Phase Change Insulation for Energy Efficiency Based on Wax-Halloysite Composites

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Abstract. Phase change materials (PCMs) have gained extensive attention in thermal energy storage. Wax can be used as a PCM in solar storage but it has low thermal conductivity. Introducing 10% halloysite admixed into wax yields a novel composite (wax-halloysite) which has a thermal conductivity of 0.5 W/mK. To increase the base conductivity, graphite and carbon nanotubes were added into the PCM composite improving its thermal energy storage. Thermal conductivity of wax-halloysite-graphite (45/45/10%) composite showed increased conductivity of 1.4 W/mK (3 times higher than the base wax-halloysite composite). Wax-halloysite-graphite-carbon nanotubes (45/45/5/5%) composite showed conductivity of 0.85 W/mK while maintaining the original shape perfectly until 91 °C (above the original wax melting point). Thermal conductivity can be further increased with higher doping of carbon nanotubes. This new composites are promising heat storage material due to good thermal stability, high thermal/electricity conductivity and ability to preserve its shape during phase transitions.

1. Introduction
Due to the increasing demand for energy and energy sustainable development, organic solid–liquid phase change materials (PCMs) have attracted considerable attention for storing thermal energy and controlling temperature by storing and releasing significant latent heat during phase change process [1-3]. Among them, paraffin wax was widely employed for thermal energy storage in many applications due to high heat of fusion, appropriate melting temperature, high specific heat capacity, chemically inert, stable, noncorrosive and nontoxic properties [2, 4-6]. However, low thermal conductivity (0.25 W/mK) and shape instability above the wax melting point limit its applications. To overcome these problems, a wide range of research has been undertaken to enhance wax thermal conductivity and form shape stabilized material. The commonly used method is to disperse in-wax carbon nanotubes, expanded graphite, copper and other metal nano/micro particles to form the composites [2-5, 7-12]. Carbon nanotubes and metal particles essentially increase the composite cost while decreasing the total volume of latent heat thermal storage. Moreover, these composites often have poor stability [3].

Halloysite nanoclay, a natural environmentally friendly low-cost material, attracted a great interest due to its hollow tubule structure, high surface area and good polymer mixability without need for exfoliation. Halloysite nanotubes are formed by rolling kaolinite aluminosilicate sheets [13-16]. The inner lumen of halloysite tubes can be loaded with various chemicals, such as metals, chemical inhibitors, dyes, antiseptics, drugs and proteins [17-21]. Zhang et al. found that halloysite maintains wax shape during heat absorption and phase change and can improve thermal conductivity [22].
Compared with the aforementioned materials, halloysite nanotubes as additives are well mixable with wax and yield a pseudo ceramic “skeleton” that maintains composite structure even above the wax melting temperature.

In this paper, a shape stabilized phase change material of wax and halloysite was developed. It has form-stable shape even when the temperature exceeds the melting point and has a higher thermal conductivity than wax. Heat shape stabilization and thermal conductivity of the composite was optimized by the additional of graphite or carbon nanotubes.

2. Experimental and Methods

2.1. Materials and preparation of wax/halloysite composites

Halloysite from Applied Minerals Inc (USA) was used without further treatment. The inner and outer diameter of halloysite is in the range 10-20 nm and 40-60 nm, while the wall thickness is 15-20 nm. The average surface area of halloysite is 54 m²/g. Technical grade wax (melting point Tm=50-53 °C), isooctane, graphite, and carbon nanotubes were purchased from Sigma-Aldrich. Halloysite clay and wax were mixed in the isooctane solution. The mixture was stirred and refluxed under 80 ºC for 3 h. Then the mixture was vacuum dried overnight. The wax/HNT composites were prepared with the different weight ratios. In order to increase thermal storage, graphite and carbon nanotubes were added in the mixture at the beginning. The following steps were consistent with the same method mentioned above.

2.2. Thermal conductivity measurement

Composites were tested in a specially designed chamber. It was fabricated from 5.8 mm thick polyacrylate with dimensions of 35 x 30 x 15 mm. Ambient temperature around the setup was maintained at 25 °C. Data was recorded and analyzed via Lab-View setup on a connected computer. The four k-type thermocouples provided temperature data which was used to determine the average thermal conductivity k of each mixture tested. Equation 1 provided the basis for this calculation where q was the heat transfer from the resistance heater (measured via heat flux sensor), A was the area of heat transfer, ∆T was the temperature gradient between thermocouple readings and ∆z was the vertical distance between them.

\[
k = \frac{q/A}{\Delta T/\Delta z}
\]

3. Results and Discussion

3.1. Thermal characteristics of PCM composites

Figure 1 shows the thermal properties of wax and wax composites by using DSC, including transition temperature (Tt), melting temperature (Tm) and latent heat (ΔH). A sharp principal peak which signifies a solid-to-liquid transition and a minor peak which represents a solid-to-solid transition appear in pure wax [23]. In shape-stabilized phase changing materials, these two peaks of paraffin wax are still exist and obvious. This could be explained as there were no chemical reactions between paraffin wax, graphite and carbon nanotubes in the preparation of the shape-stabilized PCM. The shape stabilized composites exhibit almost the same peaks as that of paraffin wax, meaning the transition temperature (Tt) and melting temperature (Tm) are constant within a standard deviation of ±1 °C, although halloysite, graphite and carbon nanotubes were dispersed throughout the paraffin wax. The solid-to-liquid phase change is discussed here because it is the main phase change of paraffin wax. One sharp phase change peak at 52.3 °C is observed for pure wax which shows the melting point is 52.3 °C. In addition, the latent heat is 171.0 J/g. The lower strength of the peaks and smaller area below the peaks indicate that all the composites have lower latent heat than pure wax due to the reduced wax content.
The thermal properties data obtained from these characterizations are also shown in Table 1 and compared with the theoretical latent heat calculated according to Equation (2).

\[ \Delta H_{\text{composite}} = \omega \Delta H_{\text{wax}} \]  

(2)

where \( \Delta H_{\text{composite}} \), \( \omega \) and \( \Delta H_{\text{wax}} \) are the calculated latent heat of the shape stabilized PCM, mass ratio of wax in the composite and latent heat of wax, respectively. The measured latent heat fits well with the calculated values, yielding differences less than -14 %.

![Figure 1. DSC curves of pure wax (a), wax/halloysite (50/50%) (b), wax/halloysite/carbon nanotubes (45/45/10%) (c), wax/halloysite/graphite (45/45/10%) (d), wax/halloysite/graphite/carbon nanotubes (45/45/5/5%) (e) and wax/halloysite/carbon nanotubes (87/10/3%) (f).](image)

| Wax:halloysite:graphite :carbon nanotubes (w%) | Transition | Melting point | Total latent heat \( \Delta H \) (J/g) | Calculated \( \Delta H \) (J/g) | Difference (%) |
|-----------------------------------------------|------------|---------------|----------------------------------|-------------------------------|---------------|
| 100:0:0:0                                     | 47.0       | 52.3          | 171.0                            | —                            | —             |
| 50:50:0:0                                     | 46.8       | 53.5          | 87.1                             | 85.5                         | -1.9          |
| 45:45:10:0                                   | 47.1       | 52.9          | 68.4                             | 76.9                         | 11            |
| 45:45:5:5                                   | 46.8       | 52.7          | 88.1                             | 76.9                         | -14           |
| 87:10:0:3                                   | 47.4       | 52.7          | 145.7                           | 148.7                        | 2.1           |
| 45:45:0:10                                | 47.1       | 52.7          | 75.7                             | 76.9                         | 1.6           |

3.2. Thermal conductivity of PCM composite

Thermal conductivity is one of the most important properties of PCMs. The thermal conductivity of different PCM composite was summarized in Table 2. Adding 10% of halloysite can increase the thermal conductivity of wax twice and the composite could keep shape above wax melting temperature 50 °C. Further increasing the ratio of halloysite to 50% resulted in the decrease of PCM composite’s thermal conductivity but increase the shape maintenance temperature to 70 °C. In order to
improve both the thermal conductivity and shape-stabilized temperature, carbon nanotubes and graphite were introduced to the PCM composite. 5% carbon nanotubes can increase the thermal conductivity whereas the composite would deform its shape at 50 °C. However, 10% graphite can enhance both the thermal conductivity as high as 1.4 W/mK and shape deformation temperature up to 81 °C. Graphite alone dispersed into paraffin wax can increase the thermal conductivity to 0.65 W/mK, but it cannot enhance the shape stable temperature. When wax/halloysite composite contains both graphite and carbon nanotubes, shape deformation temperature can be increased to 91 °C.

| Wax:halloysite:graphite:carbon nanotubes (wt %) | Thermal conductivity (W/mK) | Shape deformation T (°C) |
|-----------------------------------------------|----------------------------|-------------------------|
| 100:0:0:0                                    | 0.25                       | —                       |
| 0:100:0:0                                    | 0.10                       | 53                      |
| 90:10:0:0                                    | 0.50                       | 60                      |
| 50:50:0:0                                    | 0.36                       | 70                      |
| 85:10:0:5                                    | 0.57                       | 53                      |
| 45:45:10:0                                   | 1.40                       | 81                      |
| 90:0:10:0                                    | 0.65                       | 53                      |
| 45:45:5:5                                    | 0.85                       | 91                      |

3.3. Stable performance of wax/composites

The leakage tests above the melting temperature of wax were executed to compare the form-stable performance of the as-prepared composite PCMs. Figure 3 shows the photographs of pure wax, and different mixtures of wax/halloysite/graphite kept at 90 °C for 20 min. As seen from the photographs of the 3 cm diameter cylindrical samples, all the pure wax and wax/carbon nanotubes (90/10%) melted to liquid and wax/halloysite (50/50%) had minimal liquid leakage while wax/halloysite/graphite (45/45/10%) and wax/halloysite/graphite/carbon nanotubes (45/45/5/5%) maintained form without liquid release from the matrix.

**Figure 3.** Photographs of pure wax (a), wax/halloysite (50/50%) (b), wax/graphite (90/10%) (c), wax/halloysite/graphite (45/45/10%) (d) and wax/halloysite/graphite/carbon nanotubes (45/45/5/5%) (e) at 90 °C.

The leakage test confirms that halloysite provides mechanical strength for the phase changing composites and prevents the seepage of the melted paraffin wax. In the shape stabilized composites, halloysite, graphite and carbon nanotubes serve as supporting materials and thermal conductivity promoter of wax. However, graphite or carbon nanotubes alone cannot improve the stability of wax
significantly, and must be combined with halloysite to produce shape-stabilized material (Figure 3c). The wax undergoes phase transition in the network of halloysite, graphite and carbon nanotubes. Because of the uniform dispersion of halloysite into wax and the interfacial adhesion between wax, halloysite, and graphite, these composites could maintain their shapes even heated above the phase change temperature. There is no leakage of the wax even above melting point. These composite samples could maintain shape perfectly even after subjection to 50 melting–freezing cycles.

4. Conclusion
Doping wax with 50-nm diameter halloysite clay nanotubes provide a skeleton to maintain wax shape during heat absorption and phase transition even when the temperature of the phase change material exceeds the melting point. Therefore, such composite containing of 40-50% halloysite nanotubes allows wax melting without its leakage (while melting temperature is preserved). Halloysite also improves the thermal conductivity of wax composite. The thermal conductivity can be further adjusted by adding graphite or carbon nanotubes to the wax/halloysite composite. Due to good thermal stability, high thermal conductivity, ability to preserve shape during wax melting, and abundant availability of this natural tubule clay, the phase change insulation composite based on halloysite can be used to conserve energy in large scale practical applications.

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