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Preparation of Capsules Containing L-Cysteine with Melting Dispersion Cooling Method

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Abstract

It was tried to prepare the capsules containing L-cysteine with the melting dispersion cooling method. Tripalmitin was selected as the shell material in order to keep out water and a few fatty acid esters such as ethyl laurate, ethyl stearate, ethyl myristate, ethyl oleate, ethyl palmitate and bees wax were added in the shell material as the modification materials in order to improve the water proof of the capsule shell. Furthermore, the capsules were coated by the coating materials such as oleic acid, ethyl oleate, triolein and ethyl laurate. It was investigated how the concentration of oil soluble surfactant and the combination of the shell material with both the modification materials and the coating materials affected the characteristics of capsules such as the content and the release feature of core material, the water proof and the swelling degree of capsules. With increasing the concentration of oil soluble surfactant, the released ratio decreased, become minimum and then, increased. The content could be increased by addition of modification materials. It was found that the released ratio was considerably depressed by ethyl laurate and ethyl palmitate as the modification materials and by oleic acid as the coating material and promoted by bees wax as the modification materials.

Index terms— L-cysteine containing capsules, tripalmitin, melting dispersion cooling method, release controlling, fatty acid esters

1 Introduction

any kinds of (micro) capsules have been prepared and applied in the various fields such as cosmetics, paintings, drugs, food, information recording materials, agricultural materials and so on [1][2][3][4].

The important functions of (micro) capsules are to protect the core material from environment and to controlly release the core materials [2,3]. These functions are largely dependent on the structure of (micro) capsules and the chemical and physicochemical properties of shell materials.

In general, the hydrophilic shell materials for the hydrophobic core materials and the hydrophobic shell materials for the hydrophilic core materials are used in order to protect the core materials from leaving into the continuous phase and to obtain the higher encapsulation efficiency. The hydrophilic solid powder as a fire retardant has been microencapsulated by the droplet coalescence method [5], the in-situ gelation method [6] and the interfacial reaction method [7].

Author : Graduate School of Science and Technology, Niigata University, Niigata, Japan. e-mail: tanaka@eng.niigata-u.ac.jp These microencapsulation methods have been designed so as to increase the content by using the hydrophobic shell materials. B. Erdem, et al have microencapsulated TiO2 powder with the mini emulsion polymerization method, where the content of solid powder could be increased with the help of oil soluble surfactant having the larger hydrophilic groups [8][9][10].

Wang W, Zhon W have prepared the crystalline carbohydrate microcapsules containing soy sauce powder by the spray drying method [11]. The spray drying method can microencapsulate the hydrophilic solid powder with

the hydrophilic shell materials. However, the microcapsules made by the hydrophilic shell material are easily swollen and rapidly release the core material. Especially, when the (micro) capsules will be applied to the limited fields such as food, drug and cosmetics, it is necessary to use the nontoxic edible shell materials and the materials suitable to the living body to prepare the (micro) capsules.

L-cystein is well known to be an essential amino acid and to have a few physiological effects such as anti-inflammation effect, anti-poison effect, whitening effect of skin and antiaging effect, but degenerate due to contact with water. Accordingly, it is worth encapsulating L-cystein with the hydrophobic shell materials.

In this experiment, it was tried to encapsulate Lcystein powder with tripalmitin with help of a few fatty acid esters as the modification materials and the coating materials in order to protect the core material from water attack and to controlly release the core material.

The purposes of this study are to try to encapsulate L-cystein powder with the melting dispersion cooling method by using tripalmitin as the shell material, to investigate how the modification materials and the coating materials affected the some characteristics of capsules such as the released ratio, the content of core materials and the swelling degree. The modification materials and the coating materials were from Kanto Chemical, Co., Ltd.

2 b) Preparation of capsules

The reactor was the separable flask with the effective volume of 300cm 3 . The impeller used to form the (O/W) emulsion was the six bladed disc turbine with the diameter of 5.4cm which was set at one third of the liquid depth.

Figure **??** shows the flow chart for preparing the capsules. L-cysteine (Cys) of a given weight was added into Lecithin (SBL) and stirred to form the (S/O) dispersion. The (S/O) dispersion was added into the melted Tripalmitin (TP) and stirred for ten min to form the (S/(O+O')) dispersion. Next, the (S/(O+O')) dispersion was added into the continuous water phase dissolving Furthermore, the capsules were coated with a few coating materials as follows.

The capsules of 0.2g were added into the bottle with the effective volume of 10cm 3 in which the melted coating materials of 50cm 3 were poured beforehand as shown in Figure **??**. After soaking the capsules for a given time, the capsules were dried at room temperature. In the fundamental experiment stated above, the concentration of Lecithin (SBL), the kinds of modification materials and coating materials and the soaking time were changed. The experimental conditions were shown in Table 1. The diameters of capsules were obtained directly from the photographs taken by the optical microscope. The mean diameters were the Sauter mean diameters.

ii. Content of core material

The content (Y) of core material encapsulated was defined as equation (1).

methyl cellulose (MC) and stirred for ten min to form the (S/(O+O')/W) dispersion. The operation stated just above was performed at 74 ? . After stirring the (S/(O+O')/W) dispersion to form the (S/(O+O')) droplets with the desired diameter for twenty min, the (S/(O+O')/W) dispersion was cooled down to 30? to solidify the Tripalmitin (TP) shell and then, the capsules containing L-cysteine (Cys) were prepared. In this fundamental operation, the modification agents were added in Tripalmitin (TP). Here, the content of core material was obtained as follows.

Figure **??** : Flow chart for preparing microcapsules

The capsules of 0.2g and distilled water of 10cm 3 were added into the beaker with the volume of 100cm 3 . This beaker was kept in the refrigerator for 24h in order to swell the capsules by water. After breaking the capsules by the homogenizer and adding the distilled water of 100cm 3 , ultrasonic irradiation to the capsule slurry was performed for twenty min in order to break the capsules and to dissolve out L-cysteine (Cys) perfectly. The aqueous solution dissolving L-cysteine (Cys) was filtered with the filter paper of 0.45µm, poured into the ultra filter vessel and then, filtered with the centrifugal separator.

The sample solution obtained by the procedure stated just above was sent to the high performance liquid chromatography (HPLC) and the amount of Lcysteine (Cys) was measured. The moving phase used in this measurement was prepared as follows. 0.58g of phosphoric acid of 85wt%, 0.342g of perchloric acid tetra-n-butylammonium and distilled water of 1000cm 3 were stirred. Then, pH of this aqueous solution was adjusted to pH 3.8 by adding 5N sodium hydride. The aqueous solution of 1000cm 3 thus adjusted was used as the moving phase.

Also, the colum used was Inertsil OD-3 (4.6? × 150mm) (GL Science Ind. Ltd). In this measurement, temperature, the wave length and the liquid velocity were 40?, UV 210nm, 0.7mol/min, respectively.

iii. Observation of capsules The capsules were observed by optical microscope and scanning electron microscope (SEM: JSM-5800). In order to observe the inner structure of capsule, a capsule was cut into two pieces with the knife and was observed by scanning electron microscope. iv. Released ratio of core material Capsules of 0.2g were added in the beaker where distilled water of 100cm 3 was poured beforehand, and soaked for 24h at room temperature. Here, 5cm 3 of ampicillin sodium aqueous solution of 0.01vol% was dissolved in distilled water in order to prevent L-cysteine (Cys) from being consumed by microorganism.

Then, the aqueous solution was sampled out at the constant time intervals and the concentration of Lcysteine (Cys) dissolved was measured by HPLC after filtrating with filter paper of 0.45µm. Thus, the released ratio (R)

was estimated by equation (2).R(%) = ??????????? ???? ?????? ???????????????? ??????????? ???? ?????? ??????????????????????????? × 100**(2)**

v. Swelling and break up of capsule After soaking the capsules into distilled water for 24h, the photographs of capsules were taken by digital camera. From these photographs, the swelling feature was observed and the number of capsules broken was counted.

3 vi. Contact angle of water for composite shell film

In order to obtain the informations about the capsules swollen by water, the composite shell film composed of Tripalmitin (TP) and the modification materials was prepared on the slide glass plate.

Then, a water droplet of 0.01cm 3 was formed on the composite shell film by microsyringe and taken the photograph by digital camera. From this photograph, the width(L) and height(H) of a water droplet were measured directly and the contact angle ( ) was estimated by equation (3).? ? = 2tan -1 (2H/L) (3) III.

4 RESULTS AND DISCUSSION

a) Effect of concentration of SBL Figure 2 shows the dependences of mean diameters (dp) of capsules and the content (Y) of Lcysteine (Cys) on the concentration of Lecithin (SBL) (C SL). The mean diameters slightly increased from 2.0mm to 3.0mm with the concentration of SBL because of increase in viscosity of oil phase composed of Lecithin (SLB) and Tripalmitin (TP). Namely, the viscous force against the destructive force for an oil droplet become larger with the viscosity of oil phase [12,13]. As a result, the oil droplets become larger, because it is hard for an oil droplet to break up. On the other hand, the content rapidly increased with the concentration of SBL, become maximum at C SL =0.75 and then, decreased at C SL =1.0. Figure 3 shows the optical microscopic photographs (a) and the SEM photographs of surface (b) and the cross sections (c) of capsules prepared by changing the concentration of SBL. From these photographs, it was found that the surface of capsules was rough and the many tiny holes were in the matrix. These tiny holes may be caused by difference in crystal structures of Tripalmitin (TP) and Lecithin (SBL). Namely, Tripalmitin (TP) has the property of film formation, but Lecithin (SBL) is crystallogenic. Accordingly, many tinny holes may occur due to difference in phase separation and crystalline. The sudden decrease in the content at C SL =1.0wt% as shown in Figure 2 may be due to these tinny holes. Namely, L-cysteine (Cys) may be dissolved by water permeating into the matrix through these tinny holes. Figure **??** shows the transient features of released ratios for the capsules prepared by changing the concentration of SBL. With the concentration of SBL, the released ratio decreased, but increased at C SL =1.0wt%. The decrease in the released ratio with the concentration of SBL may be due to the protection effect of Lecithin (SBL) against permeating of water. But, the increase in the released ratio at C SL =1.0wt% is coincident with the lower content at C SL =1.0wt% shown in Figure 2. From these results, it was found that the released ratio could be controlled by the concentration of SBL. As the content, the swelling and the released ratio are strongly affected by permeation of water into the matrix of capsules, it may be necessary to give the hydrophobicity to the shell in order to prevent water from permeating. So, it was tried to modify the shell by adding the modification materials. For this, the effect of modification materials on the contact angle of water for the capsule shell was investigated. Figure 6 shows the photographs of a water droplet on the composite shell film and the dependence of contact angle of a water droplet on the modification materials. It was found that the contact angles were not changed largely by adding the modification materials, but slightly increased by adding ethyl laurate (EL) (?=119.8), ethyl myristate (EM) (?=112.6) and ethyl stearate (ES) (?=110.1).

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Figure **??** shows the optical microscopic photographs of capsules immersed in water. Just after (0h) immersion of capsules into water, any differences in the shape of capsules were not observed, but after 24h, the degrees of swelling increased with the concentration of SBL. However, the capsules broken were not observed irrespective of the concentration of SBL. The released ratios decreased in the region of the concentration from 0 to 0.75wt% within 150min as shown in Figure **??**. However, after elapsing 24h, the capsules prepared by the concentration of SBL from 0~1.0wt% may be swollen by permeation of water. Figure **??** shows the transient features of the released ratios measured for the capsules prepared by adding the modification materials. The released ratio was considerably decreased by addition of ethyl laurate (EL), ethyl palmitate (EP) and ethyl stearate (ES). Contrary to this, the released ratios were decreased by addition of ethyl myristate (EM) and ethyl oleate (EO) until elapsing 1h and increased by addition of Bees wax.

Figure **??**0 shows the dependences of degree of swelling on the modification materials. Just after (t=0) immersion of capsules, the capsules were not changed irrespective of the kinds of modification materials, but after elapsing 24h, all the capsules swelled to the almost same degree and did not dissolved. In order to increase the releasing time of core material, the capsules were coated moreover by the coating materials. Namely, the capsules have the dual shell film.

Figure 11 shows the transient features of the released ratios for the capsules prepared by being immersed in the coating materials for 3days and 10days. The capsules immersed for 3days show that the released ratios are largely decreased, especially the effect of coating by oleic acid (OA) is considerably.

Furthermore, the capsules immersed for 10days show the extreme decrease in the released ratio, especially the effect of coating by oleic acid (OA) is considerably. CONCLUSION L-cysteine powder was tried to encapsulate with tripalmitin as the shell material and the effects of modification materials and the coating materials on the characteristics of capsules were investigated. The following valuable results were obtained 1. L-cysteine powder could be encapsulated with tripalmitin by using the melting dispersion cooling method. 2. The released ratio of L-cysteine could be controlled by addition of modification agents. Especially, ethyl laurate and ethyl palmitate could decrease the released ratio. 3. The content of core material could be increased by addition of modification agents. 4. The release ratio of L-cysteine could be largely decreased by coating the capsules with the coating materials. Especially, oleic acid could be considerably decreased the released ratio. 5. The time span for releasing L-cysteine could be controlled over the wide range by adding the modification materials and by coating with the coating materials.

6 Volume

7 References Références Referencias

Figure 1:

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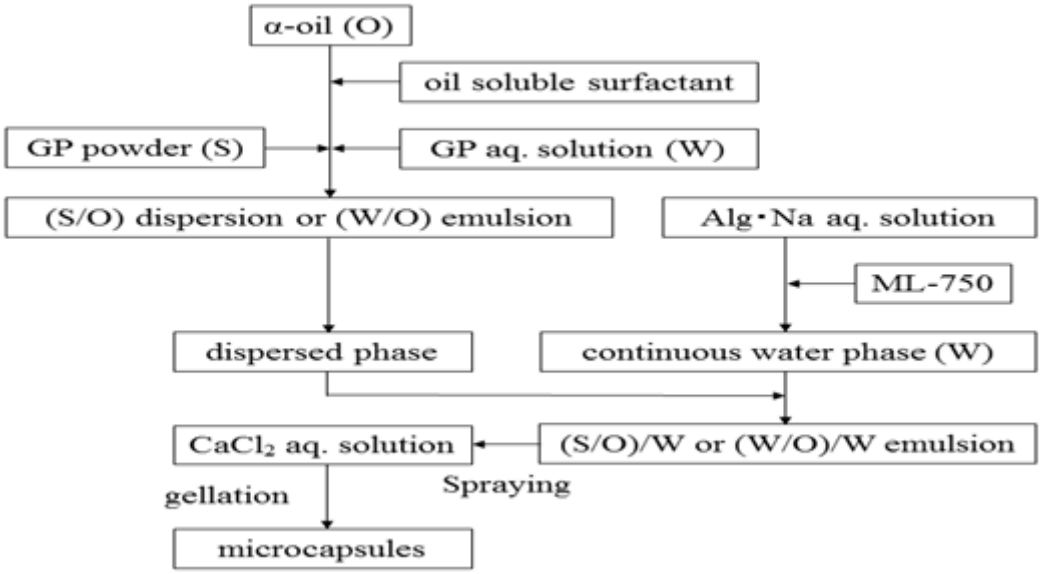

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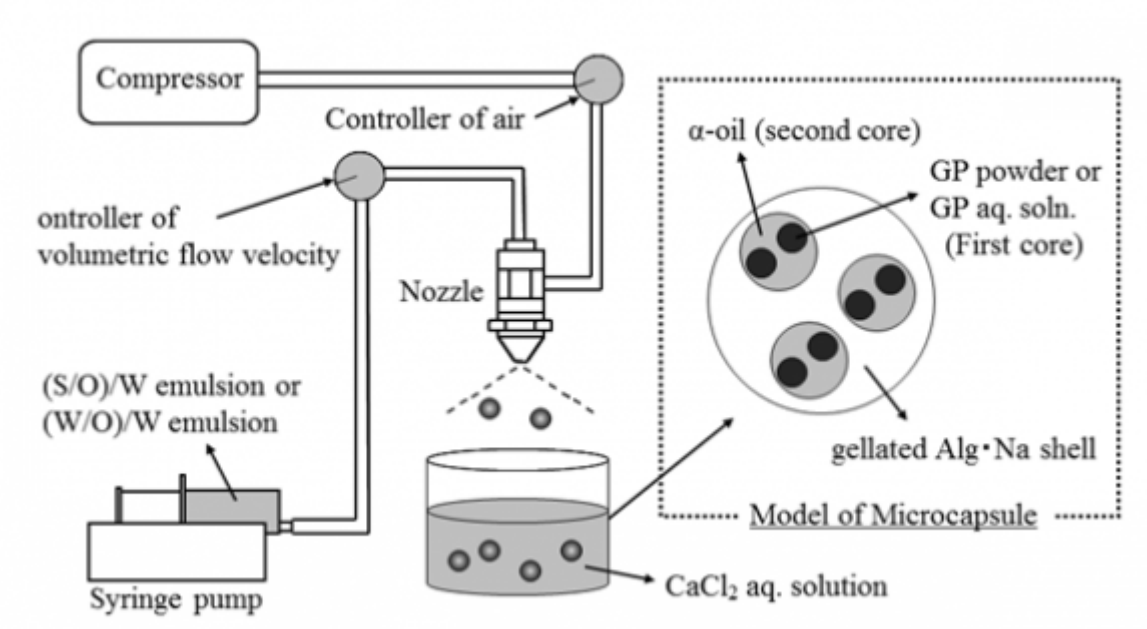

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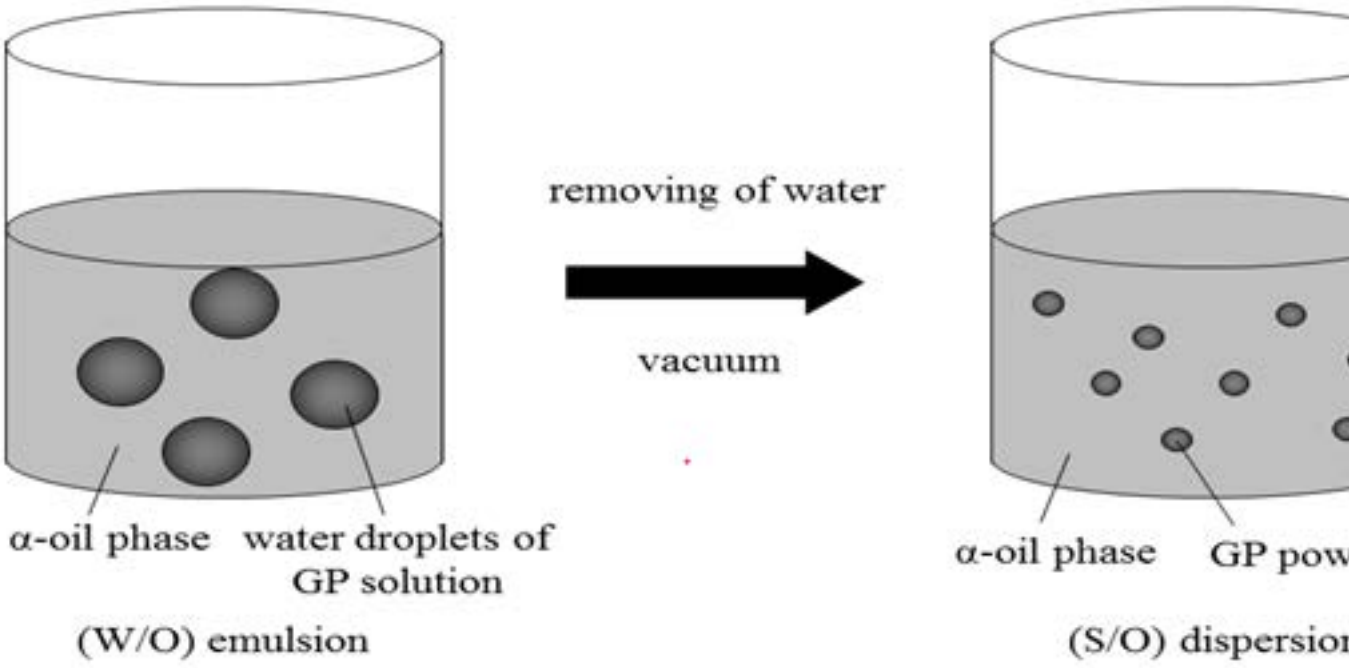

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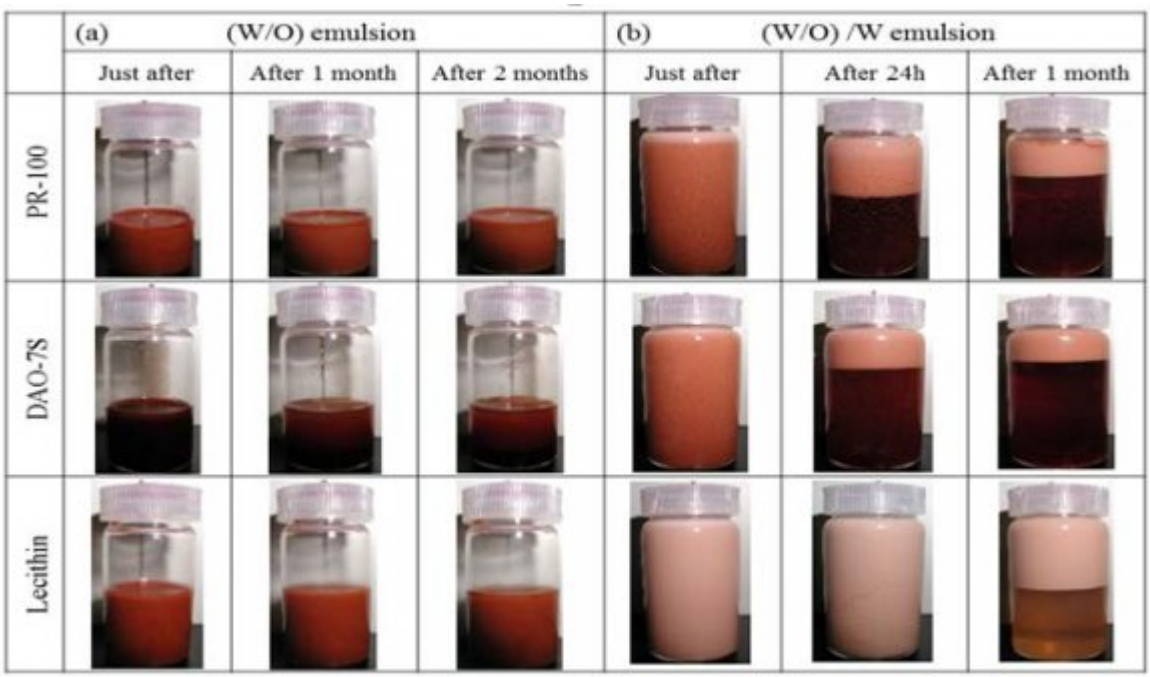
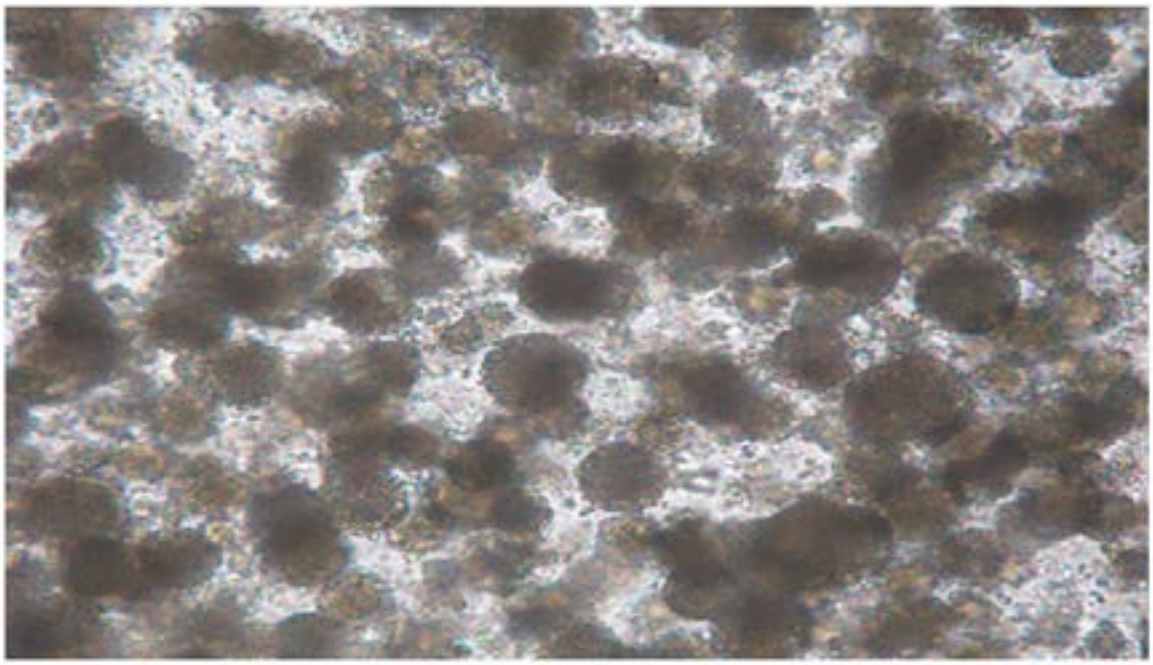


Figure 5: C



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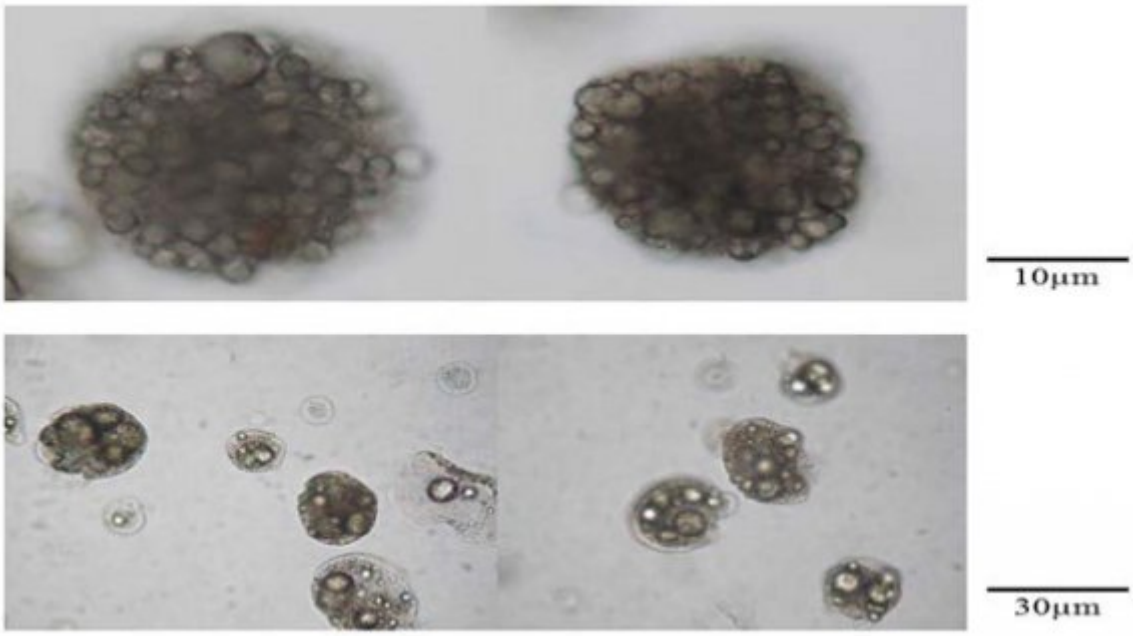

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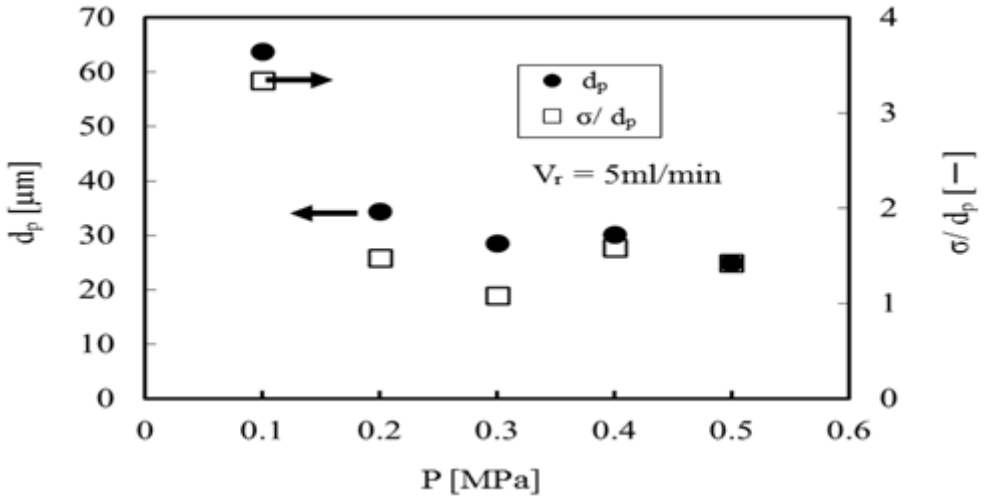

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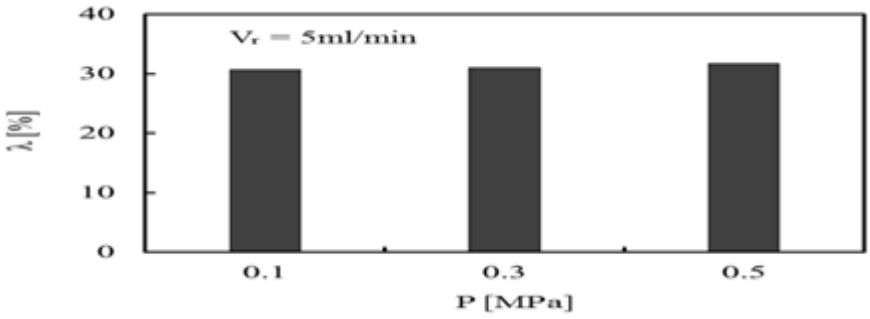

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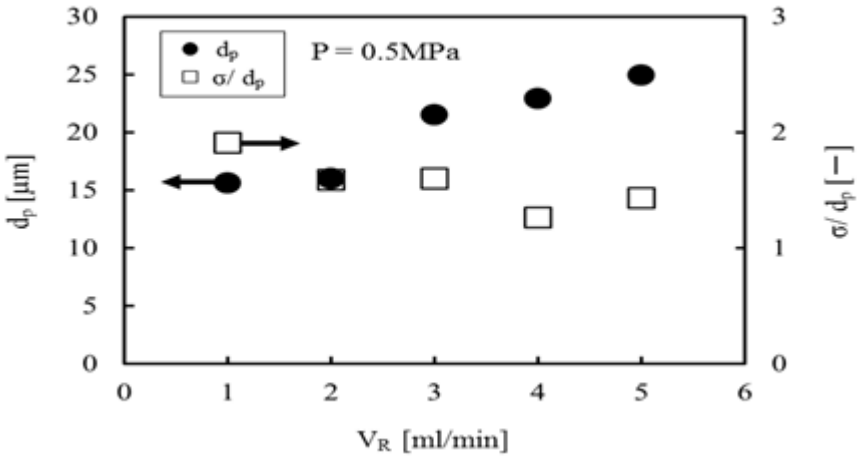
Figure 9: Figure 9 :Figure 10 :



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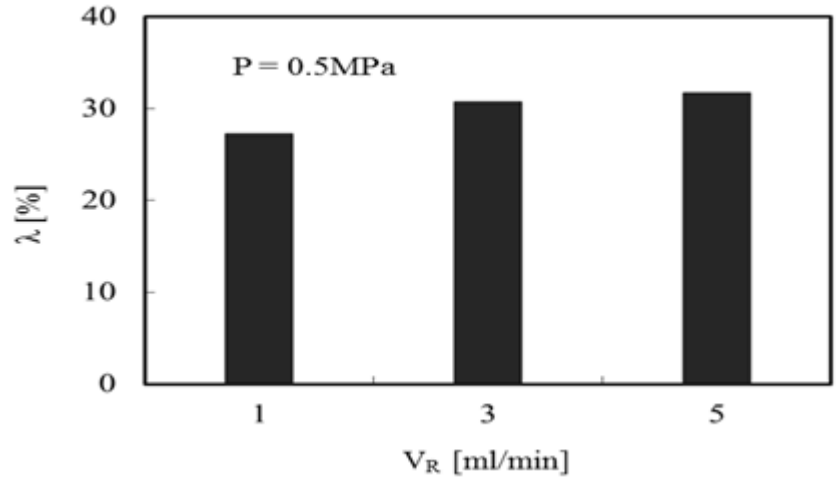

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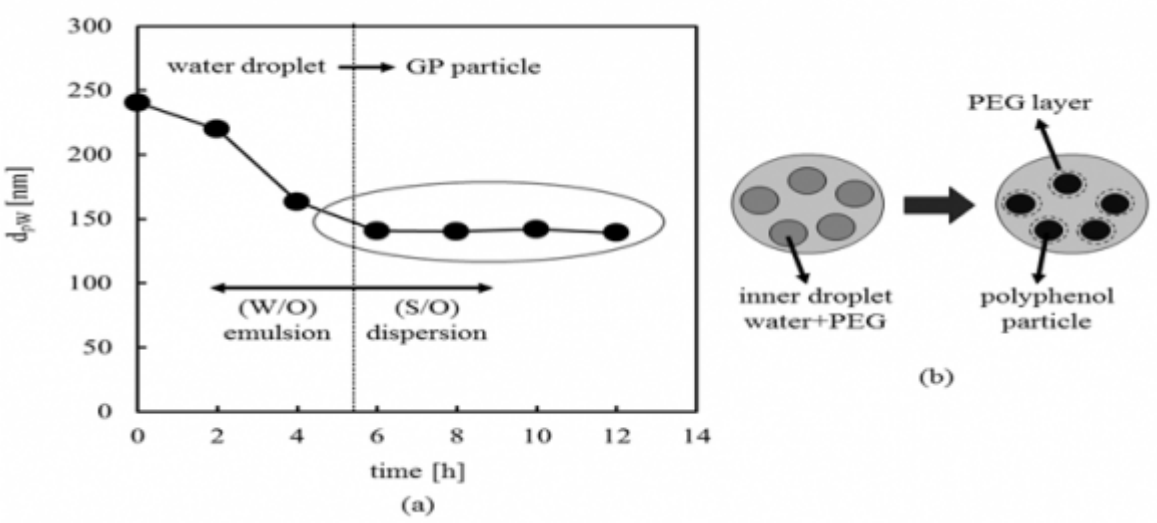
Figure 11: Figure 12



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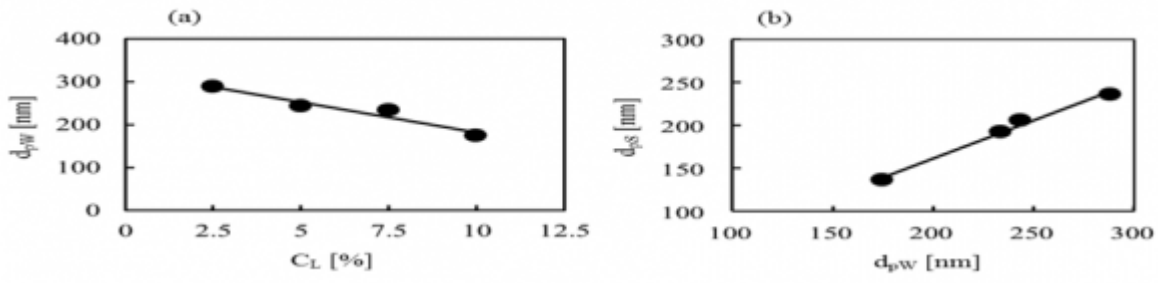

Figure 13:

1

Continuous water phase	
distilled water	290 cm 3
Methyl cellulose	0.29g (0.1 wt%)
Dispersed phase	
L-cysteine (core)	8.0 g
Tripalmitin (shell)	8.0 g
Soy bean Lecithin	2.0, 4.0, 6.0, 8.0 g
Preparation of dispersion	
Impeller speed	10 s -1
Temperature	
Melting	74 ?
Cooling	30 ?
Modification materials:	0.8 g
Soaking time	24
c) Characterization	
i. Diameters of capsules	

[Note: Ethyl laurate, Ethyl stearate, Ethyl myristate, Ethyl oleate, Ethyl palmitate, Bees wax Coating materials: Oleic acid, Ethyl oleate, Triolein, Ethyl laurate]

Figure 14: Table 1 :

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