Superhydrophobic Copper Foam Supported Phase Change Composites with High Thermal Conductivity for Energy Storage

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Superhydrophobic and superoleophilic oxidized copper foam (OCF) was prepared by oxidation of copper foam using (NH4)2S2O8 to generate rough surface then followed by modification with low surface energy substance polydimethylsiloxane (PDMS) and stearic acid (SA). Based on sperwetting, form-stable phase change materials (PCMs) composites were obtained by facile absorbing of organic PCMs into PDMS-OCF network. In this way, the organic PCMs can be spontaneously adsorbed and remain stable without leakage even at high temperature over their melting points, and the thermal storage capacity of the as-synthesized PCMs composites were analyzed using a differential scanning calorimeter (DSC). The latent heats of the PDMS-OCF/PCMs composites were measured to be 36.87 J g⁻¹ and 36.81 J g⁻¹ for PDMS-OCF/paraffin and PDMS-OCF/SA, respectively, which is greater than that of untreated copper form (CF)/paraffin composite (8.50 J g⁻¹). The PDMS-OCF/PCMs composite shows better thermal stability and the loaded organic PCM has been reduced by 0.64% after 100 times of melting-cooling recycling for PDMS-OCF/paraffin. The thermal conductivity of PDMS-OCF/paraffin composite is about 9 times that of pure paraffin. Such excellent thermal conductivity as well as good thermal stability of the PDMS-OCF/PCMs makes it promising candidate for thermal energy storage.

Keywords: superhydrophobic, copper foam, phase change material, thermal conductivity.

1. Introduction

With the continuous development of human society and economy, the consumption of energy was sharp increase, and environmental protection have been the focus of global studies. Although the kind of eco-friendly energy such as solar energy and geothermal energy may substitute the conventional source of energy. However, these energy is under a mismatch of demand and supply issues in time and space¹. In this regard, thermal energy storage for those renewable energy is a possible solution to this issue. And phase change materials (PCMs) can be used for thermal energy storage when or where in excess and deliver it when or where needed, e.g. waste heat recovery²,³ and building energy saving⁴.

Usually, PCMs is a substance which is capable of storing and releasing large amounts of thermal energy during the state between melting and solidifying at a certain temperature. In this way, heat is absorbed or released when the material changes from solid to liquid and vice versa⁵. PCMs are mainly divided into organic compounds, inorganic salts and their eutectics⁶. Generally, inorganic salts PCMs possess higherenthalpy than that of those organic PCMs and have widely been adapted as a heat storage medium at high temperature environment. However, the obvious drawbacks such as super-cooling and high corrosion of inorganic PCMs limit their practical applications. In comparison, organic PCMs have little phenomenon of super-cooling and low corrosion, which are generally used at a relative low temperature environment. However, organic PCMs have limitations in their low thermal conductivity due to their inherent organic compound nature, which would lead to a low diffusion and delivery of heat thus lower their thermal storage performance.

Although organic PCMs have been widely studied due to their high latent heat storage capacity and appropriate thermal properties⁷. However, there is a serious problem need to be addressed for direct applying of organic PCMs, that is, leakage of organic PCMs would occur when PCMs are melted. Along this line, many approaches have been exploited to overcome this issue. For example, organic PCMs as the core were encapsulated by microcapsules which acted as the shell⁸. However, this method has some drawbacks, such as high cost and complicated manufacturing processes. Accordingly, a cost-effective method has been developed by utilizing porous materials as supporting materials to load the organic PCMs to construct form-stable PCMs composites. To date, porous materials, including plaster⁹, carbon aerogel¹⁰, graphene¹¹, carbon nanotubes¹², exfoliated graphite nanoplatelets¹³, halloysite nanotube¹⁴,¹⁵, conjugated microporous polymers¹⁶ and ceramic composites¹⁷, have been reported for incorporation of organic PCMs to this end. In fact, the stability of such form-stable PCMs composites depends on the interaction between the organic PCMs and supporting materials to some extent. In our previous

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studies, we have developed a series of porous materials with superwetting wettability, including graphene-nickel \(^\text{18}\) and PDMS-HNTs \(^\text{19}\), for loading of organic PCMs to fabrication of PCMs composites. In such systems, the affinity of organic PCMs, especially for those lipophilic organic PCMs, e.g. paraffin, to the supporting materials could be significantly enhanced, which would result in an enhancement in the thermalstability of resulting PCMs composites.

In this work, we developed a new approach utilizing copper foam as supporting material, and paraffin and stearic acid as organic PCMs, to prepare novel PCMs composites. Firstly, the petal-like nanometer-sized roughness surface of copper foam was generated by oxidation method, followed by modification of the OCF with PDMS via the chemical vapor deposition (CVD) method. Under such treatment, the PDMS-OCF exhibits an interesting superhydrophobic and superoleophilic wettability. By employment of PDMS-OCF as support material, PCMs composites were prepared by direct loading of paraffin wax and stearic acid into PDMS-OCF through a simple vacuum impregnation. Our design relies in not only the utilization of superwetting PDMS-OCF to enhance the thermal stability but also taking advantage of excellent thermal conductivity of copper foam to enhance the thermal conductivity of resulting PCMs composites, which maybe expected to increase the comprehensive performance of PCMs composites.

2. Experimental

2.1 Preparation of rough surface with copper foam (CF)

First, a copper foam (10mm*10mm*1.5mm, diameter of the hole is about 1mm) was washed by using a 1.0 M HCl aqueous solution and Acetone for 15 min respectively, subsequently washed with deionized water three times to remove surface impurities. The washed copper foam was then immersed into a mixed solution of 2.5M NaOH and 0.1 M \((\text{NH}_4)_2\text{S}_2\text{O}_8\). After a given reaction time, the sample was taken out of the solution, washed with deionized water three times, and dried in vacuum, then the OCF was obtained.

2.2 Preparation of superhydrophobic surface

Some amount of OCFs and a piece of polydimethylsiloxane (PDMS) film were placed on a glass container and immersed into the molten paraffin in atmospheric pressure, then the composite was named a-PDMS-OCF/paraffin.

2.3 Preparation of PCMs composites

The supporting materials were placed on a glass container and immersed into the molten PCM (such as paraffin and SA) in vacuum (0.07 MPa) with a impregnation ratio is 1:8. Then, the PDMS-OCF/PCMs and SA-OCF/PCMs composites were dried to obtain a constant weight (70 °C). In order to compare, the PDMS-OCF was placed on a glass container and immersed into the molten paraffin in atmospheric pressure, then the composite was named a-PDMS-OCF/paraffin.

2.4 Analytical instrumentation

The micro-morphology of the supporting material and PCM composites were observed by using field emission scanning electron microscopy (SEM, JSM-6701F, JEOL, LED.) after coating samples with a layer of Au film. Contact angle (CA) measurements for the samples were performed on a contact angle meter (DSA100, Kruss). X-ray diffraction (XRD) measurements were performed on a X-ray diffractometer (D/Max-2400, Rigaku) with a Cu tube source, and 2 θ scans were obtained from 10° to 80°. The thermodynamic properties of pure paraffin, pure SA and PCM composites were determined by differential scanning calorimetry (TGA/DSC1, METTLERTOLEDO) at a heating and cooling rate of 5 °C min\(^{-1}\) in the temperature range of 20-110 °C under nitrogen atmosphere. The thermal diffusivities and the specific heat for the PDMS-OCF/PCMs composites were measured at 25 °C by the thermal conductivity testing instrument (LFA 457 MicroFlash, NETZSCH, laser flash method).

3. Results and Discussion

Characterization of morphologies of supporting materials and PCMs composites. SEM was performed to evaluate the morphology and structure of materials. As seen in Figure 1a, the OCF exhibited nano- or micro- size along with rough surface that composed of the petal shapes of copper oxide sheets roughly 800nm in diameters, in line with the results reported in the literature \(^\text{20}\). However, because of the hydrophilic nature of OCF, the adsorb ability for superhydrophobic PCM (such as paraffin or SA) is poor. Therefore, to improve its hydrophobic property, the modification with PDMS or SA is necessary. After modification with PDMS or SA, the water CA was detected to be 155.8° for PDMS-OCF (Figure 1e) and 154.7° for SA-OCF (Figure 1f), respectively. And the oil (decane) CA was observed to be 0° with a phenomenon in which decane is absorbed into PDMS-OCF in 40 milliseconds (Figure 1h). That shows that PDMS-OCF has good lipophilicity. The morphology of the PDMS-OCF (Figure 1b) and SA-OCF (Figure 1c) remains unchanged after the modification, indicating that the surface modification has no obvious influence on the surface structure of the OCF. As shown in Figure 1d, the paraffin attached to the surface of the PDMS-OCF well.
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Figure 1. SEM images of OCF (a), PDMS-OCF (b), SA-OCF (c) and PDMS-OCF/paraffin composite (d); water CA images of PDMS-OCF (e) and SA-OCF (f); the image of PDMS-OCF on the water and two drops of heliandrin B on it (g), oil CA images of PDMS-OCF in 40, 440 and 480 milliseconds.
XRD analysis. Figure 2 shows the XRD patterns of pure paraffin, PDMS-OCF and PDMS-OCF/paraffin composite. As seen in the Figure 2b, two broad intensity peaks at around 35.68° and 38.92° were observed for (002) and (111) of CuO, and the obvious and sharp peaks at 43.52°, 50.60° and 74.22° were ascribed to (111), (200) and (220) of Cu, respectively, there are in good agreement with previous literature. In the Figure 2c, the diffraction peak positions of PDMS-OCF composite and pure paraffin in the PDMS-OCF/paraffin composite remain nearly unchanged compared to PDMS-OCF and pure paraffin, indicating that the paraffin has been incorporated successfully into PDMS-OCF without occurring chemical reaction. However, the peak intensity of PDMS-OCF/paraffin composite is much weaker than that of pure paraffin and little weaker than that of the PDMS-OCF, suggesting that the crystallinity of paraffin in the PDMS-OCF/paraffin composite was reduced and the paraffin covering the surface of the PDMS-OCF.

XPS analysis. As shown in Figure 3, the characteristic peaks of Cu2p, O1s, C1s and Si2p appear on the line with the binding energy (BE) of 933.96 eV, 532.47 eV, 285.13 eV and 102.68 eV, respectively. The appearance of the peak of Si2p is mainly because the Si-O bond of PDMS ruptures at a certain temperature and then deposited on the surface of OCF forming a layer of PDMS membrane. The existence of Cu (II) in the PDMS-OCF is evidenced by a phenomenon that there are four peaks in the Figure 3(inset). This characterization proves that the surface of PDMS-OCF contains CuO, which is consistent with the results of XRD.

Thermal stability of supporting materials and composite. Figure 4a shows the TGA curves of OCF, SA-OCF and PDMS-OCF. As shown in Figure 4, the whole weight loss of OCF, SA-OCF and PDMS-OCF samples were found to be 1.68 %, 2.28 % and 2.11 %, respectively, that suggesting a high thermal stability for these samples. For SA-OCF, the thermal decomposition temperature is higher than 240 ºC with weight loss 0.95 %, that as a result of the decomposition of cupric stearate. Moreover, the PDMS-OCF, SA-OCF and OCF samples are lose weight above 700 ºC due to copper oxide was decomposed into cuprous oxide and oxygen. Thermal durability and stability of PCM composites are very important for evaluating their performance and shown on Figure 4b. As can be seen from the curves, rapid weight loss of the pure paraffin and PDMS-OCF/paraffin composite is observed between 200 ºC and 340 ºC, due to the evaporation of paraffin. And the total weight loss of PDMS-OCF/paraffin is 27.16 %. At the same weight loss rate, the temperature of the composite is slightly higher than that of the pure paraffin, which indicates that the thermal stability of the composite is improved by the supporting material.

Thermal behavior analysis. DSC was performed to evaluate thermal properties such as the phase change latent heat and phase change temperature of the as-prepared PCMs. As shown in Figure 5, The phase change latent heat of the shape-stabilized PCMs is calculated by the area under the exothermic peak in DSC curves and presented in Table 1. The latent heat of the composites depends on the amount of PCM loaded in the supporting materials. The mass fraction of PCM in the composites can be calculated by the following equation:

\[
\omega_{i}(\text{PCM percent})\% = \frac{\Delta M(\text{pure PCM})}{\Delta M(\text{PCM composite})} \times 100\% \quad (1)
\]

where \(\Delta M(\text{pure PCM})\) and \(\Delta M(\text{PCM composite})\) are the mass of pure PCM and the mass of its relevant composites. Moreover, the PCM latent heat percent of pure PCM and PCM be calculated by the following equation:

\[
\omega_{i}(\text{PCM latent heat percent})\% = \frac{\Delta H(\text{PCM composite})}{\Delta H(\text{pure PCM})} \times 100\% \quad (2)
\]
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Figure 4. TGA curves of (a) OCF, SA-OCF and PDMS-OCF; (b) PDMS-OCF/paraffin and pure paraffin

Table 1. Thermal properties of PCMs and PCM composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating PCM percent (%)</th>
<th>Onset T/(°C)</th>
<th>Latent heat (J g⁻¹)</th>
<th>Cooling PCM latent heat percent (%)</th>
<th>Onset T/(°C)</th>
<th>Latent heat (J g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure paraffin</td>
<td>100</td>
<td>35.10</td>
<td>195.89</td>
<td>100</td>
<td>53.10</td>
<td>189.68</td>
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<tr>
<td>CF/paraffin</td>
<td>12.67</td>
<td>34.40</td>
<td>8.50</td>
<td>4.34</td>
<td>54.10</td>
<td>8.15</td>
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<tr>
<td>OCF/paraffin</td>
<td>16.83</td>
<td>33.30</td>
<td>22.14</td>
<td>11.30</td>
<td>53.20</td>
<td>22.04</td>
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<td>SA-OCF/paraffin</td>
<td>19.03</td>
<td>33.40</td>
<td>25.90</td>
<td>13.22</td>
<td>53.80</td>
<td>24.82</td>
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<tr>
<td>PDMS-OCF/paraffin</td>
<td>26.91</td>
<td>32.90</td>
<td>36.87</td>
<td>18.82</td>
<td>53.50</td>
<td>36.81</td>
</tr>
<tr>
<td>a-PDMS-OCF/paraffin</td>
<td>25.44</td>
<td>32.91</td>
<td>31.79</td>
<td>16.23</td>
<td>53.98</td>
<td>31.06</td>
</tr>
<tr>
<td>PDMS-OCF/paraffin(100cycles)</td>
<td>26.27</td>
<td>32.70</td>
<td>36.11</td>
<td>18.46</td>
<td>54.18</td>
<td>35.85</td>
</tr>
<tr>
<td>Pure SA</td>
<td>100</td>
<td>61.90</td>
<td>203.40</td>
<td>100</td>
<td>52.50</td>
<td>205.20</td>
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<tr>
<td>SA-OCF/SA</td>
<td>18.44</td>
<td>57.90</td>
<td>28.58</td>
<td>14.05</td>
<td>52.50</td>
<td>28.00</td>
</tr>
<tr>
<td>PDMS-OCF/SA</td>
<td>22.78</td>
<td>58.80</td>
<td>36.81</td>
<td>18.10</td>
<td>52.50</td>
<td>37.19</td>
</tr>
</tbody>
</table>

Figure 5. DSC curves for heating (a) and cooling (c) of pure paraffin, PDMS-OCF/paraffin, SA-OCF/paraffin, OCF/paraffin and CF/paraffin; heating (b) and cooling (e) of PDMS-OCF/paraffin, PDMS-OCF/paraffin after 100 cycles of heating and cooling, and a-PDMS-OCF/paraffin; heating (c) and cooling (f) of SA, SA-OCF/SA and PDMS-OCF/SA
where $\Delta H$ (PCM composite) refers to the latent heat of the PCM composites and $\Delta H$ (pure PCM) refers to the latent heat of the relevant pure PCM. The PCM latent heat percentage in the PCM composites and the mass fraction of crystallized PCM in the PCM composites are listed in Table 1. It can be seen from Table 1 that the heating and cooling latent heat of pure PCMs and their composites. The heating latent heat was calculated to be 195.89 J g$^{-1}$ for paraffin, 8.50 J g$^{-1}$ for CF/paraffin composite, 22.036 J g$^{-1}$ for OCF/paraffin composite, 25.90 J g$^{-1}$ for SA-OCF/paraffin composite and 36.87 J g$^{-1}$ for PDMS-OCF/paraffin composite, respectively. Obviously, the heating latent heats of CF/paraffin composite, OCF/paraffin composite, SA-OCF/paraffin composite and PDMS-OCF/paraffin composite are lower than those of pure paraffin. However, the PCM latent heat percentage of OCF/paraffin composite, SA-OCF/paraffin composite and PDMS-OCF/paraffin composite was higher than that of the CF/paraffin composite, improving by 6.96%, 8.88% and 14.48%. In addition, a PCM composite has a smaller latent heat what prepared at atmospheric pressure than in a vacuum. As shown in Table 1, the latent heat of PDMS-OCF/paraffin is 2.59% higher than that of a-PDMS-OCF/paraffin. The cyclic utilization of PCM composites is great importance to evaluate their properties, especially in practical applications. This property is measured by thermal cycling test. After 100 cycles of heating and cooling, the PDMS-OCF/paraffin composite maintain excellent thermal stability, resulting in PCMs weight change curves shown in Figure 5b, Figure 5e and dates shown in table 1. Compared with PDMS-OCF/paraffin, the mass of PDMS-OCF/paraffin is reduced by 0.64% and the latent heat of PDMS-OCF/paraffin is reduced by 0.36% after 100 cycles of cooling and heating. This also shows that the PCM has no leakage and the composite has goodthermal stability.

Thermal conductivity is another important parameter to measure the rate of heat conduction in practical applications. It is helpful to increase the thermal conductivity of materials to accelerate the rate of heat exchange of materials. In order to study the effect of PDMS-OCF supporting materials on the thermal conductivity of PCMs, the thermal conductivity of the sample was measured by means of thermal conductivity testing instrument. As shown in table 2, the thermal conductivity of PCMs (paraffin and SA) and PDMS-OCF/PCM composites is listed. Compared with PCMs, the composite has higher thermal conductivity. For example, the thermal conductivity of PDMS-OCF/paraffin composite is about 9 times that of pure paraffin. It is indicated that PDMS-OCF can improve the thermal conductivity of PCMs, which is of great importance to practical industrial applications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal diffusivity (mm$^2$s$^{-1}$)</th>
<th>Specific heat (J g$^{-1}$K$^{-1}$)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Thermal conductivity (W m$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure paraffin$^{16}$</td>
<td>0.139</td>
<td>2.800</td>
<td>0.889</td>
<td>0.335</td>
</tr>
<tr>
<td>Pure SA$^{16}$</td>
<td>0.073</td>
<td>2.400</td>
<td>0.861</td>
<td>0.150</td>
</tr>
<tr>
<td>PDMS-OCF/paraffin</td>
<td>3.590</td>
<td>1.054</td>
<td>0.859</td>
<td>3.082</td>
</tr>
<tr>
<td>PDMS-OCF/SA</td>
<td>5.121</td>
<td>0.773</td>
<td>0.792</td>
<td>3.136</td>
</tr>
</tbody>
</table>

4. Conclusions

In summary, we have demonstrated the preparation of superhydrophobic and superoleophilic PDMS-OCF for construction of form-stable PCMs composites by facile absorbing of organic PCMs into PDMS-OCF network. In this way, the organic PCMs can be spontaneously adsorbed and remain stable without leakage even at high temperature over their melting points. The latent heats of the PDMS-OCF/PCMs composites were measured to be 36.87 J g$^{-1}$ and 36.81 J g$^{-1}$ for PDMS-OCF/paraffin and PDMS-OCF/SA, respectively, which is greater than that of untreated CF/paraffin composite (8.5 J g$^{-1}$). The PDMS-OCF/PCMs composite shows better thermal stability and the latent heat is reduced by 0.36% after 100cycles of cooling and heating. The thermal conductivity of PDMS-OCF/paraffin composite is about 9 times that of pure paraffin. Such PCMs composites with enhanced thermal stability as well as thermal conductivity may have great potentials for practical applications in solar energy or thermal energy saving and storage.

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6. References


