Preparation and Evaluation of Thermosensitive Microcapsules Using Double Tube Nozzle

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1. Introduction

Recently, stimuli-responsive polymers have been developed and application of these polymers is also being tried. Among them, N-isopropyl acrylamide (NIPAAm) is well known to have thermo-responsive properties, and Kuckling et al reported to prepare thermo-sensitive gel beads which consisted of NIPAAm and alginate as an application of thermo-responsive polymers [1)].

On the other hand, microcapsule has attracted interests for applications of controlled release delivery or micro-reactor. Application of the stimuli responsive polymers for the microcapsule is an interesting topic, and for the application, it is important to establish simple preparation method of stimuli responsive microcapsule, which can easily produce capsules with controlled capsule size and shell thickness. Microcapsule preparation using double tube nozzle is one of the method which is possible to achieve above conditions. Therefore, in this study, preparation of thermo-responsive microcapsule which consisted of NIPAAm and alginate was tried using double tube nozzles.

2. Experimental

Fig. 1 shows the experimental set up to prepare microcapsules using double tube nozzles. At first, microcapsule formation using the double tube nozzles was tested using only sodium alginate as shell material. As a core material, cocoa suspension was used. In the experiment, 2 wt% sodium alginate solution was pumped out from the outer tube, and cocoa suspension was pumped out from inner tube. The formed double layered droplets were then dropped into consolidation solution (0.4 M $CaCl_2$ solution). In the solution, gellation and consolidation of the alginate in the outer layer occurred due to the calcium cation crosslinkage of the alginate molecules. After 90 min., the capsules were recovered from the solution. The effect of the flow rate of the solution from the outer tube (F_{out}) and that from the inner tube (F_{in}) on the size and shell thickness of the capsules was examined.

Then, the preparation of thermo-responsive microcapsules was tried. In the experiment, NIPAAm was also used to form capsule shell in addition to sodium alginate. The solution which contained NIPAAm monomer (9.6 wt%), and sodium alginate (1 wt%) was pumped out from outer tube, and cocoa suspension was pumped out from inner tube. Consolidation solution contained ammonium peroxide sulfate (APS) as polymerization initiator (0.5 wt%) and N,N,N',N'-Tetramethyl ethylenediamine (TEMED) as promoter (0.25 vol%) and 0.1 M $CaCl_2$. In the solution, at first gellation and consolidation of the alginate in the outer layer occurred and it formed support structure of the capsule. Since polymerization reaction of NIPAAm monomer is not so fast, NIPAAm monomers were then polymerized within the alginate gell layer, and the capsules with alginate-NIPAAm complex shell were obtained. Crosslinkage of the NIPAAm polymer in the capsule shell was also tried by using N, N'-Methylenebisacrylamide (MBAAm) as cross linking agent. Furthermore, alginate-NIPAAm beads were prepared by using single tube nozzle without changing other conditions for comparison. Crosslinked alginate-NIPAAm beads were also prepared. Thermo-responsive volume change of the capsules and beads were measured with changing temperature from 27 to 40°C using microscope.

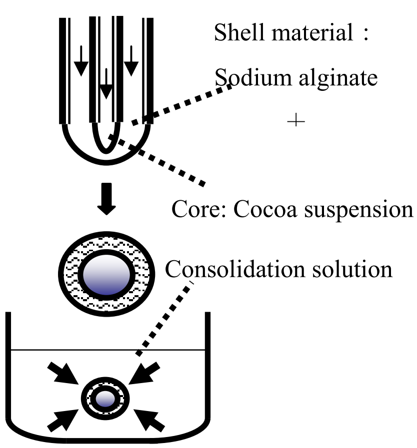
3. Results and Discussion

The effect of the flow rate of the solution from the outer tube (F_{out}) and that from the inner tube (F_{in}) on the size and shell thickness of the alginate capsules were shown in Fig. 2 and 3. The results showed that the size of the capsules increased and the shell thickness decreased with the increase of the flow rate ratio (F_{in} / F_{out}). This suggests that capsule size and shell thickness could be controlled by changing F_{in} / F_{out}. Figure 3 also showed that although F_{out} was different, if F_{in} / F_{out} was the same, shell thickness was essentially the same for three different F_{out}. This means that shell thickness is not dependent on the absolute value of the flow rate in the range used in this study. However, when the flow rate ratio (F_{in} / F_{out}) exceeded 0.45, formation of the capsule became difficult.

Then, temperature-responsive volume change of the alginate-NIPAAm capsules and beads was measured. The result showed that the capsule started to shrink when the temperature increased, and it swollen when the temperature decreased. The temperature responsive volume change was reversible. The swelling ratio was calculated based on the measured volume change. To calculate the swelling ratio, the volume at each temperature was standardized by the volume at the lowest temperature for each capsules and beads. The results were shown in Fig. 4. From the results, it was found that the tendency of the volume change in the case of capsule and beads was almost the same. For both cases, the volume changed greatly with temperature in the case with crosslinkage.

Reference

1. Kuckling D, Schmidt T, Filipcsei, Adler HJ P, Arndt KF, Preparation of filled temperature -sensitive poly(N-isopropylacrylamide) gel beads, Macromol. Symp. 2004; 210, 369-376



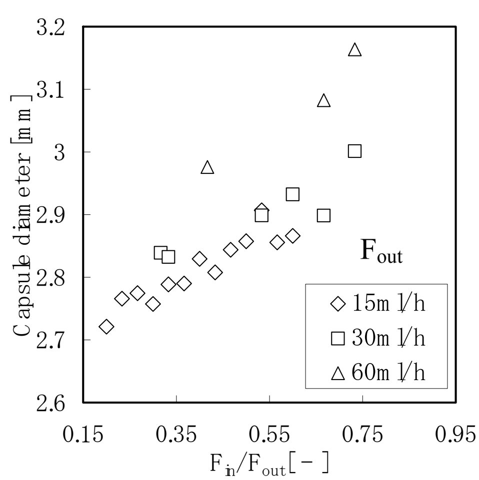


Fig.1 Experimental set up to prepare micro-capsules using double tube nozzle.

Fig.2 Effect of F_{in}/F_{out} on capsule diameter

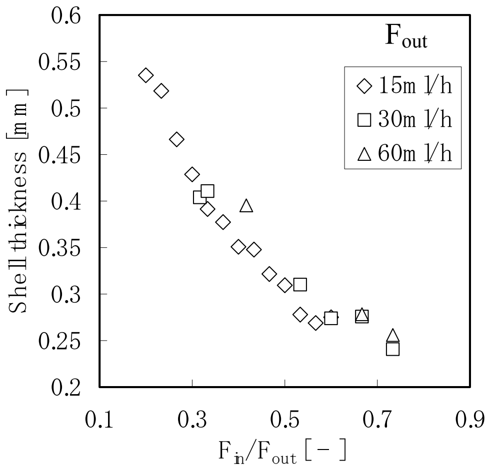


Fig.3 Effect of F_{in}/F_{out} on shell thickness

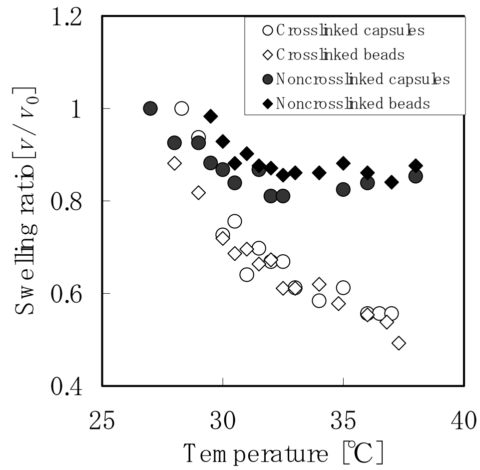


Fig.4 Swelling ratio of the capsule and beads vs temperature