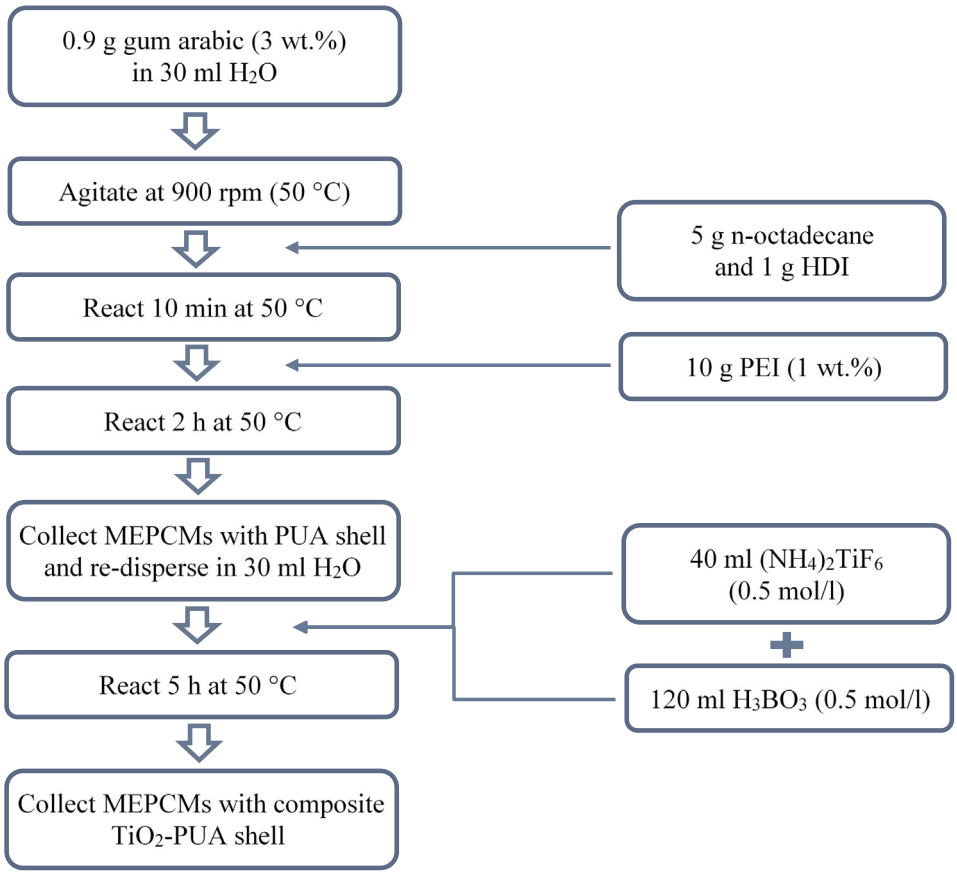

Fig. 1. Flow chart of synthesis of MEPCMs with composite TiO_2-PUA shell.

reported that MEPCM-modified skim coat possess higher heat capacity and effectively reduces envelope heat gain [20]. Despite higher toughness and good anti-leakage performance of the organic shell, utilization of organic shell MEPCMs is sometimes restricted due to their high flammability and low thermal conductivity.

These shortcomings might be overcome by encapsulating PCMs with inorganic shell [21]. Several studies have reported microencapsulation of PCM with silica (SiO_2) shell through interfacial polycondensation or sol gel synthesis [22–24]. In another work, MEPCM with calcium carbonate ($CaCO_3$) shell was fabricated [25]. However, such MEPCM is not suitable for many applications due to poor chemical stability of the $CaCO_3$ shell. Titanium dioxide (TiO_2) with several times higher thermal conductivity [26] and better mechanical properties than SiO_2 [27] can be a potential inorganic shell material for MEPCMs. In addition, it is plausible to impart photocatalysis into MEPCM through the TiO_2 shell and thus the resulting MEPCMs can be multi-functional. To the best of our knowledge, MEPCMs with TiO_2 shell is rarely studied and reported. Fang et al. [28] synthesized MEPCMs with palmitic acid as the core material and TiO_2 as the shell through the sol-gel process. The other work was reported by Chai et al. [29] where *n*-eicosane was encapsulated into a crystalline TiO_2 shell through in-situ polycondensation in the sol-gel process using titanium butoxide (TBT) as the TiO_2 precursor. In these studies, the inorganic shell was directly deposited onto the surface of organic PCM micro-droplets which stabilized by surfactant [22–29]. However, emulsions are thermodynamically unstable systems which break down over time [30]. The organic PCM micro-droplets stabilized by surfactant can easily coalesce if the synthesis conditions change, such as stirring speed and temperature. Therefore, fabrication of MEPCMs with inorganic shell using PCM micro-droplets as soft template requires strict control of experimental conditions. Moreover, while pure inorganic shells may have improved flame retardancy and thermal conductivity [31], they are brittle and the anti-leakage performance is often not satisfactory [24].

To integrate the advantages of both organic shell (i.e. toughness and anti-leakage) and inorganic shell (i.e. flame retardancy and thermal conductivity), metal films were deposited onto organic shell [32] by means of sputtering, chemical vapor deposition, and electrochemical deposition [33]. However, these methods require high temperature and/or high pressure under which organic shell microcapsules are inclined to degrade. As such, deposition of inorganic material onto organic shell under mild condition using electroless deposition is highly desired.

This study presents a novel approach to synthesize MEPCMs with composite titania-polyurea (TiO_2-PUA) shell via a two-step liquid phase deposition (LPD) at low temperature. In the first step, MEPCM pre-microcapsules with polyurea (PUA) shell is synthesized through interfacial polymerization in oil-in-water emulsion. The thin PUA shell is to stabilize and prevent coalescence of PCM micro-droplets and to serve as the hard template for deposition of TiO_2. In the second step, TiO_2 deposits on the surface of pre-microcapsules in solution by means of the LPD method at low temperature. The two-step synthesis approach shall increase the yield of microcapsules and the resulting MEPCMs with composite TiO_2-PUA shell shall integrate advantages of both organic and inorganic shells. Formation mechanisms are discussed in detail and the microcapsules are characterized by means of scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, infrared spectroscopy (IR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Parametric studies are carried out to reveal the influence of key synthesis parameters on the core fraction and thermal stability of the MEPCMs. Thermal performance of cement paste incorporating the newly developed TiO_2-PUA MEPCMs were evaluated to demonstrate their potential applications.