Preparation of Poly(urea-urethane) Microcapsules by Using Microreactor

Hideto Shosenji, Yuichi Miyazaki, Yutaka Kuwahara, Tsuyoshi Sawada and Soomin Park[1]

Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan
E-mail: sawada@gpo.kumamoto-u.ac.jp
[1]Department of Textile Engineering, Pusan National University, Busan 609-735, Korea

1. INTRODUCTION

Microencapsulation of active substances with polymeric substances has been remarkably developed, offering technique to prepare microcapsules with a variety of size, hardness and properties of controlled release of encapsulated substances. They have been used in foods, carbonless copying papers, liquid crystals, adhesives, cosmetics, insecticides and pharmaceutical and medical applications [1,2]. Recent research interest is focused on the reduction of the size to meet the requirement for their rapidly developing application especially in the pharmaceutical and medical area.

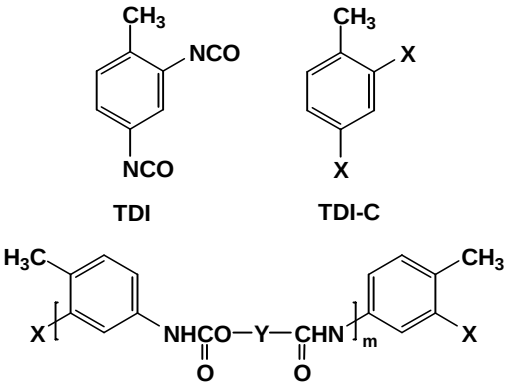
Microreactor system provides unique characteristics such as short molecular diffusion distance, large specific interfacial area and small heat capacity, promoting the research of highly effective chemical reactions. Recently we have developed the preparation of melamine microcapsules with particle sizes much smaller than those prepared by batch method [3].

Preparation of poly(urea-urethane) microcapsules has been well established [4]. In this study, we prepared poly(urea-urethane) microcapsules by using microreactor method and investigated particle size and size distribution of microcapsules obtained.

2. EXPERIMENTAL

2.1 Material

Toluene-2,4-diisocyanate (TDI), polyethylene glycol (PEG, MW=600), ethylenediamine (EDA), polyvinyl alcohol (PVA), dibutyltin dilaurate (DBTDL) and other materials were commercially available from Wako Pure Chemicals Industries and Nakalai Tesuque Cooperation. Blocked TDI (TDI-C) was prepared by the reaction of TDI and *m*-cresol [*]. Prepolymer (TDI-CP) was prepared by the reaction of TDI and PEG followed by the reaction with *m*-cresol.



2.2 Preparation of microcapsules from TDI-C

2.2.1 Batch method

To 0.18g of TDI in 16.6 ml of toluene, *n*-hexane *n*-heptane or *n*-octane was added 0.23g of *m*-cresol. The resulting solution of TDI-C was added to 100 ml of aqueous solution of 0.026% PVA. The mixture was stirred with a homogenizer for 5 min, giving o/w emulsion. To the emulsion was added 0.19g of PEG, 0.05g of DBTDL and 0.03 g of EDA under stirring with a homogenizer at 90°C. After stirring for 2h, solid polymeric materials was collected by centrifuge and dried under reduced pressure at room temperature for 24h.

2.2.2 Microreactor method

The capillary microreactor system used was composed of a microsyringe pump, a pair of gas-tight syringe, a Y connector, deactivated fused silica capillary tubes with a diameter of 150-320 μm and an air oven.

The solution of TDI-C prepared from 0.018g of TDI, 0.023g of *m*-cresol and 1.66ml of toluene was added to 10 ml of aqueous PVA solution (0.026wt%) containing 0.005g of DBTDL. The o/w emulsion obtained from the mixture by stirring with a

homogenizer for 5 min was placed in one of the syringe of the microreactor system, while 10 ml of an aqueous solution of PEG (0.019g) and EDA (0.003g) was placed in another syringe. Both solutions were injected to the capillary system at a controlled rate. The solution eluted from the capillary tube gave polymeric solid including microcapsules.

2.3 Preparation of microcapsules from TDI-CP

2.3.1 Batch method

To 0.18g of TDI in 16.6 ml of toluene, *n*-hexane, *n*-heptane or *n*-octane was added 0.19g of PEG at room temperature. To this mixture was added 0.23g of *m*-cresol, giving m-cresol adduct of urethane prepolymer (TDI-CP). The adduct was added to 100ml of aqueous 0.026wt% PVA solution and the mixture was stirred with a homogenizer to give o/w emulsion. Under stirring the emulsion was treated with DBTDL and 0.03g of EDA, giving microcapsules.

2.3.2 Microreactor method

The solution of TDI-CP prepared from 0.018g of TDI, 0.019g of PEG, 0.012g of *m*-cresol and 1.66ml of toluene was added to 10 ml of aqueous PVA solution (0.026wt%) containing DBTDL. The o/w emulsion obtained from the mixture by stirring with a homogenizer for 5 min was placed in one of the syringe of the microreactor system, while 10 ml of an aqueous solution EDA (0.003g) was placed in another syringe. Both solutions were injected to the capillary system at a controlled rate, producing microcapsules.

3. RESULTS AND DISCUSSION

Attempted preparation of microcapsules from TDI gave polymeric materials of unspecified shapes as main products along with small amount of microcapsules for both of batch and microreactor method. The encapsulation process is considered to provide hydrolysis of isocyanato on TDI which resulted in formation of urea resin, reducing yield of the microcapsules.

To avoid hydrolysis, TDI was converted to TDI-C by treating with *m*-cresol. TDI was also converted to TDI-CP by treating with PEG and then with *m*-cresol. TDI-C as well as TDI-CP gave microcapsules in high yields along with trace of polymeric materials of unspecified shape. Fig. 1 shows SEM photograph of the microcapsules prepared from TDI-CP. The microcapsules have spherical shapes with average diameter of 0.12 mm.

Fig. 2 shows the particle size distribution of the microcapsules prepared from TDI-C as well as from TDI-CP by using batch and microreactor method. TDI-CP gave microcapsules with smaller average particle size and narrower particle size distribution than the microcapsules prepared from TDI-C. In the organic solvents used for encapsulation *n*-octane gave the microcapsules with the smallest size.

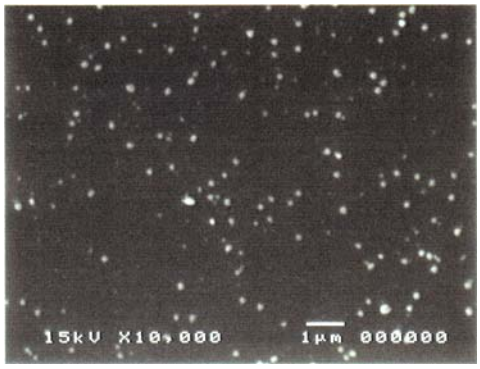


Fig. 1 The SEM photograph of microcapsules prepared from TDI-CP using microreactor method.

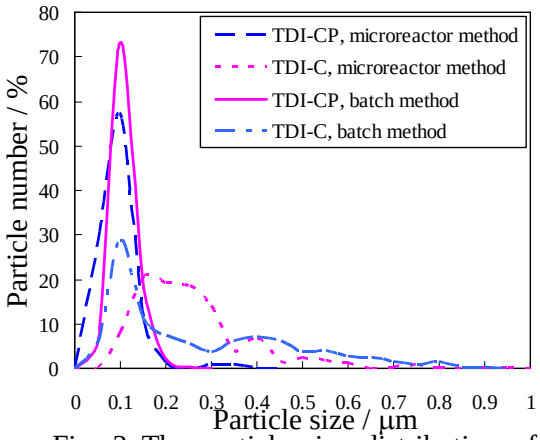


Fig. 2 The particle size distribution of microcapsules prepared from TDI-C or TDI-CP

4. REFERENCES

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