Preparation of Polyurea Microcapsules Containing Pyrethroid Insecticide with Hexamethylene Diisocyanate Isocyanurate

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ABSTRACT: Polyurea microcapsules containing a pyrethroid insecticide were prepared by the reaction between hexamethylene diisocyanate isocyanurate and ethylenediamine in an oil-in-water emulsion. This study was performed to establish the operational conditions of preparing microcapsules by interfacial polymerization and to investigate how the operational conditions affected the characteristics of microcapsules such as the morphology, wall thickness, mean diameter, and particle size distribution. Microcapsules prepared in this study were found to be spherical and monocore. The microcapsule yields, ranging from 94 to 98%, were almost equal to the theoretical values. The wall thickness of the microcapsules increased with the diameter of the microcapsules and the concentration of hexamethylene diisocyanate isocyanurate. In comparison with the results for microcapsules prepared with a mixture of hexamethylene diisocyanate uretidione and isocyanurate, the diameters and wall thickness of the microcapsules were found to be larger. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2000–2006, 2008

Key words: composites; core-shell polymers; dispersions; interfaces; microencapsulation

INTRODUCTION

It is well known that the microencapsulation method by interfacial polycondensation polymerization is a useful way to microencapsulate a liquid-core material. In particular, polyurea and polyurethane microcapsules have been extensively investigated in various fields.[1]

For example, aliphatic hexamethylene diisocyanate (HMDI) monomer and aliphatic ethylenediamine (EDA) were used to prepare polyurea microcapsules containing insecticide.[2] Kubo et al.[3] prepared polyurea microcapsules with HMDI monomer and discussed the growth rate of the wall of microcapsules by modeling the formation kinetics of polyurea microcapsules. Mizuno et al.[4] also prepared polyurea microcapsules with HMDI monomer and discussed the effect of the surfactant on the growth rate of the wall. However, they did not discuss the mechanical strength and thermal stability of the polyurea microcapsules.

We have tried to prepare polyurea microcapsules containing insecticide by interfacial polycondensation polymerization with HMDI monomer and EDA and to give the textile a dust-mite-repellent effect.[5]

However, we could not prepare microcapsules with efficient mechanical strength. Furthermore, as HMDI monomer has irritating swelling, the microencapsulation process with HMDI monomer is not suitable for the field of textiles. Although HMDI isocyanurate may result in a stronger polyurea resin[6] and has no bad smell, there is little information about the operational conditions of preparing microcapsules with HMDI isocyanurate and their characteristics.

Therefore, we tried to prepare polyurea microcapsules containing a pyrethroid insecticide by the reaction between HMDI isocyanurate and EDA.

The purpose of this study was to establish operational conditions to prepare microcapsules by interfacial polymerization and to investigate how the operational conditions affected the characteristics of microcapsules such as the morphology, wall thickness, mean diameter, particle size distribution, and microcapsule yield.

EXPERIMENTAL

Materials

HMDI isocyanurate (Desmodur N3300) and EDA as wall-forming materials were purchased from Sumika Bayer Urethane Co. (Hyogo, Japan) and Tosoh Co. (Tokyo, Japan), respectively. Insecticide containing 30 wt % permethrin (Dancide PS-150) as a core material and poly (vinyl alcohol) (PVA; L-25) as a stabi-

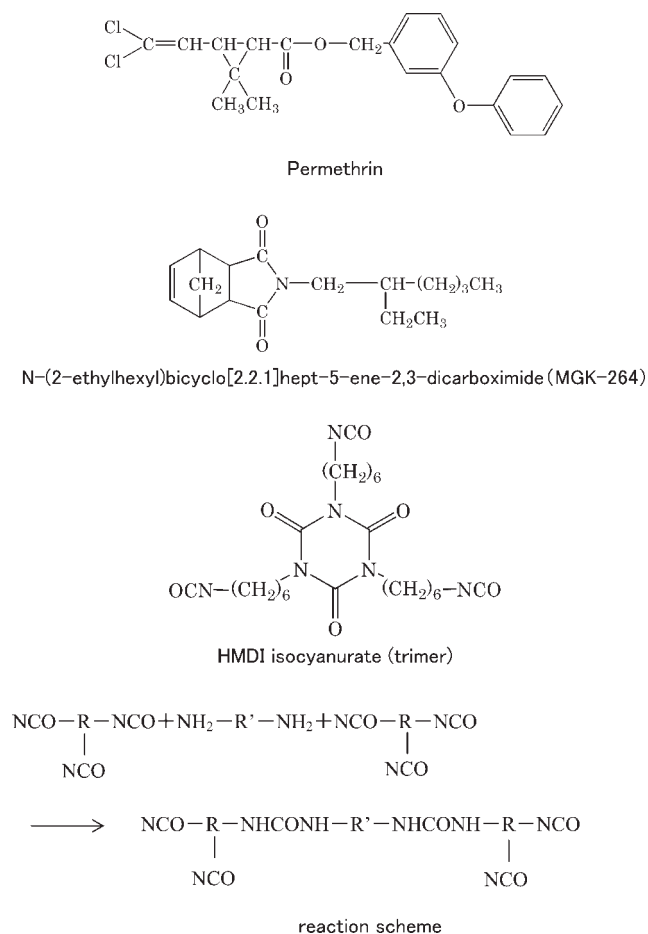*Correspondence to:* M. Tanaka (tanaka@eng.niigata-u.ac.jp).

Figure 1 Chemical structures of permethrin and HMDI isocyanurate and reaction scheme of HMDI isocyanurate and EDA.

lizer in the continuous phase were purchased from Shinto Fine Co. (Osaka, Japan) and Shin-Etsu Chemical Co. (Tokyo, Japan), respectively. Figure 1 shows the chemical structures of permethrin (MGK-264) and HMDI isocyanurate and the reaction scheme between HMDI isocyanurate and EDA.

Preparation of microcapsules

The flow chart for microencapsulation by interfacial polymerization is shown in Figure 2. Experimental conditions and operating conditions are shown in Tables I and II, respectively. To prepare the dispersed phase, 100 g of insecticide and a given weight of HMDI isocyanurate (condition A, 12.5 g; condition B, 25.0 g; condition C, 50.0 g) were mixed in a 200-mL beaker. The dispersed phase was poured into the continuous water phase with a 4 wt % concentration of PVA to form the oil-in-water (O/W) emulsion. Emulsification was carried out for 15 min with a homomixer (T.K. Homomixer Mark II, Tokushu Kika Co., Osaka, Japan). The revolution speed of emulsification was changed to 50 (3000

rpm), 75 (4500 rpm), and 100 s^{-1} (6000 rpm), respectively. After emulsification, the O/W emulsion was poured into a round-bottom flask of 1000 mL with four inlets and then stirred at the revolution speed of 5.0 s^{-1} by a two-bladed turbine impeller with a diameter of 8×10^{-2} m, which was fixed at half the liquid height from the flask bottom. After EDA (condition A, 2 g; condition B, 4 g; condition C, 8 g) diluted with distilled water (condition A, 143 g; condition B, 128.5 g; condition C, 99.5 g) was added to the O/W emulsion at 25°C, the reaction was carried out for 1 h at 25°C and then for 1 h at 60°C.

Characterization

Particle size distribution

The mean sizes [i.e., particle diameter (D_p)] and particle size distributions were determined with a particle size analyzer (SALD-3000, Shimadzu Co., Tokyo, Japan).

Microcapsule yield

At first, a microcapsule suspension of 5 g was centrifuged by a centrifugal separator (MX-300, Tomy Seiko Co., Tokyo, Japan) for 45 min at 12,000 rpm. After a supernatant liquid containing PVA and unmicroencapsulated core material was removed, the precipitated microcapsules were washed with distilled water by stirring with a glass rod. The microcapsule suspension was centrifuged again. These treatments were repeated five times to completely remove PVA and unmicroencapsulated core
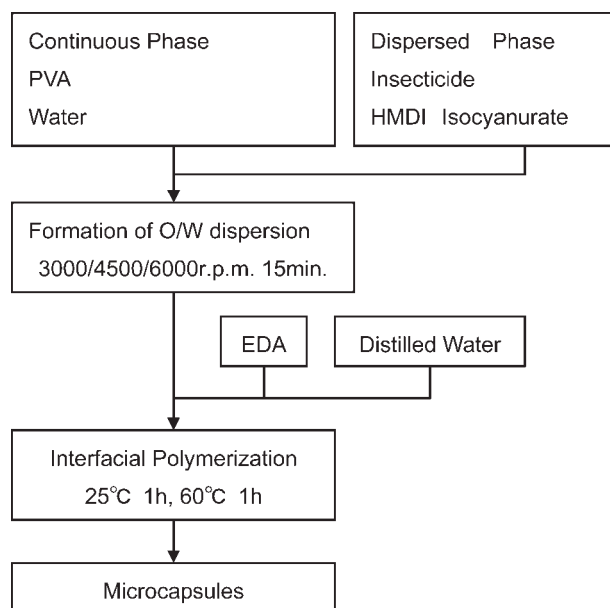

Figure 2 Flow chart for preparing polyurea microcapsules.

Dispersed phase	
Concentration of insecticide	100 g (20 wt % dispersion)
Concentration of HMDI isocyanurate	12.5–50 g (2.5–10 wt % dispersion)
Continuous phase	
Concentration of PVA	9.7 g (4.0 wt % water)
Concentration of deionized water	243 g
Diamine phase	
Concentration of EDA	2–8 g (0.4–1.6 wt % dispersion)
Concentration of distilled water	99.5–143 g (28.6–19.9 wt % dispersion)

material. After these treatments, the microcapsules were dried in a glass dish for 1 week at room temperature. The microcapsule yield (Y_E) was defined and estimated with the following equation:

$$Y_E(\%) = \frac{\text{dried microcapsule weight per unit volume}}{\text{initial weight of core and wall material per unit volume}} \times 100$$

(1)

Observations of microcapsules

The surface and wall thickness of the microcapsules were observed by scanning electron microscopy (SEM; SM-300, Topcon Co., Tokyo, Japan).

Measurement of the liquid properties

The viscosity and interfacial tension were measured with a viscometer (TV-10, Toki Sangyo Co., Tokyo, Japan) and a tension meter (CBVP-A3, Kyowa Interface Science Co., Saitama, Japan), respectively.

TABLE II
Operating Conditions

Condition A	
Insecticide	20.0 wt % (100 g)
HMDI isocyanurate	2.5 wt % (isocyanurate, 0.025 mol)
EDA	0.4 wt % (0.033 mol)
Distilled water	28.6 wt %
Condition B	
Insecticide	20.0 wt % (100 g)
HMDI isocyanurate	5.0 wt % (isocyanurate, 0.050 mol)
EDA	0.8 wt % (0.066 mol)
Distilled water	25.7 wt %
Condition C	
Insecticide	20.0 wt % (100 g)
HMDI isocyanurate	10 wt % (isocyanurate, 0.100 mol)
EDA	1.6 wt % (0.133 mol)
Distilled water	19.9 wt %

Fourier transform infrared (FTIR) spectrometer analysis

IR spectra of the core material and the microcapsules were obtained with an FTIR spectrometer (FT/IR 300E, Shimadzu).

RESULTS AND DISCUSSION

FTIR spectra

Figure 3 shows FTIR spectra of the core material, the HMDI isocyanurate as the wall-forming material, and the polyurea microcapsules synthesized at C_i (concentration of HMDI isocyanurate) = 10.0 wt %. In Figure 3(b), the absorption peak of the carbonyl group of HMDI isocyanurate can be observed at 1688 cm^{-1} (isocyanurate, ⟨NCON⟩, stretching). C—H stretching and bending vibrations in the aliphatic methylene group can be observed at 2850–2940 (stretching), 1462 (bending vibration), and 1342 cm^{-1} (bending vibration). Moreover, a characteristic NCO peak can be observed at 2270 cm^{-1}. This peak was presented by Hong and Park.[1]

FTIR spectra of polyurea microcapsules prepared from HMDI isocyanurate are shown in Figure 3(c). Absorption peaks appearing from polyurea bonds
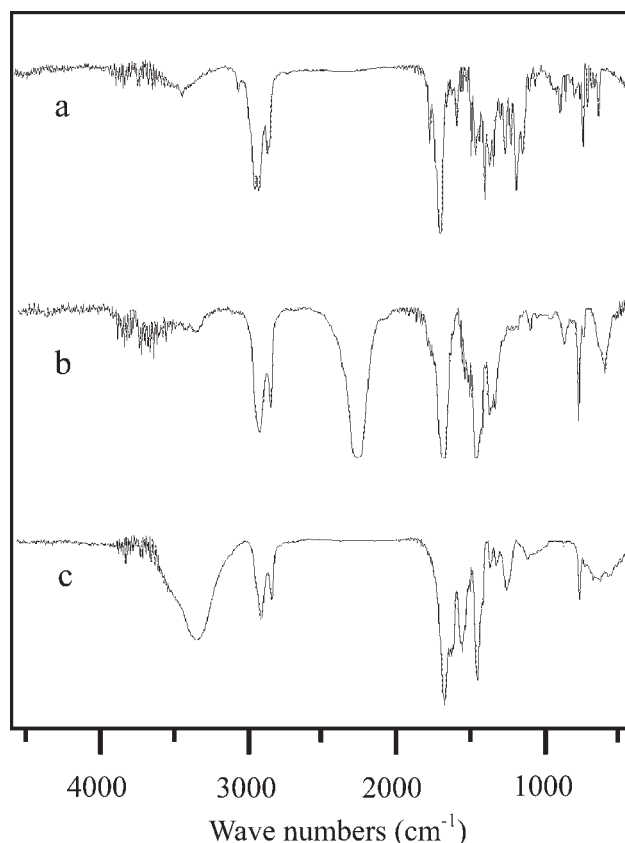

Figure 3 FTIR spectra of (a) the core material, (b) HMDI isocyanurate as the wall-forming material, and (c) polyurea microcapsules synthesized at C_i = 10.0 wt %.
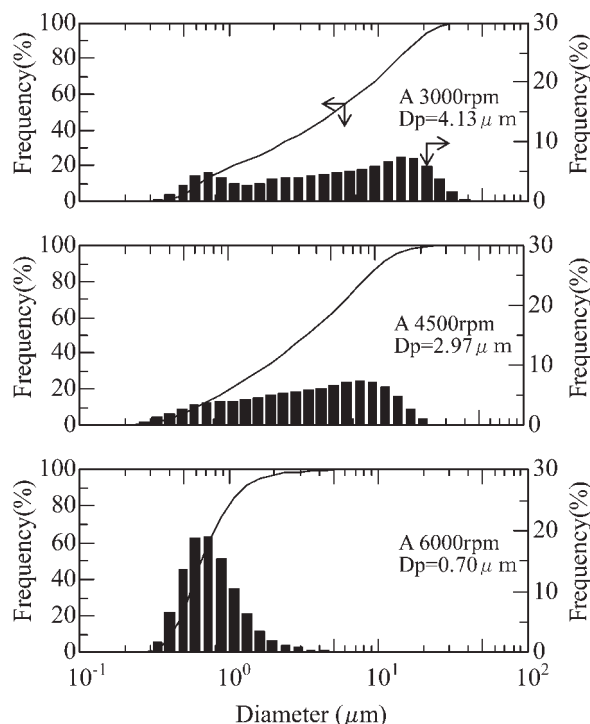
Figure 4 Size distributions and mean sizes of microcapsules prepared under condition A (C_i = 2.5 wt %).

can be observed at 3340 (urea N—H, stretching), 1646 (amide I, urea C=O, stretching), 1563 (amide II, urea N—H, bending), and 1262 cm^{-1} (amide III,

urea C—N, N—H, C=O). By the reaction between HMDI isocyanurate and EDA, the NCO peak at 2270 cm^{-1} disappears. From these results, we can conclude that polyurea microcapsules were prepared in this study.

Particle size distributions and mean sizes

The size distributions and mean sizes of the polyurea microcapsules prepared under conditions A, B, and C are shown in Figures 4–6. From these results, no remarkable effects due to the concentration of HMDI isocyanurate are observed. Moreover, the size distribution at 3000 rpm is in the range of 0.3–46.0 μm, whereas that at 6000 rpm is in the range of 0.4–14.0 μm. As the emulsification speed increases, the size distributions become narrower. In other words, microcapsules with a polydisperse size distribution are prepared at 3000 and 4500 rpm, whereas microcapsules with a monodisperse size distribution are prepared at 6000 rpm. Moreover, the mean sizes at 3000 and 6000 rpm are 3.58 and 0.77 μm, respectively.

In comparison with the results for microcapsules prepared with the monomer and the mixture of the dimer and trimer, as shown in Figure 7, the mean diameters and size distributions are larger and broader.
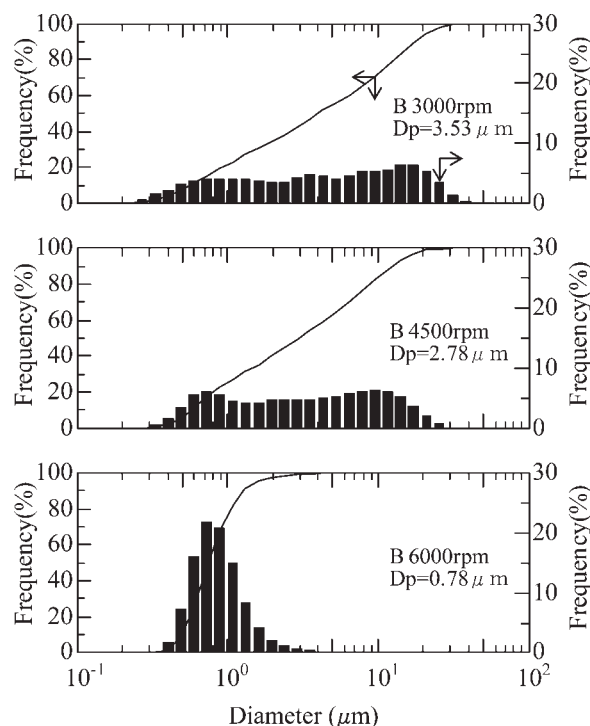

Figure 5 Size distributions and mean sizes of microcapsules prepared under condition B (C_i = 5.0 wt %).
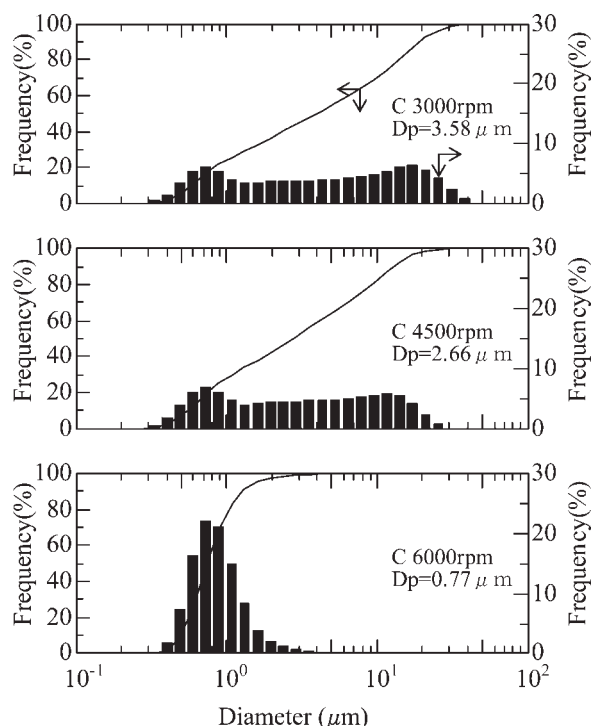

Figure 6 Size distributions and mean sizes of microcapsules prepared under condition C (C_i = 10.0 wt %).
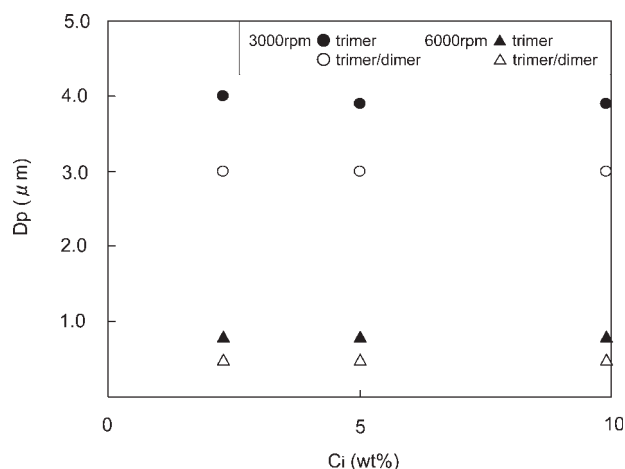
Figure 7 Dependence of mean sizes on the concentration of HMDI isocyanurate.

Microcapsule yield

Table III shows the measured values of the microcapsule yield. The microcapsule yields are in the range of 94–98%. This result should mean that the O/W emulsion is very stable and that the microencapsulation process proceeded satisfactorily under the experimental conditions adopted here. This seems to be due to the slower reaction between HMDI isocyanurate and EDA.

Observations of microcapsules

SEM photographs of cross sections of microcapsules prepared at 6000 rpm are shown in Figure 8. The microcapsules are spherical and single-cored. Furthermore, it can be clearly observed that the wall thickness is getting thicker as the concentration of HMDI isocyanurate increases from $C_i = 2.5$ wt % to $C_i = 10$ wt %.
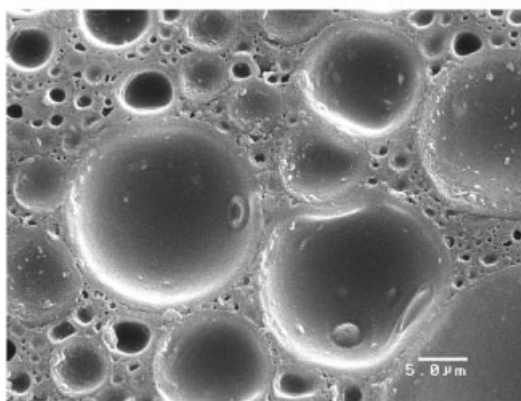
Photographs of the dried polyurea microcapsules prepared at 6000 rpm are shown in Figure 9. In the case of $C_i = 2.5$ wt %, polyurea microcapsules with a clear wall are prepared, whereas polyurea microcapsules with an opaque, white wall are prepared in

TABLE III
Microcapsule Yield

Sample		Theoretical content (%)	Microcapsule yield (%)
A ($C_i = 2.5\%$)	3000 rpm	22.88	95.3
	4500 rpm		98.8
	6000 rpm		95.7
B ($C_i = 5.0\%$)	3000 rpm	25.75	94.0
	4500 rpm		95.5
	6000 rpm		96.7
C ($C_i = 10\%$)	3000 rpm	31.50	95.2
	4500 rpm		95.2
	6000 rpm		96.5

the cases of $C_i = 5.0$ wt % and $C_i = 10$ wt %. From these results, it is concluded that microcapsules with the transparent wall are prepared in the case of $C_i = 2.5$ wt % because the insecticide is covered by the relatively thin wall. On the other hand, microcapsules with the transparent wall are not formed in the case of $C_i = 5.0$ and 10.0 wt %.

(A) C_i=2.5wt%
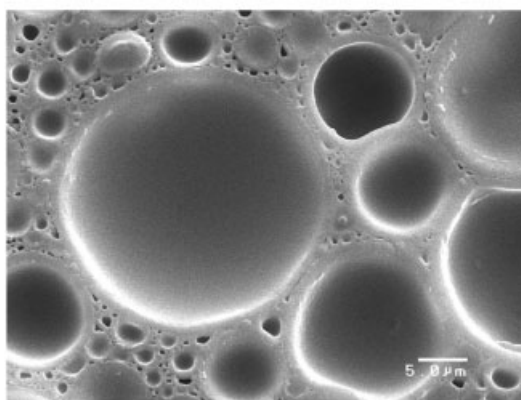
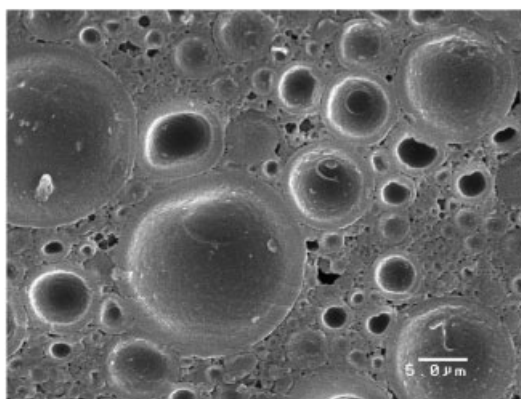**(B) C_i=5.0wt%**

(C) C_i=10.0wt%

Figure 8 SEM photographs of cross sections of polyurea microcapsules.
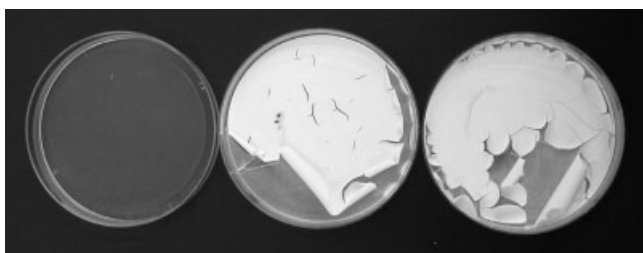
Figure 9 Photograph of dried polyurea microcapsules prepared at 6000 rpm (left, $C_i = 2.5$ wt %; center, $C_i = 5.0$ wt %; right, $C_i = 10$ wt %).

Wall thickness

To investigate the wall thickness in detail, the relationships between the microcapsule size (D_p) and the ratio of the wall thickness to the microcapsule size (W/D_p) for microcapsules prepared at 3000 and 6000 rpm are shown in Figures 10 and 11.

In Figure 10, the values of W/D_p decrease from 0.20 to 0.03 at $C_i = 2.5$ wt %, from 0.20 to 0.04 at $C_i = 5.0$ wt %, and from 0.3 to 0.07 at $C_i = 10.0$ wt % with the microcapsule size.

In Figure 11, the values of W/D_p decrease from 0.13 to 0.04 at $C_i = 2.5$ wt %, from 0.22 to 0.05 at $C_i = 5.0$ wt %, and from 0.24 to 0.07 at $C_i = 10.0$ wt % with the microcapsule size. Comparing the curves of W/D_p for $C_i = 2.5$ wt %, $C_i = 5.0$ wt %, and $C_i = 10.0$ wt %, we find that the wall thickness is getting thicker as the concentration of HMDI isocyanurate increases from $C_i = 2.5$ wt % to $C_i = 10$ wt %. As the microcapsule size increases, the value of W/D_p decreases considerably in the smaller size region and comes up to a certain constant value.
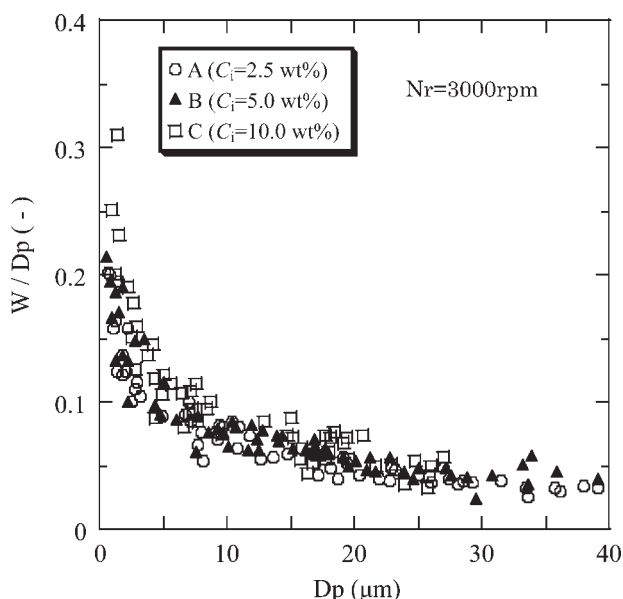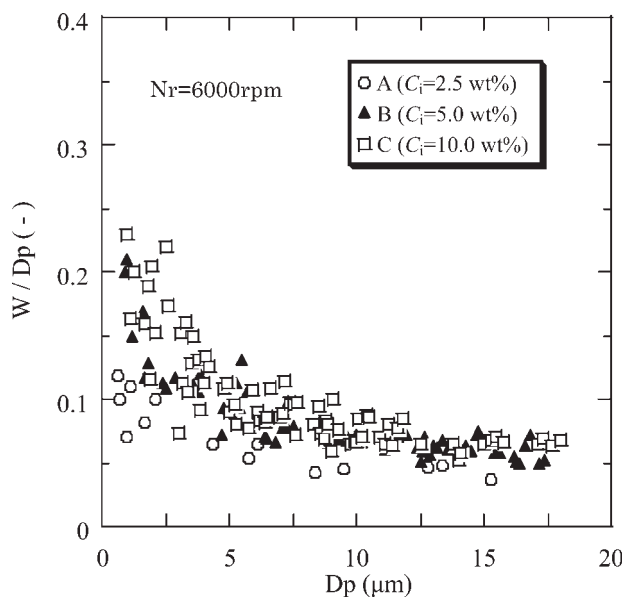

Figure 11 Relationship of D_p and W/D_p. The emulsification speed was 6000 rpm.

This result may be attributable to the fact that the final wall thickness depends on the total amount of isocyanate in the microcapsule.[3,7,8] In the smaller size region ($D_p < 5$ μm), the rate of increase in the wall thickness is nearly equal to that in the concentration of HMDI isocyanurate. That is, at the same microcapsule size, the wall thickness about doubles according to the double increase in the concentration. However, in the larger size region ($D_p > 5$ μm), the wall thickness does not increase according to the rate of increase in the concentration. This result may be considered as follows. Because the larger the microcapsule size is, the thicker the wall thickness
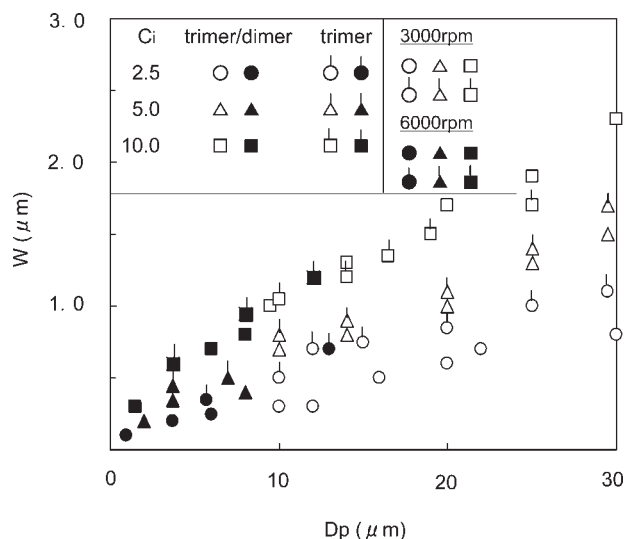

Figure 10 Relationship of D_p and W/D_p. The emulsification speed was 3000 rpm.

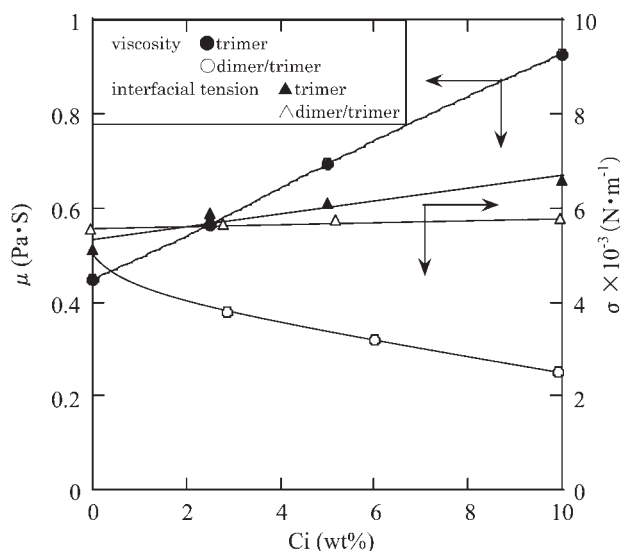**Figure 12** Dependence of the wall thickness (W) on the droplet size (D_p).

Figure 13 Dependence of the viscosity (μ) and interfacial tension (σ) on the concentrations of HMDI isocyanurate and HMDI uretidione/isocyanurate (C_i).

is,[3,4] the mass-transfer resistance of EDA in the polymer wall may become low in the smaller size region and limiting in the larger size region, respectively. For this reason, the values of W/D_p become constant in the larger size region. Figure 12 shows a comparison of the dependence of the wall thickness on the droplet size for microcapsules prepared with the trimer and the mixture of the trimer and dimer. The wall thickness for microcapsules prepared with the trimer is thicker than that for microcapsules prepared with the mixture of the trimer and dimmer at each revolution speed.

In general, it is well known that the size distributions of microcapsules prepared by interfacial polycondensation are almost the same as those of the core droplets in the O/W dispersion. The sizes of dispersed droplets depend strongly on the physical properties of the liquids concerned. As shown in Figure 13, the viscosity and interfacial tension at C_i = 0 equal the viscosity of the insecticide and the interfacial tension between the insecticide and the continuous phase, respectively. The interfacial tension is almost constant (6.0×10^{-3} N/m), regardless of the concentration of HMDI isocyanurate.

On the other hand, the viscosity of the dispersed phase increases according to the increase in the concentration of HMDI isocyanurate. As the increase in the viscosity due to the concentration is relatively large, the viscous force to break up a droplet becomes larger.[9] As a result, the size distribution

and mean sizes of microcapsules prepared with HMDI isocyanurate become broader and larger. However, as the disruptive force at 3000 rpm is not equal to that at 6000 rpm, the curves of W/D_p in Figure 10 may not correspond to those in Figure 11.

CONCLUSIONS

Polyurea microcapsules containing a pyrethroid insecticide were prepared by the reaction between HMDI isocyanurate and EDA in an O/W emulsion. This study was performed to establish the operational conditions of preparing microcapsules by interfacial polymerization and to investigate how the operational conditions affected the characteristics of microcapsules, such as the morphology, wall thickness, mean diameter, and particle size distribution.

Microcapsules prepared in this study were found to be spherical and single-cored. All the microcapsule yields obtained ranged from 94 to 98% and agreed with the theoretical values. The size distribution of the microcapsules at 3000 rpm was in the range of 0.3–46.0 μm, whereas that at 6000 rpm was in the range of 0.4–14.0 μm. As the revolution speed at emulsification increased, the size distributions became narrower. It was concluded that the size distribution and the mean sizes were strongly affected by the viscosity of HMDI isocyanurate and the revolution speed at emulsification.

The wall thickness of microcapsules increased with the diameter of the microcapsules and the concentration of HMDI isocyanurate. It may be necessary to investigate how the size, wall thickness, and wall transparency of the microcapsules prepared in this study affect the release property of the core material.

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