Nanosilicon dioxide hydrosol as surfactant for preparation of microencapsulated phase change materials for thermal energy storage in buildings

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Abstract

Microencapsulated phase change materials (MEPCMs) have been recognized as potential energy storage materials for applications such as balancing of heating and cooling loads in buildings. However, current MEPCMs do suffer from low thermal conductivity and low mechanical strength thus limiting their full potential. Past investigations have shown that nanomaterials could be used as a surfactant for the preparation of O/W emulsion and for thermal enhancement in encapsulation processes of phase change materials. For that reason nanosilicon dioxide hydrosol was selected as a surfactant for the encapsulation of samples of n-octadecane due to its excellent thermal stability and good combination properties with both organic and inorganic phase change materials. To this end, the focus of the study was on the synthesis and characterization of the fabricated MEPCM samples. Analysis of the results did show good particle dispersion and shell integrity with the best fabricated sample (MF-2) achieving a significant increase in thermal stability temperature by approximately 78°C (i.e. from 133°C to 211°C) and also higher core material content ranging from 8% to 25% in comparison with other samples. However, there was a reduction of about 17% in the energy storage capacity and a slight reduction of 0.57°C in its melting temperature when compared with the original sample of n-octadecane. The results also revealed that the nucleating agent (ammonium chloride) did affect the morphology, particle size distribution and the content of the base materials. Further enhancement studies are therefore encouraged.

Keywords: microencapsulated phase change material; poly (melamine formaldehyde); thermal energy storage; buildings

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1 INTRODUCTION

Microencapsulated phase change materials (MEPCMs) have been recognized as potential energy storage materials for applications such as balancing of heating and cooling loads in buildings [1–4]. MEPCMs can be produced by various methods but in situ polymerization method is probably the commonest technological method [5] used for the encapsulation process. Regarding shell materials, poly (melamine formaldehyde) (PMF) is the most widely used material due to its ability to be cross-linked at different molecular ratios such as: 1:2.66 [6], 1:2, 1:1.5, 1:1.3, 1:1.25 [7] and 1:2.5 [8]. PMF also possesses high density and relatively high thermal conductivity with good mechanical strength thus making it a good candidate for encapsulation of phase change materials.

However, MEPCMs do suffer from low thermal conductivity and mechanical strength thus limiting their application. Some investigators have therefore tried to enhance these properties by...
using different types of nanomaterials. For instance, Shi and Cai [9] were able to increase the mechanical strength and sealing property of MEPCM capsule by adding 24.5 and 62% of titanium oxide nanoparticles (TiO₂), respectively. Tong et al. [10] used nano-SiO₂ to enhance the thermal and mechanical properties of an encapsulated paraffin wax material. Jiang et al. [11] prepared MEPCM with nano alumina (nano-Al₂O₃) and achieved a significant enhancement in its thermal conductivity. Song et al. [12] also used nanosilver particles to enhance the mechanical properties and thermal stability of an encapsulated bromo-hexadecane (BrC₁₆) without experiencing any particle agglomeration problem. Furthermore, Yang et al. [13] successfully prepared MEPCM by using inorganic silicon nitride as a surfactant and organic PMMA hybrid as the shell material. The results showed significant thermal enhancement and a maximum increase of 16.24 mN in mechanical strength. Other investigations carried out by Dinsmore et al. [14], Wei et al. [15] and Köhler et al. [16] have also established that nanomaterials can be used as surfactants for general preparation of oil-in-water (O/W) emulsions since they can spontaneously be adsorbed on the interface of oil and water emulsion to help reduce the total surface energy. This phenomenon is based on the fact that oil–water surface energy is much larger than the difference between the particle–oil and particle–water surface energies [17]. Meanwhile, good-quality MEPCMs can also be produced by combining appropriate proportions of surfactants with various core and PMF shell materials. For example, Mohaddes et al. [18] prepared MEPCM sample with polyvinyl alcohol (PVA) and eicosane as a surfactant and core material, respectively. Zhang et al. [19] used various surfactants (i.e. SDS, SMA and PVA) to produce samples of MEPCM. Khakzed et al. [20] developed MEPCM with mixtures of surfactants, which contained 80% of SDS and 20% of Triton X-100. Su et al. [21] also combined two surfactants (Brj-30 and Brj-58) to develop MEPCM samples. Wang et al. [22] stabilized oil/water emulsion with organically modified SiO₂/TiC nanoparticles as Pickering agents and developed organic–inorganic hybrid shell MEPCMs.

In view of these highlighted investigations [9–13, 22], nanosilicon dioxide hydrosol was selected as a surfactant and combined with the shell monomers (melamine and formaldehyde) and ammonium chloride as a nucleating agent for the development of MEPCM samples. Nanosilicon dioxide hydrosol has the added advantages of being non-toxic [23] with excellent stability and good combination properties of both organic and inorganic components [24] as well as high thermal conductivity [25]. The focus of this study was therefore on the synthesis and characterization of the fabricated MEPCM samples.

### 2.1 Materials

Table 1 shows a list of basic materials which were obtained from different sources and used for the fabrication process of the MEPCM samples (MF-1, MF-2 and MF-3). For instance, high-purity paraffin n-octadecane was acquired from Alfa Aesar (China) Chemical Co., Ltd and used as a phase change material. Melamine (99% purity) and 37 wt% formaldehyde solution were obtained from Sinopharm Chemical Reagent Co., Ltd and used as shell monomers. Nanosilicon dioxide hydrosol (ZS-30, 30 wt%, Zhejiang Yuda Chemical Industry Co., Ltd) was used as a surfactant. Citric acid (99.5%), sodium hydroxide (96%) and ammonium chloride (purity 99.5%) were supplied by Sinopharm Chemical Reagent Co., Ltd and used to prepare solutions for controlling the pH values.

### 2.2 Fabrication process

In situ polymerization method was adopted for the fabrication process because it is one of the most commonly and widely used methods for the production of MEPCMs as already highlighted [5].

| MEPCM samples | Shell monomers | Emulsifier | PCM | Nucleating agent |
|---------------|----------------|------------|-----|-----------------|
|               | Melamine (g)   | Formaldehyde (g) | Nano-SiO₂ hydrosol (g) | n-Octadecane (g) | Ammonium chloride (g) |
| MF-1          | 2.0            | 3.2        | 1.2 | 10              | 0.250             |
| MF-2          | 2.0            | 3.2        | 1.2 | 10              | 0.125             |
| MF-3          | 2.0            | 3.2        | 1.2 | 10              | 0.000             |

Figure 1. In situ polymerization process [6–8].
The method is also linked with other processes that involve synthesis of prepolymer solution, preparation of O/W emulsion and formation of shells [6–8, 19]. The prepolymer solution was prepared at a pH value of 8.5–9 in accordance with the procedure shown in Figure 1. Initially, melamine (2.0 g) and 37% formaldehyde solution (3.2 g) were mixed with 10 ml of deionized water at a stirring speed of 200 rpm and then the pH value was adjusted to between 8.5 and 9 by adding 0.9–2 ml (0.2 wt%) of sodium hydroxide solution. The blended mixture was then heated up to 70°C and maintained at that temperature until the suspension became transparent. The O/W emulsions were prepared at a recommended speed of 7000 rpm for 10 min in order to achieve
stability and uniformity, whereas shell cross-linking of the solution was maintained at a stirring speed of 500 rpm and at a temperature of 70°C for 4 h after decreasing the pH value to between 3 and 4 with 0.5–2 ml (5 wt%) of citric acid solution. As shown in Figure 2, fabrication of the MEPCM was completed by cross-linking the capsules with PMF resin before being finally washed with water and then dried in an oven at a temperature of 60°C for 20 h.

2.3 Material characterizations

2.3.1 Microscopy

As shown in Figure 3, Upright Optical Microscope (Axio Imager, Carl Zeiss AG Light Microscope) was used to observe and examine the microstructure of the MEPCM particles at 500x magnification during the fabrication process. The fabricated MEPCM samples were however analysed with a scanning electron microscope (SEM) manufactured by Sigma VP (Carl Zeiss Co. Ltd) paired with energy-dispersive X-ray spectroscopy (EDS) (Oxford X-act), which enabled the fine details of the particles to be measured and assessed via image analysis. Since the shell material is a non-conductive material, the samples were initially coated with 5-nm-thick gold layer in order to increase...
their electrical conductivity before the microscopy analysis was carried out as explained in the study carried out by Suzuki [26].

2.3.2 Particle sizing
Particle size distribution (PSD) analysis is one of the most important processes for evaluating uniformity of microcapsules [27]. In this regard, a laser particle size analyzer as shown in Figure 4 (Bettersize 2000, Bettersize Instruments Ltd, China) was used to evaluate the slurry samples after encapsulation.

2.3.3 Energy storage capacity
A differential scanning calorimetric (DSC6220, SII Nanotechnology, see Figure 5) equipment was used in determining the enthalpies of fusion and melting temperature of the MEPCM samples in accordance with ISO 11 357 Standards under the dynamic testing method. The samples were tested at atmospheric pressure of 101 kPa and at a heating rate of 2°C/min from 5°C to 50°C.

2.3.4 Thermal stability
Figure 6 shows a thermogravimetric (TG) analysis instrument (EXSTAR6000 TG/DTA6300, SII NanoTechnology Inc.) that was used to evaluate the thermal stabilities of the samples. This was achieved by measuring the amount of weight changes in the samples as a function of increasing temperatures under nitrogen gas (N₂) protection covering a heating range of 50–500°C at a rate of 10°C/min.

3 RESULTS AND DISCUSSION

3.1 Microscopy analysis
As described in the MEPCM fabrication process, the total PMF shell cross-linking process for each sample lasted 4 h but they were analysed and dried after every 2 h (i.e. 2 and 4 h) in order to evaluate the effect of the nucleating agent on the fabrication process. The microscopic images of the three samples (MF-1, MF-2 and MF-3) in slurry and dried states are presented in Figures 7–9 with all showing good particle dispersion and shell integrity after drying except sample MF-3 in Figure 9c which appears somehow deformed and was attributed to lack of nucleating agent. This outcome is in agreement with the findings by Tang et al. [28] which highlighted the importance of nucleating agents in encapsulation processes.

3.2 Particle size distribution
Particle distribution frequency (Diff%) is usually used to assess the PSD profile of particle numbers from the total that are

Figure 8. Microscopic images of MF-2 samples in (a, b) slurry and (c, d) dried forms after 2 and 4 h.
within a specified size range. As shown in Figure 10, sample MF-2 which contains comparatively less amount of ammonium chloride displayed the narrowest peak particle distribution profile with most of the particles falling within the range of 15–40 μm. The profiles for MF-1 and MF-3 samples were however much wider covering particle sizes of 15–55 and 10–90 μm, respectively. These results demonstrate that the dosage of ammonium chloride can affect PSD of microcapsules and therefore needs to be optimized.

3.3 SEM examination
3.3.1 Morphologies of samples
The morphologies of the three MEPCM samples are presented in Figure 11a, c and e through the SEM images. It can be seen that most of the capsules in MF-1 and MF-2 were fully encapsulated, whereas MF-3 did suffer from a considerable amount of deformation and separation during the encapsulation process due to lack of ammonium chloride (NH₄Cl) as a nucleating agent. However, the surface of MF-1 looks relatively rough as compared with MF-2 and MF-3. This could also be due to the relatively larger amount (0.250 g) of NH₄Cl in that sample which caused the PMF cross-linking reaction to speed up. It could also be attributed to the fact that NH₄Cl was able to reduce the pH value by the generation of hydrogen chloride in water solution after the release of ammonia gas. Consequently,
Figure 11. SEM and EDS test results of fabricated MEPCMs. (a) MF-1; (b) EDS results of MF-1; (c) MF-2; (d) EDS results of MF-2; (e) MF-3; (f) EDS results of MF-3.
deposition of nanoparticles of PMF could either occur on the surfaces of the microcapsules or on the surface of the larger PMF particles. Therefore, a certain level of deposition rate of nanoparticles of PMF should be expected to affect sample MF-2 which contains 0.125 g of NH4Cl. The overall analysis of the images shows that sample MF-2 achieved the best morphology in comparison with the other samples. From the SEM images and past highlighted studies [6–8, 17], it is evident that the morphology and the shell integrity of the microcapsules can significantly be affected by the dosage of nucleating agent and therefore requires some form of optimization.

3.3.2 Energy-dispersive X-ray spectroscopy
EDS (Oxford X-act) is a rapid elemental analysis and chemical characterization analytical technique for a sample [29]. The EDS test results are as shown in Figure 11b, d and f has revealed the presence of silicon (Si), carbon (C), nitrogen (N) and oxygen (O) in all the MEPCM samples. The images also confirm that the nanosilicon dioxide particles were successfully retained in the capsules and could therefore be used to enhance the thermal conductivity of the capsules since its thermal conductivity (1.4 W/mK [25]) is much higher than that of n-octadecane (0.2 W/mK) [5] and PMF (0.34 W/mK [30]).

3.4 Energy storage capacity
Analysis of the results in Figure 12 shows that the melting temperatures of the samples were slightly reduced by 0.57–0.98°C after encapsulation due to the effect of the PMF shell and retention of nanosilicon dioxide in the capsules. As summarized in Table 2, sample MF-2 achieved the highest energy storage capacity of 179 kJ/kg with a melting temperature of 23.55°C. There was however a reduction of about 17% in its energy storage capacity when compared with that of n-octadecane (pure paraffin). The lower energy storage capacities for the other samples were as a result of a relatively less amount of core material and poor level of encapsulation as captured by the SEM images in Figure 11 and summarized in Table 2. For the sake of comparison, the maximum core material content of MF-2 was 83% as against 59% for MEPCM sample (with the same core/shell materials and core/shell ratios) that was fabricated with SMA as a surfactant [19]. This means that nanosilicon dioxide could be used to enhance the content of a core material during microencapsulation process.

3.5 Thermal stability
In Figure 13, the n-octadecane started to experience weight loss when it was heated to a temperature of 133.1°C and eventually lost 98% of its core content when it reached a temperature of 260°C. However, after encapsulation, the weight losses in the other samples were reduced over a wider heating temperature range with MF-2 achieving the highest thermal stability well beyond 211.7°C. This compares more favourably against the samples produced by Zhang et al. [31] where the highest weight loss temperature achieved was 197°C with TA as a surfactant and PMF as the shell material for the encapsulation of

| Table 2. Thermal properties of PCM and MEPCMs. |
|-----------------------------------------------|
| Name             | Melting temperature (°C) | Latent heat (kJ/kg) | Core material (wt%) |
|------------------|--------------------------|--------------------|---------------------|
| n-Octadecane     | 24.12                    | 216                |                     |
| MF-1             | 23.20                    | 126                | 58                  |
| MF-2             | 23.55                    | 179                | 83                  |
| MF-3             | 23.14                    | 161                | 75                  |

Figure 12. Enthalpy profiles of n-octadecane and MEPCM samples.
n-octadecane. This result clearly shows the potential of nanosilicon dioxide for thermal stability enhancement of MEPCMs and also corroborates with the results from other related studies, where the thermal stabilities of those MEPCMs were improved by using nanomaterials, i.e. nano-TiO₂ [9] and nanosilver [12]. It is also due to the fact that the polymer shell of the MEPCMs were reinforced by the large surface areas of the nanoparticles which enabled them to be closely combined with polymer matrix to create composite structured walls.

4 CONCLUSIONS

This study was focused on evaluating the suitability of nanosilicon dioxide hydrosol as a surfactant for microencapsulation of PCM. To this end, in situ polymerization method was adopted for the fabrication process of three different MEPCM samples. Analysis of the results has shown that nanosilicon dioxide hydrosol could be used as a surfactant and for improving the shell integrity/core material content of MEPCMs. It also has an added benefit of being used as a thermal conductivity enhancement material. The specific findings of this study may therefore be summarized as follows:

(a) The DSC test results demonstrated that the melting temperatures of the samples were slightly reduced by 0.57–0.98°C after encapsulation.
(b) The TG test results showed that the thermal stability temperatures were increased by more than 45°C.
(c) Sample MF-2 achieved the best morphological structure with the highest latent heat value of 179 kJ/kg and a thermal stability temperature of 211.7°C.

The results however did reveal that the ammonium chloride affected the morphology, PSD and the content of the base materials. Further studies are therefore encouraged to address these effects.

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