Phase separation on ricinoleic acid freezing

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Abstract. Phase separation material essentially influence storage capacity or heat release. Ricinoleic acid is potential to be used as a heat storage material. However, the nature of the phase separation of the material has not been studied yet. Therefore, this research was aim to determine the nature of the material. The test of characteristics of heat fusion and crystallization temperature of the material are carried were examined by using differential scanning calorimetry (DSC). The test was carried out using 15-20 mg of ricinoleic acid with cooling rate of 2°C/min, 3°C/min, 4°C/min, 5°C/min, 10°C/min, and 15°C/min. Coagulation testing was done by using a digital microscope of data aquisition. For comparison, characterization on oleic acid was also done. The result that hydroxyl functional group affects the occurrence of phase separation on the ricinoleic acid freezing process.

1 Introduction

Currently latent heat utilization applications in the field of energy conservation are increasing. To take advantage of latent heat, heat storage media are required. The material used as a latent heat storage medium known as PCM (phase change material). In addition to latent heat, sensible heat can also be utilized. However, the most efficient thermal energy storage is in the form of latent heat [1]. Babay [2] stated that there is currently a lot of (situation of) energy wasted due to being in the wrong place and or time. Therefore, energy storage with a wide range of that circumstances is required. PCM application on such a situation is right. This is supported by statements of Sharma [3] that the PCM application is very broad for latent heat storage system.

Good PCM must meet several criteria, including thermodynamic characteristic, namely high latent heat, high thermal conductivity, high density, low volume changes, and economical [4]. Thermophysic material properties, such as melting point, density, and thermal conductivity, greatly affects the latent heat storage. This statement is supported by Cailean [5] that the amount of heat that can be stored in the PCM is strongly influenced by the nature of the thermophysic material. Materials having high thermal conductivity has capability of storing heat in a short time. Material specific heat also affects the heat storage capacity. The greater the specific heat the greater the capacity of the heat material storage.

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Compared with other fatty acid, ricinoleic acid has the advantages such as non-corrosive to the container material and environmentally friendly. In addition, the raw material is not of groceries, so it will not interfere with national food security. Based on these considerations, ricinoleic acid is potential to be used as PCM. This statement is supported by Mehling [6] that the PCM organic materials have advantages such as the material is compatible with conventional material, stable chemical properties, high heat fusion, and non-toxic. However, Mehling [6] also argues that one of the main problems in the process of heat storage is phase separation and supercooling. So far, research on phase separation and supercooling of ricinoleic acid are very few. Therefore, this study is very important to be carried out. Both heat absorption and extraction take place due to the atomic diffusion or molecular diffusion. According to Mehling [6], the most common diffusion is molecule diffusion. This diffusion occurs if there is displacement of a silent molecule layer in the solid or liquid phase. But according to Mehrer [7], the congruent melting nature is a material melting perfectly. The material melting perfectly has the same composition whether it is in the solid phase or in liquid phase. Phase separation occurs if the composition comprises two or more components. If there is a cis double bond in the chain, the molecule can not form a neat and incompressible lattice, but tend to be circular [8]. Cis double bond on ricinoleic acid forms a kink chain, and disturbs the crystal order. Therefore, only a little energy is needed to melt the ricinoleic acid.

2 Materials and Methods

The material used in this experiment was ricinoleic acid ($C_{18}H_{34}O_3$) Testing the melting temperature (Tm), crystallization temperature (Tc), and the heat fusion (Q) was done by using an equipment named Differential Scanning Calorimetry (DSC). Tests were carried out using 15-20 mg of ricinoleic acid and the cooling rate of (Φ) 2°C/min, 3°C/min, 4°C/min, 5°C/min, 10°C/min, and 15°C/min. Morphology testing through isothermal cooling and freezing characteristic and melting was done by using a digital microscope data acquisition (as shown in Figure 1). For comparison, characterization on oleic acid was also done.
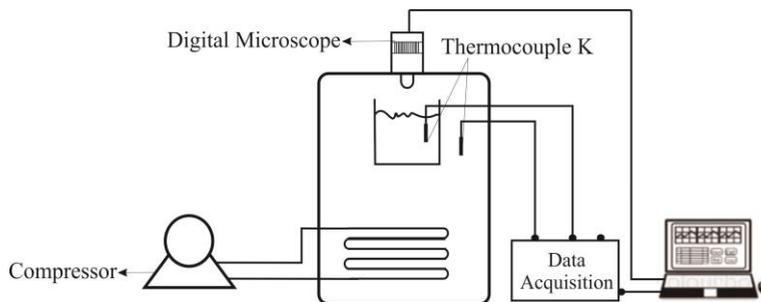

Fig. 1. Scheme of data acquisition morphological test.

This image of morphology during freezing process was captured using digital microscope and then it was recorded into computer memory. The cooling temperature was recorded by K type thermocouple. The analog signal from the thermocouple was converted into a digital signal through an analog to digital converter (adc) before it was recorded into the computer.

3 Result and Discussions

In the cooling rate of 2°C/m, 3°C/m, and 4°C/min crystalization temperature is undetectable. Crystallization temperature of -7.17°C occurs at a cooling rate of 5°C/min and the crystalization temperature of -8.17°C with the cooling rate of 10°C/min. However, the crystallization temperature was undetectable at the cooling rate of 15°C/min. On the other hand, the crystalization temperature of oleic acid was detected in each cooling rate of 2°C/min up to 15°C/min.
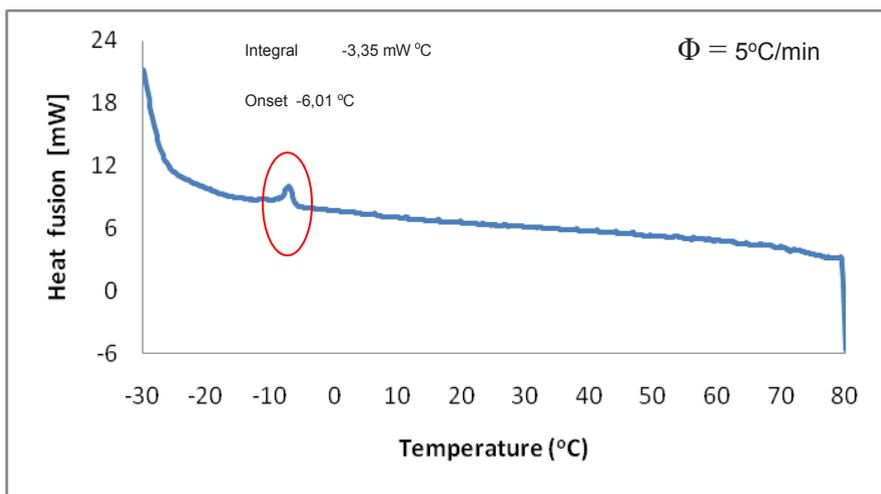

Fig. 2. The heat fusion of ricinoleic acid vs temperature

For the testing with cooling rate of 5°C/min as shown in Figure 2, the peak occurs at -7.17°C and transition temperature at -6.01°C. This means that the process of crystal formation begins at -7.17°C and further solidifies at 8.58°C. The state of crystal formation below the freezing point is supercooling condition.
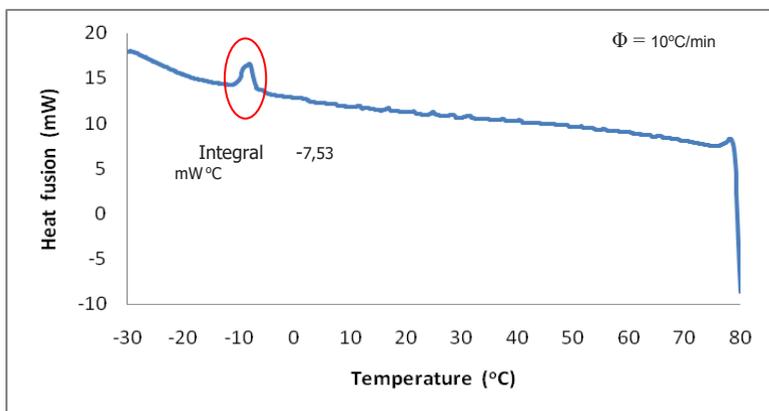

Fig. 3. The heat fusion of ricinoleic acid vs temperature.

Figure 3 shows a peak at -8.17°C crystallization temperature and the transition temperature at -6.82°C with 7.53 mW/°C heat fusion. This means that the process of crystal

formation begins at -8.17°C and further solidifies at 8.58°C. These results indicate that the greater the cooling rate, the lower the crystallization temperature.
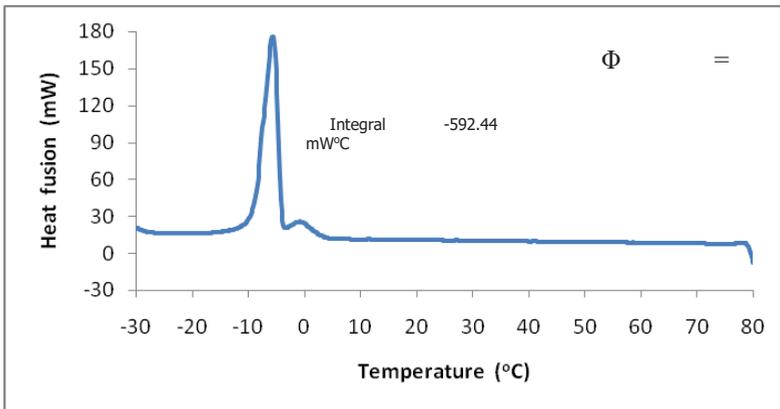

Fig. 4. The heat fusion vs. temperature of oleic acid..

Testing of oleic acid freezing at a rate of 10°C/min as shown in Figure 4 shows the peak at -5.50°C, transition temperature at -3.89°C, and heat fusion of 592.44 mW/°C. The process of crystal formation begins at -5.50°C and then solidifies at 6.58°C. The results also indicate the occurrence of supercooling. This supercooling occurence resulted in the release of sensible heat of 592.44 mW/°C. Testing of oleic acid freezing on the cooling rate 15°C/min is shown in Figure 5.
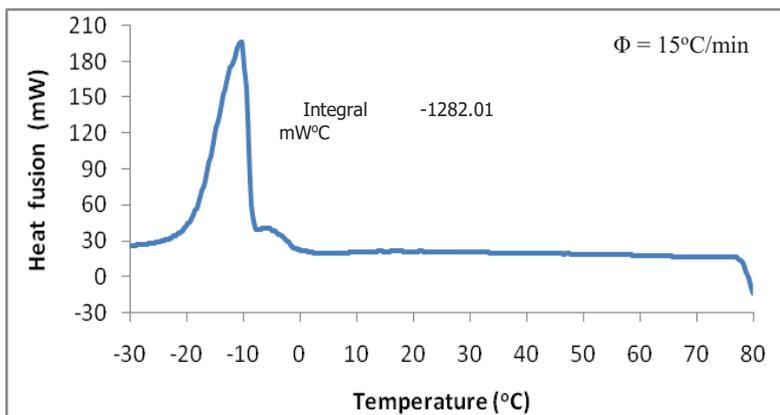

Fig. 5. The heat fusion vs temperature of oleic acid.

Figure 5 shows the peak at -10.50°C, transition temperature at -8.07°C, and heat fusion of 1282.01 mW/°C. The process of crystal formation begins at -5.50°C and further solidifies at 6.58°C.

(a)   (b)
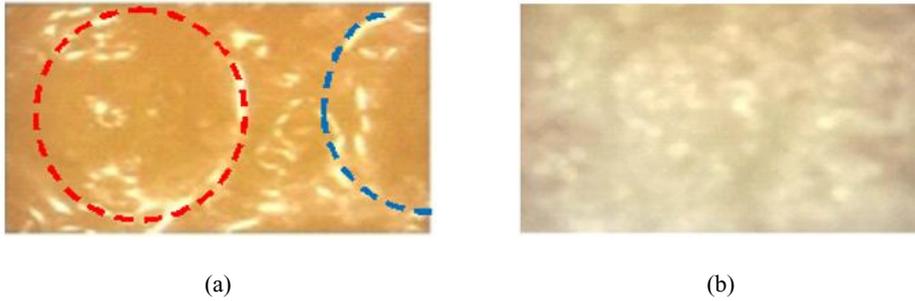
Fig. 6. Material morphology of (a) ricinoleic acid (b) oleic acid at 7°C temperature.

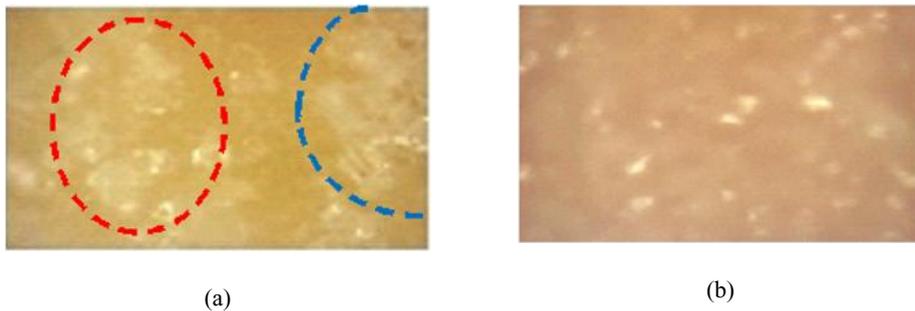(a)   (b)

Fig. 7. Material morphology of (a) ricinoleic acid (b) oleic acid at 4°C temperature.

Figure 6 and 7 shows the morphology of ricinoleic acid (a) and the morphology of oleic acid (b) at 7°C and 4°C temperature respectively. The process of crystal formation in oleic acid is more rapidly and more neatly than ricinoleic acid. In the freezing process, ricinoleic acid crystal formation is not simultaneous and multi-phase form. At the morphological image there is a visible form of micelles (red circles) and other crystal forms (blue circles). This form of multi-phase is also reported by the Nishizawa [9], the freezing of polymer material can form a multi-phase morphology.

Ricinoleic acid and oleic acid are unsaturated fatty acids with a double bond (cis) on atom C-9 and C-10. However, the C-12 atom has hodroxyl group on ricinoleic acid, but not present in oleic acid [10]. According to Petrucci [11] hydroxyl group is a polar functional group, namely polar covalent bond between oxygen and hydrogen. Hydroxyl group causes dipole-dipole interaction, so that the energy required to freeze the material is greater. In contrary, the energy needed to mold it is lower. As a result, the material melting point is lower as well. This is supported Fessenden [8] that the molecules can not form a lattice that is neat and rapid, but tend to be circular. Correspondingly, it is strengthened by Zhang [12] that the fatty acid composition affects the crystallization process very much. As a result, heat storage decreased during the smelting process..

4 Conclusion

The results show that phase separation and supercooling occur on the freezing process of ricinoleic acid. Supercooling occurs at the cooling rate of 5°C/min and 10°C/min with successive crystallization temperature of -7.17°C and -8.17°C. Crystallization temperature was not detected in the cooling rate below 5°C/min and above 10°C/min. It can be concluded that hydroxyl groups influences the occurrence of phase separation on the

freezing process of ricinoleic acid. Therefore, ricinoleic acid has better latent heat storage characteristics than oleic acid.

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