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Scientific Paper

Effect of calcium source and exposure-time on basic caviar spherification using sodium alginate

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Abstract

Gelation speed is directly proportional to the concentration of calcium. Although the kinetics of gelation are altered by the source of calcium, the final alginate gel strength nor the resistance to calcium diffusion are altered. Calcium chloride reaches a gel strength plateau fastest (~100 s), followed by calcium lactate (~500 s) and calcium gluconoate (~2000 s). Calcium chloride is the best option when the bitter taste can be masked and a fast throughput is required, while calcium gluconoate may have an advantage when the membrane thickness/hardness needs to be manipulated.

Keywords: Spherification; Calcium chloride; Calcium lactate; Calcium gluconate; Sodium alginate

Introduction

Spherification, an old technique in the world of modernist cuisine, was pioneered at El Bulli in 2003 and is a cornerstone in experimental kitchens across the world (Vega and Castells, 2012). In modernist cuisine this technique is central to the formation of faux caviar, eggs, gnocchi and ravioli. These spherical elements of a dish range from having a thin membrane, which are filled with a non-gelled liquid to elements that are gelled throughout. Although alginate gels, more specifically partially gelled orbs using alginates and a calcium source, were introduced in 2003 the technology has been around for decades in the food industry, which first used alginates to restructure red peppers for manufacturing pimentos in olives. Unlike most edible gels, which are solid throughout, alginate spheres typically contain a physical outer gel membrane with a liquid core.

Alginates are an attractive ingredient because they are derived from marine brown algae (Mabeau and Fleurence, 1993) making them non-toxic, biodegradable and naturally occurring (Silva et al., 2006). They are classified as a hydrocolloid, which are large water-soluble molecules that enhance the viscosity and are often used as texturizers (Vilgis, 2012). Alginates are unbranched copolymers of 1,4-linked-β-D-mannuronic acid and α-L-guluronic acid (Chrastil, 1991). Alginates have an affinity for alkaline earth metals and the affinity increases in the order $Mg^{2+} \ll Ca^{2+} < Sr^{2+} < Ba^{2+}$ (Kohn, 1975). In the absence of divalent ions (i.e., Ca^{2+}, Mg^{2+}) alginates only enhance the viscosity; however, when in the presence of divalent ions, especially calcium, they form strong gels. In the deprotonated state, at pH levels less than 5, the regions of the copolymer concentrated in guluronic acid (i.e., depleted in mannuronic acid) are able to strongly interact with calcium forming a divalent salt bridge between alginate polymers (Martinsen et al., 1989). Therefore, the gel forming properties of alginates are derived from their capacity to bind a large number of divalent ions and the gel strength is correlated with the proportion and length of the guluronic acid blocks

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(G-blocks) in their polymeric chains (Mancini and McHugh, 2000). The salt bridges that are responsible for the skin formation (outer gel layer) of alginate spheres have been described using the "egg-box" model (Fig. 1).

Spherification can occur using the basic technique, where a liquid containing sodium alginate is submersed and cooked in a bath of calcium. Herein, cooked does not refer to a tradition thermal process but instead the gelation process which is often described as chemical cooking. The reverse or external technique utilizes a calcium source added to the edible liquid and is cooked in a sodium alginate bath. In basic spherification, a very thin membrane is formed around the liquid. Typically calcium chloride is used as the cooking agent because it reacts rapidly with the alginate forming the divalent salt bridges and gel. External gelation results in Ca^{2+} first cross-linking at the film surface drawing the polymer chains closer together. This results in the formation of a less permeable surface slowing the diffusion of Ca^{2+} (Chan et al., 2006). In reverse spherification, a calcium source is typically added to the edible liquid, which must either be calcium gluconoate or calcium lactate, and is cooked in an alginate bath. Calcium chloride is probative for use in reverse spherification due to the bitter taste it imparts on the food. When alginates are applied from the cooking solution, typically thicker membranes are formed; however; the versatility of the ingredients that may be manipulated using the reverse technique is much greater compared to basic spherification.

Depending on the source of calcium, the gelation process may be further sub-categorized into internal and diffusion set gels (Mancini and McHugh, 2000). Diffusion set gels utilize readily soluble calcium salts. Salts solutions are used in the setting bath and small drops of sodium alginate solution are extruded into the bath. For internal set gels, the calcium is released in a controlled manner simultaneously throughout the entire system. This is typically achieved using calcium sulfate dihydrate in neutral gels and dicalcium phosphate in acid products (Mancini and McHugh, 2000; Liu et al., 2002). Internally set gels produce a more homogeneous network, which forms a less dense matrix than diffusion set gels (Choi et al., 2002; Vanderberg and De La Noüe, 2001; Quong et al., 1997).

In Nathans Myhrvold's Modernist Cuisine the authors have artistically assembled a detailed repertoire of uses and methods for spherification (Myhrovold et al., 2011). However, questions remain unanswered about the spherification technique. Specifically, how does calcium source and exposure time influence gel formation? Herein, we provide the first report on the effect of the calcium source on the cooking time and hardness of the gel.

Methods

Pre-hydrated sodium alginate (Tica-algin® 400F, White Marsh, MD) was obtained from TIC Gums and was used as received. Food grade calcium chloride (Terra Spice Company, Walkerton, IN), calcium lactate (Terra Spice Company, Walkerton, IN) and calcium gluconoate (Mhcmp Industrial Co., Ltd., Xiamen, China) were also used without further purification. Sodium alginate was mixed at 1 wt% in hot water

Fig. 2. Faux caviar created from 1 wt% calcium chloride and 1 wt% sodium alginate.

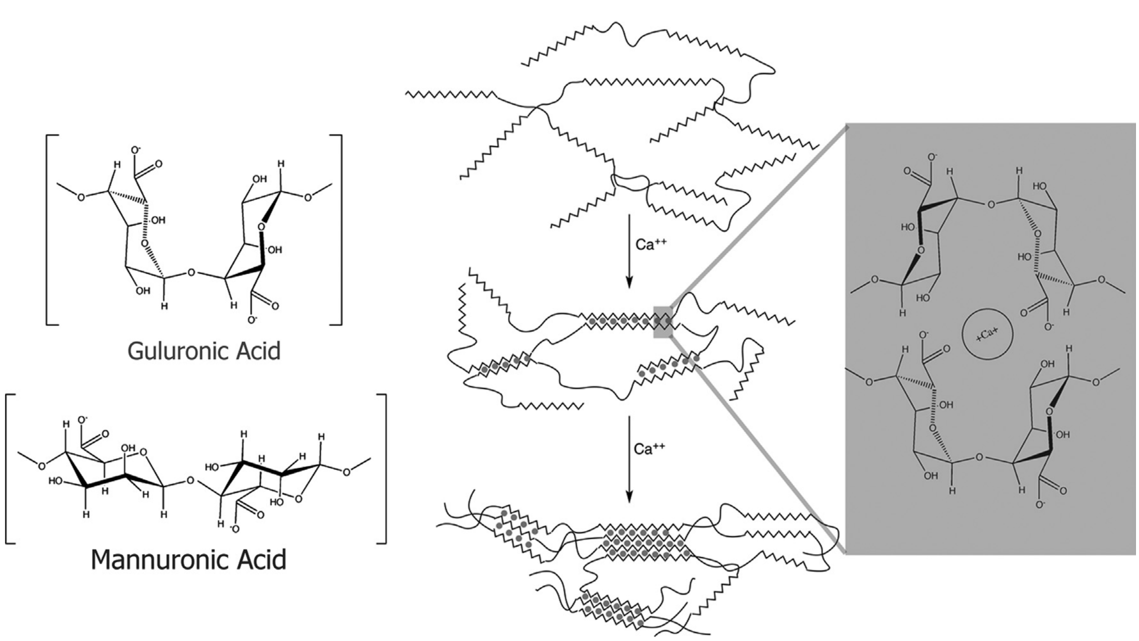

Fig. 1. Chemical structure of monomeric units in alginate and a diagrammatic representation of the divalent ion salt bridges (i.e., the "egg-box" model).