THE ROLE OF HETEROGENEOUS NUCLEATION IN WATER BASED PHASE CHANGE MATERIAL FOR MEDIUM TEMPERATURE REFRIGERATION

I M. Rasta¹, I N. G. Wardana², N. Hamidi³ and M. N. Sasongko²
¹Mechanical Engineering, Bali State Polytechnic, Bali, Indonesia
²Mechanical Engineering, Brawijaya University, Malang, Indonesia
E-Mail: maderasta@pnb.ac.id

ABSTRACT

This paper presents an experimental investigation on effects of corn oil to ice nucleation phenomenon of a corn oil - water solution immersed in a tank containing super-cooled liquid mixture of water and propylene glycol. Temperature of water and propylene glycol mixture was to be maintained as low as -20 °C. The corn oil-water solution is a new PCM candidate to be investigated for medium temperature refrigeration applications. Thermal energy storage characteristics of the PCM candidate were established and tested at various concentrations using a T-history method. Ice nucleation below freezing point in water/ice at temperatures ranging from -6 °C to -4 °C was induced by mixing corn oil with water to form an oil-water solution. As most of the solution consisted of water, this PCM became a strong candidate for under 0 °C applications. The PCM should be capable to maintain product temperatures of a medium temperature refrigeration system between -1 °C and +5 °C.

Keywords: heterogeneous nucleation, phase change materials, medium temperature refrigeration.

INTRODUCTION

In recent years, the both perceived global energy crisis and environmental degradation have encouraged the search for ways to store energy (ES) [1-4]. ES can help to manage energy more efficiently by bridging the gap between the availability (including storing) and demand as well energy quality, and also improve the system’s efficiency [5]. There are three ways to store energy, among others thermo-chemical heat storage, sensible and latent heat storage (LHS), each to answer the specific needs [6, 7]. Among these ways, the LHS is the most attractive one because of storing and releasing ability of large quantities of energy per unit weight of a PCM at a nearly constant temperature during the melting and solidification process [8-11]. There are many PCMs such as inorganic compounds, organic compounds, and their binary mixtures that melt and solidify at a range of temperatures, making them attractive in many applications [12, 13]. PCMs have been widely used in energy-efficient buildings, central air-conditioning systems, refrigeration, food industry, solar thermal energy storage, industrial waste heat recovery and temperature-adapted greenhouses [14, 15]. PCMs have received a great interest in cold storage applications [15-17].

One of the main difficulties in designing the system thermal energy storage (TES) based PCMs is matching materials so that they are appropriate for the thermal conditions required [18]. By the far best-known PCM is water [19]. Water has been used for cold storage for more than 2000 years [13, 20]. Water is widely used as a phase change material for cold storage because it has very good thermal properties such as; reliability, low cost, high specific heat, high density, high latent capacity of 334 kJ/kg and is safe [21,22]. Furthermore, it has been employed in many applications especially for air conditioning systems with shifting peak loads. This technology is ready for use and available commercially. Unfortunately, at temperatures below 0 °C water is not suitable. Water has a high super-cooling degree during the solidification process [23-25]. The effect of super-cooling makes it necessary to reduce the temperature well below the phase change temperature to start crystallization and to release the latent heat stored in the PCMs. If that nucleation does not occur and temperature is not reached, the PCM will not solidify at all and thus only store sensible heat [26-28]. The high super-cooling degree of water during solidification process leads to a degradation of the coefficient of performance of the system and can cause storage charging problems when the heat transfer medium is not at a low enough temperature to overcome the effect of super-cooling [29]. In practical applications of PCMs, super-cooling therefore can be a serious problem [16, 30, 31].

A PCM at freezing point temperatures that can easily be adjusted is vital. Both freezing and melting points are the most important factors for PCMs in any application [6]. The PCM must have freezing and melting points for practical operations. For freezing to come about or ice to form, ice nucleation must first occur, this is so as small embryonic ice crystals are needed to ice and to grow into larger ones [32]. Thus the importance of finding nucleate agents to stimulate the formation of ice nuclei in PCM materials and if this method can be developed so as to induce ice nucleation, significant progress can be made in limiting and minimizing super-cooling and phase separation. Sensitive freezing cold temperatures can be adapted.
This paper reports the results of studies into the effects of vegetable oil ice nucleates (commercial corn oil) in water as organic PCM for use in medium temperature refrigeration. Vegetable oil contains various types of fatty acids. Fatty acids and binary mixtures are also good organic PCM materials. An additional advantage is that vegetable oils offer a continuous supply [6]. PCM for applications on medium temperature refrigeration with product temperature between -1 °C and +5 °C requires evaporating temperature of refrigerant lower than -8 °C [33]. Ice nucleation below freezing point in water/ice at temperatures ranging from -6 °C to -4 °C was induced by mixing corn oil with water to form an oil-water solution. Most of solution content is water which makes the oil-water solutions become strong PCM candidates for below 0 °C temperature applications.

MATERIALS AND METHODS

Materials

Commercial corn oil to be mixed with water was chosen for this investigation. The corn oil contains polyunsaturated fatty acids (PUFA) which reduces both freezing and melting point temperatures of water to relatively low levels. Hence, these mixtures of oil and water can be strong PCM candidates for medium temperature refrigeration applications. The chemical composition of the investigated corn oil was checked by Gas Chromatography Mass Spectrometry (GCMS) and the results are shown in the Table-I.

Preparation of PCM Solutions

The main aims of adding commercial corn oil to water was to induce ice nucleation; to reduce supercooling as low as possible and to lower freezing points of water. The mixture, therefore, can be applied as a PCM with useful characteristics similar to those of water for use in medium temperature refrigeration.

Various corn oil in water mixture compositions were set up, namely, 5/95, 10/90, 15/85 and 20/80. Each mixture consisted of 10 ml and was mixed in liquid form in a laboratory. The mixtures were found to be complete solutions with no sediment was observed. This phenomenon can be explained by GCMS tests that indicated corn oil contained molecules of OH. Water has a chemical formula of H₂O, one atom of oxygen and two of hydrogen. When 2 molecules of water combine, there are both positive and negative attractions. Oxygen and hydrogen atoms form a bond known as the hydrogen bonds. These hydrogen bonds are not just present within the molecules but also between molecules. Hydrogen bonds in water bind hydrogen atoms of the corn oil and result in corn oil molecules spread evenly throughout the water molecules.
Table-1. Chemical composition of the investigated corn oil which is commercially available in local markets.

<table>
<thead>
<tr>
<th>Component name</th>
<th>Formula</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Isopropoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris (trimethysilox)</td>
<td>C_{16}H_{32}O_{15}Si_{7}</td>
<td>0.61</td>
</tr>
<tr>
<td>Benzene, 1-(1,5-dimethyl-4-hexenyl)</td>
<td>C_{13}H_{12}</td>
<td>17.45</td>
</tr>
<tr>
<td>1,3-Cyclohexadiene, 5-(1,5-dimethyl-4-hexenyl)</td>
<td>C_{13}H_{24}</td>
<td>8.29</td>
</tr>
<tr>
<td>Copaene</td>
<td>C_{13}H_{24}</td>
<td>0.28</td>
</tr>
<tr>
<td>8-Nonenoic acid, 5,7-Dimethylene-, methylester</td>
<td>C_{13}H_{20}O_{2}</td>
<td>0.50</td>
</tr>
<tr>
<td>Cyclohexene, 1-methyl-(5-methyl-1-methylene-4-hexenyl)</td>
<td>C_{15}H_{32}</td>
<td>8.45</td>
</tr>
<tr>
<td>Dodecanoic acid, methyl ester</td>
<td>C_{12}H_{26}O_{2}</td>
<td>10.92</td>
</tr>
<tr>
<td>Beta-sesquiphellandrene</td>
<td>C_{13}H_{34}</td>
<td>23.83</td>
</tr>
<tr>
<td>Hexadecanoic acid, methyl ester</td>
<td>C_{17}H_{36}</td>
<td>13.28</td>
</tr>
<tr>
<td>3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris (trimethylsilyl)</td>
<td>C_{19}H_{43}O_{7}Si_{7}</td>
<td>0.68</td>
</tr>
<tr>
<td>Dodecanoic acid, (2,2-dimethyl-1,3-dioxolan-4-yl) methyl ester</td>
<td>C_{16}H_{24}O_{4}</td>
<td>2.95</td>
</tr>
<tr>
<td>Hexadecanoic acid, (2,2-dimethyl-1,3-dioxolan-4-yl) methyl ester</td>
<td>C_{17}H_{26}O_{4}</td>
<td>2.95</td>
</tr>
<tr>
<td>2-Heptadecane, 1- (2,2-dimethyl-1,3-dioxolan-4-yl) methoxy</td>
<td>C_{19}H_{43}O_{7}Si_{7}</td>
<td>0.68</td>
</tr>
<tr>
<td>Anodendroside G, monoacetate</td>
<td>C_{16}H_{26}O_{11}</td>
<td>0.48</td>
</tr>
<tr>
<td>9-Octadecenoic acid (Z), methyl ester</td>
<td>C_{19}H_{34}O_{2}</td>
<td>6.21</td>
</tr>
<tr>
<td>7-Hexadecenoic acid, methyl ester</td>
<td>C_{17}H_{36}O_{2}</td>
<td>6.21</td>
</tr>
<tr>
<td>9-Octadecenoic acid, methyl ester</td>
<td>C_{19}H_{34}O_{2}</td>
<td>6.21</td>
</tr>
<tr>
<td>Cyclopropanebutanoic acid</td>
<td>C_{12}H_{22}O_{2}</td>
<td>1.38</td>
</tr>
<tr>
<td>Oxiraneoctanoic acid, 3-octyl, methyl ester, trans</td>
<td>C_{16}H_{34}O_{6}Si_{7}</td>
<td>1.63</td>
</tr>
<tr>
<td>Heptasiloxane, hexadecamethyl</td>
<td>C_{16}H_{36}O_{2}</td>
<td>1.99</td>
</tr>
<tr>
<td>Octadecanoic acid, methyl ester</td>
<td>C_{18}H_{36}O_{2}</td>
<td>1.99</td>
</tr>
<tr>
<td>Heptasiloxane, hexadecamethyl</td>
<td>C_{16}H_{36}O_{6}Si_{7}</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Method and Characterization of PCM Ice Nucleation

T-history Method was implemented for this research. Test results of the PCM sample were compared with common water material references which had well known thermo-physical properties. Therefore, the degree of super-cooling in the PCM candidate could be tested and discussed. A schematic diagram of the super-cooling measurement system is shown in the Figure-1. The system comprises of a thermostatic bath and a data logging system. The ice nucleation process during the phase change was observed visually during test and was recorded by a web-cam. The arrangement of web-cam can be seen in the Figure-2.

The PCM solution samples were placed in glass tubes and inserted into a cooling medium of the test system. The cooling medium was a mixture of 40% polypropylene glycol and water which was circulated by a pump via the evaporator of a refrigeration system. The temperature of the cooling medium could reach as low as -25 °C. For this research the temperature was maintained at -20 °C by using a digital thermostat of ± 0.2 °C accuracy. The data logging system (Figure-1) was equipped with data acquisition modules and a computer for recording data as well as a display system. The data acquisition modules utilized a Data scan 7000 series from MSL (Measurement Systems Ltd.) which included a data scan 7320 measurement processor and 7020 expansion modules. Each data scan module contained 16 differential input channels individually configurable for voltage and thermocouple readings. T-type thermocouples were used to take temperature readings from the PCM samples. The thermocouples had a temperature measurement range from -250 °C to 350 °C with a specific error of ± 0.5 °C. All thermocouples were calibrated by using a calibration bath and a precision thermometer with an uncertainty level of ± 0.4 °C. Calibration temperature range was between -25 °C and -50 °C.
RESULTS AND DISCUSSIONS

Conventional PCM Characteristics in Medium Temperature Refrigeration Applications

Figure-3 shows the curve characteristics of both tap and commercially bottled water when the temperature dropped progressively. At temperature reached their phase change point (0 °C), both tap and bottled water remained in their liquid form even though their temperature was below freezing point. Crystallization commenced after their temperatures fell far below the freezing points. The phenomenon is called super-cooling.

From Figure-3, it can be seen that there were differences between tap and commercially bottled water with respect to their super-cooling levels. The commercially bottled water had higher super-cooling temperatures than tap water. Water becomes super-cooled because of the length of time it takes for nucleation to occur and for ice crystals to form. Time difference taken to form ice (ice nucleation delay) between the tap and commercially bottled water was due to their different particle levels.

Super-cooled water is trapped in a meta-stable condition in spite of its temperature being below freezing point. This can only happen in liquids that do not contain crystal seeds (ice nuclei) that can induce crystallization (nucleation), as freezing initially happens on the surfaces of matter, this means that some heat is still held within them. Then the heat spreads throughout the substance and the temperature rises again until freezing point is reached. The crystallization of ice from super-cooled water is generally started with the formation of nuclei.

Without a nucleation agent, water molecules remain liquid until they are finally forced to form crystals due to their low temperature, as shown in the Figure-3. This is called homogeneous nucleation which usually occurs at temperatures lower than heterogeneous nucleation. The formation of ice crystals is due to combination of water molecules is known as homogeneous nucleation, while the formation of nuclei near suspended particles is called as heterogeneous nucleation. Homogeneous nucleation occurs in water where there are no particles that serve as nuclei for ice crystals to form. Heterogeneous nucleation takes place when water molecules become one nucleation agents or particles suspended in it [34, 35].

Figure-4 demonstrates the curve characteristics of salt solutions which has lower freezing point than pure water. This indicated that eutectic salt solutions have good
thermo-physical characteristics. In addition of that, salt solutions are also cheap. Unfortunately, the solutions have serious drawbacks. They are chemically unstable, corrosive and have relatively high super-cooling degrees. These make the solutions poor to be PCM candidates.

Water cannot be employed as a PCM for applications at temperatures below 0 °C because of its freezing point, as shown in the Figure-3. Therefore it requires nuclei agent in order to drop its freezing point below 0 °C. Using corn oil as the nuclei agent, freezing process of the mixture of corn oil and tap water (as a PCM candidate) has significantly changed. Detailed of the changes are demonstrated in the Figures 4, 5, 6, 7 and 8 respectively.

Figures 5, 6, 7 and 8 also indicate that increasing levels of corn oil concentration led to significant drops in solution freezing points. Furthermore, the corn oil additive in water also worked to reduce or even to prevent super-cooling. This shows that the corn oil solutions can be as an ideal PCM candidate for use in medium temperature refrigeration. However, there were significant differences between corn oil individual nuclei forming capabilities and thus their suitability as a PCM. In addition, little is known about their inter-particle spacing. Without particles to induce nucleation, drops of pure water can reach temperatures as low as -37 °C at which point they freeze homogeneously [36,37].
One more thing shown in Figures 5, 6, 7 and 8 is that the addition of 5%, 10%, 15%, 20% corn oil to tap water can cause the solution’s freezing point to drop to \(-2.5 \text{ ºC}, -6 \text{ ºC}, -7 \text{ ºC}, -8.5 \text{ ºC}\) respectively. This drop caused its vaporization to become more difficult. Thus more energy is needed to reach boiling point. While particle attraction strength releases more heat to reach freezing point which cause its freezing point to fall.

CONCLUSIONS

The role of corn oil as nuclei agents in water solutions has been studied. Heterogeneous nucleation occurs where water molecules bind with corn oil particle agents to enable the process of crystallization to occur. In this study, the use of 5%, 10%, 15% and 20% corn oil to water solutions were investigated. The solutions were found to have freezing temperatures below 0 ºC and minimum or ignorable super-cooling temperatures. Sensitive freezing points and cooling could be adjusted indicating that water based corn oil solutions were suitable for PCMs in medium temperature refrigeration applications.

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REFERENCES


