Fabrication and characterization of microencapsulated n-heptadecane with graphene/starch composite shell for thermal energy storage

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ABSTRACT

Microencapsulated n-heptadecane phase change material with self-assembled graphene/starch composite shells were prepared through a facile method. The compositions of the microcapsules were chemically evaluated by Fourier transform infrared spectroscopy. The results of Raman spectroscopy, optical microscopy images and scanning electron microscopy observations revealed the presence of the graphene nanoplatelets in the microcapsule shells. The step by step mechanism of the microencapsulation was explained, based on the obtained results. The thermogravimetric analysis results showed that graphene increased the microcapsule thermal stabilities. The graphene contents also facilitated the heat transfer of the microcapsules and improved the temperature control performance by 54% in the presence of 11.35 wt.% of graphene. Phase change properties and thermal reliability of the microcapsules were investigated by differential scanning calorimetry. The microcapsules had remarkable encapsulation ratios, encapsulation efficiencies and long-time operation reliability to use for thermal energy storage applications such as surface coatings for buildings.

1. Introduction

Thermal energy management by solid-liquid phase change materials (PCMs) is an efficient technique to store the latent heat when the phase changes [1,2]. Despite the high heat storage density and small temperature deviation of the PCMs, low thermal conductivity and leakage in the liquid phase are some of the main challenges to use these materials. Microencapsulation of the PCMs is developed to overcome the drawbacks by increasing the heat transfer area and isolating the core materials [3]. The microencapsulation is a process to wrap the micron-sized materials, which is named the core, with a specially featured shell to confine or protect them from the surroundings [4]. Various kinds of organic or inorganic materials were utilized to coat the PCM cores [5,6]. However, the low thermal conductivities of the most shell materials lead to limit the heat transfer across the microencapsulated PCM (MPCM) walls. The insertion of thermal conductivity promoter materials into the PCMs is a confirmed route to enhance the rate of heat transfer [7]. Carbon allotropes are noteworthy substances to improve the MPCM phase change performances, due to their high thermal conductivity, thermal stability and compatibility with the most PCMs [8,9]. Graphene with high substantial thermal conductivity (3000 W/mK) and low density has attracted a tremendous attention in several fields. The planar structure of graphene causes the thermal resistance of the matrix/graphene interface to decrease and facilitates the heat exchange through the matrix more efficient than other types of carbon nanofillers [10–13]. Dao and Jeong [14] encapsulated stearic acid with the self-organized graphene around the PCM cores through electrostatic attraction between the negatively charged core particles and the positively charged graphene. They [15] also prepared stearic acid and poly(vinyl alcohol) functionalized graphene microcapsules by a Pickering emulsion method. Shang and Zhang [16] prepared the graphene oxide (GO) shell for hexadecanol core by a Pickering emulsion templating to improve the thermal stability and leakage protection of the core. The thermal conductivity of MPCMs coated with GO is remarkably improved, compared to the same weight of embedding GO in the core, due to the connection between the conductive elements on the MPCM shells [17]. However, the balance of hydrophobic/hydrophilic properties of the GO through the oxygenic group adjustments on the nanoplatelets is a considerable challenge to achieve an intact monolayer shell. For the MPCM shells composed of graphene only, the adjacent flake interactions are not effective enough to prevent the wall crack formations caused by the volume changes of the PCM phase transitions. The preparation of the graphene-organic or inorganic materials hybrid shells can be considered as a feasible route to improve the thermo-physical
properties of the MPCMs. Wu et al. [18] fabricated microencapsulated n-hexadecane with melamine-urea-formaldehyde wall and graphene via an emulsion polymerization method to improve the heat transfer, thermal stability and leakage prevention performance of the PCM. The silica wall of paraffin/SiO$_2$ microcapsules were modified with GO by Yuan et al. [19]. The embedded GO promoted the thermal, physical and photo-thermal conversion properties of a slurry composed of MPCMs. Zhang et al. [20] synthesized microcapsules containing paraffin as a core and melamine-formaldehyde resin as a shell and a protective GO layer placed between the core and the outer covering. Jiang et al. [21] prepared the microencapsulated paraffin with calcium carbonate and GO shells. The incorporated GO into the shell made cracks on the surface of the microcapsules, although GO reduced the PCM leakage from MPCM due to its barrier property. The PCM microcapsules with self-assembled graphene/methanol modified melamine formaldehyde shells were fabricated by Wang et al. [22] to enhance the thermal properties. The hybrid shells were absorbed onto the core by electrostatic attraction force and chain entanglement.

From our literature survey, the incorporation of graphene in the microcapsule shell improves the thermal properties of the MPCMs. The complex, multi-stage and certain material-dependent process may restrict the use of graphene in the MPCM fabrication. Starch which is known as a multi-source, cheap, eco-friendly and processable material can be used as one part of the MPCM shell. The capabilities of starch to prepare the shape stable cellular skeleton of graphite-PCM composites were reported by Vitorino et al. [23,24]. In our previous work [25], the microcapsules of n-heptadecane, as a paraffin organic PCM, with starch shells were prepared and characterized. In this study, n-heptadecane was microencapsulated with a graphene/starch composite shell by a facile method. Graphene was self-assembled onto the paraffin cores by cooperating with starch and hence the MPCM shells had a hybrid structure of graphene/starch composite. The effects of graphene weight ratios on the size distribution, thermal performance and stability of the microcapsules containing paraffin with graphene/starch shell was investigated. Accordingly, the mechanism of the microencapsulation process was proposed to explain the driving forces and steps of the shell formation onto the paraffin core.

2. Experimental

2.1. Materials

An unmodified food grade potato starch (Alborz Starch Company, Iran) was utilized as the shell materials. Graphene was purchased from Xiamen Knano Graphene Technology Co., Ltd (China). The graphene properties are reported in Table 1. n-Heptadecane, C$_{17}$H$_{36}$, was used as the core materials (Merck, Germany).

2.2. Preparation of microcapsules

n-Heptadecane was microencapsulated by self-assembly of a graphene/starch composite onto the paraffin drops in an aqueous medium. Graphene was dispersed in deionized water by sonication for 60 min (SKL 950-1DN, Ningbo Haishu Sklon Electronic Instrument Co., Ltd, China). Starch was mixed with the graphene/water dispersion and heated to the boiling temperature. The materials were stirred and boiled for 15 min. After that, this aqueous suspension was added to n-heptadecane at 50°C and stirred at 1100 rpm for 60 min to prepare the microcapsules. The amounts of raw materials are presented in Table 2. Finally, the suspension was diluted with distilled water. The top layer of the mixture containing the microcapsules was filtered, washed repeatedly with deionized water and dried for 48 h at the ambient temperature.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum One) was used to study the microcapsule chemical compositions. Raman spectra were obtained by a (Teksan Takram P50C0R10) Raman spectrometer using a laser wavelength of 532 nm.

The microcapsule morphologies were studied by using scanning electron microscope (SEM, LEO 1455 V P) and optical microscope (OM, Optika) equipped with a Canon digital camera. Before the SEM tests, samples were coated with a layer of gold in vacuum conditions.

The mean sizes of the microcapsules were obtained by OM images combined with image analysis (Digimizer software). The averages of 100 measurements were utilized to specify the particle sizes of the samples.

The OM, SEM, FTIR and Raman spectroscopy were carried out at the ambient temperature.

Thermogravimetric analysis (TGA, Pyris Diamond Perkin Elmer) was performed to measure the mass loss of the samples from 25 to 550°C with a heating rate of 10°C/min under flowing 100% nitrogen gas.

The melting and freezing temperatures and latent heats of the microcapsule samples and n-heptadecane were obtained by differential scanning calorimetry (DSC, TA Instrument, Q100). All DSC measurements were performed at a heating and cooling rate of 10°C/min in the nitrogen atmosphere.

To evaluate the thermal reliability, the prepared microcapsules were heated to 50°C and maintained for 10 min, then cooled to 5°C and maintained for 10 min by a laboratory made temperature test chamber. The phase change properties of the sample were investigated by DSC after 100 heating/cooling cycles [26].

The thermal energy performances of the microcapsules were studied through the monitoring of the temperature fluctuations over time. The microcapsules were dispersed in deionized water (10 g/l) at room temperature. The prepared suspensions were placed in water baths at 10°C and 35°C, for solidifying and melting condition, respectively. The temperatures of water were recorded in each condition. The time-temperature curves of the microcapsules were plotted for 3 consecutive measurements.

3. Results and discussion

3.1. FTIR analysis

Table 1

<table>
<thead>
<tr>
<th>Carbon content (wt.%</th>
<th>True density (g/cm$^3$)</th>
<th>Bulk density (g/cm$^3$)</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 99.5</td>
<td>2.25</td>
<td>0.3</td>
<td>40-60</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Deionized water (g)</th>
<th>Paraffin (g)</th>
<th>Starch (g)</th>
<th>Graphene (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>60</td>
<td>1</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>MSG.1</td>
<td>60</td>
<td>1</td>
<td>3</td>
<td>0.1</td>
</tr>
<tr>
<td>MSG.5</td>
<td>60</td>
<td>1</td>
<td>3</td>
<td>0.5</td>
</tr>
</tbody>
</table>
1161 cm\(^{-1}\) are associated with the C–O stretching vibrations [29] in the starch spectrum. The stretching and bending vibrations of OH groups are found at 3435 and 1644 cm\(^{-1}\), respectively [30]. The OH and C–O characteristic bands in the graphene spectrum can be the results of either physical moisture adsorption or small defects on the nanoplatelets. The typical bands of n-heptadecane and starch observed in the MS and MSG.5 spectra revealing that the microcapsules formed completely. There are no strong interactions between the microcapsule cores and shells, because of the negligible shifts in the band wave-numbers, compared to the raw materials.

3.2. Raman spectroscopy

The presence of graphene in the microcapsule shells is demonstrated by Raman spectroscopy. The Raman spectra of MS, graphene and MSG.5 are represented in Fig. 2. In the MS spectrum, the bands at 1065 and 1130 cm\(^{-1}\) are ascribed to the stretching vibrations of C–C and C–O groups. The bending vibrations of C–H groups are identified at 1310 and 1450 cm\(^{-1}\). The peaks in the range of 2690 to 3000 cm\(^{-1}\) are attributed to the C–H stretching vibrations [31,32]. For graphene, three characteristic bands at 1364, 1561 and 2641 cm\(^{-1}\) are ascribed to the D-band, G-band and 2D-band, respectively. The G-band is associated with the in-plane stretching vibrations of sp\(^2\) carbon atoms of graphene sheets. The disordered or amorphous carbons at the edge or inside the graphene flakes appear in the D-bands. The 2D-band corresponds to the D-band overtone caused by two high-frequency phonons with opposite momentum vibrations [33]. In addition of MS distinctive bands, the typical peaks of graphene exist in the MSG.5 spectrum confirming that the n-heptadecane was coated with a graphene/starch composite shell.

3.3. Morphology and particle size analysis

The spherical shapes of the prepared microcapsules are shown in OM images of Fig. 3. The graphene flakes are observed on the surfaces of MSG.1 and MSG.5 in the form of black aggregates. The mean particle sizes of MS, MSG.1 and MSG.5 are 50 ± 5, 60 ± 10 and 50 ± 5 μm, respectively.

Fig. 4 represents the SEM micrographs of graphene, MS and MSG.5. The two dimensional multi-layer graphene nanoplatelets with the diameter of 1–20 micrometers are observed in the SEM morphology. The core-shell structure of the samples can be observed from the SEM images of the damaged microcapsules in Fig. 4. The SEM images show the intact shell of MS with a rough surface which can be attributed to the accumulation of starch components onto the n-heptadecane core droplets. The layered structure of the MSG.5 shells is associated with the self-assembled graphene onto the core drops. In the damaged SEM image of MSG.5, the attached graphene nanoplatelets to the fractured shell demonstrate the presence of graphene in the MSG.5 microcapsule shell. The graphene/starch composite adsorbed on the outer layer of the core and changed the MSG.5 shell surface morphology compared to MS.

3.4. Mechanism of the microencapsulation

The microencapsulation mechanism of n-heptadecane with the
graphene/starch composite shell can be interpreted based on the material features and the results of the microcapsule characterizations. In the process of the microencapsulation, starch was mixed with the graphene/water dispersion and the suspension was heated to the boiling temperature. The heating and shearing of the suspension caused the starch components, including amylose, amylopectin and polar lipids, to extract from the granules into water. Amylose chains configured as helices to reduce the surface energy. The helix configuration was sustained via hydrogen bondings among polar groups of amylose. Therefore, the effective hydrogen bonds were not created between the helices and water, and the dispersion of helices was not stable in water. The polar lipids, which typically consisted of a polar head and a non-polar tail, migrated into the amylose helices by their tail to make a stable position. This structure is known amylose-lipid complex that the lipid heads are placed at the outer end of the helix, and so the complex has a polar head and a less polar tail [34]. The dual functional amylose-lipid complexes migrated to the graphene surfaces, as the non-polar particles, by the helix tails [35]. Some other starch components may attach onto the adsorbed amylose-lipid complexes of graphene over time, because of the chemical similarity and instability of their dispersion in water. The increasing of the graphene content led to decrease the starch coating thickness on graphene, because of the more available surfaces to adsorb the starch components. For MSG.1, the starch adsorbed layer on graphene and final shell were thicker than that of MSG.5. Subsequent to the addition of n-heptadecane into graphene/starch/water suspension, the globular shaped paraffin droplets formed at once, due to the high shear stirring. The non-polar n-heptadecane droplets may coat with the remaining free amylose-lipid complexes, same as graphene. The adsorbed amylose-lipid complex formed a first layer of the starch shell around the paraffin cores. After that, the graphene/starch composite adsorbed gradually onto the first layer of the shell, caused by the tendency to accumulate the starch components of both to each other. Conclusively, the graphene/starch composite shells formed through the adsorption of the amylose-lipid complex at first, and multi-stage self-assembly of the graphene/starch composite onto the first layer (Fig. 5). The remaining starch components and graphene settled down the

Fig. 3. OM images and particle size distribution curves of MS, MSG.1, and MSG.5.
beaker after the mixing was stopped.

3.5. Thermal stability

Thermal stability of the microcapsules was evaluated by TGA. The TGA curves of graphene, n-heptadecane, starch, MS, MSG.1 and MSG.5 are demonstrated in Fig. 6. The degradation temperatures, weight loss values and ash contents are reported in Table 3. Graphene had no significant weight loss from 25 to 550 °C. n-Heptadecane decomposed completely in one stage between 101 °C and 183 °C. Starch lost about 10% of its weight at around 100 °C attributed to the moisture in the starch granules. The main weight loss of starch began at 263 °C, and the residual weight was zero at 550 °C. The microcapsule samples exhibited two steps degradation. The first weight loss stage is attributed to evaporation of the core material, while the second mass loss corresponds to the wall decomposition. The microcapsule shells made a protective barrier around the paraffin cores and delayed their thermal decomposition, compared to the pure n-heptadecane. The thermal stability of the microcapsule cores and shells improved in MSG.1 and MSG.5. Degradation of the microcapsules occurred at higher temperature with increasing the graphene content. The increasing the shell thermal stabilities of MSG.1 and MSG.5, compared to MS, indicate the presence of
Graphene in the microcapsule shells. It can be ascribed to the formation of more intact and stable shells onto the n-heptadecane core in the presence of graphene. Consequently, graphene caused the microcapsules thermal stabilities to improve. For MSG.1 and MSG.5, the final ash contents were 7.57% and 11.35%, respectively. The residue is attributed to the graphene weight ratios in the microcapsule shells, due to the thermal stability of graphene. The graphene contents of the microcapsules do not correspond to the incorporated graphene in the raw materials caused by the sedimentation of the non-adsorbed graphene nanoplatelets and the starch components at the end of the process. The starch part of the shell decreased from 38.31% for MSG.1 to 14.25% for MSG.5. The more initial graphene content of MSG.5, compared to MSG.1, caused less adsorbed starch component on the graphene flakes and the core/shell ratio to increase, as mentioned in the microencapsulation mechanism.

3.6. Phase change characterization

The temperatures and enthalpies of melting and solidifying of the microcapsules were evaluated using DSC. The DSC thermograms of n-heptadecane, MS, MSG.1 and MSG.5 are shown in Fig. 7. The obtained results of the DSC curves are reported in Table 4. The supercooling (difference between melting and solidifying temperatures) of n-heptadecane was 5.71 °C. The MS supercooling slightly increased to 5.91 °C, due to the limited nucleation in the microcapsules. For MSG.1 and MSG.5, the supercooling reduced to 5.29 and 4.41, respectively. The reduction of supercooling in MSG.1 and MSG.5 can be attributed to the change of shell morphology in presence of graphene and facilitation of heterogeneous nucleation in the microcapsules. n-Heptadecane had melting and solidifying enthalpies of 239.26 and 233.29 J/g, respectively. For the microcapsule samples, the phase change occurs through n-heptadecane as the core, and the starch shell has no effect on the amounts of heat absorption and release. The encapsulating ratio (R) and encapsulation efficiency (E) are two important parameters to characterize the thermal properties of the MPCMs. These parameters are calculated from the below equations [36]:

$$R = \frac{\Delta H_{m,MPCM}}{\Delta H_{m,PCM}}$$  
$$E = \frac{(\Delta H_{m,MPCM} + \Delta H_{c,MPCM})}{(\Delta H_{m,PCM} + \Delta H_{c,PCM})}$$

![Fig. 5. Schematic Mechanism of the microencapsulation of n-heptadecane with graphene/starch composite shell.](image)

![Fig. 6. TGA curves of n-heptadecane, starch, MS, MSG.1, MSG.5 and graphene.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>First stage decomposition</th>
<th>Second stage decomposition</th>
<th>Final ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T onset (°C)</td>
<td>T endset (°C)</td>
<td>T onset (°C)</td>
</tr>
<tr>
<td>Graphene</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>n-Heptadecane</td>
<td>101</td>
<td>183</td>
<td>–</td>
</tr>
<tr>
<td>Starch</td>
<td>40</td>
<td>100</td>
<td>9.27</td>
</tr>
<tr>
<td>MSG.1</td>
<td>131</td>
<td>208</td>
<td>54.12</td>
</tr>
<tr>
<td>MSG.5</td>
<td>142</td>
<td>210</td>
<td>74.13</td>
</tr>
<tr>
<td>MSG.1</td>
<td>131</td>
<td>208</td>
<td>54.12</td>
</tr>
<tr>
<td>MSG.5</td>
<td>142</td>
<td>210</td>
<td>74.13</td>
</tr>
</tbody>
</table>

![Table 3. TGA results of n-heptadecane, starch, MSG.1, MSG.5 and graphene.](image)
Where $\Delta H_{m,PCM}$ and $\Delta H_{m,MPCM}$ are the melting enthalpies of n-heptadecane and the prepared MPCMs, respectively and $\Delta H_{c,PCM}$ and $\Delta H_{c,MPCM}$ are the solidifying enthalpies of n-heptadecane and the prepared MPCMs, respectively. The encapsulation efficiency describes the relative performance of the microcapsules for latent heat storage, respect to the PCM [28]. The encapsulation ratio can be attributed to the weight ratio of the core involving in the phase change. The R and E results of MSG.5 and MS are close together indicating the graphene/starch composite shell had no considerable negative effect on the phase change properties of the microcapsules. However, MSG.1 showed the least R and E results, compared to the other samples. The less thermal enthalpy of MSG.1 can be attributed to its thicker shell and less core content, due to large amounts adsorption of starch onto the graphene flakes, as mentioned in the mechanism of the microencapsulation and TGA results.

3.7. Temperature control performance

The microcapsule temperature control performances were investigated by monitoring the variations of water temperature, as the surrounding medium, versus time. The PCMs can postpone the changes of the temperature via absorbing and releasing the thermal energy as the latent heat. The increasing the rate of heat exchange to the PCM causes its effectiveness to improve. The temperature control functions of the microcapsules are depicted in Fig. 8. The variation rates of water temperature slowed down by about 13% in presence of MS, compared to the pure water. MSG.5 had the maximum delay of 54% for the temperature variations of surrounding medium. The temperature control performance in MSG.5 improved by 36% compared to MS. The temperature change delay was 15% for MSG.1, in comparison to MS, even with the lower thermal efficiency. Graphene facilitated the heat transfer through the shell of the microcapsules and accelerated the rates of heat absorption and release. Therefore, the heat transfer improvement can compensate the lack of high thermal efficiencies. The n-heptadecane core operated more efficiently as a PCM, in the microcapsules with graphene/starch composite shells.

3.8. Thermal reliability

Thermal reliabilities of the microcapsules were investigated by DSC results after thermal cycling test. The DSC thermogram of MSG.5 after 100 heating-cooling cycles (MSG.5–100) is shown in Fig. 9. The summarized results of the DSC curves are also tabulated in Table 4. The melting and solidifying temperature of MSG.5–100 increased by 0.46 °C and decreased by 0.17 °C, respectively, compared to MSG.5. The melting and solidifying enthalpies of MSG.5 decreased by 4.19 J/g and 1.2 J/g, respectively after 100 heating-cooling cycles. The negligible

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melting $T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>Solidifying $T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>Encapsulation ratio (%)</th>
<th>Encapsulation efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Heptadecane</td>
<td>21.50</td>
<td>239.26</td>
<td>15.79</td>
<td>233.29</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MS</td>
<td>23.13</td>
<td>174.30</td>
<td>17.22</td>
<td>171.92</td>
<td>72.85</td>
<td>73.27</td>
</tr>
<tr>
<td>MSG.1</td>
<td>22.87</td>
<td>130.14</td>
<td>17.58</td>
<td>113.60</td>
<td>54.39</td>
<td>51.58</td>
</tr>
<tr>
<td>MSG.5</td>
<td>21.69</td>
<td>172.28</td>
<td>17.28</td>
<td>171.34</td>
<td>72.01</td>
<td>72.72</td>
</tr>
<tr>
<td>MSG.5-100</td>
<td>22.15</td>
<td>168.09</td>
<td>17.11</td>
<td>170.14</td>
<td>70.25</td>
<td>71.58</td>
</tr>
</tbody>
</table>

Fig. 7. DSC thermograms of n-heptadecane, MS, MSG.1 and MSG.5.

Fig. 8. Temperature control performances of the prepared microcapsules.

Fig. 9. Thermal reliability of MSG.5 after 100 thermal cycles.
fluctuations in phase change properties of the MSG.5 after thermal cycling showed the high thermal reliability of the n-heptadecane microcapsules with the graphene/starch composite shells.

4. Conclusions
An innovative facile method was proposed to microencapsulate n-Heptadecane, as a phase change material, with a graphene/starch composite shell. The regular spheroid microcapsules formed through the adsorption of the amyllose-lipid complex around the n-heptadecane core followed by self-assembly of the graphene/starch onto the first layer. The increasing of the graphene incorporation amounts caused the graphene contents in the shell to increase. The presence of graphene in the microcapsule shells increased the thermal stability. The prepared microcapsules had high encapsulation ratios, encapsulation efficiencies and a remarkable thermal reliability. The shell graphene content of 11.35 wt.% improved the temperature control performances of the microcapsules by 54%. The microencapsulated n-heptadecane with the graphene/starch composite shell had proper properties to be applied in surface coatings, fluids and other related media for thermal energy storage.

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