JOURNAL OF MATERIALS SCIENCE **34** (1999) 3161–3164

Morphologies and release behavior of polyurea microcapsules from different polyisocyanates

K. HONG, S. PARK*
Department of Textile Engineering, Pusan National University, #30, Changeon-dong, Kumjeong-ku, Pusan 609-735, Republic of Korea
E-mail: soomin@hyowon.pusan.ac.kr

Polyurea microcapsules were prepared by emulsion polymerization after adding an aqueous solution with poly(vinyl alcohol) as protective colloid into an organic solution with migrin oil as core material, 1,4-diamino anthraquinone (DAA) as penetrator, and different molar ratios of isophorone diisocyanates (IPDI) and toluene diisocyanates (TDI) as wall materials. The effects of diisocyanate types on the morphologies and release behavior of the resultant microcapsules were investigated. The transmittance (%) of the completely dissolved microcapsule in dimethyl acetamide (DMAc) by UV/visible spectrophotometer decreased with the content of aliphatic IPDI in the wall by increasing the wall thickness due to its inferior reactivity compared to aromatic TDI. Also in SEM images, these polyurea microcapsules from higher TDI content had rougher surfaces. In conclusion, the release profiles of the microcapsules in extraction solution showed that release rate of DAA depended on the roughness of the microcapsules. © *1999 Kluwer Academic Publishers*

1. Introduction

Microencapsulation is a coating technique which envelopes unstable or susceptible functional materials with polymer matrix, which protects the contents and releases a sustained amount into the environment over a long duration [1–3]. The characteristics of the microcapsule wall depend on the chemical and physical processing condition such as the type and concentration of the constituents as well as the microencapsulation methods. If the other processing conditions are the same, the characteristics of the microcapsules depend mainly on the types of wall-forming materials. Polyisocyanates used in this study are very important constituents as hard segments which result in urethane or urea groups by reaction with alcohol or amine [4–8]. These polyurethanes or polyureas have been previously studied mostly for the effects of polyols with high molecular weight or of polyamines with higher reactivity as compared with diisocyanates, but as such the diisocyanates themselves were not the principal object of investigation. In particular, microcapsules studied for the controlled release of sensitive or unstable core materials have rarely been prepared using only diisocyanates as wall material in an emulsion polymerization [9, 10]. In this work, the morphologies of polyurea microcapsules from different molar ratios of diisocyanates and the release behavior of 1,4-diamino anthraquinone as a penetrator were investigated.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI) and 2,4-toluene diisocyanate (TDI) from Merck were used after being dried in a vacuum oven for 3 hours. Poly(vinyl alcohol) (PVA, Mw, 1500) (Junsei Chem., Japan), 1,4-diamino anthraquinone (DAA) (Fluka) and migrin oil (Seil Perfume Co., Korea) were used without any further purification.

2.2. Preparation of microcapsules

Oily solutions with the different molar ratios of 0.1 M IPDI and TDI (1 : 0, 0.67 : 0.33, 0.5 : 0.5:, 0.33 : 0.67, 0 : 1) as wall-forming materials, 20 g of migrin oil as core material and disperse dyes, 0.2 g of DAA as a penetrator were prepared. O/w emulsion was formed by adding the organic solution into the aqueous solution of 1.5% PVA as a stabilizer and stirring vigorously. 200 ml of distilled water was added into the o/w emulsion after stirring for 15 min to prevent agglomeration between the resultant globules. After reaching 80 °C, reaction for more 60 min formed polyurea microcapsules containing migrin oil and DAA. 500 ml of distilled water was added into the microcapsule slurry to maintain the monodispersed microparticles. Slow stirring was administrated to the microcapsule slurry until reaching room temperature. The microcapsule slurry

* Author to whom all correspondence should be addressed.

was decanted and washed with 10% ethanol to remove the migrin oil, and DAA and unreacted isocyanates on the surface, and dried in a vacuum oven at 25 °C for 24 hours.

2.3. Microcapsule characterization

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 gold and examined in the microscope. Loading content and release profiles of the penetrator, DAA from 0.12 g polyurea microcapsules from the different molar ratios of polyisocyanates were obtained by adding into 100 ml of N, N'-dimethyl acetamide (DMAc), water, ethanol and methanol while stirring and maintaining 20 °C. The solution was assayed for the amount of the released DAA by utilizing a UV/visible spectrophotometer.

3. Results and discussion

3.1. Morphologies of microcapsules

Fig. 1 shows SEM photographs of polyurea microcapsules from the different molar ratios of IPDI and TDI. The surface of the microcapsules from TDI alone became rougher than the other samples and their walls appeared thicker. This was mainly due to the more active reaction on the emulsion globules by the addition of aromatic TDI with superior reactivity. The surface of microcapsule from the same molar ratio of IPDI and TDI (0.5 : 0.5) was much smoother than that from TDI alone. It is proposed that addition of aliphatic IPDI with inferior reactivity as a wall material determines the roughness of the microcapsules. Polyurea microcapsules from IPDI alone were completely spherical with clear surfaces and this was due to slow wall-formation by inferior reaction of IPDI. Thus the prepared walls had a thin, tight and clear surface which influenced the release properties of penetrator through the microcapsules, as compared with that of TDI.

The surface of polyurea microcapsules is shown in Fig. 2 to demonstrate the effects of the reactivity difference. The surface of the microcapsules became increasingly smoother with an increase of IPDI content, due to its lower reactivity.

3.2. Loading content and release behavior

Table I shows the transmittance of penetrator, DAA in polyurea microcapsules after dissolution in DMAc to determine the relative wall thickness of the microcapsules from the different molar ratios of polyisocyanate. The transmittance of the completely dissolved solution was investigated at 475 nm as λ_{max} of DAA. UV/Vis spectrophotometer was utilized after the dissolution of 0.12 g polyurea microcapsules in 100 ml of DMAc. Generally, the content of penetrator in the microcapsules at the same processing procedure like stirring speed is the same. However, the transmittance of the microcapsule solution progressively decreased and resulted in a greatly cloudy solution as the TDI content in the wall increased. This shows that TDI enhanced reaction on the globule surface due to its superior reactivity as compared with IPDI. Thus it was confirmed that the wall membrane became thicker with increase of TDI content as shown in the SEM results.

TABLE I Transmittance of the DMAc solution with polyurea microcapsules from different molar ratios of polyisocyanate

Molar ratio (TDI : IPDI)	Transmittance (%)
TDI alone	41
0.67 : 0.33	44
0.5 : 0.5	50
0.33 : 0.67	51
IPDI alone	65

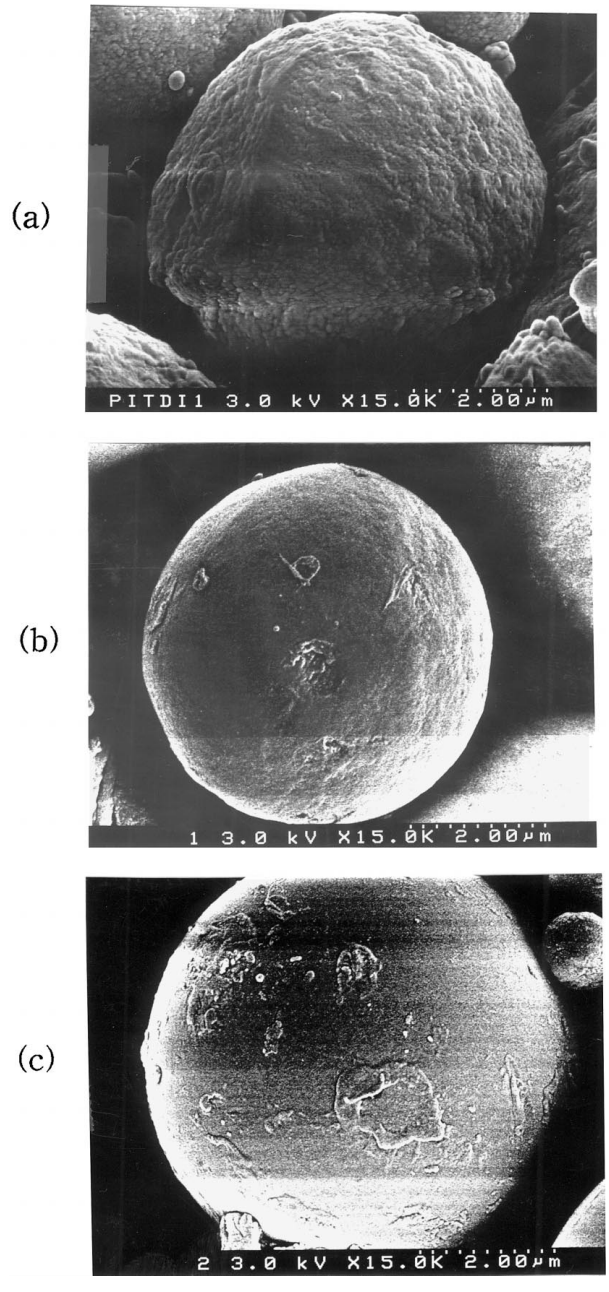

Figure 1 SEM photographs of polyurea microcapsules from different molar ratios (15,000×): (a) TDI alone, (b) 0.5 : 0.5 (TDI : IPDI), (c) IPDI alone.

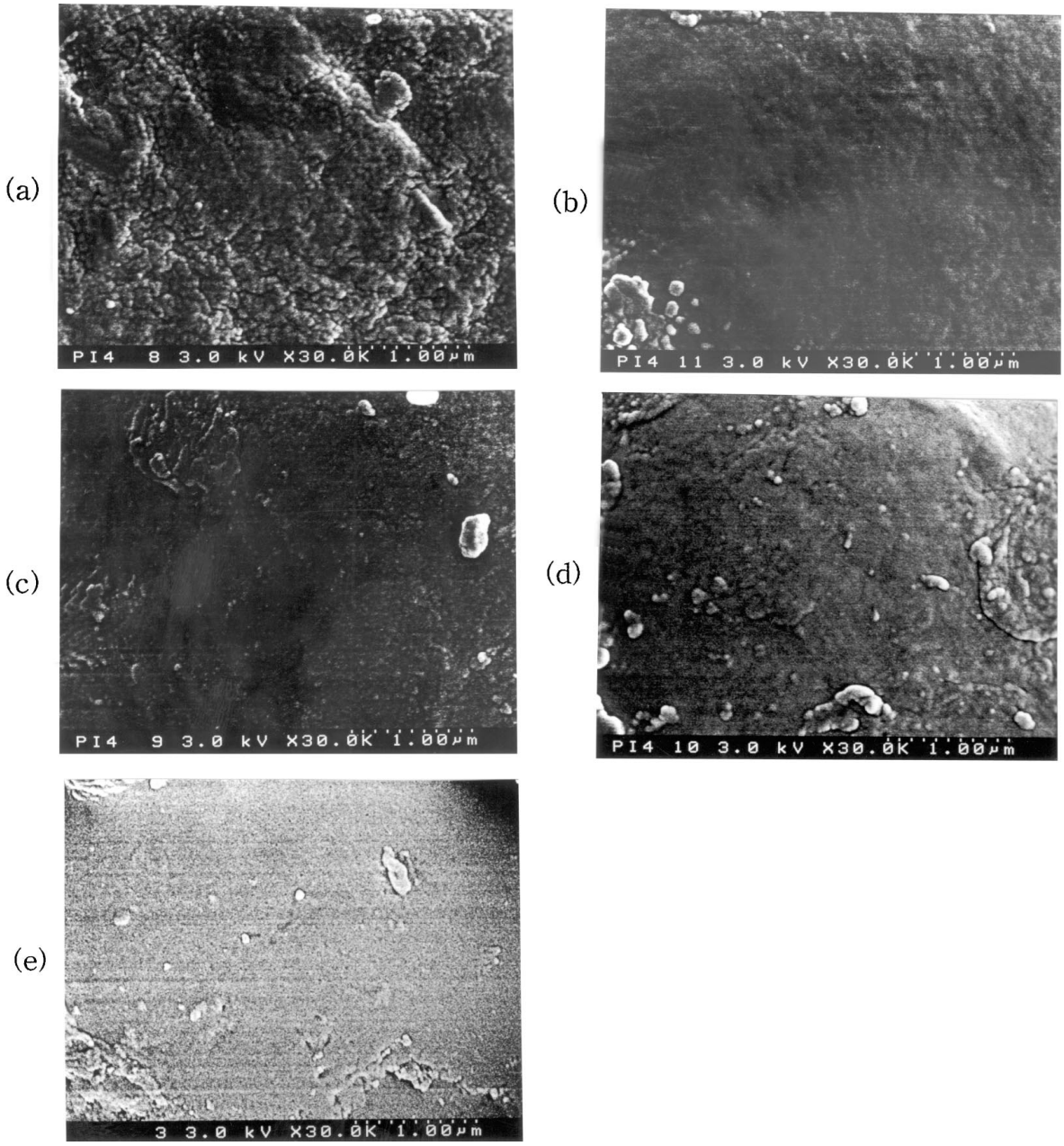

Figure 2 SEM photographs of polyurea microcapsules from different molar ratios (30,000×): (a) TDI alone, (b) 0.67 : 0.33 (TDI : IPDI), (c) 0.5 : 0.5, (d) 0.33 : 0.67, and (e) IPDI alone.

The dissolved DAA was analyzed spectrophotometrically by adding 0.12 g of microcapsules into 100 ml of extraction medium, and stirring to investigate the release properties of penetrator in water, ethanol, and methanol with different hydrophilicity. There was no release of penetrator through any microcapsules in this study using water as extraction medium, regardless of time and strong stirring, due to its incompatibility with hydrophobic migrin oil and DAA (figure not shown). In Fig. 3, there is a release of DAA in the case of ethanol and methanol as extraction media, although the extent of this release quickly decreased depending on the content of IPDI in the wall.

The incompatibility of microcapsules from IPDI alone with ethanol is shown in Fig. 3a with regard to the transmittance increase of penetrator, as compared with the initial concentration. This resulted from the agglomeration of the dispersed microcapsules. Release profiles in both extraction mediums showed the release rate of DAA depended on the TDI content in the microcapsule wall. This was related with the roughness of the microcapules prepared by rapid and random polymerization on the globule surface due to the TDI with superior reactivity. Thus it made the thickness and roughness of the microcapsule wall an important determinant in the release properties of the microcapsules.

4. Conclusion

In this study, polyurea microcapsules from different molar ratios of IPDI and TDI were prepared and the effects of polyisocyanate types on the morphologies and release behavior of the microcapsules were investigated. The transmittance of the completely dissolved

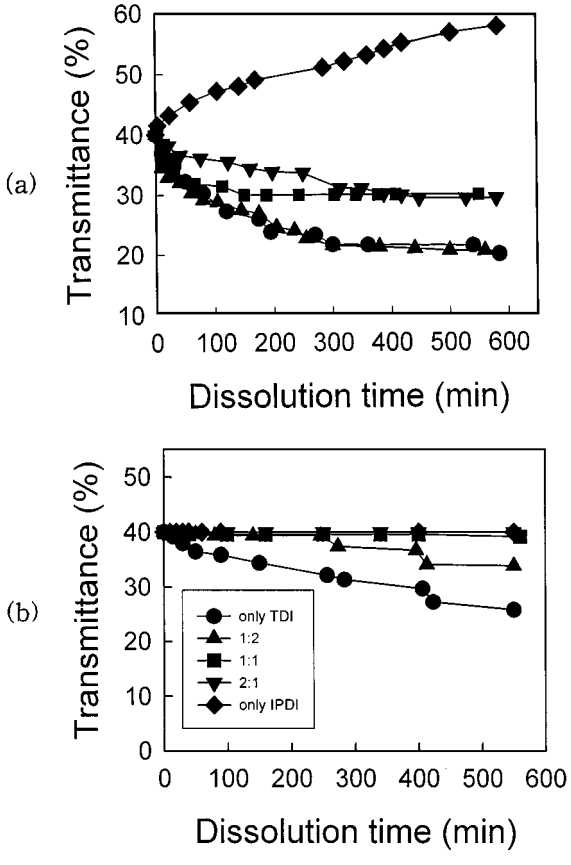

Figure 3 Release profiles of DAA through polyurea microcapsules from different molar ratios of TDI and IPDI in (a) ethanol and (b) methanol.

microcapsule slurry increased with the content of aliphatic IPDI in the walls due to its inferior reactivity, compared with aromatic TDI. This corresponded with the morphological results taken by SEM, which demonstrated that polyurea microcapsules from a higher TDI had rougher surfaces. Release profiles in extraction media showed that the release rate of DAA depended on the roughness of the microcapsules.

References

1. R. ARSHADY, *Polym. Eng. and Sci.* **29** (1989) 1746.
2. *Idem., ibid.* **30** (1990) 905.
3. *Idem., ibid.* **30** (1990) 915.
4. S. KOHJIYA, Y. IKEDA, S. TAKESAKO and S. YAMASHITA, *Reactive Polymer* **15** (1991) 165.
5. N. YUI, K. KATAOKA, A. YAMADA, Y. SAKURAI, K. SANUI and N. OGATA, *Macromol. Chem. Rapid Commun.* **7** (1988) 197.
6. K. SHAMA, K. KNUTSON and S. W. KIM, *J. Controlled Rel.* **7** (1988) 197.
7. K. HONG and S. PARK, *Reactive and Functional Polymer* (1998), in press.
8. *Idem., Materials Research Bulletin* (1998), in press.
9. H. KATAOKA and M. MURATA, JAPAN Patent 09012447 (1997).
10. R. GRAS and E. WOLF, EUROPE Patent 787754 (1997).

Received 27 July 1998
and accepted 13 January 1999