Physical Properties and Thermal Storage Characteristics of a Phase Change Emulsion

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Abstract:

An emulsion dispersed nano-size particles of phase change material is produced. We discuss with the thermophysical properties, the stability of emulsion, and the heat transport characteristics as a thermal functional fluid. The testing emulsion, which has nano-size particles as the discrete phase, is produced with a D-phase emulsification method. The diameter of discrete phase in the emulsion is measured for evaluation of the long-term stability of emulsion. In addition, the DSC curve of emulsion is determined. The results reveal that the emulsion with the D-phase emulsification method has the superior stability. From the differential thermal analysis, the DSC curve of present emulsion indicates a discontinuous change at the phase change temperature of phase change material due to its latent heat.

Keywords:

Thermal Storage, Emulsion, Phase Change Material, Thermophysical Properties.

1. Introduction

A dispersed system which contains phase change materials for the dispersed phase attracts increasing attentions as one kind of thermal storage media. A microcapsule system [1-3] has a reputation as a thermofunctional fluid. However, the microcapsule fluid has a bunch of very real problems such as a lack of long-term stability and durability for the practical usage of thermal storage devices.

An emulsion is a type of dispersed system [4]. In the emulsion, one of two liquids which will not mix with each other is dispersed as particles (the dispersed phase) in the other (the continuous phase). Especially, the emulsion which contains nano-size phase change materials for the dispersed phase has great advantages against other type of phase change materials. For instance, the nanoemulsion indicates a low viscosity, a high fluidity, and a long-term stability comparison with the microemulsion [5].

The aim of our research group is to propose more sophisticated latent heat storage technologies and new thermofunctional fluids. As part of that effort, we have replaced the dispersed phase in emulsions with alkane-based phase change materials, and by reducing the size of those materials to nano-size, we have developed phase change emulsions and also examined the thermal properties and stability of these emulsions [6].

On the other hand, a diverse variety of techniques for preparing emulsions have been proposed in the field of cosmetics science, but these techniques have not been described based on their long-term stability and convenience from the perspective of use as thermofunctional fluids, and that research amounts to nothing more than selecting preparation techniques which have empirically been successful in many cases. There, in this research, an emulsion was prepared using the D-phase

emulsification method, which is easy and requires little energy compared to the phase inversion emulsification method which has previously been the most common technique for emulsion preparation [7-9] . Then the stability of that emulsion was evaluated, and its thermal properties were measured. Heat storage and radiation characteristics were also experimentally examined.

2. Phase change emulsion

Generally speaking, emulsion preparation methods can be divided into two types: mechanical techniques and surface chemistry techniques. With mechanical techniques, the dispersed particles are reduced to microparticles using a homogenizer with high shearing force or high pressure, and this technique is suitable for large-scale mass production. With surface chemistry techniques, on the other hand, the hydrophilic-lipophilic balance (HLB value) of the emulsifier (surfactant) is adjusted, and emulsification is achieved by obtaining the D-phase, which is a surfactant associate, through adjustment of the temperature or adding an additive. This method does not require large-scale equipment, and energy consumption for producing the emulsion can be reduced. In this research, the emulsion was prepared using a surface chemistry technique called the D-phase emulsification method, and the particle size distribution and characteristics of the obtained emulsion were examined. Also, the emulsion which was the subject of this research was the O/W type in which the continuous phase is water. The D-phase emulsification method is a technique developed by Sagitani et al. [10]. With this method, an emulsion is produced by adding water-soluble polyalcohol to a nonionic surfactant, oil and water system, adjusting the HLB value, and obtaining a D-phase and O/D gel. The details of the preparation procedure are given in the references [10], but since energy consumed in emulsion production can be reduced because the method requires no heating or cooling as with the PIT method, and no great mechanical force for agitation, it was thought to be suitable for the application which was the subject of this research. Furthermore, the method can use a water soluble surfactant with a comparatively wide range of HLB values, and thus the impact on the environment is low and the amount which can be prepared at one time is larger than with the PIT method.

Figure 1 shows the emulsification process of the D-phase emulsification method. In Fig. 1, the components of the O/W emulsion are placed at the vertices of a tetrahedron. The mixture rates are indicated by taking each vertex as 100%, and the opposing side as 0%. For example, a solution at point A in the diagram indicates a blend of a mixed liquid of water-polyalcohol (50%) and surfactant (50%). Moving along the arrow from point A to point B means that oil is added until it accounts for approximately 80% of the mixed liquid. In the D-phase emulsification method, the first step is formation of an O/D gel emulsion by dispersing an oil phase (point B in Fig. 3-1) into a solution containing water, polyalcohol and surfactant (point A). This is then made into an O/W solution by diluting the gel emulsion with water (point C). Photographs of the appearance at points A, B and C in Fig. 1 are shown, respectively, in Fig. 2 (A) , (B) and (C). For preparing an emulsion using the D-phase emulsification method in this research, polyoxyethylene sorbitan monooleate (HLB value 15.0) was selected as the nonionic surfactant. This surfactant is highly hydrophilic, and thus the cloud point which indicates hydrophobicity as the temperature rises is not near the ordinary use temperature and it is thought that the emulsion can be kept in a stable condition even through repeated cycles of heating and cooling. Regarding the substances used as emulsion materials in this research, purified water was used as the continuous phase, and hexadecane ($C_{16}H_{34}$, melting point 18.2ºC) as the solute which is the phase change material. In addition, polyoxyethylene sorbitan monooleate ($C_{64}H_{124}O_{26}$) was used as the surfactant, and 1,3-Butane diol ($C_4H_{10}O_2$) as the polyalcohol. In this experiment, an emulsion blended with 10% hexadecane was produced by mixing purified water, hexadecane, surfactant and polyalcohol in the ratios given in the table to yield a total of 100g.
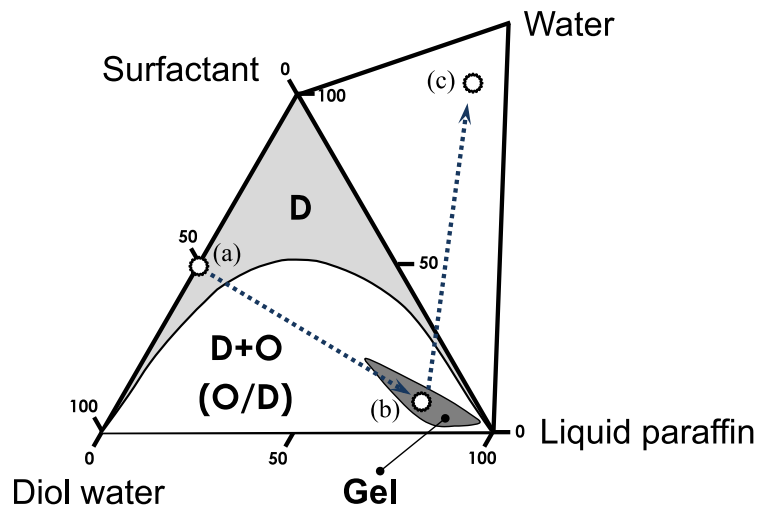
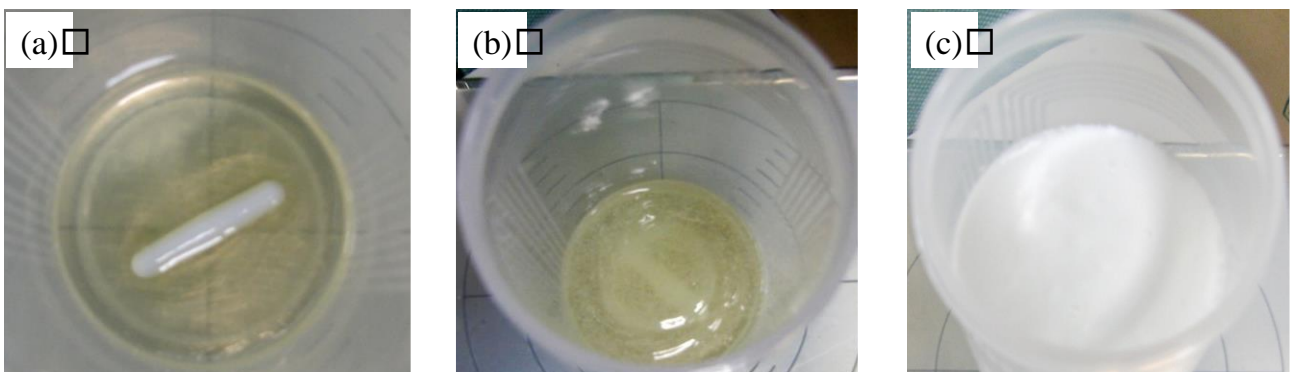*Fig. 1. Phase diagram for production of emulsion by D-phase emulsification method.*

Fig. 2. Photos of emulsion process: (a) diol aqueous solution; (b) O/D phase emulsion; (c) diluted with water.

3. Physical properties of emulsion

3.1. Stability

There is a correlation between emulsion particle size and emulsion stability, and in general the smaller the particle size, the higher the stability of the emulsion. Therefore, it is crucial to ascertain the particle size of the prepared emulsion. In order to determine the size of the hexadecane particles dispersed in the emulsion, and their changes over time, the particle size and particle size distribution of the prepared emulsion were measured from immediately after the emulsion was finished until 65 days later. This section describes the results of those measurements. A laser diffraction particle size analyzer (Shimadzu, SALD-3000) was used to measure particle size.

Figure 3 shows the particle size distribution of the emulsion immediately after preparation. The horizontal axis of the graph indicates particle size, and the vertical axis indicates the number of particles of a certain size as a percentage of the total number of particles. Immediately after preparing the emulsion, the minimum particle size was 0.333 μm, maximum particle size 0.604 μm , and most common particle size (median diameter) 0.422 μm. On the other hand, Fig. 4 shows changes in the most common particle size over the 65-day interval. It can be confirmed from the

figure that a highly stable emulsion was prepared, with almost no evident changes in particle diameter even after 65 days had elapsed.
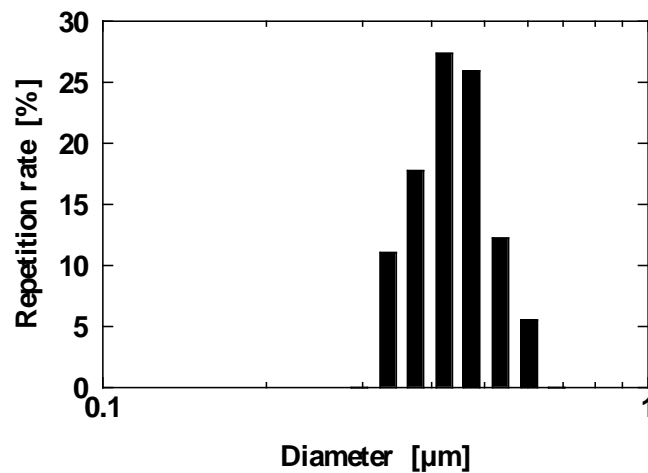

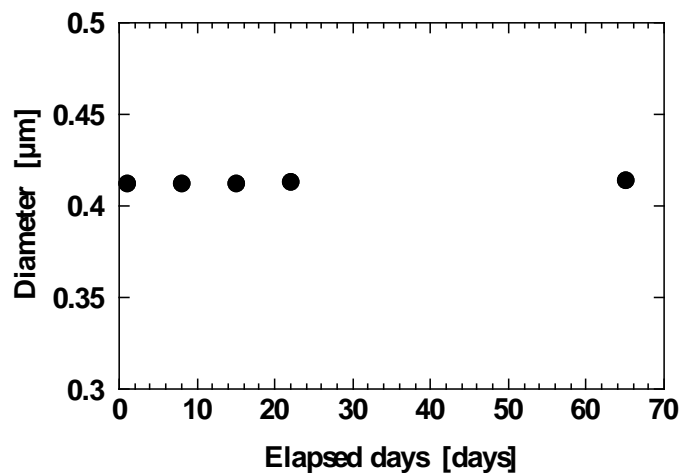*Fig. 3. Reprtition rate of diameter of dispersed phase in emulsion.*

Fig. 4. Stability of emulsion.

3.2. Viscosity

In this research, a rotating viscometer (Brookfield, Digital Viscometer Model DV-II Pro) was used to measure the viscosity of the prepared emulsion. In the experiment, temperature control was carried out by connecting the rotating viscometer with a thermostatic chamber, and the emulsion viscosity was measured from 25°C to 0°C. In addition, the rotation speed of the viscometer was set to 200 rpm.

Figure 5 shows the relationship between temperature and viscosity. From the figure, it was found that viscosity of the prepared emulsion is 2.2 times that of water at 10°C, and 2.1 times that of water at 20°C.
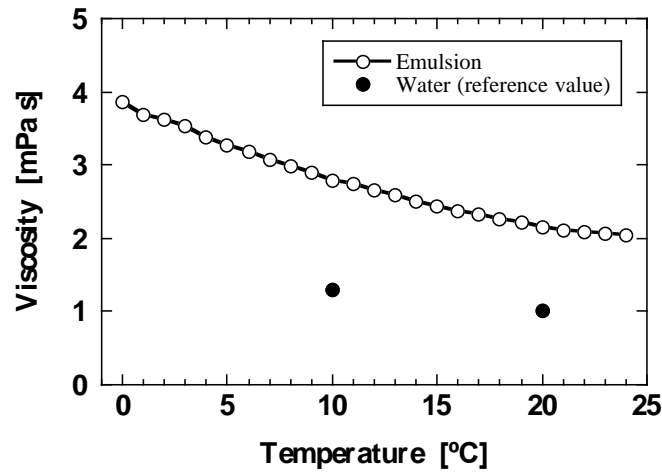
Fig. 5. Viscosity of emulsion.

3.3. Thermal characteristics

The melting point of the hexadecane dispersed in the prepared emulsion is 18.2℃. On the other hand, it is known that liquid phase change materials dispersed in an emulsion exhibit lower crystallization temperature with smaller particles sizes [11], and to enable industrial use, it is necessary to know the solidifying point of the hexadecane dispersed in the emulsion. In this research, differential scanning calorimetry (DSC; Rigaku, Thermo plus EVO2) was used to measure the melting point and solidifying point of the prepared emulsion.

Figure 6 shows the DSC measurement results and their relationship with heat flow and temperature. The vertical axis of the figure indicates heat flow, and the horizontal axis temperature. The line at the top of the figure is the DSC curve during cooling, and the line at the bottom is the DSC curve during heating. The rate of temperature rise was set to 2 K/min.

From the graph it is observed that, in the cooling process, there is a peak accompanying latent heat absorption near 1℃. Since latent heat is released as the sample material solidifies, this peak is thought to be due to the solidification heat of the hexadecane contained in the emulsion. In addition, a peak is evident at approximately 18℃ in measurement of the heating process, and it is inferred that release of latent heat occurred here. Due to the above results, it was found that the degree of supercooling of the hexadecane dispersed in the emulsion prepared in this research was approximately 17 K. These results are almost the same as the results of Eric Dickerson et al. [12].
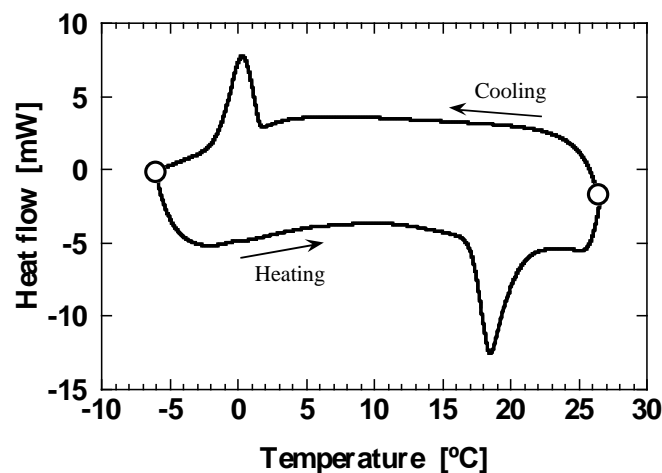

Fig. 6. Heat flow measurement of emulsion with DSC.

3.4. Heat transport characteristics

In order to ascertain the heat exchange characteristics of the phase change emulsion in this research, a convection heat dissipation experiment was carried out using a parallel flow type double-pipe heat exchanger.

Figure 7 shows a schematic system diagram of the experimental apparatus. The apparatus is comprised of a cooling water circulation system and emulsion circulation system. The cooling water circulation system is comprised of a cooling water pipe, low-temperature thermostatic chamber, testing section, and temperature measurement system. The emulsion circulation system is comprised of an emulsion storage tank, emulsion transport pipe, pump, flow control valve, test section, and temperature measurement system.
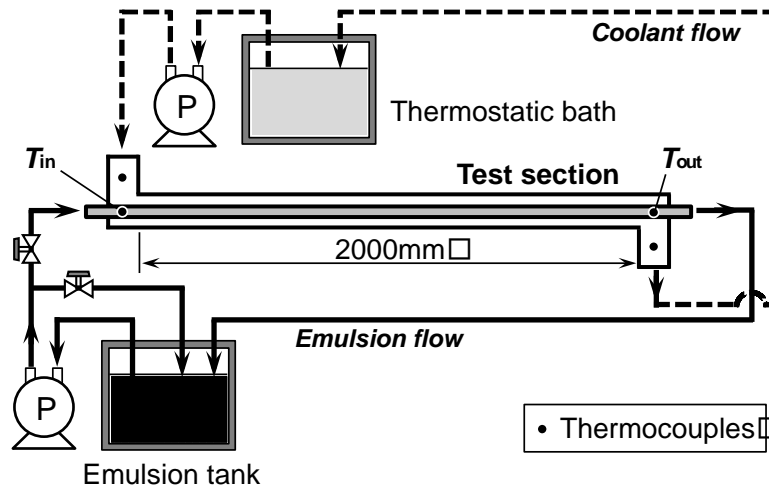

Fig.7. Schematic drawing of experimental apparatus.

The test section is a double-pipe heat exchanger, and it has a structure in which cooling water and emulsion flow in the same direction, the former on the outside and the latter on the inside. In addition, thermocouples are provided at the inlet and outlet of each unit, so that inlet and outlet temperature can be measured for each channel.

Table 1 shows the experiment conditions. In this experiment, an aqueous solution of propylene glycol with adjusted concentration (approximately 33 wt%) was used as the cooling liquid. The cooling liquid flows through the ring-shaped channel on the outside of the test section.

Table 1. Experimental condition.

Condition No.	Inlet temperature of emulsion, T_{in} [°C]	Inlet temperature of coolant [°C]
1	30	5
2	20	−5
3	15	−10

In all experiment conditions, the temperature difference was set to 25°C at the test section inlet for the sample liquid and cooling liquid. This was done in order to set the difference in temperature of each sample fluid between the test section inlet and outlet to approximately 10°C, and ensure an

adequate temperature difference between the inlet and outlet. For example, in experiment Condition 1, the emulsion inlet temperature was 30℃, and the outlet temperature was approximately 20 ℃.

In order to ascertain the effects on heat exchange duty due to the phase change of hexadecane dispersed in the emulsion, experiments were conducted under a condition (Condition 1) not straddling the 18.2℃ phase change temperature of hexadecane, and under conditions (Condition 2 and 3) straddling the phase change temperature of hexadecane where there is a possibility of a phase change by hexadecane.

Also, it was possible to estimate through a preliminary experiment that heat loss when the cooling liquid inlet temperature is 5℃ is 5% or less of the quantity of heat obtained by the cooling liquid. Similarly, heat loss at −5℃ was estimated to be 8% or less, and at −10℃ to be 10% or less.

Fig. 8 shows the emulsion temperature at the outlet of the test section. The horizontal axis of the figure indicates the numbers of the experiment conditions given in Table 1, and the vertical axis indicates the water temperature at the test section outlet.
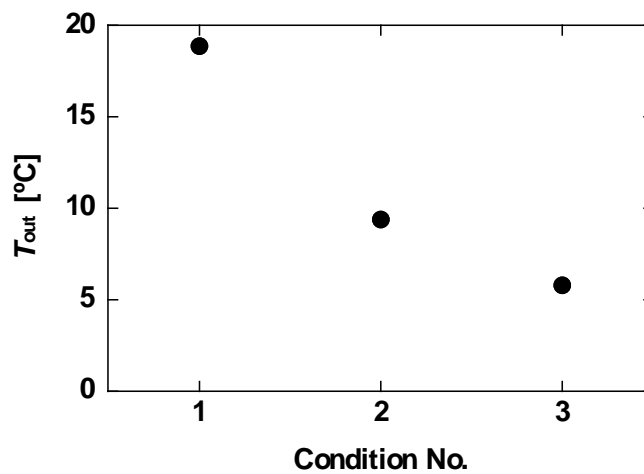

Fig. 8. Outlet temperature of emulsion as a function of experimental condition.

It can be seen from the graph that the outlet temperature is approximately 18℃ in Condition 1, approximately 10℃ in Condition 2, and approximately 5℃ in Condition 3. On the other hand, Fig. 9 shows the emulsion temperature differences between the test section inlet and outlet.
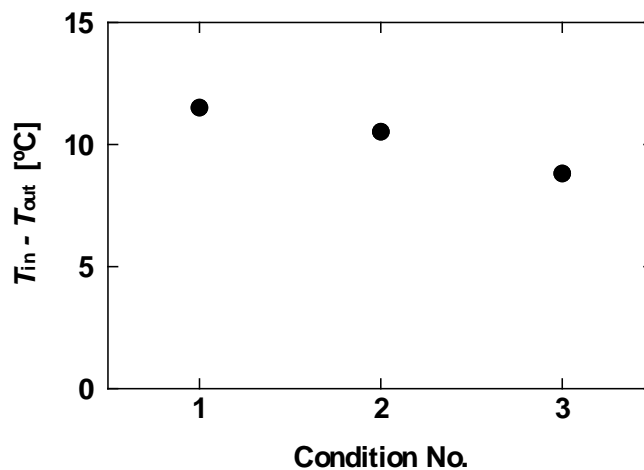

Fig. 9. Temperature difference between Tin and Tout of emulsion.

The horizontal axis in the figure indicates the experiment condition number, and the vertical axis indicates the emulsion temperature difference $T_{in}-T_{out}$ between the test section inlet and outlet. It is evident from the figure that the temperature difference is approximately 11K for Condition 1, approximately 10K for Condition 2, and approximately 8K for Condition 3. These results show that the temperature difference is smaller to the extent that a condition has a lower set temperature. As is evident from the value for the drop in solidification temperature shown in Fig. 6, it is likely that the actual solidifying point of hexadecane is about 1℃, and this is believed to be due to the fact that the effects of latent heat absorption were seen in the experiment for Condition 3 where that temperature was passed through.

4. Conclusions

In order to ascertain the thermal properties and heat transport characteristics of a phase change emulsion, the particle size distribution, phase change point, and viscosity were measured for hexadecane contained in the emulsion prepared in this experiment. In addition, the heat transport characteristics of the phase change emulsion were experimentally ascertained using a double-pipe heat exchanger. As a result, the following conclusions were reached within the scope of this experiment:

(1) Particle diameter in the emulsion prepared using the D-phase emulsification method was in the range 0.333-0.604 μm.

(2) Through an experiment using a DSC to measure the degree of supercooling, it was found that the degree of supercooling of hexadecane in the produced emulsion was 17K.

(3) When viscosity of the emulsion produced in the research was compared with the viscosity of water, it exhibited a value roughly twice as high.

(4) Due to the results of experiments using a parallel flow double-pipe heat exchanger, it is thought that, in the low-temperature condition, there was a phase change of the hexadecane phase change material contained in the emulsion, and an accompanying release of latent heat.

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