



# Producing liquid-core hydrogel beads by reverse spherification: Effect of secondary gelation on physical properties and release characteristics



Fu-Hsuan Tsai <sup>a,b</sup>, Po-Yuan Chiang <sup>a,\*</sup>, Yutaka Kitamura <sup>c</sup>, Mito Kokawa <sup>c</sup>, M.Z. Islam <sup>b</sup>

<sup>a</sup> Department of Food Science and Biotechnology, National Chung Hsing University, 250 Kuokuang Road, Taichung, 40227, Taiwan, ROC

<sup>b</sup> Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8577, Japan

<sup>c</sup> Faculty of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8577, Japan

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## ABSTRACT

Burdock leaf contains abundant chlorogenic acid (CGA) and phenolic compounds and is a popular material for research. We used reverse spherification, where burdock leaf extracts mixed with calcium ion are dropped into sodium alginate solution to produce liquid-core hydrogel beads (LHB), and evaluated the effect of different calcium concentration in secondary gelation on the swelling capacity, hardness, microstructure, and release kinetics and mechanisms of LHB during thermal and simulated gastrointestinal fluid (*in vitro*) treatments. The LHB were prepared by 0, 0.5, and 1.0 g/100 mL CaCl<sub>2</sub> in secondary gelation, and expressed as CA0, CA0.5, and CA1, respectively. As calcium concentration in secondary gelation increased, flake structure on the surface of LHB disappeared, and a rough, bumpy surface emerged. Furthermore, the stability of LHB increased, the change of swelling capacity and hardness decreased, the number of cavities on the surface of LHB and release rate of CGA during thermal and *in vitro* treatments decreased. The CGA release profile of CA0 conformed to zero-order kinetics model ( $R^2 = 0.990\text{--}0.993$ ) and CA0.5 and CA1 were conformed to Higuchi kinetics model ( $R^2 = 0.899\text{--}0.980$ ). The release exponent ( $n$ ) of CA0 during thermal treatment ranged from 0.525 to 0.597, indicating the release mechanism was anomalous transport, and release mechanisms of CA0.5 and CA1 were Fickian diffusion ( $n = 0.229\text{--}0.373$ ). CA1 exhibited the highest quality among the three conditions, but low release amount and rate of CGA in simulated small intestinal fluid needed improvement.

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## 1. Introduction

Spherification is a technique used in avant-garde and modernist cuisine, which was invented by Pescharde in 1946 and carried forward by elBulli, one of the most distinguished restaurants in the world. It is a technique where a liquid material is coated by a polymer film, forming a sphere with a liquid core (Fu et al., 2014; Hoffman, 2009; Lee & Rogers, 2012). The utilization of hydrogel

**Abbreviations:** CGA, chlorogenic acid; LHB, liquid-core hydrogel beads; SA, sodium alginate; M-block,  $\beta$ -D-mannuronic acid unit of SA; G-blocks,  $\alpha$ -L-guluronic acid unit of SA; RVS, reverse spherification; BLE, burdock leaf extracts; CA0, the LHB prepared by 0 g/100 mL CaCl<sub>2</sub> in secondary gelation; CA0.5, 0.5 g/100 mL CaCl<sub>2</sub> in secondary gelation; CA1, 1 g/100 mL CaCl<sub>2</sub> in secondary gelation; SGF, simulated gastric fluid; SIF, simulated small intestinal fluid; SC, swelling capacity; SEM, scanning electron microscope.

\* Corresponding author. Tel.: +8864 2285 1665; fax: +8864 2285 1665.

E-mail address: [pychiang@dragon.nchu.edu.tw](mailto:pychiang@dragon.nchu.edu.tw) (P.-Y. Chiang).

particles, capsules or microcapsules which could be produced entirely by edible biopolymers such as proteins and polysaccharides, to deliver functional compounds and drugs has attracted attention for decades (Li, Hu, Du, Xiao, & McClements, 2011). Hydrogel particles are often termed as hydrocolloid gel particles or hydrogel beads, and have been used widely in fields such as food technology, biotechnology, medical and pharmaceutical sciences, and waste treatment, with objectives such as treatment of waste water, enzyme immobilization, drug delivery and controlled release, and covering bad flavors of ingredients (Belščak-Cvitanović et al., 2015; Burey, Bhandari, Howes, & Gidley, 2008; Luo, Chen, & Wang, 2005). In brief, spherification is a method of preparing hydrogel particles with a liquid center, namely, liquid-core hydrogel beads (LHB). Although the use of the term spherification has been limited to the field of cooking, we consider it an adequate term to be used in other fields such as food technology since it accurately captures the formation of the hydrogel particle.

Sodium alginate (SA) is composed of (1–4)-linked  $\beta$ -D-mannuronic acid (M-blocks) and  $\alpha$ -L-guluronic acid (G-blocks), and is a biodegradable, low-cost, biocompatible, and non-immunogenic biopolymer that is generally regarded as safe (GRAS) by the FDA. It is widely used to prepare hydrogel beads because it forms gels with multivalent cations (crosslink agents) such as calcium ions under gentle conditions. Gelation occurs while G-blocks coordinate with calcium ions, forming calcium alginate, a three-dimensional gel network known as an egg-box structure (George & Abraham, 2006; Paques, Van Der Linden, Van Rijn, & Sagis, 2014).

Depending on the preparing method, spherification techniques can be divided into two types: basic spherification and reverse spherification (RVS). Taking SA and calcium ion for example, basic spherification refers to the method where the SA solution is injected into the calcium solution. This causes calcium ions to permeate into the SA droplet, and calcium alginate is formed from the surface to inside the droplet (Fig. 1a). Conversely, in RVS, the calcium solution is injected into SA, causing calcium ions to diffuse from the calcium solution to the surrounding SA, and a calcium alginate outer layer is formed (Fig. 1b) (Lee & Rogers, 2012). This study adopted RVS to prepare LHB for the following reasons: in basic spherification, gelation can occur before SA is combined with calcium ions while it is mixed with low pH and low polar materials, such as alcoholic solutions. In contrast, if RVS is used, the calcium solution can be mixed with various materials before being suspended into SA solution.

Previous studies indicate that LHB need an additional hardening process by calcium solution after membrane formation in SA (Dembczynski & Jankowski, 2002; Nussinovitch, Gershon, & Nussinovitch, 1997; Yoo, Seong, Chang, & Park, 1996). However, there is no paper indicating the effect of the additional hardening step on the quality of LHB. Herein, we clearly defined the step of suspending the calcium solution into SA as “first gelation” (Fig. 1b), and the step of additional hardening as “secondary gelation” (Fig. 1c). We provided the first report on the effect of secondary gelation on physical properties of LHB.

First gelation occurs when the core material is extruded into the SA solution. The osmotic gradient between the droplet and SA

solution causes the calcium ions to diffuse from the droplet to the surrounding SA. When G-blocks are coordinated with calcium ions, a water insoluble calcium alginate outer layer is formed. In the following secondary gelation, the semifinished beads are suspended into calcium solution. The osmotic gradient between the semifinished bead and calcium solution causes the calcium ions to permeate into the beads. In brief, the outer layer is formed in first gelation and strengthened in secondary gelation.

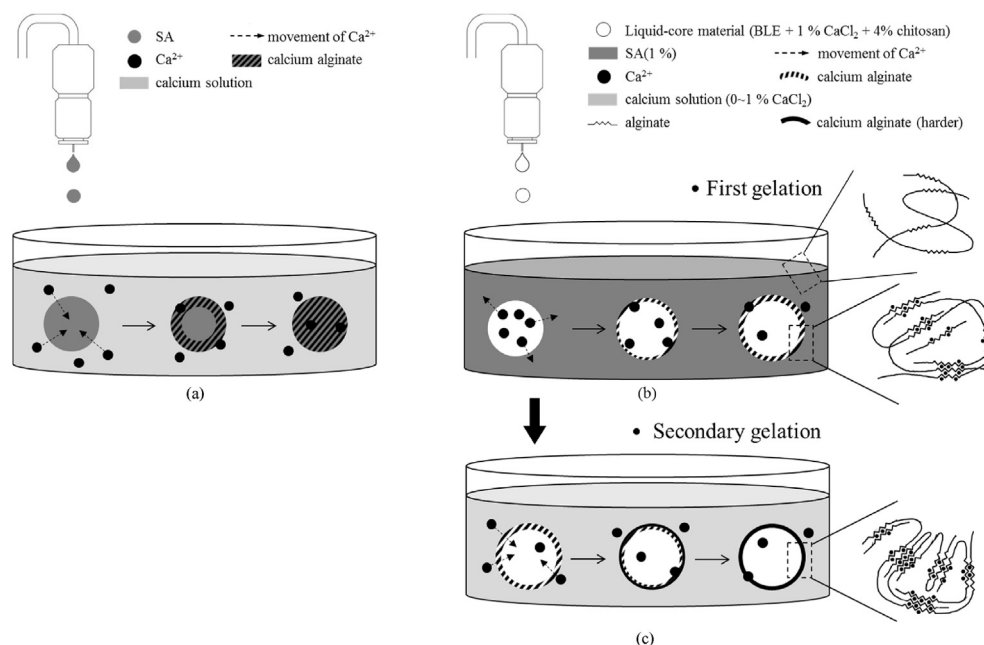
The root of burdock (*Arctium lappa* L.) has been cultivated as an ingredient of beverages, cuisine, functional foods and folk medicines in Asia. On the other hand, the leaf and stem, so-called by-products, are usually disposed as waste. However, they contain abundant phenolic compounds in higher concentrations than the root and have higher antioxidant abilities (Ferracane, Graziani, Gallo, Fogliano, & Ritieni, 2010). We reused these leaves and stems by encapsulating their extracts with alginate by RVS and produced a functional compound carrier.

In this study, LHB were made by RVS with different concentration of calcium solution in secondary gelation. Swelling capacity, hardness, microstructure, and chlorogenic acid (CGA) release amount during simulated gastrointestinal fluid (*in vitro*) and thermal treatments of the LHB were evaluated and analyzed. Release kinetics of LHB were characterized by zero-order, first-order, and Higuchi kinetics model and Korsmeyer–Peppas model.

## 2. Materials and methods

### 2.1. Materials

Burdock leaves and stem, by-product and wastes during harvesting and processing, were obtained from a local farmer. Following washing and cutting, the leaves were stored at  $-80^{\circ}\text{C}$ . In this study, burdock leaf extracts (BLE) were mixed with calcium chloride and then extruded into SA by a coaxial bead generator with gentle stirring. In this case, burdock leaf extracts mixed with calcium chloride solution needed to contain a thickener to prevent the liquid-core being deformed by shear stress when suspended in the alginate solution. Chitosan was used as a thickener in this study.



**Fig. 1.** Gelation mechanism of (a) basic spherification; (b) first gelation of reverse spherification; (c) secondary gelation of reverse spherification. The materials and their concentration be used in the study were given in parenthesis.

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