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Development of edible bubbles of calcium alginate for encapsulating energy drinks

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ABSTRACT

The edible bubbles of calcium alginate for encapsulating energy drinks were fabricated by frozen reverse spherification technique. The influences of bubble forming time, calcium salt type and concentration, and concentration of sodium alginate on the physicochemical characteristics, for example, size, shape, mechanical strength, and calcium alginate membrane thickness, were studied. To examine the feasibility of bubble formation, several calcium salts like calcium lactate, calcium lactate gluconate, and calcium chloride were tested. It became apparent that the concentration elevation of sodium alginate and calcium salts increased the shell thickness and mechanical strength. The bubble spheres with sphericity index of 0.98-1.00 were emerged and their size varied from 49.3 to 52.1 mm. The justified preparation for encapsulating energy drinks was 1% w/v calcium lactate gluconate, 1% w/v sodium alginate, and 10-min bubble forming time that provided a bubble thickness of 0.46 mm and mechanical strength of 0.94 N/mm².

Keywords: bubble, reverse spherification, calcium lactate gluconate, sodium alginate

1. INTRODUCTION

Recently, to totally meet the needs of people's lifestyles, a single-use plastic bottle has been considered the packaging of choice for food, including energy drinks and water. The plastic packaging contains a significant amount of hazardous material that is potentially detrimental to humans and other animals. Furthermore, plastic is not biodegradable and contributes to global environmental contamination.

The utilization of renewable resources, which can lessen waste disposal issues, is being investigated for the production of biopolymer films and coatings. These films are particularly ideal for food and nonfood packaging applications because to their renewability, degradability, and edibility. Edible films and coatings play an essential role in the quality, safety, transportation, storage, and presentation of a wide variety of fresh and processed foods. They can reduce primary alteration by preventing moisture losses and lowering undesirable chemical reaction rates (Tavassoli-Kafrani et al., 2016).

Water-soluble hydrocolloids, such as polysaccharides, frequently provide edible films and coatings superior mechanical characteristics than hydrophobic compounds

(Tavassoli-Kafrani et al., 2016; Koedcharoenporn and Siriwongwilaichat, 2019). Sodium alginate has recently received a lot of interest as a source of film-forming ingredients. Sodium alginate, a naturally occurring anionic polymer from seaweed, is versatile in food and pharmaceutical applications (Mabeau and Fleurence, 1993; Sriamornsak et al., 2006; Silva et al., 2006; Gong et al., 2011). Its responsibility encompasses binder, stabilizer, thickening agent and viscosity inducing agent. Affectionately, it is biodegradable, generally safe and cheap. Sodium alginate structural characterization reveals a linear polysaccharide composing of 1,4 β-D-mannuronic and 1,4 α-L-guluronic acid unit (Smardel et al., 2008). Alginates demonstrate stronger affinity with alkaline earth metals in the following order: $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$ (Kohn, 1975).

Mixing alginates with divalent cations, especially calcium, intensifies the viscosity of liquid and transform into strong gel due to alginate polymer crosslinking. A divalent salt bridge between alginate copolymer results from an immense interaction between calcium and deprotonated form of guluronic acid in alginate at pH < 5 (Martinsen et al., 1989). As a result, the ability of alginates to attach a substantial number of divalent ions is crucial to their ability to form gels. The proportion and length of the guluronic acid blocks (G-blocks) in their polymeric chains correlate with the gel strength of the substance (Mancini and McHugh, 2000). The "egg-box" model by Lee and Rogers (2012) has been employed to illustrate the salt bridges for the outer gel layer of alginate spheres.

Recently, spherification technique is accepted for producing semi-solid and/or frozen spheres containing a non-gel liquid as core body coating with thin membrane layer. This sphere will provoke a burst-in-the-mouth phenomenon when exposed in liquid. Dhrubo et al. (2017) has delineated the procedure for encapsulating a liquid inside a gelled sphere and found that the flavor and texture of sphere was affected by the spherification technique. Calcium alginate gel emerging from gelification or cross-linking could be utilized as thin membrane layer of sphere. Spherification techniques are classified into two types: basic spherification and reverse spherification. The reverse spherification technique is performed by dissolving a calcium source in edible liquid before submerging into sodium alginate solution. Contrarily, the basic spherification is accomplished by mixing edible liquid and gelling solutions such as sodium alginate before soaking in calcium chloride solution to create a thin gel shell (Lee and Rogers, 2012). Thus, it is intriguing to apply this technique to encapsulate energy drinks with the right qualities and customer acceptance.

Recently, sweet water balls prepared by basic spherification technique (Gaikwad et al., 2019) and mock pomegranate seeds balls prepared by reverse spherification technique (Dholvitayakhun and Pumpho, 2018) were reported. Nevertheless, the sphere should be consumed instantly due to its fast destruction. Therefore, the goal of this research was to use frozen reverse spherification to create edible bubbles that would encapsulate energy drinks. On the physicochemical properties of the edible bubbles, the impacts of sodium alginate concentration, bubble forming time, calcium salt type (calcium chloride, calcium lactate, and calcium lactate gluconate), and calcium salt concentration were also investigated.

2. MATERIALS AND METHODS

2.1 Materials

Sodium alginate (Manugel® DMB) was obtained from International Specialty Products (Bangkok, Thailand). Dextrose, calcium chloride, calcium lactate and calcium lactate gluconate were obtained from P.C. Drug Center Co., Ltd. (Bangkok, Thailand). Juice was purchased from a local market in Nakhon Pathom, Thailand. All other chemicals were of reagent grade.

2.2 Preparation of edible bubbles by frozen reverse spherification technique

Calcium salts (1% w/v, calcium equivalent) and dextrose (10% w/v) were dissolved and mixed with 10% v/v fruit juice and they were poured into bubble ice tray. After that they were frozen at -8°C for 24 h. The frozen liquids were immersed into the bath containing various concentrations (0.5-2.0% w/v) of sodium alginate solution for 10 min to form the bubble membrane. The obtained bubbles were then removed from the bath and transferred to a distilled water bath to rinse off any excess sodium alginate. To investigate the effect of immersing time, the bubble formation time was varied from 5-15 min using 1% w/v sodium alginate. Different calcium salts were also compared, including calcium chloride, calcium lactate, and calcium lactate gluconate.

2.3 Physical properties determination

The diameter of bubbles was measured using a digital vernier caliper (Digital Caliper, China), and their weights were weighed with a Mettler analytical balance (model AG204, Mettler–Toledo, Switzerland); the findings were reported as the mean of six measurements. The bubble shell thickness was measured with a caliper (Mitutoyo Dial Thickness Gauge, Mitutoyo, Japan), and the findings were represented as the mean of ten measurements. Sphericity index was calculated from Equation (1) (Cruz-Matías et al., 2019):

$$Sphericity\ index\ (\psi) = \frac{S_n}{S} = \frac{\sqrt[3]{36\pi V^2}}{S} \quad (1)$$

2.4 Mechanical properties testing

Using a TA-XT Plus texture analyzer (Stable Micro Systems, England) and a spherical probe (P/5s, diameter 5.0 mm), the maximum force, strength, and Young's modulus of the bubble shells were measured in order to explore their mechanical characteristics. The compression mode was performed using pre-test speed, test speed and post-test speed of 1.0, 2.0 and 10.0 mm/s, respectively and trigger force of 0.04903 N.

2.5 Measurement of pH

The pH measurement of the energy drink inside the bubbles (i.e., before and after burst of bubble) was made using a calibrated desktop pH meter (Mettler Toledo, Greifensee, Switzerland) at 25°C.

2.6 Bubble syneresis

The percentage relative weight change was used to describe the syneresis of the bubbles which calculated from Equation (2):

$$Weight\ change\ (\%) = \frac{W_t}{W_0} \cdot 100 \quad (2)$$

where W_t is final weight (g), and W_o is initial weight (g).

2.7 Statistical analysis

Minitab version 19 for Windows (SPSS Inc., USA) was used to run ANOVA and Levene's test for variance homogeneity. Post hoc testing (p<0.05) for multiple comparisons was carried out using either the Scheffé or Games–Howell tests, depending on whether Levene's test was insignificant or significant, respectively.

3. RESULTS AND DISCUSSION

3.1 Preparation and physical properties of edible bubbles of calcium alginate

Sodium alginate is generally recognized as safe material, as defined by United States Food and Drug Administration, thereby it is considered as edible films and coatings (Tavassoli-Kafrani et al., 2016). The sodium alginate used in all bubble formulations has previously been described in terms of mannuronic/guluronic acid ratio and viscosity at 1% (0.59 and 300 cps, respectively). In this study, sodium alginate was used to prepare calcium alginate bubbles by frozen reverse spherification method. Calcium salt was added to the solution of fruit juice and sugar and then frozen; the frozen liquids were dipped into various concentrations of sodium alginate solution in order to create the shell or membrane. The bubbles are best served immediately or can be stored temporarily in the fruit juice base. Figure 1 shows appearance of frozen and edible bubbles containing 10% v/v fruit juice and 10% w/v dextrose. It is clearly seen that the edible bubbles had a clear and translucent surface with liquid inside (Figure 1b). The prepared edible bubbles exhibited a spherical shape, as shown by the sphericity index close to 1 (Table 1). The shell thickness and the diameter of bubble were 0.92±0.06 mm and 49.97±0.12 mm, respectively (Table 1). Increasing the sodium alginate concentration resulted in a slight increase in shell thickness, which resulted in an increase in maximum force and mechanical strength of the bubbles.

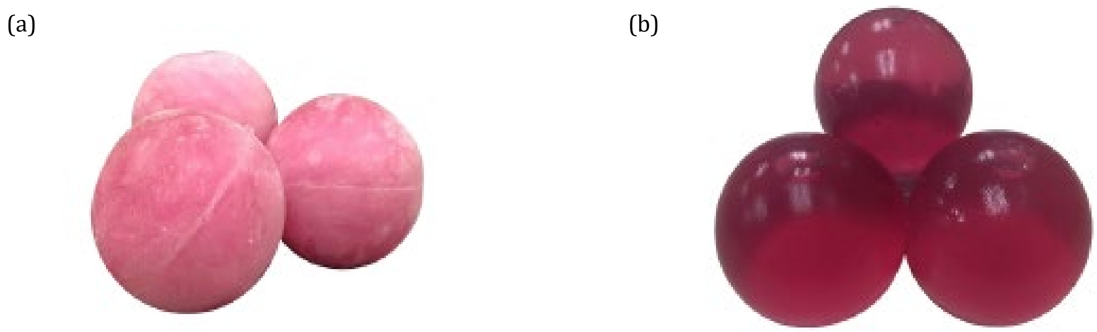

Figure 1. Photos showing the appearance of bubbles prepared by frozen reverse spherification technique; (a) frozen bubbles, (b) edible bubbles

Table 1. Impact of sodium alginate concentration on the physical and mechanical properties of the edible bubbles

Properties	Sodium alginate concentration (% w/v)			
	0.5	**0.75**	**1.0**	**2.0**
Sphericity index	0.98±0.01	1.00±0.00	0.99±0.00	0.99±0.00
Diameter (mm)	0.35±0.04	0.44±0.03	0.67±0.01	1.2±0.08
Shell thickness (mm)	0.77±0.06	0.81±0.02	0.92±0.06	0.98±0.11
Maximum force (N)	0.61±0.06	0.78±0.04	1.19±0.01	2.12±0.14
Mechanical strength (N/mm^2)	49.6±0.35	50.33±0.06	49.97±0.12	51.57±0.25
Young's modulus (N/mm^2)	0.01±0.00	0.01±0.00	0.02±0.00	0.02±0.01

The pH of the energy drink before and after bubble bursting did not differ significantly (p<0.05) for any of the calcium salts (Figure 2). For those created with calcium chloride at 0.5, 1 and 1.5% w/v, the pH of the energy drink after bubble breaking was 3.77, 3.58, and 3.55, respectively. After bubble bursting, calcium lactate had a pH of 5.27-5.70 while calcium lactate gluconate provided the pH of 5.17-5.72, which is significantly higher (p>0.05) than calcium chloride (Figure 2). The higher pH of the energy drink in the bubbles using calcium lactate and calcium lactate gluconate, compared to those using calcium chloride, could be due to the high pH of lactate salt or lactate gluconate salt (Lovera et al., 2014).

Cross-linked alginate gel is generated during the spherification process only when particular ions, such as calcium, are present (Mancini and McHugh, 2000). Calcium chloride is frequently chosen because it can quickly create gel by bridging with alginate. Since of its great solubility, an intriguing calcium source for spherification is calcium chloride. It immediately segregates when it was incorporated to solution (Lee and Rogers, 2012). However, the pH of the bubbles using calcium chloride, after the bubble burst, was relatively low (Figure 2), which may irritate the oral mucous membrane.

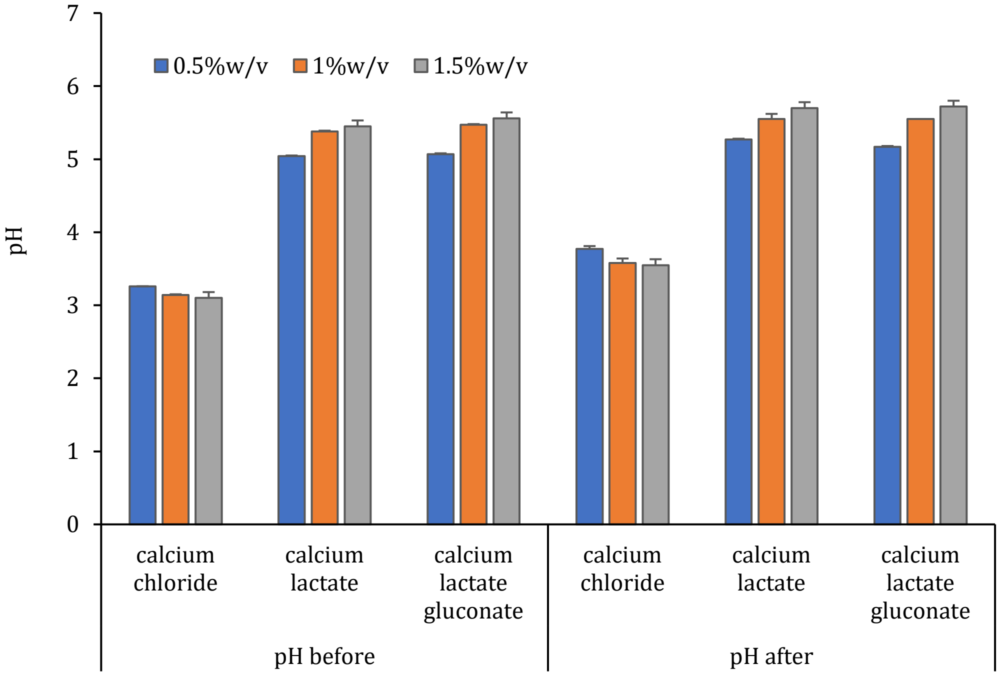

Figure 2. Impact of type and concentration of calcium salt on pH of the energy drink before and after bubble bursting

3.2 Mechanical properties of bubble shells

It is essential to choose edible bubbles that are easy to rupture yet have quite enough membrane strength to remain stable as a spherical ball during storage. As a result, for edible bubbles, the mechanical parameters of the bubble shells were measured using maximum force, strength, and Young's modulus. The maximum force and mechanical strength increased with increasing sodium alginate concentration, but the modulus did not change significantly, as indicated in Table 1. Previous research found that the mechanical properties of a gel of calcium alginate increased in direct proportion to the square of the alginate concentration (Yamagiwa et al., 1992). This reflects the fact that formation of calcium alginate gel is a bimolecular mechanism (Martinsen et al., 1989; Mancini and McHugh, 2000). As shown in Table 2, increasing the immersion time of frozen bubbles in sodium alginate resulted in the increase of the maximum force, mechanical strength, and thickness of bubble shells. The effect of immersion time on bubble shell thickness was comparable to that reported by Gaikwad et al. (2019). The bubble shell was reinforced due to the cross-linking between guluronic groups of sodium alginate and calcium ions (Gaikwad et al., 2019). The cross-linking reaction increased when immersion time was increased.

Table 2. Impact of immersion time on the bubbles' physical and mechanical properties of the edible bubbles

Properties	Time of immersion (min)		
	5	**10**	**15**
Sphericity index	1.00±0.00	1.00±0.00	0.99±0.00
Diameter (mm)	0.34±0.03	0.67±0.01	0.86±0.26
Shell thickness (mm)	0.42±0.05	0.92±0.06	0.87±0.14
Maximum force (N)	0.96±0.33	1.19±0.01	1.52±0.45
Mechanical strength (N/mm^2)	48.30±0.36	49.97±0.12	50.43±0.25
Young's modulus (N/mm^2)	0.02±0.00	0.02±0.00	0.02±0.00

Note: The bubble formation time was varied from 5-15 min using 1% w/v sodium alginate.

According to the findings, increasing the immersion time in 1% w/v sodium alginate increased shell thickness, resulting in an increase in maximum force and mechanical strength of the bubbles. A bubble forming time of 10 min provided the acceptable mechanical properties (maximum force more than 0.5 N), whereas sodium alginate at a concentration of 2% w/v or a bubble forming time of 15 min exhibited a stronger membrane that may be more difficult to burst.

The most important decision to make when attempting to generate edible bubbles is which calcium salts to use. In this research, different types of calcium salts were investigated. It was discovered that the sort of calcium salt used affected how strong the bubbles with energy drink were. When compared to calcium lactate and calcium lactate gluconate at 0.5, 1 and 1.5% w/v, calcium chloride gave the highest maximum force of 0.51, 0.67 and 0.79 N and mechanical strength of 1.09, 1.18 and 1.28 N/mm^2, respectively, as shown in Figure 3. This is most likely due to the fact that there is the high calcium content (36%) and great water solubility of calcium chloride, whereas calcium lactate has 13% calcium and somewhat soluble in room temperature water, and calcium lactate gluconate has 9% calcium (Trailokya et al., 2017; Weerapol et al., 2010). In terms of taste, calcium chloride has an unpleasant taste, but calcium lactate does not necessarily taste bitter or unpleasant, and calcium lactate gluconate has no perceptible taste (Ecarma and Nolden, 2021). As a result, calcium chloride might not be a good choice, in terms of taste, for edible bubbles.

The higher the calcium salts concentration, the stronger the membrane of bubble, as measured by maximum force value and mechanical strength value. Calcium cross-links the polymers as it diffuses into the alginate solution, enhancing the gel's elastic component. Because of its high solubility, calcium chloride has the fastest gelation rate (Lee and Rogers, 2012). The bubble membrane generated from calcium lactate demonstrated a relatively low mechanical strength (0.80-1.04 N/mm^2) and maximum force (0.42-0.62 N). Compared to calcium lactate, calcium lactate gluconate showed a greater bubble membrane strength. Calcium lactate gluconate produced bubble membrane with a maximum force and mechanical strength of 0.38-0.75 N and 0.73-1.33 N/mm^2. Calcium concentrations of 0.5, 1 and 1.5% w/v, respectively, resulted in bubble shell thicknesses of 0.51, 0.72, and 0.90 mm for calcium chloride, 0.33, 0.43, and 0.51 mm for calcium lactate gluconate and 0.39, 0.45, and 0.52 mm for calcium lactate. All bubble shells had a Young's modulus of roughly 0.02 N/mm^2. The sphericity value of 0.98 to 1.00 indicated that the bubbles were round and ranged in size from 49.3 to 52.1 mm.

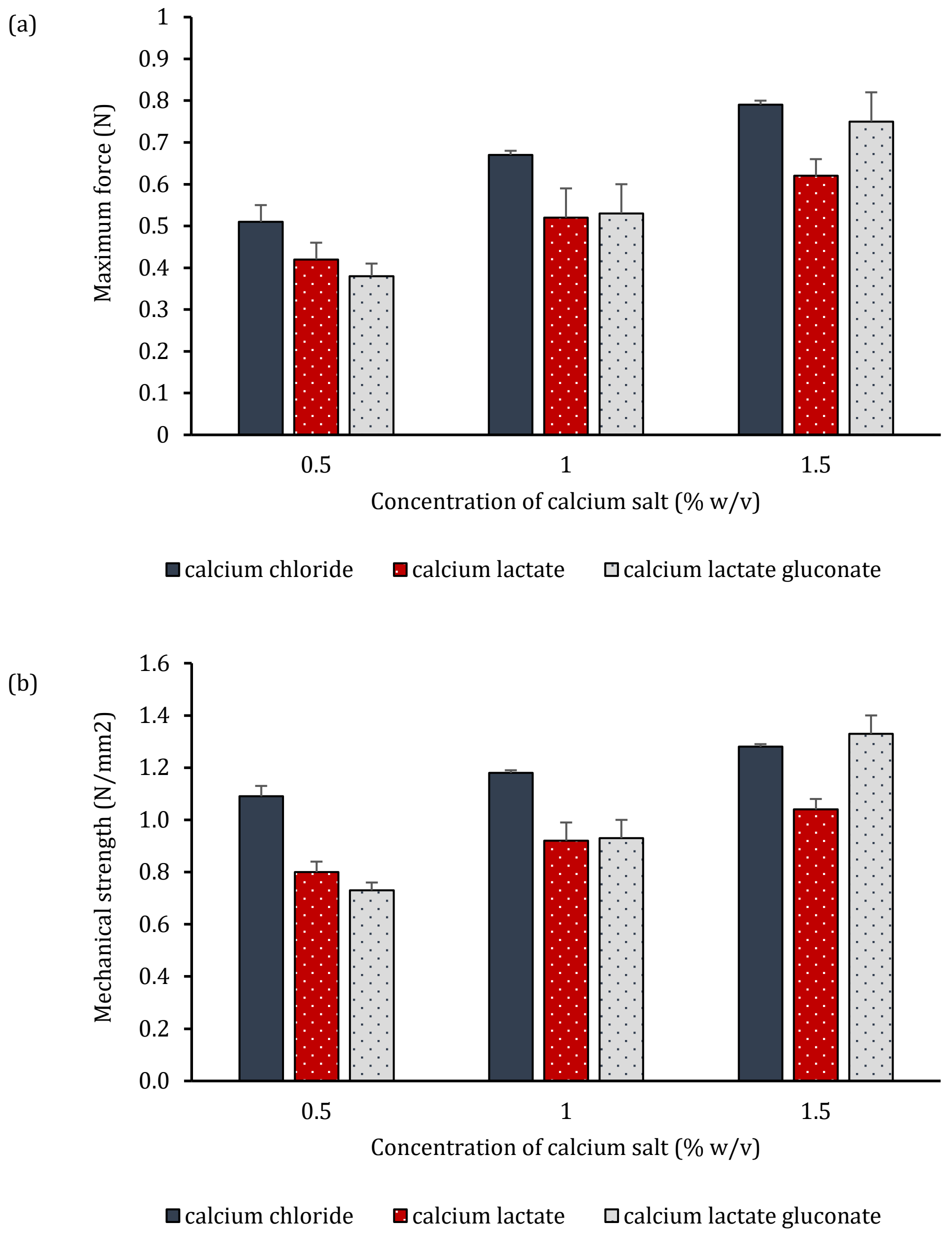

Figure 3. (a) Maximum force and (b) mechanical strength of bubbles with different types and concentrations of calcium salts

3.3 Bubble syneresis

Figure 4 shows the weight change of bubbles with different types and concentrations of calcium salts. The percentage weight change was quite low, ranging from -0.22% to -1.03%. In most cases, the bubbles containing 0.5% w/v calcium salts demonstrated a greater percentage weight loss during gelling than those containing higher concentrations of calcium salts. It is probable that a lower calcium amount produced a looser cross-linked gel than a higher calcium content, resulting in gel syneresis during curing (Smardel et al., 2008). Helgerud et al. (2010) also suggested that syneresis may occur due to a greater calcium concentration inside the bubbles, compared to the exterior calcium concentration, enabling water to diffuse out of the calcium alginate shell. This phenomenon can be explained by the greater osmotic pressure of the calcium solution than of the sodium alginate. Therefore, until equilibrium was attained, water migrated from the sodium alginate solution into the calcium solution (Enobakhare et al., 2006).

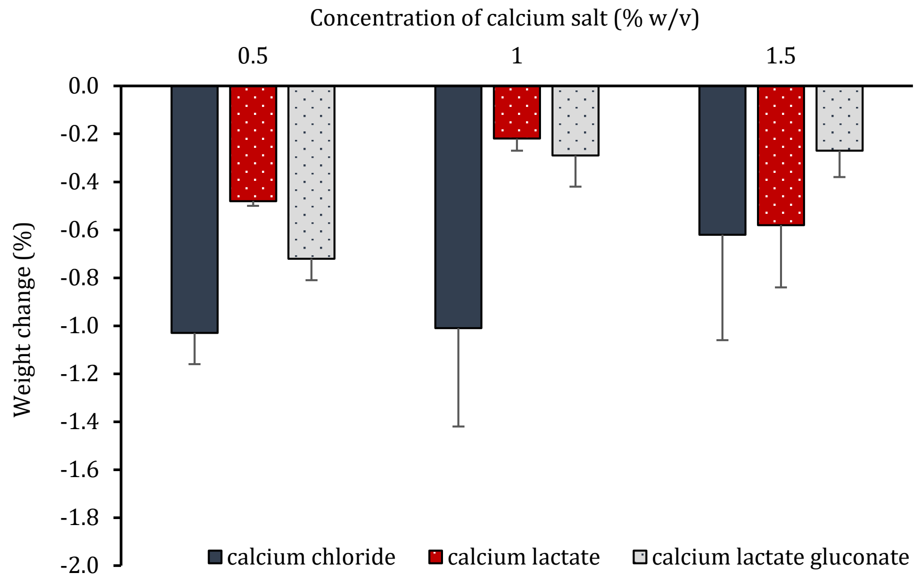

Figure 4. Weight change of bubbles with different types and concentrations of calcium salts

In summary, this study revealed that the formulation containing 1% w/v calcium lactate gluconate, 1% w/v sodium alginate was recommended to create the encapsulating energy drinks with 10-min bubble forming time. These resulted in a mechanical strength of 0.94 N/mm^2 and shell thickness of 0.46 mm.

5. CONCLUSION

The frozen reverse spherification technique was used to successfully prepare edible bubbles of calcium alginate for encapsulating energy drinks comprising 10% v/v fruit juice and 10% w/v dextrose. The bubbles were created by freezing calcium salt-containing energy drinks and dropping them into sodium alginate solution. The strength of the bubble membrane increased with increasing sodium alginate concentration and immersion time. The mechanical characteristics of the edible bubbles comprising energy drinks were affected by the type of calcium salts used in this study, including lactate, lactate gluconate, and chloride. Based on flavor, pH after bubble break, and mechanical strength of bubble shell, calcium lactate gluconate was shown to be the best option for edible bubbles. However, additional study on the stability of the bubbles formed is needed.

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