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## Preparation of microencapsulated phase change materials (MEPCM) for thermal energy storage

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### Abstract

Microencapsulated phase change materials (MEPCM) could be used for energy saving applications in buildings due to their relatively high energy storage capacities at constant temperature, which could passively reduce peak cooling loads in summer. In this study, poly(methyl methacrylate-co-methacrylic acid) (PMMA-MAA) was used as a shell material to fabricate MEPCM by crosslinking methyl methacrylate (MMA) and methacrylic acid (MAA) through in-situ suspension-like polymerization method. The effects of initiator weight percentage and the ratio of shell monomers for the preparation of MEPCM were also investigated. The experimental results showed that the best MEPCM sample was achieved with a shell monomer weight ratio of 80% MMA : 20% MAA and thermal initiator of 1 wt%. Differential scanning calorimetric (DSC) analysis also showed a latent heat value for the best sample as 170 kJ/kg with a melting temperature of 23.68°C which makes these materials suitable for application in residential buildings. Meanwhile, the core material contents and encapsulation efficiencies were calculated according to the measured results of the DSC. Finally the thermogravimetric (TG) analysis on the samples showed very good thermal stability behaviours ranging between 162.3°C and 204.4°C and therefore satisfies the environmental requirements for most applications.

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## 1. Introduction

According to the International Energy Agency (IEA) there has been a rapid increase in global energy consumption over the past few decades due to population growth and human activities. Currently the building sector is responsible for approximately 40% of final global energy consumption and CO<sub>2</sub> emissions [1]. It is also estimated that 85% of a building's gas emissions is caused by heating, cooling and lighting activities [2]. Integration of microencapsulated phase change materials (MEPCM) into various construction materials have been identified as one of the key potential technologies which could minimise energy consumption in buildings including residential buildings because they could be used to reduce the diurnal indoor air temperature variations and the occurrence of peak indoor temperatures in summer [3-5]. For example, an experimental study carried out on a novel translucent full scale passive solar MEPCM wall by Berthou et al. [6] revealed a significant improvement of indoor temperatures in both cold and sunny climates. Darkwa et al. developed a non-deform MEPCM [7] for thermal energy storage application and further evaluated its thermal performance [8] in a model room to achieve a maximum temperature reduction of 5°C. Chen et al. [9] developed MEPCM/diatomite composite as a novel hygroscopic phase change material for improving room comfort level. Jeong et al. [10] reported a reduction of the peak temperature in a building which was painted with composite MEPCM/paint. Even though MEPCMs could make positive impact on the indoor thermal comfort in residential buildings, there are several challenges for the encapsulation process in relation to their thermal properties and stability and which are yet to be resolved.

Shell material is the key parameter to ensure the thermal and long term stabilities for MEPCM applications. Previous research proved that the PMMA based polymers are probably the commonest shell materials for MEPCMs preparation although MEPCMs can be produced by various methods [11]. For instance, the MMA can be self-polymerized and crosslinked with the other monomers to form various kinds of polymers, such as methacrylic acid (MAA) [12], Allyl methacrylate (AMA) [13], Styrene (St) [14], Ethylene glycol dimethacrylate (EGDMA) [13] and Pentaerythritol tetraacrylate (PETRA) [15]. Meanwhile, previous researchers have shown that the crosslinking reaction can be triggered by various initiators, such as Benzoyl peroxide (BPO) [14], 2,2-azobisisobutyronitrile (AIBN) [16] and redox (Tertbutylhydroperoxide (TBHP) and sodium thiosulphate) [12].

To this end, three MEPCM samples were developed by encapsulating paraffin wax with poly (methyl methacrylate-co-methacrylic acid) (PMMA-MAA) for thermal energy storage application in buildings. Meanwhile the effect of weight percentage of initiator and the ratio of shell monomers for MEPCM properties were also studied since the PMMA-MAA resins have the ability to be crosslinked at different MMA/MAA molecular ratios.

## 2. Materials and methods

### 2.1. Materials

As summarized in Table 1, the n-octadecane was introduced as a phase change material and as a core material because of it has a relatively high latent heat capacity and suitable phase change temperature that is within indoor thermal comfort ranges [11]. Methyl methacrylate (MMA) (purity of 98%) and methacrylic acid (MAA) (purity of 98%) were used as shell monomers and supplied by Sinopharm Chemical Reagent Co.,Ltd. Benzoyl peroxide (BPO) (purity of 98%, Sinopharm Chemical Reagent Co.,Ltd.) was used as an oil-soluble thermal initiator in the range of 0.5% to 1.5% based on the weight of shell monomers. Sodium 1-dodecanesulfonate (S-1DS) was obtained from Sinopharm Chemical Reagent Co.,Ltd and used as an emulsifier.

Table 1: Raw materials of MEPCM preparation with PMMA-MAA shell

Items	MMA (g)	MAA (g)	n-octadecane (g)	S-1DS (g)	BPO (g)	Initiator (%)
PMMA-MAA1	2.40	0.60	7.00	0.10	0.030	1.0%
PMMA-MAA2	1.80	1.20	7.00	0.10	0.045	1.5%
PMMA-MAA3	1.50	1.50	7.00	0.10	0.015	0.5%

## 2.2. Fabrication process

Fig. 1 shows a typical procedure for using oil-soluble initiators to fabricate MEPCMs with PMMA and PMMA-MAA shells. The oil phase was prepared by mixing the shell monomers (MMA and MAA) and the melted n-octadecane at 40°C with a predetermined amount of thermal initiator (BPO). The oil phase was then homogenized into water phase with 90ml of deionized water and a certain amount of emulsifier (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 40°C with a stirring speed of 250 rpm. The microencapsulation reaction was carried out in the flask which was immersed in a water bath and was continuously agitated under a speed of 250 rpm and at a constant temperature of 80°C for 5 hours. Finally, the microcapsules were collected, washed and then dried in an oven at 60°C for 20 hours.

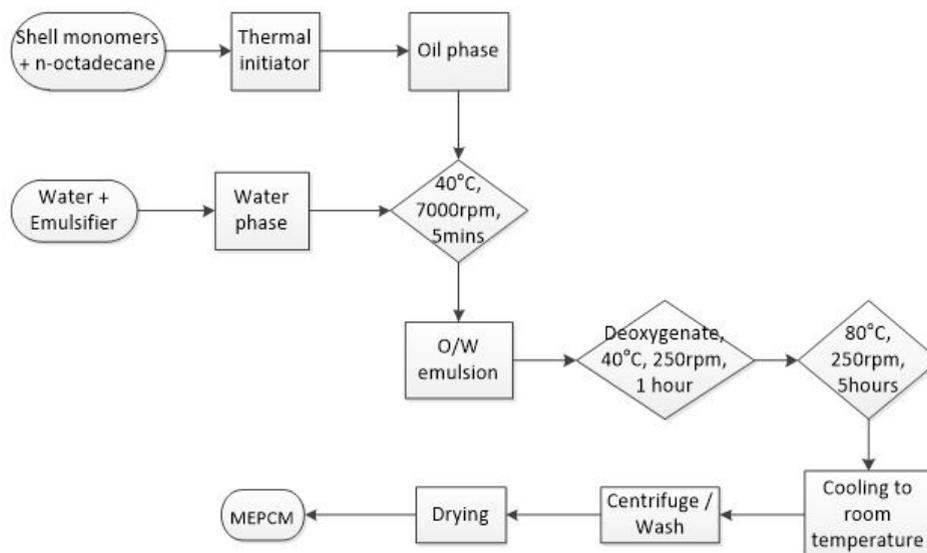


Figure 1: Illustration of MEPCM fabrication

## 2.3. Sample characterizations

The fabricated MEPCM samples were depicted by means of scanning electron microscope (SEM) by using Sigma VP (Carl Zeiss Co. Ltd.). 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 [17]. Differential scanning calorimetric (DSC) (DSC6220, SII Nanotechnology) equipment was used in determining the enthalpies of fusion and melting temperature (onset temperature for heating) of the MEPCM samples in accordance with ISO 11357 Standards under the dynamic testing method. The samples were tested at atmospheric pressure and at a heating rate of 2°C/min from 5°C to 50°C.

Thermal stabilities of the MEPCMs were examined by Thermogravimetric (TG) (EXSTAR6000 TG/DTA6300, SII Nanotechnology) analysis. The TG tests for this study were carried out under nitrogen gas protection covering a heating range of 50°C to 500°C and at a heating rate of 10°C/min.

### 3. Results and discussion

#### 3.1. Scanning electron microscopy (SEM) analysis

The SEM images in Fig.2 show the particle sizes of PMMA-MAA capsules to be in the range of 2-10  $\mu\text{m}$ . It can also be seen that the PMMA-MAA1 demonstrated the best particle morphology, while PMMA-MAA2 and PMMA-MAA3 had a lot of wrinkles on the surfaces of the capsules. That means the morphologies of microcapsules were particularly influenced by the molar ratios of shell monomers (MMA:MAA) and the use of the thermal initiator. For instance the optimization of the capsules morphology was achieved with MMA:MAA weight ratio of 4:1 and 1 wt% thermal initiator.

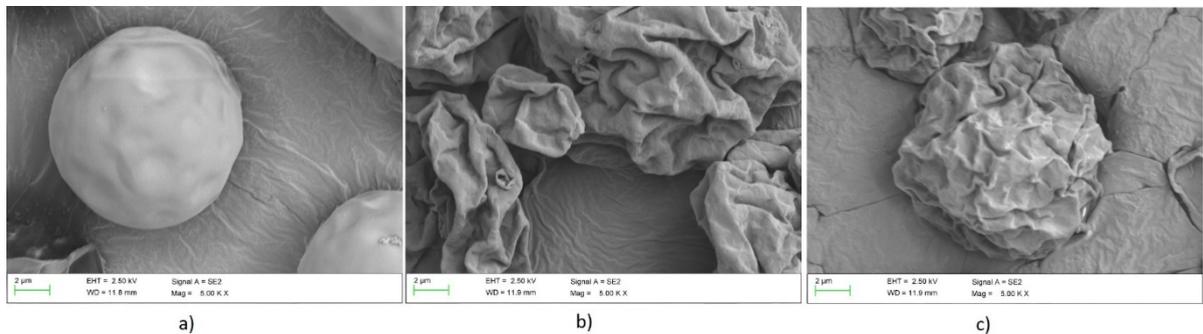


Figure 2: (a) PMMA-MAA1; (b) PMMA-MAA2; (c) PMMA-MAA3

#### 3.2. Energy storage capacity

The mass weight of the samples used for the DSC measurements were 1.190 mg for n-octadecane, 1.147mg for PMMA-MMA1, 4.258 mg for PMMA-MAA2 and 3.224 mg for PMMA-MAA3. As shown in Fig. 3 the melting temperatures of the fabricated MEPCM samples were reduced by 0.44-1.56 $^{\circ}\text{C}$  after encapsulation against the initial melting temperature of 24.12 $^{\circ}\text{C}$  for n-octadecane. The PMMA-MAA1 sample achieved the highest energy storage capacity of 170 kJ/kg with a melting temperature of 23.68 $^{\circ}\text{C}$ . While the energy storage capacities of PMMA-MAA2 and PMMA-MAA3 were obtained as 164 kJ/kg and 150 kJ/kg respectively. Therefore the samples are suitable for thermal comfort applications in residential buildings due to the melting temperature between 22 $^{\circ}\text{C}$  and 28 $^{\circ}\text{C}$  [18].

The DSC results were also used to determine the encapsulation efficiency which is defined as the ratio of the actual core content of the microcapsules to the theoretical core content [19]. Therefore, the core material contents of the three samples were in the range of 70.4-79.8% (see Table 2) based on the latent heat of n-octadecane (216 kJ/kg) which was even higher than the theoretical values of 70% in Table 1. That means the encapsulation efficiencies were more than 100%. However, the high encapsulation efficiency was mainly due to the weight percentage of shell which was reduced by the evaporation of shell monomer. This is because of the low flash point of MMA which is only 9 $^{\circ}\text{C}$  as against the evaporation which happened during self-crosslinking reaction temperature at 80 $^{\circ}\text{C}$ . This phenomenon also appeared in the investigation by Qiu X. et al.[15].

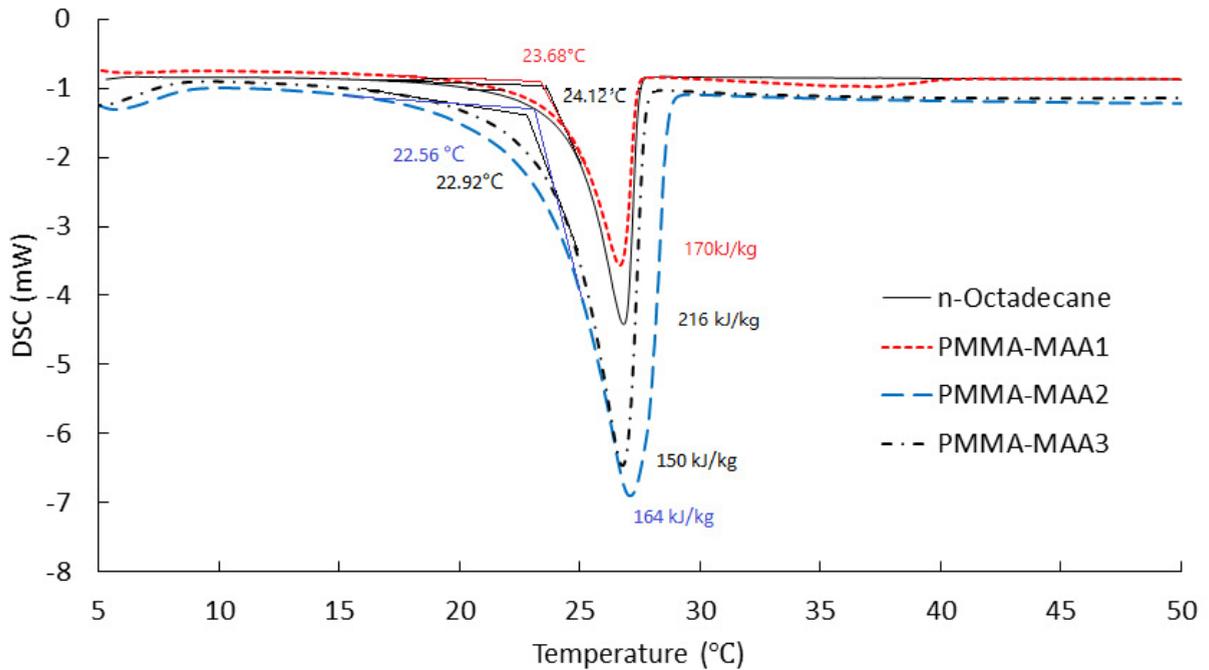


Figure 3: DSC curves of MEPCM samples

Table 2: Properties of MEPCMs with PMMA-MAA shell

Items	Melting point (°C)	Latent heat (kJ/kg)	Core material (wt%)	Encapsulation efficiency (%)
n-Octadecane	24.12	216	--	--
PMMA-MAA1	23.68	170	79.8%	114%
PMMA-MAA2	22.56	164	77.0%	110%
PMMA-MAA3	22.92	150	70.4%	101%

### 3.3. Thermal stability

As shown in Fig. 4, the thermal stabilities of MEPCMs were significantly enhanced after encapsulation. For instance the weight loss starting temperatures for n-octadecane, PMMA-MAA1, PMMA-MMA2 and PMMA-MAA3 were obtained as 129.0°C, 204.4°C, 162.3°C and 192.9°C respectively. Compared with the original core material, the weight loss starting temperature was significantly increased (more than 33.3°C) after encapsulation. Especially for the PMMA-MAA1, the thermal stability was increased by 75.4°C due to the integrated nature of the shell.

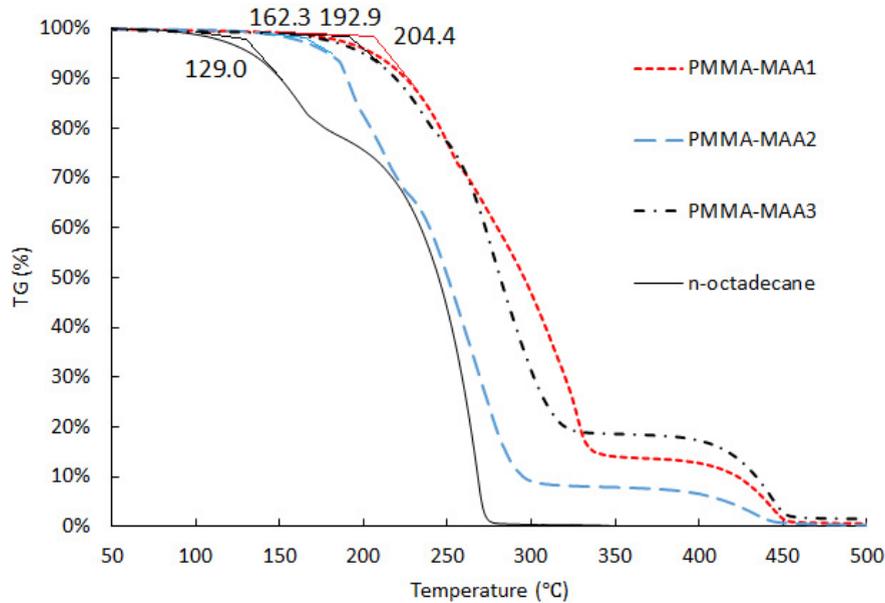


Figure 4: TG curves of MEPCM samples

#### 4. Conclusions

This study has successfully led to the development of MEPCM samples for thermal energy storage application in buildings. The experimental results proved that the qualities of capsules were mainly dependent on the ratio of shell monomers and the usage of initiators. 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 may therefore be summarized as follows:

- (a) The core material contents and encapsulation efficiencies of the MEPCM samples were higher than theoretical values due to the shell monomers evaporation during the encapsulation processes.
- (b) The experimental results show that the thermal stability of PMMA-MMA samples was enhanced by more than 33.3°C.
- (c) The best MEPCM sample with PMMA-MAA shell was manufactured with a weight ratio of 80% MMA : 20% MAA and thermal initiator of 1 wt%. The latent heat and thermal stability of the PMMA-MAA1 were obtained as 170 kJ/kg and 204.4°C respectively.

Overall, these types of MEPCMs are suitable for improving thermal comfort in residential buildings where the use of active techniques (e.g. AC) for thermal comfort purposes becomes often financially prohibitive for the high number of nonaffluent families in the world.

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