Microencapsulation of Hydrophilic Solid Powder as Fire Retardant Agent with Epoxy Resin by Droplet Coalescence Method

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ABSTRACT: To give water resistance to Bistetrazol–diammonium (BHT–$2NH_3$) as a fire retardant agent, microencapsulation with epoxy resin was tried by the droplet coalescence method. In this method, two kinds of epoxy resin droplets were prepared; one is the larger epoxy resin droplet containing BHT–$2NH_3$ as a core material and the other the smaller droplets containing Imidazole as a gelation agent. The larger epoxy resin droplets were made to coalesce with the many smaller droplets during the microencapsulation process to prepare microcapsules. In the experiment, the agitation velocities for preparation of the droplets and for coalescence were mainly changed. With increase in the impeller speed, the content of core material increased, became maximum because of increase in the coalescence frequency, and then decreased because of breakup of droplets. With increase in the impeller speed, the leakage ratio of core material decreased, became minimum, and then increased. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1671–1676, 2008

Key words: microencapsulation; composites; core-shell polymers; droplet coalescence method; fire retardant agent

INTRODUCTION

In general, one of the purposes of microencapsulation is to protect the core material from environment.[1] For example, when the core material is hydrophilic or water soluble, the core material is microencapsulated with hydrophobic polymer to protect from water or to give water resistance.[2] Because dispersion stability of hydrophilic core material in the hydrophobic shell solution is very poor in the microencapsulation process such as the suspension polymerization method[3] and the drying in liquid method,[4,5] it is important to investigate how to prevent the core material from leaking from the shell solution droplet and to establish the optimum operating conditions to increase the content.

Until now, many works for this purpose have been reported, for example, surface modification of core materials with some coupling agents or surfactants,[6] adjustment of physical property of shell solution such as viscosity or density,[7] addition of effective surfactants,[8] shortening of microencapsulation process,[9] and so on.

In this experiment, the droplet coalescence method is tried to increase the microencapsulation efficiency of the hydrophilic powdery core material. Namely, the droplets (mother droplets) of the shell solution containing the hydrophilic powdery core material are made to coalesce with the droplets (daughter droplets) containing the gelation agent. As a result of coalescence between these droplets, it is expected to gradually gelate from the periphery part of a shell solution droplet. In other words, because the leakage of core material from a droplet could be rapidly prevented, the content of core material may be considerably increased by this microencapsulation method. In detail, Bistetrazol–diammonium ($C_2H_8N_{10}$, BHT–$2NH_3$) of a fire retardant agent for polymers was adopted as the hydrophilic powdery core material, and epoxy resin and Imidazole were adopted as the shell material and the gelation agent for epoxy resin, respectively. Epoxy resin droplets containing BHT–$2NH_3$ are made to coalesce with them containing Imidazole during the microencapsulation process.

The purpose of this study is to investigate whether the content of hydrophilic powdery core material could be increased with the droplet coalescence microencapsulation method or not.

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EXPERIMENTAL

Materials

Materials used to prepare microcapsules are as follows. Epoxy resin was Bis phenol A (Epicot815; Japan Epoxy Resins, Tokyo, Japan). Solid powdery

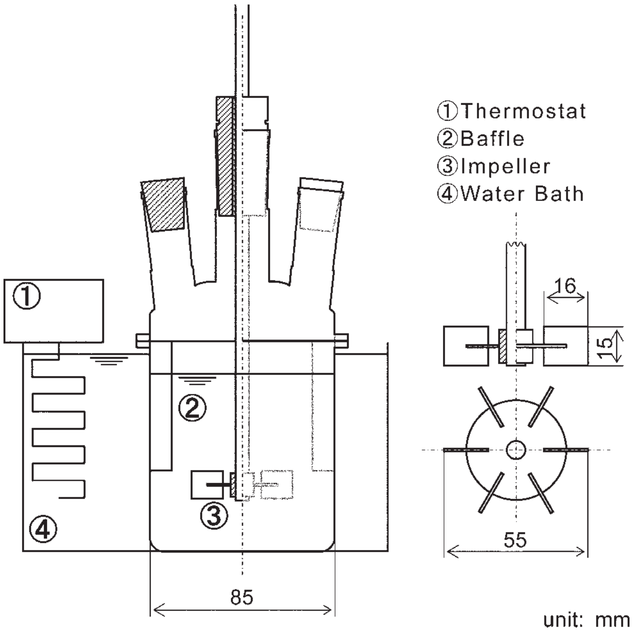

Figure 1 Experimental apparatus.

fire retardant agent was Bistetrazol diammonium (BHT–$2NH_3$; Eiwa Chemical, Kyoto, Japan), which is water soluble and completely insoluble in epoxy resin. Gelation agent for epoxy resin was Imidazole (Wako Pure Chemical Industries, Osaka, Japan). As a water-soluble stabilizer, polyvinyl alcohol (PVA) was used (degree of polymerization 500; Wako Pure Chemical Industries, Osaka, Japan).

Experimental apparatus

Experimental apparatus used here is shown in Figure 1. A separable flask with flat bottom is a reactor to prepare microcapsules. Four baffles made of aluminum plate with a width of 1.0 cm and a length of 6.0 cm are installed on the inside wall of the reactor as shown in Figure 1. An impeller used during the microencapsulation process is the six blade disk turbine with a length of 5.0 cm and a width of 1.0 cm, which is fixed at one third the liquid height from the reactor bottom.

Preparation of microcapsules

Droplet coalescence method

Figure 2 shows the flow chart of preparing microcapsules containing BHT–$2NH_3$ by the droplet coalescence method. In brief, the epoxy resin droplets (mother droplets) containing BHT–$2NH_3$ were dispersed in the continuous water phase dissolving PVA as a stabilizer. Then, another epoxy resin droplets (daughter droplets) containing Imidazole were added and dispersed in the continuous water phase.

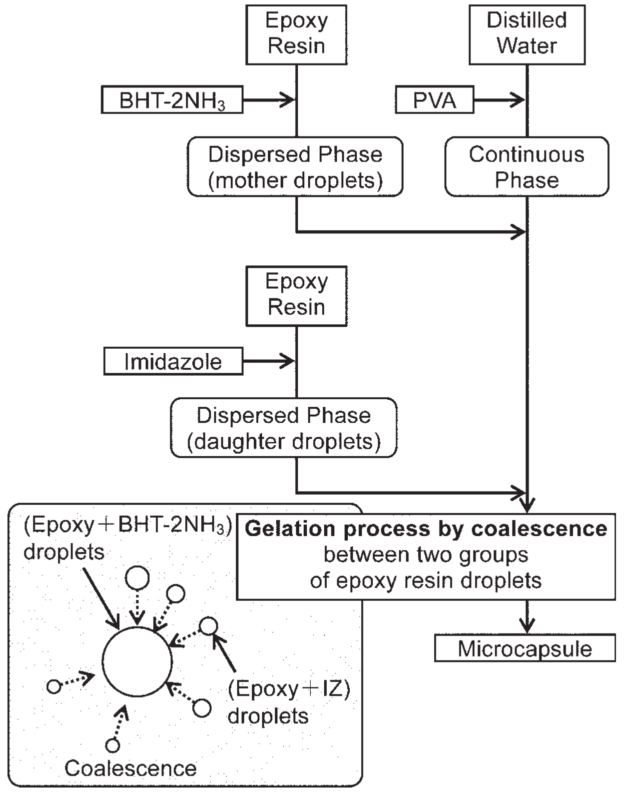

Figure 2 Flow Chart for preparing microcapsules with the droplet coalescence method.

As the diameters of daughter droplets are very smaller than those of mother droplets, the number of daughter droplets is very larger than that of mother droplets. Accordingly, the mother droplets may mainly coalesce with the daughter droplets. Microencapsulation was carried out by coalescence between the mother droplets and the daughter droplets as shown in Figure 2. The experimental conditions are listed in Table I.

TABLE I
Experimental Conditions (the Droplet Coalescence Method)

Fixed conditions	
Dispersed phase	
Bis phenol A—epoxy resin (Epicot 815)	10.0 g
Imidazole (IZ)	1.0 g
Bistetrazol–diammonium (BHT–$2NH_3$)	8.0 g
Continuous phase	
Distilled water	200.0 g
Polyvinyl alcohol (PVA) (polymerization degree: 500)	1.0 g (0.5 wt %)
Time for agitation	4 min
Temperature of gelation	70 °C
Gelation time	5 h
Operation conditions	
Impeller speed for preparing (O/W) dispersion	Nr_1 = 50–83.3 s^{-1}
Impeller speed at gelation process	Nr_2 = 1.7, 3.3 s^{-1}

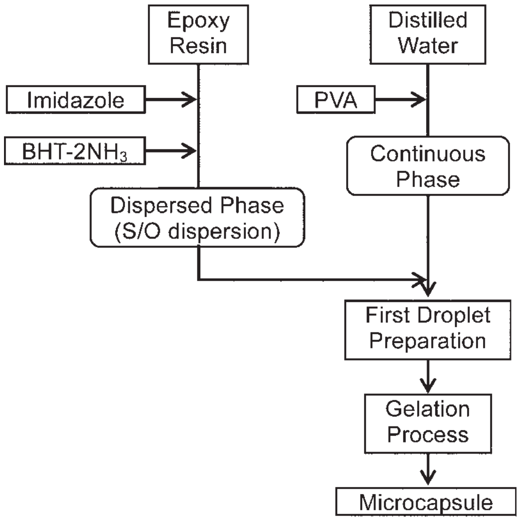

Figure 3 Flow Chart for preparing microcapsules with the *in situ* gelation in droplet method.

In situ gelation in droplet method

For comparison, microencapsulation by the *in situ* gelation in droplet method was tried. The flow chart for this method is shown in Figure 3. In brief, epoxy resin containing Imidazole and BHT–2NH_3 was the dispersed phase and distilled water dissolving PVA was the continuous phase. After addition of the dispersed phase into the continuous phase, the (S/O)/W dispersion was formed by homogenizing with the rotor-stator homogenizer (BM-2; Nihonseiki Kaisha, Tokyo, Japan) for four min. Then, microencapsulation was carried out under stirring at the given impeller speed and the temperature of 70°C for 5 h. Microcapsules were prepared by gelation of epoxy resin droplets. The experimental conditions are listed in Table II.

TABLE II
Experimental Conditions (the *In-Situ* Gelation in Droplet Method)

Fixed conditions	
Dispersed phase I	
Bis phenol A—epoxy resin (Epicot 815)	10.0 g
Bistetrazol–diammonium (BHT–2NH_3)	8.0 g
Dispersed phase II	
Bis phenol A—epoxy resin (Epicot 815)	5.0 g
Imidazole (IZ)	1.0 g
Continuous phase	
Distilled water	200.0 g
Polyvinyl alcohol (PVA) (polymerization degree: 500)	1.0 g (0.5 wt %)
Impeller speed for preparing O/W dispersion	$Nr_1 = 83.3\ s^{-1}$
Time for agitation	4 min
Temperature of gelation	70°C
Time of gelation process	5 h
Operation conditions	
Impeller speed during microencapsulation process	$Nr_2 = 2.5–6.3\ s^{-1}$

Characterization

Observation of droplets and microcapsules

Epoxy resin droplets and microcapsules were observed in the PVA aqueous solution and on the glass plate by the optical microscope (BH-2; Olympus, Tokyo, Japan), respectively, and their photographs were taken. The surface and inner structure of microcapsules were observed by scanning electric microscope (JSM-5800, JEOL, Tokyo, Japan).

Measurements of mean diameters and diameter distributions

The mean diameters (the Sauter diameter) and diameter distributions of microcapsules were measured by size distribution analyzer (SALD-3000; Shimadzu,

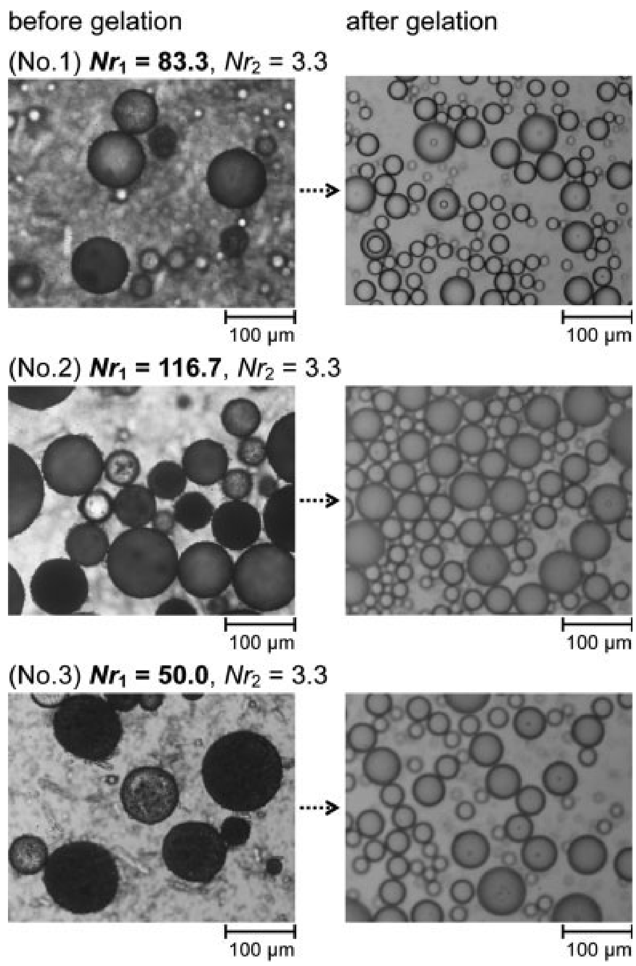

Figure 4 Optical microscopic photographs (the *in situ* gelation in droplet method).

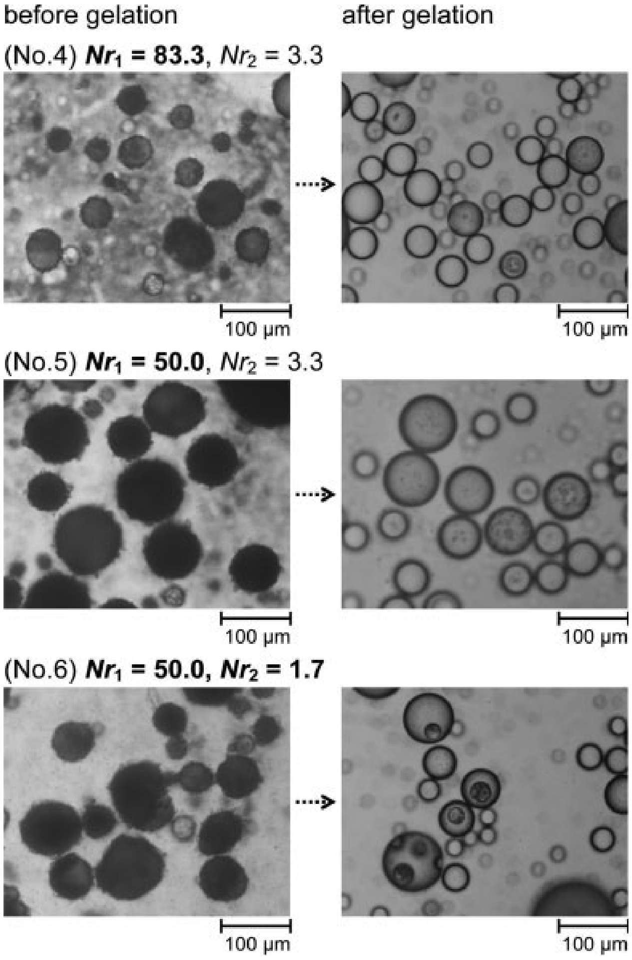

Figure 5 Optical microscopic photographs (the *in situ* gelation in droplet method).

Kyoto, Japan). The mean diameters (the Sauter diameter) and diameter distributions of epoxy resin droplets were measured from their photographs.

Measurement of content of core material

The weight of core material microencapsulated was measured by thermal balance (DTG-50/50H, Shimadzu, Kyoto, Japan). The content of core material (F) is defined as follows.

$$F = \frac{\text{Weight of core material contained}}{\text{weight of microcapsule}} \qquad (1)$$

Measurement of leakage of core material

Microcapsules of a given weight were added in hot water ($T = 95°C$) of 100 g and stirred for 10 min. After cooling temperature of hot water to room temperature, electric conductivity of water was measured by electric conductivity meter (CM-55; DKK-TOA, Tokyo, Japan). By comparing the measured value of electric conductivity with the correlation curve plotting the value of electric conductivity with the concentration of core material, the leakage amount of core material was evaluated.

RESULTS AND DISCUSSION

In situ gelation in droplet method

Figure 4 shows the optical microscopic photographs of epoxy resin droplets just after preparation of the (S/O)/W dispersion and microcapsules prepared by the *in situ* gelation in droplet method. From these photographs, it is found that epoxy resin droplets contain core material, which is identified by dark color, but microcapsules contain no core material. To prevent core material from leaking, microencapsulation was tried under the condition of the saturated concentration of BHT–$2NH_3$ in the continuous water

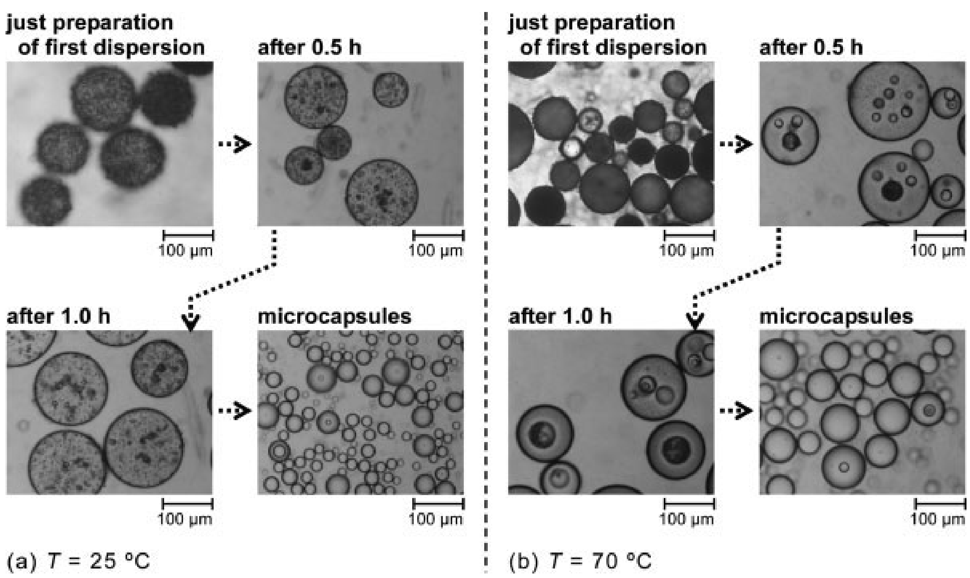

Figure 6 Temporal change of epoxy resin droplets from after preparation of (S/O)/W dispersion.

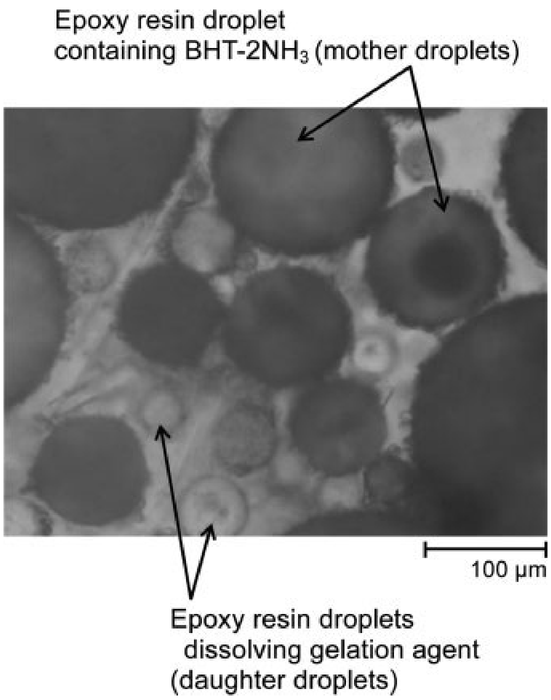

Figure 7 Optical microscopic photographs of two kinds of epoxy resin droplets just after first droplet preparation in the droplet coalescence method.

phase. The optical microscopic photographs of epoxy resin droplets and microcapsules prepared thus are shown in Figure 5. Although a few core materials are observed in microcapsules, a large amount of core material contained in epoxy resin droplets is found to leak out during the microencapsulation process. To investigate when core material leaks out from epoxy resin droplets, epoxy resin droplets were observed at some time interval from after preparation of the (S/O)/W dispersion. Figure 6 shows the optical microscopic photographs of epoxy resin droplets and microcapsules prepared at 25 and 70°C, respectively. At the temperature of 25°C, core material gradually leaks from an epoxy resin droplet with elapsing time. At the temperature of 70°C, core material leaks faster than at 25°C. This result may mean that the larger the gelation degree becomes,

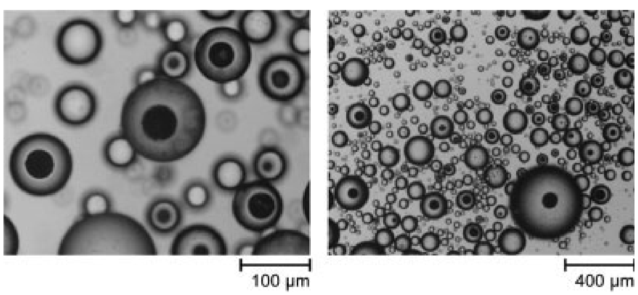

Figure 8 Optical microscope photographs of microcapsules prepared with the droplet coalescence method.

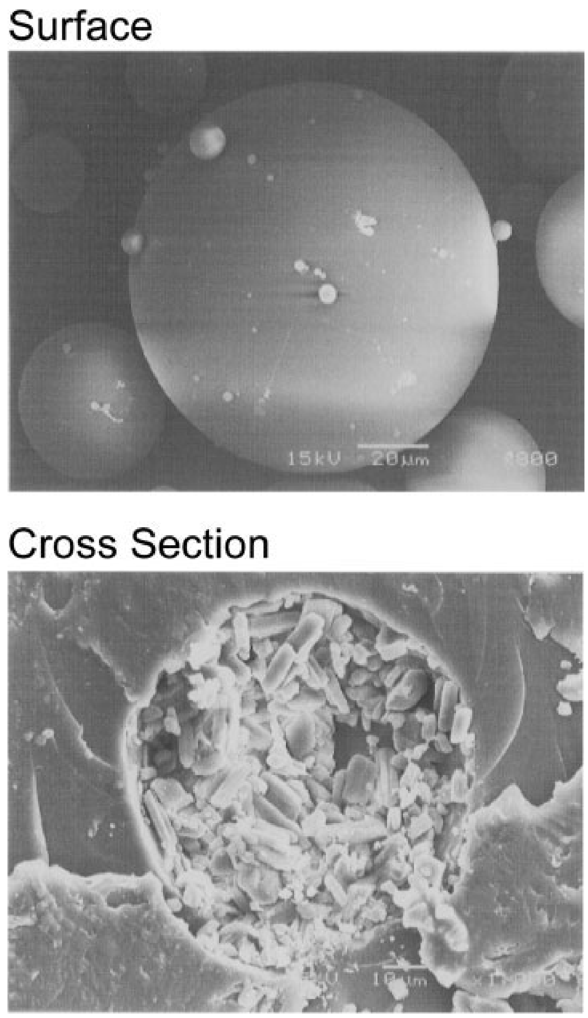

Figure 9 SEM photographs of Microcapsule prepared with the droplet coalescence method.

the faster the core material leaks. In other words, hydrophilic core material may be pushed out from the inner part of a hydrophobic epoxy resin droplet

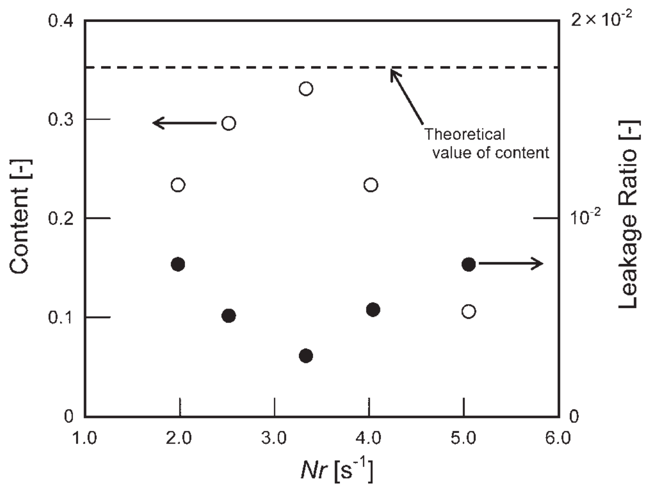

Figure 10 Dependence of content and leakage ratio of core material on impeller speed.

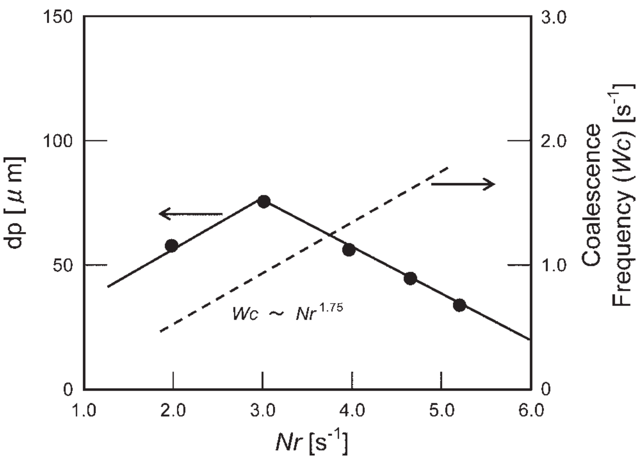

Figure 11 Effect of agitating speed on mean microcapsule diameter and coalescence frequency.

by gelation. From this point of view, if gelation could be proceeded from the periphery part of a epoxy resin droplet, leakage of core material could be prevented.

Droplet coalescence method

Thus microencapsulation by the droplet coalescence method was tried.

Figure 7 shows the optical microscopic photographs of two kinds of epoxy resin droplets prepared in the droplet coalescence method. In this figure, the larger dark droplets are the mother droplets of epoxy resin droplets containing BHT–2NH_3 and the smaller transparent droplets are the daughter droplets of epoxy resin droplets containing Imidazole.

Figures 8 and 9 show the optical microscopic photographs of microcapsules and the SEM photographs of the surface and cross section of a microcapsule, respectively. From these photographs, it is found that the surface is very smooth and powdery core material is microencapsulated well.

Figure 10 shows the dependences of content and leakage ratio of core material on the impeller speed. With increasing the impeller speed, the content increases, becomes maximum at $Nr_2 = 3.3\ s^{-1}$, and then decreases. On the other hand, with increasing the impeller speed, the leakage ratio decreases, becomes minimum at $Nr_2 = 3.3\ s^{-1}$, and then increases.

It is well known that coalescence frequency between droplets increases with the impeller speed as shown in Figures 10.[10,11] Accordingly, with increasing the impeller speed, the mother droplets containing core material must frequently coalesce with the daughter droplets containing Imidazole. Then if $r_{O/W} > (r_{O'/W} + r_{O'/O})$, the daughter droplets spread on the surface of a mother droplet, or dissolve into the mother droplet. Here, $r_{O/W}$, $r_{O'/W}$, $r_{O'/O}$ are the interfacial tensions between mother droplet and the continuous phase, between daughter droplet and the continuous water phase, between mother droplet and daughter droplet, respectively. In either case, as gelation from the periphery part of a mother droplet may be accelerated by increasing the impeller speed, the content of core material is increased.

However, as the droplets are broken at the higher impeller speed as shown in Figure 11, core material may leak easily.

CONCLUSIONS

It was tried to microencapsulate Bistetrazol–diammonium (BHT–2NH_3) as a core material with epoxy resin by the droplet coalescence method to give water resistance.

Epoxy resin droplets containing BHT–2NH_3 were made to coalesce with them containing Imidazole as gelation agent for epoxy resin. The following results were obtained:

1. It was found that hydrophilic core material was rapidly pushed out from hydrophobic epoxy resin droplets.
2. The content of core material could be considerably increased by the droplet coalescence method on comparison with the *in situ* gelation in droplet method.
3. With increasing the impeller speed during the microencapsulation process, the content of core material increased, became maximum and decreased due to droplet breakup.

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