Preparation of Melamine Resin Microcapsules by Using Microreactor with Telomeric Surfactants

Hideto Shosenji(1), Misaki Korenori(1), Katsuki Ito(1), Yutaka Kuwahara(1), Tsuyoshi Sawada(1) and Soo Min Park(2)

(1) Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

(2) Department of Textile Engineering, Pusan National University, Pusan 609-735, Korea

Abstract

Melamine resin microcapsules with mean sizes from 500 to 600 nm were prepared by using a micro-tubular reactor (microreactor) with toluene and sodium dodecylsulfate (SDS) as emulsifiers. Conventional stirring method with telomeric surfactant in place of SDS produced microcapsules with mean sizes from 100 to 200 nm. Preparation by means of microreactor method with telomeric surfactant gave microcapsules with sizes below 200 nm in narrow particle size distribution. TG analysis revealed that the microcapsules contained 50 wt% of toluene.

Introduction

Microencapsulation of active substances with polymeric substances have been remarkably developed, offering technique to prepare microcapsules with a variety of size, hardness and properties of controlled release of encapsulated substances[1,2]. They have been used in a variety of applications including textile finishing[3]. Conventional method of vigorous stirring in batch reactor produces microcapsules with size above 1μm[4]. 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[5].

We have recently prepared telomer type surfactants with multi hydrophilic and hydrophobic functions[6,7]. These telomeric surfactants stabilized emulsion at concentrations much lower than the case of conventional surfactants with monoalkyl chain.

Recently much attention has been directed to microreactor systems, which provide noble characteristics such as short molecular diffusion distance, large specific interfacial area, and small heat capacity, promoting highly selective chemical reactions[8]. Few reports have been published on the application of microreactor system to the preparation of microcapsules.

In this study, we prepared melamine resin microcapsules using a microreactor with telomeric surfactants ($1.6R_6A$-3.5AA) as emulsifying agents, and compared its properties with those prepared using a batch reactor with sodium dodecylsulfate (SDS).

$$NH_2(CH_2)_2S\text{-}(CH_2CHX)_{1.6}\text{-}(CH_2CHY)_{3.5}\text{-}H$$

$1.6R_6A$-3.5AA $X=CO_2C_6H_{13}$, $Y=CO_2Na$

Experimental

Materials

Telomeric surfactant was synthesized as described elsewhere[6]. Other chemicals were commercially available.

Preparation of microcapsules

(a) Batch reactor method

The preparation was undertaken by modifying the method of K. Hong and S. M. Park[4]. A mixture of 3.9 g of melamine and 3.0g of formaldehyde in 300 ml of water were stirred at pH 9 at 70 °C for 10 min, giving a melamine-formaldehyde precondensate. A mixture of 20 mg of $1.6R_6A$-3.5AA or SDS, 30 ml of toluene, 50 ml of water and 0.2mg of 1,4-diaminoanthraquinon (DAA) was stirred for 3 min by homogenizer, giving o/w emulsion. 50 ml of melamine-formaldehyde precondensate was added to the emulsion, and the pH of the mixture was adjusted from 4.0 to 4.5 with formic acid. The mixture was stirred at 3000 rpm at 70°C for 1 h, giving microcapsules, which was collected by a centrifuge, and dried under reduced pressure at room temperature for 24 h.

(b) Microreactor method

The capillary microreactor system used in this work was composed of a microsyringe pump, a pair of gas-tight syringe, a Y-connector, deactivated fused silica capillary tubes with a diameter of 0.25 mm, and an air oven. A mixture of 2 mg of $1.6R_6A$-3.5AA or SDS, 3 ml of toluene, 5 ml of water and DAA was stirred for 3 minutes by homogenizer, giving an o/w emulsion. Five ml of melamine-formaldehyde precondensate was added to the o/w emulsion. The mixed emulsion was placed in one of the syringe, while aqueous formic acid was placed in another syringe. Both of the solutions were injected to the capillary system at a controlled rate, while the outgoing solution was adjusted to pH4. The observation at the Y-connector with a CCD microscope confirmed the laminar flow of the emulsion as well as the formic acid solution.

Results and Discussions

FT-IR spectra of the microcapsules showed strong bands of N-H stretching at 3335 cm^{-1}, C-H stretching at 2935 cm^{-1}, C-N stretching at 1343 cm^{-1} and C-O stretching at 1163 cm^{-1}, indicating a formation of melamine resin as wall material of microcapsules.

The DSC thermogram showed a melting point of microcapsules at 432°C. The TG thermogram shows a weight loss of about 50%, revealing that the microcapsules contained about 50wt% of toluene.

The shapes of the melamine microcapsules were examined by scanning electron microscope (SEM). The batch reactor method with SDS as an emulsifier gave microcapsules with rough surfaces, and the particle sizes were from 0.5 to 8 μm. Microreactor method gave microcapsules with smooth surfaces as shown by Fig. 1. Preparation with 1.6R_6A-3.5AA by using batch reactor gave microcapsules with particle sizes of 0.5-2.0 μm, along with a significant amount of polymers of unspecified shapes. As shown by Fig. 1, the microreactor method gave predominantly cubic microcapsules along with trace of irregularly shaped polymers.

The particle size distributions of microcapsules were estimated from the SEM photographs. The microcapsules prepared with SDS showed size range from 0.3 to 0.8 μm, while the diameter of 91% of the microcapsules prepared with 1.6R_6A-3.5AA was in the range from 0.02 to 0.2 μm.

Preparation by using microreactor gave microcapsules of smaller diameter in narrower size distribution than those prepared by the batch reactor method. The laminar flow in the microreactor is considered to keep the emulsion so stable as to form microcapsules of uniform cubic shape. Vigorous stirring in the batch reactor may cause destruction as well as combination of emulsion, which results in a formation of microcapsules of irregular shapes. With telomeric surfactant microcapsules in narrow size distribution were obtained, plausibly owing to the function of this surfactant to forms stable, fine and well-dispersed emulsion.

Conclusion

a

b

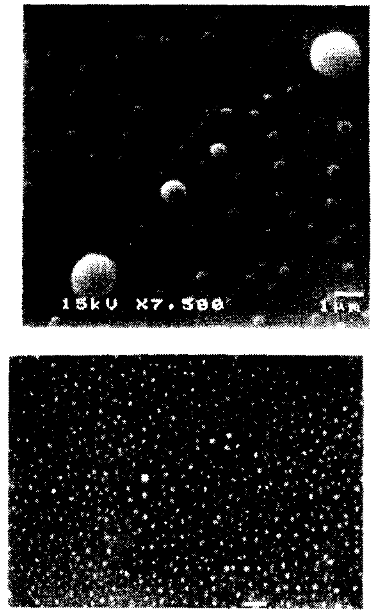

Fig. 1. The SEM photographs of microcapsules prepared by using microreactor.
Emulsifier: a, SDS; b, 1.6R_6A-3.5AA.

Encapsulation of melamin resin with telomeric surfactant in a microreactor gave microcapsules with sizes below 200 nm in narrow size distribution. The microcapsules are considered to be formed by the reaction in laminar flow in the microreactor from the melamin precondensate in well dispersed emulsions stabilized by the telomeric surfactant.

References

1. T. Kondo, *J Oleo Sci.*, **50**, 1 (2001).
2. R. Arshady, *Polym. Eng. Sci.* (a) **30**, 915 (1990); R. Arshady, *ibid.* (b) **33**, 865 (1993).
3. G. Nelson, *Rev. Progr. Color. Rel. Topics.*, **31**, 57 (2001).
4. K. Hong and S. Park, *Materials Chem. Phys.*, **58**, 128 (1999).
5. G. Lambert, E. Fattal, H. Pinto-Alpahandary, A. Gulik and P. Couvreur, *Pharm. Res.*, **17**, 707 (2000).
6. T. Yoshimura, Y. Koide, H. Shosenji and K. Esumi, *J. Jpn Oil Chen. Sci.*, **49**, 801 (2001); T. Yoshimura, K. Hontake, H. Shosenji and K. Esumi, *J. Oleo Sci.*, **50**, 103 (2001).
7. Y. Seino, H. Shosenji and S. Natsuo. *PCT Int. Appl.*, 42 (2002).
8. H. Hisamoto, T. Saito, M. Tokeshi, A. Hibara, and T. Kitamori, *Chem. Commun.*, 2662 (2001).