Development of form stable Poly(methyl methacrylate) (PMMA) coated thermal phase change material for solar water heater applications

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Abstract. Phase change material (PCM) is one of the most popular and widely used thermal energy storage material in solar water heater because it able to absorb and release a large amount of latent heat during a phase change process over a narrow temperature range. However the practical application of PCM is limited by two major issues; 1) leakage which leads to material loss and corrosion of tank and 2) large volume change during phase change process which cause pressure build up in the tank. In this work, form-stable PCM was prepared by coating myristic acid with Poly(methyl methacrylate) (PMMA) to prevent leakage of PCM. PMMA was mixed with different weight percentage (0.1, 0.2, 0.3, 0.4 and 0.5 wt%) of dicumyl peroxide (DCP). The purpose of adding DCP to PMMA is to crosslink the polymer and to increase the mechanical strength of PMMA to hold the myristic acid content inside the coating during the phase change process. Leakage test results showed that PMMA mixed with 0.1% DCP exhibit 0% leakage. This result is further supported by Field Emission Scanning Electron Microscopy (FESEM) images and Fourier transform infrared spectroscopy (FTIR) analysis results, where a compact and uniform coating without cracks were formed for PCM coated with PMMA with 0.1% DCP. Differential scanning calorimetry (DSC) results shows that the melting point of form-stable PCM is 55°C, freezing point is 50°C, the latent heat of melting and freezing is 67.59 J/g.

1. Introduction

Phase change material (PCM) is the most common and prospective technique being used to store latent heat energy. This is because of its storing and releasing capability of very large amount of energy for each unit mass at nearly a constant temperature [1]. In solar water heater (SWH), effective application of PCM could increase the reliability of the system during low solar gain hours without the need for back up electrical power. The size of the storage tank on the roof will reduce significantly because PCM able to store fourteen to fifteen times extra heat for each unit volume compared to sensible storage materials such as rock masonry or water [2-3].

However throughout the phase change process, PCM tends to melt and corrodes the wall of the SWH heat storage tank [4-5]. Moreover the PCM will also go through large volume change during the melting and freezing cycle which can cause pressure build up in the tank during melting and inefficient heat transfer due to air gap during freezing. Thus, PCM must be well contained to avoid them from leaking out and minimize the volume change during the phase change process. This measure must be taken into consideration in order to use them practically.
A form-stable PCM is a composite structure with solid-liquid PCMs covered or entrapped in a supporting material. When the surrounding temperature rises and the PCM changes from solid to liquid state, the supporting material prevent leakage or changes in shape, yet, the heat exchange or heat transfer process will occur normally [6].

One method to produce form stable PCMs is to coat the PCM with polymer material such as PMMA. PMMA is a flexible, transparent polymer which is compatible with PCM materials such as paraffin wax and fatty acids as evidenced from microscopic investigation and FT-IR analysis [7-8]. In previous work PMMA coating was used to produce form stable fatty acid PCMs with reduced leakage and good thermal properties for applications in under floor space heating for buildings [9]. However no attempt was made to introduce crosslinking to this coating material.

Thus in this work, effort are taken to introduce crosslinking into PPMA coating through addition of DCP. Crosslinking of polymer coating chains will form a strong three dimensional network [10]. The crosslinking is expected to produce more compact and thin coating, thus act more efficiently in eliminating leakage and retaining the shape of PCMs.

2. Methodology

2.1. Materials
Polymethyl methacrylate, PMMA (120, 000 molecular weight) was purchased from Sigma Aldrich. Myristic acid (purity ≥ 98%), chloroform (stabilized with 0.6-1.0% ethanol) and dicumyl peroxide (molecular weight of 270.37 g/mol and purity >98%) were purchased from R&M Chemicals, Malaysia.

2.2. Coating of Myristic Acid with PMMA
PMMA solution was prepared by solution blending method. PMMA was dissolved in a fixed amount of chloroform with a ratio of 10ml of chloroform to 2g of PMMA powder. The mixture was stirred using the aid of hot plate magnetic stirrer (Model: Stuart SB 162-3) at 25°C for 30 minutes. Then, dicumyl peroxide (DCP) at different weight percentage (0.1, 0.2, 0.3, 0.4, and 0.5% w/w) were added to the solution and the stirring was continued for another 10 minutes. Myristic acid was then dipped into this coating solution at fixed immersion time of 5 second. The coated samples were placed on Teflon sheet and dried in oven at 45°C for 24 hours.

2.3. Characterizations of Form Stable PCMs
The infrared spectra of PCMs with coating were recorded using Thermo Scientific Nicolet iS10 FTIR-ATR. Attenuated Total Reflectance (ATR) was used for this analysis because it can analyse the composite PCMs with coating in their natural states without grinding and destroying the coating. Analysis was conducted in the wavelength range of 4000 to 400 cm\(^{-1}\) with 32 scans.

Thermal properties of composite PCMs were measured by using Mettler Toledo TOPEM differential scanning calorimetry (DSC). The analysis for latent heat were carried out at the temperature of 25-100 °C and 10 °C/min heating rate under a constant stream of nitrogen gas at the flow rate of 10 mL/min.

Morphology of the form-stable PCM at magnification of X2000 was examined using Filed Emission Scanning Electron Microscopy (FESEM) model JOEL JSM 6701F at accelerating voltage of 2kV. Prior to scanning, the samples were placed on a disc and held in place using a double-sided carbon tape. The samples were then coated with platinum particles to avoid sample charging.

2.4. Leakage Test
Leakage test method was adapted from the selection of proper mass percentage of different form stable PCMs by Huang et al [11]. Coated PCMs were placed in oven at the temperature of 65 °C for 72 hours. The leakage percentage can be calculated by Eq. (1).

\[
\text{Percentage Leakage} (\%) = \frac{M_1-M_2}{M_2} \times 100
\]

Where;
$M_1 =$ Mass of PCM before thermal cycle
$M_2 =$ Mass of PCM at the end thermal cycle

In addition, the leakage was also characterized using the leakage area. The form stable PCM samples were placed on blue litmus paper and put in oven at the temperature of 65 °C for 72 hours. The leakage of PCM can be observed through the color change of litmus paper from blue to pink and the area of color change was calculated.

3. Results and Discussions
100% PMMA without DCP exhibit high amount of leakage (>12%) which indicates that PMMA does not form a compact and continuous coating, Figure 1. Leakage was fully eliminated when PCMs were coated with PMMA + 0.1 wt% DCP. However, the leakage percentage increases when the weight percentage of DCP in the coating are more than 0.1 wt%. Generally when more DCP is added, more crosslink network will be formed and will cause the material to become brittle and lose its flexibility. When the PCM inside the heavily crosslink PMMA coating melt and undergo a volume change, the brittle and non-flexible coating will be pushed outward to expand and this will cause cracks.

Figure 2 shows no leakage could be observed for PCMs coated with PMMA+ 0.1 wt% DCP when the samples were exposed in oven at 65˚C for 72 hours. All the other samples exhibit leakage during melting, which could be observed by change in color of the blue litmus paper to pink due to the contact with leaked myristic acid. The amount of crosslinking in the PMMA with 0.1 wt% DCP, is sufficient to form a compact and flexible coating which is expected to expand without cracking when the PCM inside the coating is melted and undergo volume change.

Figure 3 shows that the PCM coated with PMMA + 0.1 wt% DCP have smooth surface without any cracks or pin holes. This image could be correlated to 0% leakage of myristic acid from this sample. However all the other samples have micro cracks on the surface and the amount of cracks increase as the percentage of DCP increased. Besides, crystals like structure can be seen through the cracks for samples in Figure 3 (c-f). This structure was the exposed myristic acid. When the myristic acid melts, it will leak out through these cracks. The leakage increases when the percentage of DCP in PMMA increases because there are more cracks on the coating layer. In addition, the sample coated with 100% PMMA has major cracks and holes due to low physical property of PMMA as compared to the crosslinked PMMA. Thus from these results it could be concluded that PCM coated with PMMA +0.1% DCP able to eliminate leakage fully.
Figure 2: Leakage test using blue litmus paper for PCMs coated with PMMA crosslink with different percentage of DCP; A) Before exposure in oven, B) After exposure in oven

Figure 3: Myristic Acid Coated with (a) PMMA+0.1%DCP (b) PMMA+0.2%DCP (c) PMMA+0.3%DCP (d) PMMA+0.4%DCP (e) PMMA+0.5%DCP (f) 100% PMMA.
Thermal properties of coated PCMs are summarized in Table 1. The latent heat of coated PCMs decreased around 30% compared to the original latent heat of myristic acid with 98% purity. However the latent heat around 120-125 kJ kg\(^{-1}\) for form stable PCMs are comparable with any other reported works. For example the latent heat values for polyethylene glycol coated with thermosetting is 99kJkg\(^{-1}\) [12], for lauric acid modified sepiolite composite form stable PCMs is 125 kJ kg\(^{-1}\)[13], phenolic resin/PEO-PPO copolymer composite PCMs is 102 kJ kg\(^{-1}\) [14] and stearyl alcohol/high density polyethylene/expanded graphite form stable PCMs is 109 kJ kg\(^{-1}\) [15]. The latent heat of these form stable PCMs are influenced by the latent heat of both PCM and coating material and mass fraction of coating material used. The latent heat of form stable PCM is lower compared to the pure PCM material because some mass fraction of the high latent heat PCM material had been substituted by mass fraction of low latent heat coating material during the coating process. Thus it is important to form a compact and as thin as possible coating on the surface of PCM to avoid large reduction of PCM mass fraction. Formation of compact crosslink network in PMMA with DCP makes it an excellent choice for thin coating on the surface of PCMs. However future work had to be carried out to optimize the crosslink formation in PMMA.

| PCMs                          | Melting point (°C) | Latent Heat of Melting (kJ Kg\(^{-1}\)) | Freezing Point (°C) | Latent Heat of Freezing (kJ Kg\(^{-1}\)) |
|-------------------------------|-------------------|----------------------------------------|---------------------|----------------------------------------|
| Without coating               | 56.62             | 170                                    | 51.51               | 172                                    |
| PMMA without DCP              | 58.00             | 109                                    | 49.64               | 107                                    |
| PMMA with DCP (%)             |                   |                                        |                     |                                        |
| 0.1 %                         | 60.00             | 120                                    | 48.55               | 119                                    |
| 0.2 %                         | 61.65             | 122                                    | 47.68               | 120                                    |
| 0.3 %                         | 62.34             | 121                                    | 48.32               | 118                                    |
| 0.4 %                         | 64.37             | 119                                    | 46.33               | 117                                    |
| 0.5 %                         | 65.11             | 123                                    | 47.43               | 121                                    |

4. Conclusion
The major drawback of using myristic acid as PCM in SWH storage tank is the acid tend to corrode the wall of the tank during the phase change process. Therefore, this PCM was coated with PMMA + DCP in this work. It was found at 0.1% concentration of DCP leakage could be totally eliminated due to formation of compact and continuous coating layer as evidenced from FESEM micrographs. Moreover incorporation of DCP does not influence the latent heat of melting and freezing of the coated PCMs compared to PCM coated with only PMMA. The latent heat value around 120-125 kJ kg\(^{-1}\) is comparable with other research work reported.

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