막유화법에 의한 에멀젼 액적 및 알지네이트 미립자의 제조

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Preparation of Emulsion Droplets and Alginate Microspheres by Membrane Emulsification Method

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1. Introduction

The membrane emulsification method is a new technology that allows producing uniform emulsions at low energy input compared to the conventional emulsification methods such as a high-pressure homo genizer, rotor/stator system and colloid mill. Also the membrane emulsification method is highly attractive given its simplicity, potentially lower energy demands, need for less surfactant and the resulting narrow droplet size distribution. Over the last 10 years, there has been an increasing interest in a technique for making O/W and W/O emulsions and polymer microspheres using the membrane emulsification method [1~3].

This research aims to obtain some information concerning how O/W emulsion droplets grow and detach from the membrane pore mouth and to prepare alginate microspheres using the membrane emulsification method. We used a microscopic visualization system to observe the emulsion droplets formation process from a disk-type polyester track-etched membranes. Based on the visualization experiments, the rate of droplet formation, the droplet size and its distribution were determined and also the droplet formation dynamics was discussed. The uniform microspheres of a natural polymer, calcium alginate, were prepared by controlling various conditions of membrane emulsification procedure using a lab-scale batch type system having a Shirasu porous glass (SPG) hydrophobic membrane. To prepare alginate microspheres, we considered various process parameters such as the ratio of dispersed phase to continuous phase, the type and concentration of sufactants, the concentration of alginate, stabilizer and cross-linking agent, the stirring speed of continuous phase and the transmembrane pressure.

2. Experimental

A schematic diagram of the membrane emulsification system for the visualization of O/W emulsion droplets formation is shown in Fig. 1. The continuous phase (pure water) containing an emulsifier (SDS; sodium dodecyl sulfate) was fed into the membrane cell and the dispersed phase (soybean oil) in a reservoir was permeated through the track-etched membrane into the continuous phase under N_2 gas pressure. The track-etched polyester membranes (Osmonics Co., USA) having 5, 8 and 10 ㎛ mean pore size were used. The formation dynamics of emulsion droplets were recorded real-time by using a microscopic visualization system (a optical microscope equipped with a digital camcorder and a LCD monitor) and saved into a PC.

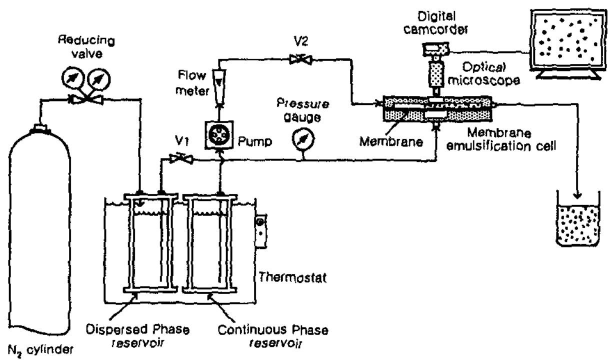


Fig. 1. Schematic diagram for the visualization of emulsion droplets formation in a membrane emulsification system.

A schematic diagram of the batch-type membrane emulsification system for preparation of alginate microspheres is shown in Fig. 2. The continuous phase (isooctane) with emulsifier (Span 80, 83 and 85) was stirred in the vessel and the dispersed phase (Na-alginate solution) in a reservoir was permeated through the SPG membrane into the continuous phase. The dispersed phase flux was calculated on the basis of data obtained from the weight change of the dispersed phase reservoir with an electronic balance and a PC. Used SPG membrane tube was 2.9 ㎛ mean pore size, 10 mm outer diameter, and 30 mm length, and treated with octadecyltrichlorosilane and trimethylchlorosilane to render hydrophobic SPG membrane.

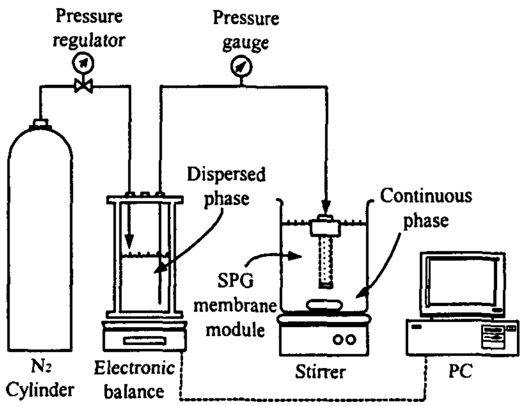
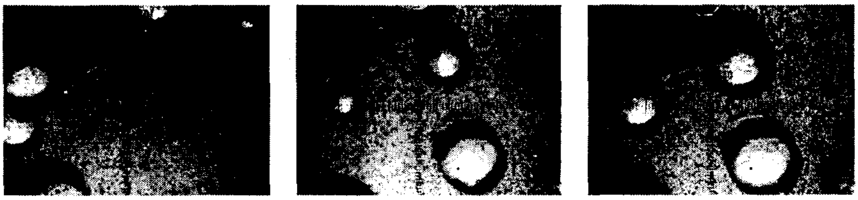


Fig. 2. Schematic diagram for the preparation of alginate micospheres by membrane emulsification method.

3. Results and Discussion

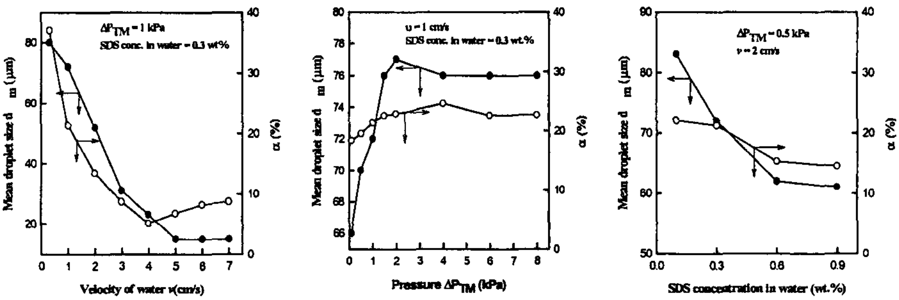
The real-time observation using a microscope with digital camcorder system made it possible to measure the mean emulsion droplet size and distribution and the mean rate of droplet formation. Fig. 3 illustrates the progress of droplet formation on the isopore membrane surface. After just an emulsion droplet is formed, it grows until detaching from the pore mouth. The growing time is shortening with increasing the continuous phase velocity. Fig. 4 shows that the mean droplet size and the standard deviation are decreased with increasing the continuous phase velocity, decreasing the transmembrane pressure and increasing SDS concentration in the continuous phase.

Fig. 5 shows that effects of the ratio of dispersed phase to continuous phase (D/C ratio), emulsifier concentration in the continuous phase and Na-alginate concentration in the dispersed phase on the mean size and size distribution of alginate microspheres prepared by membrane emulsification. Increasing D/C ratio, the mean size of alginate microspheres increases gradually and the size distribution becomes broader. As emulsifier (Span 80) concentration in the continuous phase increases, the mean size and the size distribution decrease. Also increasing the Na-alginate concentration in the dispersed phase, the mean size increases but the size distribution becomes narrower. Fig. 6 shows SEM photographs of alginate microspheres prepared with various alginate concentrations. The matrix structure of microspheres prepared at higher alginate concentration was much denser. When the alginate



(a) After formation (0.1 s) (b) Growing (1.2 s) (c) Before detaching (2 s)

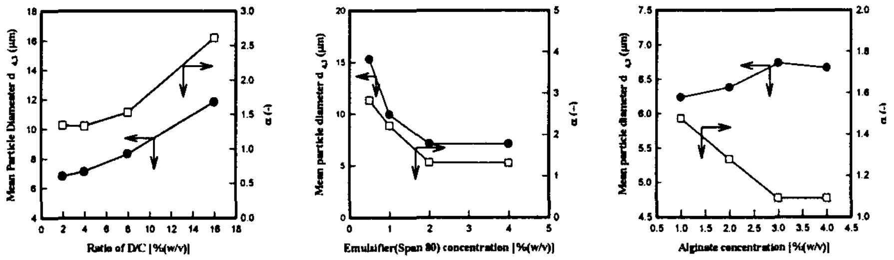
Fig. 3. Dynamics for the formation of O/W emulsion droplet with time. [Membrane; hydrophilic polyester 5 μm, Dispersed phase; soybean oil, Continuous phase; water, ΔP_{TM} = 0.1 kPa, v = 0.3 cm/s, SDS concentration in water = 0.3 wt.%]



(a) (b) (c)

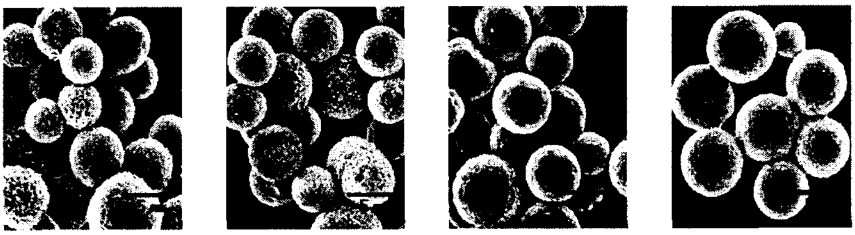
Fig. 4. Mean size and standard deviation of O/W emulsion droplets with variation of (a) v, (b) ΔP_{TM} and (c) emulsifier (SDS) concentration in water. [Membrane; hydrophilic polyester 5 μm, Dispersed phase; soybean oil, Continuous phase; water]

concentration was 1%(w/v), the mean size of microspheres was the smallest but the size distribution was broad owing to low viscosity of alginate solution. On the other hand, the mean size of microspheres at high concentration of alginate solution was larger than that at low concentration because of the increase in viscosity.



(a) (b) (c)

Fig. 5. Effect of **(a)** D/C ratio, **(b)** emulsifier (Span 80) concentration and **(c)** alginate concentration on mean size and size distribution of the alginate microspheres. [**(a)** alginate concentration = 3%(w/v); stabilizer concentration = 11%(w/w); emulsifier (Span 80) concentration = 2%(w/v); ΔP_{TM} = 40 kPa; stirring speed = 700 rpm; membrane pore size = 2.9 ㎛, **(b)** D/C ratio = 4%(w/v); stabilizer concentration = 11%(w/w); ΔP_{TM} = 40 kPa; alginate concentration = 3%(w/v); stirring speed = 700 rpm; membrane pore size = 2.9 ㎛, **(c)** D/C ratio = 4%(w/v); emulsifier (Span 80) concentration = 2%(w/v); stabilizer concentration = 5%(w/w); ΔP_{TM} = 30 kPa; stirring speed = 700 rpm; membrane pore size = 2.9 ㎛]



(a) (b) (c) (d)

Fig. 6. SEM photographs of alginate microspheres prepared with various alginate concentrations. **(a)** 1%(w/v) solution **(b)** 2%(w/v) solution, **(c)** 3%(w/v) solution, and **(d)** 4%(w/v) solution [D/C ratio =4%(w/v); emulsifier(Span 80) concentration = 2%(w/v); stabilizer concentration = 5%(w/w); ΔP_{TM} = 30 kPa; stirring speed = 700 rpm; SPG membrane pore size = 2.9 ㎛].

4. Conclusions

The visualization of O/W emulsion droplet formation through the track-etched polyester membranes by using a microscope with digital camcorder system shows that the mean droplet size and size distribution are decreased with increasing the continuous phase velocity, decreasing the transmembrane pressure and increasing SDS concentration in the continuous phase. Emulsion droplets having about 20~30 ㎛ size are prepared at the higher velocity of continuous phase.

Uniform alginate microspheres with the mean diameter of about 6 ㎛ were finally prepared using SPG membrane having 2.9 ㎛ pore size and the optimal preparation conditions are as follows; D/C ratio = 4%(w/v), alginate concentration = 3%(w/v), emulsifier concentration = 2%(w/v), stabilizer concentration = 5%(w/w), ΔP_{TM} = 30 kPa, stirring speed = 700 rpm and concentration of crosslinking ($CaCl_2$) agent = 10%(w/v). The mean size of alginate microspheres increases with increasing D/C ratio, transmembrane pressure and alginate concentration in the dispersed phase. But the mean size of alginate microspheres decreases with increasing emulsifier concentration, stabilizer concentration, stirring speed and concentration of the crosslinking agent in the continuous phase.

References

1) S. M. Joscelyne and G. Tragardh, "Membrane Emulsification: A Literature Review", *J. Memb. Sci.*, **169**, 107(2000).
2) T. Nakashima, M. Shimizu and M. Kukizaki, "Particle Control of Emulsion by Membrane Emulsification and Its Applications", *Advanced Drug Delivery Review*, **15**, 47(2000).
3) L. Giorno, N. Li and E. Drioli, "Preparation of Oil-in-Water Emulsions Using Polyamide 10 kDa Hollow Fiber Membrane", *J. Memb. Sci.*, **217**, 173(2003).