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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 gluconate (~ 2000 s). Calcium chloride is the best option when the bitter taste can be masked and a fast throughput is required, while calcium gluconate may have an advantage when the membrane thickness/hardness needs to be manipulated.
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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 gluconate 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 gluconate (Mhcmp Industrial Co., Ltd., Xiamen, China) were also used without further purification. Sodium alginate was mixed at 1 wt% in hot water

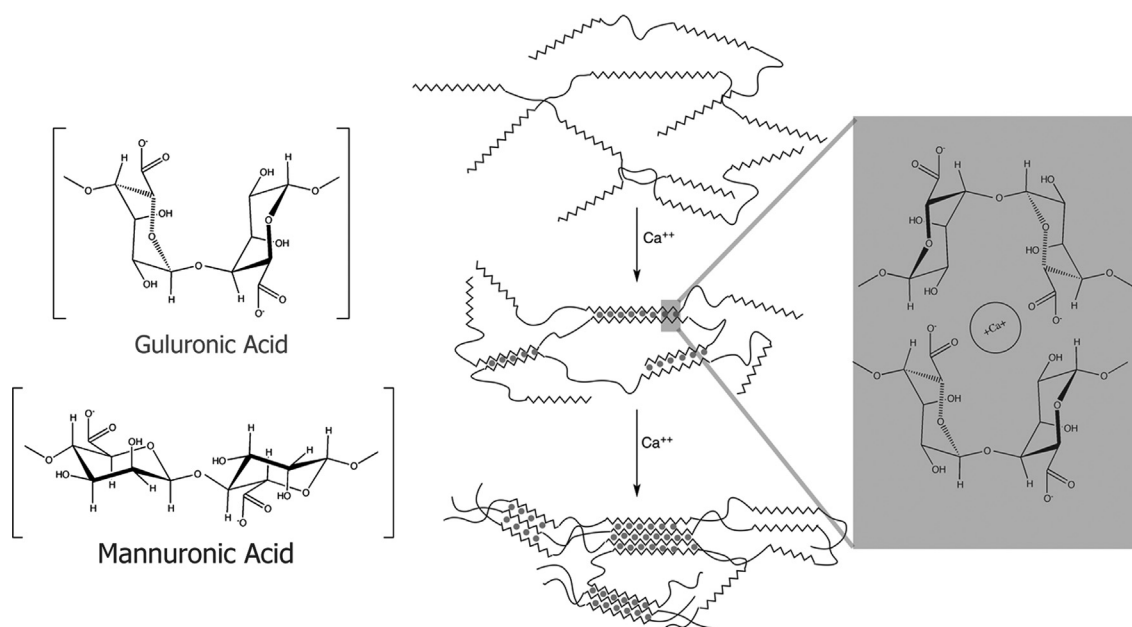Fig. 2. Faux caviar created from 1 wt% calcium chloride and 1 wt% sodium alginate.

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).
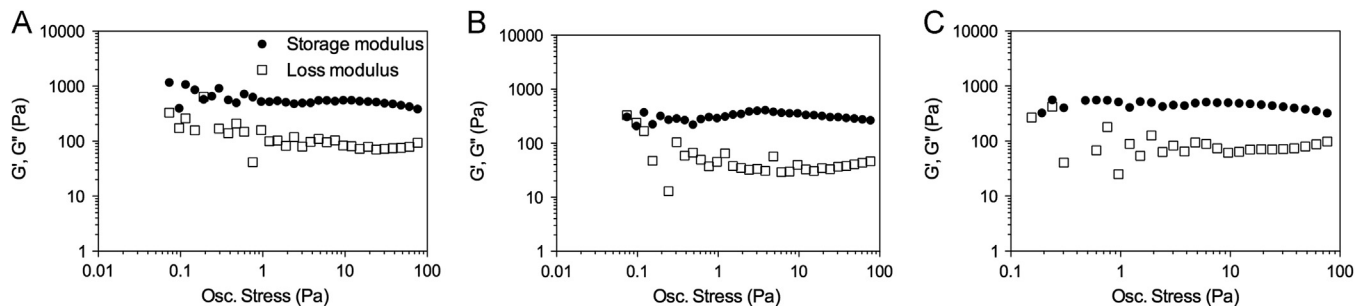
Fig. 3. Rheological assessment of the linear viscoelastic region of alginate gels exposed to (A) 1 wt% calcium chloride solution, (B) 1 wt% calcium lactate solution and (C) 1 wt% calcium gluconate for 4000 s.

($\sim$80 °C) using an ultra turrax mixer (T25 basic model, IKA, Wilminton, NC) for 5 min and was then allowed to hydrate for 24 h before cooking (Fig. 2). Calcium salt solutions were made at 1 wt% in water and were stirred using a magnetic stirrer until the solution was clear and was then stored for 24 h. A single drop of alginate solution was added to the different calcium salt baths and cooked between 1 and 4000 s. The diameter of the faux caviar was measured using a vernier caliper and caviar that were 8 mm in diameter, were selected for rheological assessment.

Small deformation oscillatory rheology (AR-G2, TA Instruments, New Castle, DE) was utilized to determine the elastic (G') and loss (G'') modulus using an 8 mm crosshatched stainless steel spindle and sandblasted flat parallel plate. G' and G'' were both obtained from the linear viscoelastic region using a controlled stress oscillatory sweep at 1 Hz and 25 °C. Alginate gels are often described as viscoelastic materials exhibiting both a viscous and elastic component when exposed to a stress or deformation. G', the elastic component, is a measure of the hardness; G'' is the viscous component, which is a measure of the viscous dissipation.

Discussion

As the alginate solution was added drop-wise into the calcium bath, a gelled membrane instantly formed around the caviar sphere. Regardless of the calcium source, the linear viscoelastic region (LVR) and magnitude of G' and G'' were not statistically ($p < 0.05$) different (Fig. 3A–C) after 4000 s of cooking. Since G' is greater than G'' and these parameters are frequency independent, they are classified as a strong gels using Clark and Ross-Murphy's classical definitions of gels (Clark and Ross-Murphy, 1987). After 4000 s, the LVR extends from 0.01 Pa to 100 Pa. As exposure time decreased, the LVR got shorter and the hardness decreases. It is important to note that regardless of the exposure time, G' and G'' were obtained from the LVR for subsequent analysis.

Calcium chloride rapidly dissociates when added to solution because of its high solubility, making it an attractive calcium source for spherification. Although commonly used in basic spherification the applications in reverse spherification are limited due to the bitter taste it contributes to the food. Upon addition of the alginate solution to the calcium bath, chemical cooking begins instantaneously and proceeds very rapidly

(Fig. 4A,B). After 100 s of exposure of an 8 mm caviar alginate to the 1 wt% calcium chloride bath, the elastic properties of the gel remained constant. This has tremendous advantages because the rapid gelation reduces preparation time and ensures a consistent product. In a calcium lactate bath, the calcium solubility (8 g/100 ml) is reduced compared to calcium chloride (75 g/100 ml), however there is no bitter perception. Compared to the calcium chloride solution, the alginate caviar takes much longer to reach the maximum hardness (G') (Fig. 4C,D). After approximately 500 s G' remains constant. The least soluble of the calcium sources is calcium gluconate (3 g/100 ml) (Fig. 4E,F). G' does not reach the maximum value (i.e., maximum hardness) until approximately 3000 s. Although this may be problematic in a facility that requires a fast throughput, there may be advantages in being able to further manipulate the physical properties of the caviar to tailor its sensory properties.

When calcium is exposed to the interface of the alginate sphere it will react with the guluronic acid enriched zones forming egg-box junctions and ultimately leads to gelation. Upon mixing, there is an osmotic gradient between the inner sphere and the cooking bath providing a driving force for the calcium to migrate through the gelled alginate matrix. The calcium diffuses through the matrix until it reaches area where it is able to form a physical non-covalent interaction with alginate.

The process of diffusion through alginate gels has been modeled using a binomial diffusion equation. Herein, we assume that modeling diffusion of calcium is generated by concentration gradient that is time dependent and leads to a correlation between the diffusion distance and G'. Using this assumptions we can adapt the binomial diffusion equation to account for G' which has been used for numerous other diffusion-limited reactions and takes the following form (Chrastil, 1991; Chrastil, 1990):

$$G' = G'_{max}[1-e^{-kt}]^n \qquad (1)$$

where t is time, G' is a measure of the hardness, which is correlated to the diffusion process for the calcium ions, G'_{max} is the maximum G' at $t \sim \infty$, k is the gelation rate constant and n is the heterogeneous structural resistance constant which is indirectly proportional to the resistance of calcium diffusion. As calcium diffuses into the alginate solution it will cross-link the polymers increasing the elastic component of the gel. Statistically ($p < 0.05$) there was no difference in the maximum
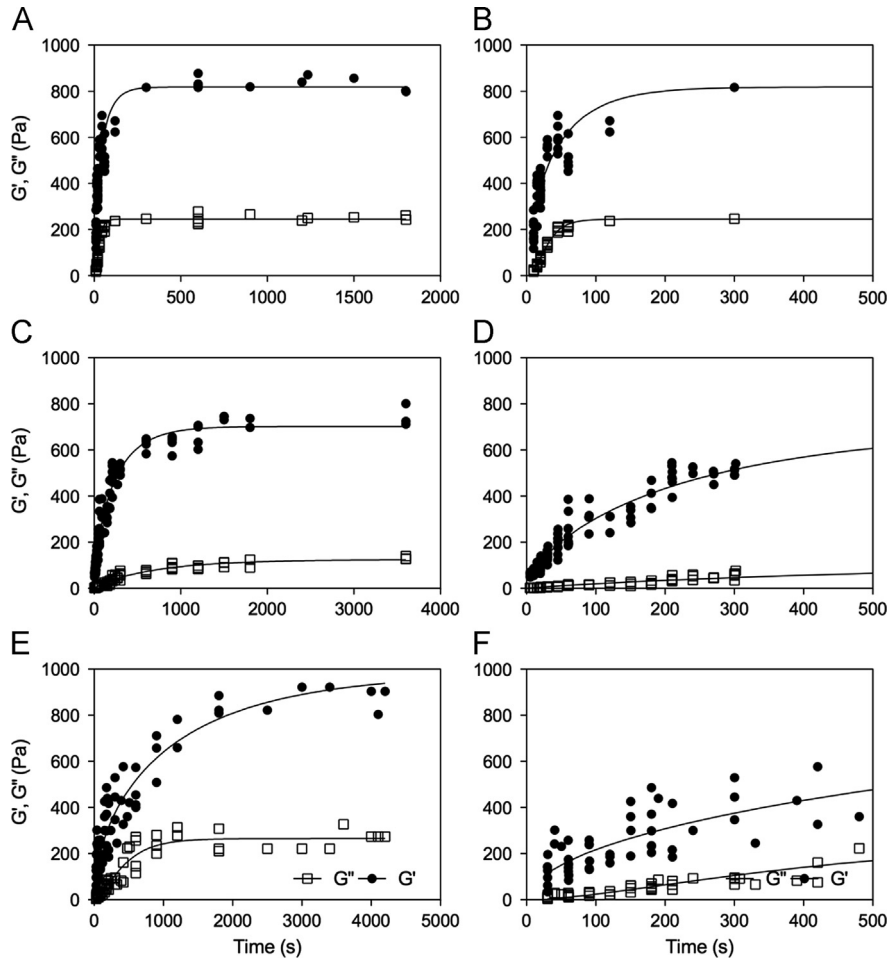
Fig. 4. Evolution of the storage and loss modulus of 8 mm diameter alginate spheres exposed to (A, B) 1 wt% calcium chloride solution, (C, D) 1 wt% calcium lactate solution, and (E, F) 1 wt% calcium gluconate solution for times ranging from 1 to 4000 s.
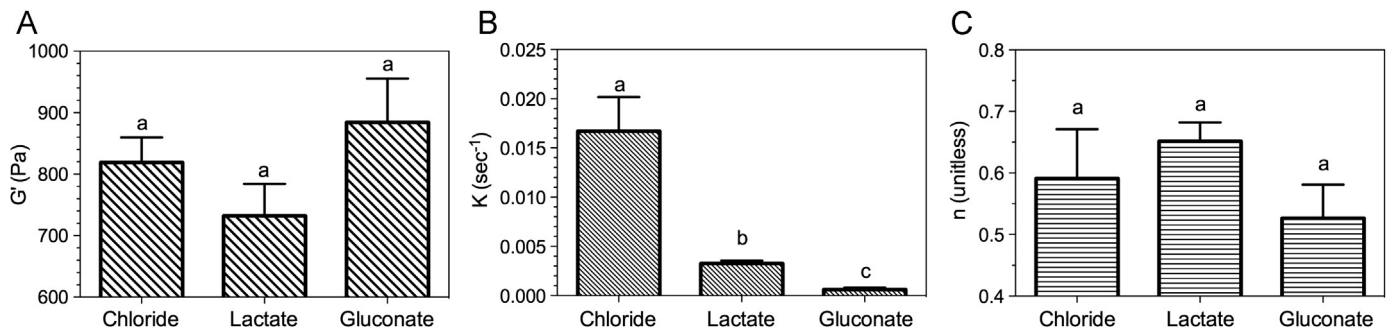

Fig. 5. Fitted parameters calculated using the binomial diffusion equation derived for diffusion-limited reactions for 1 wt% sodium alginate exposed to different 1 wt% calcium salt solutions.

hardness (G') obtained using different calcium salts, which is expected (Fig. 5A). However, the rate constants (k) were all statistically different from one and other (Fig. 5B). Finally, the resistance to diffusion is not statically different for the gels (Fig. 5C). Therefore, it is possible to control the rate of the reaction without altering the final physical properties of the gel.

The rate of calcium diffusion closely follows the concentration of calcium ions present in solution (Fig. 6). All salt solutions studies were examined below the solubility limit of

the salt. For calcium chloride the solubility is 75 g/100 ml, for calcium lactate it is 8 g/100 ml and for calcium gluconate it is 3 g/100 ml at 20 °C. For this study the overall weight concentration of the salt was maintained constant at 1 wt%. However the molar mass of the anion varied which meant that the alginate solution was exposed to different concentrations of Ca^{2+} in the setting bath. The Ca^{2+} concentration was calculated to be 0.09 wt%, 0.18 wt% and 0.36 wt% for calcium gluconate, calcium lactate and calcium chloride, respectively.
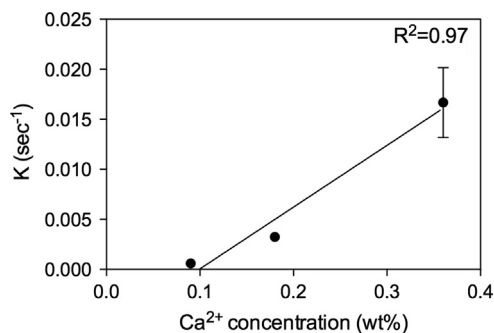
Fig. 6. Gelation rate constant for calcium gluconate, calcium lactate and calcium chloride as a function Ca^{2+} concentration.

It was found that the rate of gelation was positively correlated with the concentration of Ca^{2+} ions in the setting bath.

Conclusion

The rate of gelation is greatest for calcium chloride and is slowest for calcium gluconoate. Although the gelation kinetics are affected by the source of calcium neither the final alginate gel strength nor the heterogeneous structural resistance to calcium diffusion are altered. Calcium chloride reaches a maximum hardness after 100 s, while calcium lactate takes 500 s and calcium gluconoate takes well over 3000 s. For fast throughput, calcium chloride is the best option when the bitter taste can be masked, while for a tailorable membrane thickness/hardness calcium gluconoate may be preferable.

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