Polyurea Microcapsules with Different Structures: Preparation and Properties

K. HONG, S. PARK

Department of Textile Engineering, Faculty of Applied Chemical Engineering, Pusan National University, #30 Changeon-dong, Kumjeong-ku, Pusan 609-735, Republic of Korea

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ABSTRACT: Polyurea microcapsules were formed by carrying out an interfacial polycondensation reaction in emulsion globules between various diisocyanates and ethylenediamine to investigate the effects of the chemical structure on various characteristics. FTIR showed that very reactive aromatic 2,4-toulene diisocyanate produced many more hydrogen-bonded N—H groups than did other aliphatic diisocyanates. All the microcapsules in this study had prominent thermal stabilities from the results of DSC and TG. It was evident that both the molecular weight and the reactivity of diisocyanates determined the mean diameter and particle-size distribution at the same time.
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Key words: polyurea; microcapsules; FTIR; thermal properties; particle-size distribution

INTRODUCTION

The concept of entrapping materials within a polymeric coating is commonly called microencapsulation. Much of the technology in the area derives from the "carbonless" paper work at NCR in which the release of pigment occurred when the microcapsules were broken by pressure. Entrapment can control the release of active ingredients, sustain the effectiveness of such ingredients, permit liquids to be handled as solids, protect reactive components until time of use, allow the safe handling of toxic materials, extend the shelf life of delicate materials, and overcome product incompatibilities.[1]

Polyurea microcapsules are completely insoluble in water and other common solvents and can incorporate both hydrophobic and hydrophilic active materials. We studied the microencapsulation of fragrant materials with various polymer matrices.[2–4] Fragrance, as a core material, can be released from the microcapsules by diffusing through the wall. The release rate of the functional material from the microcapsules can be controlled by the chemical structure of the capsule wall, its thickness, and the particle size of the microcapsules.[5] Especially, the chemical structure of the monomer in the encapsulation by interfacial polycondensation is one of the important parameters determining the physical properties of the microcapsules. In the present study, the effect of the chemical structure on the physical properties of polyurea microcapsules was investigated by varying the type of monomeric diisocyanates.

EXPERIMENTAL

Materials

Hydrogenated biphenyl methane diisocyanate (H_{12}MDI, M_w = 262.4), isophorone diisocyanate

Correspondence to: S. Park (soominpark@hyowon.cc.pusan. ac.kr).

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(IPDI, M_w = 224), and 2,4-toluene diisocyanate (TDI, M_w = 174) from Merck were used after being dried in a vacuum oven for 3 h. Poly(vinyl alcohol) (PVA, M_w = 1,500; Junsei Chemicals Co. Ltd., Japan) and fragrant migrin oil (Seil Perfume Co. Ltd., Pusan, Korea) were used without any further purification. All the chemicals purchased were reagent grade.

Preparation

Polyurea microcapsules were formed in the present study by carrying out an interfacial polycondensation reaction in emulsion globules between the various diisocyanates and ethylenediamine (EDA). An organic phase with 0.5*M* of the various diisocyanates as wall-forming material and migrin oil as the core substance with the same weight percent as that of the diisocyanates was prepared. The o/w emulsion was formed by adding the organic solution into the aqueous solution of 1.0 wt % PVA as a protective colloidal agent and by stirring vigorously at ambient temperature. EDA, 0.5*M*, in 200 mL of 0.5 wt % PVA was added into the o/w emulsion after stirring for 10 min to prevent an agglomeration among the resultant emulsion globules. Reaction for more than 120 min gave the formation of polyurea microcapsules containing the fragrant migrin oil. The microcapsules were decanted, filtered out, washed with 10% ethanol to remove the migrin oil on the surface, and dried in a vacuum oven at 25°C for at least 48 h.

IR spectra were obtained using a Nicolet Impact 400D Fourier transform infrared spectrometer (Seiko Co., Japan). DSC and TG measurements for the microcapsules were carried out using a DSC Mettler Model TA-3000 (Thermal Science PL-STA, USA). The samples of about 40 mg each were heated to 400°C at the rate of 10°C/min under a constant N_2 flow. The mean volume diameter and particle-size distribution were determined using a Galai CIS-1 particle sizer (Galai Production Ltd., Israel). The test with a few drops of microcapsule slurry was carried out after sonication for 3 min. Scanning electron microscopy (SEM) was performed using a JSM-5400 (JEOL Co. Ltd., Japan). Microcapsules were sprinkled onto a double-sided tape, sputter-coated with platinum, and examined under the microscope.

RESULTS AND DISCUSSION

Figure 1 shows FTIR spectra of polyurea microcapsules from the various diisocyanates: H_{12}MDI, IPDI, and TDI. All the samples prepared in these experiments have strong bands known for a hydrogen-bonded N—H stretching vibration at 3300 cm^{-1}, and a free N—H stretch at a higher frequency region of about 3600 cm^{-1} is observed. C—H stretching vibrations are shown at both 2950 and 2850 cm^{-1}. By the reaction of the diisocyanates and EDA, the NCO peak in the diisocyanates at 2270 cm^{-1} disappears and two carbonyl stretching bands are observed: a hydrogen-bonded urea carbonyl at 1676 cm^{-1} and a free urea carbonyl absorption band at 1705 cm^{-1}. From these characteristic peaks, it is evident that the polyurea microcapsules were successfully prepared. In the sample prepared from H_{12}MDI, the intensities of the C—H peak to the N—H peak and of C—H to C═O are considerably strong due to its structure with a long methylene chain. The microcapsules from aliphatic H_{12}MDI would have many more C—H groups than those from aliphatic IPDI with a difference of chemical structure. For samples from H_{12}MDI and IPDI, the intensity of hydrogenated-bonded N—H to free N—H is stronger than that from aromatic TDI, which is related to the difference of reactive activity. The very reactive aromatic TDI could produce many more hydrogen-bonded N—H groups than could the other aliphatic diisocyanates. Furthermore, polyurea microcapsules from TDI are presumed to show different thermal properties in that the intensities of the C—H peak to the N—H peak and of N—H to C═O in the sample from TDI are less than those from aliphatic H_{12}MDI and IPDI.

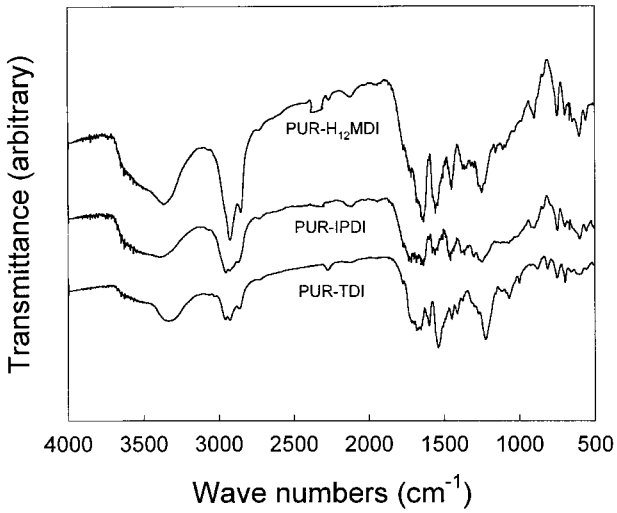

Figure 1 FTIR spectra of polyurea microcapsules from different diisocyanates.

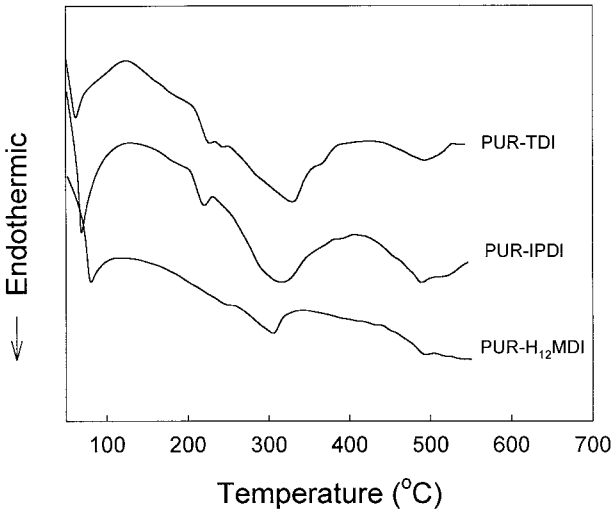

Figure 2 DSC diagrams of polyurea microcapsules from different diisocyanates.

Figure 2 shows DSC diagrams of polyurea microcapsules from the different diisocyanates. All the samples have maximum absorption peaks above 300°C, which is considered to be the melting temperature and indicating that polyurea microcapsules in this study have a prominent thermal stability. In particular, the thickness of the wall membrane from aromatic TDI may be greater than that from aliphatic H_{12}MDI and IPDI by the difference of reactive activity. Much random polymerization could proceed onto the resultant emulsion globules using TDI. Yadav et al. reported that the degree of crystallinity depended proportionally on the polymeric wall thickness in the study on poly(hexamethylene)-urea microcapsules at different preparation conditions.[6] In our studies, the microcapsules with only different diisocyanates were synthesized to determine the effect of the difference of the chemical structure on the thermal properties. Polyurea microcapsules from aromatic TDI may have rough surface morphologies, due to the abrupt reaction of TDI with EDA on the emulsion globules. As a result, the melting temperature and heat capacity of the samples increased slightly in the order H_{12}MDI, IPDI, and TDI.

Figure 3 shows TG diagrams of polyurea microcapsules from the different diisocyanates. The first weight loss is seen above 300°C for all the samples, and the magnitude of the weight loss corresponds to the result of the DSC. The release of core material in the microcapsule increases in the order TDI, IPDI, and H_{12}MDI. As shown in Figure 3, the microcapsules from aromatic TDI have the highest thermal stability among all the samples, which seems to be related to the difference of reactivity with EDA, producing various wall properties. The weight loss of the microcapsules from H_{12}MDI is greater due to many more methylene chains in it than in IPDI.

Surface morphologies of one microcapsule wall from the different diisocyanates are shown in Figure 4. As a result, the smoothness of the capsule surface increases in the order TDI, IPDI, and H_{12}MDI. In the microcapsule from TDI, it is confirmed that a rapid random reaction occurred between TDI in the organic phase and EDA in the water-soluble phase on the emulsion globules, producing a very rough wall membrane. The difference of diisocyanate reactivity induced from the chemical structure brings about the various membrane morphologies, which can significantly determine the permeability, crystallinity, and thickness of the resultant microcapsules. Figure 5 shows the surface morphologies of the samples from IPDI and H_{12}MDI to determine the relationship between the molecular weight and the particle size. Particles with a much greater diameter are prepared from H_{12}MDI with a greater molecular weight than that from IPDI, and the smoothness of the wall membranes is prominent due to its longer and more linear structure than that of IPDI.

Figure 6 shows the particle-size distribution of the samples with various structures. Mean volume diameters of the microcapsules from TDI, IPDI, and H_{12}MDI are 6.5, 5.6, and 4.6, respec-

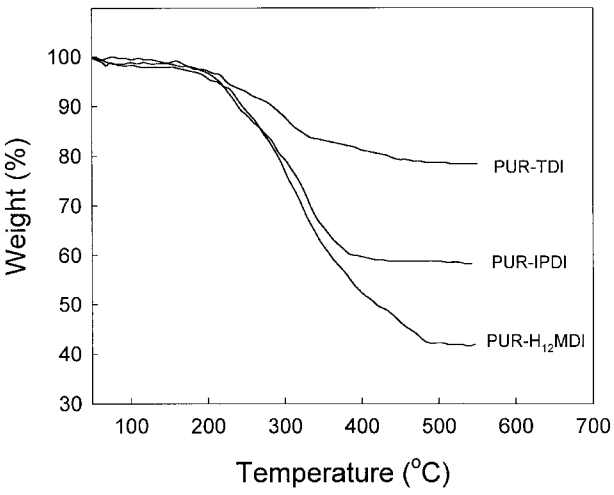

Figure 3 TG diagrams of polyurea microcapsules from different diisocyanates.

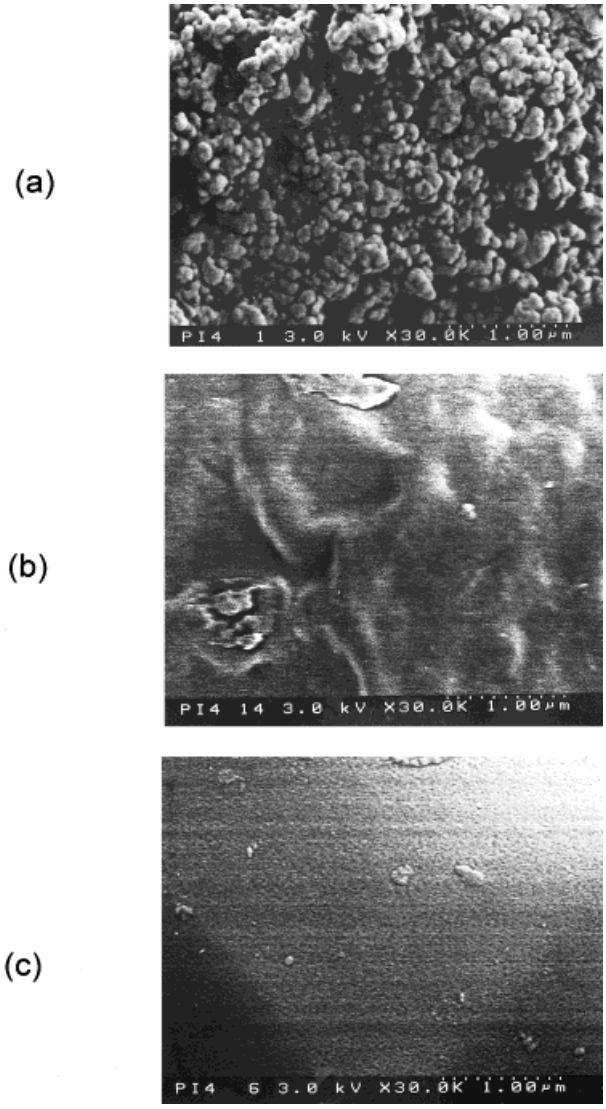

Figure 4 SEM photographs of polyurea microcapsules from different diisocyanates (30,000×): (a) TDI; (b) IPDI; (c) H_{12}MDI.

tively. The sample from H_{12}MDI has many large particles, which is due to the highest molecular weight among these diisocyanates. However, the molecular weight does not seem to influence the final diameters of the samples from TDI and IPDI even though the molecular weight of IPDI is larger than that of TDI. This indicates that both the molecular weight and the reactivity determine the mean diameter of the particles at the same time. As shown in the particle-size distribution, the differences of the chemical structure and physical properties in diisocyanates used to prepare wall membranes bring out microcapsules with various mean diameters and particle-size

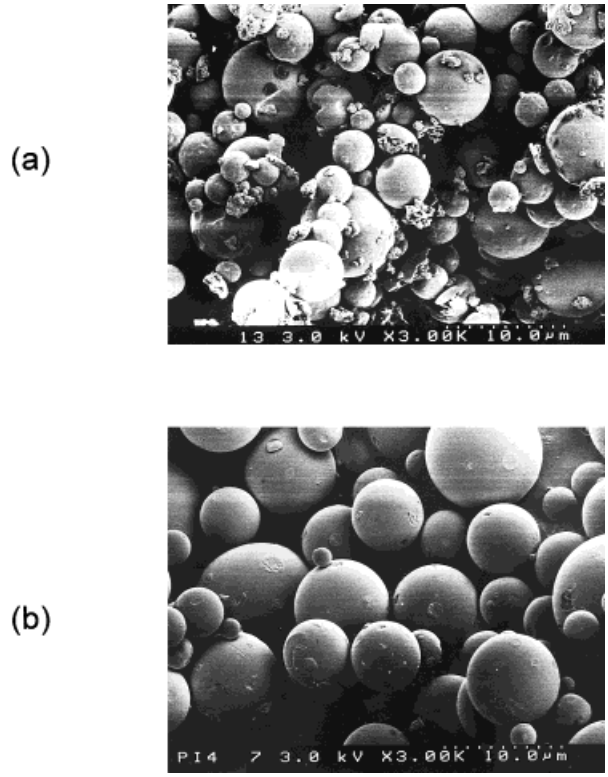

Figure 5 SEM photographs of polyurea microcapsules from different diisocyanates (3000×): (a) IPDI; (b) H_{12}MDI.

distributions. It is evident that the size distribution of microcapsules from aromatic TDI is much broader than that from aliphatic IPDI regardless of the molecular weight.

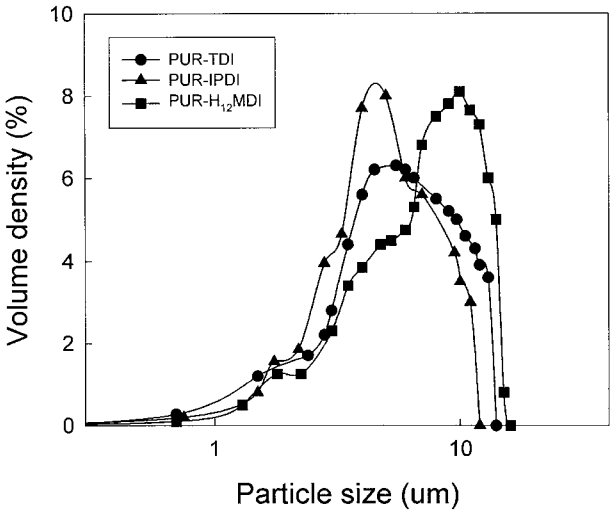

Figure 6 Particle-size distribution of polyurea microcapsules from different diisocyanates.

CONCLUSIONS

Polyurea microcapsules were formed by carrying out an interfacial polycondensation reaction in emulsion globules between various diisocyanates and EDA. For samples from H_{12}MDI and IPDI, the intensity of hydrogenated-bonded N—H to free N—H was stronger than that from aromatic TDI, which was related to the difference of reactive activity. The melting temperature and heat capacity of the samples increased slightly in the order H_{12}MDI, IPDI, and TDI by thermal analysis. Furthermore, the roughness of the capsule surface increased in the same order by the results of the SEM.

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