Thermal Performance of the Microencapsulated PCM

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Abstract

Microencapsulated pcm (MPCM) particles are mixed with distilled water and utilized to evaluate its characteristics and performance as a thermal storage medium transporting heat. For the present study, tetradecane ($C_{14}H_{30}$, T_m=5.5℃) is capsulated in the core, coated with the melamine for their surface. The size of particles is well-controlled under 10 μm in the process of in-situ polymerization with melamine-formaldehyde resin. For the experiment, the concentrations of slurries are prepared for 20 wt%, 30 wt%, and 40 wt%. The results are compared with those of water and 100% tetradecane oil. The pure water and tetradecane start solidifying within 20 minutes after introducing cooling water into the thermal storage tank whose flow rates are varied by 125 cc/min, 250 cc/min, and 500 cc/min. However, MPCM slurries are required relatively longer period of time for their phase change than pure phase change materials. That is, the entrained MPCM particles restrict their heat transfer in terms of natural convection and conduction to them.

Nomenclature

C_p : specific heat [J/kg℃]
G : mass flow rate [kg/s]
h : heat transfer coefficient [W/m²℃]
k : thermal conductivity [W/m℃]
Q : heat storage rate [W]
r_1, r_2 : radius (equation (4), (5)) [m]
T : temperature [℃]
U : overall heat transfer coefficient [W/m²℃]

Subscripts

1~9 : thermocouple numbers
c : cooling water
coil : circulating cooling coil
inlet : inlet
out : outlet

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1. Introduction

Today the development of thermal energy storage systems is considered an advanced energy technology in terms of enhancing heat transfer with high heat capacity. Generally, phase change materials like paraffin and salt hydrates as an organic compound suffer certain limitations with their practical use, i.e. flammability, low thermal conductivity and volumetric change during phase change. Incongruent melting is another problem with some phase change materials such Glauber's salt. In addition, many phase change materials, especially salt hydrates, have a tendency to supercool.[1]

Attempts have been made to address the problems mentioned above. That is, direct contact heat exchange, which may alleviate the problem of poor heat transfer rate and incongruent melting, has been studied.[1] In such a design, an immiscible heat transfer fluid flows through a pool of phase change material to transfer heat and stir the material. The heat transfer medium circulates around capsules which are filled with phase change material and transports heat to the demand in type of sensible heat. Recently, for maximizing latent heat of phase change materials, ice slurry,[2,3] or HDPE (Cross linked High Density Polyethylene)[4] are investigated for transporting latent heat as well as heat transfer media.

A new technique of utilizing phase change materials in energy storage and thermal control systems such as microencapsulated phase change materials is studied.[5-9] In this approach, the phase change material is microencapsulated and suspended in a heat transfer fluid to form a phase change slurry. They are pumped and circulated to the system to cool or heat a building. That is, the slurry serves as both the storage and a heat transfer media; therefore, the requirement of a heat transfer media separate from the storage media is eliminated. In addition, encapsulating the phase change material in separate, small enclosures is expected to eliminate the problem of incongruent melting.

Microencapsulated phase change materials (MPCM) are applied for many fields such as electonic cooling device,[5,6] heating or cooling buildings.[7-9]

Goel et al.[7] have presented numerical studies to analyze thermal and fluid dynamical characteristics of MPCM slurry to transport them into a duct. With their results, there are some limitation to understand their thermal phenomena while they are pumped through the duct and changed them into melting and solidifying. Inaba et al.[8] have measured density, latent heat, and thermal conductivity of MPCM slurry and found their empirical correlations with temperature. Yamagishi et al.[9] have introduced the feasibility of MPCM slurry and measured the supercooling of MPCM induced by smallness of microcapsules through differential scanning calorimetry (DSC). In his study, it has been found that the smaller size of microcapsules withstood the stress from the slurry flow and the volumetric expansion of phase change.

The present work describes the preparation of MPCM particles, which capsulate tetradecane ($CH_3(CH_2)_{12}CH_3$) with melamine surface, and analyses their size distribution and thermal characteristics. With prepared MPCM particles under 10 μm, they are mixed with distilled water for different concentrations such as 20 wt%, 30 wt% and 40 wt%, respectively, and thermal performance test as a heat storage medium is conducted.

2. Preparation of MPCM slurry and experimental set-ups

2.1 Preparation of MPCM slurry

A variety of techniques for manufacturing MPCM have been applied in various fields for many years. The selection from these techniques is highly dependent on the specifications of MPCM; materials of the core and walls, capsule size and thickness of MPCM.[9] MPCM offers many advantages, as the possibility of using the same medium for both energy transport and storage, thereby reducing losses during the heat exchange process, high heat transfer rate to the phase change component due to large surface area to volume ratio, a lower pumping rate and a higher heat transfer coefficient than the conventional single phase working fluid. The fundamental concept of the encapsulation process requires dispersion of the material to be encapsulated in a liquid medium containing the wall material in solution. The wall material is then caused to separate from solution by physical mixing and chemical driving forces and deposit around the material to be encapsulated. It is later solidified or hardened by thermal, cross-linking or desolvation techniques. The basic requirement on the core material to be encapsulated is that it remain insoluble and nonreactive with the medium in which it is dispersed with the wall material.

For the preparation of MPCM in the present work, in-situ polymerization process, which has advantages of low cost and mass production for their manufacture, is adopted for tetradecane as the core material and melamine-formaldehyde (MF) as the shell material.[(10)] Tetradecane for which has 5~6℃ for its melting temperature is filled in the capsule of MF polymer with water soluble surfactant, SMA (styrene-maleic acid anhyride copolymer). The reactor constructed with double shells so as to circulate heating or cooling water for its temperature control is used to make MPCM particles. Mole ratio of melamine, which is 1.9 kg (15.079 mole/g), to formaldehyde, which is 3.1 kg (30.233 mole/g), is 1 : 2.54. The mixture dissolved in 5 kg of water keeps stirring for 1~1.5 hours. Water mixed slurry is produced by 400 rpm stirring machine with 60℃ controled temperature for 3~4 hours.

The thermal characteristics of the produced MPCM capsules are analysed by DSC (Instrument Specialists Inc.), and the droplet and size distributions of the dispersed MCPM are measured by optical microscope from Olympus BX50 and FRITSCH analysette 22 (Zerkleinern Partikel messen Teilen Kartoffelstarke [Nr.482508]). The characteristics of MPCM capsules are scrutinized with SEM (Scanning Electron Microscopy, Philips EX30).

2.2 Evaluation of MPCM thermal performance

The thermal storage tank for the present study is constructed with acrylic tube that is composed of copper coil of 1/4 inches, which places at the inner surface of the tube circulating cooling water. The dimensions of the tube are 10 cm in diameter and 20 cm in length. To measure temperature variations during experiment, 9 T-type thermocouples locate at the different heights as shown in Fig. 1. The outer surface of the thermal storage tank is insulated

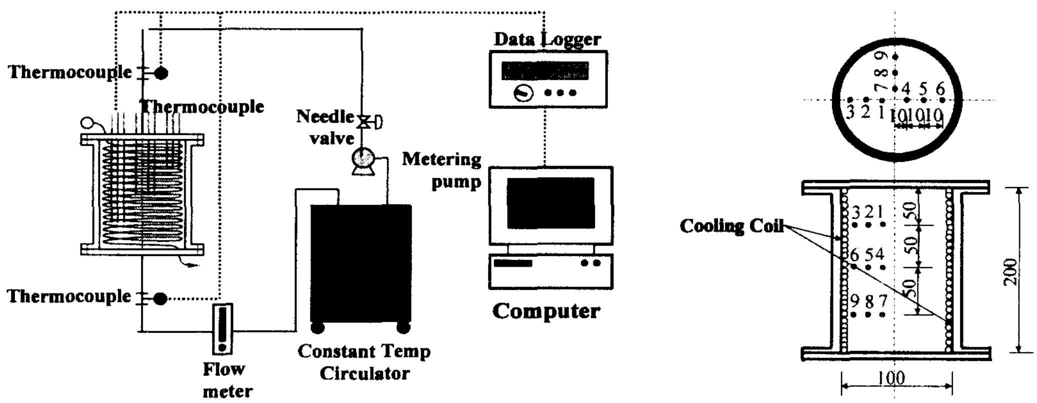


Fig. 1 Schematic diagram of the experimental thermal storage system.

with the glass fiber of 2 cm thickness. The temperature of the thermal storage tank is controled by circulating cooling water contained with 26 vol% ethylene glycol for which the iso-thermal bath, which has controled an accuracy of ±0.5℃, is used. Fig. 1 introduces the schematic diagram for the experimental apparatus, and also the dimension of thermal storage tank with the locations as well as their numbers of thermocouples.

Experiments perform for 100% phase change material, tetradecane and distilled water. Then, the results of the test from pure phase change materials have been compared with the MPCM slurry in terms of their concentrations, such as 20 wt%, 30 wt% and 40 wt%, respectively. The flow rates of circulating cooling water in the copper coil are varied by 125 cc/min, 250 cc/min and 500 cc/min, respectively, in order to examine supercooling effect. To confirm of repeatability for the results, the experiments are conducted twice under the same condition. It is found that all of data are distributed within 95% confidence curve.

The total heat supplied or recovered from the cooling water into MPCM slurry is calculated from equation (1), for which both the inlet and outlet temperatures of cooling coil are measured with T-type thermocouples.

$$Q = UA\overline{\triangle T} \tag{1}$$

Here, log mean temperature difference from equation (1) is obtained by equation (2).[11]

$$\overline{\triangle T} = \frac{(T_3 - T_{inlet}) - (T_9 - T_{out})}{\ln \frac{(T_3 - T_{inlet})}{(T_9 - T_{out})}} \tag{2}$$

From equation (1), the heat transported into MPCM slurry, Q, is computed, and then the overall heat transfer coefficient, U in equation (3) and (4) is obtained.

$$UA\overline{\triangle T} = G_c C_{pc}(T_{inlet} - T_{out}) \tag{3}$$

$$U = \frac{G_c C_{pc}(T_{inlet} - T_{out})}{2\pi r_1 L \overline{\triangle T}} \tag{4}$$

In the equation (3) and (4), the parameters, such as the flow rates, G (kg/s), specific heat of cooling water, C_{PC} (J/kg℃), and the length of thermal storage tank, L (0.2 m), are applied. And then the heat transfer coefficient in the thermal storage tank is converted in the following equation.

$$h = \frac{1}{\frac{1}{U} - \frac{r_1 \ln(r_2/r_1)}{k_{coil}} - \frac{r_1}{r_2 h_c}} \tag{5}$$

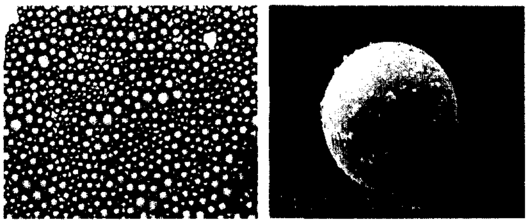
3. Results and discussions

3.1 MPCM capsules

For the present work, paraffin oil, tetradecane, is selected as a core material, and melamine is for shell material of MPCM capsules. Encapsulation is conducted by emulsifying tetradecane into melamine mixed with water soluble surfactant. During encapsulation process, there are many variable parameters for the determination of the characteristics of capsules; type, dimension, axial location of stirred device for the operation. Besides that, the rpm of stirred device is one of essential factors to determine it.

It is consisted of two steps for encapsulating processes, i.e., emulsification and polymerization. In these processes, it is noted that the proper selection of surfactant decides uniform sizes of the oil droplets and it keeps stable during the process. For the purpose of mass production of MPCM particles, it is concluded that the operating time for emulsifying process has been highly depended on the viscosity of emulsified liquid for the maximum amount of capsule production with a homogenization mixer.

During polymerization process, the reacting time of oil droplets with melamine, polymer,



(a) (b)

Fig. 2 (a) MPCM slurry with melamine wall and (b) its magnified particle.

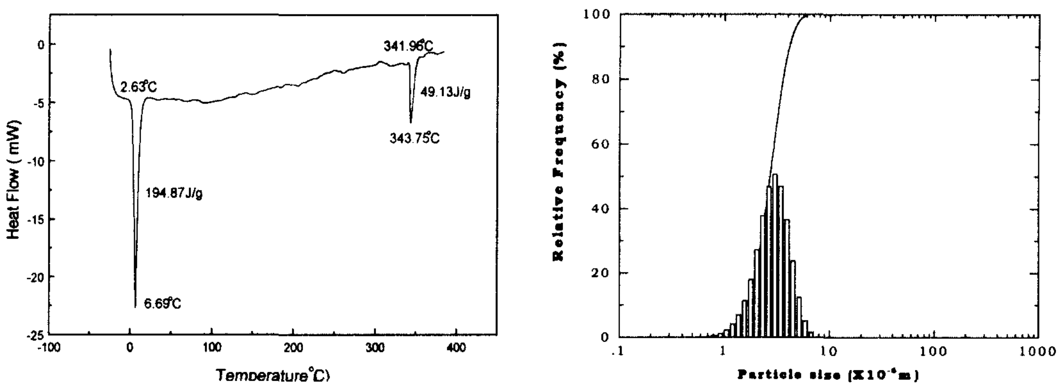
should keep short as the prepolymer grows in size and ultimately phase-separates as a liquid prepolymer-rich phase. Fig. 2 shows capsules whose sizes are distributed by 1 ~ 10 μm, produced from the reactor for the mass production in which the volume has 150 liters. The photograph of the surface of a capsule taken by SEM, which has appeared a rough skin of melamine, is also introduced.

The results of DSC analyze have shown in Fig. 3 (a). Accordingly, two peeks, one for tetradecane and the other for melamine, are obtained. As a result, the melting temperature is 6.69℃ and the latent heat of it is about 195 J/g. It is confirmed that the capsule is clearly composed of two different materials. Fig. 3 (b) describes the size distributions of the prepared capsules. The mean diameter of capsules is found to be as small as 5 μm, and uniformly ranged below 10 μm. The smaller sizes of capsules are able to withstand repeated mechanical thermal stress.[9]

3.2 Performance as a thermal storage media

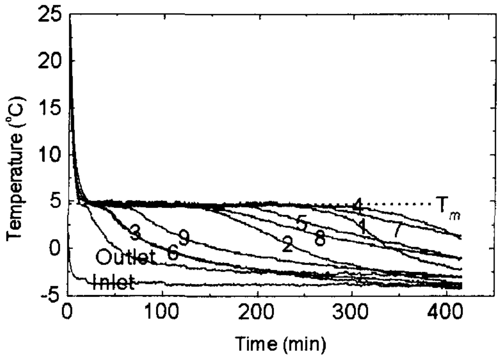
Fig. 4 shows the results of the experiment to temperature history in MPCM slurry during charging process. In the figure, it describes the temperature variation of MPCM slurry as the time of charging the storage by circulating cooling water has been changed. For the experiment, different concentrations of MPCM slurry for 20 wt%, 30 wt% and 40 wt%, respectively, have been applied for comparing with the results of pure phase change materials such as tetrandecane and water, while the circulating cooling water is controled at the flow rate of 125 cc/min. During the test, the circulating cooling water is controled at −4℃, therefore, temperatures for MPCM slurry is dropped below the melting/freezing temperatures of phase change materials, called it by supercooling, whose melting temperatures are 0℃ for water and 5.5℃ for tetradecane, after certain charging time.

Figs. 4 (a) and (b) have shown temperature changes for pure tetradecane and water during charging process. It is noted that the solidification at T/C-7, 8 and 9, where they are placed at the bottom part of the storage tank, ini-

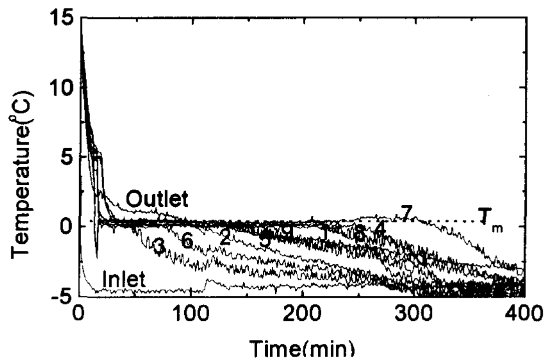


(a) (b)

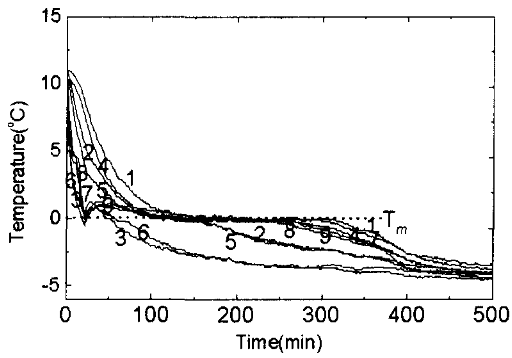
Fig. 3 (a) DSC results and (b) particle size distribution of MPCM.



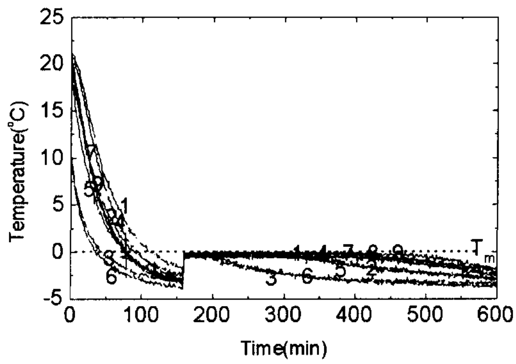
(a) Tetradecane 100%



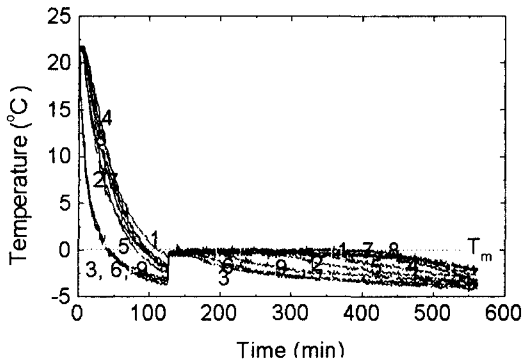
(b) Water



(c) MicroPCM 20 wt%



(d) MicroPCM 30 wt%



(e) MicroPCM 40 wt%

Fig. 4 Transient temperature variations for different thermal storage media at 125 cc/min of cooling water flow rate.

tiates. Supercooled temperature has firstly appeared at the locations near the cooling coil, which are T/C-3 and 6, finally, they have moved to the center of the storage tank, T/C-1, 4 and 7, after 200 minutes during charging of MPCM slurry.

From the results, it is shown that there is a temperature jump up to their freezing temperature after some charging time except Fig. 4 (a). It is assumed that smaller particle could transport heat into the core of capsule and circulate rigorously the fluid by convection, and thereby the core plays a role of nucleation agent. But it requires for further research on this field. As shown in Fig. 4, for pure phase change materials, heat has transferred to the center of the storage in short period of time and it completes the absorption of sensible heat in 20 minutes after the initiation, and then latent heat is absorbed.

According to Figs. 4 (a) and (b), MPCM slurry is reached to the freezing temperature within 20 minutes, while T/C-1 locating at the center of the storage becomes to be solidified after 100~180 minutes, as shown in Figs. 4 (c)~(d). However, T/C-4, 7 have reached to the solidification faster than T/C-1 since heat transfer is enhanced due to natural convection effect. For investigating the effect of the flow rate of circulating cooling water, besides of 125 cc/min, 250 cc/min and 500 cc/min are examined. As results, most of temperature histories are similar to Fig. 4, while the period of charging time is appearing shorter than the low flow rate. As results, temperature distribution in MPCM slurry during charging process shows similar to the case of 125 cc/min, while the period of charging time for 250 cc/min is requiring for 1.5~4 times to 500 cc/min.

Fig. 5 shows the variation of heat transfer coefficient within 20 minutes after starting the charging process during which sensible heat is dominated. It is noted that heat transfer is restricted due to the addition of MPCM, which is known as very low conductivity. During the initial stage of the process, heat is transferred by both conduction and convection. As the concentration of slurry becomes thick, conduction/diffusion becomes relatively dominant instead of convection, as shown in Fig. 5. It has resulted that pure phase change materials of both tetradecane and water shows a better heat transfer characteristics than MPCM slurry. As compared with between tetradecane and water, tetradecane dramatically increase the heat transfer coefficient at the initial stage of the charging due to lower specific gravity, 0.6, than water, and after while it is dropped because solidified tetradecane, whose melting/freezing temperature is around 5.5℃, at the cooling coil temperature of −3~−4℃, is coated on the surface of the cooling coil. On the other hand, in case of water, heat transfer coefficient becomes decreasing within the initial 20 minutes during which sensible heat is absorbed. And then, it is jumped up because the ice covered around the cooling coil, which is a relatively high thermal conductivity, has enhanced it. As mentioned above, MPCM slurry shows low heat transfer coefficient due to much lower convection as well as conduction than pure phase change materials.

Total absorbed heat into phase change materials during the charging process is intro-

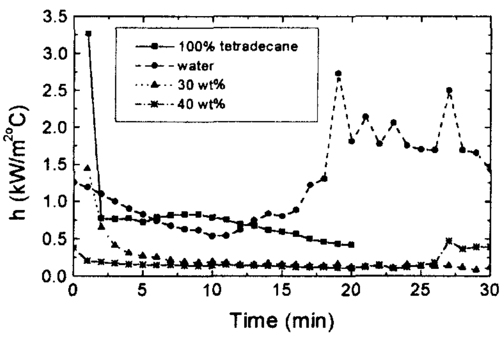


Fig. 5 Transient heat transfer coefficients for different thermal storage media.

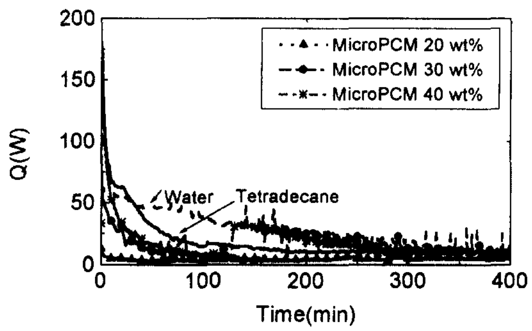


Fig. 6 Transient thermal stored rate for different storage media at 125 cc/min.

duced in Fig. 6. After 20 minutes in the charging process, both water and 20 wt% MPCM slurry are significantly increasing the rate of heat storage, 30 wt% and 40 wt% show their increasing after 120~150 minutes in the charging. It causes by initiating the solidification of phase change material after supercooling, as shown in Fig. 4, since the conversion from the absorption of sensible heat to latent heat is taken place. As described in the Fig. 6, it is found that the absorption of latent heat for water ends up in 150~250 minutes at the center of the storage tank. For MPCM slurry, the latent heat absorption for 20 wt% slurry continues by 200 minutes, and 30 wt% and 40 wt% slurry are lasting up to 300 minutes for it. However, tetrandecane ends up absorbing latent heat within 150 minutes.

Conclusively, it should prevent supercooling from the initial stage of charging process to be able to reduce the charging time. In present work, it results that 40 wt% slurry absorbs the highest amount of heat in other phase change materials. So, 40 wt% of slurries is to be optimum as well as the maximum concentration, because the slurry as a working fluid is too thick to flow in pipe if it has added up more concentration.

4. Conclusions

In present work, an experiment is conducted to investigate the characteristics of MPCM slurry, which is mixed with both water and microencapsulated phase change materials. For the first stage of the project, optimum conditions of manufacturing capsules are examined and the characteristics of MCPM slurry as thermal storage media are investigated.

For the preparation of capsules, tetradecane, paraffin oil, is adopted to store a cool energy. It is dispersed with melamine as a shell material of capsules in water soluble surfactant. The size distribution of produced capsules is ranged of 1~10 μm. And it is analyzed of thermal property with DSC. As a result, it confirms that there are two peeks of heat absorption, which mean that the capsule is composed of both core material of 6.69℃ as melting temperature and shell wall of 342℃.

It is found that the capability of thermal storage for MPCM slurry is between water and tetradecane. It has shown that MPCM slurry is restricted heat transfer by natural convection due to particles existing in the fluid of MPCM slurry during the initial stage of charging process. In order to prevent supercooling of the slurry, it is essential to control properly the temperature of cooling water circulating in coil. Finally, the total amount of heat stored in MPCM slurry is increasing as their concentrations are increasing. In view of pumping and mixing of MPCM slurry, 40 wt% is the maximum and optimum concentration.

Acknowledgement

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