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Study on Thermal Properties of Bio-PCM Candidates in Comparison with Propylene Glycol and Salt Based PCM for sub-Zero Energy Storage Applications

I M Rasta[1], I N Suamir

Mechanical Engineering Department, Bali State Polytechnic, Kuta Selatan, Badung, Bali, 80364, Indonesia

[1]E-mail: maderasta@pnb.ac.id

Abstract. Phase Change Materials (PCMs) provide a greater density of energy storage with a smaller temperature difference between storing and releasing heat compared to sensible heat storage methods. This paper reports results of study on bio-PCM made of vegetable oil ester and water mixtures. T-history thermal analysis method was implemented in determining thermal properties of the bio-PCM candidates. Comparison analysis was also performed in order to evaluate how favorable the investigated bio-PCM compared with conventional salt based PCM and propylene glycol. The study results showed that with right amount vegetable oil ester, the bio-PCMs can reduce freezing point and reduce or even eliminate super-cooling of water. On the other hand, salt based PCMs and propylene glycol showed high super-cooling and lower latent heat storage. This study has shown that the investigated water based bio-PCMs are strong PCM candidates for sub-zero energy storage applications.

1. Introduction

Thermal energy storage (TES) technology using phase change materials (PCMs) not only improves the performance and reliability of energy systems but is useful to improve energy efficiency and energy savings and reduce discrepancies between energy supply and demand [1-5]. The latent heat thermal energy storage (LHTES) technique is the most attractive because of the ability of PCMs to store a very large amount of energy per unit of mass then release at almost constant temperature [6,7]. In addition, LHTES can achieve higher energy storage densities, smaller sizes of systems and narrower temperature ranges in melting and freezing processes with PCMs from sensible heat storage (SHS) [8-10].

PCM is classified in different groups depending on material properties. Various kinds of inorganic and organic PCMs and blends have been investigated for LHTES applications [11,12]. Among all ingredients, those who have a high storage density for a small temperature range are considered PCM [13,14]. Organic PCM has the advantage of keeping their properties stable from the number of times they melt or freeze [15,16]. One of the most popular organic PCM is paraffin wax, because the temperature range of the phase change is wide, super-cooling is negligible and chemically stable [17]. However, compared to water / ice, paraffin has higher costs, high volume changes (14%), lower latent heat and lower thermal conductivity.

Salt hydrates can be considered as potential PCMs because they have a large latent phase transition phase and melting temperature is suitable but melts incongruently. As a result, the amount of water released is not enough to dissolve the crystalline salt formed during the dehydration process. This causes differences in density, phase separation and sedimentation in containers causing serious technical problems in practical applications. Another disadvantage of salt hydrate is poor core formation ability, which causes significant super-cooling [18]. In addition, the problem of corrosion of metal components in energy storage installations [19,20].

The main problem of research on phase change TES technology is to develop effective PCMs for energy storage [21]. Temperatures and enthalpies of phase change PCMs are the most important thermal parameters, because they involve thermal stability and energy storage characteristics of PCMs [22-24]. Water is widely used as a phase change material for cold storage because it is cheap, safe and has a high specific heat (334 kJ kg^{-1}) [25, 26]. However, the high level of water super-cooling [27-29] during the freezing process causes degradation of the system performance coefficient and can cause charging storage problems when the heat transfer medium is not at sufficiently low temperatures to overcome the super-cooling effect.

This paper reports the investigation of ester vegetable oil in water solution as a good PCM candidate for applications below 0 ºC. Investigations include freezing behavior under different conditions to determine the suitability of prospective PCMs applications. A particular aspect of the investigation is (i) cooling rate and use of vegetable oil esters for constant reduction and varying coolant temperature, and (ii) determining the minimum temperature difference required to fill PCM.

2. PCM Characterization

2.1 Material

Vegetable oil ester (Corn oil and soya oil ester) was chosen because it contains a lot of unsaturated fatty acids so it has freezing point and low melting point. The composition of corn oil and soya oil ester can be seen in [30].

2.2 Preparation of Vegetable Oil in Water Mixture

Generally, pure water has a freezing point of 0 ºC. It is higher than the temperature desired to build energy conservation below 0 ºC. Two types of ingredients can be mixed in their eutectic proportions to reach the lowest eutectic temperature, namely the temperature of the phase change. To reduce the temperature of the water phase change, vegetable oil as a dispersed phase and tap water as a continuous phase (O / W = oil in water) is made in various solution concentrations (in% volume). Various percentages of vegetable oil solution (5%, 7.5%, 10% and 12.5% soya oil or corn oil), propylene glycol and in water salt are made to reduce the temperature of the water phase change. With the addition of a small amount of vegetable oil in the water, it is hoped that the characteristics of a good PCM can be produced (approaching water). There is no or little super-cooling. The total sample volume (100%) of PCM material that will be tested in this study is 10 ml (10 cc).

2.3 Characterization of PCM

- *Measurement of super-cooling degree*

Super-cooling degrees are important parameters for PCMs. Super-cooling is the presence of liquid water below 0 ºC. On the one hand, with a greater degree of super-cooling, a lower evaporation temperature would reduce the efficiency of the refrigerator. On the other hand, before freezing PCMs, energy storage is only dependent on the sensible heat at the time, which is not a lot of storage capacity can store cool (cool storage capacity). Figure 1 shows a schematic diagram of the measurement degree of a super-cooling system. This consists of a thermostatic bath and a data acquisition system.

The water temperature is added with propylene glycol (40% volume) in the tub as the cooling medium can reach -20 ºC. Test tubes sink in a thermostatic water bath. The temperature in the test tube is measured with a thermocouple (Type T). Thermocouple precision tests are ± 0.2 ºC, and they are calibrated with a precision thermometer. All thermocouples are connected to the ADAM4000 data acquisition system.

Testing for water-based PCM materials, which have high super-cooling [31,32], which relate to practical matters is not quite right with DSC. The T-history method is a simple method for determining the melting point, melting heat, type heat and PCM thermal conductivity. Temperature - Time curves from PCM samples taken and their thermo-physical properties obtained by comparing curves with Temperature-Time curves from other materials known to function as references (usually pure water) [3]. The T-history method has the following features: (i) has been designed to test large samples (ii) simple experimental unit, (iii) it is able to measure several thermo-physical properties of several samples from PCM simultaneously, and (iv) allow one to observe the phase change process of each PCM sample.

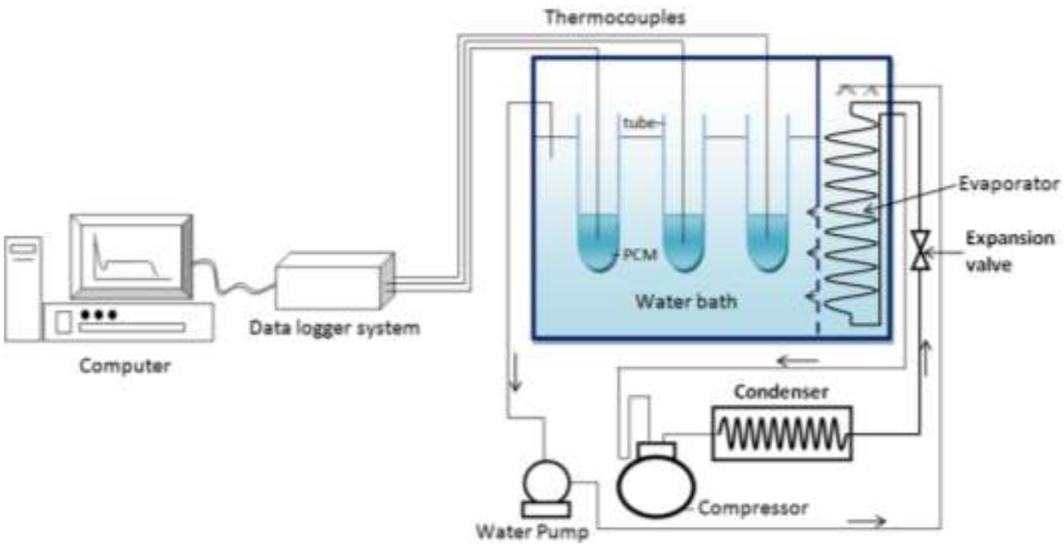

Figure 1. Schematic diagram of T-history method

- *Visualization of solidification PCMs*

To observe the phase change process of each PCM sample the test equipment is equipped with a webcam camera connected to a computer. Thus the process of forming ice cores until freezing can be observed, which is very suitable for practical applications.

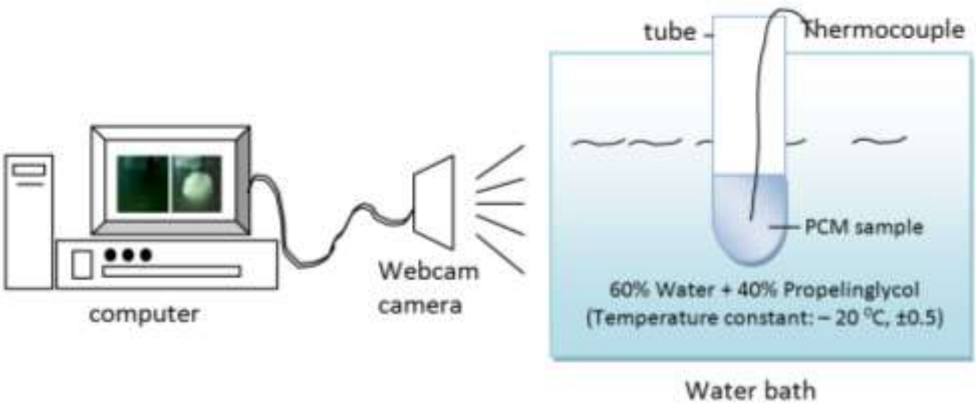

Figure 2. Visualisasi proses perubahan fase dari sampel PCM.

3. Results and Discussion

Super-cooling is a condition that is experienced by a liquid that has a dramatic decrease in temperature to below freezing without being solid. This is because the molecules in the liquid have thermal motion which prevents them from crystalizing. Freezing itself starts to occur on the surface of the substance first, so that there is heat that is still trapped in the solution. Then one day when the heat spreads evenly to all substances, the temperature will rise again until the freezing point is reached. Super-cooling is related to the internal structure of a liquid that is not compatible with crystallization.

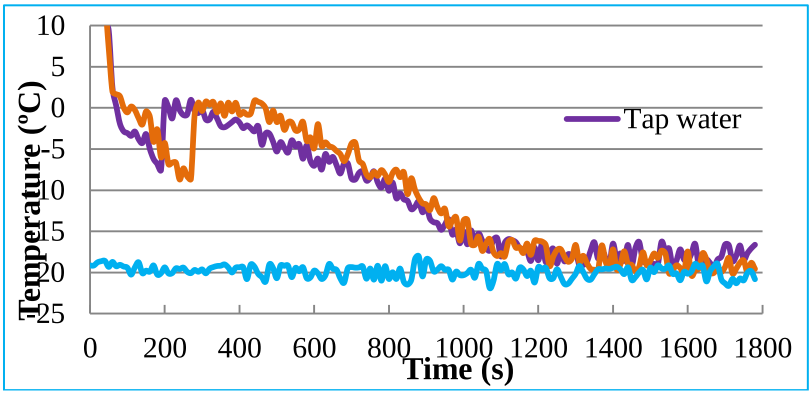

Figure 3. Water temperature on center of sample in the bath at constant temperature of -20 ºC

Large super-cooling levels make refrigerator evaporation temperature lower, which will reduce cooling efficiency. In addition, before freezing PCMs, energy storage is only based on sensible heat at that time, which means that not much storage capacity can be stored. Figure 3 shows the super-cooling behavior of tap water and mineral water samples (10 ml) in a water bath - propylene glycol. This number shows the temperature variation of the sample center with time. It can be seen that at insertion in a water bath, the temperature of the water sample rapidly decreases to -3.5 ºC and then slower until the inner temperature reaches -9 ºC. Then the ice begins to form and the temperature rises to 0 ºC. After this point, the center temperature of the water remains constant at the temperature of the phase change while the temperature of the ice in the container wall drops again, following the temperature of the water in the tub.

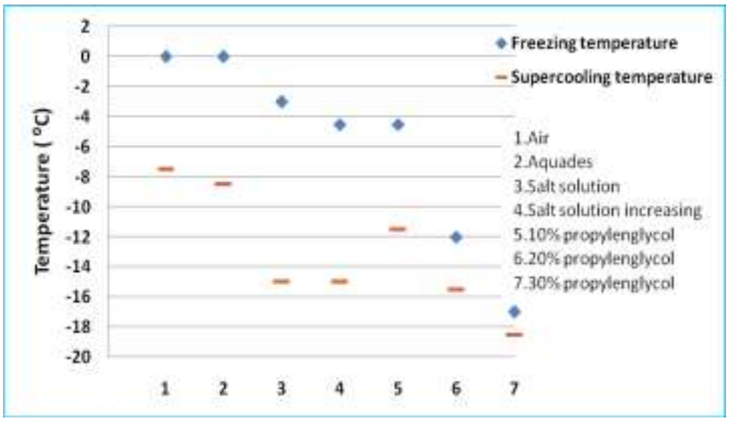

Figure 4. Freezing and super-cooling temperature of tap water with different nucleate agent concentration in T-history method

Figure 3 shows tap water and mineral water samples which occur at high levels of super-cooling. The sample does not freeze until the temperature reaches -7.5 ºC and -8.5 ºC. Thus each gives a super-cooling effect of 7.5 ºC and 8.5 ºC (Figure 5). The difference in the level of super-cooling between tap water and mineral water indicates the purity of the substance (water). The purer a substance the higher the level of super-cooling is. Therefore nucleation agents are needed to reduce / eliminate super-cooling tap water and distilled water. The nucleation agents commonly used for water are salt solutions (NaCl) and glycol, also adopted for this study.

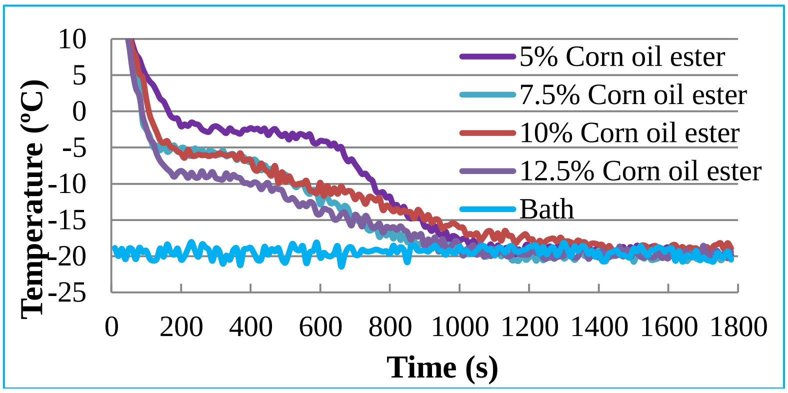

Figure 5. Freezing process of 5%, 7.5%, 10%, 12.5% corn oil ester in tap water solution

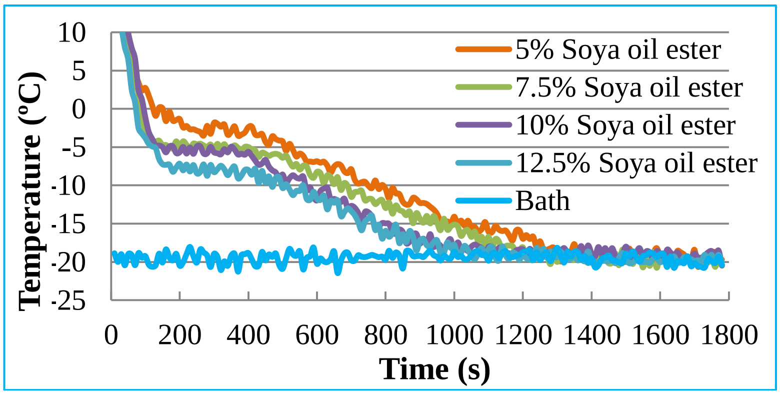

Figure 6. Freezing process of 5%, 7.5%, 10%, 12.5% soya oil ester in tap water solution

Figure 4 shows that dissolving salt or glycol into the tap water causes a decrease in the freezing point of tap water (below 0 °C), increasing significantly with an increase in the amount of salt or glycol. The freezing point of a solution (a sample of a salt solution in water) is the temperature at which the vapor pressure is equal to the solvent vapor pressure (water). Because the vapor pressure of the solution is lower than the solvent, the solution has not frozen at 0 °C. Therefore, the temperature must be lowered so that the solution can freeze. When the solvent freezes, the vapor pressure drops in the solvent faster than the liquid. As a result, at temperatures below the freezing point the solvent occurs in the vapor pressure equilibrium of the solution by solvent vaporization. At that time, the solvent will freeze while the solute is still in the liquid phase, so the solution becomes more concentrated so the freezing point is lower. Figure 4 shows super-cooling temperature due to effect of adding salt or glycol to the tap water. This can be seen by adding salt to the tap water resulting in a higher super-cooling degree effect compared to pure water. Unlike the case with the addition of 10%, 20% and 30% propylene glycol into the tap water super-cooling degrees occur respectively to 7, 3.5 and 1.5. This means that the addition of propylene glycol to the tap water results in a significant reduction in super-cooling degree compared to pure tap water.

The purpose of this study is to use vegetable oil ester (soya and corn oil ester) as a nucleation agent in water-based PCM material. Figures 5 and 6 show variations in soya oil and corn oil in water as a sample of PCM material cooled in a water bath - propylene glycol constant temperature of -20 ºC with time. This can be seen from the effect of adding 5%, 7.5%, 10% and 12.5% soya oil ester in water resulting in a decrease in the freezing temperature of the samples respectively -3 ºC; -5 ºC, -6 ºC and -8 ºC, shown in Figure 6. Addition of corn oil has decreased the freezing temperature of the samples respectively -3 ºC; -5.5 ºC, 6 ºC and -8.5 ºC, as shown in Figure 5.

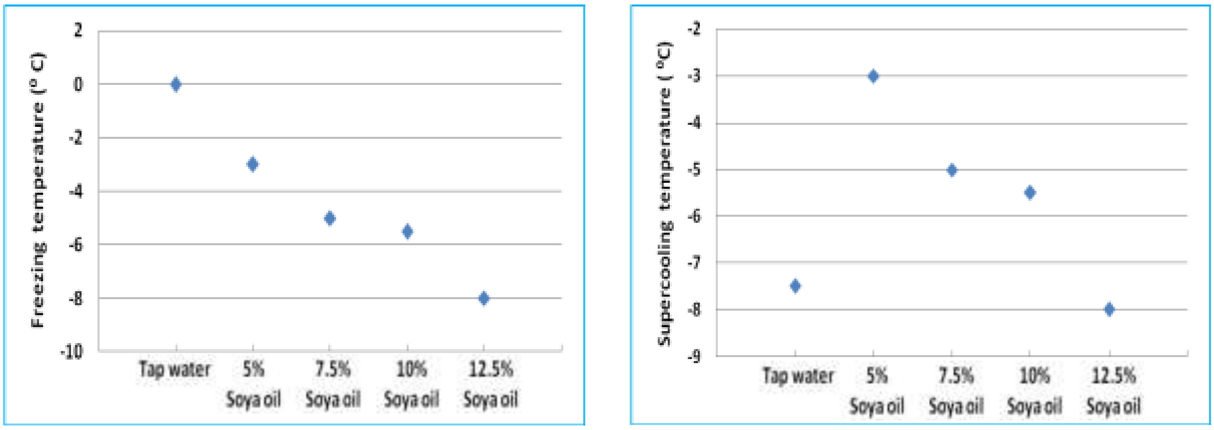

Figure 7. Freezing and super-cooling temperatures of tap water with different concentration of soya oil ester in water mixture

Figure 7 shows freezing and super-cooling temperature phenomena of corn oil ester and water mixtures at different nucleation substance concentrations (5%, 7.5%, 10%, and 12.5%). The investigation was conducted at water bath which was continuous to be cooled down to -20 ºC. While for soya oils ester mixtures can be seen in Figure 8.

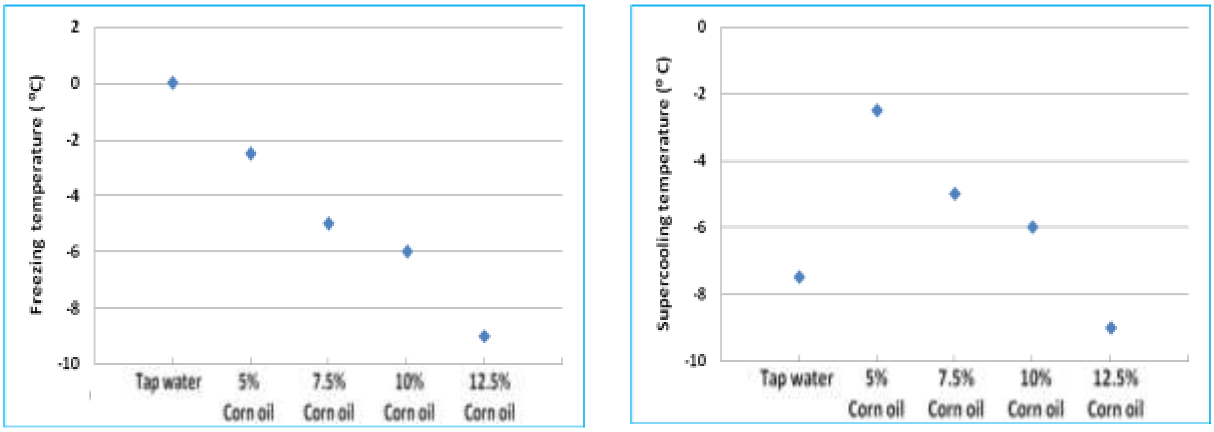

Figure 8. Freezing and super-cooling temperatures of tap water with different concentration of corn oil ester in water mixture

Figure 9 shows freezing process of water propylene glycol mixtures in a water bath at a constant temperature of -20 ºC. From the figure, it can be seen that tap water with 10%, 20% and 30% propylene glycol caused a decrease in the freezing temperature respectively down to -4.5 ºC, -12 ºC and -16.5 ºC. The figure also shows that the freezing curve is not as flat as the curve for corn oil or soya oil in water mixture as shown in Figure 5 and 6. It can be seen that propylene glycol in water mixtures require shorter time of freezing process at their freezing temperature. This indicated that latent heat storage of freezing and melting of propylene glycol and water mixture was smaller than soya or corn oil esters in water mixtures.

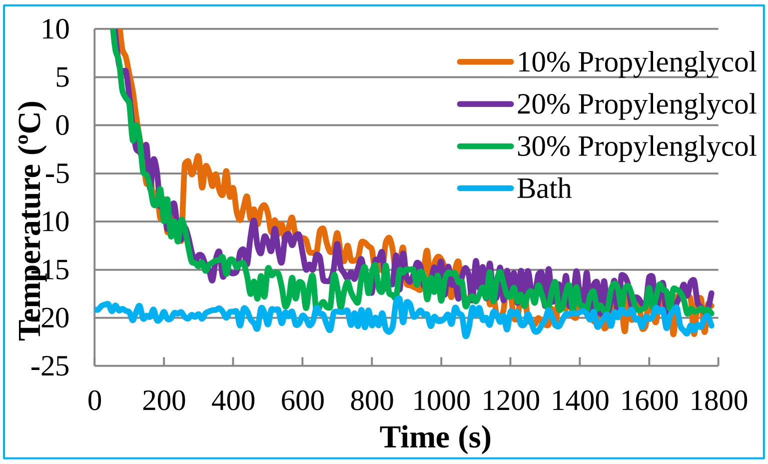

Figure 9. Freezing process of propylene glycol in water mixtures at bath temperature of -20 °C

Similar to water propylene glycol mixtures, salt based solution in water also caused a decrease in the freezing temperatures as shown in Figure 10. Salt based solution, in this study used NaCl, also has shorter time of freezing process at their freezing temperature which indicated that lower latent heat storage of freezing and melting compare with water or soya/corn oil esters in water mixtures. Both salt based solutions and propylene glycol in water mixtures have significantly high super-cooling as shown in Figure 9 and 10.

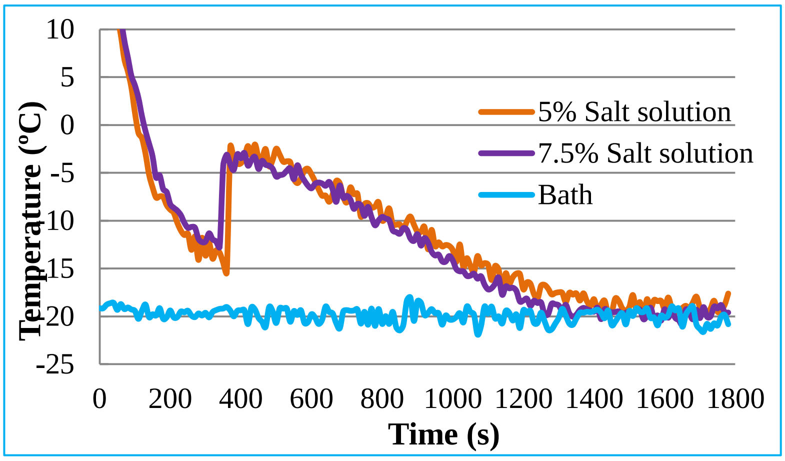

Figure 10. Freezing process of salt (NaCl) solutions at bath temperature of -20 °C

4. Conclusions

In this paper, thermal properties of bio-PCM candidates, propylene glycol as well as salt based PCM for sub-zero energy storage have been investigated. Water based PCMs with vegetable oil ester (corn and soya oil esters) nucleate agents are good candidates for sub-zero thermal energy storage. Mixtures of 5%, 7.5%, 10% and 12.5% soya oil ester in tap water can reduce freezing temperatures respectively -3 °C, -5 °C, 5.5 °C and -8 °C. Similar effects were also found for mixtures of 5%, 7.5%, 10% and 12.5% corn oil in tap water can cause a decrease in freezing temperatures respectively -3 °C, 5.5 °C, 6 °C and -8.5 °C. Smaller amount of vegetable oil ester (soya and corn oil ester) required to provide the same reduction on freezing temperature compare with propylene glycol or salt based solutions make the mixture more favorable as PCM candidates. The mixtures also found to have thermal properties very closed to water even better with regards to super-cooling. The vegetable oil ester and water mixture could eliminate degree of super-cooling.

5. Acknowledgements

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