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Preparation of Microcapsules Containing Camellia Oil with Heterocoagulation between Chitosan and Oleic Acid

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Abstract

It was tried to microencapsulate camellia oil using heterocoagulation between fatty acid dissolved in camellia oil and chitosan dissolved in the continuous water phase. Oleic acid as a fatty acid was dissolved in camellia oil in order to certainly form the microcapsule shell made from oleic acid and chitosan. The microcapsules were observed with optical microscope and characterized about the diameters, ζ-potential, FTIR analysis and adhesion feature on human hair. Microcapsules with the mean diameter in the range from ca. 1.5 μm to 4.5 μm could be prepared with the preparation method presented in this study. The oil droplets of camellia oil charged negatively to be −54.6 mV and the microcapsules charged positively to be 59.6 mV. The microcapsules adhered well on the negatively charged human hair and were kept stably before and after drying at room temperature for 24 h and blowing.

Keywords

Microencapsulation, Camellia Oil, Heterocoagulation, Hair Dressing Material, Fatty Acid

1. Introduction

As the microcapsules can contain the core materials such as gas, liquid and solid and have the various functions, until now a deal of microcapsules have been prepared and applied in the various fields such as cosmetics, foods, drugs, textiles, electric materials, latent heat storage, paintings and adhesives [1] [2] [3].

The main important functions of microcapsules are to protect the core materials from environment for a long time, to optionally release the core materials according to stimuli such as mechanical pressure, heat and pH of solvent, to

modify the surface of core materials and to change the core materials such as liquid and gas to the fine solid particles [1] [2] [3]. The microcapsules with these functions can be prepared with the physicochemical methods such as the coacervation method, the drying in liquid method, the spray dried method, the heterocoagulation method and the chemical methods such as the suspension polymerization method, the interfacial polymerization method, the mini emulsion polymerization method, the gelling in liquid method and the *in-situ* polymerization method [1] [2] [3].

Recently, many works about the microencapsulation of essential oils have been reported [4]-[10]. For example, many kinds of oil species have been microencapsulated with the interfacial gelling reaction method [11] [12] [13], the *in-situ* polymerization method [14] [15], the interfacial polycondensation reaction method [16] [17], the coacervation method [18] [19], the spray-dried method [20] [21] [22] and the melting dispersion cooling method [23]. These microcapsules have been applied to the textiles, fragrance, aromatherapy, antibiosis and so on.

In Japan, camellia oil which was produced from camellia tea seed was rich in oleic acid and has been said to be good for hair.

So, it is well known that camellia oil has been used from long ago as the hair dressing material and the face treatment material in the cosmetic field [24]. Here, if the microcapsules are going to be applied in the cosmetic field, it is very important to microencapsulate camellia oil with biocompatible materials. Furthermore, if camellia oil could be microencapsulated with harmless materials and broken with the hand pressure, the soft microcapsules like the microencapsulated camellia oil may be positively recommended as a hair dressing material, because camellia oil can be retained stably and prevented from oxidation.

Taking these things into consideration, the fundamental experiment about microencapsulation of camellia oil with chitosan was conducted using the heterocoagulation method.

The purposes of this study are to investigate whether camellia oil could be microencapsulated with chitosan on the basis of heterocoagulation or not and to characterize whether the microencapsulated camellia oil could be applied as the hair dressing material or not.

2. Experimental

2.1. Materials

Materials used to prepare the microcapsules were as follows. Camellia oil (CO: Oshima Tsubaki Co. Ltd., Japan) was microencapsulated as a core material. Oleic acid (OA: Wako Pure Chemicals Co., Ltd., Tokyo, Japan) was dissolved into camellia oil in order to stably form the microcapsule shell regardless of fluctuation of components in natural camellia oil.

Chitosan (Wako Pure Chemicals Co., Ltd., Tokyo, Japan) was used to form the microcapsule shell using heterocoagulation with oleic acid. Citric acid (Wa-

ko Pure Chemicals Co., Ltd., Tokyo, Japan) was used to dissolve chitosan in the water phase. Soybean lecithin (SBL: Wako Pure Chemicals Co., Ltd., Tokyo, Japan) was used as an oil soluble surfactant.

2.2. Preparation of Microcapsules

Figure 1 shows the flow sheet for preparing the microcapsules.

Camellia oil (CO) and Oleic acid (OA) of given volume were mixed together to form the oil dispersed phase (O), in which soybean lecithin (SBL) was dissolved beforehand.

The oil dispersed phase was added into the continuous water phase (W) and stirred with the rotor stator homogenizer to form the (O/W) emulsion.

Then, the chitosan aqueous solution of a given concentration was added to the (O/W) emulsion. The (O/W) emulsion was stirred with the impeller for a given time (ca. 4 h) to form the microcapsules. The fundamental operation described above was performed changing mainly the revolution velocity to form the (O/W) emulsion. The microcapsules prepared thus were collected with filtration paper and characterized. The experimental conditions are shown in Table 1.

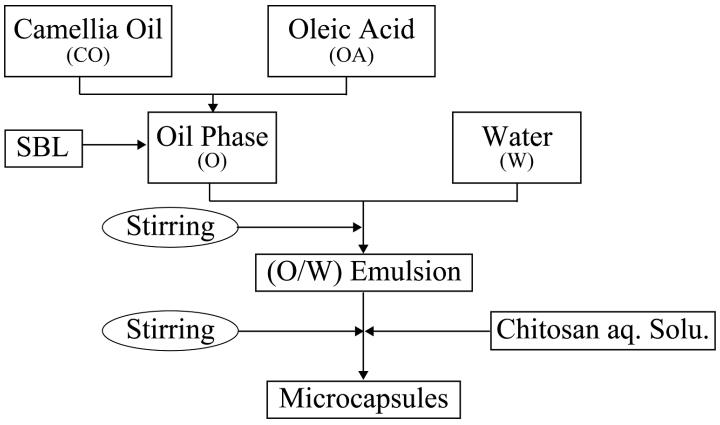


Figure 1. Flow sheet for preparing microcapsules.

Table 1. Experimental conditions.

Oil Phase		Formation of (O/W) Emulsion	
Camellia Oil	2.0 g	Nr	2000 - 10,000 rpm
Oleic Acid	0.2 g (10 wt%-Oil)	t	5 min
Continuous Phase		T	40˚C
Water	300 g		
Chitosan aq. Solution		**Microencapsulation Process**	
Chitosan	0.2 g (1.0 wt%-Water)	Nr	60 rpm
Water	20 g	t	4 h
Citric Acid	0.2 g (1.0 wt%-Water)	T	40˚C

2.3. Characterization

2.3.1. Diameter Distribution and Mean Diameter

The diameter distributions and the mean diameters of the oil droplets and the microcapsules were measured by Particle Size Analyzer (SALD-3000, Shimazu Seisakusho, Ind., Co., Ltd., Kyoto, Japan). Here, the mean diameters were the Sauter mean diameters.

2.3.2. ζ-Potential

The ζ-potentials of the oil droplets in the (O/W) emulsion and the microcapsules dispersed in the continuous water phase were measured with Particle Size Analyzer (ELSE-2: Otsuka Electronics, Co., Ltd., Tokyo).

2.3.3. Observation of Emulsion and Microcapsules

The (O/W) emulsion and the microcapsules were observed by stereo optical microscope (BH-2VMA: Olympus, Co., Ltd., Tokyo, Japan). From these photographs, the stability of the (O/W) emulsion and the microcapsules were estimated.

Here, the magnification times of the objective lens is 20.

2.3.4. FTIR Analysis

In order to confirm whether camellia oil is microencapsulated with chitosan or not, the microcapsules were analyzed with FTIR (FTIR-800PC, Shimazu Seisakusho, Ind., Co., Kyoto, Japan).

2.3.5. Adhesion of Microcapsules on Human Hair

It was observed with the optical microscope (BH-2VMA: Olympus, Co., Ltd, Tokyo, Japan) how the microcapsules adhered on the surface of human hair.

Namely, human hair was immersed in the microcapsules slurry for 5 min at room temperature. After this, human hair was dried over night at room temperature and observed with the optical microscope. Then, human hair was dried with blower for a few minutes and observed with the optical microscope. From these photographs, adhesion feature of the microcapsules on human hair was discussed.

3. Results and Discussion

3.1. Observation of Oil Droplets before and after Microencapsulation

In order to investigate whether the oil droplets were microencapsulated with chitosan due to heterocoagulation or not, first the (O/W) emulsion before and after microencapsulation was observed.

Figure 2 shows the diameter distributions of oil droplets in the (O/W) emulsion which was formed by stirring with the rotor stator homogenizer under the experimental conditions such as Nr = 5000 rpm, t = 5 min and T = 40˚C.

The oil droplets with the mean diameter of 3.9 μm and the value of CV = 0.11 were formed, where CV is the coefficient of variation and defined as the ratio

(σ/dp) of the standard deviation (σ) of diameter distribution to the mean diameter (dp).

The smaller the CV values are, the more uniform the diameters become.

Also, Figure 3 shows the optical microscopic photograph of the oil droplets in the (O/W) emulsion before microencapsulation.

The mean diameter and the CV value were 3.9 μm and 0.11, respectively. Furthermore, the (O/W) emulsion formed was found to be extremely stable, because the diameters of oil droplets were kept almost constant for 24h. This stability of the (O/W) emulsion may be due to the repulsive force based on carboxyl group.

Figure 4 shows the optical microscopic photographs of the oil droplets after microencapsulation. The mean diameter and the CV value of the oil droplets after a few days were dp = 3.9 μm and CV = 0.11, respectively and those of the oil droplets after a week were dp = 4.0 μm and CV = 0.12, respectively. From this result, it was found that the (O/W) emulsion was kept almost unchanged. Accordingly, it may be imagined that microencapsulation of oil droplets was satisfactorily performed.

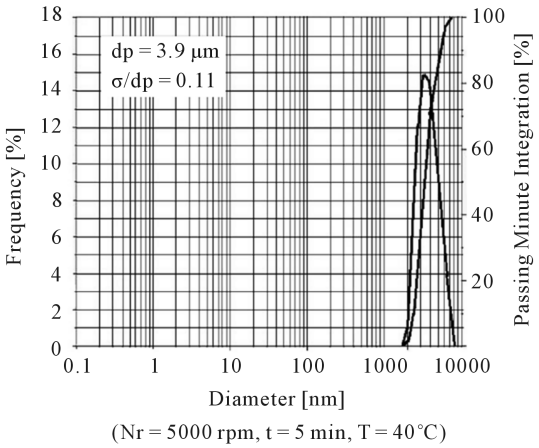
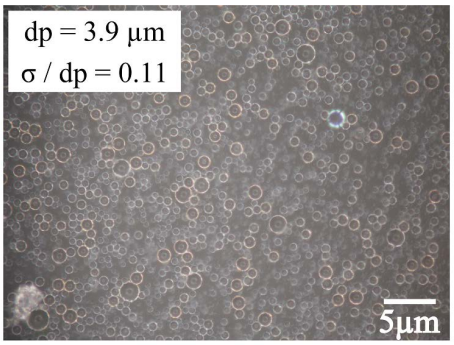


Figure 2. Diameter distribution of oil droplets.



(O/W) Emulsion
(Nr = 5000 rpm, t = 5 min, T = 40 ℃)

Figure 3. Optical microscopic photograph of oil droplets before microencapsulation.

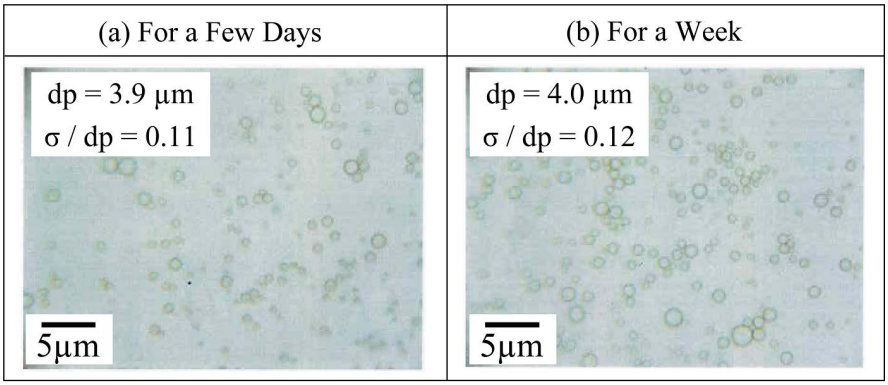


Figure 4. Optical microscopic photographs of oil droplets after microencapsulation.

3.2. ζ-Potential of Oil Droplets before and after Microencapsulation

In this study, as it was tried to microencapsulate camellia oil due to heterocoagulation between OA with carboxyl group and chitosan of polycation, the ζ-potentials of oil droplets before and after microencapsulation were measured. **Figure 5** shows the ζ-potentials of oil droplets measured before and after microencapsulation. The ζ-potentials of oil droplets before and after microencapsulation are −54.6 mV and 59.6 mV, respectively. From these results, it may be capable of being thought that the oil droplets were miroencapsulated with chitosan due to heterocoagulation between OA and chitosan. Furthermore, as the oil droplets are microencapsulated with chitosan positively charged, adhesion of these oil droplets onto the negatively charged human hair will be promoted.

3.3. FTIR Analysis

In order to analyze the chemical composition on the surface of oil droplets, the results of FTIR analysis for chitosan and the oil droplets after microencapsulation are shown in **Figure 6**. As the adsorption peaks at = 1500 cm^{-1} and 3400 cm^{-1} are due to NH_2 of chitosan, the oil droplets are found to be microencapsulated with chitosan. From the results obtained above, it is confirmed that the microcapsules containing camellia oil could be prepared according to the formation mechanism presented in this study, which was shown in **Figure 7**. Namely, as the oil droplets made from CO and OA were charged negatively, the microcapsule shell was formed with heterocoagulation between OA and chitosan of polycation.

3.4. Dependence of Diameters of Oil Droplets and Microcapsules on Revolution Velocity

Here, when the microcapsules are going to be applied as a spray type hair dressing material, the diameters of microcapsules are very important to use them efficiently.

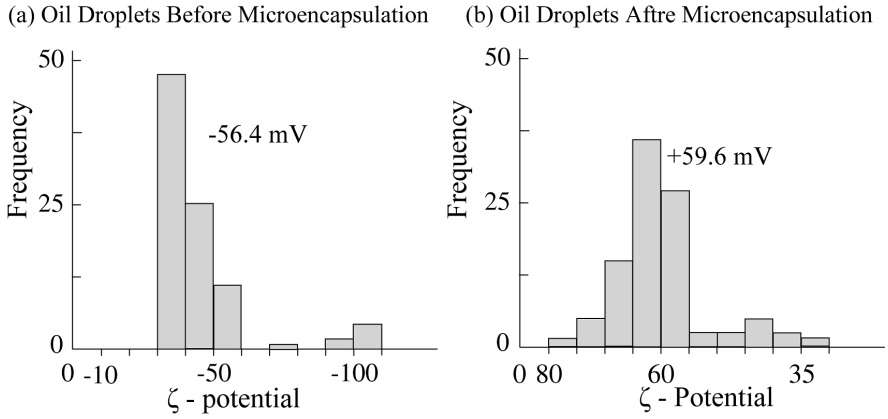


Figure 5. ζ-potential of oil droplets before and after microencapsulation.

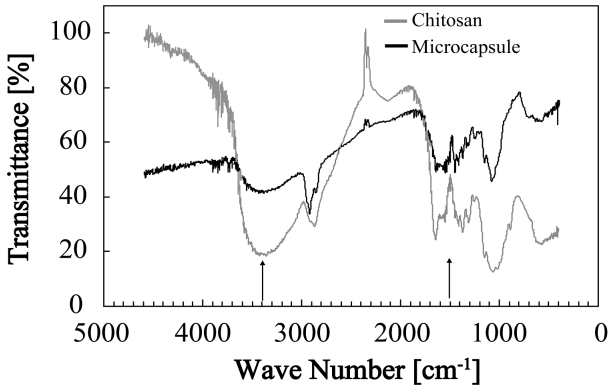


Figure 6. FTIR analysis of microcapsule and chitosan.

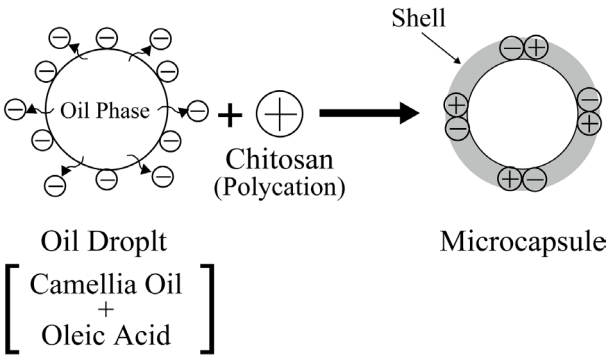


Figure 7. Formation mechanism of microcapsules.

So, in order to investigate the controllable region of the diameters of the microcapsules, the mean diameters of the microcapsules were measured by changing the revolution velocity to form the (O/W) emulsion.

On preparing the microcapsules with the heterocoagulation method under the experimental conditions adopted in this study, the diameters of the microcapsules approximately equal to those of the oil droplets in the (O/W) emulsion.

Figure 8 shows the dependence of the mean diameters of the microcapsules on the revolution velocity (Nr) to form the (O/W) emulsion.

From Figure 8, the following experimental equation could be obtained.

$$dp \sim Nr^{-1.17} \quad (1)$$

This dependency agrees well with that ($\sim Nr^{-1.20}$) for the (O/W) emulsion formed in the disruptive dominant field [25] [26]. Accordingly, the diameters of the microcapsules are able to be controlled using Weber Number ($\rho Nr^2 di^3/\gamma$) as a criteria, where ρ, di, γ are the density of the continuous water, the impeller diameter, the interfacial tension, respectively. In this study, the mean diameters of the microcapsules could be changed in the region from 1.5 μm to 4.5 μm with the revolution velocity.

Also, the CV values for all the microcapsules prepared in this study were in the range from 0.09 to 0.16. As a result, the diameters of the microcapsules were found to be more uniform.

3.5. Adhesion of Microcapsules

It is well known that, as the human hair is negatively charged, the positively charged particles are easily adhered on the surface of human hair. So, it was investigated whether the microcapsules adhered well on the surface of human hair or not.

Figure 9 shows the optical microscopic photographs of human hair on which the microcapsules adhered after drying at room temperature. From these photographs, it was found that the microcapsules adhered well on the surface of human hair.

Also, Figure 10 shows the optical microscopic photographs of microcapsules on the glass plate after drying due to blowing. The microcapsules appeared due to flattening larger than those before blowing as shown in Figure 4, but were found to be stable even after drying.

From these results, it is expected that the microencapsulated camellia oil can be applied as a hair dressing material.

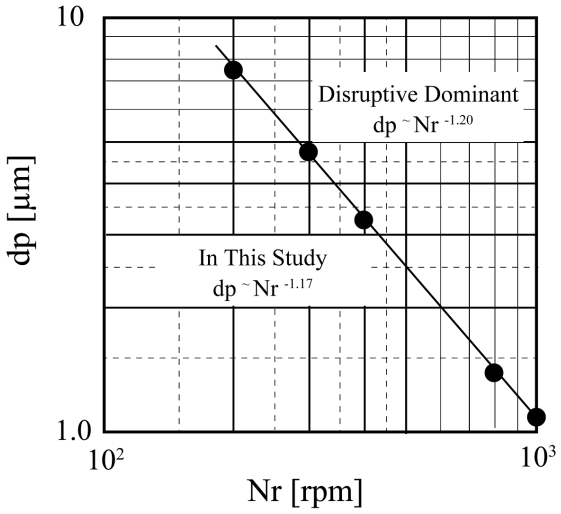


Figure 8. Dependence of mean diameters of oil droplets on revolution velocity.

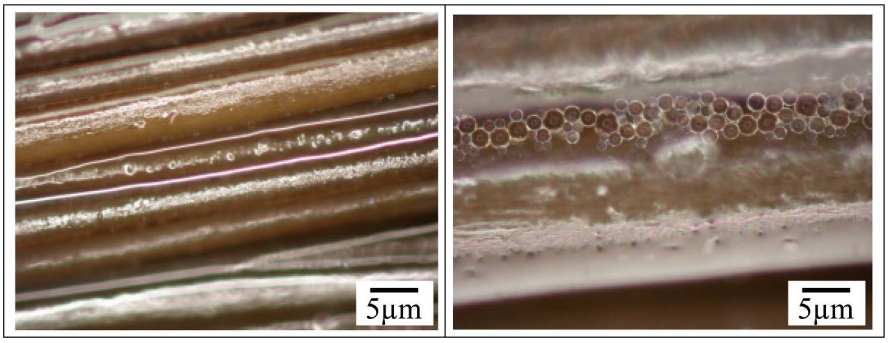


Figure 9. Observation of adsorption of microcapsules.

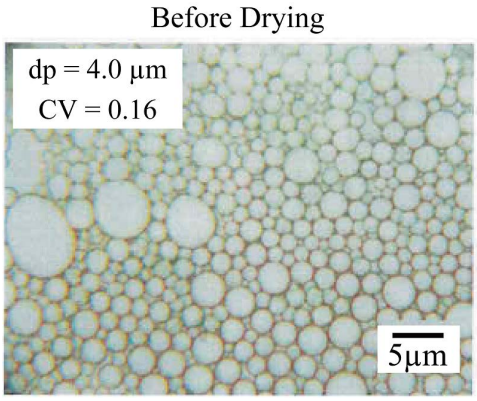


Figure 10. Optical microscopic photograph of microencapsulation after and drying due to blowing.

4. Conclusions

It was tried to microencapsulate camellia oil with heterocoagulation between oleic acid and chitosan and it was investigated whether the microcapsules could be applied to the hair dressing material or not. The following fundamental results were obtained.

The microcapsules with the mean diameters in the range from 1.5 μm to ca. 4.5 μm could be prepared with the formation mechanism presented in this study.

The microcapsules were positively charged in the continuous water and adhered well on the surface of human hair. The microcapsules were kept stably on the human hair before and after drying. In the near future, it will be necessary to investigate the dispersing behavior of microcapsules in the water phase with the various pH values and the hair dressing effect of the microencapsulated camellia oil and to compare with other dressing materials such as various essential oils.

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