Preparation and Characterization of Phase Change Materials Microcapsules for Thermal Energy Storage

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Abstract
The main purpose of this research is preparing microencapsulated phase change materials (MEPCM) by using a UV-curable pickering emulsion polymerization with PMMA-graphene oxide hybrid shell. Phase change materials (PCMs) with high latent heat are used in thermal energy storage (TES) which is an efficient and sustainable way for storing energy. Bio-based PCMs are less flammable than paraffins and can absorb, store and release large amounts of latent heat. Therefore, coconut oil which is a bio-based PCM was used as the core in this project. The emulsion was stabilized by graphene oxide (GO), in which GO was absorbed spontaneously on the surface of methyl methacrylate to produce hybrid shell. The polymerization process was carried out at ambient temperature for 30 minutes by utilizing LED as a source of ultraviolet radiation. The effect of agitation speed (i.e. 900 and 1200 rpm) on particle size and core content of microcapsules were investigated by optical microscopy (OM) and differential scanning calorimetry (DSC). In addition, the thickness of shell for two conditions was calculated. According to OM results, microcapsules produced at 900 and 1200 rpm conditions had a mean size of 28 and 12 µm, respectively. In addition, the core content of the samples was found to be 55.37% and 56.25%.

Keywords: Phase Change Materials, Bio-based PCM, Thermal Energy Storage, Energy Saving, Microcapsule, Pickering Emulsion, UV Curing.

Introduction
Nowadays, energy saving is an important issue since it is estimated that energy consumption only by buildings will raise to 115.7 EJ/year until 2030 [1]. Phase change materials with high latent heat capacity are able to store and release thermal energy isothermally. As shown in Fig. 1, the number of articles related to PCMs for thermal energy storage is increasing. PCMs are used in building industry, textile industry, electronics and solar energy storage. Appropriate melting point, high thermal conductivity and high latent heat are the most desired properties in selecting PCMs [2]. PCMs are classified into two main types containing organic and inorganic. Inorganic PCMs such as salt hydrates have high latent heat and high thermal conductivity. However, these materials undergo irreversible cycles and phase segregation which limit their application. On the other hand, organic PCMs are chemically inert, noncorrosive, nontoxic, long-lasting without phase segregation and are available in wide range of melting points. The drawback of organic PCMs is their relatively low thermal conductivity which requires high contact area [3, 4]. Organic PCMs are divided into paraffinic
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and non-paraffinic type. Paraffinic PCMs are extensively used due to their appropriate properties. However, this type of organic PCMs have low ignition resistance in comparison with non-paraffinic type. Bio-based PCMs are a class of non-paraffinic materials with low flammability and low cost. Coconut oil is one of the bio-based PCMs with melting points from 23-26℃ and relatively high latent heat of approximately 100 J/g [4, 5].

As it was mentioned, organic PCMs suffer from low thermal conductivity. Microencapsulation can be a way to enhance this problem by increasing surface area. Microencapsulation also prevents leakage of PCM during phase transition, reduced reactivity with environment and controls the volume change. Shell of the microcapsules can be generated from several polymers. It has been reported that using melamine-formaldehyde resin and urea-formaldehyde resin may cause environmental problems due to remnant formaldehyde monomer after shell formation. While poly(methylmethacrylate) (PMMA) is a nontoxic and commercial resin with high chemical and impact resistance [6, 7]. There are various ways in order to encapsulate PCMs. Recently, pickering emulsion is considered as an efficient method for encapsulating PCMs. In pickering emulsion, solid particles are used instead of organic surfactants. Lower toxicity, excellent droplet stability, smaller droplets, less foam and combination of properties in shell are some advantages of pickering emulsion over conventional methods [8, 9]. Particles used for pickering emulsion must show amphiphilic behavior. Graphene oxide (GO) is a two-dimensional nanoparticle that possess amphiphilic property due to its structure; hydrophilic groups at the edges and hydrophobic aromatic structure at the center of particles [10].

The polymerization process can be done by thermal initiation polymerization mechanism but this process requires high temperature for several hours which results in high energy consumption. In contrast, photopolymerization can be done in ambient temperature and very short time. Wang et al. prepared PMMA/paraffin microcapsules by modified silica particles by pickering emulsion polymerization and using UV irradiation [8]. The quality of the shell formation such as morphology, microcapsule size distribution and core content are impacted by the homogenization time and speed. Khakzad et al. had investigated effective parameters on hexadecane microcapsules with melamine-formaldehyde shell [3].

![Figure 1](image.png)

**Fig 1.** The number of articles related to PCMs for thermal energy storage during 1998–2019. Source: Science Direct, “phase change materials” and “thermal energy storage”.
In this project, coconut oil was selected as a bio-based PCM and MMA was used as shell main constituent. Among the studied parameters, homogenization speed showed an effective control on the microcapsule size. Hence, the effect of two agitation speed on core content, particle size and shell thickness of the synthesized microcapsules were studied.

**Experimental**

**Materials**

Coconut oil was used as the phase change material with a melting point of 25.35°C which is near to room temperature. It also possess relatively high amount of latent heat (98.25 and 96.40 J/g for melting and crystallization, respectively). The thermal conductivity of coconut oil is in the range of 0.32-0.35 W/m.K at 25-45 °C. Coconut oil is non toxic and its density is 0.903 g/cm³.

Coconut oil had the role of core in this project. Methylmethacrylate (MMA), trimethylolpropane triacrylate (TMPTA) and 2-isopropylthioxanthone (ITX) were used as shell former, crosslinking agent and photoinitiator, respectively. The UV absorption spectrum of ITX indicates high absorption at 380 nm.

Pickering emulsion polymerization was performed by using graphene oxide (GO) with the flake diameter of 0.5-2 microns and thickness of 0.5-1 nm. LED lamps with emission peak at 380 nm were used for the photopolymerization. The characteristics of LEDs (Table 1) were compatible with the absorption spectrum of ITX. A 19 mm quartz cylinder was used as reactor to facilitate the transmission of UV irradiation. The cylindrical shape of reaction container allowed uniform radiation from each side and uniform polymerization as the result. For emulsification and homogenization, a three blade mechanical mixer with diameter of 15 mm was used.

<table>
<thead>
<tr>
<th>Property</th>
<th>LED</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (lux)</td>
<td>205.4</td>
</tr>
<tr>
<td>peak wave length (nm)</td>
<td>380</td>
</tr>
<tr>
<td>Power density (W/m²)</td>
<td>3167.4</td>
</tr>
</tbody>
</table>

**Preparation**

The oil in water emulsion was prepared by mixing two phases for 30 minutes. While mixing, the emulsion was irradiated by LEDs for another 30 minutes at ambient temperature. The prepared MEPCM was then filtered and dried. Table 2 summerizes the formulation and Fig. 2 shows a schematic illustration of the process. The experiments were performed in two different agitation speed (i.e. 900 and 1200 rpm). MEPCM-900 and MEPCM-1200 stand for microencapsulated PCM with mixing rate of 900 and 1200 rpm, respectively.

<table>
<thead>
<tr>
<th>material</th>
<th>Amount (g)</th>
<th>Ratio to MMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>TMPTA</td>
<td>0.45</td>
<td>0.3</td>
</tr>
<tr>
<td>ITX</td>
<td>0.075</td>
<td>0.05</td>
</tr>
<tr>
<td>Coconut oil</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>GO</td>
<td>0.0015</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Characterization

First, the UV absorbance through the quartz container was measured by JENWAY UV-vis spectrometer and the transmittance of UV radiation through it was calculated. Then, the thermal properties were obtained from METTLER differential scanning calorimetry (DSC) with the rate of 5°C/min from -30°C to +70°C under nitrogen atmosphere. Morphology and particle size of the final microcapsules were observed by LEICA optical microscopy (OM). At last, shell thickness of the microcapsules was calculated using MATLAB software.

![Schematic illustration of preparing MEPCM](image)

Results and discussion

UV transmittance

The UV absorption spectrum of the quartz cylinder reactor used in this study is shown in Fig. 3.

According to LEDs emission peak, the absorbance of the quartz at 380 nm was measured and transmission of UV radiation through it was calculated. This result reveals that the emulsion receives 88.61% of input radiation energy at 380 nm which is sufficient for curing.

![UV absorption spectrum of the quartz cylinder reactor](image)

DSC analysis

The thermal properties of coconut oil as the PCM and the two samples of MEPCM were characterized by DSC analysis and the results are presented in Fig. 4. The core content was calculated by using the ratio of MEPCM latent heat to coconut oil latent heat (Eq. 1).
The thermal properties and core content of the samples are summarized in Table 3. As it can be seen melting points and crystallization points did not change significantly by microencapsulation. The latent heats changed and resulted in core contents of 55.37 and 56.25% for MEPCM-900 and MEPCM-1200, respectively. Moreover, these core contents approve the core to shell ratio that was used (1:1).

Table 3. Thermal properties of coconut oil and MEPCMs

<table>
<thead>
<tr>
<th>Property</th>
<th>Coconut oil</th>
<th>MEPCM-900</th>
<th>MEPCM-1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>25.35</td>
<td>25.46</td>
<td>25.12</td>
</tr>
<tr>
<td>Melting latent heat (J/g)</td>
<td>-98.25</td>
<td>-54.40</td>
<td>-55.27</td>
</tr>
<tr>
<td>Crystallization point (°C)</td>
<td>6.51</td>
<td>4.54</td>
<td>3.85</td>
</tr>
<tr>
<td>Crystallization latent heat (J/g)</td>
<td>96.40</td>
<td>54.65</td>
<td>54.82</td>
</tr>
<tr>
<td>Core content (%)</td>
<td>-</td>
<td>55.37</td>
<td>56.25</td>
</tr>
</tbody>
</table>

Microcapsules morphology

The OM images of MEPCMs are shown in Fig. 5 that reveals smooth and spherical morphology for the microcapsules. The average particle size of 28 and 12 µm were determined for MEPCM-900 and MEPCM-1200, respectively. Also, the shell thickness for the samples was calculated to be 4.0 and 1.7 µm, respectively. Table 4 summarized the properties of synthesized microcapsules.

Fig 5. OM images of a) MEPCM-900 and b) MEPCM-1200

\[
\text{core content (\%)} = \frac{\Delta H_{m,\text{MEPCM}}}{\Delta H_{m,\text{coconut oil}}} \times 100
\]
The feasibility of microencapsulation of coconut oil, as a phase change material, by a PMMA-GO hybrid shell by using UV curable pickering emulsion polymerization was demonstrated. The morphology of microcapsules was found to be dependent on mixing rate, however, the core content was found to be independent from stirring speed.

References


[9] Chevalier, Y. and Bolzinger, M., “Emulsions stabilized with solid nanoparticles: