Thermophysical Properties Characterization of Microencapsulated Phase Change Material Slurry

Jorge L. Alvarado
University of Illinois at Urbana-Champaign

Charles Marsh Chang Sohn
U. S. Army Corps of Engineers

Dave Kessler
University of Illinois at Urbana-Champaign

Follow this and additional works at: http://docs.lib.purdue.edu/iracc

http://docs.lib.purdue.edu/iracc/644

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.
Complete proceedings may be acquired in print and on CD-ROM directly from the Ray W. Herrick Laboratories at https://engineering.purdue.edu/Herrick/Events/orderlit.html
THERMOPHYSICAL PROPERTIES CHARACTERIZATION OF MICROENCAPSULATED PHASE CHANGE MATERIAL SLURRY

Jorge ALVARADO¹, Charles MARSH², Chang SOHN², Dave KESSLER³

¹University of Illinois at Urbana-Champaign, Department of Mechanical and Industrial Engineering, Urbana, Illinois, USA
(800) 872-2375, Fax (217) 373-6740, j-alvarado@cecer.army.mil

²U.S. Army Corps of Engineers, Engineer and Research Development Center Construction Engineering Research Laboratory Champaign, Illinois, USA
(800) 872-2375, Fax (217) 373-6740, Charles.P.Marsh@erdc.usace.army.mil, Chang.W.Sohn@erdc.usace.army.mil

³University of Illinois at Urbana-Champaign, Department of Theoretical and Applied Mechanics, Urbana, Illinois, USA
(800) 872-2375, Fax (217) 373-6740, d-kessler@cecer.army.mil

ABSTRACT

Current chilled water systems require vast amount of water and pumping power to meet increasing cooling demands. Existing cooling and heating distribution systems have an inherent thermal capacity limitation (e.g., specific heat, mass flow rate, delta T), which is often neglected when adding new buildings to military, industrial or commercial facilities, resulting in higher equipment and infrastructure costs. Through the use of an advanced material concept, namely Microencapsulated Phase Change Materials (MPCM), performance enhancement of an improved heat transfer fluid is now being pursued. This paper discusses the status of experimental efforts using a linear alkane phase change material intended for a secondary coolant for space cooling applications. Initial quantitative characterization of MPCM material properties including latent heat of fusion, melting and freezing points, and temperature- and concentration-dependent viscosity data are presented. State-of-the-art equipment was used to characterize the MPCM slurry including the use of a differential scanning calorimeter and a temperature-controlled concentric viscometer. Results indicate that the freezing and melting points of microencapsulated n-Tetradecane differed by 5°C or more when no effective nucleating agent was used. Current efforts have yielded the identification of a very effective nucleating agent, which can suppress supercooling almost entirely. Other experimental results indicate that MPCM slurry viscosity significantly depends not only on volume fraction but also on temperature, which can have an impact on the heat transfer process. MPCM slurry has the potential to become a successful heat transfer fluid, which may result in significant energy and cost savings.

1. INTRODUCTION

In the last few years, several researchers around the world have investigated the impacts and benefits of phase change materials in an attempt to boost the heat capacity of secondary heat transfer fluids. For many years, phase change materials (PCMs) have been studied to determine their potential benefits in district cooling systems. Recently, research activities have demonstrated that the heat capacity of heat transfer fluid can be increased four fold by adding PCMs to cooling systems (Bo et al., 1999). Despite their potential benefits, wide spread use of PCM has been limited by other factors including clogging of pipes and limited heat conductivity in heat exchangers (Yamagishi et al., 1999, Choi, 1993). Recent developments have demonstrated that microencapsulation of phase change material can be applied to cope with some of the drawbacks posed by PCM (Yamagishi et al., 1996). By encapsulating and isolating the phase change material from its surroundings, the phase change material is less likely to hamper the heat transfer process.
To estimate the full potential of microencapsulated phase change material (MPCM), the essential thermophysical properties must be determined through experimentation. Yamagishi et al. (1999) measured the thermal and physical properties for microencapsulated octadecane. A previous publication (Yamagishi et al. 1996) presented experimental results from several differential scanning calorimetry experiments, which were used to determine basic thermal properties, including latent heat of fusion, and melting and crystallization temperature points. Bo et al. (1999) also made use of differential scanning calorimetry to measure latent heat of fusion, and melting and crystallization temperature points of PCM. Many other researchers have used differential scanning calorimetry (DSC) to measure basic thermal properties of other materials with great accuracy.

Several investigators have studied, described and reported on the impact of spherical particles on the apparent viscosity of slurries. Vand (1948) carefully studied the interactions among particles in liquids, and proposed a model which has been regarded as the basis for the study of slurry viscosity. Thomas (1965) also studied in detail and proposed viscosity models for dilute and concentrated suspensions that depend on volume fraction. Yamagishi et al. (1996) presented viscosity data that were acquired from several experiments by using a cylindrical Couette viscometer and pressure drop measurements. In the study, the apparent viscosity of MPCM slurry clearly showed a Newtonian fluid behavior when a 1% anionic surfactant was used. A later study (Yamagishi et al., 1999) showed that the relative viscosity of MPCM slurry was fairly independent of temperature suggesting a strong correlation with changes in the viscosity of pure water.

This publication presents the status of experimental efforts using a microcapsulated n-Tetradecane intended for cooling applications. Also presented are data that qualify MPCM thermophysical properties including latent heat of fusion, melting and freezing points, and temperature- and concentration-dependent viscosity.

2. MEASUREMENT OF THERMOPHYSICAL PROPERTIES

2.1 Physical Characteristics of MPCM
Substantial amount of work has been undertaken to fully characterize MPCM. For this study, MPCM particles were made by microencapsulating 99% pure n-Tetradecane with gelatin through the process of complex coacervation. The process produces cross-linked microcapsules in the range of 70-260 µm in diameter. The average microcapsules diameter is 145 µm. On average, the particles contained 2% by weight of an effective nucleating agent. Based on microscopic observations and DSC analysis, each capsule is about 88% PCM and 12% shell material. A characteristic micrograph of MPCM can be seen in Figure 1.
2.2. Thermal Properties of MPCM

A differential scanning calorimeter (DSC) was used to determine the thermal properties of MPCM. The DSC measured the amount of heat absorbed or released by a sample in comparison to a standard reference. The energy absorbed or released was recorded as a function of time and temperature. The resulting energy-temperature profile or curve was used to determine latent heat of fusion, crystallization and melting points as described by several experts in the field of differential scanning calorimetry (Charsley and Warrington, 1992; Hatakeyama and Quinn, 1994; Speyer, 1994). Figure 2 shows a typical endotherm curve for MPCM slurry at 17.4% mass fraction. As shown in Figure 2, the melting point for MPCM slurry was calculated by reading the temperature at which the tangent to the maximum rising slope of a DSC endotherm intercepts the baseline. This is defined as the onset temperature, transition temperature, or melting point (Hatakeyama and Quinn, 1994). The area enclosed by the baseline and endotherm is equivalent to the sample’s latent heat of fusion. ASTM E 1269 gives more information on DSC methods and equipment.
Experimental Apparatus and Conditions

A TA Instruments 2920 Modulated Differential Scanning Calorimeter was used to measure the thermal properties. Hermetically sealed aluminum pans were used to contain the samples and to minimize evaporation during testing. Helium gas at a flow rate of 26 cm³/min was used as purge gas. As part of the calibration process, baseline slope offset values, and cell constant values were determined. Also, water and octadecane melting points were used to calibrate and determine the required temperature corrections. Cell constant calibration runs data were used to accurately determine the level of adjustment necessary for temperature readings and heat flow signal. A cell constant value of 1.09 was used for all the experimental runs, and used to determine as accurately as possible the real amount of heat being absorbed or released by each sample. All the DSC experiments were run by using a heating and cooling rate of 3° C/min. The temperature range was maintained as narrow as possible to obtain the highest possible resolution.

Water samples of known mass were used to verify and validate the accuracy of the calibration process. The average melting point for the water samples was 0.04° C. The average value of latent heat of fusion for the water samples was 334.4 J/g, with a standard deviation of 3.4 J/g or a 0.2% relative error when compared to the well-established value of 333.8 J/g (ASHRAE, 2001). The water sample DSC results indicate that the equipment used was reliable, accurate, and consistent.

MPCM sample preparation consisted of placing and magnetically stirring a small amount of bulk slurry in a vial to ensure a homogeneous mixture. A pipette was used to transfer samples from the vial to each aluminum pan. The MPCM samples weighed between 9 and 11 mg. The mass fraction of the samples was determined by weighing the samples before and after a controlled evaporation of the carrier fluid (water).

Results

Figure 3 shows the melting and crystallization point data for MPCM slurry at several mass fractions. Figure 4 shows the latent heat of fusion experimental results of MPCM slurry at several mass fractions as measured by the DSC.
2.3 Viscosity of MPCM Slurry

A temperature-controlled concentric viscometer was used to determine the apparent viscosity of MPCM slurry. A typical concentric viscometer consists of a rotating cylinder or spindle inside a temperature-controlled container which spins at constant and discrete rotational speeds. The device measures the viscosity of a sample by measuring the torque exerted by the fluid against the rotating cylinder. A Brookfield viscometer, model LVT with a UL adapter was used to measure the viscosity of the MPCM slurry. For temperature control, the container or UL Adapter was connected to a water bath that circulated water at a fixed temperature. A solution of laboratory grade Propylene Glycol-water mixture at 34.6% and known viscosity values was prepared to calibrate the viscometer. The viscometer was calibrated at different temperatures and spindle rotational velocities after the system had reached a constant temperature for at least 30 minutes. It was determined that the viscometer was within a 1% margin of error as suggested by the viscometer manufacturer.

The viscosity of MPCM samples of different mass fractions was measured at 12, 30 and 60 revolutions per minute to determine if the slurry behaved as a Newtonian fluid. Each sample was in the UL adapter for 30 minutes and stirred magnetically to make sure all the microcapsules were suspension before measuring the viscosity. Three measurements were taken for every sample. The mass fraction of each sample was determined by taking about three 20 μl of MPCM slurry from the UL adapter. Each 20 μl sample was dried to determine the water content and mass fraction of the sample. An analysis of variance (ANOVA) was used to determine which set of data points was suitable for further analysis. The next section shows the statistically significant results.

Results

Figure 5 shows the viscosity of MPCM slurry as a function of temperature and mass fraction.
3. DISCUSSION AND ANALYSIS OF RESULTS

3.1 Thermal Properties of MPCM: Discussion and Analysis

Figure 3 shows that the melting point for the MPCM slurry is independent of mass fraction. This should be expected because only the microencapsulated phase change material undergoes phase change at a constant temperature. The average melting point value for microencapsulated n-Tetradecane is 5.6 °C with a standard deviation of 0.06 °C. Figure 3 also shows that the crystallization and melting temperatures can differ noticeably. The difference between melting and crystallization temperatures is usually termed as supercooling. The right amount and type of a nucleating agent must be selected to suppress supercooling effectively. Classical Nucleation Theory (CNT) suggests that microemulsions may exhibit a certain degree of supercooling due to the limited number of nucleating sites inside each microdroplet. CNT also suggests that liquid-to-solid transformations take place because of the preferred type of mechanism, namely homogeneous or heterogeneous nucleation. Homogeneous nucleation, which is the main crystallization mechanism of nanodroplets (Montenegro and Landfester, 2003), has a greater nucleation barrier than heterogeneous nucleation and requires greater supercooling or lower temperature for stable nuclei to form and grow. Selection and the required amount of nucleating agents still relies on experimental trials because of the lack of a complete understanding of all the elements necessary to accurately predict the required conditions for nucleation. Figure 3 also shows that supercooling can be decreased considerably when approximately 2% of an effective nucleating agent is used.

Figure 4 shows that the latent heat of fusion for MPCM particles is linearly dependent on mass fraction. The amount of latent heat of fusion available at different mass fraction values is an important and essential piece of information necessary for thermal system simulations. The information presented in Figure 4 can also be used to estimate the amount of MPCM slurry flow rate and piping size necessary to deliver a desirable heat capacity.

3.2 Viscosity of MPCM slurry: Discussion and Analysis

Figure 5 clearly shows that the apparent viscosity of MPCM slurry depends on temperature and mass fraction. Specifically, the viscosity dependence on temperature is noted to be stronger at higher mass fractions. The relative viscosity of MPCM slurry is more dependent on temperature at higher mass fractions, contradicting the results presented by Yamagishi et al. (1999). Relative viscosity is defined as the ratio between the apparent viscosity of
MPCM slurry to that of water at a given temperature. There are two possible explanations; the difference may be attributable either to particle size or to temperature range. Yamagishi et al. used microcapsules filled with octadecane in the 2-10 µm diameter range and measured the viscosity in the 10° - 50° C temperature range. The results presented in this publication are for microcapsules in the 70 – 260 µm particle size range and the temperature was varied from 0° to 15° C. The data depicted in Figure 5 can indeed be used for thermal system simulations. The impact of higher viscosity at lower temperature and higher mass fraction should also be taken into consideration when selecting operating conditions or sizing equipment because higher viscosity represents higher pumping power, and lower turbulence and thermal conductivity.

4. CONCLUSIONS

The results presented clearly shows the potential and advantaged of using MPCM slurry as a heat transfer fluid. The thermal properties indicate that, at higher concentrations of microencapsulated n-Tetradecane, the greater the amount of latent heat of fusion will be available to increase the overall heat capacity of a thermal system. On the other hand, increased mass fractions represent higher viscosity, especially at low temperatures. The findings suggest an optimum point of operation for a particular thermal system. The results also indicate that careful consideration must be given to nucleating agent selection to be able to suppress the supercooling phenomenon effectively. The MPCM slurry thermophysical data presented in this publication can also be used for extensive thermal system simulations. MPCM Slurry has the potential to become a successful heat transfer fluid, which may result in significant energy and cost savings.

REFERENCES

American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE), 2001, ASHRAE Handbook Fundamentals, Ch. 38.


**ACKNOWLEDGMENTS**

The authors would like to thank Dr. Gary Phetteplace, Mr. Vince Hock of the U.S. Army Corps of Engineers Construction Engineering Research Lab, Mr. Jose J. Parrilla of the University of Puerto Rico at Mayagüez, and University of Illinois Professors Shelly Schmidt and Ty Newell for the valuable support provided during the execution of this research project.