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CHARACTERIZATION OF SUPERCOOLING SUPPRESSION OF MICROENCAPSULATED PHASE CHANGE MATERIAL BY USING DSC

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Supercooling suppression of microencapsulated *n*-tetradecane was measured using differential scanning calorimetry. Results indicate that the degree of supercooling is positively affected by the amount and type of nucleating agent present in bulk and microencapsulated *n*-tetradecane which it is used as a phase change material (MPCM). Results also demonstrate that the melting point of the *n*-tetradecane is fairly independent of nucleating agent concentration (0 – 4%). Conversely, the latent heat of fusion of *n*-tetradecane decreases considerably with nucleating agent amount and the initiation of crystallization point is inversely proportional to cooling rate.

Keywords: *cooling rate, crystallization point, DSC, latent heat of fusion, melting point, microencapsulated phase change material*

Introduction

In recent years, research has been directed at finding ways to increase the apparent heat capacity of heat transfer fluid. In the past, phase change materials (PCMs) have been studied to a great extent to determine their potential benefits in district cooling systems [1, 2]. Past research has shown that the heat capacity of heat transfer fluid can be increased fourfold by adding PCMs to cooling systems [3]. Researchers have also studied the impacts of using ice slurries to increase the thermal capacity of existing chilled water systems [4]. Others have used specific paraffins to match the PCM melting point with particular system operational conditions [2, 5–7]. However, full implementation has been hampered by energy-intensive pumping and clogged pipes associated with their use.

In the last two decades, PCM research has brought to light very important issues concerning the PCM's effectiveness in improving heat capacity. Several publications indicate the importance of key parameters such as the Stefan number, mass fraction, and the PCM latent heat of fusion in improving performance [8–10].

Recently, more emphasis has been put on determining the feasibility of using microencapsulated phase change materials (MPCM) as heat capacity enhancers [3]. Several investigators have reported on the benefits of MPCM slurry as a heat transfer fluid [11–14]. Roy and Sengupta [11] measured the latent heat of fusion of MPCMs that varied in size between 50 to 250 μm. Mulligan *et al.* [13] experimented with MPCMs made of *n*-octadecane, *n*-eicosane, *n*-heptadecane and *n*-dodecane as core material that varied in size between 10 to 30 μm, in silicon oil or water as the carrier fluid. The results indicate that the effective specific heat increased noticeably with mass fraction. Yamagishi *et al*. [15] measured the latent heat of fusion, melting and crystallization temperature points of microencapsulated *n*-dodecane and *n*-tetradecane as a function of capsule size. The results indicate that the degree of supercooling or difference between melting and crystallization temperature points increases with decreasing particle diameter, specifically for microcapsules of 100 μm in diameter or less.

For MPCM slurry to be successful in transferring heat in a cost effective manner, the supercooling phenomenon should be understood and controlled effectively. Supercooling suppression in organic compounds such as polymers has been studied using DSC in recent years [16–18]. Mucha and Krolikowski [16] studied the impact of several nucleating agents or fillers on the crystallization kinetics of polypropylene.

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Avella *et al.* [17] showed that $CaCO_3$ nanoparticles at 3 mass% could act as an efficient nucleating agent in isotactic polypropylene. In the case of microencapsulated octadecane, Fan *et al.* [19] used and tested sodium chloride at 6 mass% and octadecanol at 9 mass% as nucleating agents to suppress supercooling. However, such amounts of nucleating agent have an adverse effect on heat capacity.

In this paper, the thermal properties of bulk and microencapsulated *n*-tetradecane with the inclusion of effective nucleating agents are presented.

Experimental

Description and preparation of MPCM samples

The MPCM particles used in the experiments were made by microencapsulating 99% pure *n*-tetradecane with gelatin through the process of complex coacervation. This process produces cross-linked microcapsules in the range of 90–125 μm in diameter with an average size of 100 μm. On average, the particles contained nucleating agent at 0.2% of silica, and 1, 2 and 4 mass% of tetradecanol, respectively. Each particle is made of 88.3% *n*-tetradecane and nucleating agent, and 11.7% capsule material. The latent heat of fusion for bulk *n*-tetradecane was about 215 J g^{-1}.

All MPCM samples were prepared by using the same experimental procedure. In order to make sure all samples were accurate representations of the bulk slurry, approximately 15 mL of MPCM slurry was placed in a vial and magnetically stirred to make sure all the particles remained in suspension. The same pipette tip was used for all samples, which had an opening large enough to ensure that representative samples were taken every time. All MPCM sample masses were between 9 and 11 mg, consisting of water as the carrier fluid and microcapsules containing phase change material. The mass fraction of all the samples was determined by weighing the samples before and after the experiments. All the specially designed sealed pans for DSC use were carefully reopened to allow carrier fluid or water evaporation in order to determine the mass of MPCM. This value was used to determine mass fraction.

Methods

Research efforts were directed at measuring the initiation of freezing and melting points, and latent heat of fusion of MPCM. Differential scanning calorimetry was used to measure the amount of heat absorbed or released by each sample in comparison with a standard reference. The energy absorbed or released was recorded as a function of time and temperature. The resulting energy and temperature profile or curve was used to determine latent heat of fusion, specific heat, and melting point based on previous proven methodologies [1, 6, 11, 15, 20, 21–23]. More information on DSC methods and equipment can be found in ASTM E 1269.

Apparatus

The thermal behavior of the MPCM slurries under study was recorded using a TA Instruments 2920 Differential Scanning Calorimeter. Hermetically sealed aluminum pans were used. Helium gas at a flow rate of 26 cm^3 min^{-1} was used as purge gas. As part of the calibration process, a baseline calibration was performed to determine the heat signal when no samples were present. In addition to baseline calibration, cell constant and temperature calibration runs were conducted. Three cell constant calibration runs were performed to accurately measure the amount of heat supplied to the samples and to determine the adjustments necessary for temperature readings and heat flow signal. Samples of less than 10 mg of octadecane, water, and indium were used as calibration material. The information collected from the baseline, temperature, and cell constant runs were taken into consideration by the software built into the DSC for computing thermal properties. The built-in software compared the data from all the calibration runs and determined baseline slope, baseline offset, cell constant values, and temperature corrections. The cell constant values from each material were within acceptable limits. The combined average value for the cell constant was 1.09. The cell constant value was used as a correction factor to determine how much energy was actually delivered and received by each specimen.

The calibration and experimental runs were performed by using a heating and cooling rate of 3°C min^{-1} for all the experiments. The temperature range was kept as narrow as possible to obtain the highest possible resolution.

As part of the calibration process, water samples of known mass were used to validate the calibration process. All water samples had a mass of 10 mg or less. Eleven samples were tested throughout all the DSC experiments in order to make sure the experimental results were consistent. The average melting point for the water samples was 0.11°C. The average value of latent heat of fusion for the same 11 samples was 337.2 J g^{-1}, a standard deviation of 3.8 J g^{-1} and 0.8% relative error when compared with the well-established value of 335 J g^{-1}. The latent heat relative error for each sample fluctuated between –2.0 and 1.6%. The results of these water sample tests provide confidence that the DSC equipment used in the research can provide reliable, accurate, and consistent data.

Results and discussion

Several batches of bulk and microencapsulated tetradecane were tested using DSC to determine which combination of nucleating agent type and concentration could suppress supercooling effectively. As shown in Fig. 1, 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 [23]. The amount of area enclosed by the baseline and endotherm is equivalent to the latent heat of fusion of the sample, corresponding to the microencapsulated phase change material only. To determine the initiation of freezing point, the DSC was run in cooling mode at the same rate (3°C min^{-1}) to obtain an exotherm. The initiation of freezing point was determined by the same approach described above and using the corresponding exotherm.

Table 1 shows the DSC results for 100% bulk tetradecane, 99.8% bulk tetradecane with 0.2% silica fume, and 99.8% microencapsulated tetradecane with 0.2% silica fume. T_m, T_sol and λ are the melting point, initiation of freezing point, and latent heat of fusion, respectively. The results clearly indicate that silica fume is not effective in suppressing supercooling in MPCM. The considerable degree of supercooling of MPCM particles containing 0.2% of silica fume as a nucleating agent indicates that careful selection of nucleating agent type and concentration should be considered in all future studies. Table 1 also shows that silica fume is more effective in suppressing supercooling when the phase change material is in bulk form than in microdroplets. Montenegro and Landfester [24] found that nanodroplets (125–500 nm) showed considerable degree of supercooling, indicating homogeneous nucleation as the preferred type of nucleation mechanism. Classical nucleation theory (CNT) asserts that liquid-to-solid transformations take place because of homogeneous or heterogeneous nucleation. Homogeneous nucleation has a greater nucleation barrier than heterogeneous nucleation and entails greater supercooling or a lower temperature for stable nuclei to form and grow [25].

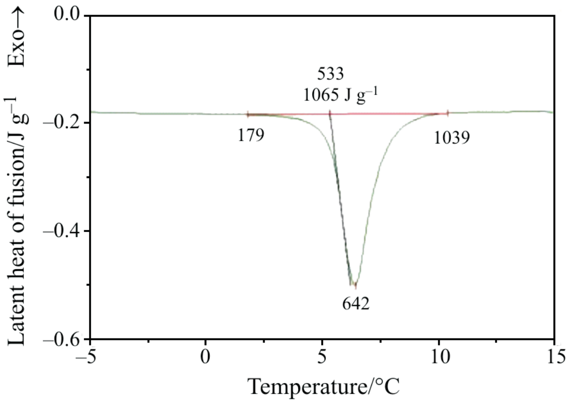

Fig. 1 Typical MPCM slurry DSC endotherm

Table 1 Tetradecane thermal properties

Sample description	T_m/°C	T_sol/°C	λ/J g^{-1}
100% bulk tetradecane	5.5	0	215
99.8% bulk tetradecane with 0.2 mass% silica fume	5.3	3.7	211
99.8% microencapsulated tetradecane with 0.2 mass% silica fume	5.3	0.1	192

Given the ineffectiveness of silica fume at 0.2 mass% as a nucleating agent, two courses of action to successfully improve the nucleation process in MPCM were contemplated. One approach was to increase the concentration of silica fume at the expense of latent heat of fusion. However, recently Danch and Osoba [18] found out that polyethylene combined with chalk exhibits unstable thermal properties in time and temperature. This suggests a second course of action which entails the use of a more appropriate and stable type of nucleating agent [18] when dealing with carbon-based molecules such as polymers and paraffins. As a result, bulk and microencapsulated tetradecane with 1, 2 and 4 mass% of tetradecanol was prepared and tested.

Figure 2 shows how the concentration of tetradecanol in tetradecane affects the initiation of freezing point in bulk and microencapsulated tetradecane samples. For bulk and microencapsulated tetradecane ($C_{14}H_{30}$), it can be seen that 2% of tetradecanol ($C_{14}H_{30}O$) is sufficient to suppress supercooling almost entirely. This suggests that heter-

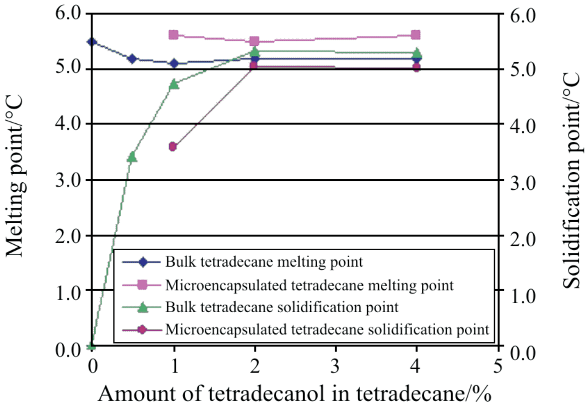

Fig. 2 Melting and initiation of freezing points of bulk and microencapsulated tetradecane with tetradecanol

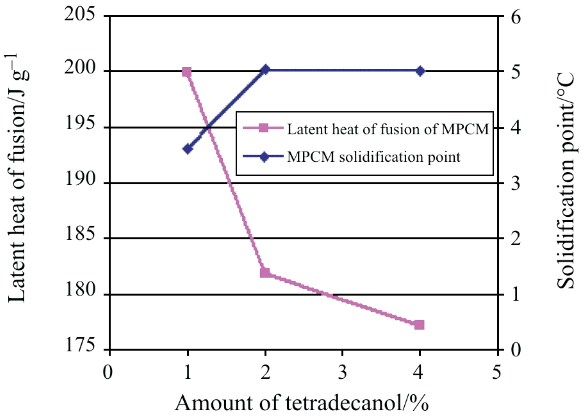

Fig. 3 Latent heat of fusion of microencapsulated tetradecane with tetradecanol

ogeneous nucleation is more favorable in the presence of tetradecanol, which is a homologous or tetradecane-like molecule. A recent study [26, 27] has shown that tetradecanol induces the formation of a rotator phase during the nucleation process, which acts as a precursor for the crystallization of tetradecane as a triclinic crystal at a higher temperature. Further combined X-ray diffraction and DSC studies should be conducted in the future to understand the impact of nucleating agent concentration on the crystal structure of MPCM.

Figure 3 shows the adverse effect of increasing nucleating agent concentration on latent heat of fusion. High latent heat of fusion is a highly desirable property for MPCM slurry in heat transfer applications. Therefore, selection of nucleating agent concentration should be as small as possible but sufficient to suppress supercooling. The loss of heat capacity is directly attributed to the presence of a nucleating agent whose melting point is at least 30°C higher than the phase change material.

Figure 4 shows that the initiation of freezing point is inversely proportional to cooling rate which clearly shows a linear trend. This behavior has been observed in bulk polymers [17] and bulk paraffins [28]. Crystallization of tetradecane, like in polymers [17] starts at a higher temperature when there is more time to overcome the nucleation energy barrier. This also entails that common kinetic mechanisms are at play which control the nucleation process in a similar fashion regardless of molecular mass or chemical structure at the cooling rate range of interest. This also indicates that a heterogeneous nucleation mechanism is responsible for supercooling suppression phenomena at higher temperatures [17].

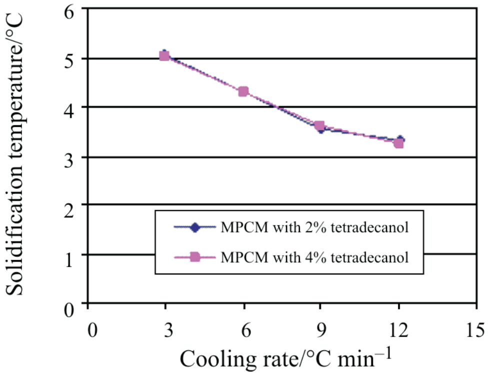

Fig. 4 Cooling rate effect on initiation of freezing point of MPCM

Conclusions

Supercooling suppression of microencapsulated *n*-tetradecane was successfully characterized using differential scanning calorimetry. Results indicate that silica fume at 0.2 mass% is ineffective in suppressing supercooling of bulk or microencapsulated tetradecane. However, supercooling of microencapsulated tetra- decane can be effectively suppressed when combined with 2 or 4% of tetradecanol. Conversely, the latent heat of fusion of *n*-tetradecane decreases considerably with nucleating agent concentration. DSC results also indicate that the initiation of freezing point decreases with cooling rate in a linear fashion which is typical of hydrocarbons at low cooling rates.

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