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## Development of microencapsulated phase change material with poly (methyl methacrylate) shell for thermal energy storage

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### Abstract

This research focused on the development of MEPCMs for thermal energy storage in low carbon buildings with poly (methyl methacrylate) (PMMA) shell. The experimental results showed that the best MEPCM sample was prepared with 1 wt% of the thermal initiator and the surfactant of S-1DS. The differential scanning calorimetric (DSC) analysis showed that the best sample has a latent heat of 170 kJ/kg and a melting temperature of 22.68 °C. Meanwhile, the core material contents and encapsulation efficiencies were calculated according to the measured results of the DSC. Those two values for the sample of PMMA-3 and PMMA-5 were even higher than theoretical values due to the evaporation of shell monomer during encapsulation processes. Finally, the thermogravimetric (TG) analysis of the fabricated MEPCM samples showed good thermal stability behaviors above 161 °C and therefore satisfy the environmental requirements for most applications.

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### 1. Introduction

Previous studies have proved that microencapsulated phase change material (MEPCM) was one of the key potential materials for saving energy consumption in buildings because it can balance the mismatch between heating

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and cooling demands automatically [1, 2]. The researches pointed that the latent heat thermal energy storage materials suitable for various applications in buildings, such as melting temperatures up to 21°C are more suitable for cooling applications [3], 22–28°C for thermal comfort applications, 29–60 °C for hot water supply and over 120°C for waste heat recovery applications [4]. For instance, an experimental study carried out on a novel translucent full scale passive solar MEPCM wall by Berthou *et al.* [5] revealed that it could be used to provide significant improvement of indoor temperatures in both cold and sunny climates. Darkwa *et al.* developed a non-deform MEPCM [6] for thermal energy storage application. Su *et al.*[7] developed MEPCM for hot water supply in low carbon buildings and proved the energy storage density would increase from 84,000 kJ/m<sup>3</sup> to 128,735 kJ/m<sup>3</sup> by added 50 wt% MEPCM.

Previous researches also showed that polymers based methyl methacrylate (MMA) are the commonest shell materials for MEPCMs preparation with in-situ suspension-like polymerization method [8] since the MMA can be self-polymerized [9] and crosslinked with the other monomers [10]. Meanwhile, good quality MEPCMs can be produced by combining appropriate proportions of surfactants. For example, Su *et al.* [10] also combined two surfactants (Brij-30 and Brij-58) to develop MEPCM samples. Wang *et al.* [11] stabilized oil/water emulsion with organically modified SiO<sub>2</sub>/TiC nanoparticles as surfactants and developed organic-inorganic hybrid shell MEPCMs. Su *et al.* [12] also successfully fabricated MEPCM samples with the surfactant of nanosilicon dioxide hydrosol. To this end, different types of surfactants (i.e. nano-silicon dioxide hydrosol and Sodium 1-dodecanesulfonate (S-1DS)) were used to prepare MEPCM samples with paraffin wax and poly (methyl methacrylate) (PMMA) in this research. Meanwhile, the effects of weight percentage of initiator and types of surfactants were also studied.

## 2. Materials and methods

### 2.1. Materials

As summarized in Tab.1, the paraffin of n-octadecane was introduced as a core material because of its relatively high latent heat capacity and appropriate phase change temperature. While the MMA (purity of 98 %, Sinopharm Chemical Reagent Co.,Ltd.) was used as shell monomer. Nano-SiO<sub>2</sub> hydrosol (ZS-30, 30 wt%, Zhejiang Yuda Chemical Industry Co., Ltd) and sodium 1-dodecanesulfonate (S-1DS) (Sinopharm Chemical Reagent Co.,Ltd) were used as a surfactants. Usually, based on the weight of shell monomer, thermal initiators in the range of 0.5 wt% to 3wt% are used for crosslinking PMMA [13]. To this end, the AIBN (purity of 98 %, Aladdin) with the weight percentages of 0.5 %, 1.0 %, 2.0 % and 3.0 % was used as oil-soluble thermal initiator.

Table 1: Raw materials of MEPCM preparation with PMMA shell

Sample	MMA (g)	PCM (g)	Surfactant material	Surfactant (g)	AIBN (g)	Initiator weight (wt%)
PMMA-1	3	7		0.5	0.090	3.0%
PMMA-2	3	7	Nano-SiO <sub>2</sub> hydrosol	0.5	0.060	2.0%
PMMA-3	3	7		0.5	0.030	1.0%
PMMA-4	3	7		0.5	0.015	0.5%
PMMA-5	3	7	S-1DS	0.5	0.030	1.0%
PMMA-6	3	7		0.5	0.015	0.5%

### 2.2. Fabrication process

The typical procedure for using oil-soluble initiators to fabricate MEPCMs with PMMA shell is as following: The oil phase was prepared by mixing the shell monomer (MMA) and the melted n-octadecane at 40 °C with a predetermined amount of thermal initiator (AIBN). The oil phase was then homogenized into water phase with 90 ml of deionized water and a certain amount of surfactant (nano-SiO<sub>2</sub> hydrosol or S-1DS) at a speed of 7000 rpm for 5 minutes to form a stable O/W emulsion. The next stage was to transfer the homogeneous emulsion into a three-neck round bottom flask before it was deoxygenated with nitrogen gas for one hour at a stirring speed of 250 rpm.

The microencapsulation reaction was then carried out in the flask immersing in a water bath of 80 °C and was continuously agitated under a speed of 250 rpm for 5 hours. Finally, the microcapsules were collected, washed and then dried in an oven at 60 °C for 20 hours.

### 3. Results and discussion

#### 3.1. Morphology analysis of MEPCM samples

The fabricated MEPCM samples were depicted by a scanning electron microscope (SEM) manufactured by Sigma VP (Carl Zeiss Co. Ltd.), as demonstrated in Fig. 1. The SEM images showed that the particle sizes of PMMA capsules are in the range of 5–20  $\mu\text{m}$  and that is the same as the initial diameters of MEPCM particles in slurry. However, most of the capsules manufactured with the surfactant of nano-SiO<sub>2</sub> hydrosol in Fig. 1 (a) to (d) were deformed after drying due to some weakness of the PMMA shell. On the other hand, the capsules fabricated with the surfactant of S-1DS showed much better morphology and integrity, and the PMMA-5 demonstrated the best particle morphology and integrity, while the PMMA-6 showed a lot of wrinkles on the surfaces of the capsules. That means the morphologies of microcapsules were particularly influenced by the type of surfactant and the dosage of the thermal initiator. In this research, the optimization of the capsules morphology was achieved with the surfactant of S-1DS and 1 wt% thermal initiator.

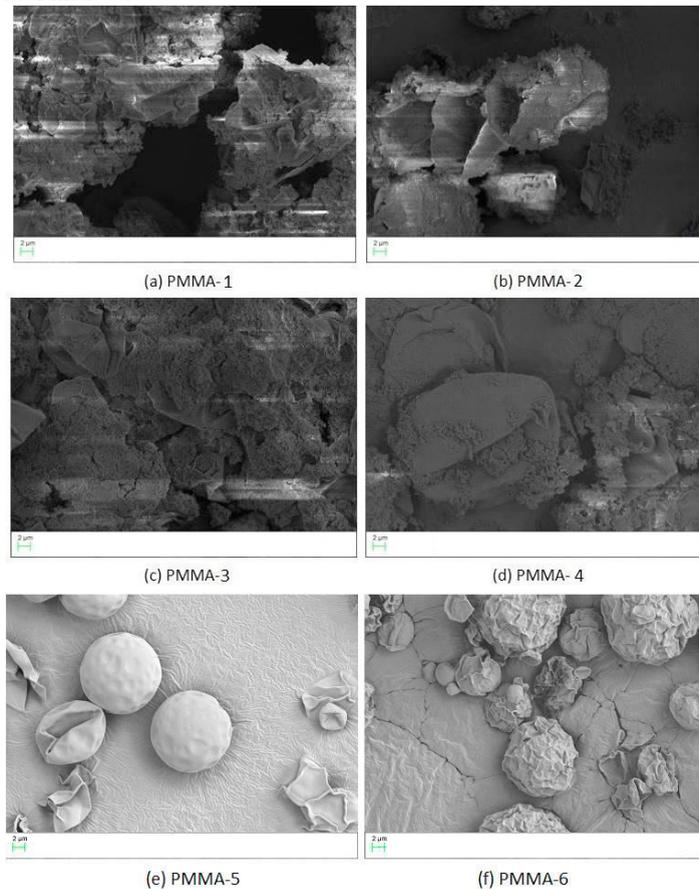


Figure 1: SEM images of fabricated MEPCM samples

### 3.2. Energy storage capacity

According to differential scanning calorimetric (DSC) (DSC6220, SII Nanotechnology) measurement results, the melting points of MEPCMs were reduced by 0.2-1.87 °C compared with the n-octadecane (PCM core material), as shown in Fig. 2. Meanwhile, the thermal energy storage capacities of fabricated MEPCM samples were achieved as much as 149 kJ/kg, 143 kJ/kg, 166 kJ/kg, 142 kJ/kg, 170 kJ/kg and 150 kJ/kg for the PMMA-1, PMMA-2, PMMA-3, PMMA-4, PMMA-5 and PMMA-6, respectively. The DSC analysis results also showed that the dosage of thermal initiator did effect on the thermal energy storage capacities and the core material contents of MEPCM samples, and the highest core material contents for the surfactant of nano-SiO<sub>2</sub> and S-1DS were achieved by using 1 wt% of thermal initiator. The research outcomes by Romio et al. [14] showed that the polymerization rate of MMA was increased by a higher initiator dosage. To this end, the dosage of AIBN need to be optimized and the best concentration of initiator is 1 % in this study.

According to the initial core/shell ratio in Tab.1, the theoretical core material content should be 70 % with the latent heat of 151.2 kJ/kg. However, the experimental results in Tab.2 showed the energy storage capacity of PMMA-3 and PMMA-5 were higher than 70 % and that means the encapsulation efficiencies [15] were more than 100 %. However, the high encapsulation efficiency did not mean good encapsulation quality since deform of MEPCM capsules existed in Fig. 1. On the contrary, the high encapsulation efficiency was mainly due to the reducing of weight percentage of shell that caused by the evaporation of shell monomer. The evaporation resulted by the low flash point of MMA which is only 9 °C and relatively high reaction temperature of 80 °C for the self-crosslinking of MMA [16].

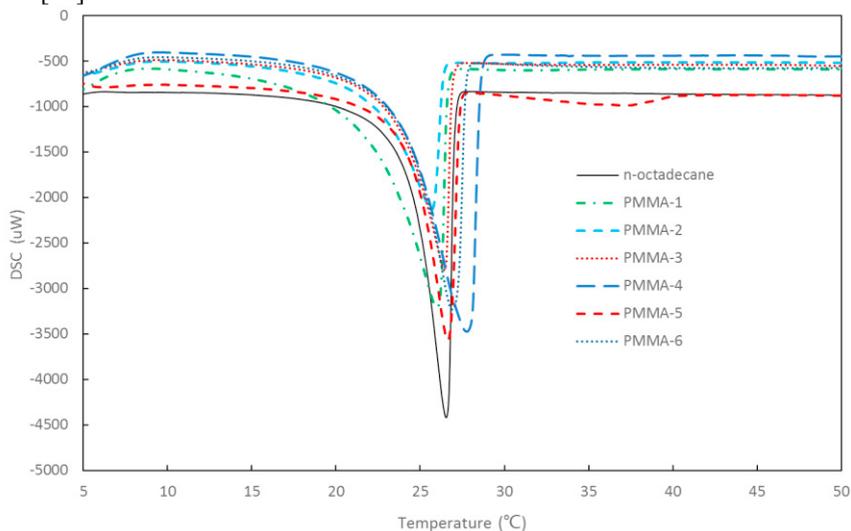


Figure 2: DSC curves of MEPCM samples

Table 2: Properties of paraffin and MEPCM samples

Material	Melting temperature (°C)	Latent heat (kJ/kg)	Core material (wt%)	Encapsulation efficiency (%)
Paraffin	23.12	216	--	--
PMMA-1	21.25	149	69.0%	98.5%
PMMA-2	22.80	143	66.2%	94.6%
PMMA-3	22.66	166	76.9%	109.8%
PMMA-4	22.07	142	65.7%	93.9%
PMMA-5	22.68	170	78.7%	112.4%
PMMA-6	22.92	150	69.4%	99.2%

### 3.3. Thermal stability

As shown in Fig. 3, the thermogravimetric (TG) (EXSTAR6000 TG/DTA6300, SII NanoTechnology Inc.) analysis results showed that the weight loss starting temperatures for n-octadecane, PMMA-1, PMMA-2, PMMA-3, PMMA-4, PMMA-5 and PMMA-6 were at 129.0 °C, 178.6 °C, 167.6 °C, 161 °C, 165.8 °C, 204.4 °C and 192.9 °C, respectively. That means the thermal stability of the MEPCMs was enhanced more than 32 °C by the PMMA shell compared with the paraffin core of n-octadecane after encapsulation. However, due to the deformed state of the capsules fabricated with the surfactant of nano-SiO<sub>2</sub>, the thermal stability of those samples (PMMA-1 to PMMA-4) was demonstrated much lower than the capsules fabricated with the surfactant of S-1DS (PMMA-5 and PMMA-6). For instance, compared with the original core material the weight loss starting temperature at 129.0 °C, the weight loss starting temperatures for PMMA-5 and PMMA-6 were increased more than 63.9 °C while the maximum value for the capsules manufactured with the surfactant of nano-SiO<sub>2</sub> was only 49.6 °C. Especially for the PMMA-5 the thermal stability was increased by 75.4 °C due to the integrated nature of the shell. The TG analysis also proved the best MEPCM sample of PMMA-5 has the highest thermal stability.

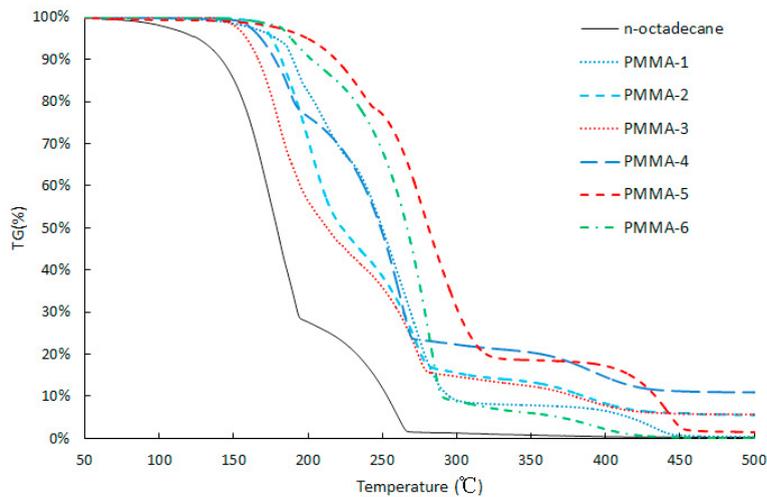


Figure 3: TG curves of MEPCM samples

## 4. Conclusions

In general this study has developed several MEPCM samples for thermal energy storage in low carbon building. The experimental results proved that the qualities of capsules were mainly affected by the type of surfactants and the dosage of initiator. Meanwhile, capsule morphologies, thermal storage capacities, core material contents, encapsulation efficiencies and thermal stabilities were analysed and evaluated by SEM, DSC and TG, respectively. The key findings are summarized as follows:

- 1) The core material contents and encapsulation efficiencies of the PMMA-3 and PMMA-5 were higher than theoretical values due to the evaporation of MMA (shell monomer) during encapsulation processes.
- 2) The experimental results show that the thermal stabilities of PMMA samples were between 161 °C and 204.4 °C and enhanced by more than 32 °C.
- 3) The best MEPCM sample with PMMA shell was manufactured with the surfactant of S-1DS and thermal initiator of 1 wt%. The latent heat and thermal stability of the best PMMA samples were obtained as 170 kJ/kg and 204.4 °C respectively.

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