

# Effect of Viscosity of Shell Solution on the Content of Solid Powder as Core Material in Microencapsulation by the Drying-in-Liquid Method

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**ABSTRACT:** Solid powder generating minus ion was microencapsulated by polystyrene with the drying-in-liquid method. In the microencapsulation, (R)-(+)-limonene as the solvent for polystyrene and ethylene glycol as the continuous phase were adopted instead of the conventional organic solvent such as dichloromethane, benzene and toluene, and water, respectively. It was mainly investigated whether the solvents adopted here could be applied to the drying-in-liquid method or not and how the viscosity of the shell solution and the oil soluble surfactant affected the content of core material. The oil soluble surfactant made hydrophilic solid powder

more hydrophobic and resulted in an increase of the content. Microcapsules containing solid powder could be prepared with the drying-in-liquid method using (R)-(+)-limonene and ethylene glycol. An increase in the viscosity of the shell solution repressed the movement of solid powder particles in a droplet of the shell solution during the microencapsulation process and resulted in the higher content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1585–1593, 2008

**Key words:** microcapsule; drying-in-liquid; liquid–liquid dispersion; polystyrene

## INTRODUCTION

Microcapsules have been applied in various fields such as recording materials, cosmetics, coating materials, food, agriculture, and so on. Recently, it is strongly demanded to develop the microencapsulation method using the low loaded materials to environment. For example, organic solvents such as dichloromethane, toluene, and benzene as the solvent for polystyrene as the most popular shell material have been used in the drying-in-liquid method.<sup>1–3</sup> However, these solvents are strongly restricted for use at present.

It is well-known that (R)-(+)-limonene is good solvent for polystyrene.<sup>4</sup> We prepared composite particles composed of polystyrene and solid powders by using (R)-(+)-limonene as the solvent for polystyrene and ethylene glycol as the continuous phase.<sup>5</sup> These composite particles had the structure that solid powder coated the surface of a polystyrene bead. If the preparation method in the previous research could be applied to microencapsulation of solid powder, (R)-(+)-limonene may be used instead

of organic solvents stated earlier in the drying-in-liquid method.

In microencapsulation of solid powder with the drying-in-liquid method, it is required to stably retain solid powder in a droplet of the shell solution.<sup>6,7</sup>

As the viscosity of the shell solution plays an important role to retain solid powder in a droplet of the shell solution, it is necessary to investigate the effect of the viscosity of the shell solution on the content of solid powder as core material.

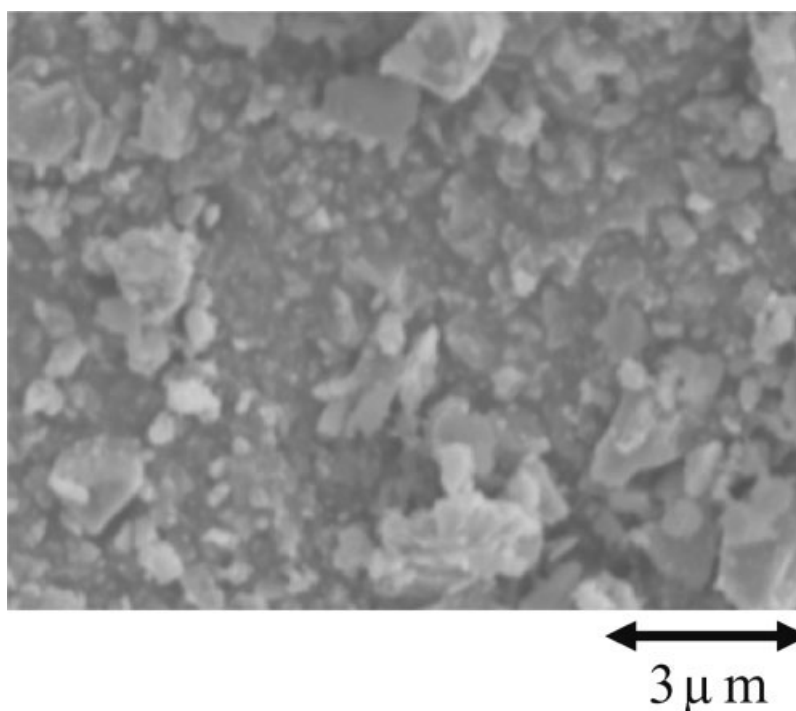
The purpose of this study is to investigate whether the (R)-(+)-limonene/ethylene glycol system may be applied to microencapsulation of solid powder with the drying-in-liquid method or not and to estimate the effect of the viscosity of the shell solution on the content of solid powder as core material. In the experiment, solid powder generating minus ion (hereafter called NIP as an abbreviation) was selected as core material. It is well-known that minus ion has the various physiological efficacies such as an anodyne, mental stabilizer, and air purification.

## EXPERIMENTAL

### Materials

(R)-(+)-limonene (Kanto Chemical) was used as the solvent for polystyrene (Wako Pure Chemical Industries; Degree of Polymer, 2000) of the matrix of microcapsule.

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**Figure 1** SEM photograph of NIP.

Solid powder generating minus ion (NIP) used as the core material is the composite mineral ore containing xenotime, titanium oxide, zirconium oxide, zinc-aluminum oxide, etc. It has the mean diameter of  $3.9 \mu\text{m}$ . The SEM photograph of NIP is shown in Figure 1. Ethylene glycol (Wako pure Chemical Industries) was used as the continuous phase. Hydroxy-functional carboxylic acid ester (BYK-Chemie Japan KK; Disperbyk 108) (D108) was used as the oil soluble surfactant. Tricalcium phosphate (TCP) (Wako Pure Chemical Industries) was used as the stabilizer in the continuous phase, and sodium dodecyl benzene sulfonate (DBS) (Kanto Chemical) was used as the costabilizer.

### Experimental apparatus

Figure 2 shows the experimental apparatus used for preparing microcapsules.

A separable flask with an inner diameter of  $8.5 \times 10^{-2} \text{ m}$  and a capacity of  $5 \times 10^{-4} \text{ m}^3$  was used as the reactor and installed in a mantle heater. Four baffles with  $8.5 \times 10^{-2} \text{ m}$  long were installed on the wall of the reactor to prevent air entrainment from the free surface of the dispersion with stirring. A high speed homogenizer of rotor-stator type (Nihon Seiki; BM-T) was used to form (S/O)/W dispersion.

The impeller of a six-bladed disk turbine with  $5.0 \times 10^{-2} \text{ m}$  in diameter was used as a stirrer during the microencapsulation process and installed at one-third of the liquid depth.

The cold trap equipment (Iwaki Glass; CLT-050) and circulating aspirator (SIBATA Scientific Technology; WJ-15) were used for removing the solvent during the microencapsulation process.

### Preparation of microcapsules

Figure 3 shows the flow sheet of preparing microcapsules.

Polystyrene (PS) of the given weight as the shell material was dissolved in (R)-(+)-limonene of the constant volume ( $2.5 \times 10^{-6} \text{ m}^3$ ) to prepare the polymer solution as the dispersed phase. The given weight of solid powder (NIP), which generates minus ion, was added in the polymer solution under ultrasonic irradiation to form the (S/O) dispersion. The amount of minus ion generated is found to be proportional to the weight of NIP.

Ethylene glycol of the constant volume of  $3.0 \times 10^{-4} \text{ m}^3$  was poured as the continuous phase into the reactor, which was kept at 373 K. Two kinds of stabilizer (hydrophilic solid powder as stabilizer and water soluble surfactant as costabilizer) were pre-mixed in the continuous phase.

The dispersed phase was poured into the continuous phase under stirring by the homogenizer to form the (S/O)/W dispersion. The drying-in-liquid was performed for 3.5 h stirring with the impeller speed of  $4.17 \text{ s}^{-1}$  and removing the solvent for PS at 373 K to prepare microcapsules.

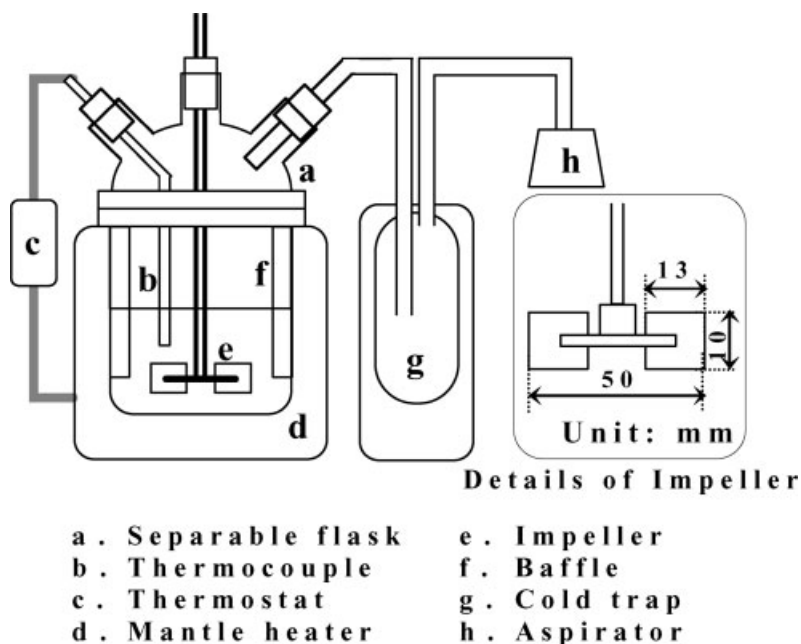


Figure 2 Experimental apparatus.

Microcapsules were washed twice with distilled water and dried under reduced pressure for 24 h.

Microencapsulation stated earlier was performed by changing the added amount of oil soluble surfactant and the PS concentration.

Experimental conditions are shown in Table I.

### CHARACTERIZATION

#### Observation of microcapsules

The surface and cross section of microcapsules were observed with scanning electron microscopy (SEM) (JEOL; JSM-5800).

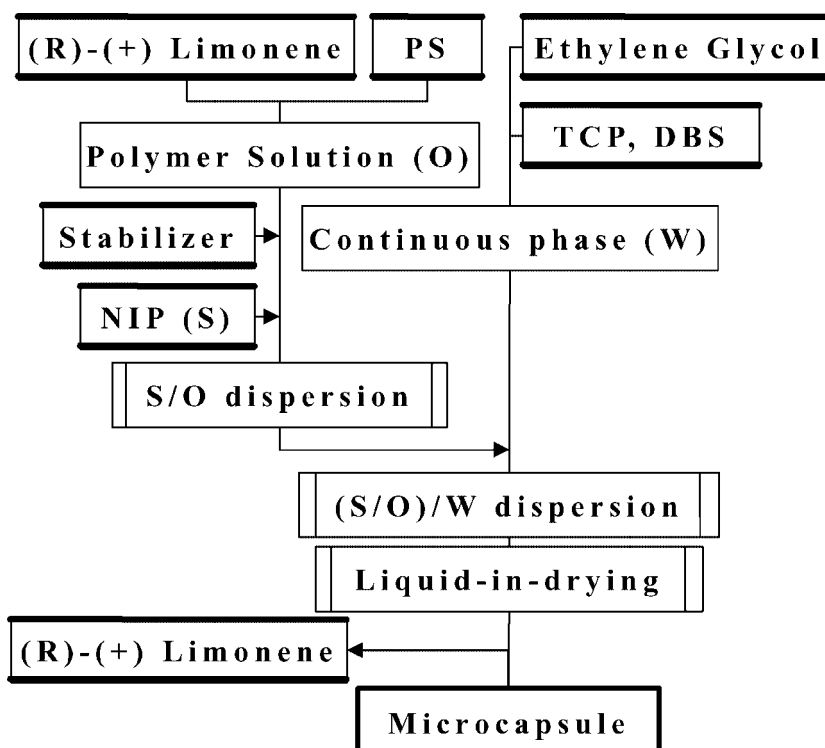


Figure 3 Flow sheet of experiment.

**TABLE I**  
**Experimental Conditions**

Core material (S phase)	
Solid powder generating minus ion	5 g
Shell material (O phase)	
(R)-(+)-Limonene solution dissolving PS	
Concentration of PS	5–33.3 wt %
Volume of shell solution	$2.5 \times 10^{-5} \text{ m}^{-3}$
Continuous phase (W phase)	
Ethylene glycol	$3.0 \times 10^{-4} \text{ m}^3$
Dispersion stabilizer for continuous phase: TCP	
Concentration of TCP	0.99 wt %
Costabilizer for continuous phase: DBS	
Concentration of DBS	$3.33 \times 10^{-3} \text{ wt %}$
At formation of (S/O) dispersion	
Ultrasonic intensity	125 W
Ultrasonic wavelength	42 kHz
Irradiation time	10 min
Temperature	298 K
At formation of (S/O)/W dispersion	
Impeller speed	50 or $133 \text{ s}^{-1}$
Stirring time	10 min
Temperature	298 K
At drying in liquid	
Impeller speed	$4.17 \text{ s}^{-1}$
Time of drying in liquid	3.5 h
Temperature	373 K

### Diameter distribution and mean diameter

The Sauter mean diameter of microcapsules were measured with laser diffraction particle size analyzer (Shimadzu; SALD 3000).

### Content of NIP

The given weight of microcapsules was set in the thermal balance (Shimadzu; DTG-50) and PS of the shell was removed by thermal decomposition.

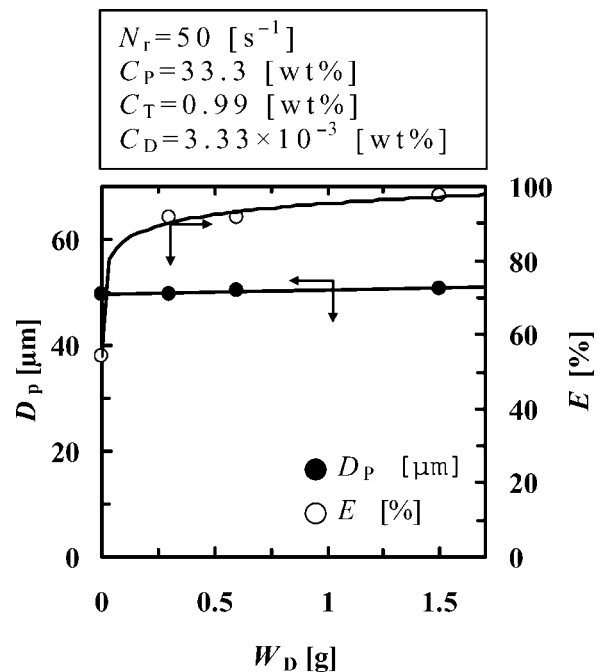
The content of NIP in the microcapsules was obtained by measuring the change in the weight of microcapsules with the thermal balance. Namely, the content ( $F$ ) was calculated by the following equation.

$$F = 100 \times (W_a - W_b) / W_a \quad (1)$$

where  $W_a$  and  $W_b$  are the weight of microcapsules before and after thermal decomposition, respectively. The calculated content ( $F_{\text{theo}}$ ) was obtained by the following equation.

$$F_{\text{theo}} = 100 \times W_C / (W_C + W_S) \quad (2)$$

where  $W_C$  and  $W_S$  are the weight of core material NIP and shell material PS given by experimental



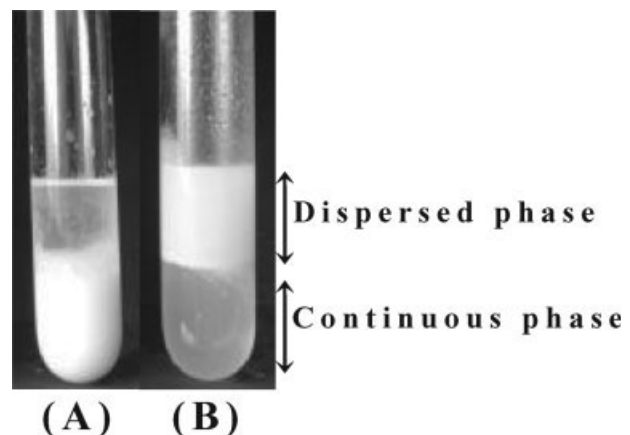
**Figure 4** Effect of amount of D108 on mean diameter and content of NIP at 33.3 wt % PS.

condition, respectively. The microencapsulation efficiency ( $E$ ) was calculated by the following equation.

$$E = 100 \times F / F_{\text{theo}} \quad (3)$$

### Physical properties of liquids concerned

Interfacial tension and viscosity of liquids concerned were measured with surface tension meter (Kyowa Interface Science) and a vibration viscometer (Yamaichi Electronics; Viscomate VM-1A), respectively.



**Figure 5** Effect of oil soluble surfactant on hydrophobicity of NIP: (A) without D108, (B) with D108.

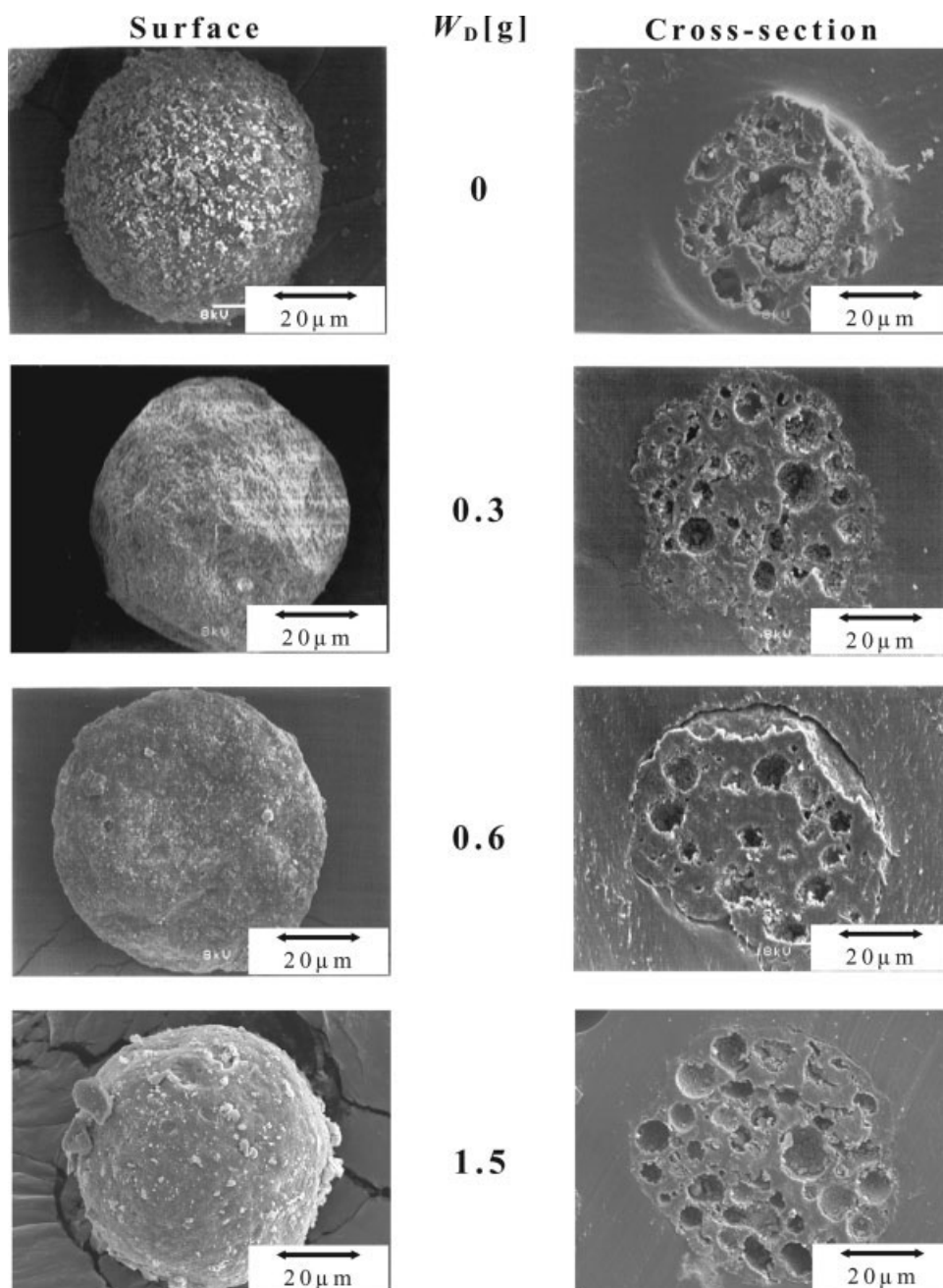


Figure 6 SEM photographs of microcapsules (effect of oil soluble surfactant at 33.3 wt %  $C_p$ ).

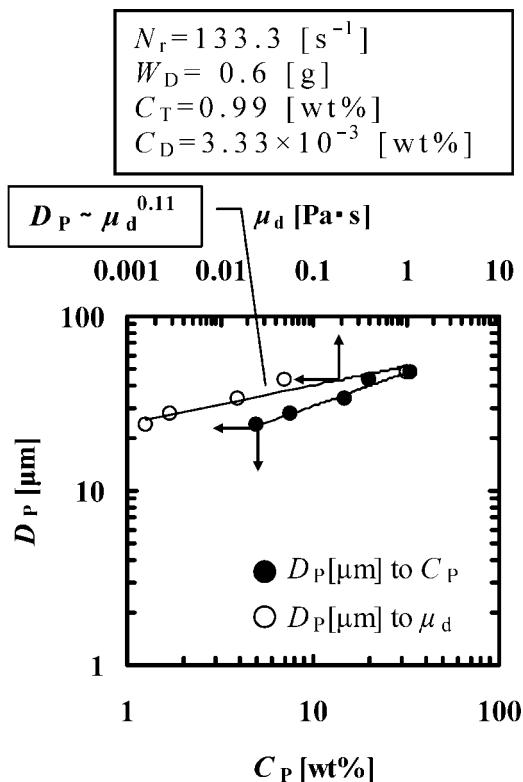
## RESULTS AND DISCUSSION

### Effect of the oil soluble surfactant

Figure 4 shows the dependence of the mean diameter ( $D_p$ ) of microcapsules and the microencapsulation efficiency ( $E$ ) on the amount ( $W_D$ ) of D108. The mean diameters slightly increase with the amount of D108. The content was about 60% without D108 and abruptly increased to about 95% with an addition of D108. It is considered that an increase in the mean diameter is attributable to the increase of the microencapsulation efficiency of the core material.

To investigate in detail the effect of D108, the dispersion stability of NIP was estimated in the dispersed phase and in the continuous phase. Namely, the continuous and the dispersed phase of the constant volume ( $10 \times 10^{-6} \text{ m}^3$ ) were poured into a test tube. After an addition of NIP into the dispersed oil phase, this test tube was shaken for 5 min with the tube shaker. After settling the test tube, it was observed that NIP was in the continuous water phase or in the dispersed oil phase.

Figure 5 shows the dispersion (B) with D108 and (A) without D108. From this figure, it is found that



**Figure 7** Dependence of the mean diameter on the PS concentration  $C_P$  and the viscosity of the shell solution  $\mu_d$ .

NIP was in the continuous water phase (A) without D108 and in the dispersed oil phase (B) with D108. The most part of the composition of NIP are metal oxide. When metal oxide powder with the hydrophilic surface was added to the dispersed oil phase, they move to the interface between the dispersed oil phase and the continuous water phase, and then defect to the continuous water phase. Therefore, the result of Figure 5 may suggest that D108 makes hydrophilic NIP hydrophobic. Then, it may suggest that the hydrophilic group of D108 adsorbed on the hydrophilic surface of NIP. As the stability of NIP in the dispersed oil phase increases with an addition of D108, the content may be increased.

Figure 6 shows the SEM photographs of the surface and the cross section of microcapsules without and with D108. Microcapsules were spherical irrespective of an addition of D108. The inner structure of microcapsules was multicore. Several holes in the cross section may be the traces of (R)-(+)-limonene volatile, which evaporated from the microcapsule. Large numbers of NIP were observed in the surface of holes and the shell of microcapsule in the cross section. It is found that the number of NIP increases with the amount of D108. This may be due to the increase in the microencapsulation efficiency.

### Effect of the PS concentration

Figure 7 shows the dependence of the mean diameter of microcapsule on the PS concentration (or the viscosity of the shell solution). The mean diameter increased with the PS concentration. This is attributable to an increase in the viscous force against the disruptive force for a droplet, because the interfacial tension is almost constant ( $10.4 \times 10^{-3}$  N/m).

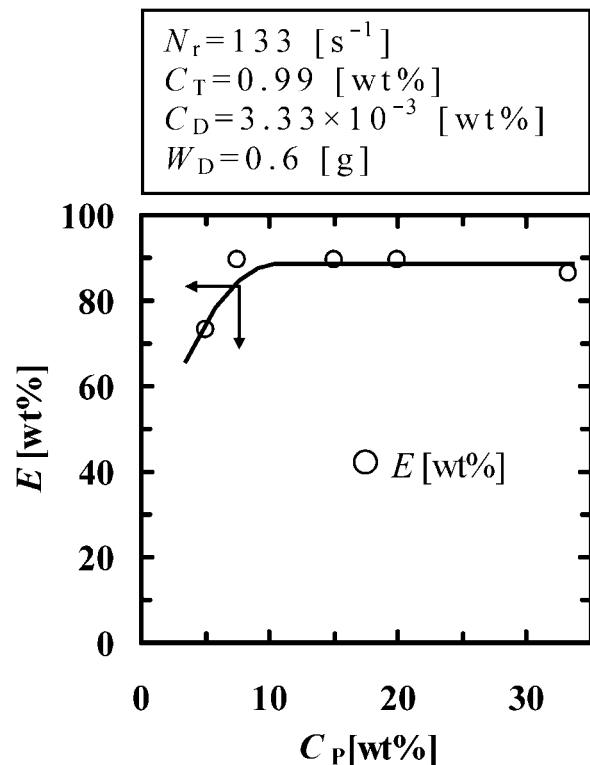
In the case of  $\mu_d > 1.0 \times 10^{-1}$  Pa s, the following dependence of the mean diameter on the viscosity of the dispersed phase was derived.<sup>8-12</sup>

$$D_P \sim \mu_d^{0.1 \sim 2.5} \quad (4)$$

The dependence of the mean diameter on the viscosity of the dispersion phase in the liquid-liquid adopted here,  $D_P \sim \mu_d^{0.11}$ , is in agreement with that in eq. (4).

Figure 8 shows the dependence of the microencapsulation efficiency on the PS concentration. The microencapsulation efficiency increased with the PS concentration and became almost 90% over the PS concentration of 10 wt %.

Figure 9 shows the SEM photographs of the surface and the cross section of microcapsules. It is found that microcapsule was irregular at the lower PS concentration and microcapsules became more spherical with the higher PS concentration. This is



**Figure 8** The dependence of the encapsulation efficiency on the PS concentration.

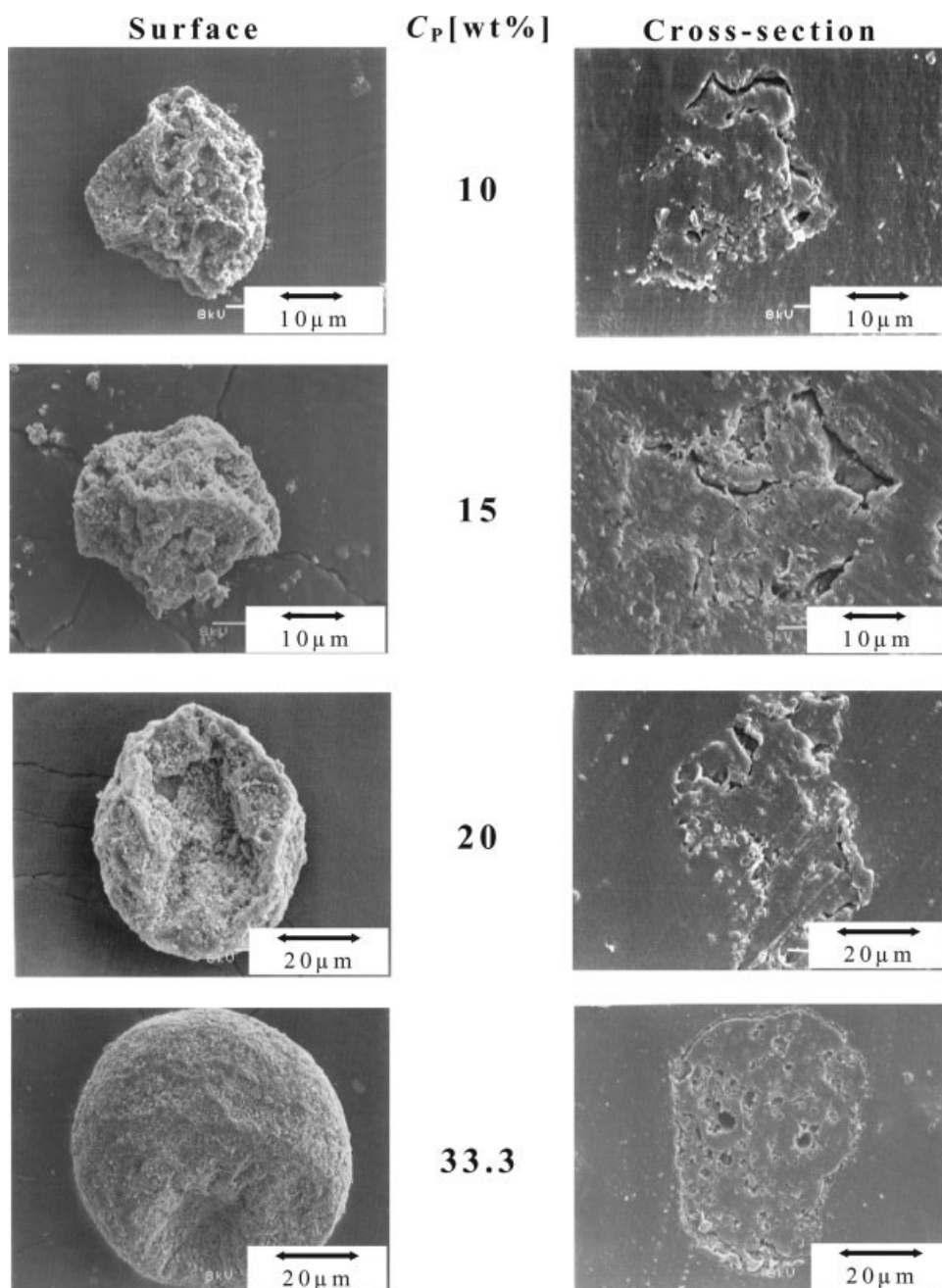


Figure 9 SEM photographs of microcapsules (effect of various PS concentrations).

attributable to the depression effect against deformation based on the viscous force in the microencapsulation process.

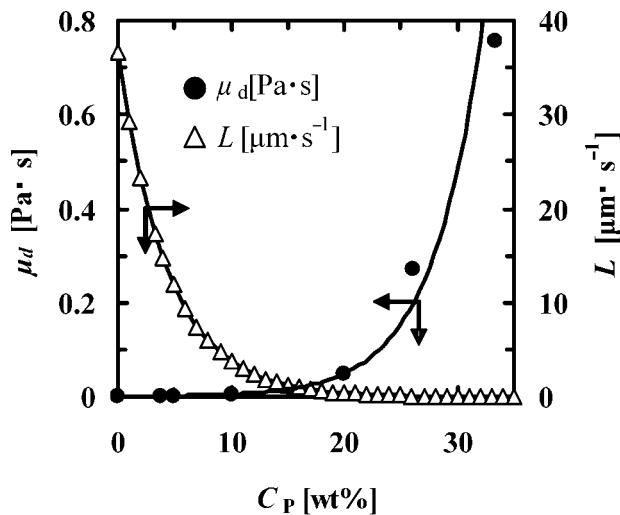
The effect of the viscosity of the shell solution on the content of solid powder as core material in the microencapsulation process is estimated as follows.

If the movement length ( $L$ ) per unit time of a solid particle in a droplet of the shell solution is very smaller than the droplet diameter  $d_p$ , ( $L < d_p$ ), the possibility which the solid particle is stayed in a droplet and microencapsulated may increase. The viscosity of the droplet of the shell solution may

be controlled by the concentration of the shell material and the removal rate of the solvent of the shell solution.

Figure 10 shows the dependence of the viscosity of the shell solution and the movement length of a solid particle on the PS concentration. Here, the movement length of a solid particle was calculated by the Stokes settling velocity.

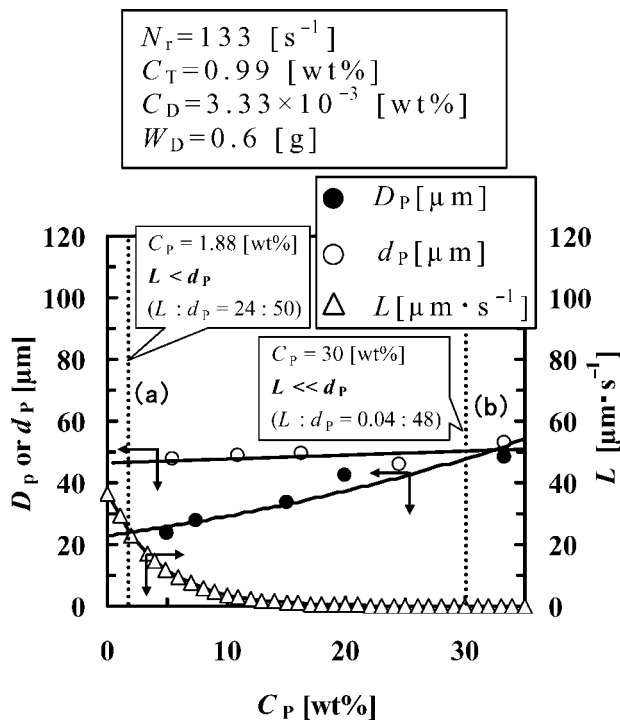
$$L = \frac{g(\rho_p - \rho)d_{PS}^2}{18\mu} \quad (5)$$



**Figure 10** The dependence of the viscosity of the shell solution ( $\mu_d$ ) and the movement length per unit time ( $L$ ) of a solid particle on the PS concentration.

where  $\rho_p$  and  $d_{ps}$  are the density and the diameter of a solid particle,  $\rho$  and  $\mu$  are the density and the viscosity of the shell solution, respectively.

The movement length sharply decreased with the PS concentration. Figure 11 shows the dependence of the mean diameter of microcapsule ( $D_p$ ), the mean



**Figure 11** The dependence of the mean diameter of microcapsule ( $D_p$ ), the mean diameter of primary droplet ( $d_p$ ), and the movement length per unit time ( $L$ ) of a solid particle NIP on the PS concentration.

diameter of primary liquid droplet ( $d_p$ ), and the movement length per unit time ( $L$ ) of a solid particle NIP on the PS concentration. The mean diameter of primary liquid droplets and microcapsules increase with the PS concentration. The difference between the mean diameter of primary droplets and those of microcapsules is due to the removal of the solvent. Two dotted lines (a) and (b) in Figure 11 are the ratio of the movement length to mean diameters of primary droplets at the lowest and the highest viscosity of the shell solution in this experiment, respectively. Namely, the value of dotted line (a), the mean diameter at the viscosity of shell solution of  $7.9 \times 10^{-4}$  Pa s, is larger than the movement length of a solid particle ( $L < d_p$ ). The microencapsulation efficiency may become smaller as shown in Figure 8.

Contrary to this, as the value of dotted line (b), the mean diameter at the viscosity of shell solution of  $4.8 \times 10^{-1}$  Pa s, is much larger than the movement length ( $L < d_p$ ), the microencapsulation efficiency may be about 90%.

From this result, it is found that the microencapsulation efficiency can be controlled by the relative value of the movement length to the microcapsule diameter.

## CONCLUSIONS

It was investigated to microencapsulate solid powder by polystyrene with the drying-in-liquid method using (R)-(+)-limonene as the solvent for polystyrene and ethylene glycol as the continuous phase.

The following results were obtained:

1. Microcapsules containing solid powder could be prepared by using the solvents adopted here.
2. The oil soluble surfactant made hydrophilic solid powder more hydrophobic and resulted in the higher content.
3. The viscosity of the shell solution played an important role for the morphology, the diameter, and the content.

## NOMENCLATURE

$C_D$	concentration of DBS in continuous phase [wt %]
$C_P$	concentration of PS in dispersion phase [wt %]
$C_T$	concentration of TCP in continuous phase [wt %]
$d_p$	mean diameter of primary liquid droplet [ $\mu\text{m}$ ]



$d_{PS}$	mean diameter of solid particle [ $\mu\text{m}$ ]
$D_P$	mean diameter of microcapsules [ $\mu\text{m}$ ]
$E$	microencapsulation efficiency [%]
$F$	content of NIP in microcapsules [%]
$F_{\text{theo}}$	calculated content of NIP in microcapsules [%]
$g$	acceleration of gravity [ $\text{m} \cdot \text{s}^{-2}$ ]
$L$	movement length per unit time [ $\mu\text{m} \cdot \text{s}^{-1}$ ]
$W_a$	weight of microcapsules [g]
$W_b$	weight of microcapsules after thermal decomposition [g]
$W_C$	weight of core material NIP [g]
$W_S$	weight of shell material PS [g]
$\mu$	viscosity of shell solution [ $\text{Pa} \cdot \text{s}$ ]
$\mu_d$	viscosity of dispersion phase [ $\text{Pa} \cdot \text{s}$ ]
$\rho$	density of shell solution [ $\text{g} \cdot \text{cm}^{-3}$ ]
$\rho_P$	density of solid particle NIP [ $\text{g} \cdot \text{cm}^{-3}$ ]

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