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Preparation of microcapsules by electrostatic atomization

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Abstract

A new method for preparing microcapsules based on a one-step gelling process combined with an electrostatic atomization technique is proposed. In the process, capsules with polymer shells are produced by dripping viscous solution, which contains a crosslinker agent, into a consolidation solution with agitation. In this study, sodium alginate and $CaCl_2$ were used as a polymer material for shell formation and crosslinker agent, respectively. Carboxymethyl cellulose (CMC) was used as a non-gelling polymer to modulate the viscosity and the density of the core solution to prevent deformation during the shell formation process. The CMC in the core of the capsule obtained was then enzymatically decomposed using cellulase. The results show that the microcapsules with alginate shell and water core are obtained successfully. By combining the one-step gelling process with the electrostatic atomization technique, the capsule size can be reduced to 500 μm in diameter.

To demonstrate a practical application, enzyme immobilization was performed within the capsules. Invertase, which catalyzes the decomposition of sucrose into fructose and glucose, was used as a model enzyme in this study. The results show that invertase is immobilized with high efficiency (87–98%). Enzyme activity is increased with increasing of the applied voltage in the electro-dripping process because of the smaller capsule diameter at the higher applied voltage.

Keywords: Microcapsule; Electrostatic atomization; Enzyme immobilization; Carboxymethyl cellulose (CMC); Calcium alginate

1. Introduction

Microcapsules with shells made of functional materials have attracted increasing interest because of their diverse potential of applications such as drug delivery, cell or enzyme immobilization, separation in biomedicine, and microreactors. A variety of functions of microcapsules with having unique properties can be realized by applying functional components such as nanoparticles [1], biomacromolecules [2], photosensitive dyes [3], smart polymers [4], and multivalent ions [5] into the capsule wall or into the interior of the capsule.

In general, the performance of a capsule is dependent on its shell properties such as thickness, pore-size, surface charge, and mechanical properties, as well as the specific surface area and capsule size distribution. For example, the permeability of the capsule shell or the release rate of encapsulated materials depends on the shell properties. A smaller diameter of the capsule also results in faster radial mass transfer.

The manufacture of such capsules is usually carried out by coacervation, emulsion, or spraying techniques. However, these techniques present difficulties in controlling uniform capsule size, shell thickness, and shape. Therefore, a simpler method, which can easily control such properties, is desired. The one-step gelling process reported by Blandino et al. [6] is a new, simple, and versatile method for preparing spherical microcapsules. The concept of the one-step gelling process is shown in Fig. 1. Capsules with polymer shells are produced by dripping viscous solution, which contains a crosslinker agent, into a polymer solution with agitation. Because viscous solution prevents the deformation of droplets due to shear stress arising from agitation in the solution, crosslinker agent in the droplets can diffuse out to the surface of the droplet while maintaining an individual spherical shape, and a polymer shell is formed around the droplets. In the study, sodium

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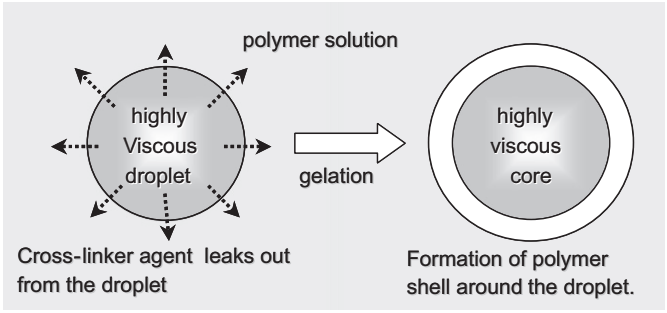

Fig. 1. Concept for a one-step gelling method of preparing microcapsules.

alginate and $CaCl_2$ were used as the polymer for shell formation and crosslinker agent, respectively. Carboxymethyl cellulose (CMC) was used as a non-gelling polymer to modulate the viscosity and density of the core solution.

Although capsules are easily produced by this method, the core of the resulting capsule remains relatively viscous because CMC cannot diffuse out from the capsule through the alginate shell [7]. This works as a diffusion resistivity in the capsule. If the high molecular-weight thickener, CMC could be decomposed and eliminated from the capsules; then capsules with liquid-core could be obtained to reduce the diffusion resistivity. To realize this goal, we tried to decompose the CMC in the capsules using cellulase to obtain calcium alginate-gel microcapsules with liquid-cores. Cellulase is an enzyme that hydrolyzes CMC into reducing sugars having low molecular weight, so that the decomposed residues can penetrate the alginate shell to the outer solution.

In addition to the above, the electrostatic atomization technique is applied to reduce the size of the capsules. Electrostatic atomization is a well-known phenomenon where liquid is dispersed into fine droplets due to an electrostatic repulsive force working on the surface of the liquid. Electrostatic atomization has some significant advantages, e.g. relative ease of droplet generation, ability to avoid aggregation of droplets due to electric charge of same polarity on the droplets, and ability to produce a narrow-sized distribution of generated droplets [8,9]. Therefore, it is expected that the technique allows the production of mono-dispersed droplets of a viscous liquid of few submicrometers in size to produce smaller capsules combined using the above mentioned one-step gelling process.

To investigate one possible application of the microcapsules obtained, enzyme immobilization was attempted. In this study, invertase, which catalyzes the decomposition reaction of sucrose into fructose and glucose, was used as a model enzyme.

2. Materials and methods

2.1. Materials

Sodium alginate and calcium chloride ($CaCl_2$) were purchased from Kanto Chemical Co. Ltd. CMC was purchased from ICN Biomedicals, Inc. Cellulase derived from *Aspergillus niger* (EC 3.2.1.4) and invertase derived from *Saccharomyces cerevisia* (EC 3.2.1.26) were purchased from Wako Pure Chemical Industries, Ltd. The enzyme activities of the cellulose and the invertase were 1.92 and l163 IU/mg, respectively. Glucose C2, which is the reagent kit for glucose assay based on enzymatic method with a combination of mutarotase and glucose oxidase, was also purchased from Wako Pure Chemical Industries, Ltd. All other chemicals were of analytical grade.

2.2. Preparation of Alg(Liq) capsules by gravitational dripping

CMC solutions of 1% or 2% (w/v) containing 5.5% (w/v) $CaCl_2$ were prepared. To form droplets, the $CaCl_2$–CMC solution was dripped through an injection needle (o.d. = 0.50 mm, i.d. = 0.32 mm), using a microsyringe pump (Model-100, Neuroscience), into 50 ml of 1% (w/v) sodium alginate solution at a flow rate of 1 ml/h. The sodium alginate solution was constantly stirred at about 1000 rpm using a magnetic stirrer in order to prevent the aggregation of the droplets. A dropping height of 6 cm was used to ensure the formation of spherical droplets. Prior to the collection of the formed capsules, the sodium alginate solution was diluted three-fold by adding distilled water and was stirred for 1 min. The capsules were collected by filtration, and rinsed several times by distilled water, followed by a hardening process in a solution of 0.4 M $CaCl_2$ solution for 1 h. The prepared capsules were stored in a refrigerator at 4 °C until used. We refer to the CMC-core/alginate-shell capsule obtained as the Alg(CMC) capsule.

In the CMC-decomposition experiments, the capsules were transferred into cellulase solution of 1% (w/v) for 48 h at 8 °C. We refer to the liquid-core/alginate-shell capsule obtained as the Alg(Liq) capsule.

2.3. Electrostatic atomization

A schematic illustration of the experimental setup for the electrostatic atomization process is shown in Fig. 2. A 2%(w/v) CMC solution containing 5.5% $CaCl_2$ was supplied to a nozzle electrode (o.d. = 0.65 mm, i.d. = 0.40 mm) using a microsyringe pump at a flow rate of 1 ml/h. High voltage from 0 to +4.5 kV DC was applied to the nozzle against a ring ground electrode (i.d. = 15 mm). The distance between the nozzle and the ring ground electrode was fixed to 8.7 mm throughout this study. The $CaCl_2$–CMC solution was electrostatically dripped into 50 ml of 1% (w/v) sodium alginate solution. The subsequent processes to form capsules were the same as those described above.

2.4. Measurement of capsule diameter and shell thickness

The image processing software A-zoukun ver.2.20 (Asahi KASEI Engineering Corporation) was used to