

PCM USING PARAFFIN/EXFOLIATED GRAPHITE COMPOSITES AS ENERGY SAVING BUILDING MATERIALS FOR THERMAL COMFORT

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Abstract

The building sector is known to make a large contribution to total energy consumption and CO₂ emissions. Phase change materials (PCMs) have been considered for thermal energy storage in buildings. The aim of this study was to improve the thermal conductivity of PCMs applicable as building materials. Using exfoliated graphite nanoplatelets (xGnP), composite PCMs were prepared by mixing and melting techniques for high dispersibility, thermal conductivity and latent heat storage. xGnP of 3 and 5 wt.% added to three types of liquid pure PCMs has different melting points. The thermal conductivity of composite PCMs was increased with the xGnP loaded contents. The DSC results showed that the melting temperature and latent heat of the composite PCMs loaded with xGnP was maintained. The latent heat of composite PCMs did not decrease when loading with xGnP. As a result, composite PCMs loaded with xGnP can be considered as energy saving building materials.

1 Introduction

The building sector is known to contribute significantly to total energy consumption and CO₂. Thermal energy storage is a useful tool for improving energy efficiency and increasing energy savings. There are three ways to store thermal energy: chemical energy (reversible reactions), sensible heat and latent heat [1]. Among these, latent heat storage is the most attractive because of its high storage density and small temperature variation from storage to retrieval [2]. In latent heat thermal energy storage systems, energy is stored during melting and recovered during the freezing of a phase change material. A great variety of inorganic and organic PCMs and their mixtures have been investigated as latent heat storage materials [3].

Among the investigated PCMs, paraffins have been widely used for latent heat thermal energy storage applications because of their high latent heat and proper thermal characteristics such as little or no supercooling, low vapor pressure, good thermal and chemical stability, and self-nucleating behavior [4]. However, they also have some inherent limitations, such as low thermal conductivity, and the need for a container to prevent leak and flammability properties. To solve these problems, some investigators have studied the possibility of a container that can prevent the leaking of liquid PCMs by using Shape-stabilized PCM and Microencapsulated PCM techniques [5, 6]. Shape-stabilized PCM and Microencapsulated PCM can maintain their shape even when the PCM changes from solid to liquid by physical

combination with polymer or mineral [7, 8]. Several other investigators have studied the flame-retardant characteristic of PCMs. The heat release rate of PCM remarkably decreases with the loading of carbon-containing substance and non-flammable mineral, contributing to the improved flammability properties [9, 10]. Other investigators have studied the improvement of the thermal conductivity of PCM by mixing with a particle of metal or carbon-containing substance that has a high thermal conductivity [11, 12].

Recently, the radiant floor heating system has become widely used around the world because of its energy savings and health benefits [13]. Similarly to other countries, in Korea, the energy consumption for buildings constitutes a large proportion of the total energy consumption. Especially, Korean residential buildings that use radiant floor heating systems consume more than half of the building energy in heating. Therefore, efforts have been made to reduce heating energy in many ways, including the use of vacuum insulation panels, high performance window systems, and high performance ventilation systems. However, in the absence of sufficient research on the application of PCM as a building material, further study is required on the application of PCMs in proper heating systems. The most important characteristic to consider is the heat capacity and melting point of the PCM in its application to building materials. However, the residential building using radiant floor heating systems presents a different thermal distribution compared with that using convection heating systems [14]. In the case of the radiant floor heating system, hot water pipes are built in the floor as the heating medium. In addition, the temperature of the hot water in the pipe can rise to as high as 80°C. Therefore, the flooring materials that are applied when radiant floor heating systems are used require a significantly higher melting point than the ceiling and wall.

This study aims to prepare the composite PCMs loaded with a low mass fraction of xGnP to obtain high thermal conductivity composite PCMs that can be considered as energy saving building materials of residential buildings using radiant floor heating system. This study also aims to investigate the effect of the xGnP addition on the dispersibility, thermal conductivity and latent heat capacity of composite PCMs.

2 Materials and testing methods

2.1 Materials

Exfoliated graphite nanoplatelets (xGnP) are prepared from sulfuric acid-intercalated expandable graphite (3772), (obtained from Asbury Graphite Mills, NJ), by applying a cost and time effective exfoliation process initially proposed by Drzal's group (Kim and Drzal, 2009). The Hexadecane (with melting temperature of 18-20°C), octadecane (26-30°C) and paraffin (53-57°C) were purchased from the Sigma-Aldrich company and used directly as PCMs.

2.2 Preparation of composite PCMs

The samples were prepared by adding xGnP at different mass fractions into hexadecane, octadecane and paraffin wax using mixing and melting techniques. To establish the relationship between the thermal conductivity of the composite PCM and the mass fraction of xGnP, and to determine the minimum mass fraction of xGnP that is adequate to obtain composite PCMs loaded with xGnP as applicable building materials, the composite PCMs were prepared by stirring and sonication of xGnP in liquid paraffin with a mass fraction of 3 and 5 wt.%. K type thermocouples are extended into the PCMs module through one sidewall to record the transient temperature response of the PCMs. The PCMs were melted by heating

them at over the melting temperature of each PCM, and the xGnP was then mixed into the liquid PCMs. After stirring for 20 min and at 1000 rpm, the mixtures were ultrasonicated for 20 min. Lastly the liquid mixtures were injection-molded and cooled, and as shown in table 1 the nine types of composites PCM samples were obtained.

Table 1. Composite PCM samples with xGnP mass fraction.

| No | Sample | No | Sample | No | Sample |
|----|------------------------|----|------------------------|----|----------------------|
| 1 | Pure hexadecane | 4 | Pure octadecane | 7 | Pure paraffin |
| 2 | Hexadecane/xGnP 3 wt.% | 5 | Octadecane/xGnP 3 wt.% | 8 | Paraffin/xGnP 3 wt.% |
| 3 | Hexadecane/xGnP 5 wt.% | 6 | Octadecane/xGnP 5 wt.% | 9 | Paraffin/xGnP 5 wt.% |

2.3 Characterization techniques

The morphology and composition of the pure PCMs and composite PCMs at different loadings were observed by means of scanning electron microscopy (SEM, JEOL JSM-6360A) at room temperature. An SEM with an accelerating voltage of 12kV and working distance of 12 mm was used to collect SEM images. The samples were coated with a gold coating of a few nanometers in thickness.

The thermal conductivity of pure PCMs and Composite PCMs was measured using a TCi thermal conductivity analyzer. The Tci developed by C-Therm Technologies Ltd. is a device for conveniently measuring the thermal conductivity of the small sample by using the MTPS method. Contrary to other devices, TCi can measure the thermal conductivity of materials in the states of solid, liquid, powder, and mixed. The TCi consists of a sensor, power control device, and computer software. A spiral-type heating source is located at the center of the sensor, and heat is generated at the center. The heat that has been generated enters the material through the sensor during which a voltage decrease occurs rapidly at the heating source, and the thermal conductivity is calculated through the voltage decrease data.

Thermal properties such as the melting temperature and latent heat capacity of pure PCMs and composites PCMs loading xGnP were measured using a DSC instrument (DSC Q 1000, TA instrument, USA). DSC measurements were performed at a 5 °C/min heating rate and a temperature range of 20–80 °C. The melting temperature was measured by drawing a line at the point of maximum slope of the leading edge of the peak and extrapolating to the base line. The latent heats of the PCMs were determined as total by numerical integration of the area under the peaks that represents the solid–solid and solid–liquid phase transition.

3 Results and discussion

3.1 Morphology and dispersibility of composite PCMs

The Scanning electron microscopy observations were performed for the pure PCMs and the composite PCMs loaded with xGnP. The pure PCMs and composite PCMs loaded with xGnP specimens were broken up in liquid nitrogen and the fractured surfaces were coated with gold before SEM investigations. Fig. 1 shows SEM micrographs of pure paraffin and paraffin/xGnP composites containing 3 wt.% xGnP. It is observed from Fig. 1b that the dispersions of the xGnP in the paraffin are uniform and that xGnP was well-dispersed in the paraffin. In fact, it appears as though the paraffin slightly covered the xGnP surface. The xGnP particles are either embedded in the paraffin matrix, evidenced by the white lines protruding from the background, or lying on the surface, as suggested by their irregular but sharp edges, which differs from the smooth and soft paraffin. The morphology and

dispersibility of octadecane/xGnP composites and hexadecane/xGnP composites appear to follow the same trend.

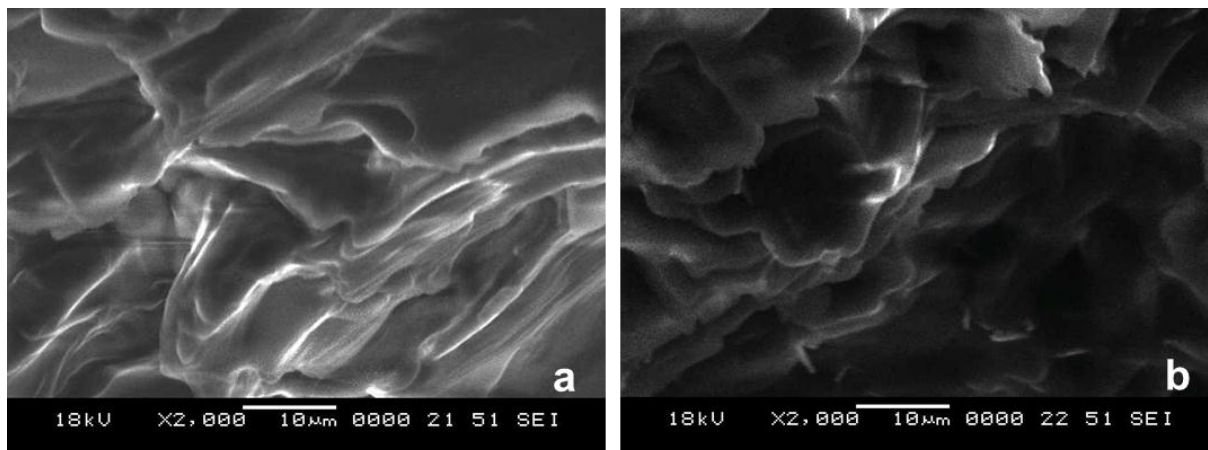


Figure 1. SEM micrographs of a) pure paraffin and b) paraffin/xGnP 3 wt.%.

3.2 Thermal conductivity of composite PCMs

The thermal conductivity result of pure PCMs and composite PCMs are shown in table 2. It can be seen that the thermal conductivity of the composite PCMs loaded with xGnP clearly improve compared to that of pure PCMs. The thermal conductivity of hexadecane/xGnP composites, octadecane/xGnP composites and paraffin/xGnP composite was linearly increased with the xGnP loaded contents. However, no more than 5 wt.% xGNPs were added because it has a very low weight density. The greatest increase of thermal conductivity by loading xGnP appeared in the octadecane/xGnP composite. The thermal conductivity of the octadecane/xGnP composite PCMs with a mass fraction of 3 and 5 wt.% xGnP increased by 76% and 101%, respectively. When the thermal conductivity of pure octadecane is 0.497 W/mK, the thermal conductivity of the octadecane/xGnP 5 wt.% composite PCM is found to be 0.999. The thermal conductivity of hexadecane, octadecane and paraffin showed a significant increase by about 75~100% in spite of the addition of the 5 wt.% mass fraction of xGnP. This result leads the better heat transfer with various temperatures in building materials, when PCM is applied to building materials. This means that latent heat storage performance was improved

Table 2. Thermal conductivity and rate of increase of Composite PCMs

| PCM Samples | Hexadecane | | | Octadecane | | | Paraffin wax | | |
|-----------------------------|------------|------|------|------------|------|------|--------------|------|------|
| | 0 | 3 | 5 | 0 | 3 | 5 | 0 | 3 | 5 |
| xGnP loading content (wt.%) | | | | | | | | | |
| Thermal conductivity (W/mK) | 0.69 | 0.99 | 1.16 | 0.50 | 0.87 | 1.00 | 0.36 | 0.45 | 0.62 |
| Rate of increase (%) | - | 49 | 74 | - | 76 | 101 | - | 28 | 73 |

3.3 Thermal storage performance of composite PCMs

The heating and freezing curves from the DSC measurements of the pure PCMs and composite PCMs are presented in Fig. 2. The thermal characteristics of the composite PCMs are very close to those of the pure PCMs. The latent heat of the PCMs is obtained as the total area under the peaks of the solid-liquid transitions of the PCMs in the composite by numerical integration. It can be seen that the latent heat of the composite PCMs approaches that of the pure PCMs. It can be seen from the heating curve in Fig. 2a that octadecane and hexadecane has one phase change peak, while the paraffin has two phase change peaks. The one phase change peak of hexadecane corresponds to the solid-liquid phase change. The first

phase change peak of paraffin is lower and corresponds to the solid–solid phase transition of the paraffin, and the second peak is very high, corresponding to the solid–liquid phase change. The DSC curve of the paraffin/xGnP composite PCMs is shown in Fig. 2b. There are also one and two peaks in the DSC curve of the composite PCMs loaded with xGnP, and the thermal characteristics of the composite PCM are very close to those of the pure paraffin. This is because there is no chemical reaction between the paraffin and the xGnP. The latent heat of the PCMs is obtained as the total area under the peaks of the solid–solid and solid–liquid transitions of the PCM in the composite by numerical integration. From Fig. 2, it can be seen that the latent heat of the composite PCMs approaches that of the pure PCMs.

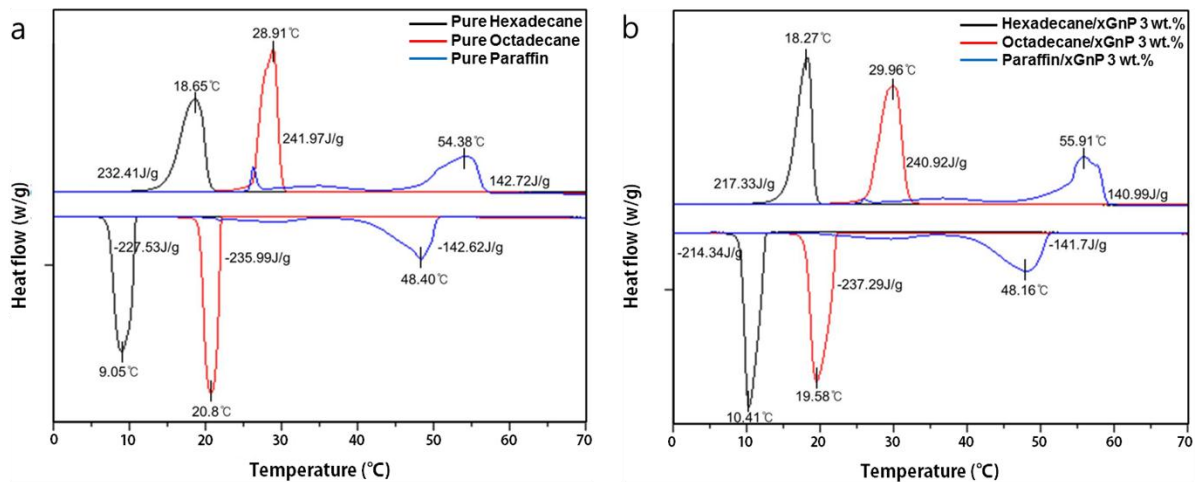


Figure 2. The heating and freezing curves by DSC of a) pure PCM and b) composite PCM.

From these results, it has been found that although the thermal conductivity of composite PCM loading was increased, the latent heat of PCM was not decreased with the xGnP loaded contents because of the good dispersion of xGnP in paraffin with a high surface area and nanoparticle size.

4 Conclusions

Composite PCMs loaded with xGnP were prepared for high thermal conductivity and latent heat storage using mixing and melting techniques. From the cryogenically fractured surface of the composite PCMs, xGnP was well-dispersed into octadecane, hexadecane and paraffin, and it led to high thermal conductivity. As the xGnP loading contents were increased, thermal conductivity was increased. The greatest increase of thermal conductivity by loading with xGnP appeared in the octadecane/xGnP composite. The thermal conductivity of the octadecane/xGnP composite PCMs with a mass fraction of 5 wt.% xGnP increased by 101%. The results clearly indicated an almost linear relationship between the thermal conductivity and mass fraction of xGnP in the composite PCM. On the other hand, latent heat storage was slightly decreased with the xGnP loading contents. When xGnP 3 wt.% was blended into each PCM, the thermal conductivity of the composite PCM sample increased to a maximum of about 76%, while the latent heat capacity decreased to a maximum of about 6%. This is because of the good dispersion of xGnP, which has a high thermal conductivity in paraffin with a high surface area and nanoparticle size. As a result, the effective composite PCMs loaded with xGnP, using octadecane, hexadecane and paraffin as phase change materials, can be considered as energy saving building materials for residential buildings using radiant floor heating systems.

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