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Thermal evaluation of high heat storage montmorillonite with phase change material containing exfoliated graphite nanoplatelets

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Abstract

In this experiment, we used a vacuum impregnation method to prepare shape stabilized PCM that contained sodium montmorillonite (Na-MMT) and Exfoliated graphite nanoplatelets (xGnP), to improve the thermal conductivity of PCMs, and prevent leakage of the liquid state of PCMs. Na-MMT has low cost and natural abundance, high adsorption and absorption capacities, and fire retardant heating rate. In the used materials, xGnP, usually produced from graphite intercalated compounds, are particles consisting of several layers of graphene sheets. As a result, we found that the FTIR adsorption spectra of paraffinic PCMs did not change, and there was no chemical interaction between paraffinic PCMs and xGnP/Na-MMT mixture. From the DSC analysis, xGnP made an impact on the thermal properties of the paraffinic PCMs/Na-MMT composites. The oxidation rate of paraffinic PCMs based composite with xGnP was greater than that of the composite without xGnP. FTIR, DSC, TGA and TCi were used to determine the characteristics of the paraffinic PCMs/Na-MMT composites.

Keywords – paraffinic PCMs; sodium montmorillonite; xGnP; heat storage; thermal properties; vacuum impregnation

1. Introduction

Latent heat storage technology has been widely used in building. The storage and application of heat is achieved through phase change materials. This has the advantages of high heat storage density, and keeping the temperature stable during the heat storage/release process. The application of PCM (Phase change materials) in building can not only save energy, but also decrease the temperature fluctuation. The application of PCM in building has been one of the hot topics in latent heat storage technology [1]. Unlike conventional sensible storage materials, PCMs absorb and release heat at a

nearly constant temperature. A large number of PCMs are known to melt with a heat of fusion in any required range. They also play an important role in solving energy imbalance, by improving thermal efficiency, and protecting the environment [2]. PCMs can be categorized into two major groups: inorganic compounds, and organic compounds. And organic PCMs are classified into paraffinic PCMs, and non-paraffinic PCMs, such as fatty acids [3]. Paraffinic PCMs are considered one of the most promising candidates, due to their large latent heat, low vapor pressure in the melt, good chemical stability, self-nucleating behavior and safety [4]. However, paraffinic PCMs have flowability during the phase change process, as a solid–liquid PCM. Therefore, it is necessary to prepare form-stable paraffinic PCM with a micro capsulation methods or incorporation methods or shape stabilized process. Also, paraffinic PCMs suffer from low thermal conductivity and liquid leakage, when they undergo the solid–liquid phase change.

In previous work, we studied the effect of exfoliated graphite nanoplatelets (xGnP) addition on the thermal properties of the paraffin wax/xGnP composite prepared as a form-stable PCM, and reported that the thermal conductivity of PCM increased with increasing graphite mass fraction [5]. Therefore, we prepared PCM/montmorillonite composite with xGnP, to improve the thermal conductivity for energy saving. This study also aims to investigate the effect of the xGnP addition on the dispersibility, thermal conductivity, and latent heat capacity of form stable PCM [6]. Actually, paraffinic PCMs should be incorporated into porous materials, such as gypsum wallboard, plaster, concrete, clay minerals, and others. Clay minerals have been used for years in many applications, such as nanocomposites, catalysts, adsorbents for removal of hazardous compounds, and supports for highly fluorescent probes. The demand for clays in diverse scientific and technological areas lies in their low cost and natural abundance, high adsorption and absorption capacities, and fire retardancy, among other properties. Among clay minerals, the most common smectite clay mineral is montmorillonite (MMT). MMT evolves from volcanic ashes by weathering or hydrothermal effects, like other aluminum-rich minerals, and composes the highest part of the volcanic ash clay termed bentonite. Therefore, this paper uses Na-MMT (Sodium montmorillonite) as a container of PCM [7]. We prepared thermal enhanced paraffinic PCM/Na-MMT composite by compounding xGnP, to improve the thermal conductivity of the PCMs.

In this study, we prepared thermal enhanced paraffinic PCM/Na-MMT, by using a vacuum impregnation process with xGnP. The vacuum impregnation method guarantees the high heat storage of paraffinic PCMs, due to capillary forces and surface tension forces during the incorporation process. The Na-MMT is needed for applying grouting materials of ground heat exchange system because the Na-MMT is used to grouting materials, originally. So we developed the ground heat energy storage composite

through mixture of Na-MMT and paraffinic PCMs. And we enhanced thermal conductivity of Na-MMT/Paraffinic PCM composites by mixing xGnP. And the thermal conductivity enhanced composite brought preventing super-cooling phenomenon of paraffinic PCMs.

2. Experimental

This study used two types of liquid paraffinic PCMs, with different melting points. In the experiment, we used n-hexadecane and n-octadecane as PCM, which have 254.7J/g and 247.6J/g of latent heat capacity, and melting points of 20.84°C and 30.4°C, respectively. The paraffinic PCMs were obtained from Celsius Korea, South Korea. xGnP is a graphitic carbon-based material. The graphite was obtained from Asbury Graphite Mills, Inc., NJ, USA, by applying a cost- and time-effective exfoliation process initially proposed by Drzal's group [4]. The used Na-MMT has 8-12% free moisture, 8-14cc/2g swelling, 0.75-0.85g/cm³ loose bulk density and more than 80% particle size (200 mesh pass). This Na-MMT was obtained from Ilsung chemical Co., Ltd, South Korea. The paraffinic PCMs/Na-MMT with xGnP or without xGnP composites were prepared by an impregnation method in a vacuum, following the manufacturing process. 5wt% of xGnP according to weight percentage of Na-MMT was mixed in Na-MMT, before the vacuum process. The xGnP/Na-MMT mixture was placed inside a filtering flask, which was connected to a water trap apparatus, to evacuate air from its porous surface. Then, the valve between the flask and the container of 200g of liquid paraffinic PCMs was turned open, to allow it to flow into the flask, to cover the xGnP/Na-MMT mixture. After the vacuum process was continued for 90min, air was allowed to enter the flask again, to force the liquid paraffinic PCMs to penetrate into the pore space of the xGnP/Na-MMT mixture. To find the maximum PCM amount in the xGnP/Na-MMT mixture, we impregnated 200g of paraffinic PCMs into xGnP/Na-MMT mixture. In this case, no impregnated excess of paraffinic PCMs remained in the flask. Therefore, we needed to remove the excess of paraffinic PCMs in the flask through filtering. The colloid state of SSPCM was filtered by 1µm filter paper, until a granule type of sample appeared on the filter paper. Then the granule type of thermal enhanced SSPCM was dried in a vacuum drier, at 80°C for 48h.

Fourier transform infrared spectroscopy (FTIR: 300E Jasco) was utilized to monitor the change of chemical groups upon curing. Clear potassium bromide (KBr) discs were molded from powder, and used as backgrounds. The samples were analyzed over the range of 525 – 4000cm⁻¹, with a spectrum resolution of 4cm⁻¹. All spectra were averaged over 32 scans. This analysis of the composites was performed by point-to-point contact with a pressure device. Thermal properties of thermal enhanced paraffinic PCMs/Na-MMT, such as the melting and freezing temperature and latent

heat capacity, were measured using differential scanning calorimetry (DSC: Q 1000). Thermal durability of the thermal enhanced paraffinic PCMs/Na-MMT was carried out using thermo gravimetric analysis (TGA: TA Instruments, TGA Q5000) on approximately 2-4mg samples, over the temperature range 25°C-600°C, at a heating rate of 10°C/min, under a nitrogen flow of 20 ml/min. The thermal conductivity of thermal enhanced paraffinic PCMs/Na-MMT 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 a small sample, by using the Modified Transient Plane Source (MTPS) method.

3. Results and discussion

3.1. FTIR analysis and chemical stability test of n-octadecane based composite PCMs

Fig. 1 shows the FTIR absorption spectra of the n-hexadecane/Na-MMT and n-octadecane/Na-MMT composites, and n-hexadecane/Na-MMT and n-octadecane/Na-MMT composites with xGnP. The molecular formulae of n-hexadecane and n-octadecane are $C_{16}H_{34}$ and $C_{18}H_{38}$, respectively. Therefore, these PCMs contained $-CH_2$ and $-CH_3$ bonding. Because all the PCMs have the same group bonding, the FTIR absorption spectra shown are similar. These FTIR absorption spectra were almost the same, with absorption peaks of 2918 , 2850 , 1468 , and 720cm^{-1} , caused by stretching vibration of functional groups of $-CH_2$ and $-CH_3$ bonding. Na-MMT is composed of more than 60% silica, of which the molecular formula is SiO_2 . So, the silica peak showed in the FTIR graph. The most intense band at 1085cm^{-1} is due to asymmetric stretching of the Si-O-Si bonding. This band usually appears between 1200 and 1000cm^{-1} . These stretching vibration bands have appeared

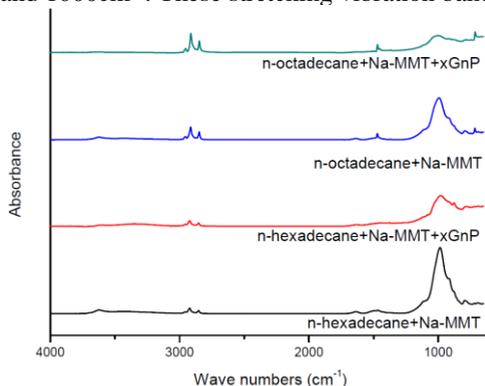


Fig. 1 FTIR spectra of paraffinic PCM based composites.

after the compositing process with PCMs. This means that the chemical properties of silica fume were not changed. Of course, other peaks also appeared in the FTIR graphs, but these peaks did not indicate the characteristics of the n-hexadecane and n-octadecane. In this experiment, we impregnated the paraffinic PCMs into the 5wt% of xGnP/Na-MMT mixture for shape stabilization and thermal enhancement of the paraffinic PCMs. In previous works, we confirmed from FTIR analysis that the xGnP has no strong peak [6]. Therefore, we found the FTIR peaks of thermal enhanced paraffinic PCMs/Na-MMT composites have almost the same peaks. However, in the case of the paraffinic PCMs/Na-MMT composites that contained the xGnP, these composites showed low value of the FTIR peaks, as loaded with xGnP. We confirmed that the FTIR peaks that indicated the characteristics of paraffinic PCMs did not shift in the FTIR graphs. This means the characteristics of paraffinic PCMs did not change. Therefore, this indicates that the heat storage properties of PCM remained after the compositing process. Consequently, we determined that the heat storage characteristics of paraffinic PCMs could integrate into the structure of xGnP and Na-MMT due to its physical bonding, without change of its chemical properties.

3.2. Thermal properties analysis

Fig. 2 presents the heating and freezing curves from DSC measurements of the paraffinic PCMs/Na-MMT composites and the composites with xGnP. In the graph, the phase transition of the n-hexadecane/Na-MMT composite occurred between 15°C and 23°C during heating, and the corresponding heat capacity was 61.36J/g. The solidification temperature range of this composite was lowered to between 10°C and 15°C, compared to the melting temperature. In the case of the n-octadecane based composite, this composite showed melting temperature range of from 20°C to 35°C, and freezing

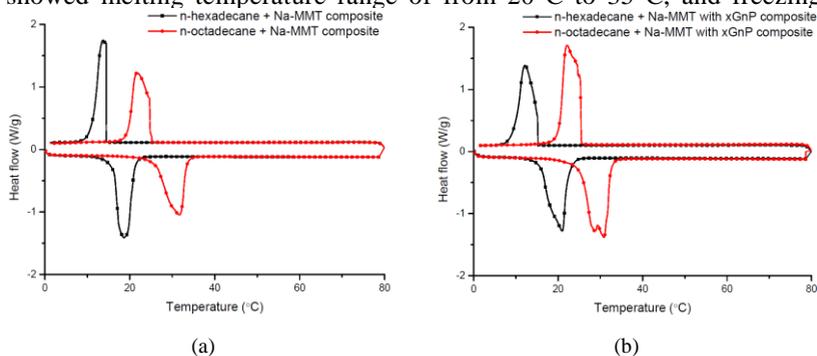


Fig. 2 DSC graph of (a) paraffinic PCM based composite PCM, and (b) paraffinic PCM based composites with xGnP.

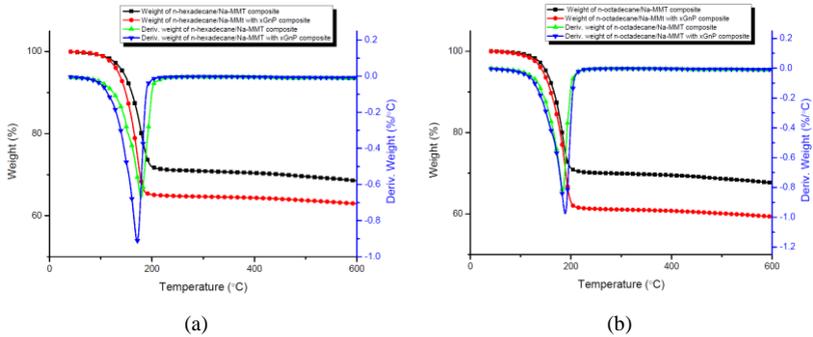


Fig. 3 Thermo gravimetric analysis of (a) n-hexadecane based composites, and (b) n-octadecane based composites.

temperature range of from 17°C to 25°C, and the corresponding heat capacity was 56.58J/g. The value for latent heat capacity of each the paraffinic PCMs based composite PCMs was nearly 24% that of the pure paraffinic PCMs. This incorporated rate is smaller than the general incorporated rate of other PCMs, which have nearly 50% of the incorporated rate. Also we analyzed thermal properties of the paraffinic PCMs/Na-MMT with xGnP composites. The n-hexadecane/Na-MMT composite with xGnP and n-octadecane/Na-MMT composite with xGnP have 68.95J/g and 80.16J/g of latent heat capacity, respectively. However, from the latent heat capacity analysis, the paraffinic PCMs/Na-MMT composites with xGnP showed high latent heat capacity, in comparison with the prepared composite without xGnP. This means that the xGnP is more porous than Na-MMT powder, so more PCM could incorporate into the porous structure of xGnP.

3.3. Thermo gravimetric analysis

Fig. 3 shows thermal gravimetric analysis of the paraffinic PCMs based composites and the composite with xGnP. As shown in the derivative weight curve of paraffinic PCMs, we found the thermal oxidation degradation peak of the n-hexadecane and n-octadecane based composites occurred at 178.78°C and 183.87°C, respectively. The n-hexadecane based composite with xGnP and the n-octadecane based composite with xGnP show 171.03°C and 188.71°C of peak of derivative weight, respectively. Also, we measured the thermal oxidation degradation of paraffinic PCMs based composites and the composites with xGnP. From the thermal degradation analysis, we confirmed that the oxidation rate of n-hexadecane/Na-MMT and n-hexadecane/Na-MMT with xGnP show 68.51% and 62.94%, respectively. n-octadecane/Na-MMT and n-octadecane/Na-MMT with xGnP show 67.64% and 59.33%, respectively. As a result, the oxidation rate of paraffinic PCMs based composite with xGnP is greater than that of the composite without

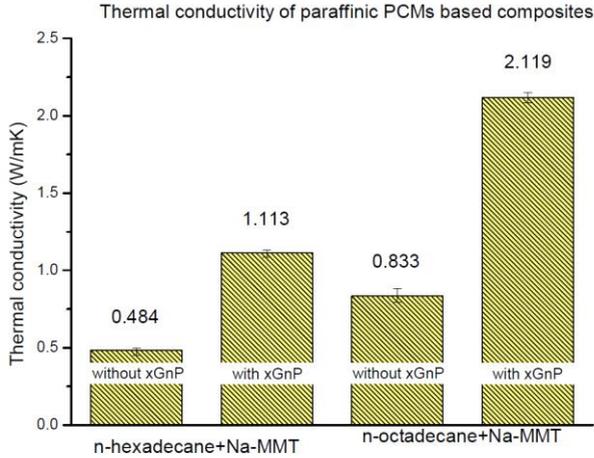


Fig. 4 Thermal conductivity of paraffinic PCM based composites.

xGnP. This means that xGnP has more porous structure, compared to the Na-MMT. Therefore more paraffinic PCMs were well incorporated into the nanostructure of xGnP.

3.4. Thermal conductivity analysis

Fig. 4 shows the thermal conductivity analysis of the n-hexadecane and n-octadecane based composite PCMs. The analysis indicated the thermal conductivity of n-hexadecane and n-octadecane based composite PCMs to be 0.484 and 0.833W/mK respectively. n-hexadecane and n-octadecane show 0.154 and 0.557W/mK, respectively. Also, we measured the thermal analysis of the thermal enhanced composite PCMs with xGnP. As a result, the n-hexadecane based thermal enhanced composite PCM shows 1.113W/mK thermal conductivity value. It has a 230% increase of thermal conductivity, compared to that of the n-hexadecane based composite PCM. The n-octadecane based thermal enhanced composite PCM shows 2.119W/mK of thermal conductivity value. It has a 254% increase of thermal conductivity, compared to that of the n-octadecane based composite PCM. This means xGnP led to an enhancement of the thermal conductivity of composite PCMs.

4. Conclusion

In this experiment, we used a vacuum impregnation method to prepare shape stabilized PCM that contained sodium montmorillonite and xGnP, to improving the thermal conductivity of PCMs, and prevent leakage of the liquid state of PCMs. As a result, we found that the FTIR adsorption spectra of paraffinic PCMs did not change, and there was no chemical interaction

between paraffinic PCMs and xGnP/Na-MMT mixture. From the DSC analysis, we confirmed that the values for latent heat capacity of each paraffinic PCMs based composite PCMs were nearly 24% of the pure paraffinic PCMs. The n-hexadecane/Na-MMT composite with xGnP and n-octadecane/Na-MMT composite with xGnP have 68.95J/g and 80.16J/g of latent heat capacity, respectively. The oxidation rate and thermal conductivity of paraffinic PCMs based composite with xGnP are higher than those of the composite without xGnP. Consequently, we expect the paraffinic PCMs based composites with xGnP to be useful in applications in various fields, due to their high thermal properties.

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