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

Georgios Kokogiannakis, Sustainable Buildings Research Centre (SBRC), University of Wollongong
gkg@uow.edu.au

Weiguang Su¹, Jo Darkwa, Georgios Kokogiannakis, Tongyu Zhou, Yiling Li

¹School of Mechanical & Automotive Engineering, Qilu University of Technology, Jinan, China
Introduction - MEPCMs

- Phase Change Materials (PCMs): mitigate peak heat gains in buildings and lower peak summer indoor temperatures by storing latent heat as a result of phase change.

- Microencapsulated PCMs (MEPCMs) are PCMs enclosed by a shell (0.05 μm and 5000 μm)

Microencapsulation is a process in which tiny particles or droplets are surrounded by a coating, or embedded in a homogeneous or heterogeneous matrix, to give small capsules with many useful properties.
Microencapsulated Phase Change Materials (MEPCM) - Benefits

- Benefits of microencapsulated Phase Change Materials (MEPCM):
  - Could be integrated in surface layers of building structures: No leaking of the PCM from the surface
  - Have higher heat-transfer area
  - Restricting the core material within a specified volume when phase change occurs
  - A small and portable thermal energy storage system

MEPCM: Challenges

- MEPCMs could make positive impact on the indoor thermal comfort in residential buildings, but the encapsulation process in relation to their thermal properties and stability is still challenging.
- Shell material is the key parameter to ensure the thermal and long term stabilities for applications with MEPCMs.
- A disadvantage in comparison with traditional PCMs is a rather small mass-fraction of PCM that can be used and thus less total heat storage capacity.
Three MEPCM samples were developed and compared by encapsulating paraffin wax within poly(methyl methacrylate-methacrylic acid copolymer) (PMMA-MAA) shells.

The effect of the weight percentage of the initiator and the ratio of shell monomers for MEPCM properties were studied since the PMMA-MAA resins have the ability to be crosslinked at different MMA/MAA molecular ratios.

MMA+MAA=PMMA-MAA
Materials and methods

- n-Octadecane was introduced as a PCM and as a core material: relatively high latent heat capacity and suitable phase change temperature that is within indoor thermal comfort ranges
- Methyl methacrylate (MMA) and methacrylic acid (MAA): shell monomers
- Benzoyl peroxide (BPO): oil-soluble thermal initiator (starts a chain reaction for the monomers to result as a PMMA-MAA polymer)
- Sodium 1-dodecanesulfonate (S-1DS): emulsifier

<table>
<thead>
<tr>
<th></th>
<th>MMA (g)</th>
<th>MAA (g)</th>
<th>n-octadecane (g)</th>
<th>S-1DS (g)</th>
<th>BPO (g)</th>
<th>Initiator (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-MAA1</td>
<td>2.40</td>
<td>0.60</td>
<td>7.00</td>
<td>0.10</td>
<td>0.030</td>
<td>1.0%</td>
</tr>
<tr>
<td>PMMA-MAA2</td>
<td>1.80</td>
<td>1.20</td>
<td>7.00</td>
<td>0.10</td>
<td>0.045</td>
<td>1.5%</td>
</tr>
<tr>
<td>PMMA-MAA3</td>
<td>1.50</td>
<td>1.50</td>
<td>7.00</td>
<td>0.10</td>
<td>0.015</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
Materials and methods

- The morphology, latent heat storage capacity and thermal stability of MEPCM is affected by:
  - The weight percentage of initiator (Benzoyl peroxide)
  - The ratio of shell monomers (MMA vs. MAA)

<table>
<thead>
<tr>
<th></th>
<th>MMA (g)</th>
<th>MAA (g)</th>
<th>n-octadecane (g)</th>
<th>S-1DS (g)</th>
<th>BPO (g)</th>
<th>Initiator (% wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-MAA1</td>
<td>2.40</td>
<td>0.60</td>
<td>7.00</td>
<td>0.10</td>
<td>0.030</td>
<td>1.0%</td>
</tr>
<tr>
<td>PMMA-MAA2</td>
<td>1.80</td>
<td>1.20</td>
<td>7.00</td>
<td>0.10</td>
<td>0.045</td>
<td>1.5%</td>
</tr>
<tr>
<td>PMMA-MAA3</td>
<td>1.50</td>
<td>1.50</td>
<td>7.00</td>
<td>0.10</td>
<td>0.015</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
MEPCM fabrication

Shell monomers + n-octadecane → Thermal initiator → Oil phase

Water + Emulsifier → Water phase

40°C, 7000rpm, 5mins → O/W emulsion

Deoxygenate, 40°C, 250rpm, 1 hour → 80°C, 250rpm, 5hours

MEPCM → Drying → Centrifuge/Wash → Cooling to room temperature
The scanning electron microscope (SEM, Sigma VP (Carl Zeiss Co. Ltd.) was used to observe the morphology of MEPCM samples.

The samples were coated with 5 nm thick gold layer in order to increase their electrical conductivity before the microscopy analysis.
Sample characterizations for latent heat capacity: DSC

- Differential scanning calorimetric (DSC) was used in determining the enthalpies of fusion and melting temperature (onset temperature for heating).
- The samples were tested at atmospheric pressure and at a heating rate of 2°C/min from 5°C to 50°C.
Sample characterizations for thermal stability: TGA

- The thermal stability of the MEPCMs at high temperatures were examined by Thermogravimetric Analysis (TGA).
- The TGA tests 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.
The particle sizes of PMMA-MAA capsules were in the range of 2-10 μm
PMMA-MAA1 demonstrated the best particle morphology
PMMA-MAA2 and PMMA-MAA3 had a lot of wrinkles on the surfaces
Morphologies were particularly influenced by the molar ratios of shell monomers (MMA:MAA) and the use of the thermal initiator.
Best morphology: MMA:MAA weight ratio of 4:1 and 1 wt% thermal initiator.
DSC results for energy storage capacity

DSC curves of n-Octadecane and MEPCM samples
TGA results for thermal stability

TGA curves of MEPCM samples: %weight change as a function of temperature
# Summary of MEPCM properties

<table>
<thead>
<tr>
<th>Items</th>
<th>Melting point (°C)</th>
<th>Latent heat (kJ/kg)</th>
<th>Core material (wt%)</th>
<th>Weight loss starting temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Octadecane</td>
<td>24.12</td>
<td>216</td>
<td>--</td>
<td>129.0</td>
</tr>
<tr>
<td><strong>PMMA-MAA1</strong></td>
<td>23.68</td>
<td>170</td>
<td>79.8%</td>
<td>204.4</td>
</tr>
<tr>
<td><strong>PMMA-MAA2</strong></td>
<td>22.56</td>
<td>164</td>
<td>77.0%</td>
<td>162.3</td>
</tr>
<tr>
<td><strong>PMMA-MAA3</strong></td>
<td>22.92</td>
<td>150</td>
<td>70.4%</td>
<td>192.9</td>
</tr>
</tbody>
</table>
Conclusions

- MEPCMs: easier to integrate in buildings than PCMs
- Three MEPCM samples were successfully fabricated and compared.
- The thermal stability (i.e. measured with weight loss at high temperatures) of PMMA-MMA samples was significantly enhanced.
- The best MEPCM sample was manufactured with a weight ratio of 80% MMA : 20% MAA and thermal initiator of 1 wt%.