

Shell Thickness and Chemical Structure of Polyurea Microcapsules Prepared with Hexamethylene Diisocyanate Uretidione and Isocyanurate

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ABSTRACT: To investigate the dependence of the shell thickness on both the microcapsule size and the concentration of hexamethylene diisocyanate (HMDI) and to analyze the chemical structure of the polyurea shell, polyurea microcapsules were prepared by using the reaction between HMDI uretidione/isocyanurate and ethylene diamine (EDA) in an oil-in-water emulsion. In the experiment, the concentrations of hexamethylene diisocyanate and EDA were changed. The shell thickness was correlated well with the mean size and the concentration of HMDI on the surface area per unit volume of microcapsule. From the solid-state ¹³C NMR spectroscopy analysis, the uretidione and isocyanurate ring structures were

found to be not changed before and after the reaction. From the wide-angle X-ray diffraction analysis, it was suggested that the chemical structure of the polyurea shell was amorphous. From the FTIR spectra analysis, it could be concluded that polyurea microcapsules were prepared by the reaction between HMDI uretidione/isocyanurate and EDA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3786–3791, 2007

Key words: microencapsulation; hexamethylene diisocyanate (HMDI); uretidione; isocyanurate; nuclear magnetic resonance; wide-angle X-ray diffraction; Fourier transform infrared spectrometer

INTRODUCTION

Various microencapsulation techniques have been used to obtain fine particles with a controlled release property in many industrial fields such as textiles, agricultural chemicals, cosmetics, food, medicines.^{1,2} Especially, polyurea and polyurethane microcapsules have been extensively investigated in various application.^{3–9}

Among them, the aliphatic hexamethylene diisocyanate (HMDI) monomer and aliphatic ethylene diamine (EDA) have been used most frequently to prepare polyurea microcapsules.

We prepared polyurea microcapsules using the mixture of HMDI uretidione of dimer and HMDI isocyanurate of trimer, to prepare the mechanically stronger microcapsules.¹⁰

The many important findings such as size distributions, microcapsule yield, and mechanical strength were able to be obtained.

The chemical structure of polyurea shell as well as the size and the shell thickness of microcapsules may influence the properties of microcapsule such as mechanical strength, thermal stability, and release rate of core material.

Many studies on the chemical structure of polyurea microcapsules prepared with HMDI monomer have been reported.

The chemical structures have been investigated by FTIR spectrometer measurement.^{3–7,11,12} The crystal structure was investigated by the wide-angle X-ray diffraction (WAXD) measurement.^{4,6}

However, little is known about the chemical structures of polyurea microcapsules prepared with HMDI uretidione and isocyanurate.

Here, it may be expected that the solid-state ¹³C NMR spectroscopy measurement is also effective in investigating the chemical structures as well as FTIR spectrometer measurement.

The purpose of this study is to investigate the dependence of the shell thickness on both the microcapsule size and the concentration of HMDI and to analyze the chemical structures of polyurea microcapsules prepared with HMDI uretidione/isocyanurate by the solid-state ¹³C NMR spectroscopy, FTIR spectrometer, and WAXD.

EXPERIMENTAL

Materials

The mixture of HMDI uretidione and HMDI isocyanurate (Desmodur N3400) was purchased from Sumika Bayer Urethane, Japan. Figure 1 shows the chemical

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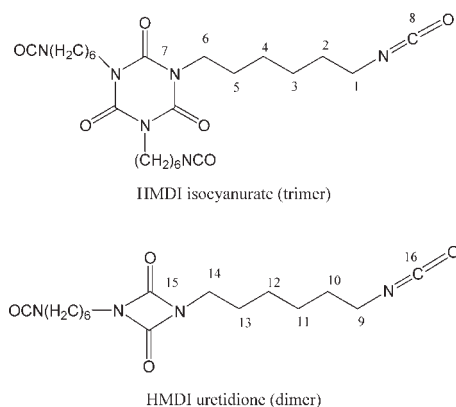


Figure 1 Chemical structures of HMDI uretidione and HMDI isocyanurate.

structures of HMDI uretidione and isocyanurate. Insecticide (ANINSEN PER-30) containing 30 wt % of permethrin as core material and polyvinyl alcohol (polymerization degree = 500) as stabilizer were purchased from Daiwa Chemical Industry, Japan. EDA was purchased from Toso, Japan. These chemical species were used as received.

Preparation of microcapsules

Polyurea microcapsules containing insecticide as core material were prepared according to the previous work.¹⁰ The experimental conditions are shown in Table I.

Other conditions were the same as the previous work.

In the experiment, the concentration (C_i) of HMDI uretidione/isocyanurate was mainly changed together with that of EDA.

Size distribution and mean size of microcapsules

The size distribution and mean size (D_p) of microcapsules were measured by the particle size analyzer (SALD-3000; Shimadzu, Japan).

Observations of microcapsules

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

WAXD measurement

The WAXD measurement was performed by the RIGAKU RU-200 (Rigaku, Japan) system, in which Cu $K\alpha$ radiation ($\lambda = 0.1541$ nm) was used as the source. The WAXD patterns of microcapsule shell were recorded at 25°C in the range $2\theta = 15\text{--}35^\circ$ at a scan speed $2^\circ/\text{min}$.

Nuclear magnetic resonance analysis

Solution nuclear magnetic resonance (solution ^1H NMR and ^{13}C NMR) spectra of HMDI and core materials were recorded on BRUKER AVANCE DSX300WB (300 MHz for ^1H , 76 MHz for ^{13}C) NMR spectrometer (Bruker BioSpin, Japan) using tetramethylsilane as an internal reference and CDCl_3 as the solvent. To determine the chemical structure of polyurea shell, solid-state ^{13}C NMR spectra were measured by BRUKER AVANCE DSX300WB (76 MHz) NMR spectrometer using tetramethylsilane as an internal reference. The sample was put in a cylindrical rotor and spun at 5 kHz. The contact time was 2 ms and the repetition time was 5 s. The spectral width and data points were 30 kHz and 64 k, respectively.

Fourier transform infrared spectrometer analysis

Infrared spectra of core material and polyurea shell were obtained by Fourier transform infrared spectrometer (FTIR 300E; Shimadzu, Japan).

RESULTS AND DISCUSSION

Shell thickness of microcapsules

Figure 2 shows the SEM photographs of the surface (a) and the cross section (b) of microcapsules. It is

TABLE I
Experimental Conditions

Condition A	
Aninsen PER-30	20.0 wt % (100 g)
HMDI uretidione/isocyanurate	2.5 wt % (12.5 g)
Uretidione	0.027 mol
Isocyanurate	0.007 mol
Ethylene diamine	0.5 wt % (0.042 mol)
Distilled water	28.5 wt %
Condition B	
Aninsen PER-30	20.0 wt % (100 g)
HMDI uretidione/isocyanurate	5.0 wt % (25 g)
Uretidione	0.053 mol
Isocyanurate	0.014 mol
Ethylene diamine	1.0 wt % (0.083 mol)
Distilled water	25.5 wt %
Condition C	
Aninsen PER-30	20.0 wt % (100 g)
HMDI uretidione/isocyanurate	10 wt % (50 g)
Uretidione	0.107 mol
Isocyanurate	0.028 mol
Ethylene diamine	2.0 wt % (0.167 mol)
Distilled water	19.5 wt %
Condition D	
HMDI uretidione/isocyanurate	10 wt % (50 g)
Uretidione	0.107 mol
Isocyanurate	0.028 mol
Ethylene diamine	2.0 wt % (0.167 mol)
Distilled water	19.5 wt %

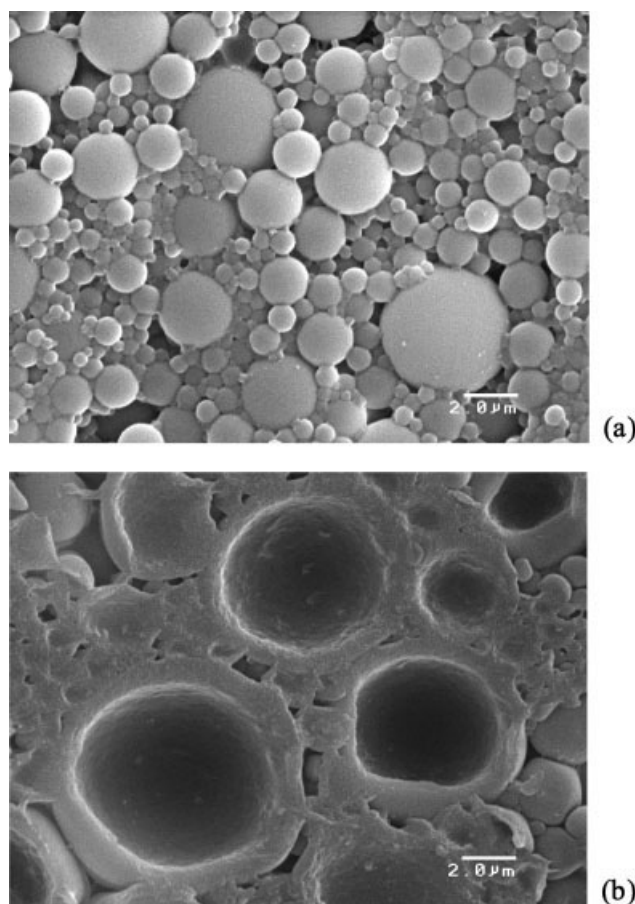


Figure 2 SEM photographs of surface (a) and cross section (b) of polyurea microcapsules.

found that microcapsules prepared in this study are spherical and the mono core type.

The relationship among the microcapsule size (D_p), the shell thickness (W), and the concentration of (C_i) HMDI is shown in Figure 3. It is observed that the shell thickness (W) is getting thicker with an increase in the concentration of HMDI and the microcapsule size. These results are the same as those in the previous works.^{8,9} From this figure, it is found that the shell thickness is proportional to $D_p^{0.87}$ at each concentration of HMDI uretidione/isocyanurate.

To investigate the dependence of the shell thickness on the concentration of HMDI in detail, the concentration of HMDI in the dispersion phase was recalculated as the concentration (C_s) on the surface area per unit volume of microcapsule using the mean microcapsule size and the concentration of HMDI.

Figure 4 shows the dependence of the shell thickness on the concentration of HMDI (C_s) on the surface area per unit volume of microcapsule. From this figure, it is found that the shell thickness is proportional to $C_s^{0.58}$.

Accordingly, the following expression relating the shell thickness with the mean size and the concentra-

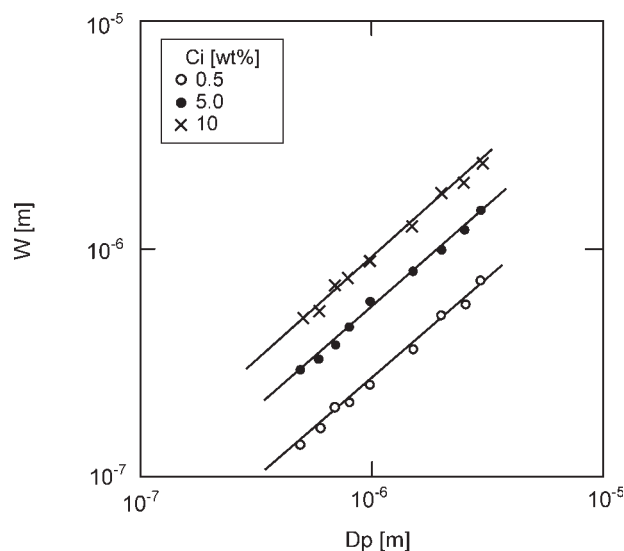


Figure 3 Dependence of the shell thickness on the mean size.

tion of HMDI on the surface area per unit volume of microcapsule is able to be derived.

$$W \sim D_p^{0.87} C_s^{0.58} \quad (1)$$

WAXD measurement

Figure 5 shows the WAXD pattern of polyurea microcapsules without the core material prepared at the experimental condition (D) in Table I.

As characteristic peaks for the crystalline region are not observed in this X-ray diffraction pattern, it is easy to understand that polyurea shell is an amorphous structure. The thermal property of polyurea shell was measured with the differential scanning calorimetry to confirm the melting behavior of crystalline region.

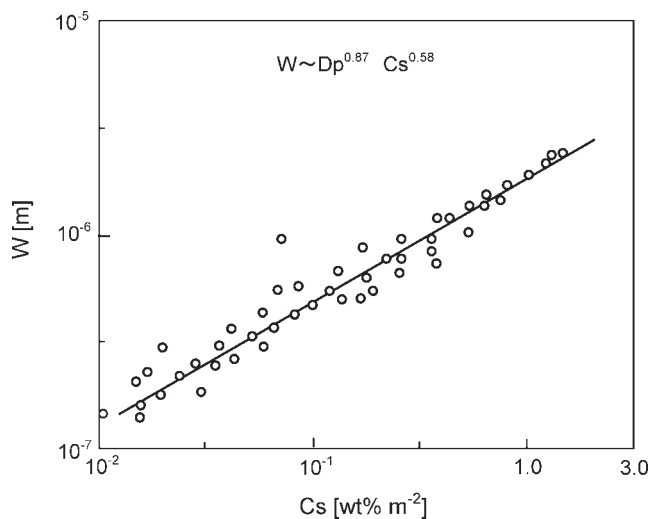


Figure 4 Dependence of the shell thickness on the concentration of HMDI.

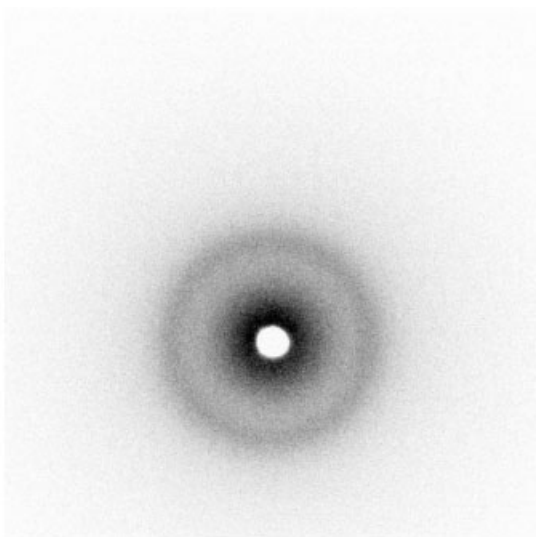


Figure 5 The wide-angle X-ray diffraction pattern of polyurea microcapsule without core material.

As no endothermal peaks due to melting behavior were observed and the crosslink structures are thought to be formed in the polyurea chains, it may be reasonable to suggest that the shell structure is amorphous.

Yadav et al.² reported that polyurea microcapsules containing cyclohexane were synthesized by the reaction between HMDI monomer and 1,6-hexamethylene diamine and the degree of crystallinity of microcapsule shell was in the range of 21–33%. In this case it is suggested that the linear structure is formed in the polyurea chains. Therefore, it is considered that the crystal structures of polyurea microcapsule shell are strongly affected by the structures of isocyanate and amine molecules. Taking these results into consideration, it is suggested that the shell structure of polyurea microcapsules prepared in this study is amorphous, because the uretidione and isocyanurate ring structures prevent the crystallization of polyurea polymer.

Solution ¹H NMR and solution ¹³C NMR

The ¹H chemical shifts of the mixture of HMDI uretidione and HMDI isocyanurate are listed in Table II.

TABLE II
¹H Chemical Shifts for the Mixture of HMDI Uretidione and HMDI Isocyanurate

Proton species	Chemical shift (ppm)	Relative intensity
H3, H4 (trimer)	1.30	13.83
H11, H12 (dimer)	1.30	
H2, H5 (trimer)	1.60	2.52
H10, H13 (dimer)	1.60	
H14 (dimer)	3.15	3.14
H1 (trimer)	3.25	
H9 (dimer)	3.25	1.00
H6 (trimer)	3.80	

TABLE III
¹³C Chemical Shifts for the Mixture of HMDI Uretidione and HMDI Isocyanurate

Carbon species	Chemical shift (ppm)
C3, C4, C11, C12 (trimer, dimer)	26.30, 26.46
C5 (trimer)	27.90
C13 (dimer)	28.83
C10 (dimer)	31.38
C2 (trimer)	31.44
C14 (dimer)	40.63
C6, C9 (trimer, dimer)	43.18
C1 (trimer)	43.21
C8, C16 (trimer, dimer)	122.29
C7 (trimer)	149.33
C15 (dimer)	158.17

The peak assignments are shown in Figure 1. For example, H1 stands for the hydrogen atoms of position 1 in Figure 1. The chemical shifts at 1.3, 1.6, 3.1, 3.2, and 3.8 ppm are assigned to proton resonances of (H3+H4) + (H11+H12), (H2+H5) + (H10+H13), H14, (H1+H9), and H6, respectively. From relative peak intensities of H6 and H14, the mole ratio of HMDI uretidione to HMDI isocyanurate in the mixture is determined to be 3.8:1.0.

The ¹³C chemical shifts of the mixture of HMDI uretidione and HMDI isocyanurate are listed in Table III. The peak assignments are shown in Figure 1. For example, C1 stands for the carbon atom of position 1 in Figure 1. Carbon resonances are observed as follows: (C3+C4) + (C11+C12) at 26.30–26.46 ppm, C5 at 27.90 ppm, C13 at 28.83 ppm, C10 at 31.38 ppm, C2 at 31.44 ppm, C14 at 40.63 ppm, (C6+C9) at 43.18 ppm, C1 at 43.21 ppm, (C8+C16) at 122.29 ppm, C7 at 149.33 ppm, and C15 at 158.17 ppm, respectively.

Solid-state ¹³C NMR spectra

Figure 6 shows the 76 MHz solution ¹³C NMR spectra of core material and 76 MHz solid-state ¹³C NMR spectra of polyurea microcapsules. The expanded spectra of carbonyl carbon resonances (140–170 ppm) are shown in Figure 7. The expanded spectra of methylene carbon resonances (0–60 ppm) are shown in Figure 8. In the spectra of microcapsules without core, carbon resonances at 150, 159, and 160 ppm are observed. The carbon resonances at 150 and 159 ppm are assigned to the carbonyl resonances of HMDI isocyanurate (C7; >NCON<) and HMDI uretidione (C15; >NCON<) ring, respectively, because each chemical shift corresponds to the result of solution ¹³C NMR spectra. The mole ratio calculated from peak intensities at 150 and 159 ppm is very close to the mole ratio of HMDI uretidione to HMDI isocyanurate

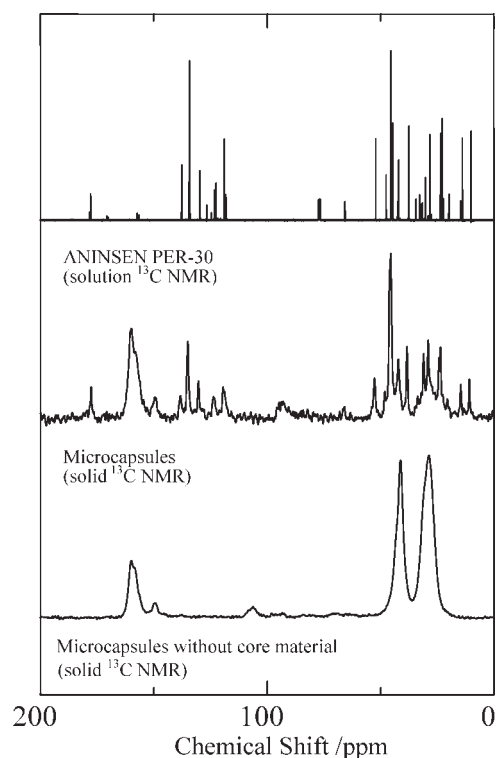


Figure 6 The solution ^{13}C NMR spectra of the core material and the solid-state ^{13}C NMR spectra of polyurea microcapsules.

in the mixture used as the wall-forming material. The carbon resonance at 160 ppm is assigned to the carbonyl resonance of polyurea bond (NHCONH).

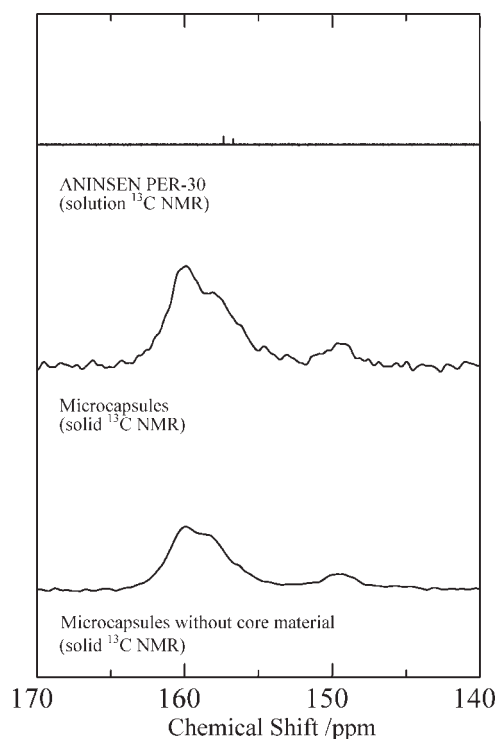


Figure 7 The expanded spectra of carbonyl carbon resonances of polyurea microcapsules.

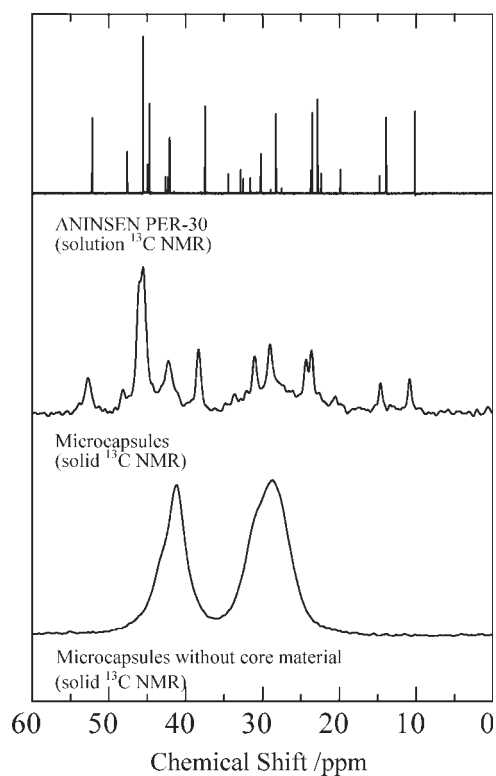


Figure 8 The expanded spectra of methylene carbon resonances of polyurea microcapsules.

In the spectra of polyurea microcapsules, it can be seen that the chemical shifts correspond to spectra of polyurea microcapsules without core. From this result, it may be reasonable to consider that the ring structures between uretidione and isocyanurate are formed even after the reaction. Besides this, the broad peaks corresponding to the chemical shifts of core material are also observed in the spectra. In general, core material of liquid as in this study is not suitable for the solid-state ^{13}C NMR measurement, because chemical shifts are not observed in the spectra. However, the reason why chemical shifts of core material appear in the solid-state ^{13}C NMR spectra is that the fluidity of core material is limited by the narrow space in a microcapsule. In other words, it is considered that liquid core material could not flow at the narrow space in a microcapsule. The solid-state ^{13}C NMR measurement is found to be very effective to analyze the structure of polyurea microcapsules prepared in this study.

FTIR spectra

Figure 9 shows FTIR spectra of the core material (a), the mixture of HMDI uretidione and HMDI isocyanurate as the wall-forming material (b), and polyurea microcapsules synthesized at $C_i = 10.0$ wt % (c).

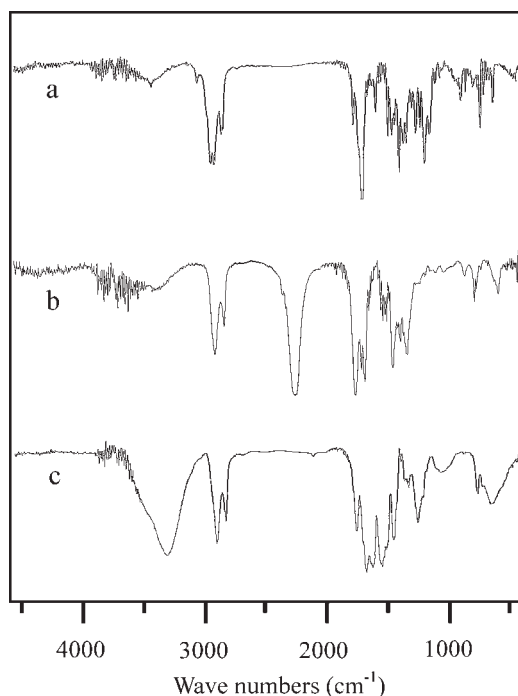


Figure 9 FTIR spectra of the core material (a), the mixture of HMDI uretidione and HMDI isocyanurate as the wall-forming material (b), and polyurea microcapsules synthesized at $C_i = 10.0$ wt % (c).

In Figure 9(b), absorption peaks of HMDI uretidione and HMDI isocyanurate carbonyl group are observed at 1768 cm^{-1} (uretidione, $>\text{NCON}<$, stretch) and 1687 cm^{-1} (isocyanurate, $>\text{NCON}<$, stretch), respectively. C—H stretching and bending vibrations in the aliphatic methylene group are observed at $2852\text{--}2936\text{ cm}^{-1}$ (stretching), 1460 cm^{-1} (bending vibration), and 1342 cm^{-1} (bending vibration). Moreover, characteristic NCO peak is observed at 2272 cm^{-1} .⁴

Absorption peaks appearing from polyurea bonds are observed at 3344 cm^{-1} (urea N—H, stretch), 1648 cm^{-1} (amide II, urea C=O, stretch), 1561 cm^{-1} (amide II, urea N—H, bending), and 1263 cm^{-1} (amide III, urea C—N, N—H, C=O). By the reaction between the mixture of HMDI uretidione and HMDI isocyanurate and EDA, NCO peak at 2272 cm^{-1} disappears. From these

results, it can be concluded that polyurea microcapsules are prepared in this study.

CONCLUSIONS

The dependence of the shell thickness on the mean size and the concentration of HMDI on the surface area per unit volume of microcapsule was expressed as follows:

$$W \sim D_p^{0.87} C_s^{0.58}$$

From solid-state ^{13}C NMR spectra of polyurea microcapsules, it was concluded that polyurea microcapsules were prepared and the ring structures between uretidione and isocyanurate were not changed after the reaction.

From the WAXD measurement, it was suggested that shell structure of polyurea microcapsules prepared from the mixture of HMDI uretidione and HMDI isocyanurate was amorphous.

From FTIR spectra of polyurea microcapsules, it was found that polyurea microcapsules were prepared by the reaction between HMDI uretidione and HMDI isocyanurate and EDA.

References

- Gao, Y.; Shen, P.; Wang, B.; Lu, S.; Huang, G.; Ho, L. *J Microencapsul* 1984, 1, 307.
- Yadav, S. K.; Khilar, K. C.; Suresh, A. K. *J Membr Sci* 1997, 125, 213.
- Hong, K.; Park, S. *Mater Res Bull* 1999, 34, 963.
- Hong, K.; Park, S. *Mater Chem Phys* 2000, 64, 20.
- Ohtsubo, T.; Tsuda, S.; Tsuji, K. *Polymer* 1991, 32, 2395.
- Kawada, H.; Ogawa, M.; Ito, I.; Abe, Y.; Tsuji, K. *J Am Mosq Control Assoc* 1994, 10, 385.
- Hirech, K.; Payan, S.; Carnelle, G.; Brujes, L.; Legrand, J. *Powder Technol* 2003, 130, 324.
- Kubo, M.; Harada, Y.; Kawakatu, T.; Yonemoto, T. *J Chem Eng Jpn* 2001, 34, 1506.
- Mizuno, K.; Taguchi, Y.; Tanaka, M. *J Chem Eng Jpn* 2005, 38, 45.
- Takahashi, T.; Taguchi, Y.; Tanaka, M. *J Chem Eng Jpn* 2005, 38, 929.
- Komoto, T.; Matsuda, H.; Imai, K.; Hirata, A.; Mori, S.; Yamano, T. *Polym J* 1996, 28, 177.
- Yamanobe, T.; Naito, Y.; Komoto, T. *J Mol Struct* 2002, 1, 437.