Preparation and properties of highly conductive palmitic acid/graphene oxide composites as thermal energy storage materials

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Abstract

PA/GO (palmitic acid/graphene oxide) as PCMs (phase change materials) prepared by vacuum impregnation method, have high thermal conductivity. The GO (graphene oxide) composite was used as supporting material to improve thermal conductivity and shape stabilization of composite PCM (phase change material). SEM (Scanning electronic microscope), FT-IR (Fourier transformation infrared spectroscope) and XRD (X-ray diffractometer) were applied to determine microstructure, chemical structure and crystalloid phase of palmitic acid/GO composites, respectively. DSC (Differential scanning calorimeter) test was done to investigate thermal properties which include melting and solidifying temperatures and latent heat. FT-IR analysis represented that the composite instruction of porous palmitic acid and GO were physical. The temperatures of melting, freezing and latent heats of the composite measured through DSC analysis were 60.45, 60.05°C, 101.23 and 101.49 kJ/kg, respectively. Thermal cycling test showed that the form-stable composite PCM has good thermal reliability and chemical stability. Thermal conductivity of the composite PCM was improved by more than three times from 0.21 to 1.02. As a result, due to their acceptable thermal properties, good thermal reliability, chemical stability and great thermal conductivities, we can consider the prepared form-stable composites as highly conductive PCMs for thermal energy storage applications.

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1. Introduction

Latent heat storage is a relatively new area of research in the improvement of efficient energy management. Because of the high energy storage during the melting process, PCMs (phase change materials) which have certain operating temperatures are widely used for heat storage. It is also noteworthy to mention that because of their small volume and less heat loss they can be applied in different applications. The most important application fields of PCM are energy conversion in buildings, solar energy systems, thermal insulation and green houses and textiles [1].

Some organic and inorganic materials are used as PCM as they have high thermal storage capability and other properties such as good thermal stability and little supercooling, but most of them have their own disadvantages. First, they have some problems in cooling process because of low thermal conductivity that causes supercooling [2–4]. The other problem observed in most of researches on PCMs is the leakage of PCMs after melting temperature; however there are some solutions for these problems. For example many supporting materials like high density polyethylene, composite materials, etc. are used to solve this problem [5–9]. Currently many researches are done to use inorganic materials such as EG (expanded graphite) and SiO2 composites as they have great porosity and surface area that help to have better performance and thermal stability. The low thermal conductivity of PCMs also was solved by adding high thermal conductivity substances such as carbon fibers, EG and other additives that can affect overall thermal conductivity of PCMs [10]. Various methods have been investigated for increasing the thermal conductivity of PCMs. These methods include dispersing high conductivity particles within the PCM, inserting a metallic matrix and adding chunks of metal tubing into the PCM, inserting carbon fibers either arranged along a brush or randomly oriented and impregnating a porous graphite matrix with PCM [11,12].

GO (graphene oxide) is novel material that has been used in many fields due to high thermal and electrical conductivity. The
main reason GO was used as a supporting material in current research because of high specific surface area and thermal conductivity.

In this research impregnation method is used for incorporation of PA (palmitic acid) as PCM in porous composite (GO). Palmitic acid is a favorable organic PCM for thermal energy storage which melts at 61.14 °C with a latent heat of 202.00 kJ/kg and solidifying at 59.84 °C with a latent heat of 208.87 kJ/kg. GO composite prepared by modified Brodie's method from graphite and characterization done by FT-IR (Fourier transformation infrared spectroscopy) and XRD (X-ray diffractometer) [6]. This research is focused on the determination of thermal properties and thermal reliability of PA/GO composite after thermal cycling by using DSC (Differential scanning calorimeter), meanwhile it tries to suggest a new way in improving thermal conductivity of composite PCM by using GO (graphene oxide).

2. Experimental

2.1. Materials

Palmitic acid (99% — Fisher Scientific Inc.) was used as phase change material. Graphite powder was from Sigma Aldrich Inc. (particle size < 20 μm, thermal conductivity 4–100 W/m K). Sodium chloride, nitric acid and hydrochloric acid were purchased from Fisher Scientific Inc.

2.2. Preparation of graphene oxide

Graphene oxide was made by modified Brodie’s method. Graphite powder (10 g) was mixed with fuming nitric acid (200 ml). The mixture was heated in a water bath to 60 °C and sodium chloride (80 g) was gradually added. The mixture was kept for 24 h at 60 °C and then it was washed and filtered with water and hydrochloric acid. The whole procedure was repeated for 5 times. GO (graphene oxide) achieved through sedimentation, finally dried at 70 °C.

2.3. Preparation of PA/GO composite PCMs

Vacuum impregnation was done to produce PA/GO composite PCM. Fig. 1 shows the process for making composite PCM step by step. The PCM materials and GO sheets were positioned in a vacuum furnace. First of all, the vacuum procedure was done by vacuuming furnace under vacuum pressure of 100 kPa for 2 h in order to discharge air from pores of GO sheets. Second, PA was melted in 90 °C in the vacuumed furnace and GO sheets were physically immersed in liquid PA for 3 h. The vacuum pump was switched off to allow the air to reenter the furnace and then composite PCM was removed from liquid PA by using a stainless mesh. The liquid PA that had not been infiltrated in the pores of GO sheets was removed by keeping composite PCM in the furnace at 120 °C. Finally, the products were taken out from the furnace and dried [13].

The procedure was done for four different GO (graphene oxide) sheets and all analyses were done for different sheets to get maximum mass percentage of impregnated PA into the pores of GO.

2.4. Analysis methods

SEM (Scanning electron microscopy) was used to observe the microstructures of the shape-stabilized composite PCMs, and the images were taken with a CARL ZEISS-AURIGA 60 microscope. The chemical structure analysis of the PA/GO composite was done before and after of thermal cycles by Fourier Transformation Infrared Spectrometer (Perkin Elmer-spectrum100 model FT-IR) in the wave ranges of 4000—400 cm⁻¹. X-ray test was done for investigation of crystalloid phase of the PA/GO composites by an X-ray diffractometer (XRD; EMPYREAN, PANALYTICAL). The melting and freezing temperatures and latent heat of PCM were obtained by differential scanning calorimeter (Mettler Toledo-DSC 820) at a heating rate of 5 °C/min in purified nitrogen atmosphere.

The weight loss and thermal stability of PCMs are obtained by TGA (thermogravimetric analysis) (Mettler Toledo-SDTA851) at a heating rate of 10 °C/min and temperature of 30—600 °C. Thermal conductivities of pure PA and composite PCMs were measured by thermal properties analyzer (KD-2 Pro Model) in a specific temperature and repeated for four times until maximum relative error of ±4 was found.

2.5. Thermal cycling test

To determine the thermal stability of PA/GO composite PCMs during melting and freezing process, a thermal cycling test was done using a thermal cycling system of in-house design (university of Malay). The thermal cycling system was designed to operate between 30 °C and 80 °C. The schematic and picture of the thermal cycling system are shown in Fig. 2. The tests were done by using a fan and a heater as cooling and heating parts, the digital Indicating Controller (Shinko-ACS-13A) for controlling the melting and freezing process, the communication converter (Shinko-IDF-400) to transfer data to personal computer (PC) and controller program, the relay (Idec-SM25) to control heater and power supplies for fans and heater. The heater was located behind the PCM container and a thermocouple was placed inside the PCM to check temperature and send data to Digital Indicating Controller. First, the specified

![Fig. 1. Vacuum impregnation set-up.](image-url)
amount of PCMs was placed in the container while the thermocouple was carefully placed inside the PCM to measure temperature and send data to communication converter. Second, by operating program in PC, cycling started and melting was done by heating up to 80 °C, then immediately freezing was started by switching off the heater while the fan was turned on until the temperature reduced to 30 °C. The cycles were done up to 2500 thermal cycles and the temperature variations of composites were automatically recorded in PC by accuracy of ±0.1 °C.

3. Results and discussion

3.1. Characterization of form-stable PA/GO composite PCM

FT-IR spectroscopy was done for characterization of composite PCM to investigate chemical compatibility between PA and GO. Fig. 3 shows FT-IR results for PA (palmitic acid) and PA/GO composite PCM. The peaks at 2915.02 cm\(^{-1}\) and 2853.57 cm\(^{-1}\) are the symmetrical stretching vibration peaks of \(\text{CH}_2\) in PA. The absorption peak at 1720 cm\(^{-1}\) is assigned to the C=O stretching vibration. The peak at 1321 cm\(^{-1}\) corresponds to the in-plane bending vibration of the –OH group of palmitic acid, the peak at 910 cm\(^{-1}\) corresponds to the out-of-plane bending vibration of the –OH functional group and the peak at 730 cm\(^{-1}\) represents the in-plane swinging vibration of the –OH functional group. It can be clearly seen from both FT-IR spectra there is no shift in the above main absorption peaks and in composite PCM can clearly indicate PA absorption peaks. This result shows that there is no chemical reaction between functional groups of PA and GO. The PA was impregnated in pores of GO sheets and leakage of PA from composite PCM was prevented.

3.2. XRD patterns of PA/GO composites PCM

Fig. 4 shows the XRD patterns of the GO (graphene oxide), PA and GO/PA composite PCM. Curve a in Fig. 4 shows that GO has peaks at around 14° and 43° that is observed in pervious works [14]. Curve b in Fig. 4 shows the XRD peaks at 8°, 13°, 24°, 25° and 27.0° are made by the PA because of its given crystallization. Curve c in Fig. 4 indicates that the XRD peaks of the PA in the composites...
PCM are also stated on the basis of the GO major peaks and it shows that the crystal formation of the PA in the composites PCM did not change during the impregnation process. The intensity of the X-ray peaks of the PA in the GO composites is lower than that of pure PA. This result shows that due to the limitation of the crystals of the PA by pores of the GO composite the crystallite size of the PA becomes smaller in the composites.

3.3. Microstructure analysis of the composite PCMs

Fig. 5 is the SEM image of the GO (graphene oxide) and Fig. 6 is image of the PA/GO composite PCM. In Fig. 6, the black and white parts are the PA and GO substances within the composite PCMs, respectively. It was observed how the PA distributed into the pores of GO sheet used as the supporting material. The composite material retains its form without having leakage of the melted PA during phase change procedure.

3.4. Thermal properties of PA and form-stable PA/GO composite PCM

DSC analyses results are shown in Figs. 7 and 8 for the PA, PCM1, PCM2, PCM3 and PCM4, also melting and freezing temperatures as well as latent heats are measured and shown in Table 1. As seen in Table 1, the melting and solidifying temperatures are determined to be 61.14 °C and 59.84 °C for the PA, respectively, and 60.45 °C and 60.05 °C for the PCM2. The melting and solidifying latent heats are measured to be 202.00 kJ/kg and 208.87 kJ/kg for the PA, respectively, 101.23 kJ/kg and 101.49 kJ/kg for the PCM2.

In the composites, during the melting and solidifying process only PA absorbs and releases thermal energy so high latent heat storage capacity in composite PCM is result of high phase change material content. The mass percentage of PCM (namely palmitic acid in this case) is calculated according to Ref. [15] as follows:
where PCM (wt%) represents the mass percentage of PA in the composites, $\Delta H_{\text{PCM}}$ indicates the melting latent heat of the composites, and the $\Delta H_{\text{PA}}$ shows the melting latent heat of PA as determined by the DSC test. Hence, the PCM mass percentages of PCM1, PCM2, PCM3 and PCM4 were 49.78 wt%, 50.11 wt%, 49.39 wt% and 40.60 wt%, respectively. The highest mass percentage of PA in GO sheets was determined to be 50.11 wt% for PCM2 that melts at 60.45 $^\circ$C with a latent heat of 101.23 kJ/kg and solidifies at 60.05 $^\circ$C with a latent heat of 101.49 kJ/kg. The differences between melting temperatures and solidifying temperature of PA and PCM composites from Table 1 show that the supercooling degree of composite PCMs is smaller than PA during solidification process. These results show that GO as supporting material protecting PA due to the porous wall of the GO acting as nucleation agent. The results also indicate that the synthesis method is repeatable.

3.5. Thermal stability of form-stable PA/GO composite PCM

The TGA and DTG (derivative thermogravimetric) curves of PA and PCM2 are shown in Figs. 9 and 10. The result shows that there are two steps of weight loss for PCM2. As shown in Fig. 10 the first step happens at temperature between 230 $^\circ$C and 310 $^\circ$C that belongs to the thermal degradation of the PA molecular chains while second step occurs after 430 $^\circ$C as for the thermal degradation of the GO. Charred residue amount of PA and PCM2 at 600 $^\circ$C was determined to be 1% and 26.36% respectively. The latent heat values of composite PCM were changed by 0.52%, 1.09% and −1.04%, −1.59% and −1.39 % for freezing process after 500, 1500 and 2500 cycles, respectively. The changes in melting and freezing temperature of composite PCM are not significant for latent heat thermal energy storage (LHTES) applications. The decrease in latent heat values is in an acceptable level for LHTES applications for composite PCM [17].

In addition, Fig. 13 shows the FT-IR spectra of PCM2 before and after 2500 thermal cycles. Fig. 13 shows that there are no essential changes in the form and wave number of main peaks after thermal cycling. These results prove that chemical structure of PA/GO composite PCM was not affected during thermal cycling. Accordingly, the form-stable PA/GO composite PCM is stable in chemical and thermal properties after 2500 thermal cycles.

Table 1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Melting Temperature (°C)</th>
<th>Latent heat (kJ/kg)</th>
<th>Solidification Temperature (°C)</th>
<th>Latent heat (kJ/kg)</th>
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<tr>
<td>PA</td>
<td>61.14</td>
<td>202.00</td>
<td>59.84</td>
<td>208.87</td>
</tr>
<tr>
<td>PCM1</td>
<td>61.25</td>
<td>100.56</td>
<td>58.21</td>
<td>101.05</td>
</tr>
<tr>
<td>PCM2</td>
<td>60.45</td>
<td>101.23</td>
<td>60.05</td>
<td>101.49</td>
</tr>
<tr>
<td>PCM3</td>
<td>61.05</td>
<td>99.78</td>
<td>60.15</td>
<td>100.07</td>
</tr>
<tr>
<td>PCM4</td>
<td>59.65</td>
<td>100.21</td>
<td>58.45</td>
<td>100.67</td>
</tr>
</tbody>
</table>

Fig. 8. Solidifying DSC curves of the PA and PCM1—PCM4.

Fig. 9. TGA curves of the PA and PCM1—PCM4.

Fig. 10. DTG curves of the PA and PCM2.

3.6. Thermal reliability of the form-stable PA/GO composite PCM

Thermal cycling test was performed to investigate properties of composite PCM after a large number of melting and freezing cycles. Thermal cycling test was done up to 2500 cycles and DSC analysis performed for PCM2 after 500, 1500 and 2500 cycles. Results are shown in Figs. 11 and 12. Thermal properties of composite PCM before and after thermal cycling are given in Table 2. After thermal cycling, the melting temperature after 500, 1500 and 2500 cycles changed 0.18, 0.48 and 0.42 $^\circ$C and freezing temperature changed by −0.38, −0.32 and −0.63 $^\circ$C, respectively. The latent heat values of composite PCM were changed by 0.52%, 1.09% and −1% for melting process and −1.04%, −1.59% and −1.39 % for freezing process after 500, 1500 and 2500 cycles, respectively. The changes in melting and freezing temperature of composite PCM are not significant for latent heat thermal energy storage (LHTES) applications. The decrease in latent heat values is in an acceptable level for LHTES applications for composite PCM [17].

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3.7. Thermal conductivity of PA/GO composites

The thermal conductivity of PA and composite PCMs was measured by a thermal conductivity apparatus (KD-2 Pro) by using the hot wire method. Thermal conductivity of composite PCMs was measured in solid state before melting temperature and after melting temperature of PA in thermal equilibrium condition. The results are presented in Table 3 for PA and PCM1–PCM4. As shown in Table 3 in solid state (25 °C) and molten state (60 °C), the thermal conductivity of PA/GO composites is much higher than PA. The thermal conductivity of the PCM2 in both molten and solid regions was increased by more than three times compared to the PA thermal conductivity.

Table 3
Thermal conductivity of the PA, PCM1–PCM4.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Thermal conductivity (W/m K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molten state (60 °C)</td>
</tr>
<tr>
<td>PA</td>
<td>0.26</td>
</tr>
<tr>
<td>PCM1</td>
<td>1.13</td>
</tr>
<tr>
<td>PCM2</td>
<td>1.08</td>
</tr>
<tr>
<td>PCM3</td>
<td>1.38</td>
</tr>
<tr>
<td>PCM4</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Fig. 11. Melting DSC curves of the composite PCM before and after thermal cycling.

Fig. 12. Solidifying DSC curves of the composite PCM before and after thermal cycling.

Table 2
Thermal properties of PA/GO composite PCM before and after thermal cycling.

<table>
<thead>
<tr>
<th>Cycling number</th>
<th>Melting temperature (°C)</th>
<th>Melting latent heat (kJ/kg)</th>
<th>Freezing temperature (°C)</th>
<th>Freezing latent heat (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60.45</td>
<td>101.23</td>
<td>60.05</td>
<td>101.49</td>
</tr>
<tr>
<td>500</td>
<td>60.63</td>
<td>101.76</td>
<td>59.67</td>
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<tr>
<td>1500</td>
<td>59.97</td>
<td>102.34</td>
<td>59.73</td>
<td>99.87</td>
</tr>
<tr>
<td>2500</td>
<td>60.03</td>
<td>100.21</td>
<td>59.42</td>
<td>100.08</td>
</tr>
</tbody>
</table>

Fig. 13. FT-IR spectra of PA/GO composite PCM before and after thermal cycling.

Fig. 14. Temperature graph of PA and PCM2 for melting process.

Fig. 15. Temperature graph of PA and PCM2 for solidification process.
The improvement of thermal conductivity in PA/GO composite PCM was also verified with comparison of the melting and freezing time of PA and PA/GO composite PCM. The melting and freezing graphs of PA and PCM2 are shown in Figs. 14 and 15. As we can see in Fig. 14 the melting time will be 38 min for pure PA and 23 min for PCM2 and as it shows that the melting time was reduced by 39.4%. Freezing time also shown in Fig. 15 decreased by 60.6% from 33 min for pure PA to 13 min for PCM2. This result also indicates that the thermal conductivity in composite PCM is more intensive.

4. Conclusions

The new composite PCM was prepared by impregnation method and palmitic acid used as a phase change material for thermal energy storage and GO (graphene oxide) used as supporting material. The highest mass percentage of PA was found 50.11% in the composite. Characterization was done by SEM, XRD and FT-IR spectroscopy techniques. The phase change temperatures and latent heats of composite PCM were measured by DSC analysis to be 60.45 and 60.05 °C and 101.23 and 101.49 kJ/kg, respectively. The composite PCM had a good thermal reliability in terms of thermal properties and chemical stability after 2500 melting/freezing cycles. In addition, thermal stability of composite has been improved according to the TGA results, it shows that thermal stability of the composites PCM was improved by GO. Thermal conductivity of the composite PCM was measured in melting and solidifying state and in both states it also increased significantly. On the whole, PA/GO composite PCM proved that can be used as promising PCM for latent heat storage systems because of the higher thermal conductivity and good thermal properties as well as reliability after high number of thermal cycling.

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