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Lu Ren
March 10, 2009

Production of Alginate Beads

A project report presented in partial fulfillment of the requirements for the degree of Master in Food Technology at Massey University, Auckland, New Zealand

Lu Ren

2008

ABSTRACT

This paper was to improve the production of calcium-induced alginate gels manufactured by a company in Auckland. Problems encountered included yield and syneresis of the beads post-gelation. Essentially the alginate, sugars and other ingredients were dissolved in water at 80ºC. The pH of the solution was adjusted and the alginate beads were extruded into a 5% $CaCl_2$ bath before being drained and dried.

The chemical reaction between sodium alginate and calcium ions is dependent upon the solubility and availability of calcium ions. Some calcium salts (e.g., $CaCl_2$, calcium lactate) were readily soluble and fully dissociated in water and resulted in an immediate gelation of the alginate. Dicalcium phosphate (DCP) was sparingly soluble at pH 7 and calcium ions were not released significantly until the pH reached about pH 4.2. Sodium hexametaphosphate (SHMP) is a chelating agent and this was used to soak up small quantities of Ca^{+2} to ensure no gelation occured while the alginate was being mixed. The optimum quantities of alginate, DCP and SHMP were defined in the laboratory trials.

The use of SHMP, maltodextrin, and gums significantly affected the hardness and stickiness of gel beads. It was found that the combination of xanthan and alginate Protanal LF 120 gave the best results in terms of minimal stickiness and maximum yield after drying.

Key words: alginate gel beads, syneresis, formula, pH, citric acid, gelation time, SHMP, setting time, yield rate, drying, hardness, stickiness, maltodextrin, xanthan gum, guar gum, stickiness by touching, leakage, apparent viscosity.

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(published in *Food Chemistry*, 2008; journal homepage: www.elsevier.com/locate/foodchem)

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1. INTRODUCTION

Alginate is a family of unbranched binary copolymers comprising a backbone of (1→4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues (Draget et al., 2006). Alginates have been used for a variety of industrial purposes, such as stabilizers, thickeners and gelling agents in food production and pharmaceutical applications. Furthermore, it has been applied in encapsulation of probiotics into the food products like yoghurt, mayonnaise (Krasaekoopt et al, 2006), drug delivery (Hari et al., 1996), and the removal of pollutant phenol in water (Pan et al., 2008).

However, the most attractive application of alginate is the calcium-induced gelation resulting from specific and strong interactions between calcium ions and guluronate residues in alginate (Grant et al., 1973). Generally, three techniques are used to produce alginate gels: the extrusion technique where the hydrocolloid solution is extruded into a hardening solution or setting bath containing a multivalent cation (usually Ca^{2+}) to form gel spheres; the emulsion technique where the polymer solution (discontinuous phase) is added to a vegetable oil (continuous phase) to produce tiny gel particles; the spray drying technique where the food material is transformed from a fluid state into a dried particulate form by spraying droplets into hot dry air (Krasaekoopt et al, 2003).

This research focused on the development of a formula for making alginate gel beads using the extrusion method. The original formula was produced by a company that produced alginate gel beads. The objective was to increase the yield and stop syneresis of the beads post-gelation prior to drying.

The goals of the research were to control the gelation rate of the alginate solution through changes in pH and calcium salts, improve the effectiveness of the process to produce beads, measure the attributes of the gel beads produced, and define the rheological properties of the alginate solution.

2 LITERATURE REVIEW OF ALGINATES

2.1 Sources of alginates

Alginates are known as natural polysaccharides extracted from brown seaweed (Nussinovitch, 1997). It has been estimated that the total worldwide production of alginates is about 30,000 metric tones per year. All commercial alginates are generated from marine algae including *Laminaria hyperborean, L. digitata, L. japonica, Lessonia nigrescence, Macrocystis pyrifera* and *Durvillea Antarctica* (Smidsrod & Draget, 1997). The locations for harvesting alginates are mainly from the cold and temperate waters of Northern Europe, the west coast of South America, the southern part of Australia and Tasmania, and around Japan. Large amounts of brown algae are cultivated in mainland China (Smidsrod & Draget, 1997).

In addition, some soil bacteria, such as *Azotobacter vinelandii* and *A. crococcum* and several species of *Pseudomonas*, are able to synthesize alginate-like polysaccharides. However, they are not commercially available (Draget et al., 2006).

2.2 Alginate extraction

The extraction of alginate from algal material consists of several steps, which is schematically illustrated in Figure 2.1. First, algal tissue is milled and extracted utilizing 0.1-0.2 M mineral acid. In this step of pre-extraction, the insoluble alginate with a counterion composition that is determined by the ion-exchange equilibrium with seawater is ion-exchanged with protons (acidified) (Draget et al., 2006; Sabra & Deckwer, 2005). In the second stage, the alginic acid obtained is brought into solution by neutralization with an alkali like sodium carbonate or sodium hydroxide to produce water-soluble sodium alginate. The removal of algal particles is carried out by separation methods such as sifting, flotation, centrifugation, and filtration. Soluble sodium alginate is then precipitated by adding alcohol, calcium chloride, or mineral acid, which

can be reconverted to the sodium form as needed, and finally dried and milled (Draget et al., 2006; Sabra & Deckwer, 2005).

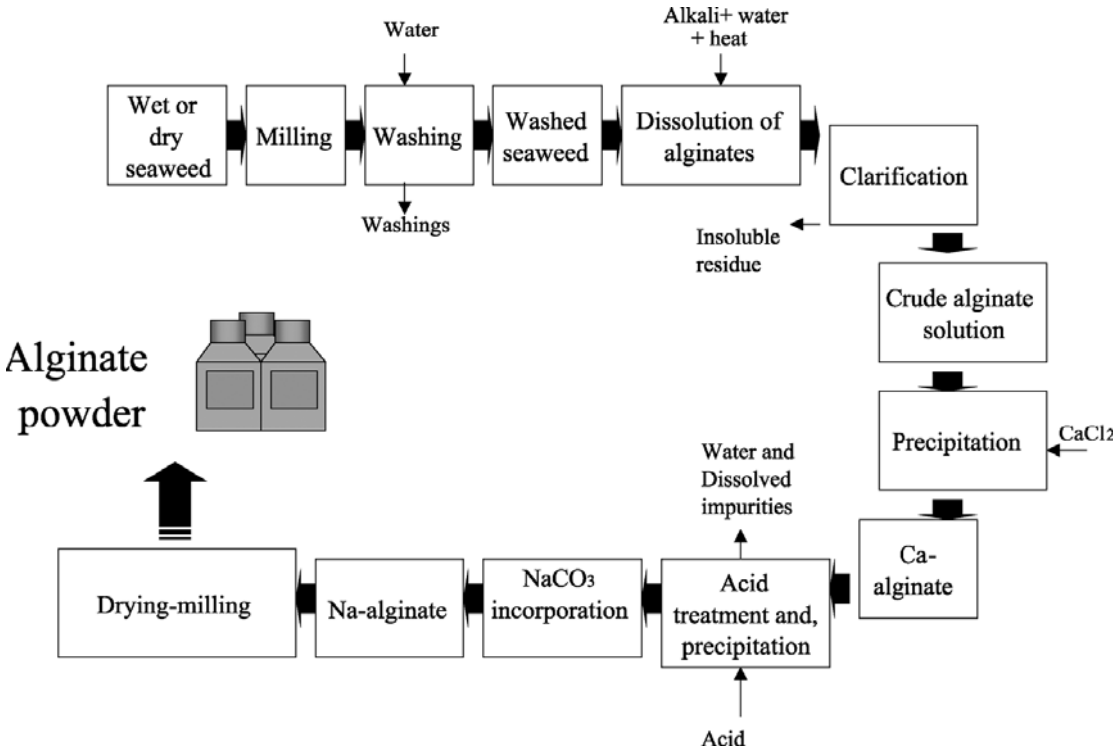


Figure 2.1 Flow diagram of the production of sodium alginate. (Sabra & Deckwer, (2005)).

2.3 Chemistry

Alginate in molecular terms is considered as a family of unbranched binary copolymers of (1→4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues (Figure 2.2) (Draget et al., 2006).

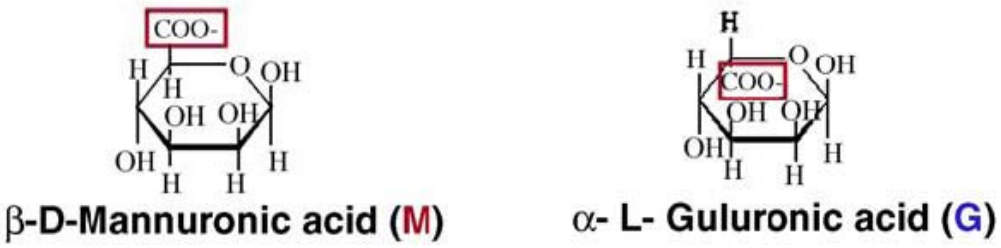


Figure 2.2 Chemical structures of G and M. (Adapted from Vos et al., (2006)).

The alginate molecule is energetically most stable in the chair conformations of M and G residues (Figure 2.3) (Smidsrod & Draget, 1997). M units are in

the conformation $^4C_1$, while G units are in the conformation $^1C_4$ (Whistler & BeMiller, 1997).

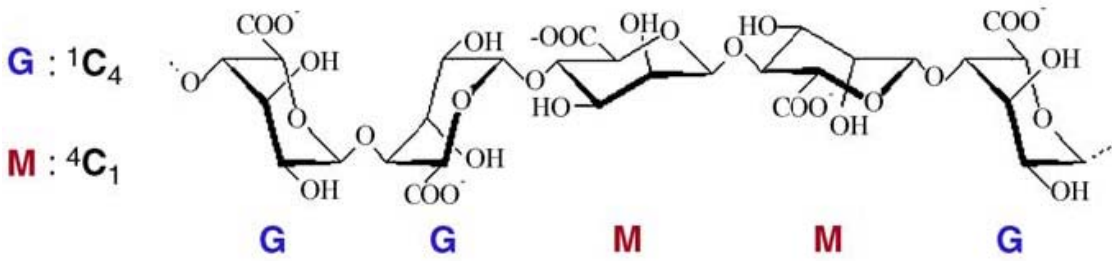


Figure 2.3 2-D conformation of the alginate backbone. (Adapted from Vos et al., (2006)).

The two monomers (M and G) can exist in four possible combinations in any one alginate polymer: diequatorial (MM), equatorialaxial (MG), axial-equatorial (GM) and diaxial (GG) (Figure 2.4) (Smidsrod & Draget, 1997). The diaxial (GG) glycosidic linkage provides a large hindered rotation which offers the G-blocks a stiff and extended nature. Also, this G-G linkage provides a special zigzag structure with cavities that are crucial in the binding of ions and subsequent gel formation (Smidsrod & Draget, 1997).

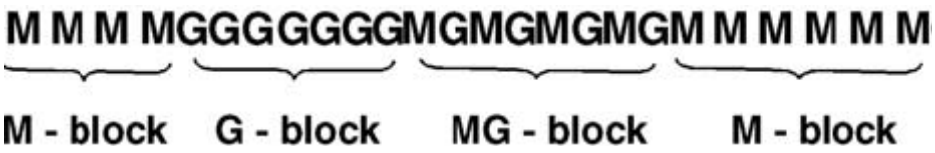


Figure 2.4 Typical combinations of M/G making up the different types of alginates. (Adapted from Vos et al., (2006)).

Alginates are typically described by parameters such as, the M/G ratio, the distribution of M- and G-units along the chain and the average molecular weight. The difference of weight-average molecular weights found in commercial alginates varies from approximately 50 to 500 kDa (Smidsrod & Draget, 1997). These parameters are relevant to the functionality of the alginates, such as solubility, interaction with metals, gel properties and viscosity (Haug et al., 1967). The composition, sequential structure and the

functionality of alginates are dependant on season, age of seaweed population, species and geographic location (Haug et al., 1974).

2.3.1 Effect of ionic strength

Ionic strength of a solution can cause significant changes in alginate solution properties. The solubility of alginate is also affected at high ionic strengths. This effect can be thermodynamically explained and provides a tool for separating the components of a polysaccharide mixture by precipitation. Alginates may be precipitated by high concentrations of inorganic salts like potassium chloride. This is used to fractionate alginates, thereby providing a precipitate enriched in mannuronate residues. A salt with a concentration less than 0.1 M is enough to slowdown the kinetics of the dissolution process and thus limit the solubility (Draget et al, 2006). This effect can be attributed to the drive of the dissolution process of alginate in water. This kind of drive is most probably the gradient in the chemical potential of water between the bulk solvent and the solvent in the alginate particle, due to the high counterion concentration in the particle. Hence, the dissolution process of alginate in water gets severely decreased when it is aiming to dissolve alginate in an aqueous solvent already containing ions. If alginates are utilized at high salt concentrations, first the full hydration of polymer should be carried out in pure water. Then, it needs to be followed by the addition of salt with mechanical stirring (Draget et al, 2006).

2.3.2 Effect of pH

Different alginates react to pH differently. Solutions of sodium alginate become unstable above pH 10. Alginates precipitate around pH 3.5 or lower because of the predominance of COOH moiety. The mannuronic and guluronic acid monomers have their dissociation constants (*pKa*) at pH 3.38 and pH 3.65, respectively (Nussinovitch, 1997; Haug, 1964). There are two types of interactions in this aqueous system: the charge repulsion between ionized carboxylate (COO^-) groups, and the hydrogen bonding formed between carboxylic acid and ionized carboxylate groups. At pH values above the *pKa* value (3.7) of the uronic acid residues, mutual repulsion of ionized

carboxyl groups leads to a loosening of the network structure (Bu et al., 2005). The *pKa* value of the alginate polymer is determined by the relative concentration of the composite monomeric residues, the ionic strength of the solution and the alginate concentration (Draget et al., 2006).

As the pH of an alginate solution is suddenly lowered from pH 7, the polymer will precipitate. However, a slow and controlled decline in pH may lead to the formation of an alginic acid gel. Alginate precipitation occurs over a relatively narrow pH range dictated by the molecular weight of the alginate (Draget et al., 2006).

Alginates isolated from *A. nodosum* have a more heterogeneous polymer sequence of alternating structure (MG-blocks). Alginates from *Laminaraia* species are characterized by more homogeneous block structure (poly-M and poly-G). The existence of homopolymeric blocks is likely to favour precipitation by forming crystalline regions stabilized by hydrogen bonds. These crystalline regions are not as readily produced in heterogeneous alginates and they will remain solubilized at a pH where *Laminaria* alginates precipitate. Some alginates from *A. nodosum* are soluble at pH values as low as pH 1.4 (Draget et al., 2006).

2.3.3 Effect of heating

An alginate solution can be broken down by heating because the heating process promotes the reaction rate of all the depolymerization processes. The monomer composition of an alginate can influence the thermal stability of this alginate. Alginates rich in mannuronic acid residues (isolated from *A. nodosum*) are far less heat stable than those rich in guluronic acid residues (isolated from *L. hyperborean*) (Oates & Ledward, 1990).

Alginate generally generates thermostable gels over the range 0-100°C (Oates & Ledward, 1990). The rigidity of an alginate gel reduces as the temperature goes up. This indicates that the properties of alginate gels are temperature-dependent (Gacesa, 1988). However, thermal degradation

(homolysis) may occur at high temperature. An alginate gel will melt if the heating temperature increases above the transition temperature of the alginate gel. And this transition temperature is well above the boiling point of water at 100°C (Oates & Ledward, 1990).

2.3.4 Digestion of alginate by microorganisms

In addition, many microorganisms, such as *Klebsiella aerogenes, Photobacterium, Littorina sp., Azotobacter vinelandii phage,* and *Pseudomonas*, may digest alginates since they are natural products (Draget et al., 2006, Gacesa, 1988). And enzymes are able to facilitate the digestion of alginate. Alginate can be enzymatically depolymerized by alginate lyase. Alginate lyases have been isolated from a variety of bacteria, including marine bacteria, *Bacillus circulans, Sphingomonas* species, *Klebsiella* species, and *Pseudomonas* species (Yoon et al., 1999). Algiante lyase cleaves the β-1–4 glycosidic linkage present in the acidic polysaccharides by β-elimination mechanism, producing 4-deoxy-α-l-*erythro*-hex-4-ene pyranosyluronate-containing oligosaccharides. Alginate lyases are classified as EC4.2.2.3, poly(M) lyase [(1→4)- β-D-mannuronan lyase] or EC4.2.2.11, poly(G) lyase [(1→4)-α-L-guluronan lyase], which is based on their dominant cleaving action on M-rich or G-rich alginates (Shen et al., 2006). The environment where the lyase-producing organism is found determines the substrate specificity of lyases. Nevertheless, the bacteria alginate is not degraded by most of alginate lyases due to its O-acetyl group. Hence, there are only a few alginate lyases, such as Al_XM_B of *Photobacterium*, PA3547 and PA1167 of *P. aeruginosa* PAO1, ALY1-I and ALY1-III of *Sphingomonas* sp. A1, degrade acetylated alginate (Shen et al., 2006).

However, the enzymes degrading alginates can be both useful and a problem. Alginate-degrading enzymes have a known specificity that are potentially useful for elucidating the fine structure of the polysaccharide and they also hold promise as therapeutic agents in the treatment of mucoid *P. aeruginosa* lung infections in patients with cystic fibrosis (Gacesa, 1988). In contrast, the involvement of alginases can be found in the disease processes of certain

phytopathogenic micro-organisms. And alginases may also be involved in the spoilage of alginates or alginate-containing foodstuffs (Gacesa, 1988).

2.3.5 Hydration of alginates

Alginates are sold usually as powders and they must be dissolved in water prior to their use. Alginates have a high affinity for water and they readily form lumps when they are added in water. Therefore, it is crucial to control the wetting and hydration of alginates to ensure their functionality (Larsena et al., 2003).

To completely dissolve alginates without forming lumps, normally they are dry-mixed with some ingredients such as sugars before placed into water, and /or a very high-shear mixer is used to break down the lumps formed. Alginates can also be dispersed after mixing with vegetable oil or glycerol (Nussinovitch, 1997).

Having successfully wet the alginate, it must be fully hydrated. This can be achieved by heating the alginate solution to at least 70ºC before it is used. This heating in water causes the alginate structure to open and allows water molecules to enter the alginate structure and hydrate fully all the active sites of the molecule. It is critical that this hydration occurs with sufficient excess of water. For example, solutions containing more than about 25% low molecular weight solute (eg. sugar) will successfully compete for water and the alginate molecule will not properly hydrate. Therefore, alginate hydration requires dissolution in water at low solute concentrations (normally less than 10% - 15% solutes), then heating to around 80ºC to properly hydrate the alginate before using it to make a gel (Nussinovitch, 1997; ISP, 2007).

2.3.6 Shelf life of alginate

In addition, there may be a shelf life of several months for dry, powdered, pure sodium alginate when stored in a dry, cool place without exposure to sunlight. In the deep freezer, sodium alginate may be maintained for several years, and no significant reduction is observed in molecular weight. In contrast, a very

limited stability is exhibited in dried alginic acid at ordinary temperatures because of intramolecular, acid-catalyzed degradation (Draget et al., 2006).

2.4 Alginate gelation with cations

Alginates are able to produce gels with divalent cations. The most suitable divalent cation for food purposes is calcium due to its low toxicity (Nussinovitch, 1997). Alginate gels have the particular feature of being ‘cold setting’ compared to most gelling polysaccharides, which means that the setting of alginate gels is more-or-less independent of temperature. Nevertheless, the properties of the final gel can be altered if gelation is conducted at different temperatures (Smidsrod & Draget, 1997). However, even though alginate gels are heat-stable, a prolonged heat treatment at low or high pH will destabilize the gels due to an increased reaction rate of depolymerizing processes such as proton catalysed hydrolysis and the β-elimination reaction (Smidsrod & Draget, 1997).

The introduction of calcium chloride into a solution of sodium alginate can cause a gel or precipitate instantaneously. Except with very small volumes of alginate, it is difficult even with high-speed stirring to produce homogeneous gels free of lumps (fisheyes) due to the rapid, strong, and irreversible formation of junctions in the gel, and thus the high rate of gelation, (Draget et al., 2006). To avoid this problem, two methods have been employed for the preparation of alginate gels: the dialysis method and the internal gelation method. The dialysis method allows calcium ions to diffuse into the alginate solution (Draget et al., 2006). Typically, aqueous sodium alginate solution is dripped into a solution of calcium ions (Draget et al., 2006). The calcium ions induce a cooperative effect between G-blocks to form a 3D network which is known as the “egg-box” mode (Figure 2.5) (Rousseau et al., 2004).

The internal gelation method uses an inactive form of the cross-linking ion, such as bound by a sequestering agent, or as an insoluble salt. After mixing the alginate and inactive cross-linker, the solution conditions are changed

(e.g., by reducing pH) and the calcium ions are slowly released (Draget et al., 2006).

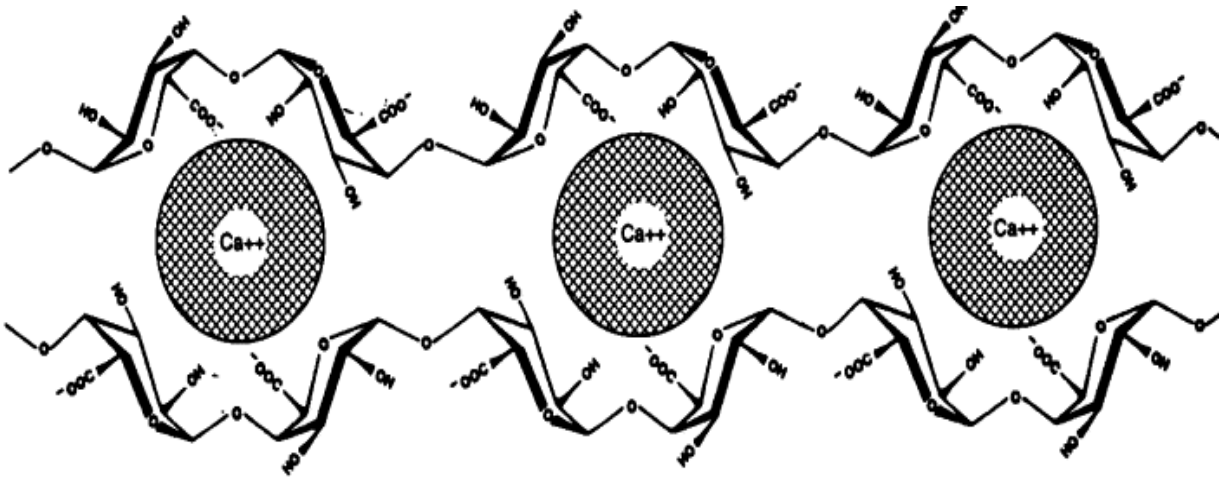


Figure 2.5 The “Eggs-box” model for alginate gelation with calcium ions (Rousseau et al., (2004)).

The dialysis method tends to result in an inhomogeneous distribution of calcium, with the largest concentration at the surface and the concentration gradually reducing towards the center of the bead. The internal setting method almost always produces homogeneous gels (Smidsrod & Draget, 1997). The gelling kinetics is considered the main difference between internal setting and diffusion setting. The gel strength of internally set alginate gels is more dependent on molecular weight and is more susceptible to syneresis than gels set by diffusion (Smidsrod & Draget, 1997).

Generally, three techniques have been utilized for the production of gels: namely extrusion technique, emulsion technique, and spray drying technique. These techniques have been employed for making gels and also microencapsulation /encapsulation of certain core materials, such as food ingredients, drug and probiotics.

2.4.1 Extrusion technique

This is a popular approach to producing capsules with hydrocolloids. It is easy, simple, low cost, and has gentle formulation conditions (King, 1995;

Krasaekoopt et al., 2003). Typically, a solution of sodium alginate is extruded through a syringe needle in the form of droplets to free-fall into a hardening solution containing a multivalent cation (normally Ca^{2+} in the form of $CaCl_2$). An insoluble layer of ionically cross-linked alginate is formed around liquid spheres (Krasaekoopt et al., 2003). The size and shape of the beads is determined by the diameter of the needle used and the distance of free-fall, respectively (Krasaekoopt et al., 2003).

2.4.2. Emulsion technique

The emulsion technique creates a water-in-oil emulsion. A small volume of an alginate solution (discontinuous phase) is added to a large volume of a vegetable oil (continuous phase). The mixture is homogenized, a solution containing a multivalent cation (normally Ca^{2+}) is added and the water-soluble alginate turns into an insolubilized (cross-linked) tiny gel particles within the oil phase (Krasaekoopt et al., 2003; Homayouni et al., 2008).

A second method (Figure 2.6) involves emulsifying an aqueous solution of sodium alginate in sunflower oil containing porous $CaCO_3$ microparticles. A slow-release acid solution (e.g., GDL) is added to lower the pH value of the water phase and Ca^{2+} cations are gradually released from $CaCO_3$ to cross-link the alginate chains to form gels. The formed alginate gel core is surrounded by the $CaCO_3$ particles. Those $CaCO_3$ particles form a shell which provides the gel bead enough stiffness for separation from the oil phase by centrifugation. The porous $CaCO_3$ microparticles play two important roles in this gel making process. One function is to act as a stabilizer for the water-in-oil emulsion. And another function is to perform as a cross-linker for the alginate gel beads (Liu et al., 2008).

The sizes of the final gel beads that are harvested later by filtration depend on the sizes of the internal phase particles of the emulsion. The size of the beads can be in a range from 25 μm to 2 mm. The bead size also is governed by the speed of agitation (Krasaekoopt et al., 2003). In addition, adding emulsifiers in the water-in-oil emulsion can form a better emulsion because the emulsifiers

are able to lower the surface tension of the emulsion. Thus the smaller spheres of gels are produced. For example, Tween 80 at 0.2% is commonly applied as an emulsifier in this production (Sheu & Marshall, 1993).

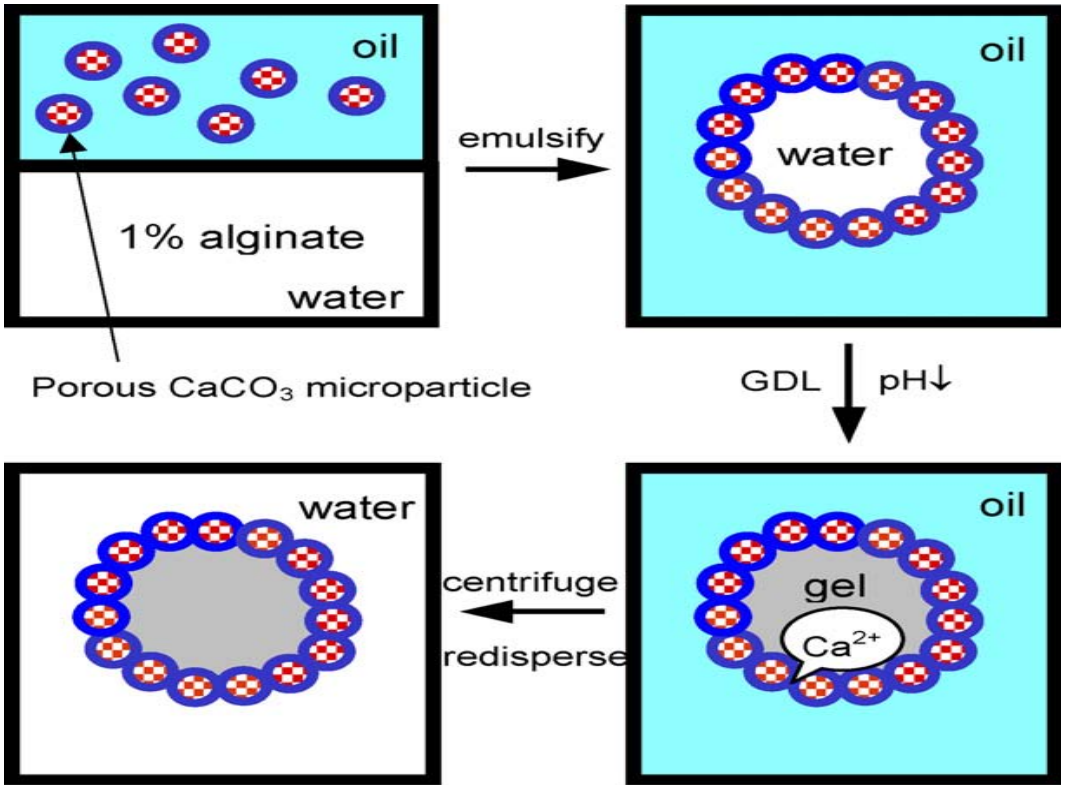


Figure 2.6 Process of making alginate gel beads through an emulsion technique (Liu et al., (2008)).

2.4.3. Spray drying technique

Spray drying technique is conducted by spraying the feed into a hot drying gas medium, which transforms an alginate solution from a fluid state into dried particulates. Spray drying is a unique process making the production of dried particles from a liquid feed in a single processing step. The process is designed to create the operating conditions that promote product recovery and yield a product of a predefined quality specification (Guola & Adamopoulos, 2005). Spray drying technique has been widely utilized because of its advantage of the rapid solvent evaporation in the production. Especially, this technique has been used for preparing the microparticulate drug delivery systems (Ré, 1998). Atomization by spraying a suspension into a hot air is the normal way to achieve spray drying. And the key factor in the achievement of

economic production of top quality products by producing optimum conditions for evaporation is to atomize a fine spray from the feed (Meenan et al., 1997).

2.4.4. Comparison of extrusion and emulsion technique

Comparatively, extrusion forming entrapped rather than an encapsulated core material is simpler than the emulsion technique. The extrusion technique has a limitation of the slow formation of beads compared to the emulsion technique, which thus is difficult for large-scale production (Krasaekoopt et al., 2003). By contrast, the emulsion technique is relatively new and can be readily scaled up for large-scale processing in the food industry. It generates both encapsulated and entrapped core materials, and the beads (25 μm to 2 mm) that are smaller than the beads produced by the extrusion method (2–5 mm). The size of beads from the extrusion method can be controlled by the size of the needle used, while the size of beads from the emulsion method is dictated by the speed of agitation and the type of emulsifier used. But the operating cost of the emulsion technique may be higher than that of the extrusion technique due to the demand for vegetable oil (Krasaekoopt et al., 2003).

2.4.5 Impact of alginate polymer

The strength of an alginate gel is greatly affected by the composition of the monomer of an alginate. Comparing the gelling behavior between high G and high M alginates, high G alginate presents greater gel strength. However, the gel obtained with high M alginates is softer and more elastic than that formed with high G alginates. Also, a more homogenous gel is formed by adding just sufficient calcium to the high M alginate solution. When excess calcium is used, the high G alginate results in a faster precipitation. In addition, syneresis is not exhibited in the gels that are made by the high M alginate with just sufficient calcium (Mancini et al., 1999; ISP, 2007).

2.4.6 Nature of the cation

The mechanical properties of alginate beads are influenced by the nature of the cation, the polymer and cation concentration, and the ionic strength (Ouwerx et al., 1998). The gelling properties of alginates depend on the ion binding properties. Alginates show characteristic ion-binding properties in that their affinity for multivalent cations is governed by the composition of alginates. It has been shown that the characteristic affinities are a property exclusive to polyguluronate, whereas polymannuronate has almost no selectivity. The affinity of alginates for alkaline earth metals exhibits an increasing order Mg<<Ca<Sr<Ba (Sabra & Deckwer, 2005), Ni< Zn<Cu<<Pb (Rouge et al., 2006). The high selectivity between ions is similar with the alkaline earth metals. This demonstrates that the mode of binding can not be by nonspecific electrostatic binding only, but that some chelations caused by structural features in the G-blocks must endow the selectivity. The explanation of this characteristic property can be found from the so-called ‘‘egg box’’ model. This model is based upon the linkage between the guluronate residues and Ca^{2+} ions in a single alginate chain (Sabra & Deckwer, 2005).

The selectivity of alginate for multivalent cations is also determined by the ionic composition of the alginate gel, because the affinity toward a specific ion increases with rising content of the ion in the gel. Therefore, since an alginate gel contains higher amount of Ca^{2+} ions than a Na alginate gel, the former has a higher affinity toward Ca^{2+} ions than the latter (Sabra & Deckwer, 2005).

2.5 Calcium-alginate gels

The alginate-calcium gels demonstrate both properties of solids and liquids with 0.5% alginate (Roopa & Bhattacharya, 2008). Although the solid characteristics to retain shape are exhibited in alginate-calcium gels, they are able to function as a semi-permeable membrane through which low molecular weight, water-soluble molecules can diffuse. Also, the breakdown of the formed gel can be expected to result from the subsequent mechanical disruption of these gels (Roopa & Bhattacharya, 2008).

The characteristics of alginate-calcium gels can be influenced by many factors, such as pH, sequestrant, water hardness, the addition of hydrocolloids, and the intake of water. pH has a significant effect on the formation of alginate gels. Alginate gels have been successfully formed by using a low pH of 2.8-4.0 (King, 1983). During the production of alginate-calcium gels, the requirement of calcium is controlled by the pH. In general, the lower the pH and the higher the level of soluble solids, the less calcium is required to form the continuous irreversible gel (ISP, 2007). While sodium alginates with excess calcium content start to gel at pH 5, the gelation with just sufficient calcium content does not occur until the pH reaches 3 to 4 (ISP, 2000).

The different rates of the acidification of alginate solutions can affect the properties of the gels produced. For example, GDL slowly hydrolyses to gluconic acid in water causing a reduction in pH. This rate depends on temperature (Cavallieri & Cunha, 2008). However, a rapid acidification can be obtained by adding large amounts of GDL to the system, causing a fast decline in pH and even reaching values below the polydispersity index (PI, is a measure of the distribution of molecular mass in a given polymer sample. PI calculated is the weight average molecular weight divided by the number average molecular weight). This can result in weaker and brittler gels. This is because the repulsive electrostatic interactions are minimal under the conditions that pH is near the PI (Alting et al., 2000).

In most situations, a calcium sequestrant is required to ensure alginate gels do not occur because of extraneous small amount of calcium naturally present in water. This avoids the premature formation of gels during mixing. The commonly used sequestrants are sodium hexametaphosphate (SHMP), tetrasodium pyrophosphate, and sodium citrate (ISP, 2007).

Although the fast gelation of alginate solution can be achieved without using a calcium sequestrant, the addition of a sequestrant is crucial in the production of gel beads. It is employed as a protective device since polyvalent ion contaminants can occur in almost any material of natural origin, such as water, chemicals, pigments (ISP, 2000). After removing those ions, more efficient

hydration is achieved and thus the gels are formed in a better quality without lumps. For instance, disodium phosphate may be also applied to remove (as insoluble dicalcium phosphate) calcium ions from tap water even though it has little affinity for calcium at pH less than 5. (ISP, 2007).

Water hardness varies in different areas. For example, in Europe, water hardness as calcium carbonate can range from 50 to over 400 ppm and it can reach 1000 ppm in certain areas. Generally, lower concentrations of alginate are more affected than higher ones. The level (50 – 350 ppm) of calcium carbonate may be insignificant, but the strength of the alginate gel can be radically altered, especially at the nominal usage rate of 0.4% of alginate (ISP, 2007).

Hence, as mentioned earlier, a sequestrant is needed in the alginate gel production in order to remove the impact of water hardness. The variations in water hardness can be overcome also by producing aerated gels, described as a mousse, which is prepared by adding a whipping agent, such as a hydrolyzed protein (ISP, 2007). Also, certain high M alginates can be used to overcome the variations in water hardness as they may be less sensitive to variations in calcium ion concentration (ISP, 2007).

2.5.1 Gel syneresis and swelling

Syneresis is described as a slow, time dependent de-swelling of a gel leading to an exudation of liquid. The phenomenon is commonly found over time in various systems undergoing a sol/gel transition (Draget et al., 2001). Although the molecular mechanisms causing syneresis in alginate gels are not clear, the degree of syneresis is strongly associated to the amount of calcium present (Draget et al., 1991). In addition, it has been discovered that low molecular weight alginate seems to bring an equilibrium state by limiting the primary network structure from further contraction (low degree of syneresis). However, more flexible elastic segments can give an equilibrium state by permitting more rapid relaxation (and a high degree of syneresis) (Draget et al., 2001). The outside surfaces of the gel beads reflect changes in syneresis:

the lower the syneresis of the gel beads, the less sticky the outside surfaces of the gel beads.

To overcome the problem of syneresis in the gel production, a combination of xanthan gum and alginate has been utilized. The higher the amount of xanthan gum added to the beads, the lower the syneresis. This is because that the incorporation of xanthan gum into the diclofenac calcium-alginate beads leads to a change in matrix structure of the beads (diclofenac is a non-steroidal anti-inflammatory drug. Its name is derived from its chemical name: 2-(2,6-dichloranilino) phenylacetic acid). The change is due to forming the intermolecular hydrogen bonding between xanthan gum and sodium alginate, and formation of small aggregates of xanthan gum after dispersing into sodium alginate. The resulting beads are able to provide higher entrapment efficiency of diclofenac sodium and increased water uptake (Pongjanyakul & Puttipipatkhachorn, 2007).

The swelling of alginate gels takes place due to water intake during the gel beads production. There are numerous processes occurring simultaneously once calcium alginate gel films contact with the aqueous media. In general, the setting solutions make the surface of the beads wet and the alginate molecules are hydrated. The shells of the beads are slowly disentangled causing the penetration of water into the centre of beads. As a result, the gel beads swell (Sriamornsak and Kennedy, 2008). Nevertheless, the extent of entanglement and the retractive force within the gelled network limit the expansion of the shell of gel beads. The retractive force is affected by several factors, such as the rigidity of alginate, the extent of calcium cross-linking and any additional inter- or intra-molecular associations. For instance, decreasing the extent of cross-linking could result in a reduced retractive force and would permit more water to be absorbed (Sriamornsak and Kennedy, 2008). Therefore, in order to reduce the swelling of gel beads, a strong gel with a firm cross-link network is suggested in the production.

2.5.2 Impact of rheological properties of alginate solutions

The properties of alginate gels are influenced by the rheological properties of the alginate solution from which they are prepared. Rheology is defined as the study of deformation and flow of matter; the study of the manner in which materials respond to applied stress and strain. Stress is defined as a force per unit area and usually expressed in Pascal (N/m^2), includes tension, compression or shear. Strain and shear are used to describe the deformation of a material (Steffe, 1992). Apparent viscosity refers to the ratio of shear stress to shear rate, which can be defined as equation (1) (Steffe, 1992).

$$\eta = \sigma/\gamma \qquad (1)$$

where: η is the apparent viscosity, σ is the shear stress (Pa), γ is the shear rate (s^{-1}).

Sodium alginate solutions are unusually high in apparent viscosity even at low concentrations due to their high molecular weight and the rigid nature of the molecules. The solutions at high concentrations are pseudoplastic and exhibited shear thinning over a wide range of shear rates (ISP, 2000).

An alginate solution incorporating other solutes tends to exhibit a yield stress. Yield stress is defined as a threshold value of stress that the flow of some materials may not commence until it is exceeded. The food is regarded to follow the Bingham plastic model when the shear rate-shear stress data follows a straight line with a yield stress (Rao, 1999). The utilization of xanthan gum in gels can cause a yield stress at very low shear stresses. The inability of the gels to flow is due to the formation of high molecular weight aggregates of stiff rod-like molecules via hydrogen bonding (Matthews et al., 2005).

To find out the value of the yield stress of an alginate solution, the values of ‘log shear stress against log shear rate’ are plotted. The linear curves gradient is the rate index of pseudoplasticity according to the Herschel–Bulkley equation (2). The value of the yield stress can be located by extending the straight line back to Y axis and the point on the Y axis is the yield stress.

$\sigma = \eta' \gamma^c + \sigma^o$ (2)

$\sigma = \eta' \gamma^c$ (3)

where σ is the shear stress (Pa), η' the 'viscosity coefficient', γ the shear rate (s^{-1}), c the 'rate index' of pseudoplasticity and σ^o is the yield stress (Pa). Equation (2) is a simple extension of a power law equation (3) (Matthews et al., 2005).

The gel point of an alginate gel occurs at the time at which storage modulus G' and loss modulus G'' cross each other at a given frequency. Thus the gelation time can be determined according to the time of G'-G'' crossover. G' expresses the magnitude of the energy stored in the material or recoverable per cycle of deformation. G'' measures the energy that is lost as viscous dissipation per cycle of deformation. Hence, G'' is zero for a perfectly elastic solid since all the energy is stored. However, G' is zero for a liquid with no elastic properties because the energy is dissipated as heat. The complex modulus G* can be calculated by employing the below equation (4) (Rao,1999).

$$|G^*| = \sqrt{(G')^2 + (G'')^2} \quad (4)$$

Similarly, if G' is much larger than G'', the material behaves more like a solid. The deformation is essentially elastic or recoverable. But if G' is much smaller than G'', the material behaves like a liquid because the energy for the deformation is dissipated viscously (Ferry, 1998).

2.6 Calcium salts

Calcium salts are introduced to react with alginate to produce gels. The most commonly used calcium sources include calcium sulfate (usually as the dihydrate), gypsum, and dicalcium phosphate (calcium hydrogen orthophosphate). The rate of calcium released from the salts to become available to the alginate molecules is dependant on a number of factors, such as pH and the amount, particle size and intrinsic solubility characteristics of

the calcium salt. In general, small particle size and low pH result in a rapid release of calcium (ISP, 2007).

The solubility of various calcium salts are often influenced by pH. For instance, even though anhydrous dicalcium phosphate (DCP) exists in an alginate solution at neutral pH, the reaction does not happen as DCP is essentially insoluble at neutral pH. However, the use of dicalcium phosphate dihydrate is not suggested because its solubility is sufficiently high at neutral pH to lead to premature gelation (ISP, 2007). Calcium sulfate is very soluble at neutral pH so this is not a suitable option in that instance (ISP, 2007). A combination of two calcium salts with different solubilities is able to offset the weaknesses using only one salt. For example, although uniform gels at neutral pH can not be formed using $CaSO_4 \bullet 2H_2O$, combining $CaCO_3$ and $CaSO_4 \bullet 2H_2O$ into one system can give control over both gelation rate and homogeneity of the alginate gels. The gelation rate increases as the proportions of $CaSO_4 \bullet 2H_2O$ and total calcium content increase (Kuo and Ma, 2001).

In the alginate gel production, the gelling reaction is controlled by the level of sequestrant, the mixing time, the concentration of calcium salts, and the amount of dissolved calcium in the solution before making beads (ISP, 2007). At low levels of calcium/alginate conversion, a thickening or “false viscosity” is observed. Soft, thixotropic, and in some cases, shear reversible gels are seen in the middle concentration region. At high calcium levels, moldable, continuous, strong gels are formed (ISP, 2007).

2.7 Practical applications of alginates

Alginates have been applied widely in various areas by exploiting their many properties. Alginates gel in the presence of Ca^{2+} ions, they may also be utilized as a stabilizer/suspending agent, a thickening agent, and the calcium gel may be made into a thread and spun using traditional weaving technology (Gacesa, 1988). The following examples will partly demonstrate a broad range of the applications of alginate.

2.7.1 Fruit-like products

Peschardt was the first one to develop a process for the production of artificial cherries in 1946 (Nussinovitch, 1997). In this method, a flavoured, coloured, alginate-sugar solution was introduced into a bath of soluble calcium salt. After instantaneously forming a calcium alginate skin, slow diffusion of calcium into the spherical particle and crosslinking with the alginate inside contributed to the gelation of the interior of the ‘cherries’. The artificial cherries were used in baked goods because of their thermostability (Nussinovitch, 1997).

2.7.2 Water dessert gels

Edible gels or jellies can be produced by alginate cross-linking with calcium and other divalent or trivalent metal ions. The reaction rates are governed by the selection of calcium ions, concentration and pH. Too rapid a gel formation produces a grainy, discontinuous gel, whereas the very soft gels can be obtained by a very slow process. These systems have been utilized in producing fruit grams and jellies, jellied salads and broths, dessert gels and candied jellies (Nussinovitch, 1997).

2.7.3 Milk puddings, ice-cream stabilizers

The imperfect solubility of alginate in milk can leave the milk pudding with inferior quality, the development of granular structures and a lack of gel strength and firmness. However, a good-quality milk pudding can be made by applying a specially treated blend of a water-soluble alkali metal alginate, a mild alkali and a small quantity of calcium salt (Nussinovitch, 1997).

Moreover, alginate can retard the rate of ice-crystal growth in ice creams. This can be performed by using alginate to obtain a smooth texture. Small amounts of sodium alginate (0.1 to 0.5%) have been employed as ice-cream stabilizers to achieve good body properties and texture protection due to their water-holding properties. The concentration of the calcium ions in the water can be reduced by the reaction with sodium alginate (Nussinovitch, 1997).

In addition, inclusion of sodium alginate in soft cheese spreads is capable of preventing the separate between water and oil. Alginate also can be introduced for the minimization of the surface hardening and the improvement of the texture of the processed cheese. The addition of 0.15% sodium alginate is found sufficient to thicken whipped cream (Nussinovitch, 1997).

2.7.4 Fish and meat preservation and sausage casings

The oxidative rancidity of fatty fish such as mackerel and herring can be prevented by the block freezing the fish in alginate jelly. An alginate film is formed around fish pieces that isolate air, and thereby reducing rancidity. Also, the off-flavors and unpleasant smells associated with fish can be contained by the jelly coating during storage (Nussinovitch, 1997).

Calcium alginate films have been used in a wide range of meat processing, such as coating poultry parts, being a carrier for proteolytic enzymes to tenderize meat, preventing salt rust of sausage and prolonging sausage shelf life. Coating beef steaks, pork chops and skinned chicken drumsticks with sodium calcium alginate and a cornstarch slurry can improve texture and juiciness, colour, appearance and odour (Nussinovitch, 1997).

2.7.5 Bakery toppings, fillings, beverages and salad dressings

Alginates are utilized for the preparation of icings for sweet yeast-dough products. Icing formulations with added alginate are non-sticky and do not crack. The texture of whipped sugar toppings can be improved and the reduction of syneresis in baking jellies can be achieved by the using alginate (Nussinovitch, 1997).

Sodium alginate or propylene glycol alginate can minimize pulp sedimentation in fruit drinks. In chocolate-milk drinks, alginate mixed with phosphate is used effectively as a stabilizer. Sodium alginates have been used for the clarification of wine and the removal of tannins, colouring material and nitrogenous substances from beverages (Nussinovitch, 1997).

Propylene glycol alginate can help to slow the separation of the oil and water phases in salad dressings, which gives the dressings or sauces greater stability at high room temperatures or in the refrigerator. The final product is a soft, smooth-textured gel without cracking or allowing oil separation upon standing (Nussinovitch, 1997).

3. EXPERIMENTAL MATERIALS AND METHODS

3.1 Materials and equipment

Calcium carbonate

Calcium carbonate ($CaCO_3$, Molecular weight (MW): 100.09) (Scharlau Chemie, S.A.). Analytical grade.

Calcium chloride

Calcium chloride ($CaCl_2 \cdot 2H_2O$, MW: 147.02) (Scharlau Chemie, S.A.) Analytical grade.

Calcium chloride bath solution

Prepared by dissolving 52.63 g calcium chloride powder in one litre deionized water.

Calcium chloride + sucrose bath solution

Prepared by dissolving 142.86 g calcium chloride powder and 1714.29 g sucrose in 1 litre deionized water.

Calcium lactate

Calcium lactate ($Ca(CH_3 \cdot CHOH \cdot COO)_2 \cdot 2H_2O$, MW: 308.30) (Fisher Chemicals, Leics UK). Analytical grade.

Calcium sulphate

Calcium sulphate ($CaSO_4 \cdot 2H_2O$, MW: 172.17) (Acros Organics, New Jersey). Analytical grade.

Castor sugar

Castor sugar (Kerry Ltd, New Zealand). Food grade.

Citric acid solution

A 1.0 N citric acid solution was prepared by dissolving 64.04 g of citric acid (VWR International Ltd, England; analytical grade) in 1 litre deionized water. It was standardized by using standardized 0.1 N NaOH, using phenolphthalein as the indicator.

Dextrose monohydrate

Dextrose monohydrate (Coopers Brewery Ltd, New Zealand). Food grade.

Dicalcium phosphate dihydrate (DCP)

Dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$, MW: 172.09) (Acros Organics, New Jersey, USA). Analytical grade.

Glucono-δ-lactone (GDL) solution

A GDL ($C_6H_{10}O_6$, MW: 178.14) (Jungbunzlauer, Swiss; food grade) solution was prepared by dissolving 29 g of GDL in 100 ml of deionized water.

Glucose syrup

Avon A2130 (Dextrose equivalent: 38.0-42.0) (Penford New Zealand Ltd). Food grade.

Glycerine

Glycerine (Relative density: USP 99.5%) (Davis Trading Co. Ltd). Food grade.

Guar gum

Guar gum Procol U Special (Particle size: minimum of 97% through 100 mesh, minimum of 80% through 200 mesh; Viscosity: 3800 and 5000 cps minimum after hydrating for 15 min and 2 h respectively) (Polypro International Inc., via Chemiplas NZ Ltd). Food grade.

Hydrochloride acid (HCl) solution

A 0.1N HCl solution was prepared by diluting 16.5 ml of the 45% (w/w) HCl (Biolab, Australia; analytical grade) to 2 litres. It was standardized by using standard 0.1N sodium hydroxide with a phenolphthalein indicator.

Maltodextrin MD1

Maltodextrin MD1 (National Starch Chemical Pty Ltd, NZ). Food grade (dextrose equivalent 9.0-13.0). It was a free flowing powder, which could be dispersed with cold water and contributes viscosity and body. The technical specification sheet is in Appendix 8.1.

Maltodextrin N-LITE LP

Maltodextrin N-LITE LP (National Starch Chemical Pty Ltd, NZ) was food grade. It was recommended for use in cold-process liquid systems where a high degree of lubricity, creaminess. The technical specification sheet is in Appendix 8.2.

Oven

An oven (LabServ, Scientific Ltd, New Zealand) was used for the dehydration test of alginate gel beads at 35ºC, and the determination of total moisture content at 105ºC.

pH meter

PB-10 pH/mV meter (Sartorius AG, Germany).

Potassium hydrogen phthalate

A $7.83x10^{-2}$ M potassium hydrogen phthalate (KHP, $KC_8H_4O_4H$, MW= 204.23) (Biolab, Australia) solution was prepared by weighing 0.8 g of $KC_8H_4O_4H$ that had been dried previously in an oven at 105ºC for 2 h and cooled. Then it was dissolved in 50 ml of deionized water.

Rheometer

AR 550 rheometer (TA Instruments Ltd, UK) was equipped with a cone-and-plate geometry with a cone angle of 2° and diameter of 60 mm, and a solvent

trap cover. The instrument was connected to a temperature unit (Peltier element) that provided a control of temperatures during the determination. The rheometer was controlled with a computer using the Rheology Advantage Software. The data obtained were analyzed by using TA Data Analysis software (2006).

Sodium alginate Manucol DH

This sodium alginate (Particle size: at least 98% through 355 µm, at least 80% through 250µm; Viscosity (in 1% aq.sol.): 40 to 90 mPa·s) (International Specialty Product Inc, Australasia via Alchemy Chemicals Ltd, NZ). Food grade. The technical specification sheet is in Appendix 8.3.

Sodium alginate Manucol LF

This sodium alginate (Particle size: at least 98% through 355 µm, at least 80% through 250µm; Viscosity (in 1% aq.sol.): 10 to 40 mPa·s) (International Specialty Product Inc, Australasia via Alchemy Chemicals Ltd, NZ). Food grade. The technical specification sheet is in Appendix 8.4.

Sodium alginate Manugel GMB

This sodium alginate (Particle size: at least 98% through 355 µm, at least 80% through 250µm; Viscosity (in 1% aq.sol.): 110 to 270 mPa·s) (International Specialty Product Inc, Australasia via Alchemy Chemicals Ltd, NZ). Food grade. The technical specification sheet is in Appendix 8.5.

Sodium alginate Protanal LF 120

This sodium alginate (Particle size: minimum of 99% through 120 mesh BS; Viscosity (in 1% aq.sol.): 200 to 400 mPa·s) (FMC BioPlymer, USA). Food grade. The technical specification sheet is in Appendix 8.6.

Sodium alginate solution

A 1% sodium alginate solution was prepared by slowly dissolving 10.10 g sodium alginate Protanal LF 120 powder in 1 litre deionized water at 80ºC that was controlled using a water bath. To ensure a complete solubilization without

lumps, the sodium alginate was added slowly in a small amount first while stirred by using a glass stick. After the sodium alginate added was almost dissolved, a further small amount of sodium alginate was added and stirred. The procedure was repeated until all sodium alginate was dissolved.

Sodium alginate + sucrose solution

Sodium alginate Protanal LF 120 (20 g) and sucrose (50 g) were dry mixed. Then the mixture was slowly dissolved in deionized water (930 g) at 80ºC that was controlled using a water bath. To ensure a complete solubilization without lumps, the mixture was added slowly in a small amount first while stirred by using a glass stick. After the mixture added was almost dissolved, a further small amount of mixture was added and stirred. The procedure was repeated until all mixture was dissolved.

Sodium hydroxide

A 0.1 N sodium hydroxide (NaOH, MW=40.00) (Biolab, Australia) was prepared by dissolving 4 g of NaOH in 1 litre deionized water. This was standardized using potassium hydrogen phthalate with a phenolphthalein indicator.

Sodium hexametaphosphate

Sodium hexametaphosphate (SHMP; $Na_{(n+2)}P_nO_{(3n+1)}$, n=6-9; MW: 672-978) (Jiangsu Chengxing Phosph-Chemicals Co, Ltd, China). Food grade.

Texture analyser

TA.XT plus Texture analyser (Stable Micro Systems Ltd, England) contained a penetrometer with a stress gauge connected to a computer. The apparatus was equipped with a 4mm Cylinder Probe (P/4), a Heavy Duty Platform, and a holed plate that was used to provide weight on the gel beads to make beads still during the penetration with a probe. The Texture Exponent 32 software was employed to drive the instrument and process the data.

Thermometer

Fluke 51 digital thermometer (John Fluke MFG. Co. INC, USA).

Water bath

GD120 Ser. Water bath (Grant Instrucments (Cambridge) Ltd, England) was used to control the temperatures for making sodium alginate solution at 80ºC and the test of gelation time of sodium alginate solution with calcium salts at 60ºC.

Wheat starch

Wheat starch (Manildra Group of Companies, Australia). Food grade.

Sucrose

White table sugar (Kerry Ltd, New Zealand). Food grade.

Xanthan gum

Xanthan gum (Particle size: 100% through USS 60 mesh, 250; 95% minimum through USS 80 mesh, 177 µ. Viscosity (1.0% in 1.0% KCl): 1200-1600 cP) (Hawkins Watts Ltd, New Zealand). Food grade. The technical specification sheet is in Appendix 8.7.

3.2 Methods

3.2.1 Preparation of sodium alginate stock solution

A sodium alginate stock solution was prepared according to the formula listed in Table 3. 1.

Table 3.1. Formula of sodium alginate stock solution

Part	Ingredient	Percentage (w/w)
A	Sodium alginate	1
	Guar gum	0.4
	Castor sugar	5
	SHMP	0.1
	Water	29
B	Castor sugar	22.5
	Glucose syrup	20
	Glycerine	7
	Dextrose	14
	Wheat starch	1

Part A was prepared by dry mixing sodium alginate, castor sugar, guar gum and SHMP. The mix was slowly added to deionized water at 80ºC and stirred well to mix, using a glass rod. This step ensured the alginate was hydrated properly before solutes were added.

Part B was prepared by dry mixing castor sugar, dextrose, and wheat starch. This dry blend was added slowly to the solution prepared in Part A while stirring with a glass rod to ensure solubilization. Glucose syrup and glycerine were added to this mixture and mixed well. This was the “stock solution” for further work.

3.2.2 Production of alginate beads

The standard method was used for making alginate gel beads started by preparing the sodium alginate stock solution at 80ºC. DCP (0.3 g) was added to 100 g of solution and mixed well with a glass rod. The pH was adjusted to 4.2 using 0.1 N HCl. Immediately, it was extruded using a syringe into a 5% (w/w) calcium chloride bath to form gel beads. The beads were left in the bath for 1 min and then collected with a sieve. To dry the harvested beads, they were placed on a paper tissue for 1 min before stored in a sealed plastic container.

3.2.3 Titration curves for alginates

Titration curves for either 1% sodium alginate or stock alginate solution (section 3.2.1) were prepared against 0.1N HCl or 0.1N citric acid. One hundred ml of the appropriate alginate solution had 0.06 ml acid added at 20ºC and the mixture was stirred for 10 minute with a glass rod. The pH was then measured. Further aliquots of acid were added using the same procedure and the titration curve was run until the pH had reached about pH 3.

Separately, 0.095 ml of 29% (w/v) GDL was added to 50 ml sodium alginate stock solution and the pH was measured over 24 hours as the GDL hydrolysed.

3.2.4 Calcium salts and gelation characteristics

Four types of calcium salt were used to test the gelation time of the alginate + sucrose solution at four pH values and two temperatures. The experimental design is given in Table 3.2. A constant concentration of calcium ions (7.2% (w/w) calcium ion : sodium alginate) from each calcium salt was used. Thus each calcium salt was added at different concentrations as shown in Table 3.2.

The test solution used was 2% alginate in 5% sucrose (all w/w). About 50 (±0.3) g of the test solution was used and the appropriate concentration of calcium salt added as a solid. The pH of the solution was adjusted to either 4, 4.5, 5, and 6 using 0.1 N HCl. The gelation time was assessed by gently stirring with a glass rod until a soft gel was formed. The time to achieve this gel was recorded. This whole procedure was repeated using fresh solutions but the reaction was run at 60ºC in a water bath.

Table 3.2. Experimental design for testing calcium salts

Calcium salt	Amount of Ca salt (g)	Temperature	pH
Dicalcium phosphate	0.3	20	6 5 4.5 4
	0.3	60	6 5 4.5 4
Calcium carbonate	0.18	20	6 5 4.5 4
	1.18	60	6 5 4.5 4
Calcium lactate	0.56	20	6 5 4.5 4
	0.56	60	6 5 4.5 4
Calcium sulfate	0.3	20	6 5 4.5 4
	0.3	60	6 5 4.5 4

3.2.5 Dicalcium phosphate and gelation

A sodium alginate stock solution (defined in 3.2.1) was prepared. DCP (0.06 g) was added to 20 g of the sodium alginate stock solution and mixed well with a glass rod. The pH of solution was adjusted to either 5.8, 5.0, 4.2 or 3.7, using 0.1 N HCl. A timer was used to measure the gelation time to create a soft gel as assessed by gently stirring with a glass rod.

3.2.6 Water uptake of the gel beads in the setting bath

A sodium alginate stock solution (defined in 3.2.1) was used. Two kinds of bath solutions were prepared. One was calcium chloride bath solution containing 5% (w/w) $CaCl_2$; the second was calcium chloride + sucrose bath solution consisting of 5% (w/w) $CaCl_2$ and 60% (w/w) sugar. Four setting baths each of 250 ml volume were made – one for each of four setting times: namely 1, 5, 30 and 60 min. Also, a calcium chloride + sucrose setting bath was made in a plastic container for the determination with a setting time of 60 min. The beads were produced in those setting baths according to section 3.2.2, allowed to remain for the desired setting time, then removed from the bath using a sieve and dried by placing on a paper tissue for 1 min.

The harvested beads were weighed and placed into aluminum dishes that had been previously dried, cooled and weighed. Then the beads and dishes were dried in an oven at 105ºC overnight to determine the total moisture content.

3.2.7 Air drying of the gel beads

Alginate gel beads using stock alginate solution (section 3.2.1) were produced according to section 3.2.2 and collected. Gel beads (about 25g) were placed onto a preweighed petri dish and accurately weighed to ±0.01 g. They were then placed in a fan assisted air oven at 35ºC. At regular intervals, the petri dish was removed from the oven and the gel beads were transferred using a spoon to a new, clean, pretared petri dish. These gel beads were then accurately weighed and the weight change of the beads was calculated. The old petri dish was reweighed to calculate the amount of leached material that

remained in the dish. The beads were placed back onto the old petri dish and then returned to the 35ºC oven.

Also, the beads were placed in an oven at 105ºC overnight as well, which aimed to calculate the total moisture content of the gel beads of each formula.

3.2.8 Texture analysis of beads

The Texture Exponent 32 software was opened to drive the texture analyzer. Firstly, the Force of the load cell and Height of the probe needed to be calibrated for the instrument before use. The probe was set at a height of 10 mm from the platform. Then, the test parameters were set. *Measure Force in Compression* was selected as the test type. Also, other parameters were set as follows: *Option: Return To Start; Pre-Test Speed: 2.0 mm/s; Test Speed: 1.0 mm/s; Post-Test Speed: 10.0 mm/s; Distance: 2 mm; Trigger Type: Auto-5 g; Tare Mode: Auto; Data Acquisition Rate: 500 pps.* In another easier way, those parameters were able to be set by selecting the existing project Adhesive Gum. The tests were carried out at 20ºC that was controlled by setting the working temperature of the texture analyzer and the room temperature by an air conditioner.

A test of hardness and stickiness of beads was performed. The name of the sample and the replicated number were set. The autosave function was set to save the obtained data. Thus, those data were saved using the sample ID followed by the replicate number. The data was exhibited as graph. The values of peak force and distance could be taken from the cursor on the position of interest. These values were able to be transferred to a result window listed at the bottom of the screen. These data could be edited using Excel software.

After all settings were conducted, the measurement of hardness and stickiness of beads was carried out. For each measurement, the bead was placed on the blank plate of the Heavy Duty Platform. A holed plate allowing the cylinder probe pass through the central hole was placed on top of the

beads. The holed plate was used to provide weight on the gel beads and make beads still, which prevented lifting of the beads when the probe was withdrawn out from the penetrated beads. This was to ensure an accurate stickiness. Also, the probe was cleaned using wet and dry tissue papers between tests.

During test, the probe pushed down at the rate of 2.0 mm/s (set in Pre-Test Speed) until a trigger force of 5 g (set in Trigger Type) was detected on the surface of the bead. Then, the probe penetrated to a depth of 2mm (set in Distance) in the bead at a rate of 1.0 mm/s (set in Test Speed). Next, the probe returned to its initial position at a rate of 10.0 mm/s (set in Post-Test Speed). A maximum force reading was used as hardness. The negative peak force indicating the resistant to withdrawal from the bead was used as stickiness.

3.2.9 Apparent viscosity of alginate stock solution

A rheometer was set up before the determinations. First of all, the air supply and water supply were turned on to the instrument. After the air bearing clamp was removed, the rheometer and the PC were started.

The Rheology Advantage Software was run to drive the rheometer. A cone-and-plate geometry (60/2º) was attached to the draw rod. This was performed by placing the draw rod in the screw thread of the geometry and the draw rod upwards was screwed (clock – wise) finger tight. Then the Zero point (datum) and the Geometry Gap were calibrated.

The Flow Procedure was selected for the measurement of the apparent viscosities of sodium alginate stock solutions. Then, three steps were set up, including *i. Conditioning step; ii. Conditioning ramp step; iii. Post –experiment step*. In the first step, *Initial temperature* was set up at *20ºC*. *Equilibration duration* was set as *10 s.* In the second step, the settings were follows. *Test type: Continuous ramp; Ramp: shear rate (1/s), From: 1.000 to 300.0; Duration: 1 min; Mode: Linear; Sampling, Delay time: 10 s.* In the third step,

the *Temperature* was set up at *20ºC.* To ensure the determination being carried out at 20ºC, the working temperature of the rheometer was further confirmed by an air conditioner in the room. After those settings, this procedure was saved.

After all those settings were completed, the apparent viscosities of sodium alginate stock solutions were conducted. To load the sodium alginate stock solution, the geometry was raised to back off position. The stock solution was loaded onto the plate by using a spoon. Then the geometry was lowed to the gap distance calibrated previously. The amount of the stock solution placed was just enough to fill the gap and ensured the stock solution to be exactly covered by the cone-and-plate.

During the determination, the shear rate was increased from 1 to 300 s^{-1} (set up Shear rate in Ramp). The solution was tested for 1 min (set in Duration). The testing data was recorded every 10 s (set in Delay time).

3.2.10 Oscillatory rheology of alginate stock solution

After the rheometer was set up, an Oscillatory Procedure was selected to measure the oscillatory rheology of the sodium alginate stock solution. Likewise, three steps were required to do the settings. In the *Conditioning step*, settings were *Initial temperature*: *20ºC*; *Equilibration duration*: *10 s.* In the *Time sweep step*, the settings were follows. *Ramp: shear rate; Frequency (Hz): 40.00 to 1.000; Duration: 3 h; Mode: Log; Point per decade: 2; Temperature: 20ºC. Controlled variable: % strain, 1.* In the *Post-experiment step*, the *Temperature* was set up at *20ºC.* To ensure the determination being carried out at 20ºC, the working temperature of the rheometer was further confirmed by an air conditioner in the room. After those settings, this procedure was saved. The procedure was performed.

To determine the oscillatory rheology of the sodium alginate stock solution, the sodium alginate stock solutions were prepared earlier. Time sweep test of oscillation procedure was selected for the deformation oscillatory

measurements of storage modulus (G') and loss modulus (G''). After all settings were done, the sodium alginate stock solution (50 g) was weighed and placed in a beaker. Then 0.15 g of DCP was added and dispersed thoroughly throughout the solution by using a glass rod. The pH was adjusted to pH 4.2 by adding 0.65 ml of 1.0 N citric acid. And the solution was quickly mixed well with a glass rod. Immediately, small amount of this solution was taken and placed on the plate by using a spoon. The stock solution was ensured to be exactly covered by the cone-and-plate. After loading, a solvent trap cover was put around the cone-and-plate and sample to prevent the evaporation. The loading of the sample should be quick to avoid the gelation occurring before the test started.

During the test, a further 10 seconds (set in Equilibration duration) were allowed for sample equilibration before the determination was started. G' and G'' were recorded over time at a fixed frequency of 1 Hz (set in Frequency) and at a strain of 1% (set in Controlled variable). The test performed for 3 h (set in Duration). The testing data was recorded every 1 min (set in Delay time).

3.2.11 Qualitative observations

The differences of the beads among those formulae were observed by the researcher. The beads were rated against 8 different attributes, namely whiteness, translucence, fractureness, springiness, dryness, stickiness by touching, central firmness, and leakage. Each attribute was assessed using a 10 - point score sheet. Score 1 represented the lowest category for the attribute. In contrast, score 10 meant the highest category.

3.3 Statistics analysis

The data of hardness and stickiness of alginate gel beads were analyzed by General Linear Model in Multifactorial analysis of variance (multifactorial ANOVA) of SPSS (SPSS 15.0 for Windows). One-way ANOVA was used to analyze the data from maltodextrin and dextrose. Also, the data of the leakage of beads were analyzed by one-way ANOVA. The comparisons were

performed to determine significant differences ($P < 0.05$) between the varying variables for making alginate gel beads.

4. RESULTS AND DISCUSSION

4.1. Titration curve for sodium alginate solution

The initial pH value of a 1% sodium alginate solution was around 7.15. The titration curve against HCl and citric acid is given in Appendix 1A and summarized in Figure 4.1. To reach the pH value at 4.2, approximately 6.0 and 15.0 ml of HCl and citric acid solution, respectively, was required.

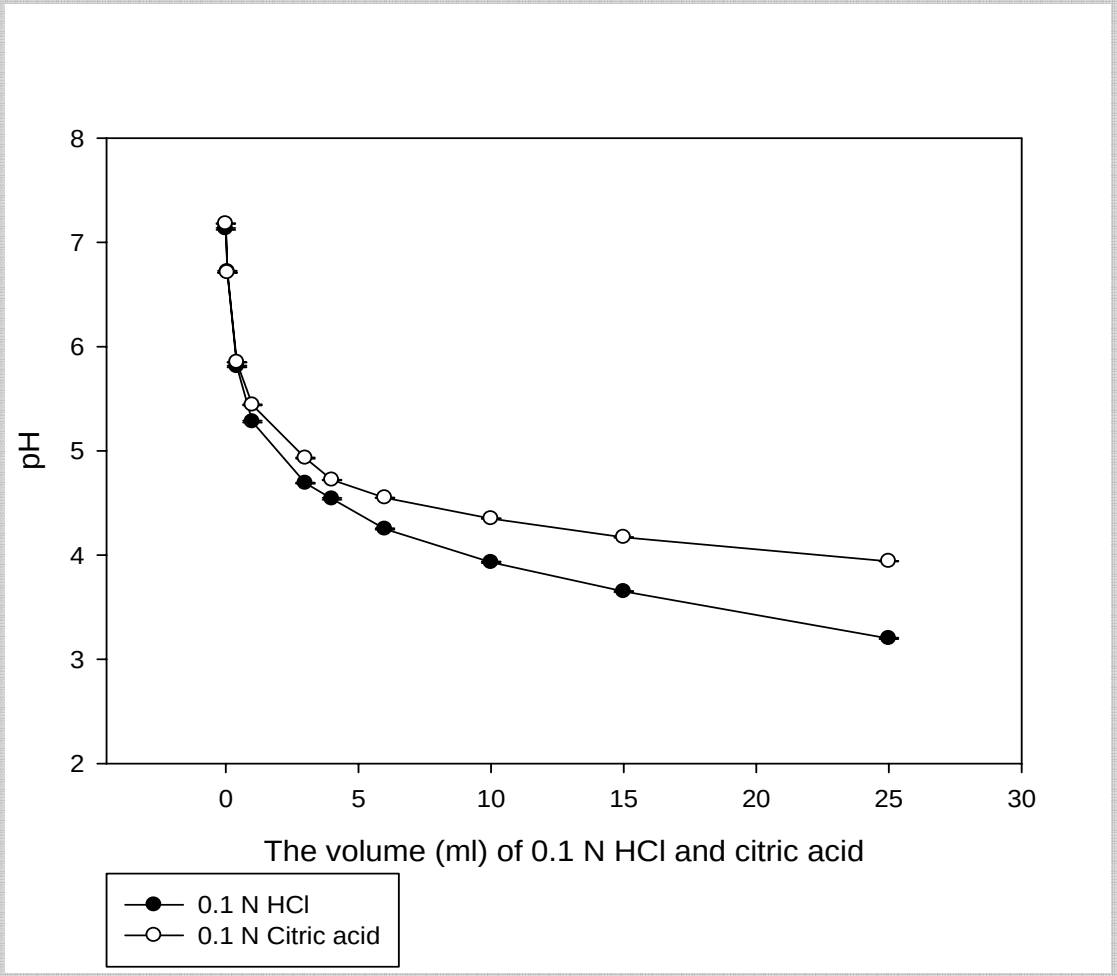
Although the two acids had the same normality, the two titration curves differed significantly. HCl exhibited a stronger ability to adjust the pH of 1% sodium alginate solution because it is a strong acid and fully dissociated in aqueous solutions. However, citric acid is a weaker acid with three acid dissociation constants (pK_{a1} = 3.13, pK_{a2} = 4.76, pK_{a3} = 6.40) (Barron et al., 1999). Citric acid is a buffer around pH 4.76 - hence the greater need for more acid to neutralize the alginate.

These results are consistent with that reported by Draget et al (2006). The results of the titration with acids could be different if other types of sodium alginate were used.

Adjusting the pH of a sodium alginate solution to less than pH 4 will result in the formation of alginic acid gels. Alginic acid gels will retard the formation of Ca-alginate gel (Draget et al., 2006).

To assess the impact of other solutes on the titration curve, the sodium alginate stock solution was tested. Results are presented in Appendix 1B and summarized in Figure 4.2. The solution originally used by the company had a pH value of 5.82. However, the addition of HCl resulted in the same rate of pH drop as the solution containing alginate alone. In this formulated sodium alginate solution, sodium alginate has the primary buffering effect.

Figure 4.1. Titration curve for 1% sodium alginate in water.



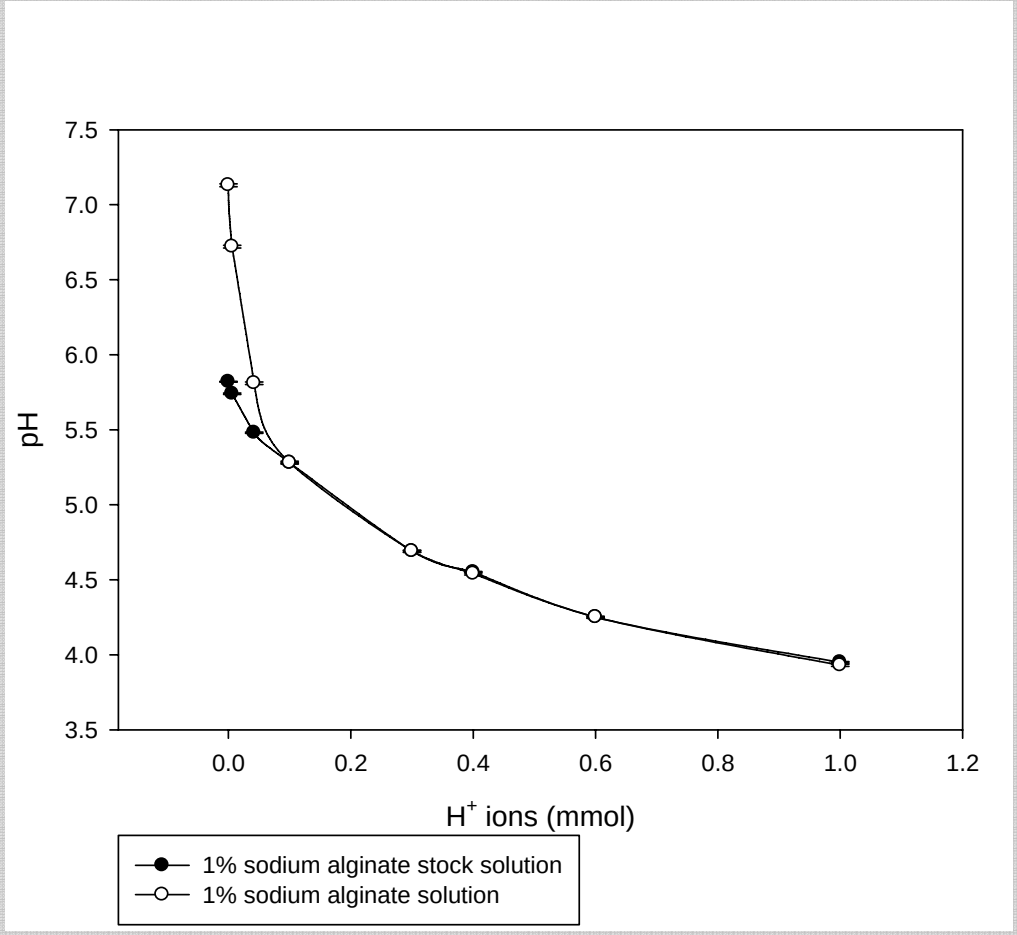
Footnotes: 100 g of 1% sodium alginate Protanal LF 120 was titrated with 0.1 N HCl and 0.1 N Citric acid at 20ºC.

• each data point represents 4 replicates

• error bars represent standard errors

• row data in Appendix 1A

Figure 4.2. Titration curve for sodium alginate stock solution



Footnotes: 100 g of 1% sodium alginate stock solution and 100 g of 1% sodium alginate solution were titrated with 0.1 N HCl at 20ºC.

• the type of the sodium alginate used was Protanal LF 120

• the stock solution was: sodium alginate 1%; guar gum 0.4%; castor sugar 27.5%; SHMP 0.1%; water 29%; glucose syrup 20%; glycerine 7%; dextrose 14%; wheat starch 1%.

• each data point represents 4 replicates

• error bars represent standard errors

• row data in Appendix 1B

The original industrial formulation involved the use of GDL to lower the pH. At the usage applied in the industry, the GDL reduced the pH in the first hour from pH 5.88 to 4.86 (Table 4.1.). The pH changed slightly in the following hours and equilibrated at pH 4.73. A pH of 4.73 was not sufficiently low to release Ca^{2+} ions from some calcium salts commonly used, like DCP. In this case, the gelation caused by sodium alginate reacting with Ca^{2+} ions would not occur.

Table 4.1. Effects of Glucono delta lactone on the pH of sodium alginate stock solution

Time (h)	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
pH	5.88	4.86	4.83	4.80	4.79	4.78	4.77	4.77	4.76	4.76
STDEV	0.01	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.01
Time	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
pH	4.74	4.74	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73
STDEV	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Footnotes: the pH value was read after 0.095 ml of 29% (w/v) GDL was added to 50 g of the sodium alginate solution

- the composition of the alginate stock solution was given in Figure 4.2.
- each value is calculated from the data of 2 replicates

4.2 Calcium salts and gelation characteristics

The gelation of sodium alginate is determined by the availability of free calcium ions in the solution. For example, adding stock solution to a $CaCl_2$ solution where the calcium is completely ionised causes a gel to form immediately.

The gelation rate of an alginate solution depends upon the particle size and intrinsic solubility characteristics of the calcium salt (ISP, 2007). About 7.2% (w/w) calcium ions, based on the weight of sodium alginate, was stoichiometrically required for complete gelation. In addition, some calcium salts are only solubilised and ionized at low pH values. In this trial, calcium salts were used at 7.2% (w/w) calcium ion : sodium alginate and the pH was adjusted down to pH 4 with HCl. It was also believed that the solution's temperature could play a role in calcium salt solubility and this variable was included in the trial.

Different calcium salts release different amounts of calcium ions into solution. The proportion of calcium for each of the salts used is shown in Table 4.2

Table 4.2 Proportion of calcium ions from different calcium salts

Calcium salt	MW	% Ca	M (g)
Dicalcium phosphate	172.09	23.29	0.031
Calcium lactate	308.3	13.00	0.055
Calcium carbonate	100.09	40.04	0.018
Calcium pyrophosphate	254.1	15.77	0.046
Calcium chloride	147.02	27.26	0.026
Calcium sulfate	172.17	23.28	0.031
Calcium citrate	570.5	7.03	0.102

Where: MW = molecular weight

M = weight of calcium salt required for a full gelation of 10 g of stock

Results are given in Appendix 2A and summarized in Table 4.3. Calcium lactate was rapidly soluble and effectively gelled the alginate immediately. There was no measurable influence of pH or temperature on this salt.

Temperature played no significant role in the rate of gelation of any of the calcium salts.

The gelling time for DCP, $CaSO_4$, $CaCO_3$ was significantly influenced by solution pH. In all instances, a lower pH resulted in a shorter (faster) gelation time. At pH 4.0, $CaSO_4$ took nearly 3 days to gel; $CaCO_3$ took much longer. Only DCP gelled in a reasonable time span (5 – 20 hours). However, calcium lactate was insensitive to pH like calcium chloride. These two salts were able to react with an alginate solution immediately due to their high solubility in water. Therefore, they both could be used for making setting bath solutions in the Ca-alginate gel beads production.

One problem with this experiment was the method used to measure formation of a gel. A simple procedure, stirring with a glass rod was used to assess when the solution viscosity changed. This was adequate for the purpose of this trial, but was qualitative. At 60ºC, for example, the solution viscosity was much less than 20ºC and this may have accounted for a failure to note a temperature effect on gelation. This problem was not an issue with the relative rates of gelation among salts and within pH variations at 20ºC.

It was assessed from the literature that adjusting to pH ≤ 4.0 caused the formation of alginic acid gels. These kinds of gels would prevent from forming Ca-alginate gels. Alginic acid gels were softer than Ca-alginate gels, causing an undesirable texture and properties of the final product. Thus a pH adjustment to pH 4.2 was used for future research work.

Table 4.3 Gelation time of alginate solution by using different calcium salts

Calcium salt	Amount of Ca salt (g)	Temperature (ºC)	pH	Gelation time (min)
Calcium lactate	0.56	20	6	3±0.00
			5	3±0.00
			4.5	3±0.00
			4	3±0.00
	0.56	60	6	3±0.00
			5	3±0.00
			4.5	3±0.00
			4	3±0.00
Dicalcium phosphate	0.3	20	6	2010±0.00
			5	875±7.07
			4.5	85±7.07
			4	5±0.00
	0.3	60	6	2045±7.07
			5	910±14.14
			4.5	95±7.07
			4	20±7.07
Calcium carbonate	0.18	20	6	19690±14.14
			5	12485±7.07
			4.5	8165±7.07
			4	5290±14.14
	0.18	60	6	more than 3 days
			5	more than 3 days
			4.5	more than 3 days
			4	more than 3 days
Calcium sulfate	0.3	20	6	165±7.07
			5	125±7.07
			4.5	95±7.07
			4	60±0.00
	0.3	60	6	180±14.14
			5	140±14.14
			4.5	115±7.07
			4	80±0.00

Footnotes: The gelation rate was determined using 50 g of the solution containing 2% Protanal LF 120 alginate and 5% sucrose (all w/w). The pH of the solution was adjusted using 0.1 N HCl.

- format of values: mean ± standard deviation
- each value is calculated from 2 replicates

4.2.1 Influence of pH on the solubility of dicalcium phosphate

The ionisation of DCP was measured by the rate of gelation of the sodium alginate stock solution. Gelation was strongly influenced by the pH of the solution (Appendix 2B and Table 4.4). The original stock solution had a pH of 5.8 and gelation time was very slow. As the pH was lowered, the gelation time became significantly shorter.

It was observed subjectively that rapid acidification of the stock solution resulted in weaker and brittle gels, consistent with Alting et al (2000).

Table 4.4 Gelation time of sodium alginate stock solution using DCP at different pH values

pH	Gelation time (h)
5.8	15.97±0.07
5	13.10±0.09
4.2	1.60±0.05
3.7	0.72±0.04

Footnotes: The gelation time was measured by adding DCP (0.06 g) to 20 g of the sodium alginate stock solution. The pH of solution was adjusted using 0.1 N HCl.

- the type of the sodium alginate used was Protanal LF 120
- format of values: mean ± standard deviation
- each value is calculated from 4 replicates

4.2.2 Influence of chelating agent (SHMP) on gelation

The stock alginate solution was prepared and the pH was adjusted to pH 4.0 using HCl. Different amounts of SHMP were added and the solution was well mixed. A constant amount of DCP (0.3 g) was then added and the gelling time was measured. Results are given in Table 4.5. Clearly, the higher the concentration of SHMP, the longer the gelation time was found.

The results confirmed comments from alginate suppliers (ISP, 2000).

Table 4.5 Effect of SHMP on the gelation time

SHMP (g)	Gelation time (min)
0	5.0±0
0.1	152.5±4
0.2	420.0±0

Footnotes: The gelation time was measured by adding DCP (0.3 g) to 50 g of the sodium alginate stock solution containing different amounts of SHMP. The pH of solution was adjusted to 4 using 0.1 N HCl before addition of DCP.

- the type of the sodium alginate used was Protanal LF 120
- format of values: mean ± standard deviation
- each value is calculated from 2 replicates

4.3 Influence of calcium chloride setting bath

The manufacture of alginate beads is a two-step procedure. Firstly, the stock alginate solution is converted to droplets and these are set by immersion in a calcium chloride solution. This creates an immediate gel “skin” and the bead shape is achieved. The second stage requires calcium ions to be released in the ungelled liquid solution inside this bead, forming a gel inside and thereby creating a solid alginate gel bead.

Given the composition of the alginate stock solution, the impact of the immersion in $CaCl_2$ was of key importance. Too long an immersion time results in excess uptake of $CaCl_2$ which impacts an undesirable bitter taste to the bead. These are also issues related to yields and water content of the beads, which needed to be quantified.

A stock solution was prepared and droplets of approximate 5 mm diameter were formed in a 5% (w/w) $CaCl_2$ solution. These beads were left to soak in the $CaCl_2$ bath for various times as shown in Table 4.6. The longer the beads were left in the water, the more water was absorbed. Detailed results are provided in Appendix 3.

By using a solution of 5% $CaCl_2$ in 60% (w/w) sucrose, there was no uptake of water into the beads (Table 4.6). This solution was roughly isoosmotic with the gel beads. This clearly shows the water uptake was from osmosis into the highly concentrated stock solution inside the gel beads.

This observation is consistent with the process of swelling of polysaccharide gels (Sriamornsak and Kennedy, 2008). It should be noted that water uptake was extremely rapid and therefore the first few minutes of immersion resulted in a big weight gain. This extra water would need to be removed again by drying.

Table 4.6 Impact of $CaCl_2$ bath immersion on total moisture of gel beads

Bath	Setting time (min)	Total moisture (%)
$CaCl_2$	**1**	42.36±1.39
$CaCl_2$	**5**	50.52±0.68
$CaCl_2$	**30**	64.06±1.73
$CaCl_2$	**60**	68.80±1.40
$CaCl_2$+sucrose	**60**	35.51±0.91

Footnotes: The total moisture contents were obtained by drying the beads in an oven at 105ºC overnight. Before the moisture test, these beads were produced and left in the two setting bathes in different setting times. Four setting times (1, 5, 30 and 60 min) were used for the 5% $CaCl_2$ bath. Another bath with 5% $CaCl_2$ and 60% sucrose had only one setting time of 60 min.

• the type of the sodium alginate used was Protanal LF 120

• format of values: mean ± standard deviation

• each value is calculated from 6 replicates

4.4 Air drying of the gel beads

After the alginate gel beads are produced, they need to be dried to reduce moisture to ensure they are shelf stable (low Aw). The gel beads are dried at 35ºC in a forced air oven in the industry. During drying, several changes happen in the beads. The inside of the beads solidify by the internal setting as calcium is released slowly within mixture. However, in industry it has been observed that the beads centre remains liquid for a long time and there is syneresis of liquid material through leaching or because the beads are squashed. This has led to some issues, such as the loss of the materials from the beads, loss of yield, and stickiness on the surface of the beads, causing the beads to stick together during drying. The clumps of beads cost more labor to separate them during the drying stage.

These problems required reformulation of the gel beads. The object was to compare the properties of those beads to find out the best formula. Six formulae were used in the trials as shown in Table 4.7. Each formula was prepared using the method stated in section 3.2.1.

Formula 1 was the original formulation from the industry that needed to be improved. Formula 2 was replaced guar gum and glucose syrup with sucrose. Formula 3 deleted wheat starch, but added table sugar, xanthan gum and maltodextrin N-LITE LP. Formulae 4-6 did not contain guar gum, glucose syrup or wheat starch, but used maltodextrin MD1. In addition the amounts of dextrose and MD1 differed among formulae 4-6.

All beads were produced at pH 4.2 with a calcium chloride bath setting time of 1 min. A short setting time (1 min) was used to avoid an excess uptake of bath solution. A large volume of solution absorbed could dilute the central materials of beads and thus result in a less severe syneresis. Also, one minute was sufficient time to build up a strong shell for a gel bead, as the reaction between Ca^{2+} ions and alginate occurred immediately. To test the changes of the weight loss of the beads and the amount of the materials leached from the centre of the gel beads as the drying time increased, the gel beads were

placed in a petri dish and dried in an oven at 35ºC for up to 66 h. During the drying, at regular intervals, the petri dish was removed from the oven and the gel beads were transferred using a spoon to a new, clean, pretared petri dish. These gel beads were then accurately weighed and the weight change of the beads was calculated. They were then returned to the original dish and returned to the oven for more drying.

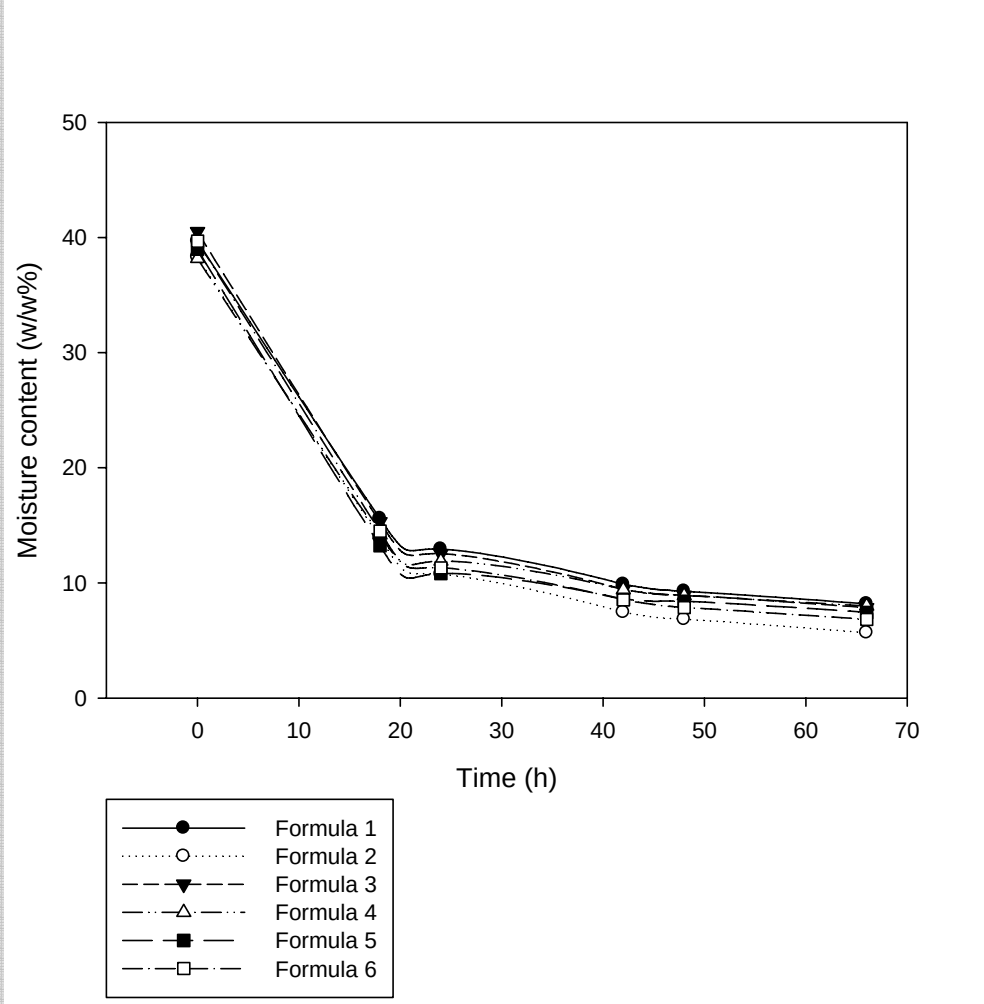
Table 4.7 Formulations used in the tests of production of alginate gel beads

Part	Ingredient	Formula					
		1 (g)	2 (g)	3 (g)	4 (g)	5 (g)	6 (g)
A	Sodium alginate	1	1	1	1	1	1
	Guar gum	0.4	-	-	-	-	-
	Castor sugar	5	-	-	5	5	5
	Sucrose	-	6.4	6.4	-	-	-
	SHMP	0.1	0.1	0.2	0.1	0.1	0.1
	Water	28.5	32.5	32.4	32.5	32.5	32.5
B	Castor sugar	22.5	22	22	23.5	23.5	23.5
	Glucose syrup	20	-	-	-	-	-
	Glycerine	7	7	7	7	7	7
	Dextrose	14	30	27	30	-	15
	Maltodextrin MD1	-	-	-	-	30	15
	Maltodextrin N-LITE LP	-	-	3	-	-	-
	Xanthan gum	-	-	1	-	-	-
	Wheat starch	1	1	-	-	-	-

The results are given in Appendix 4 and summarized in Figure 4.3. All six formulae had the similar total moisture content at around 39% (Appendix 4G). During the drying, they gave the same rate of moisture loss of the beads. The moisture of the beads was mostly lost in the first 24 h. After one day evaporation, the percentage of the moisture content of those beads dropped

to approximately 15%. At the end of the drying test at 35ºC (66 h), the moisture contents of the beads remained in a range from 5 – 8%.

Figure 4.3. Moisture content of gel beads during air drying



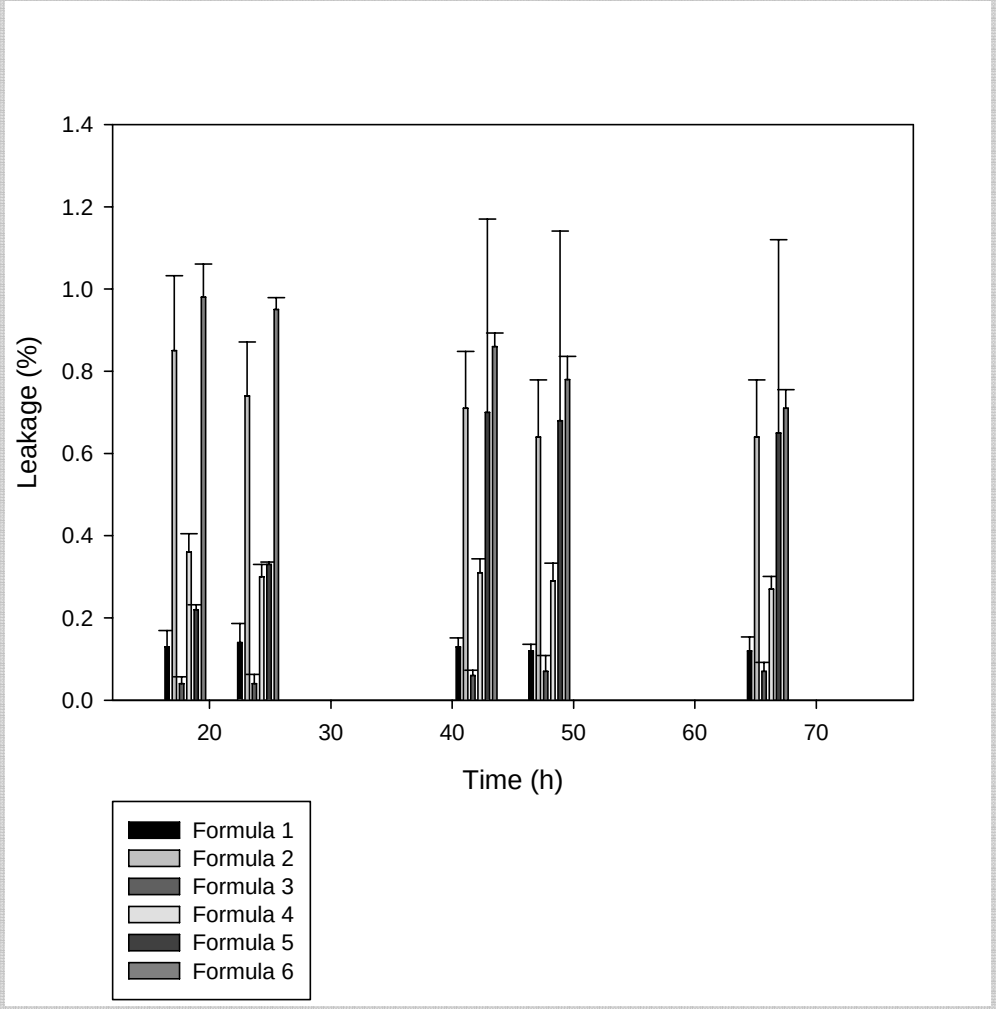
Footnotes: The beads were extruded into a $CaCl_2$ bath for 1 min. The beads were dried in an air oven at 35ºC for up to 66 h.

- the type of the sodium alginate used was Protanal LF 120
- each data point represents 4 replicates
- error bars represent standard errors

During the air drying of beads at 35ºC, a sticky fluid that leached from the beads was found in the petri dishes. The leakage of the beads was measured at each time once the beads had been removed to a clean petri dish.

The results of the weight of leached material remaining in the petri dish are shown in Figure 4.4. It is important to recognize that this material remained in the petri dish for the entire drying period. Hence there is a gradual loss of material with increased drying time, representing a gradual dehydration of the leachate as the beads dried. While there are significant differences among these leachate values, there is no consistent pattern that can be attributed to any particular materials.

Figure 4.4. Change of leaking materials from gel beads during drying



Footnotes: The beads were extruded into a $CaCl_2$ bath for 1 min. The beads were dried in an air oven at 35ºC for up to 66 h.

- formulations are same as those for Figure 4.3.
- the type of the sodium alginate used was Protanal LF 120
- each data point represents 4 replicates
- error bars represent standard errors

4.5 Controlling exudation from beads

4.5.1 Influence of SHMP, pH and maltodextrins

The focus of these trials was to stop exudation of sticky materials from the bead. It was postulated that a more rapid gelation of the alginate solution inside the bead and the addition of a starch (maltodextrin) component into the formulation would address this stickiness problem. Maltodextrins were employed due to their properties suitable for making gel beads (see the specification sheets in Appendix 9). They could be used as a bulking agent and contribute viscosity. Based on earlier work, it was decided that dicalcium phosphate dihydrate (DCP) would be used as the calcium salt. Calcium ions would be released by lowering the pH to pH 4.2. It was critical to ensure no gelation occurred until the bead had been formed in the $CaCl_2$ bath because agitation of the set alginate gel would permanently destroy the gel structure. Thus, SHMP was added to chelate free calcium until the reduced pH was able to solubilise DCP. At that point the Ca^{2+} ions would swamp the SHMP and the alginate would be able to gel.

An experiment was designed to test these theories, using four variables that included maltodextrin N-LITE LP (0 and 5% (w/w)), dextrose (25 and 30% (w/w)), SHMP (0.1, 0.2 and 0.5% (w/w)) and pH (4.2, 5 and 6). The experimental design is shown in Table 4.8.

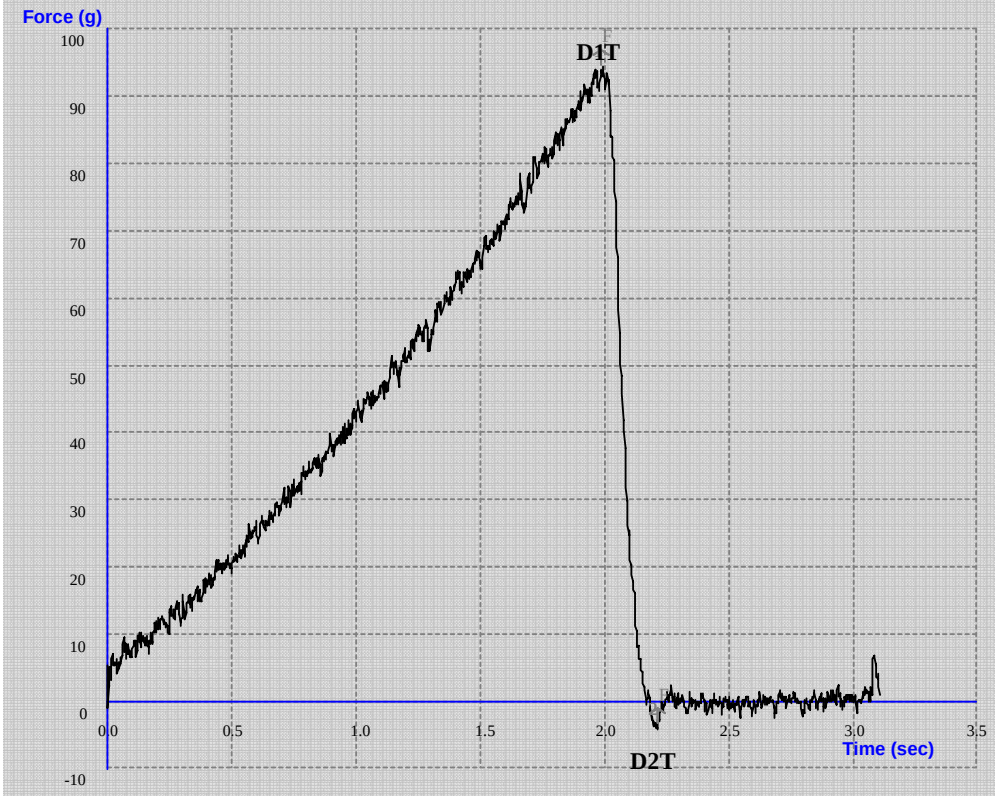
Table 4.8 Experimental design to assess exudation of beads

	Part A				Part B					
Formula	Alginate (g)	Sucrose (g)	Water (g)	SHMP (g)	Castor sugar (g)	Glycerine (g)	Wheat starch (g)	DT (g)	MDT LP (g)	pH
MSP 1	1	6.4	32.5	0.1	22	7	1	30	0	6
MSP 2				0.1				30	0	5
MSP 3				0.1				30	0	4.2
MSP 4				0.1				25	5	6
MSP 5				0.1				25	5	5
MSP 6				0.1				25	5	4.2
MSP 7				0.2				30	0	6
MSP 8				0.2				30	0	5
MSP 9	all formulae used same			0.2	all formulae used same			30	0	4.2
MSP 10	composition			0.2	composition			25	5	6
MSP 11				0.2				25	5	5
MSP 12				0.2				25	5	4.2
MSP 13				0.5				30	0	6
MSP 14				0.5				30	0	5
MSP 15				0.5				30	0	4.2
MSP 16				0.5				25	5	6
MSP 17				0.5				25	5	5
MSP 18				0.5				25	5	4.2

Where: MDT LP = Maltodextrin N-LITE LP
MSP = maltodextrin, SHMP and pH
DT = dextrose

A texture analyzer was used to determine the hardness and stickiness of the alginate gel beads produced from each formula. They were measured by penetrating the adhesive beads with a cylinder probe, where the maximum force value was taken to indicate the hardness. The probe was then removed by reversing the texture analyzer motor, and the negative peak force representing the resistance to withdrawal of the probe from the beads was measured as the stickiness (or adhesiveness, adhesion). The typical shape of a texture analyzer curves is shown in figure 4.5.

Figure 4.5 Texture analyzer curve of alginate gel beads



Footnotes: The curve was produced by Texture Exponent 32 software after the hardness and stickiness of the alginate gel beads were measured using a texture analyzer.

• The beads were penetrated by a cylinder probe. The maximum force value (D1T) was taken as the indication of the hardness. The negative peak force (D2T) representing the resistance to withdrawal of the probe from the beads was referred to the stickiness.

All beads were extruded using a syringe into a 5% (w/w) calcium chloride bath. The beads were left in the bath for 1 min and then collected with a sieve. To dry the harvested beads, they were placed into an air oven at 35ºC for 24 h before measured by a texture analyzer. The actual results of this textural analysis are provided in Appendix 5A and summarized in Table 4.9.

Table 4.9 Impact of formulation on hardness & stickiness of alginate gel beads

Formula	Hardness (force, g)		Stickiness (force, g)	
	Mean	STDEV	Mean	STDEV
MSP 1	157	7.8	-12	1.7
MSP 2	142	2.9	-6	1
MSP 3	111	13.4	-4	0.6
MSP 4	85	3.1	-4	0.5
MSP 5	93	6.5	-6	0.8
MSP 6	99	8.8	-7	0.9
MSP 7	117	3.9	-4	1.1
MSP 8	136	4.4	-4	0.9
MSP 9	138	11.3	-5	1.1
MSP 10	85	2	-6	1.9
MSP 11	105	8.6	-8	1.4
MSP 12	107	5.5	-7	1.1
MSP 13	72	4.7	-3	0.8
MSP 14	59	6.2	-2	0.8
MSP 15	48	1.8	-2	0.6
MSP 16	54	3	-3	0.7
MSP 17	70	6.8	-4	1.6
MSP 18	63	5	-3	1.3

Footnotes:

• Formula: see table 4.8

• STDEV = standard deviation

• each mean value was calculated from the data of 6 different gel beads made from one bath of beads

The data of the hardness and stickiness of the alginate gel beads was analyzed by ANOVA. The statistical results are presented in Appendix 5b.

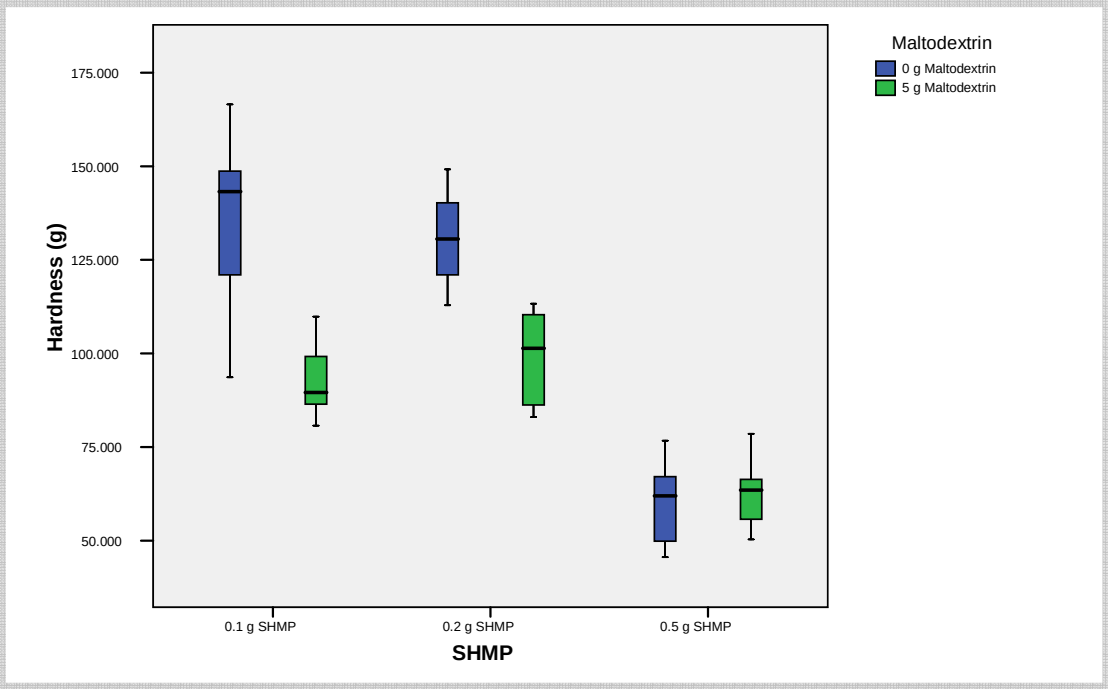
SHMP had a major influence on the hardness of gel beads ($p<0.05$). The greater the amount of SHMP added, the lower the hardness of the beads (Figure 4.6). High contents of SHMP could chelate more calcium ions, leaving less free calcium ions to react with the alginate. In addition, SHMP significantly affected the stickiness of gel beads ($p<0.05$). The stickiness of gel beads decreased as concentrations of SHMP increased (Table 4.9). The reasons for these changes in hardness and stickiness are unclear and not found in literature.

At constant SHMP concentrations, maltodextrin N-LITE LP exhibited significantly lower values of hardness than those without adding N-LITE LP ($p<0.05$) (Figure 4.6). On the other hand, stickiness of beads was insignificantly affected by the amount of N-LITE LP used.

The pH of the alginate stock solution had no significant effect on the stickiness of gel beads. However, pH had a significant effect ($p<0.05$) on the hardness of the beads. With the addition of 0.1 or 0.5 g of SHMP (but without adding maltodextrin N-LITE LP), the hardness of the beads decreased as the pH decreased. In contrast, the addition of the maltodextrin resulted in an increase in the hardness of the beads with a decreasing pH (Table 4.9).

The reasons for these changes with pH are not clear, as at pH 6.0 there would have been little, if any solubilisation of DCP. As a result, there would be very low levels of free Ca^{+2} ions at pH 6.0. From experiments in open solution, it was clear that alginate did gel at pH 4.2.

Figure 4.6 Effect of SHMP and maltodextrin on the hardness of alginate gel beads.



Footnotes: Each boxplot can be interpreted as follows:

• The box itself includes the middle 50% of the data. The upper and lower edge (hinge) of the box presents the 75 and 25 percentile of the data set, respectively. The range of the middle two quartiles is known as the inter-quartile range.

• The line in the box presents the median value of the data.

• The ends of the vertical lines (or whiskers) present the minimum and maximum data values.

4.5.2 Influence of alginates and gums

The stickiness of the surface of beads, caused by syneresis from the gel beads, is not related directly to the stickiness measured using a texture analyzer. This syneresis should be overcome by preventing the sticky materials leaching from inside the beads. If the viscosity of the sodium alginate stock solution could be increased, the materials inside the beads might be locked up. Also, different types of alginate might contribute to the different viscosities of the alginate solution.

This experiment involved 28 formulae that were designed by utilizing four types of alginates (Manucol LF, Manucol DH, Manugel GMB, and Protanal LF 120), differing amounts of xanthan gum (0, 0.1, 0.5 and 1 g) and guar gum (0.1, 0.5 and 1 g) (Table 4.10). The alginate gel beads from each formula were produced using the standard method in section 3.2.2.

The four types of alginate differed in molecular weight and viscosity. They were: Manucol LF (International Specialty Product Inc, Australasia via Alchemy Chemicals Ltd, NZ): 10 to 40 mPa·s for a 1% concentration solution at 20ºC; Manucol DH (International Specialty Product Inc, Australasia via Alchemy Chemicals Ltd, NZ): 40 to 90 mPa·s for a 1% concentration solution at 20ºC; Manugel GMB (International Specialty Product Inc, Australasia via Alchemy Chemicals Ltd, NZ): 110 to 270 mPa·s for a 1% concentration solution at 20ºC; Protanal LF 120 (FMC BioPlymer, USA): 200 to 400 mPa·s for a 1% concentration solution at 20ºC. The technical specification sheets are given in Appendix 8.

Table 4.10 Experimental design for syneresis evaluation

Formula	Part A				Part B						
	Alginate (g)	Sucrose (g)	SHMP (g)	Water (g)	Xanthan (g)	Guar (g)	Castor sugar (g)	Glycerine (g)	Dextrose (g)	MDT LP (g)	pH
AXG 1		6.4	0.2	32.5	0	0	22	7	27	3	4.2
AXG 2	*MANUCOL*				0.1	0					
AXG 3	*LF*				0.5	0					
AXG 4					1	0					
AXG 5		as	above		0	0.1		as	above		
AXG 6	1				0	0.5					
AXG 7					0	1					
AXG 8					0	0					
AXG 9	*MANUCOL*				0.1	0					
AXG 10	*DH*				0.5	0					
AXG 11		as	above		1	0		as	above		
AXG 12					0	0.1					
AXG 13	1				0	0.5					
AXG 14					0	1					
AXG 15					0	0					
AXG 16	*MANUGEL*				0.1	0					
AXG 17	*GMB*				0.5	0					
AXG 18		as	above		1	0		as	above		
AXG 19					0	0.1					
AXG 20	1				0	0.5					
AXG 21					0	1					
AXG 22					0	0					
AXG 23	*Protanal*				0.1	0					
AXG 24	*LF 120*				0.5	0					
AXG 25		as	above		1	0		as	above		
AXG 26					0	0.1					
AXG 27	1				0	0.5					
AXG 28					0	1					

The results of the hardness of the alginate gel beads measured by a texture analyzer are given in Table 4.11. Raw data are presented in Appendix 6A.

Table 4.11 Impact of formulation on hardness of alginate gel beads

Formula	Alginate (g)	Alginate viscosity (mPa.s)	Xanthan (g)	Guar (g)	Hardness (force, g)	
					Mean	STDEV
AXG 1	*MANUCOL LF*	10-40	0	0	28	1.6
AXG 2			0.1	0	27	1.6
AXG 3			0.5	0	32	1.9
AXG 4			1	0	38	2
AXG 5			0	0.1	27	3.5
AXG 6			0	0.5	26	1.2
AXG 7			0	1	24	1.6
AXG 8	*MANUCOL DH*	40-90	0	0	33	1.4
AXG 9			0.1	0	31	1.3
AXG 10			0.5	0	33	2.1
AXG 11			1	0	26	3
AXG 12			0	0.1	35	2.1
AXG 13			0	0.5	38	1.7
AXG 14			0	1	39	1.7
AXG 15	*MANUGEL GMB*	110-270	0	0	66	5.4
AXG 16			0.1	0	67	2
AXG 17			0.5	0	86	4.2
AXG 18			1	0	64	3
AXG 19			0	0.1	81	4.8
AXG 20			0	0.5	73	2.9
AXG 21			0	1	60	4.9
AXG 22	*Protanal LF 120*	200-400	0	0	70	5.3
AXG 23			0.1	0	84	2.4
AXG 24			0.5	0	59	2.5
AXG 25			1	0	51	2.7
AXG 26			0	0.1	80	6.3
AXG 27			0	0.5	64	1.5
AXG 28			0	1	75	3

Footnotes:

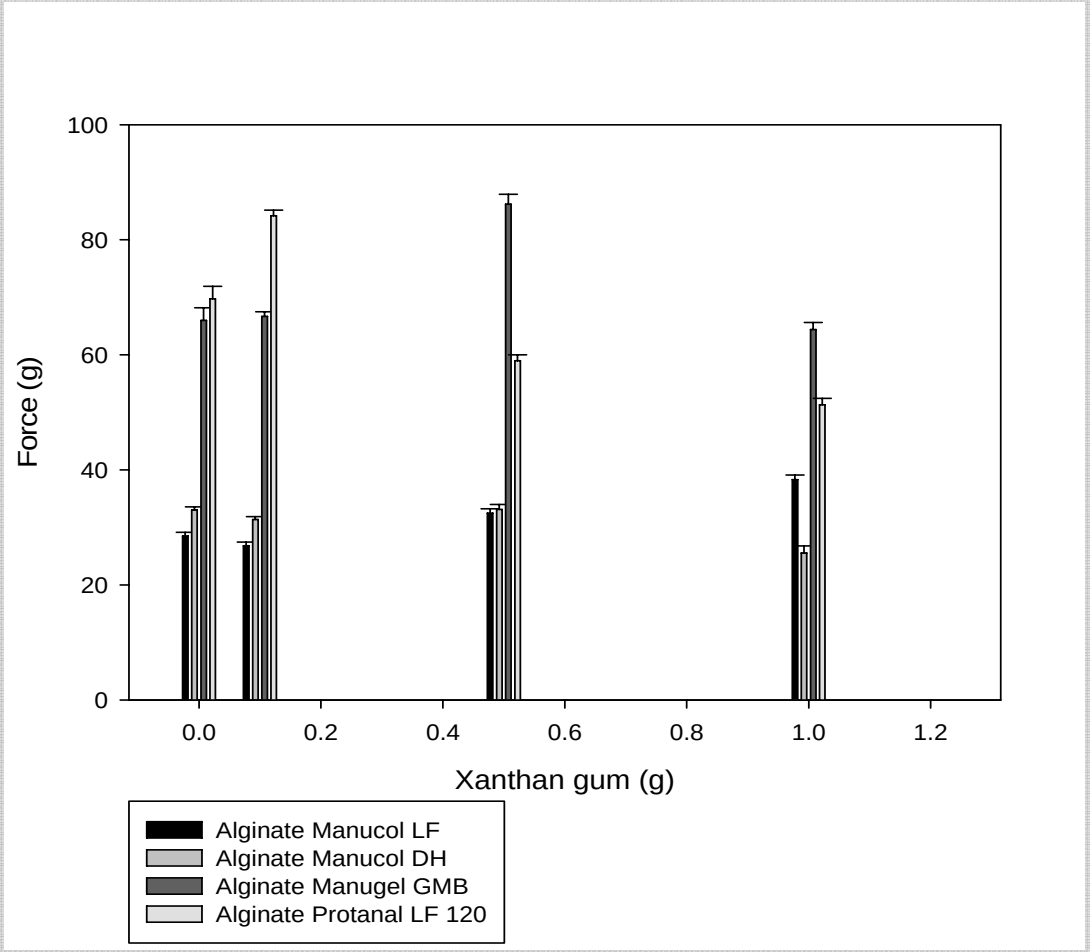
- formula relates to formulation in Table 4.10
- each mean value was calculated from the data of 6 replicates
- alginate viscosity is 1% solution measured at 20ºC

The texture data were analyzed by ANOVA (see Appendix 6B).

The alginates had a significant effect on the hardness of gel beads ($p<0.05$). In the absence of other gums, the hardness of the beads increased with increasing viscosity of the alginate used (Table 4.11). The beads using alginate Protanal LF 120 exhibited the greatest hardness at approximately 70 g force, whereas those formed from Manucol LF had the lowest hardness at around 28 g force.

Significant differences ($p<0.05$) were also found by using either xanthan or guar gum. The highest hardness was seen in the gel beads formed using alginate Protanal LF 120, Manugel GMB and xanthan (Figure 4.7).

Figure 4.7 Impact of alginate and xanthan gum on hardness of alginate gel beads



Footnotes:

• formula relates to formulation in Table 4.10

• the data columns represent hardness of beads affected by different alginates and xanthan gum

• each data column represents 6 replicates

• error bars represent standard errors

Syneresis from these beads was assessed qualitatively. The beads were allowed to rest for 24 hours on a glass petri dish, and the level of sticky fluid in the dish was assessed. A score sheet involving 8 different attributes was prepared. These included whiteness, translucence, fractureness, springiness, dryness, stickiness by touching, central firmness, and leakage. Each attribute was assessed using 1 to 10 scale where 1 represented the lowest category for the attribute and 10 the highest category. The results are given in Table 4.12.

From these observations, the following conclusions were reached:

- increased alginate viscosity reduced leakage;
- .xanthan gum completely stopped leakage at 1% concentration;
- .increased viscosity of the gel solution caused increased whiteness of the final beads;
- .increasing xanthan gum decreased fracture, leakage and translucence of the beads.

The attribute of dryness here was supposed to assess the degree of wetness on the surface of the beads. However, the results don't present reasonable assessments due to the poor assessing means that was judged by touching and watching the beads. Hence, the dryness attribute was influenced by other attributes such as stickiness and shininess, especially the differences of dryness among those beads were very close. Also, a trained panel approach was not performed because of the time limit.

Table 4.12 Attributes of the gels beads

Formula	Attribute							
	Whiteness	TLC	FTN	SGN	Dryness	SKNT	CT FMN	Leakage
AXG 1	1	7	9	7	8	9	5	9
AXG 2	1	7	9	7	8	9	6	9
AXG 3	1	7	6	8	9	8	7	1
AXG 4	2	4	5	9	9	8	7	1
AXG 5	1	9	9	7	8	7	6	9
AXG 6	1	8	9	7	8	7	6	9
AXG 7	1	7	9	7	8	7	6	9
AXG 8	1	7	7	7	8	6	6	8
AXG 9	1	7	7	7	8	6	4	8
AXG 10	2	6	4	9	9	6	7	1
AXG 11	3	5	3	9	9	6	8	1
AXG 12	1	8	8	7	8	5	6	7
AXG 13	1	7	8	7	7	5	6	7
AXG 14	2	7	8	7	7	5	6	7
AXG 15	1	9	7	7	8	6	5	5
AXG 16	1	7	7	7	8	6	7	5
AXG 17	2	6	4	8	8	6	8	1
AXG 18	3	5	3	9	9	7	7	1
AXG 19	1	9	6	7	9	7	4	2
AXG 20	1	8	6	7	9	7	4	2
AXG 21	2	7	6	7	9	7	5	2
AXG 22	3	6	6	7	8	8	2	5
AXG 23	3	5	5	8	8	7	7	5
AXG 24	3	5	4	9	9	6	8	2
AXG 25	3	5	2	9	9	5	8	1
AXG 26	2	7	7	6	7	7	3	6
AXG 27	2	6	7	6	7	7	6	6
AXG 28	2	5	5	7	8	6	6	4

Footnotes: Each attribute was assessed using 1 to 10 scores. Score 1 represented the lowest category for the attribute. In contrast, score 10 meant the highest category.

• TLC = Translucence

• FTN = Fractureness

- SGN = Springiness
- SKNT = Stickiness by touching
- CT FMN = Central firmness
- AXG = refers to the formulation in Table 4.10.

Figure 4.8 Images of gels produced by different formulae

Original formula 1 with 0.4 g guar gum

Formula AXG 25 with 1 g xanthan

Formula AXG 28 with 1 g guar gum

Formula AXG 22 without gums

Footnotes: The gels were produced at pH 4.2 with a 5% $CaCl_2$ bath setting time of 1 min using the formulae in Table 4.10.

The benefit of xanthan gum against syneresis is consistent with previous studies (Pongjanyakul & Puttipipatkhachorn, 2007; El Sayed et al., 2002). The combination of xanthan and alginate Protanal LF 120 gave the best results for every option tested and the better properties against syneresis.

4.6 Rheological Comparison of sodium alginate stock solutions

Once the best formula had been found, it was compared to the original formula provided by the company. The two formulae are as follows:

Table 4.13 Comparison of original and optimal experimental formulae

Part	Ingredient	Formula	
		Original industry (g)	Optimal experimental (g)
A	Sodium alginate	1	1
	Guar gum	0.4	-
	Castor sugar	5	-
	Sucrose	-	6.4
	SHMP	0.1	0.2
	Water	28.5	32.4
B	Castor sugar	22.5	22
	Glucose syrup	20	-
	Glycerine	7	7
	Dextrose	14	27
	Maltodextrin N-LITE LP	-	3
	Xanthan gum	-	1
	Wheat starch	1	-

Two sodium alginate stock solutions were prepared. The pH of the solution from the original formula was about pH 5.82. The pH of the solution from the optimal experimental formula was around 5.29. These pH values were not adjusted, so no gelation occurred.

The apparent viscosities of the two solutions were measured using a rheometer. During the determination, the shear rate of the rheometer was

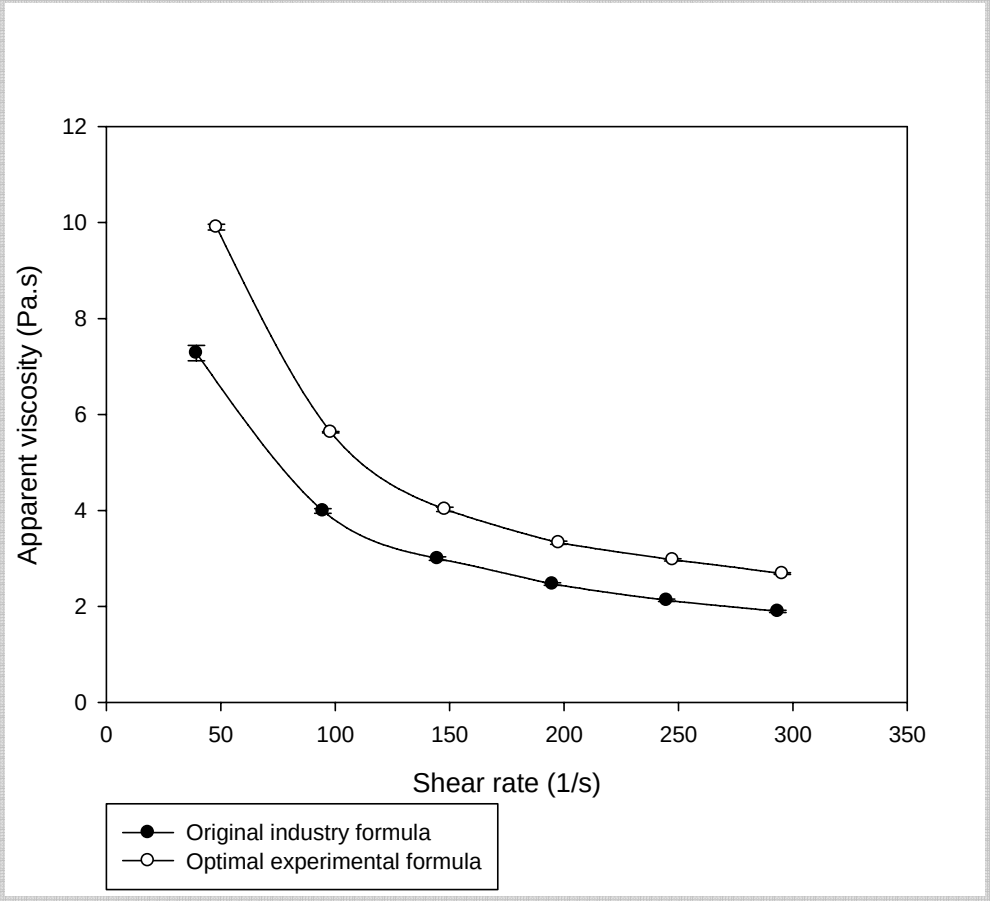
increased from 1 to 300 s^{-1}. The solution was tested for 1 min at 20ºC. The testing data was recorded every 10 s. The resulting data, such as apparent viscosity, shear rate and shear stress, were recorded on the computer connected to the rheometer. The raw data are presented in Appendix 7.

The two kinds of sodium alginate stock solutions showed shear thinning with pseudoplastic rheology (Figure 4.9). This is consistent sodium alginate solutions as studied by ISP (2000).

The stock solution with xanthan gum had an apparent viscosity of 9.9 Pa.s at the shear rate of 48 s^{-1} which was much higher than the original solution (Figure 4.9). The xanthan solution had a higher viscosity at all shear rate.

The logarithm of shear stress versus the logarithm of shear rate was plotted (Figure 4.10). If the two lines are extended back to Y axis, they will not go back to the origin, meaning that there is a yield stress in the solutions. This is consistent with Matthews et al (2005).

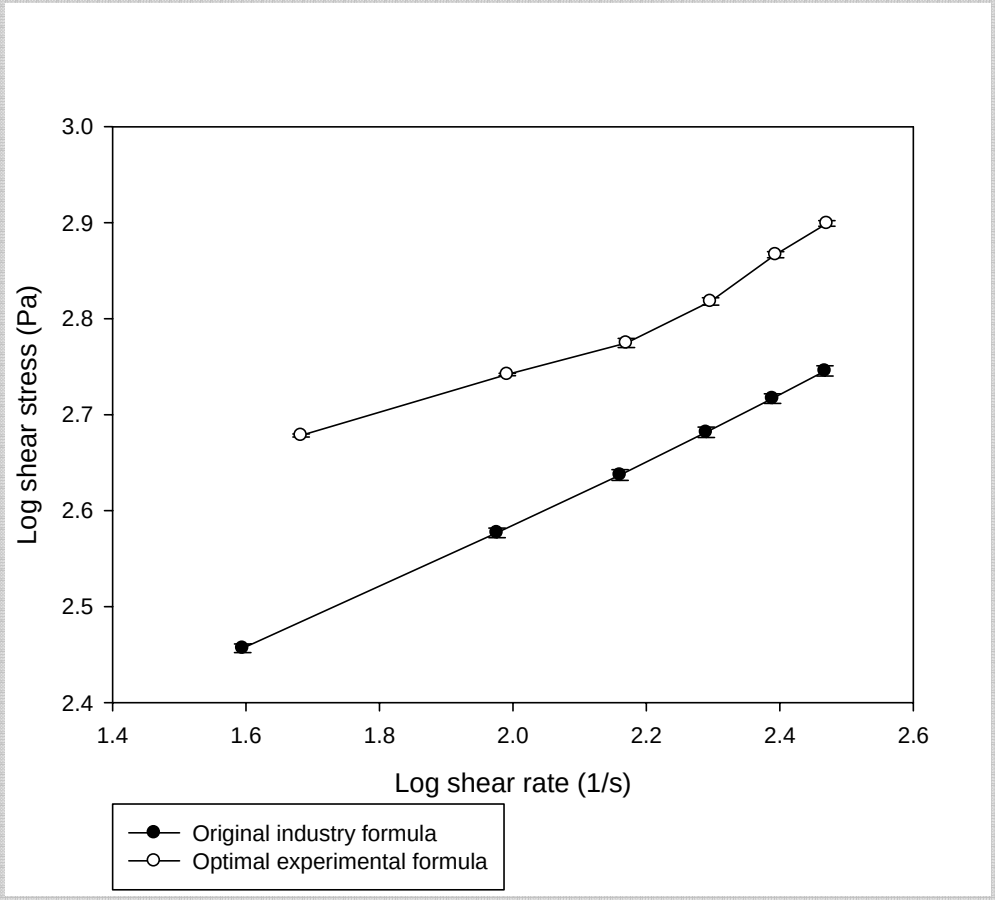
Figure 4.9 Plot of apparent viscosities versus shear rates



Footnotes: The data of apparent viscosity and shear rate were obtained from a rheometer measuring two sodium alginate stock solutions. The solutions were determined at 20ºC. During the determination, the shear rate of the rheometer was increased from 1 to 300 s^{-1}. The solution was tested for 1 min. The testing data was recorded every 10 s.

- formulae of the two stock solutions are shown in Table 4.13
- the type of the sodium alginate used was Protanal LF 120
- each data point represents 6 replicates
- error bars represent standard errors

Figure 4.10 Plot of the logarithm of shear stress versus the logarithm of shear rate.



Footnotes: The data of log shear stress and log shear rate were calculated from the data of shear stress and shear rate that were obtained from a rheometer measuring two sodium alginate stock solutions. The solutions were determined at 20ºC. During the determination, the shear rate of the rheometer was increased from 1 to 300 s^{-1}. The solution was tested for 1 min. The testing data was recorded every 10 s.

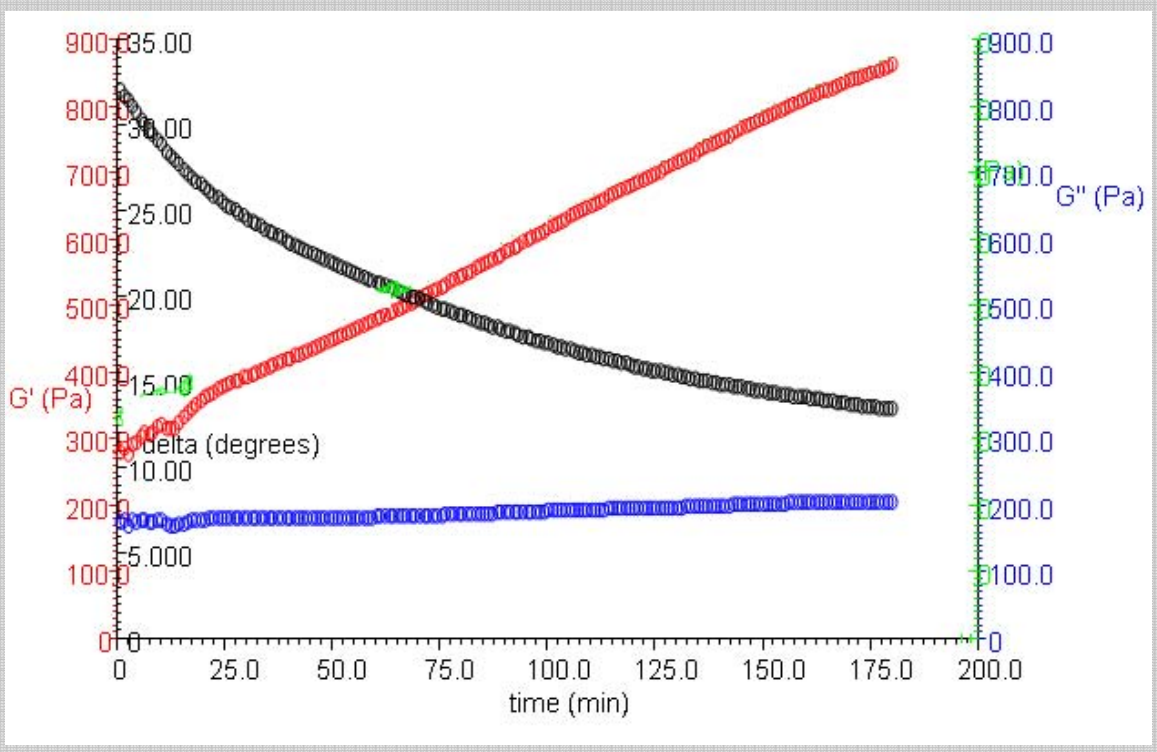
- formulae of the two stock solutions are shown in Table 4.13
- the type of the sodium alginate used was Protanal LF 120
- each data point represents 6 replicates
- error bars represent standard errors

The oscillatory rheology of the sodium alginate stock solution from the optimal experimental formula was determined also using a rheometer. The sodium alginate stock solution (50 g) was weighed and placed in a beaker. Then 0.15 g of DCP was added and dispersed thoroughly throughout the solution. The pH was adjusted to pH 4.2 by adding 0.65 ml of 1.0 N citric acid. After quickly mixing, the solution was loaded on the rheometer plate and tested.

During the test, a further 10 seconds were allowed for sample equilibration before the determination at 20ºC was started. Storage modulus (G') and loss modulus (G'') were recorded over time at a fixed frequency of 1 Hz and at a strain of 1%. The test performed for 3 h. The testing data were recorded every 1 min.

As the sodium alginate stock solution gelled gradually, the oscillatory rheology of the solution was measured. The viscoelastic properties of calcium-induced sodium alginate gels was determined by monitoring the time development of the dynamic moduli (G' and G'') of gelled systems.

Figure 4.11 Variation of G’ and G’’ of the sodium alginate stock solution during gelation



Footnote: : Storage modulus G’ (Pa); : Loss modulus G’’ (Pa);
: Time (min);

Figure 4.11 shows the recorded development of the G’ and G’’ against ageing time for the formation of alginate gel. At the start of the measurement, G’ was about 380 Pa, which was much higher than G’’ at around 160 Pa. At this stage the alginate solution had not finished its gelation yet. G’ should have been lower than G’’ if the solution was really showing a liquid-like behavior. The most likely reason was that the alginate solution was too viscous because of the addition of 1% xanthan gum. This solution appears to behave like a weak gel rather than a liquid solution.

The gel strength (G’) increased with the time, which indicated that alginate gelled gradually as more bonds or stronger bonds were formed within the network. G’’ remained constant during the determination. As a result, the G’ and G’’ curves did not intersect and therefore there was no evidence of gelation. Either the alginate gelled very quickly (before the measurements began) or the presence of xanthan made the solution too viscous and thereby buried the subsequent gelation pattern.

4.7 Factory trial

This optimum formulation was then used for a trial in the factory at Carroll Industries Ltd. The ideal process suggested to hydrate the dry mix containing the alginate, a little of the sugar, and the chelating agent (SHMP) in all the water. Then the remaining sugars, glycerine, maltodextrin and glucose were added. They were mixed well and heated for pasteurization and alginate hydration. The heating method was ineffective and this was ultimately stopped without reaching 80ºC. The DCP was added and mixed quickly throughout the entire mixture. This mixture was then pumped to the bead forming nozzles. At this point, the citric acid was metered into the mix and mixed quickly before being extruded into $CaCl_2$ bath. The beads were removed from this bath as quickly as possible.

In the trial, this formulation was modified due to the limitations of the production facilities. The amount of xanthan used was lowered to 0.5%, because 1% xanthan would have contributed a too high viscosity for the plant. Heating to 80ºC was not possible either. After the production, the centre of the beads did not gel until drying for over 2 days at 35ºC. The reasons were probably that the alginate was not hydrated completely. In addition, a lot of alginate remained as lumps in the mix as it did not wet properly. The SHMP used was probably too high for this trial and may have been a factor in the long gelation time. DCP did not appear to mix well, and perhaps some parts of the mixture did not contain enough calcium salt for the reaction.

5. CONCLUSIONS

A 1% sodium alginate solution in water had an initial pH of 7.15. Addition of various solutes used in making gel beads reduced this starting pH to pH 5.82. Both HCl and citric acid will reduce the pH of this solution and appropriate titration curves for these acids were produced. Care must be taken to avoid the formation of alginic acid (occurs significantly below about pH 4.0) as this will result in a poor gel set.

An optimum formulation was devised using dicalcium phosphate as the source of calcium ion. At pH 5.82 (starting pH of the solution) DCP was insoluble and the calcium ion was unavailable for gelling the alginate. The pH needed to drop to pH 4.2 to release the calcium ion.

SHMP is essential to avoid premature gelation of alginate in a reasonable time frame because of possible contamination of free Ca^{2+} ions from other ingredients. Generally, the higher the concentration of SHMP, the longer the gelation time. Thus, a suitable amount of SHMP needs to be defined to mop up free Ca^{2+} ion at the start of production, but not too high a level to stop gelation once DCP solubilises.

The total moisture content of the beads increased if they remained in the $CaCl_2$ bath. Also, protracted immersion time in $CaCl_2$ results in an undesirable bitter taste with the bead. The first few minutes of the setting were the critical time since the beads absorbed water extremely fast.

During drying at 35ºC, the weight loss of beads mainly occurred in the first 24 hours. In terms of hardness of the beads, the ideal formulation should provide sufficient strength to stop compression and fracturing, or releasing liquid from the centre of the beads. Thus to maximize hardness it is best to:

- increase alginate viscosity (higher molecular weight)
- reduce SHMP
- increase maltodextrin
- increase xanthan gum

A pH of 4.2 was essential to achieve gelation of the central part of the beads in a reasonable time.

In terms of stickiness of the beads, as seen in exudation (syneresis), the best options to minimize this were:

- increase xanthan gum
- increase alginate viscosity
- increase maltodextrin
- reduce SHMP
- reduce setting time in a $CaCl_2$ bath

The alginate stock solution showed shear thinning with a pseudoplastic rheology. The apparent viscosities dropped remarkably as the shear rates increased. At the same shear rate, the solution containing 1% xanthan gum always had a higher value of apparent viscosity than that containing guar gum. The oscillatory rheology measurement of the sodium alginate stock solution containing 1% xanthan gum demonstrated that G' was much higher than G'' during the test time, showing a solid-like behavior.

The optimum formulation for producing gel beads that would set completely within a reasonable time scale, maximum yield and not be sticky is:

- Sodium alginate: 1%
- Sucrose: 6.4%
- SHMP: 0.2%
- Water: 32.4%
- Castor sugar: 22%
- Glycerine: 7%
- Dextrose: 27%
- Maltodextrin N-LITE LP: 3%
- Xanthan gum: 1%

- Dicalcium phosphate 0.3g / 100 g sodium alginate stock solution
- pH: pH 4.2 (adjusted using 1.0 N citric acid)

The modified process of the industry production of gel beads is as follows:

• Dry mix sodium alginate (2 kg), SHMP (0.2 kg), and sucrose (12.8 kg).

• Dissolve the mix slowly into 60 kg (litre) water without forming lumps. Use high speed shear mixer to ensure all lumps removed. Heat to 80ºC to hydrate the alginate.

• Dry mix the xanthan gum (1 kg) with the castor sugar (44 kg). Add glycerine (15 kg), xanthan/sugar, maltodextrin (6 kg), glucose powder (25 kg), glucose syrup (25 kg) to the alginate solution. Mix well and leave for 5-10 min to ensure solubilisation. Maintain at 80ºC to ensure pasteurisation of all materials prior to extrusion.

• Add 0.6 kg of DCP, ensure it is dispersed well in the mixture by a mixer.

• Pump citric acid into the mixture during extrusion. According to the flow rates of the pumps used, the citric acid solution will be 10.98% (123.4 g of citric acid powder into 1 litre water).

• Pump the mixture to make alginate gel beads in a 5% $CaCl_2$ bath. Collect the beads formed from the bath as quick as possible.

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APPENDICES

Appendix 1: Titration data for alginate solutions

Appendix 1A. Titration curve for 1% sodium alginate Protanal LF 120 in water.

Acid	Volume (ml)	0	0.06	0.42	1	3	4	6	10	15	25
0.1 N HCl	pH (Run 1)	7.14	6.74	5.83	5.29	4.7	4.55	4.26	3.95	3.66	3.21
		7.14	6.73	5.82	5.29	4.7	4.56	4.26	3.94	3.66	3.21
	pH (Run 2)	7.1	6.7	5.79	5.25	4.68	4.52	4.23	3.92	3.64	3.18
		7.12	6.71	5.81	5.27	4.69	4.53	4.24	3.92	3.64	3.2
	Ave pH	7.13	6.72	5.81	5.28	4.69	4.54	4.25	3.93	3.65	3.20
	STDEV	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.01
0.1 N Citric acid	pH (Run 1)	7.17	6.71	5.85	5.44	4.93	4.72	4.55	4.35	4.17	3.94
		7.19	6.72	5.85	5.45	4.95	4.73	4.55	4.36	4.18	3.95
	pH (Run 2)	7.18	6.7	5.84	5.43	4.92	4.72	4.54	4.34	4.16	3.94
		7.18	6.71	5.85	5.43	4.93	4.72	4.55	4.35	4.17	3.94
	Ave pH	7.18	6.71	5.85	5.44	4.93	4.72	4.55	4.35	4.17	3.94
	STDEV	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01

Appendix 1B. Titration curve for sodium alginate stock solution

HCl (ml)	0	0.06	0.42	1	3	4	6	10
H^+ (mmol)	0	0.006	0.042	0.1	0.3	0.4	0.6	1
pH (Run 1)	5.82	5.74	5.48	5.28	4.7	4.56	4.26	3.95
	5.82	5.75	5.49	5.29	4.7	4.56	4.26	3.96
pH (Run 2)	5.81	5.73	5.48	5.27	4.68	4.55	4.25	3.94
	5.81	5.73	5.47	5.27	4.67	4.54	4.24	3.94
Ave pH	5.82	5.74	5.48	5.28	4.69	4.55	4.25	3.95
STDEV	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01

Where: H^+ (mmol) = the added amount of H^+ ions

Appendix 1C. Effects of Glucono delta lactone on the pH of sodium alginate stock solution

Time (h)	0	1	2	3	4	5	6	7	8	9
pH 1	5.88	4.86	4.82	4.8	4.8	4.77	4.77	4.76	4.76	4.75
pH 2	5.87	4.86	4.83	4.8	4.78	4.78	4.77	4.77	4.76	4.76
Ave pH	5.88	4.86	4.83	4.80	4.79	4.78	4.77	4.77	4.76	4.76
STDEV	0.01	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.01
Time	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
pH 1	4.74	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73
pH 2	4.74	4.74	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73
Ave pH	4.74	4.74	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73
STDEV	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 2A. Gelation time of alginate solution by using different calcium salts

Calcium salt	Amount of Ca salt (g)	Temperature	pH	Gelation time (min)		Ave GT (min)	STDEV
				Run 1	Run 2		
Dicalcium phosphate	0.3	20	6	2010	2010	2010	0.00
			5	870	880	875	7.07
			4.5	80	90	85	7.07
			4	5	5	5	0.00
	0.3	60	6	2040	2050	2045	7.07
			5	900	920	910	14.14
			4.5	90	100	95	7.07
			4	15	25	20	7.07
Calcium carbonate	0.18	20	6	19680	19650	19665	21.21
			5	12480	12490	12485	7.07
			4.5	8160	8170	8165	7.07
			4	5280	5250	5265	21.21
	1.18	60	6	over 3 days	over 3 days	-	-
			5	over 3 days	over 3 days	-	-
			4.5	over 3 days	over 3 days	-	-
			4	over 3 days	over 3 days	-	-
Calcium lactate	0.56	20	6	3	3	3	0.00
			5	3	3	3	0.00
			4.5	3	3	3	0.00
			4	3	3	3	0.00
	0.56	60	6	3	3	3	0.00
			5	3	3	3	0.00
			4.5	3	3	3	0.00
			4	3	3	3	0.00
Calcium sulfate	0.3	20	6	160	170	165	7.07
			5	120	130	125	7.07
			4.5	90	100	95	7.07
			4	60	60	60	0.00
	0.3	60	6	170	190	180	14.14
			5	130	150	140	14.14
			4.5	110	120	115	7.07
			4	80	80	80	0.00

Appendix 2B. Gelation time of alginate stock solution with DCP

Run	Stock (g)	0.1N HCl (ml)	pH	Gelation time (h)	Ave GT (h)	STDEV
1	20	0	5.8	16	15.97	0.07
				16.02		
2				15.87		
				16		
1	20	0.26	5	13.08	13.10	0.09
				13.05		
2				13.22		
				13.03		
1	20	1.2	4.2	1.67	1.60	0.05
				1.58		
2				1.58		
				1.58		
1	20	3	3.7	0.75	0.72	0.04
				0.67		
2				0.75		
				0.72		

Footnotes: The gelation time was measured by adding DCP (0.06 g) to 20 g of the sodium alginate stock solution. The pH of solution was adjusted using 0.1 N HCl.

• the type of the sodium alginate used was Protanal LF 120

Appendix 3. Impact of $CaCl_2$ bath immersion on total moisture of gel beads

Bath	Setting time (min)	Run	Dish	W1	Sample weight (g)	W2	W3	% T.M.	Average % T.M.	STDEV
CaCl2	1	1	1	28.8258	4.8668	33.6926	31.6946	41.05	42.36	1.39
			2	30.3054	4.8524	35.1578	33.1094	42.21		
			3	29.2737	4.4646	33.7383	31.9325	40.45		
		2	1	29.0314	4.5762	33.6076	31.6252	43.32		
			2	28.9971	4.3098	33.3069	31.4485	43.12		
			3	30.3496	4.4073	34.7569	32.8168	44.02		
CaCl2	5	1	1	30.6662	4.328	34.9942	32.81	50.47	50.52	0.68
			2	29.1608	4.3676	33.5284	31.3725	49.36		
			3	29.2173	4.4446	33.6619	31.432	50.17		
		2	1	29.2604	4.7096	33.97	31.5667	51.03		
			2	29.0446	4.6541	33.6987	31.326	50.98		
			3	30.3769	4.5321	34.909	32.5926	51.11		
CaCl2	30	1	1	28.2415	4.0382	32.2797	29.5856	66.72	64.06	1.73
			2	29.1475	4.538	33.6855	30.7983	63.62		
			3	28.5697	4.3352	32.9049	30.2442	61.37		
		2	1	29.1321	4.3251	33.4572	30.6744	64.34		
			2	32.347	4.5231	36.8701	33.95	64.56		
			3	28.3835	4.4752	32.8587	30.0058	63.75		
CaCl2	60	1	1	28.7684	4.525	33.2934	30.1847	68.70	68.80	1.40
			2	28.6193	4.2711	32.8904	30.0575	66.33		
			3	29.0147	4.3361	33.3508	30.3863	68.37		
		2	1	28.5057	4.4011	32.9068	29.8309	69.89		
			2	30.2597	4.2312	34.4909	31.5583	69.31		
			3	29.8406	4.3759	34.2165	31.1437	70.22		
CaCl2 + sugar	60	1	1	28.9926	4.1135	33.1061	31.6414	35.61	35.51	0.91
			2	30.6683	4.2398	34.9081	33.4497	34.40		
			3	34.0795	4.2808	38.3603	36.8865	34.43		
		2	1	30.7816	4.3321	35.1137	33.5602	35.86		
			2	28.075	4.5798	32.6548	30.9914	36.32		
			3	30.978	4.3275	35.3055	33.7277	36.46		

Where: W1 = weight in grams of moisture dish + lid

W2 = weight (g) of moisture dish + lid + sample (before drying)

W3 = weight (g) of moisture dish + lid +sample (after drying)

T.M = total moisture;

STDEV = standard deviation

Appendix 4. Air drying of gel beads at 35° C

Appendix 4A. Zero time weights

Formula	Run	Drying time (h)	Dish	DW (g)	DB (g)	Beads (g)	DL (g)	Leakage (g)	Leakage (%)	Ave leakage (%)	STDEV leakage	Loss of beads (%)	Ave loss of beads (%)	STDEV LB	Moisture (%)
1	1	0	1	11.86	36.81	24.95	-	-	-	-	-	-	-	-	-
			2	11.87	38.78	26.91	-	-	-			-	-		-
	2		1	11.92	37.78	25.86	-	-	-			-	-		-
			2	11.94	35.85	23.91	-	-	-			-	-		-
2	1		1	11.9	39.96	28.06	-	-		-	-	-	-	-	-
			2	11.93	38.43	26.5	-	-	-			-	-		-
	2		1	11.81	37.17	25.36	-	-	-			-	-		-
			2	11.9	-13.46	-25.36	-	-	-			-	-		-
3	1		1	11.91	33.6	21.69	-	-	-	-	-	-	-	-	-
			2	11.88	36.42	24.54	-	-	-			-	-		-
	2		1	11.89	35.61	23.72	-	-	-			-	-		-
			2	11.89	32.95	21.06	-	-	-			-	-		-
4	1		1	11.92	33.06	21.14	-	-	-	-	-	-	-	-	-
			2	11.93	42.05	30.12	-	-	-			-	-		-
	2		1	11.91	37.28	25.37	-	-	-			-	-		-
			2	11.9	-13.47	-25.37	-	-	-			-	-		-
5	1		1	11.9	33.01	21.11	-	-		-	-	-	-	-	-
			2	11.87	32.58	20.71	-	-	-			-	-		-
	2		1	11.88	32.74	20.86	-	-	-			-	-		-
			2	11.91	-8.95	-20.86	-	-	-			-	-		-
6	1		1	11.8	34.49	22.69	-	-	-	-	-	-	-	-	-
			2	11.92	37.36	25.44	-	-	-			-	-		-
	2		1	11.93	36.24	24.31	-	-	-			-	-		-
			2	11.92	-12.39	-24.31	-	-	-			-	-		-

Where: DW = dish weight; DB = the weight of dish + bead; DL = the weight of dish + leakage

Appendix 4B. 18 hours drying at 35° C

Formula	Run	Drying time (h)	Dish	DW (g)	DB (g)	Beads (g)	DL (g)	Leakage (g)	Leakage (%)	Ave leakage (%)	STDEV leakage	Loss of beads (%)	Ave loss of beads (%)	STDEV LB	Moisture (%)
1	1	18	1	11.86	30.81	18.9	11.91	0.05	0.20			24.25			
			2	11.87	32.63	20.71	11.92	0.05	0.19			23.04			
	2		1	11.92	31.32	19.38	11.94	0.02	0.08			25.06			
			2	11.94	30.01	18.06	11.95	0.01	0.04	0.13	0.08	24.47	24.20	0.85	24.08
2	1		1	11.9	32.97	20.92	12.05	0.15	0.53			25.45			
			2	11.93	31.82	19.75	12.07	0.14	0.53			25.47			
	2		1	11.81	31.27	19.17	12.1	0.29	1.14			24.41			
			2	11.9	30.42	18.23	12.19	0.29	-1.14	0.27	0.98	171.88	61.80	73.39	61.54
3	1		1	11.91	28.05	16.14	11.91	0	0.00			25.59			
			2	11.88	30.33	18.43	11.9	0.02	0.08			24.90			
	2		1	11.89	29.73	17.83	11.9	0.01	0.04			24.83			
			2	11.89	27.55	15.65	11.9	0.01	0.05	0.04	0.03	25.69	25.25	0.45	25.21
4	1		1	11.92	27.62	15.6	12.02	0.1	0.47			26.21			
			2	11.93	34.11	22.1	12.01	0.08	0.27			26.63			
	2		1	11.91	31.75	19.74	12.01	0.1	0.39			22.19			
			2	11.9	31.27	19.29	11.98	0.08	0.32	0.36	0.09	22.44	24.37	2.38	24.00
5	1		1	11.9	27.38	15.44	11.94	0.04	0.19			26.86			
			2	11.87	27.16	15.24	11.92	0.05	0.24			26.41			
	2		1	11.88	27.31	15.38	11.93	0.05	0.24			26.27			
			2	11.91	28.96	17	11.96	0.05	0.22	0.22	0.02	24.41	25.99	1.08	25.76
6	1		1	11.8	28.78	16.74	12.04	0.24	1.06			26.22			
			2	11.92	30.53	18.42	12.11	0.19	0.75			27.59			
	2		1	11.93	30.54	18.37	12.17	0.24	0.99			24.43			
			2	11.92	28.71	16.54	12.17	0.25	1.11	0.98	0.16	26.36	26.15	1.30	25.18

Where: DW = dish weight; DB = the weight of dish + beads; DL = the weight of dish + leakage

Appendix 4C. 24 hours drying at 35° C

Formula	Run	Drying time (h)	Dish	DW (g)	DB (g)	Beads (g)	DL (g)	Leakage (g)	Leakage (%)	Ave leakage (%)	STDEV leakage	Loss of beads (%)	Ave loss of beads (%)	STDEV LB	Moisture (%)
1	1	24	1	11.86	30.13	18.21	11.92	0.06	0.24			27.01			
			2	11.87	31.92	20	11.92	0.05	0.19			25.68			
	2		1	11.92	30.63	18.69	11.94	0.02	0.08			27.73			
			2	11.94	29.4	17.45	11.95	0.01	0.04	0.14	0.09	27.02	26.86	0.86	26.72
2	1		1	11.9	32.14	20.11	12.03	0.13	0.46			28.33			
			2	11.93	31.08	19	12.08	0.15	0.57			28.30			
	2		1	11.81	30.36	18.31	12.05	0.24	0.95			27.80			
			2	11.9	29.5	17.36	12.14	0.24	-0.95	0.26	0.83	168.45	63.22	70.16	62.96
3	1		1	11.91	27.48	15.56	11.92	0.01	0.05			28.26			
			2	11.88	29.59	17.71	11.88	0	0.00			27.83			
	2		1	11.89	28.97	17.08	11.89	0	0.00			27.99			
			2	11.89	27.08	15.17	11.91	0.02	0.09	0.04	0.05	27.97	28.01	0.18	27.98
4	1		1	11.92	27.12	15.12	12	0.08	0.38			28.48			
			2	11.93	33.27	21.26	12.01	0.08	0.27			29.42			
	2		1	11.91	31.21	19.22	11.99	0.08	0.32			24.24			
			2	11.9	30.75	18.79	11.96	0.06	0.24	0.30	0.06	24.45	26.65	2.69	26.35
5	1		1	11.9	26.92	14.95	11.97	0.07	0.33			29.18			
			2	11.87	26.67	14.73	11.94	0.07	0.34			28.87			
	2		1	11.88	26.81	14.86	11.95	0.07	0.34			28.76			
			2	11.91	28.45	16.47	11.98	0.07	0.31	0.33	0.01	26.77	28.40	1.10	28.07
6	1		1	11.8	28.02	16	12.02	0.22	0.97			29.48			
			2	11.92	29.7	17.55	12.15	0.23	0.90			31.01			
	2		1	11.93	29.79	17.64	12.15	0.22	0.90			27.44			
			2	11.92	27.98	15.83	12.15	0.23	1.02	0.95	0.06	29.52	29.36	1.47	28.41

Where: DW = dish weight; DB = the weight of dish + beads; DL = the weight of dish + leakage

Appendix 4D. 42 hours drying at 35° C

Formula	Run	Drying time (h)	Dish	DW (g)	DB (g)	Beads (g)	DL (g)	Leakage (g)	Leakage (%)	Ave leakage (%)	STDEV leakage	Loss of beads (%)	Ave loss of beads (%)	STDEV LB	Moisture (%)
1	1	42	1	11.86	29.35	17.46	11.89	0.03	0.12			30.02			
			2	11.87	31.07	19.15	11.92	0.05	0.19			28.84			
	2		1	11.92	29.84	17.89	11.95	0.03	0.12			30.82			
			2	11.94	28.68	16.72	11.96	0.02	0.08	0.13	0.04	30.07	29.94	0.82	29.81
2	1		1	11.9	31.28	19.25	12.03	0.13	0.46			31.40			
			2	11.93	30.25	18.19	12.06	0.13	0.49			31.36			
	2		1	11.81	29.48	17.45	12.03	0.22	0.87			31.19			
			2	11.9	28.7	16.55	12.15	0.25	-0.99	0.21	0.82	165.26	64.80	66.97	64.59
3	1		1	11.91	26.83	14.91	11.92	0.01	0.05			31.26			
			2	11.88	28.83	16.94	11.89	0.01	0.04			30.97			
	2		1	11.89	28.2	16.3	11.9	0.01	0.04			31.28			
			2	11.89	26.44	14.53	11.91	0.02	0.09	0.06	0.03	31.01	31.13	0.16	31.07
4	1		1	11.92	26.58	14.58	12	0.08	0.38			31.03			
			2	11.93	32.46	20.45	12.01	0.08	0.27			32.10			
	2		1	11.91	30.66	18.66	12	0.09	0.35			26.45			
			2	11.9	30.19	18.23	11.96	0.06	0.24	0.31	0.07	26.70	29.07	2.92	28.76
5	1		1	11.9	26.38	14.45	11.93	0.03	0.14			31.55			
			2	11.87	26.17	14.24	11.93	0.06	0.29			31.24			
	2		1	11.88	26.68	14.36	12.32	0.44	2.11			31.16			
			2	11.91	27.93	15.96	11.97	0.06	0.27	0.70	0.94	29.04	30.75	1.15	30.04
6	1		1	11.8	27.35	15.35	12	0.2	0.88			32.35			
			2	11.92	28.98	16.86	12.12	0.2	0.79			33.73			
	2		1	11.93	29.13	17	12.13	0.2	0.82			30.07			
			2	11.92	27.34	15.21	12.13	0.21	0.93	0.86	0.07	32.28	32.11	1.51	31.25

Where: DW = dish weight; DB = the weight of dish + beads; DL = the weight of dish + leakage

Appendix 4E. 48 hours drying at 35° C

Formula	Run	Drying time (h)	Dish	DW (g)	DB (g)	Beads (g)	DL (g)	Leakage (g)	Leakage (%)	Ave leakage (%)	STDEV leakage	Loss of beads (%)	Ave loss of beads (%)	STDEV LB	Moisture (%)
1	1	48	1	11.86	29.22	17.32	11.9	0.04	0.16			30.58			
			2	11.87	30.87	18.97	11.9	0.03	0.11			29.51			
	2		1	11.92	29.71	17.76	11.95	0.03	0.12			31.32			
			2	11.94	28.54	16.58	11.96	0.02	0.08	0.12	0.03	30.66	30.52	0.75	30.40
2	1		1	11.9	31.11	19.09	12.02	0.12	0.43			31.97			
			2	11.93	30.08	18.05	12.03	0.1	0.38			31.89			
	2		1	11.81	29.32	17.29	12.03	0.22	0.87			31.82			
			2	11.9	28.54	16.42	12.12	0.22	-0.87	0.20	0.75	164.75	65.11	66.43	64.90
3	1		1	11.91	26.71	14.8	11.91	0	0.00			31.77			
			2	11.88	28.72	16.81	11.91	0.03	0.12			31.50			
	2		1	11.89	28.07	16.18	11.89	0	0.00			31.79			
			2	11.89	26.34	14.42	11.92	0.03	0.14	0.07	0.08	31.53	31.65	0.15	31.58
4	1		1	11.92	26.46	14.46	12	0.08	0.38			31.60			
			2	11.93	32.29	20.3	11.99	0.06	0.20			32.60			
	2		1	11.91	30.53	18.53	12	0.09	0.35			26.96			
			2	11.9	30.05	18.09	11.96	0.06	0.24	0.29	0.09	27.26	29.61	2.91	29.31
5	1		1	11.9	26.28	14.34	11.94	0.04	0.19			32.07			
			2	11.87	26.05	14.13	11.92	0.05	0.24			31.77			
	2		1	11.88	26.55	14.24	12.31	0.43	2.06			31.74			
			2	11.91	27.8	15.84	11.96	0.05	0.22	0.68	0.92	29.57	31.29	1.16	30.61
6	1		1	11.8	27.19	15.2	11.99	0.19	0.84			33.01			
			2	11.92	28.81	16.73	12.08	0.16	0.63			34.24			
	2		1	11.93	28.98	16.86	12.12	0.19	0.78			30.65			
			2	11.92	27.21	15.09	12.12	0.2	0.89	0.78	0.11	32.81	32.68	1.49	31.89

Where: DW = dish weight; DB = the weight of dish + beads; DL = the weight of dish + leakage

Appendix 4F. 66 hours drying at 35° C

Formula	Run	Drying time (h)	Dish	DW (g)	DB (g)	Beads (g)	DL (g)	Leakage (g)	Leakage (%)	Ave leakage (%)	STDEV leakage	Loss of beads (%)	Ave loss of beads (%)	STDEV LB	Moisture (%)
1	1	66	1	11.86	28.96	17.06	11.9	0.04	0.16			31.62			
			2	11.87	30.56	18.64	11.92	0.05	0.19			30.73			
	2		1	11.92	29.43	17.49	11.94	0.02	0.08			32.37			
			2	11.94	28.28	16.33	11.95	0.01	0.04	0.12	0.07	31.70	31.61	0.67	31.49
2	1		1	11.9	30.79	18.77	12.02	0.12	0.43			33.11			
			2	11.93	29.77	17.74	12.03	0.1	0.38			33.06			
	2		1	11.81	29.04	17.01	12.03	0.22	0.87			32.93			
			2	11.9	28.28	16.16	12.12	0.22	-0.87	0.20	0.75	163.72	65.70	65.35	65.50
3	1		1	11.91	26.48	14.57	11.91	0	0.00			32.83			
			2	11.88	28.45	16.55	11.9	0.02	0.08			32.56			
	2		1	11.89	27.81	15.9	11.91	0.02	0.08			32.97			
			2	11.89	26.11	14.2	11.91	0.02	0.09	0.07	0.04	32.57	32.73	0.20	32.67
4	1		1	11.92	26.26	14.27	11.99	0.07	0.33			32.50			
			2	11.93	31.99	20	11.99	0.06	0.20			33.60			
	2		1	11.91	30.32	18.33	11.99	0.08	0.32			27.75			
			2	11.9	29.84	17.88	11.96	0.06	0.24	0.27	0.06	28.11	30.49	2.99	30.22
5	1		1	11.9	26.07	14.15	11.92	0.02	0.09			32.97			
			2	11.87	25.85	13.93	11.92	0.05	0.24			32.74			
	2		1	11.88	26.34	14.03	12.31	0.43	2.06			32.74			
			2	11.91	27.58	15.62	11.96	0.05	0.22	0.65	0.94	30.55	32.25	1.14	31.59
6	1		1	11.8	26.94	14.97	11.97	0.17	0.75			34.02			
			2	11.92	28.54	16.47	12.07	0.15	0.59			35.26			
	2		1	11.93	28.74	16.64	12.1	0.17	0.70			31.55			
			2	11.92	26.99	14.89	12.1	0.18	0.80	0.71	0.09	33.70	33.63	1.54	32.92

Where: DW = dish weight; DB = the weight of dish + beads; DL = the weight of dish + leakage

Appendix 4G. Total moisture contents of beads with different formulas

Formula	Run	Dish	W1	Sample weight (g)	W2	W3	T.M. (%)	Average T.M. (%)	STDEV
1	1	1	29.6548	4.1812	33.836	32.183	39.53	39.67	0.25
		2	29.4506	5.302	34.7526	32.6556	39.55		
		3	28.9174	3.9719	32.8893	31.3278	39.31		
	2	1	29.1577	3.9257	33.0834	31.5148	39.96		
		2	29.1011	4.6037	33.7048	31.8719	39.81		
		3	32.4992	5.8349	38.3341	36.0074	39.88		
2	1	1	30.3816	3.8924	34.274	32.7965	37.96	38.31	0.38
		2	29.1757	3.2386	32.4143	31.1701	38.42		
		3	28.8024	4.1503	32.9527	31.3811	37.87		
	2	1	29.0374	5.3616	34.399	32.354	38.14		
		2	29.7835	4.8055	34.589	32.7271	38.75		
		3	29.6178	5.9789	35.5967	33.2817	38.72		
3	1	1	30.9336	2.9319	33.8655	32.6808	40.41	40.51	0.91
		2	28.9583	2.5896	31.5479	30.5239	39.54		
		3	28.1344	4.4882	32.6226	30.8362	39.80		
	2	1	32.4748	3.9932	36.468	34.8676	40.08		
		2	29.1635	3.3839	32.5474	31.1436	41.48		
		3	29.0243	3.6665	32.6908	31.1604	41.74		
4	1	1	29.114	3.1004	32.2144	31.0553	37.39	38.18	0.46
		2	29.0789	3.1858	32.2647	31.031	38.72		
		3	29.073	2.2244	31.2974	30.4418	38.46		
	2	1	29.3541	3.2001	32.5542	31.3362	38.06		
		2	29.0123	3.1402	32.1525	30.9501	38.29		
		3	28.9852	2.9073	31.8925	30.784	38.13		
5	1	1	33.855	5.7447	39.5997	37.3484	39.19	38.99	0.31
		2	28.9223	5.1491	34.0714	32.0502	39.25		
		3	29.7028	5.1546	34.8574	32.8782	38.40		
	2	1	30.3478	5.2329	35.5807	33.5394	39.01		
		2	29.3371	5.1092	34.4463	32.4552	38.97		
		3	29.2785	5.3268	34.6053	32.522	39.11		
6	1	1	29.259	3.9429	33.2019	31.6348	39.74	39.67	0.14
		2	28.8911	3.7854	32.6765	31.1733	39.71		
		3	30.3983	4.6745	35.0728	33.225	39.53		
	2	1	29.479	3.5631	33.0421	31.6215	39.87		
		2	29.3022	3.892	33.1942	31.6561	39.52		
		3	29.0475	3.7762	32.8237	31.3272	39.63		

Where: W1 = weight in grams of moisture dish + lid

W2 = weight (g) of moisture dish + lid + sample (before drying)

W3 = weight (g) of moisture dish + lid +sample (after drying)

T.M = total moisture

STDEV = standard deviation

Appendix 4H. Moisture content of beads during drying at 35ºC

Formula	Time (h)					
	0	**18**	**24**	**42**	**48**	**66**
1	39.67	15.59	12.94	9.87	9.28	8.18
2	38.31	13.91	10.75	7.44	6.84	5.66
3	40.51	15.30	12.53	9.42	8.92	7.84
4	38.18	14.18	11.89	9.41	8.89	7.98
5	38.99	13.23	10.81	8.58	8.40	7.43
6	39.67	14.49	11.29	8.51	7.86	6.82

Footnote: the moisture contents of beads during drying at 35ºC are calculated from the data in Appendix 4A – G.

Appendix 5. Exudation from beads during drying at 35° C

Appendix 5A. Test result – row data

Beads factors				R1	R2			R1	R2		
				Hardness				Stickiness			
pH	SHMP (g)	MTD (g)	Batch	Force 1 (g)		Ave Hardness (g)	STDEV	Force 1 (g)		Ave Stickiness (g)	STDEV
			1	146.86	166.521			-14.013	-12.492		
			1	163.697	148.707			-12.492	-13.578		
4.2	0.1	0	1	156.854	157.614	156.709	7.84	-9.993	-9.993	-12.094	1.73
			2	145.448	143.384			-5.323	-4.236		
			2	142.081	143.058			-4.779	-6.626		
5	0.1	0	2	138.279	138.388	141.773	2.88	-6.735	-5.54	-5.540	0.99
			3	94.177	93.634			-4.128	-3.476		
			3	123.18	117.348			-4.997	-4.56		
6	0.1	0	3	115.359	121.011	110.785	13.36	-3.802	-4.862	-4.304	0.60
			4	86.465	85.922			-4.671	-3.91		
			4	87.66	80.708			-3.693	-3.91		
4.2	0.1	5	4	81.142	87.117	84.836	3.09	-4.779	-3.91	-4.146	0.46
			5	94.503	100.043			-6.3	-6.955		
			5	100.043	95.046			-6.952	-6.31		
5	0.1	5	5	85.27	86.031	93.489	6.52	-5.105	-5.105	-6.121	0.84
			6	106.561	88.963			-6.626	-6.3		
			6	99.174	99.174			-8.364	-7.821		
6	0.1	5	6	88.529	109.819	98.703	8.77	-6.3	-6.952	-7.061	0.85
			7	122.854	121.008			-3.476	-3.367		
			7	113.838	112.861			-3.15	-3.802		
4.2	0.2	0	7	116.771	117.206	117.423	3.91	-5.974	-4.779	-4.091	1.09
			8	141.212	130.458			-4.671	-2.933		
			8	131.544	140.017			-2.498	-3.802		
5	0.2	0	8	137.301	135.998	136.088	4.37	-4.454	-4.019	-3.730	0.85
			9	142.081	140.234			-6.083	-4.236		
			9	149.359	124.375			-4.779	-3.041		
6	0.2	0	9	123.18	147.078	137.718	11.29	-3.802	-5.214	-4.526	1.07

Where: MTD = maltodextrin

Value of Hardness = positive maximum force (g)

Value of Stickiness = negative maximum force (g)

Beads factors			Batch	R1 Hardness Force 1 (g)	R2 Hardness Force 1 (g)	Ave Hardness (g)	STDEV	R1 Stickiness Force 1 (g)	R2 Stickiness Force 1 (g)	Ave Stickiness (g)	STDEV
pH	SHMP	MTD									
			10	84.184	85.596			-7.712	-6.409		
			10	87.877	86.248			-6.735	-6.083		
4.2	0.2	5	10	82.446	83.424	84.963	1.99	-3.041	-3.585	-5.594	1.86
			11	93.852	94.177			-8.147	-7.169		
			11	108.733	112.644			-9.885	-6.626		
5	0.2	5	11	112.1	107.321	104.805	8.59	-8.038	-9.993	-8.310	1.38
			12	113.513	110.362			-8.038	-5.214		
			12	100.804	101.673			-6.517	-5.866		
6	0.2	5	12	111.883	104.243	107.080	5.51	-6.083	-7.764	-6.580	1.11
			13	76.689	76.037			-3.585	-4.019		
			13	67.13	72.127			-2.607	-2.281		
4.2	0.5	0	13	73.647	65.392	71.837	4.65	-2.39	-2.281	-2.861	0.75
			14	51.054	51.379			-2.172	-2.498		
			14	61.699	62.211			-1.412	-1.756		
5	0.5	0	14	64.632	63.437	59.069	6.17	-3.585	-1.847	-2.212	0.77
			15	49.859	47.686			-2.498	-2.281		
			15	48.555	49.859			-3.367	-2.39		
6	0.5	0	15	46.057	45.622	47.940	1.83	-1.412	-2.172	-2.353	0.63
			16	55.724	53.335			-3.802	-3.476		
			16	50.945	56.376			-3.15	-2.064		
4.2	0.5	5	16	57.571	50.293	54.041	3.00	-2.498	-2.607	-2.933	0.66
			17	64.306	78.427			-3.041	-6.192		
			17	69.628	68.651			-3.15	-2.607		
5	0.5	5	17	78.535	62.676	70.371	6.80	-5.648	-2.607	-3.874	1.61
			18	66.152	55.29			-4.997	-1.955		
			18	66.37	65.718			-1.955	-2.498		
6	0.5	5	18	57.245	64.632	62.568	4.96	-3.802	-4.345	-3.259	1.30

Where: MTD = maltodextrin

Value of Hardness = positive maximum force (g)

Value of Stickiness = negative maximum force (g)

Appendix 6. Alginate and gum formulations on gel hardness and exudation

Appendix 6A. Raw test data

Beads fators			Batch	R1	R2	Ave Hardness (g)	STDEV	R1	R2	Ave Stickiness (g)	STDEV
				Hardness				Stickiness			
Alginate (1 g)	Xanthan (g)	Guar (g)		Force 1 (g)				Force 2 (g)			
Manucol LF	0	0	1	28.351	27.047			-2.933	-3.041		
			1	30.523	26.939			-3.693	-2.172		
			1	27.808	30.306	28.496	1.57	-2.281	-3.91	-3.005	0.71
	0.1	0	2	27.482	24.875			-1.629	-2.933		
			2	28.025	28.134			-3.041	-2.933		
			2	24.658	27.591	26.794	1.59	-2.607	-1.521	-2.444	0.69
	0.5	0	3	31.175	29.98			-2.281	-2.064		
			3	33.674	35.194			-3.367	-2.172		
			3	31.936	32.913	32.479	1.86	-4.888	-4.888	-3.277	1.33
	1	0	4	37.367	36.389			-2.716	-2.933		
			4	41.169	37.041			-5.54	-3.91		
			4	37.258	40.517	38.290	2.02	-4.236	-5.105	-4.073	1.13
	0	0.1	5	31.284	25.092			-4.454	-2.064		
			5	25.201	31.936			-1.955	-4.779		
			5	25.092	24.223	27.138	3.49	-3.041	-2.498	-3.132	1.22
	0	0.5	6	24.766	27.156			-2.39	-2.824		
			6	25.527	25.853			-2.172	-2.39		
			6	27.482	24.549	25.889	1.21	-3.259	-2.498	-2.589	0.39
	0	1	7	25.853	22.377			-2.281	-3.693		
			7	24.984	24.549			-2.716	-2.607		
			7	22.594	25.961	24.386	1.57	-3.91	-2.064	-2.879	0.75

Where:

Value of Hardness = positive maximum force (g)

Value of Stickiness = negative maximum force (g)

STDEV = standard deviation

Beads fators			Batch	R1	R2	Ave Hardness (g)	STDV	R1	R2	Ave Stickiness (g)	STDV
				Hardness				Stickiness			
Alginate (1 g)	Xanthan (g)	Guar (g)		Force 1 (g)				Force 2 (g)			
Manucol DH	0	0	8	34.76	33.13			-2.39	-1.955		
			8	32.913	34.325			-2.716	-2.607		
			8	31.61	31.392	33.022	1.37	-1.847	-2.498	-2.336	0.36
	0.1	0	9	30.089	29.546			-2.607	-3.041		
			9	32.153	31.392			-2.064	-2.281		
			9	32.153	32.805	31.356	1.28	-4.019	-3.15	-2.860	0.71
	0.5	0	10	35.52	32.261			-4.562	-2.824		
			10	33.782	35.412			-2.172	-2.824		
			10	31.501	30.198	33.112	2.16	-2.824	-3.476	-3.114	0.82
	1	0	11	29.111	28.025			-4.128	-4.019		
			11	25.853	26.396			-2.498	-2.607		
			11	22.159	21.834	25.563	3.00	-3.041	-3.15	-3.241	0.69
	0	0.1	12	33.456	33.674			-2.716	-2.064		
			12	34.76	37.801			-5.105	-2.172		
			12	38.019	33.999	35.285	2.08	-2.281	-4.236	-3.096	1.27
	0	0.5	13	40.626	37.475			-5.431	-1.521		
			13	38.127	36.281			-3.259	-4.019		
			13	37.693	40.408	38.435	1.73	-2.064	-5.214	-3.585	1.61
	0	1	14	42.472	40.408			-2.281	-2.498		
			14	38.562	39.105			-2.824	-2.716		
			14	38.344	37.91	39.467	1.71	-5.54	-3.585	-3.241	1.21

Where:

Value of Hardness = positive maximum force (g)

Value of Stickiness = negative maximum force (g)

STDV = standard deviation

Beads fators			Batch	R1	R2	Ave Hardness (g)	STDEV	R1	R2	Ave Stickiness (g)	STDEV
				Hardness				Stickiness			
Alginate (1 g)	Xanthan (g)	Guar (g)		Force 1 (g)				Force 2 (g)			
Manugel GMB	0	0	15	73.213	61.156			-3.15	-4.997		
			15	62.35	72.561			-5.214	-3.585		
			15	63.328	63.219	65.971	5.42	-3.15	-1.955	-3.675	1.24
	0.1	0	16	67.021	64.74			-6.192	-4.236		
			16	69.411	68.325			-6.735	-6.083		
			16	64.088	66.478	66.677	2.04	-3.802	-5.866	-5.486	1.18
	0.5	0	17	92.114	90.701			-5.866	-6.952		
			17	83.967	81.794			-4.997	-4.562		
			17	84.727	83.858	86.194	4.18	-7.821	-6.3	-6.083	1.21
	1	0	18	62.459	67.239			-6.517	-4.997		
			18	69.085	62.459			-5.54	-6.517		
			18	63.437	61.699	64.396	3.03	-7.169	-6.409	-6.192	0.78
	0	0.1	19	76.254	86.682			-5.214	-7.712		
			19	78.427	79.622			-4.128	-4.997		
			19	86.356	76.146	80.581	4.79	-8.473	-4.562	-5.848	1.79
	0	0.5	20	74.299	74.408			-5.105	-4.671		
			20	74.842	69.302			-4.236	-2.933		
			20	68.651	74.625	72.688	2.89	-3.259	-4.236	-4.073	0.83
	0	1	21	54.529	53.335			-4.128	-4.236		
			21	60.504	64.849			-5.866	-6.3		
			21	64.632	60.287	59.689	4.88	-6.192	-3.367	-5.015	1.25

Where:

Value of Hardness = positive maximum force (g)

Value of Stickiness = negative maximum force (g)

STDEV = standard deviation

Beads fators			Batch	R1	R2	Ave Hardness (g)	STDEV	R1	R2	Ave Stickiness (g)	STDEV
				Hardness				Stickiness			
Alginate (1 g)	Xanthan (g)	Guar (g)		Force 1 (g)				Force 2 (g)			
Protanal LF 120	0	0	22	66.044	76.146			-2.172	-3.367		
			22	66.587	66.587			-3.15	-3.259		
			22	76.906	66.261	69.755	5.25	-4.019	-2.281	-3.041	0.70
	0.1	0	23	85.922	85.27			-3.15	-2.824		
			23	86.356	85.27			-4.236	-3.15		
			23	81.36	80.925	84.184	2.40	-3.693	-2.716	-3.295	0.57
	0.5	0	24	55.616	60.069			-2.39	-1.738		
			24	60.504	55.942			-1.847	-2.281		
			24	61.047	60.612	58.965	2.49	-1.195	-1.738	-1.865	0.43
	1	0	25	52.14	53.335			-3.91	-3.476		
			25	47.903	53.009			-2.281	-1.521		
			25	53.66	48.012	51.343	2.67	-2.607	-2.281	-2.679	0.87
	0	0.1	26	81.142	72.453			-3.693	-5.214		
			26	87.225	85.162			-4.019	-3.585		
			26	72.344	80.273	79.767	6.25	-4.671	-2.498	-3.947	0.94
	0	0.5	27	65.826	65.718			-4.671	-4.671		
			27	63.002	62.459			-4.236	-3.367		
			27	63.654	63.111	63.962	1.45	-4.888	-3.802	-4.273	0.59
	0	1	28	74.082	73.973			-5.214	-5.105		
			28	72.778	78.861			-4.888	-4.345		
			28	78.753	71.801	75.041	3.03	-4.779	-4.888	-4.870	0.30

Where:

Value of Hardness = positive maximum force (g)

Value of Stickiness = negative maximum force (g)

STDEV = standard deviation

Appendix 7. Apparent viscosities of alginate mixture solution at certain shear rates

Appendix 7A. Row test data

Run	Original industry formula					Optimal experimental formula				
	SR 1/s	SS Pa	T °C	time s	AV Pa.s	SR 1/s	SS Pa	T °C	time s	AV Pa.s
1	38.16	285	20	10.02	7.468	48.43	483.8	20	10.04	9.989
	94.29	376	20	20.03	3.988	98.76	555.7	20	20.05	5.627
	144.4	433	20	30.04	2.998	149	614.8	20	30.05	4.126
	195.6	479.3	20	40.04	2.451	196.7	678.3	20	40.04	3.447
	245.2	521.3	20	50.03	2.126	246.9	754.6	20	50.03	3.056
	294	554.7	20	59.65	1.887	294.9	809.4	20	59.71	2.745
2	41.59	273.5	20	10.02	6.575	49.13	479.8	20	10.02	9.766
	94.96	358.6	20	20.04	3.776	97.01	552	20	20.03	5.69
	144.8	409.6	20	30.03	2.829	147.3	608.7	20	30.02	4.132
	193.8	454.7	20	40.04	2.346	197.5	671.5	20	40.03	3.4
	244.3	494.6	20	50.03	2.025	247.8	743.5	20	50.03	3
	293.3	527.5	20	59.59	1.798	295.6	790.1	20	59.55	2.673
3	40.24	285.8	20	10.04	7.101	47.03	473.2	20	10.04	10.06
	95.32	375.9	20	20.04	3.943	97.32	548	20	20.05	5.631
	143.9	429.3	20	30.04	2.982	147.5	594.1	20	30.04	4.028
	194.3	476.7	20	40.05	2.453	197.7	646.1	20	40.04	3.268
	244.9	516.7	20	50.04	2.109	248	739.7	20	50.04	2.983
	292.9	551.1	20	59.54	1.881	295.9	799.6	20	59.7	2.703
4	39.79	294.5	20	10.03	7.4	48.2	477.2	20	10.03	9.9
	95.1	387.3	20	20.05	4.073	98.44	553.7	20	20.05	5.625
	145.5	445.9	20	30.04	3.064	148.8	575.4	20	30.04	3.866
	194.3	491.4	20	40.04	2.529	199	651.8	20	40.05	3.275
	244.8	532.5	20	50.05	2.175	246.7	728.3	20	50.05	2.952
	292.6	569.4	20	59.54	1.946	294.6	792	20	59.62	2.688
5	38.69	291.4	20	10.02	7.533	48.92	474.1	20	10.02	9.692
	94.39	385.7	20	20.04	4.086	99.13	556.1	20	20.05	5.61
	145.1	444.1	20	30.04	3.061	147.3	600.9	20	30.04	4.08
	195.9	492.5	20	40.05	2.513	197.2	657.5	20	40.05	3.334
	244	531.3	20	50.03	2.177	247.6	733	20	50.04	2.961
	294.3	570.1	20	59.64	1.937	295.3	796.9	20	59.61	2.699
6	37.77	287.4	20	10.03	7.609	47.18	473.4	20	10.04	10.03
	93.81	382.6	20	20.05	4.078	97.53	546.4	20	20.05	5.603
	144.6	441	20	30.04	3.05	147.7	578.3	20	30.04	3.915
	195.4	489.8	20	40.06	2.507	197.9	641.8	20	40.05	3.243
	245.7	531	20	50.04	2.161	248.3	716	20	50.05	2.884
	293.6	568.4	20	59.58	1.936	296.1	771.4	20	59.56	2.605

Where: AV = apparent viscosity

SR = shear rate

SS = shear stress

T = temperature

Appendix 7B. Mean values and standard deviations for Appendix 7A.

Formula	Testing time (S)	Mean of AV (Pa.s)	STDEV	Mean of SR (1/s)	STDEV	Mean of SS (Pa)	STDEV
Original industry forula	10	7.281	0.39	39.373	1.44	286.267	7.21
	20	3.991	0.12	94.645	0.57	377.683	10.50
	30	2.997	0.09	144.717	0.56	433.817	13.50
	40	2.467	0.07	194.883	0.86	480.733	14.36
	50	2.129	0.06	244.817	0.61	521.233	14.52
	59	1.898	0.06	293.450	0.65	556.867	16.53
Optimal experimental formula	10	9.906	0.15	48.148	0.88	476.917	4.24
	20	5.631	0.03	98.032	0.86	551.983	4.02
	30	4.025	0.11	147.933	0.77	595.367	15.98
	40	3.328	0.08	197.667	0.78	657.833	14.40
	50	2.973	0.06	247.550	0.63	735.850	13.30
	59	2.686	0.05	295.400	0.58	793.233	12.68

Where: each mean value is calculated at a certain testing time

AV = apparent viscosity

SR = shear rate

SS = shear stress

Appendix 5B. Statistical analysis

Univariate Analysis of Variance

Between-Subjects Factors

		Value Label	N
SHMP	.100	0.1 g SHMP	36
	.200	0.2 g SHMP	36
	.500	0.5 g SHMP	36
Maltodextrin	.000	0 g Maltodextrin	54
	5.000	5 g Maltodextrin	54
Dextrose	25.000	25 g Dextrose	54
	30.000	30 g Dextrose	54
pH	4.200	pH 4.2	36
	5.000	pH 5	36
	5.500	pH 5.5	12
	6.000	pH 6	24

Tests of Between-Subjects Effects

Dependent Variable: Hardness

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	108861.779[a]	17	6403.634	144.363	.000
Intercept	921625.386	1	921625.386	20777.037	.000
SHMP	42388.402	2	21194.201	477.800	.000
Maltodextrin	.000	0	.	.	.
Dextrose	.000	0	.	.	.
pH	1313.606	3	437.869	9.871	.000
SHMP * Maltodextrin	.000	0	.	.	.
SHMP * Dextrose	.000	0	.	.	.
Maltodextrin * Dextrose	.000	0	.	.	.
SHMP * Maltodextrin * Dextrose	.000	0	.	.	.
SHMP * pH	4258.768	3	1419.589	32.003	.000
Maltodextrin * pH	.000	0	.	.	.
SHMP * Maltodextrin * pH	.000	0	.	.	.
Dextrose * pH	.000	0	.	.	.
SHMP * Dextrose * pH	.000	0	.	.	.
Maltodextrin * Dextrose * pH	.000	0	.	.	.
SHMP * Maltodextrin * Dextrose * pH	.000	0	.	.	.
Error	3992.209	90	44.358		
Total	1125285.625	108			
Corrected Total	112853.988	107			

a. R Squared = .965 (Adjusted R Squared = .958)

Post Hoc Tests

SHMP

Multiple Comparisons

Dependent Variable: Hardness

Tukey HSD

(I) SHMP	(J) SHMP	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0.1 g SHMP	0.2 g SHMP	-.02211	1.569817	1.000	-3.76315	3.71892
	0.5 g SHMP	53.76483*	1.569817	.000	50.02380	57.50587
0.2 g SHMP	0.1 g SHMP	.02211	1.569817	1.000	-3.71892	3.76315
	0.5 g SHMP	53.78694*	1.569817	.000	50.04591	57.52798
0.5 g SHMP	0.1 g SHMP	-53.76483*	1.569817	.000	-57.50587	-50.02380
	0.2 g SHMP	-53.78694*	1.569817	.000	-57.52798	-50.04591

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

Hardness

Tukey HSD[a,b]

SHMP	N	Subset 1	Subset 2
0.5 g SHMP	36	60.97072	
0.1 g SHMP	36		114.73556
0.2 g SHMP	36		114.75767
Sig.		1.000	1.000

Means for groups in homogeneous subsets are displayed.

Based on Type III Sum of Squares

The error term is Mean Square(Error) = 44.358.

a. Uses Harmonic Mean Sample Size = 36.000.

b. Alpha = .05.

pH

Multiple Comparisons

Dependent Variable: Hardness

Tukey HSD

(I) pH	(J) pH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
pH 4.2	pH 5	-6.15156*	1.569817	.001	-10.26085	-2.04226
	pH 5.5	39.81375*	2.220057	.000	34.00234	45.62516
	pH 6	-18.57171*	1.755109	.000	-23.16604	-13.97738
pH 5	pH 4.2	6.15156*	1.569817	.001	2.04226	10.26085
	pH 5.5	45.96531*	2.220057	.000	40.15389	51.77672
	pH 6	-12.42015*	1.755109	.000	-17.01448	-7.82583
pH 5.5	pH 4.2	-39.81375*	2.220057	.000	-45.62516	-34.00234
	pH 5	-45.96531*	2.220057	.000	-51.77672	-40.15389
	pH 6	-58.38546*	2.354726	.000	-64.54939	-52.22152
pH 6	pH 4.2	18.57171*	1.755109	.000	13.97738	23.16604
	pH 5	12.42015*	1.755109	.000	7.82583	17.01448
	pH 5.5	58.38546*	2.354726	.000	52.22152	64.54939

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

Hardness

Tukey HSD[a,b,c]

pH	N	Subset			
		1	2	3	4
pH 5.5	12	55.25375			
pH 4.2	36		95.06750		
pH 5	36			101.21906	
pH 6	24				113.63921
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

Based on Type III Sum of Squares

The error term is Mean Square(Error) = 44.358.

a. Uses Harmonic Mean Sample Size = 22.154.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

c. Alpha = .05.

Univariate Analysis of Variance

Tests of Between-Subjects Effects

Dependent Variable: Stickness

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	619.113[a]	17	36.418	27.640	.000
Intercept	2432.446	1	2432.446	1846.094	.000
SHMP	178.696	2	89.348	67.810	.000
Maltodextrin	.000	0	.	.	.
Dextrose	.000	0	.	.	.
pH	4.073	3	1.358	1.030	.383
SHMP * Maltodextrin	.000	0	.	.	.
SHMP * Dextrose	.000	0	.	.	.
Maltodextrin * Dextrose	.000	0	.	.	.
SHMP * Maltodextrin * Dextrose	.000	0	.	.	.
SHMP * pH	58.443	3	19.481	14.785	.000
Maltodextrin * pH	.000	0	.	.	.
SHMP * Maltodextrin * pH	.000	0	.	.	.
Dextrose * pH	.000	0	.	.	.
SHMP * Dextrose * pH	.000	0	.	.	.
Maltodextrin * Dextrose * pH	.000	0	.	.	.
SHMP * Maltodextrin * Dextrose * pH	.000	0	.	.	.
Error	118.586	90	1.318		
Total	3404.194	108			
Corrected Total	737.699	107			

a. R Squared = .839 (Adjusted R Squared = .809)

Post Hoc Tests

SHMP

Multiple Comparisons

Dependent Variable: Stickness

Tukey HSD

(I) SHMP	(J) SHMP	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0.1 g SHMP	0.2 g SHMP	-1.07800*	.270557	.000	-1.72276	-.43324
	0.5 g SHMP	-3.61953*	.270557	.000	-4.26429	-2.97476
0.2 g SHMP	0.1 g SHMP	1.07800*	.270557	.000	.43324	1.72276
	0.5 g SHMP	-2.54153*	.270557	.000	-3.18629	-1.89676
0.5 g SHMP	0.1 g SHMP	3.61953*	.270557	.000	2.97476	4.26429
	0.2 g SHMP	2.54153*	.270557	.000	1.89676	3.18629

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

Stickness

Tukey HSD[a,b]

SHMP	N	Subset		
		1	2	3
0.1 g SHMP	36	-6.53472		
0.2 g SHMP	36		-5.45672	
0.5 g SHMP	36			-2.91519
Sig.		1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

Based on Type III Sum of Squares

The error term is Mean Square(Error) = 1.318.

a. Uses Harmonic Mean Sample Size = 36.000.

b. Alpha = .05.

pH

Multiple Comparisons

Dependent Variable: Stickness

Tukey HSD

(I) pH	(J) pH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
pH 4.2	pH 5	-.33136	.270557	.613	-1.03959	.37687
	pH 5.5	-2.42297*	.382625	.000	-3.42457	-1.42138
	pH 6	.53811	.302492	.290	-.25372	1.32994
pH 5	pH 4.2	.33136	.270557	.613	-.37687	1.03959
	pH 5.5	-2.09161*	.382625	.000	-3.09320	-1.09002
	pH 6	.86947*	.302492	.026	.07764	1.66130
pH 5.5	pH 4.2	2.42297*	.382625	.000	1.42138	3.42457
	pH 5	2.09161*	.382625	.000	1.09002	3.09320
	pH 6	2.96108*	.405835	.000	1.89873	4.02343
pH 6	pH 4.2	-.53811	.302492	.290	-1.32994	.25372
	pH 5	-.86947*	.302492	.026	-1.66130	-.07764
	pH 5.5	-2.96108*	.405835	.000	-4.02343	-1.89873

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

Stickness

Tukey HSD[a,b,c]

pH	N	Subset 1	Subset 2
pH 6	24	-5.76708	
pH 4.2	36	-5.22897	
pH 5	36	-4.89761	
pH 5.5	12		-2.80600
Sig.		.063	1.000

Means for groups in homogeneous subsets are displayed.

Based on Type III Sum of Squares

The error term is Mean Square(Error) = 1.318.

a. Uses Harmonic Mean Sample Size = 22.154.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

c. Alpha = .05.

Oneway

```
ONEWAY
  Hardness BY Maltodextrin
  /STATISTICS DESCRIPTIVES
  /MISSING ANALYSIS
  /POSTHOC = TUKEY ALPHA(.05).
```

ANOVA

Hardness

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	15851.605	1	15851.605	17.322	.000
Within Groups	97002.383	106	915.117		
Total	112854.0	107			

```
ONEWAY
  Stickness BY Maltodextrin
  /STATISTICS DESCRIPTIVES
  /MISSING ANALYSIS
  /POSTHOC = TUKEY ALPHA(.05).
```

ANOVA

Stickness

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	8.846	1	8.846	1.287	.259
Within Groups	728.853	106	6.876		
Total	737.699	107			

```
ONEWAY
  Hardness BY Dextrose
  /STATISTICS DESCRIPTIVES
  /MISSING ANALYSIS
  /POSTHOC = TUKEY ALPHA(.05).
```

ANOVA

Hardness

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	15851.605	1	15851.605	17.322	.000
Within Groups	97002.383	106	915.117		
Total	112854.0	107			

```
ONEWAY
  Stickness BY Dextrose
  /STATISTICS DESCRIPTIVES
  /MISSING ANALYSIS
  /POSTHOC = TUKEY ALPHA(.05).
```

ANOVA

Stickness

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	8.846	1	8.846	1.287	.259
Within Groups	728.853	106	6.876		
Total	737.699	107			

• Multifactorial ANOVA was used because it could be applied to analyze the significant effect of the interaction among different variables, such as SHMP * pH. However, this function was only used when the variable had more than three levels.

• The effect of maltodextrin and dextrose was analyzed using One-way ANOVA instead of Multifactorial ANOVA because the two ingredients used in this trial only had two levels: maltodextrin (0 and 5 g); dextrose (25 and 30 g).

Appendix 6B. Statistical analysis

Univariate Analysis of Variance

Between-Subjects Factors

		Value Label	N
Xanthan	.00	0 g of Xanthan gum	96
	.10	0.1 g of Xanthan gum	24
	.50	0.5 g of Xanthan gum	24
	1.00	1 g of Xanthan gum	24
Guar	.00	0 g of Guar gum	96
	.10	0.1 g of Guar gum	24
	.50	0.5 g of Guar gum	24
	1.00	1 g of Guar gum	24
Alginate	1.00	Alginate MANUCOL LF	42
	2.00	Alginate MANUCOL DH	42
	3.00	Alginate MANUGEL GMB	42
	4.00	Alginate Prantol LF 120	42

Tests of Between-Subjects Effects

Dependent Variable: Hardness

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	72690.431[a]	27	2692.238	280.970	.000
Intercept	302703.034	1	302703.034	31590.989	.000
Xanthan	926.881	3	308.960	32.244	.000
Guar	649.930	3	216.643	22.610	.000
Alginate	44497.378	3	14832.459	1547.960	.000
Xanthan * Guar	.000	0	.	.	.
Xanthan * Alginate	5334.603	9	592.734	61.859	.000
Guar * Alginate	1845.671	9	205.075	21.402	.000
Xanthan * Guar * Alginate	.000	0	.	.	.
Error	1341.472	140	9.582		
Total	505463.650	168			
Corrected Total	74031.903	167			

a. R Squared = .982 (Adjusted R Squared = .978)

Post Hoc Tests

Xanthan

Multiple Comparisons

Dependent Variable: Hardness

Tukey HSD

(I) Xanthan	(J) Xanthan	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0 g of Xanthan gum	0.1 g of Xanthan gu	-1.0297	.70644	.466	-2.8665	.8072
	0.5 g of Xanthan gu	-1.4642	.70644	.167	-3.3010	.3727
	1 g of Xanthan gum	6.3250*	.70644	.000	4.4882	8.1619
0.1 g of Xanthan gu	0 g of Xanthan gum	1.0297	.70644	.466	-.8072	2.8665
	0.5 g of Xanthan gu	-.4345	.89359	.962	-2.7580	1.8890
	1 g of Xanthan gum	7.3547*	.89359	.000	5.0312	9.6782
0.5 g of Xanthan gu	0 g of Xanthan gum	1.4642	.70644	.167	-.3727	3.3010
	0.1 g of Xanthan gu	.4345	.89359	.962	-1.8890	2.7580
	1 g of Xanthan gum	7.7892*	.89359	.000	5.4657	10.1127
1 g of Xanthan gum	0 g of Xanthan gum	-6.3250*	.70644	.000	-8.1619	-4.4882
	0.1 g of Xanthan gu	-7.3547*	.89359	.000	-9.6782	-5.0312
	0.5 g of Xanthan gu	-7.7892*	.89359	.000	-10.1127	-5.4657

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

Hardness

Tukey HSD[a,b,c]

Xanthan	N	Subset 1	Subset 2
1 g of Xanthan gum	24	44.8982	
0 g of Xanthan gum	96		51.2232
0.1 g of Xanthan gum	24		52.2529
0.5 g of Xanthan gum	24		52.6874
Sig.		1.000	.269

Means for groups in homogeneous subsets are displayed.
Based on Type III Sum of Squares
The error term is Mean Square(Error) = 9.582.

a. Uses Harmonic Mean Sample Size = 29.538.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

c. Alpha = .05.

Guar

Multiple Comparisons

Dependent Variable: Hardness
Tukey HSD

(I) Guar	(J) Guar	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
0 g of Guar gum	0.1 g of Guar gum	-5.9053*	.70644	.000	-7.7421	-4.0684
	0.5 g of Guar gum	-.4560	.70644	.917	-2.2929	1.3809
	1 g of Guar gum	.1414	.70644	.997	-1.6955	1.9782
0.1 g of Guar gum	0 g of Guar gum	5.9053*	.70644	.000	4.0684	7.7421
	0.5 g of Guar gum	5.4493*	.89359	.000	3.1258	7.7728
	1 g of Guar gum	6.0467*	.89359	.000	3.7232	8.3701
0.5 g of Guar gum	0 g of Guar gum	.4560	.70644	.917	-1.3809	2.2929
	0.1 g of Guar gum	-5.4493*	.89359	.000	-7.7728	-3.1258
	1 g of Guar gum	.5974	.89359	.909	-1.7261	2.9208
1 g of Guar gum	0 g of Guar gum	-.1414	.70644	.997	-1.9782	1.6955
	0.1 g of Guar gum	-6.0467*	.89359	.000	-8.3701	-3.7232
	0.5 g of Guar gum	-.5974	.89359	.909	-2.9208	1.7261

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

Hardness

Tukey HSD[a,b,c]

Guar	N	Subset 1	Subset 2
1 g of Guar gum	24	49.6460	
0 g of Guar gum	96	49.7873	
0.5 g of Guar gum	24	50.2433	
0.1 g of Guar gum	24		55.6926
Sig.		.880	1.000

Means for groups in homogeneous subsets are displayed.
Based on Type III Sum of Squares
The error term is Mean Square(Error) = 9.582.

a. Uses Harmonic Mean Sample Size = 29.538.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

c. Alpha = .05.

Alginate

Multiple Comparisons

Dependent Variable: Hardness
Tukey HSD

(I) Alginate	(J) Alginate	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
Alginate MANUCOL I	Alginate MANUCOL I	-4.6812*	.67549	.000	-6.4375	-2.9248
	Alginate MANUGEL (	-41.8178*	.67549	.000	-43.5742	-40.0614
	Alginate Prantol LF 1	-39.9350*	.67549	.000	-41.6913	-38.1786
Alginate MANUCOL I	Alginate MANUCOL I	4.6812*	.67549	.000	2.9248	6.4375
	Alginate MANUGEL (	-37.1366*	.67549	.000	-38.8930	-35.3803
	Alginate Prantol LF 1	-35.2538*	.67549	.000	-37.0102	-33.4974
Alginate MANUGEL (	Alginate MANUCOL I	41.8178*	.67549	.000	40.0614	43.5742
	Alginate MANUCOL I	37.1366*	.67549	.000	35.3803	38.8930
	Alginate Prantol LF 1	1.8828*	.67549	.030	.1265	3.6392
Alginate Prantol LF 1	Alginate MANUCOL I	39.9350*	.67549	.000	38.1786	41.6913
	Alginate MANUCOL I	35.2538*	.67549	.000	33.4974	37.0102
	Alginate MANUGEL (	-1.8828*	.67549	.030	-3.6392	-.1265

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

Hardness

Tukey HSD[a,b]

Alginate	N	Subset 1	2	3	4
Alginate MANUCOL LF	42	29.0674			
Alginate MANUCOL DH	42		33.7486		
Alginate Prantol LF 120	42			69.0024	
Alginate MANUGEL GMB	42				70.8852
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.
Based on Type III Sum of Squares
The error term is Mean Square(Error) = 9.582.

a. Uses Harmonic Mean Sample Size = 42.000.

b. Alpha = .05.

Univariate Analysis of Variance

Tests of Between-Subjects Effects

Dependent Variable: Stickiness

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	219.829[a]	27	8.142	8.363	.000
Intercept	1739.070	1	1739.070	1786.214	.000
Xanthan	12.839	3	4.280	4.396	.005
Guar	15.683	3	5.228	5.369	.002
Alginate	120.471	3	40.157	41.245	.000
Xanthan * Guar	.000	0	.	.	.
Xanthan * Alginate	29.729	9	3.303	3.393	.001
Guar * Alginate	17.886	9	1.987	2.041	.039
Xanthan * Guar * Alginate	.000	0	.	.	.
Error	136.305	140	.974		
Total	2638.756	168			
Corrected Total	356.134	167			

a. R Squared = .617 (Adjusted R Squared = .543)

Post Hoc Tests

Xanthan

Multiple Comparisons

Dependent Variable: Stickiness

Tukey HSD

(I) Xanthan	(J) Xanthan	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0 g of Xanthan gum	0.1 g of Xanthan gur	-.1414	.22519	.923	-.7269	.4441
	0.5 g of Xanthan gur	-.0781	.22519	.986	-.6636	.5074
	1 g of Xanthan gum	.3835	.22519	.326	-.2020	.9691
0.1 g of Xanthan gur	0 g of Xanthan gum	.1414	.22519	.923	-.4441	.7269
	0.5 g of Xanthan gur	.0633	.28484	.996	-.6773	.8040
	1 g of Xanthan gum	.5250	.28484	.258	-.2157	1.2656
0.5 g of Xanthan gur	0 g of Xanthan gum	.0781	.22519	.986	-.5074	.6636
	0.1 g of Xanthan gur	-.0633	.28484	.996	-.8040	.6773
	1 g of Xanthan gum	.4616	.28484	.370	-.2790	1.2023
1 g of Xanthan gum	0 g of Xanthan gum	-.3835	.22519	.326	-.9691	.2020
	0.1 g of Xanthan gur	-.5250	.28484	.258	-1.2656	.2157
	0.5 g of Xanthan gur	-.4616	.28484	.370	-1.2023	.2790

Based on observed means.

Homogeneous Subsets

Stickiness

Tukey HSD[a,b,c]

Xanthan	N	Subset 1
1 g of Xanthan gum	24	-4.0462
0 g of Xanthan gum	96	-3.6626
0.5 g of Xanthan gum	24	-3.5845
0.1 g of Xanthan gum	24	-3.5212
Sig.		.177

Means for groups in homogeneous subsets are displayed.
Based on Type III Sum of Squares
The error term is Mean Square(Error) = .974.

a. Uses Harmonic Mean Sample Size = 29.538.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

c. Alpha = .05.

Guar

Multiple Comparisons

Dependent Variable: Stickiness

Tukey HSD

(I) Guar	(J) Guar	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0 g of Guar gum	0.1 g of Guar gum	.4639	.22519	.171	-.1216	1.0494
	0.5 g of Guar gum	.0883	.22519	.979	-.4972	.6738
	1 g of Guar gum	.4594	.22519	.178	-.1261	1.0449
0.1 g of Guar gum	0 g of Guar gum	-.4639	.22519	.171	-1.0494	.1216
	0.5 g of Guar gum	-.3756	.28484	.553	-1.1163	.3650
	1 g of Guar gum	-.0045	.28484	1.000	-.7451	.7361
0.5 g of Guar gum	0 g of Guar gum	-.0883	.22519	.979	-.6738	.4972
	0.1 g of Guar gum	.3756	.28484	.553	-.3650	1.1163
	1 g of Guar gum	.3711	.28484	.563	-.3695	1.1118
1 g of Guar gum	0 g of Guar gum	-.4594	.22519	.178	-1.0449	.1261
	0.1 g of Guar gum	.0045	.28484	1.000	-.7361	.7451
	0.5 g of Guar gum	-.3711	.28484	.563	-1.1118	.3695

Based on observed means.

Homogeneous Subsets

Stickiness

Tukey HSD[a,b,c]

Guar	N	Subset 1
0.1 g of Guar gum	24	-4.0055
1 g of Guar gum	24	-4.0010
0.5 g of Guar gum	24	-3.6298
0 g of Guar gum	96	-3.5415
Sig.		.274

Means for groups in homogeneous subsets are displayed.
Based on Type III Sum of Squares
The error term is Mean Square(Error) = .974.

a. Uses Harmonic Mean Sample Size = 29.538.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

c. Alpha = .05.

Alginate

Multiple Comparisons

Dependent Variable: Stickiness
Tukey HSD

(I) Alginate	(J) Alginate	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
Alginate MANUCOL	Alginate MANUCOL	.0104	.21532	1.000	-.5495	.5703
	Alginate MANUGEL	2.1390*	.21532	.000	1.5791	2.6989
	Alginate Prantol LF 1	.3673	.21532	.325	-.1926	.9272
Alginate MANUCOL	Alginate MANUCOL	-.0104	.21532	1.000	-.5703	.5495
	Alginate MANUGEL	2.1286*	.21532	.000	1.5687	2.6885
	Alginate Prantol LF 1	.3569	.21532	.350	-.2030	.9168
Alginate MANUGEL	Alginate MANUCOL	-2.1390*	.21532	.000	-2.6989	-1.5791
	Alginate MANUCOL	-2.1286*	.21532	.000	-2.6885	-1.5687
	Alginate Prantol LF 1	-1.7717*	.21532	.000	-2.3316	-1.2118
Alginate Prantol LF 1	Alginate MANUCOL	-.3673	.21532	.325	-.9272	.1926
	Alginate MANUCOL	-.3569	.21532	.350	-.9168	.2030
	Alginate MANUGEL	1.7717*	.21532	.000	1.2118	2.3316

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

Stickiness

Tukey HSD[a,b]

Alginate	N	Subset 1	Subset 2
Alginate MANUGEL GMB	42	-5.1959	
Alginate Prantol LF 120	42		-3.4242
Alginate MANUCOL DH	42		-3.0673
Alginate MANUCOL LF	42		-3.0569
Sig.		1.000	.325

Means for groups in homogeneous subsets are displayed.
Based on Type III Sum of Squares
The error term is Mean Square(Error) = .974.

a. Uses Harmonic Mean Sample Size = 42.000.

b. Alpha = .05.

Appendix 8. Operations of Multifactorial ANOVA and One-way ANOVA

The Multifactorial ANOVA was conducted using SPSS 15.0 for Windows. It was done by going to: **Analyze/ General Linear Model/Univariate**. The GLM – Univariate dialog box was opened. In this dialog box, the dependent variable was clicked and moved to the box labeled **Dependent Variable** by clicking the arrow button. The factors were selected and moved to the box labeled **Fixed Factor(s)** by clicking the arrow button pointing to that box. Also, Post Hoc Multiple Comparisons test was performed by clicking **Post Hoc**. In the opened subdialog box, the factor containing three levels was moved to the box labeled **Post Hoc Tests for** using the arrow button. Then **Tukey** was selected by clicking its check box. And **Continue** was clicked for the next setting. In addition, group means of factors were able to be produced by clicking **Options**. In the Options subdialog box, the factor was moved to the box labeled **Display Means** for by clicking the arrow button. Then **Continue** was clicked to finish this setting. The GLM – Univariate dialog box was appeared again. Last, **OK** was clicked to display the results of the analysis.

One-way ANOVA was conducted by going to: **Analyze/Compare Means/One-Way ANOVA**. The One-Way ANOVA dialog box was opened. The dependent variable was moved to box labeled **Dependent List** by clicking the arrow button pointing to the box. The factor variable was moved to the box labeled **Factor** by clicking the arrow button. Also, the Post Hoc Multiple Comparisons subdialog box was opened by clicking **Post Hoc**. Then **Tukey** was selected to perform the Tukey's honestly significant different test. **Continue** was clicked to finish this setting. In addition, **Options** was clicked to open the **One-Way ANOVA: Options subdialog box**. Descriptive was selected by clicking its check box beside. This operation produced the number of cases, mean, standard deviation, standard error, minimum, maximum, and 95 per cent confidence interval of the dependent variable in each group. Continue was clicked to finish this setting. Back in the One-Way ANOVA dialog box, **OK** was clicked to produce the results of the analysis.

Appendix 9. Technical specification sheet of ingredients

National Starch
FOOD INNOVATION

Technical Service Bulletin

NATIONAL® M1

NATIONAL M1 is a tapioca maltodextrin derived from tapioca starch. It is very bland in taste and non-hygroscopic which makes it suitable for various applications.

Physical Properties:

Colour	White to off-white
Form	Powder
Moisture	Approximately 5%
pH	Approximately 4.5

Features and Benefits:

NATIONAL M1 is a free flowing powder, which can be dispersed with cold water and contributes viscosity and body. Because of its high solubility, NATIONAL M1 can be used in food systems requiring little or no heat. NATIONAL M1 is ideally suitable as a bulking agent in spray-dried flavors or seasonings.

Applications:

NATIONAL M1 is recommended for use in baked goods, rehydration/ energy beverages, confectionery, peanut butter, and spray-dried flavors or seasoning.

Baked Goods: NATIONAL M1 is of special interest to cookies, cakes and muffins to stabilise moisture and moderate texture.

Rehydration/ Energy Beverage: NATIONAL M1 provides excellent caloric density without exceeding osmotic balance. This is important in formulating rehydration/ energy beverages to provide a low residue carbohydrate source.

Confectionery: NATIONAL M1 is used as the sole agent to control sugar bloom and moderate stickiness in hard boil candy.

Peanut Butter: NATIONAL M1 can be added to peanut butter to improve body, provide smooth and creamy mouthfeel without grittiness.

Spray Dried Flavors/ Seasoning: NATIONAL M1 can be used as an effective carrier for spray-dried products. Final powders are free flowing and are readily reconstituted in water.

Label Declaration:

Tapioca Maltodextrin

$2.00/kg FIS, GST excl. < 1MT lots
21/01/08

The information given and the recommendations made herein are based on our research and are believed to be accurate but no guaranty of their accuracy is made. In every case we urge and recommend that purchasers, before using any product in full-scale production, make their own tests to determine to their own satisfaction whether the product is of acceptable quality and is suitable for their particular purposes under their own operating conditions. No representative of ours has any authority to waive or change the foregoing provisions but, subject to these provisions, our engineers are available to assist with product queries and technical support. Nothing contained herein shall be construed to imply the non-existence of any relevant patents or to constitute a permission, inducement or recommendation to practice any invention covered by any patent, without authority from the owner of this patent.

National Starch
FOOD INNOVATION

PRODUCT DATA SHEET

CONFIDENTIAL

NATIONAL® M1

Label Designation	Tapioca Maltodextrin

Physical and Chemical Characteristics (*):

Color	White to Off-white
Form	Fine Powder
Granulation	
Through USSS #100	>98%

Physical and Chemical Specifications:

DE	9.0 - 13.0
Moisture	14% maximum
pH (20% solution)	4.0 - 4.7

Microbiological Specifications:

Total Plate Count	10,000/g maximum
Yeast	200/g maximum
Mold	200/g maximum
E. coli	negative
Salmonella	negative

Packaging and Storage:

NATIONAL® M1 is packaged in multi wall Kraft paper bags with a net weight of 25 kgs. We recommend that NATIONAL® M1 be stored in a clean, dry area at ambient temperature and away from heavily aromatic material. The best before date for NATIONAL® M1 is 24 months from the date of manufacture.

(*) While this information is typical of NATIONAL® M1 it should not be considered a specification.

Data may become outdated, update yearly. 050928 AP
The above information is made in good faith but no guaranty of its accuracy is made. Purchasers should make their own determination whether the product is of acceptable quality and is suitable for their particular purposes. No representative of ours has any authority to waive or change these provisions. Nothing contained herein shall be construed to imply the non-existence of any relevant patents or to constitute a permission, inducement or recommendation to practice any invention covered by any patent, without authority from the owner of this patent.

National Starch
FOOD INNOVATION

Nutritional Data

NATIONAL M1

Calories†	4.0 KCal./gram
Calories from Fat	0.01 KCal./gram
Total Fat	<0.15%
Saturated Fat	<0.08%
Cholesterol	None Detected
Sodium	Approx. 50mg/100g
Total Carbohydrates	Approx. 90 %
Dietary Fiber	Approx. 0.4%
Sugars	Approx. 0.5%
Protein	<0.5%
Vitamin A	None Detected
Vitamin C	None Detected
Calcium	Approx. 50mg/100g
Moisture*	Approx. 10%
Ash	<0.5%

Note: Please note that while the above information is typical of NATIONAL M1, it should not be considered a specification, since the values may vary slightly between samples.

***Moisture**: The moisture content of all starches will vary, depending on environmental conditions during storage and manufacture. However, NATIONAL M1 will generally have a moisture content of around 10%.

The information given and the recommendations made herein are based on our research and are believed to be accurate but no guaranty of their accuracy is made. In every case we urge and recommend that purchasers, before using any product in full-scale production, make their own tests to determine to their own satisfaction whether the product is of acceptable quality and is suitable for their particular purposes under their own operating conditions. No representative of ours has any authority to waive or change the foregoing provisions but, subject to these provisions, our engineers are available to assist with product queries and technical support. Nothing contained herein shall be construed to imply the non-existence of any relevant patents or to constitute a permission, inducement or recommendation to practice any invention covered by any patent, without authority from the owner of this patent.

(2)

National Starch
FOOD INNOVATION

5-7 Averton Place, East Tamaki
P O Box 58 230, Greenmount,
Auckland

04 February 2008

MASSEY UNIVERSITY
IFNHH,Riddet Reception

PALMERSTON NORTH
M.U
Attention: Ray Winger

The following sample has been submitted for your evaluation.

Product Name: N-LITE LP **Batch No:**	**Application: Fat Memetic used in applications where no he**
Price valid for 3 months:	$/ kg in ton lots $6.45 / kg less ton lots (delivery charge applies for less ton lots)
Pack size:	22.7kg
Availability: **Lead Time:**	In Stock: No **In Stock: 2 – 4 days** **Non Stock: 10 – 12 weeks**
Product labelling:	Thickener E: 1440
Product manufactured in:	USA
This product is Non GM Identity Preserved, Halal and Kosher certified. (Statement (s) available on request)	

Recommendation: To decrease "stickiness" in fruit straps without decreasing viscosity

Please contact **Janet Donovan** on **273 5931** if you have any queries about this product.

This information is current and will be updated on every sample dispatched. The provided information will be valuable for your R _D and Purchasing personnel and if there is any information not supplied, please contact National Starch Chemical Pty Ltd.

National Starch
FOOD INNOVATION

Technical Service Bulletin

N-LITE®LP

N-LITE LP, a unique modified food starch, is used as a fat mimetic in cold-process liquid food systems. The "LP" designates liquid/pregel applications, N-LITE LP is very oily, bland in flavor and has outstanding viscosity stability in liquid systems. A no- or low-fat product can be prepared having the organoleptic and textural properties of a high quality fat-rich product. N-LITE LP does not require cooking and contributes virtually no viscosity to the food product.

Physical Properties:

Color	White to off-white
Form	Powder
Moisture	Approximately 7%
pH	Approximately 6

Features and Benefits:

N-LITE LP can be added to a liquid food product to improve the lubricity and coating of the palate.

N-LITE LP is designed for cold process liquid systems but is very resistant to heat and also to acid and mechanical shear.

N-LITE LP should be blended with other dries for easiest dispersal in water. Vigorous agitation is also helpful.

N-LITE LP is compatible with other ingredients commonly used in food products.

Applications:

N-LITE LP is recommended for use in cold-process liquid systems where a high degree of lubricity, creaminess and resistance to gelling is required. These include pourable salad dressings, dry mix soups and microwavable cheese sauces.

Instant Salad Dressings: Excellent no- and low-fat pourable and (instant) spoonable salad dressings can be made with N-LITE LP. Low- and no-fat products will change little in viscosity during storage.

Soups: No- and low-fat dry mix soups with N-LITE LP will have a rich, creamy mouthfeel like their full fat counterparts.

Sauces: The fat content of a dry mix cream or cheese sauce can be reduced while maintaining a smooth, creamy texture with excellent body.

Label Declaration:

Food Starch-Modified

The information given and the recommendations made herein are based on our research and are believed to be accurate but no guaranty of their accuracy is made. In every case we urge and recommend that purchasers, before using any product in full-scale production, make their own tests to determine to their own satisfaction whether the product is of acceptable quality and is suitable for their particular purposes under their own operating conditions. No representative of ours has any authority to waive or change the foregoing provisions but, subject to these provisions, our engineers are available to assist with product queries and technical support. Nothing contained herein shall be construed to imply the non-existence of any relevant patents or to constitute a permission, inducement or recommendation to practice any invention covered by any patent, without authority from the owner of this patent.

National Starch
FOOD INNOVATION

PRODUCT DATA SHEET

CONFIDENTIAL

N-LITE® LP

Label Designation	Food Starch-Modified
Source	Waxy Maize

Physical and Chemical Characteristics (*):

Color	White to Off-white
Form	Fine Powder

Physical and Chemical Specifications:

Granulation	
Through USSS #20	98% minimum
Through USSS #100	50% maximum
Moisture	14% maximum
pH (9% slurry)	4.5 - 7.5

Microbiological Specifications:

Total Plate Count	10,000/g maximum
Yeast	200/g maximum
Mold	200/g maximum
E. coli	negative
Salmonella	negative

Packaging and Storage:

N-LITE® LP is packaged in multi wall Kraft paper bags with a net weight of 50 lbs. We recommend that N-LITE® LP be stored in a clean, dry area at ambient temperature and away from heavily aromatic material. The best before date for N-LITE® LP is 24 months from the date of manufacture.

(*) While this information is typical of N-LITE® LP it should not be considered as a specification.

Data may become outdated, update yearly. 050928 AP
The above information is made in good faith but no guaranty of its accuracy is made. Purchasers should make their own determination whether the product is of acceptable quality and is suitable for their particular purposes. No representative of ours has any authority to waive or change these provisions. Nothing contained herein shall be construed to imply the non-existence of any relevant patents or to constitute a permission, inducement or recommendation to practice any invention covered by any patent, without authority from the owner of this patent.

International Specialty Products

Sales Specification

MANUCOL® DH - Sodium Alginate

Specification No. 1039

DESCRIPTION
MANUCOL DH is a medium viscosity, pure sodium alginate suitable for use in food products.

DETAILED REQUIREMENTS

1.	Viscosity (1% Solution)	40 - 90 mPa.s (cP)
2.	pH (1% solution)	5.0-7.5
3.	Loss on Drying	not greater than 13%
4.	Particle Size	at least 98% through 355 µm
		at least 80% through 250 µm
5.	(a) Appearance	cream to light brown powder
	(b) Powder Colour	not less than 48
6.	Ash (on dried solids basis)	18-27%
7.	Lead (Pb)	not greater than 5 mg/kg (ppm)
8.	Arsenic (As)	not greater than 3 mg/kg (ppm)
9.	Copper (Cu)	not greater than 10 mg/kg (ppm)
10.	Zinc (Zn)	not greater than 10 mg/kg (ppm)
11.	Mercury (Hg)	not greater than 0.5 mg/kg (ppm)
12.	Cadmium (Cd)	not greater than 0.5 mg/kg (ppm)
13.	Microbiological Limits	
	Bacteria (Total viable mesophilic aerobic count)	not greater than 5000 cfu/g
	Yeast and Mould	not greater than 300 cfu/g
	Coliform	negative by MPN
	E. coli	absent in 25 g
	Salmonella	absent in 25 g

INGREDIENT
Sodium alginate E401 CAS: 9005-38-3

REGULATORY COMPLIANCE
Complies with Purity Criteria in current EC Directives
Kosher Approved
Food Chemicals Codex
Generally recognised as safe (GRAS) in accordance with 21 CFR 184.1724

QUALITY SYSTEM
MANUCOL DH is manufactured according to a Quality System registered to ISO9002

PACKAGING
MANUCOL DH is packaged in 25 kg multi-ply sacks fitted with polyethylene liner or equivalent. All packaging materials comply with relevant UK, EC and United States food contact legislation.

STORAGE
Packages should be kept sealed and stored in a cool dry place.

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METHODS OF TESTING (Full details of test methods are available on request)

1. **Viscosity (1% Solution)**
Pour 450 g distilled water into a 600 ml glass beaker. Add 5.00 g product slowly while stirring the solution with an electric stirrer fitted with a propeller-type metal paddle. Adjust the weight of solution to 500 g with additional distilled water, rinsing the walls of the beaker. Stir for two hours at 800 rpm, then adjust the temperature to 20 degrees C, stirring by hand to eliminate any layering effects. Measure the viscosity immediately using an LV model of the Brookfield[1] viscometer at 60 rpm, with spindle 1, at 20 degrees C.

2. **pH (1% Solution)**
Measure the pH of a 1% solution at 20 degrees C using a pH meter.

3. **Loss on Drying**
Spread 5-10 g product evenly on a predried tared watch glass and weigh accurately. Dry in an oven at 105 ± 1 degrees C for four hours. Cool in a desiccator and re-weigh.

4. **Particle Size**
Sieve 10 g product on the specified British Standard Screens (200 mm diameter) for three minutes each screen using an Alpine[2] Air Jet Sieve. Use the finest mesh sieve first and progress to the coarsest mesh. Record the weight of product remaining on each screen and calculate the percentage which passes through each specified screen.

5. **Powder Colour**
Place powder in an optically flat Photovolt cuvette to a depth of 2 cm. Do not shake or tap. Using a green tristimulus filter, measure the powder colour on a Photovolt[3] reflectometer standardised against a white enamel standard of 75% reflectance.

6. **Ash**
Use the procedure given in the current edition of the Food Chemicals Codex.

7-12. **Lead, Arsenic, Copper, Zinc, Mercury and Cadmium**
These metals may be determined by atomic absorption techniques.

13. **Microbiological Limits**
For bacteria (TVMAC), E coli, salmonella, yeast and mould, follow the procedures as given for microbial limit tests in the current edition of the United States Pharmacopoeia. Method for coliform is available on request. For bacteria, plate out 1 ml of 1% solution and incubate for 48 hours at 30-35 degrees C. For yeast and mould plate out 1 ml of 1% solution on acidified potato dextrose agar and incubate for 5 days at 20-25 degrees C. Express results as colony forming units (c.f.u.) per gram.

SUPPLIERS OF TESTING EQUIPMENT
[1] Brookfield Engineering Laboratories, Stoughton, Massachusetts.
[2] Hosakawa Micron Ltd, Augsburg, Germany.
[3] Photovolt Corporation, Indianapolis, Indiana

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International Specialty Products

Sales Specification

MANUCOL® LF - Sodium Alginate

Specification No. 1034

DESCRIPTION

MANUCOL LF is a low viscosity, pure sodium alginate suitable for use in food products.

DETAILED REQUIREMENTS

1.	Viscosity (1% Solution)			10 - 40 mPa.s (cP)
2.	pH (1% solution)		5.0-7.5	
3.	Loss on Drying			not greater than 13%
4.	Particle Size			at least 98% through 355 µm
				at least 80% through 250 µm
5.	(a) Appearance			cream to light brown powder
	(b) Powder Colour			not less than 38
6.	Ash (on dried solids basis)			18-27%
7.	Lead	(Pb)		not greater than 5 mg/kg (ppm)
8.	Arsenic	(As)		not greater than 3 mg/kg (ppm)
9.	Copper	(Cu)		not greater than 10 mg/kg (ppm)
10.	Zinc	(Zn)		not greater than 10 mg/kg (ppm)
11.	Mercury	(Hg)		not greater than 0.5 mg/kg (ppm)
12.	Cadmium	(Cd)		not greater than 0.5 mg/kg (ppm)
13.	Microbiological Limits			
	Bacteria			not greater than 5000 cfu/g
	(Total viable mesophilic aerobic count)			
	Yeast and Mould			not greater than 300 cfu/g
	Coliform			negative by MPN
	E. coli			absent in 25 g
	Salmonella			absent in 25 g

INGREDIENT

Sodium alginate E401 CAS: 9005-38-3

REGULATORY COMPLIANCE

Complies with Purity Criteria in current EC Directives
Kosher Approved
Food Chemicals Codex
Generally recognised as safe (GRAS) in accordance with 21 CFR 184.1724

QUALITY SYSTEM

MANUCOL LF is manufactured according to a Quality System registered to ISO9002

PACKAGING

MANUCOL LF is packaged in 25 kg multi-ply paper sacks fitted with polyethylene liner or equivalent. All packaging materials comply with relevant UK, EC and United States food contact legislation.

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STORAGE

Packages should be kept sealed and stored in a cool dry place.

METHODS OF TESTING (Full details of test methods are available on request)

1. **Viscosity (1% Solution)**
   Pour 450 g distilled water into a 600 ml glass beaker. Add 5.00 g product slowly while stirring the solution with an electric stirrer fitted with a propeller-type metal paddle. Adjust the weight of solution to 500 g with additional distilled water, rinsing the walls of the beaker. Stir for two hours at 800 rpm, then adjust the temperature to 20 degrees C, stirring by hand to eliminate any layering effects. Measure the viscosity immediately using an LV model of the Brookfield[1] viscometer at 60 rpm, with spindle 1, at 20 degrees C.

2. **pH (1% Solution)**
   Measure the pH of a 1% solution at 20 degrees C using a pH meter.

3. **Loss on Drying**
   Spread 5-10 g product evenly on a predried tared watch glass and weigh accurately. Dry in an oven at 105 $\pm$ 1 degrees C for four hours. Cool in a desiccator and re-weigh.

4. **Particle Size**
   Sieve 10 g product on the specified British Standard Screens (200 mm diameter) for three minutes each screen using an Alpine[2] Air Jet Sieve. Use the finest mesh sieve first and progress to the coarsest mesh. Record the weight of product remaining on each screen and calculate the percentage which passes through each specified screen.

5. **Powder Colour**
   Place powder in an optically flat Photovolt cuvette to a depth of 2 cm. Do not shake or tap. Using a green tristimulus filter, measure the powder colour on a Photovolt[3] reflectometer standardised against a white enamel standard of 75% reflectance.

6. **Ash**
   Use the procedure given in the current edition of the Food Chemicals Codex.

7-12. **Lead, Arsenic, Copper, Zinc, Mercury and Cadmium**
   These metals may be determined by atomic absorption techniques.

13. **Microbiological Limits**
   For bacteria (TVMAC), E coli, salmonella, yeast and mould, follow the procedures as given for microbial limit tests in the current edition of the United States Pharmacopoeia. Method for coliform is available on request. For bacteria, plate out 1 ml of 1% solution and incubate for 48 hours at 30-35 degrees C. For yeast and mould plate out 1 ml of 1% solution on acidified potato dextrose agar and incubate for 5 days at 20-25 degrees C. Express results as colony forming units (c.f.u.) per gram.

SUPPLIERS OF TESTING EQUIPMENT

[1] Brookfield Engineering Laboratories, Stoughton, Massachusetts.
[2] Hosakawa Micron Ltd, Augsburg, Germany.
[3] Photovolt Corporation, Indianapolis, Indiana.

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(5)

International Specialty Products

Sales Specification

MANUGEL® GMB - Sodium Alginate

Specification No. 1007

DESCRIPTION

MANUGEL GMB is a high viscosity, pure sodium alginate suitable for use in food products where high gel strength is required.

DETAILED REQUIREMENTS

1.	Viscosity (1% Solution)		110 -270 mPa.s (cP)
2.	pH (1% solution)	5.0-7.5	
3.	Loss on Drying		not greater than 13%
4.	Particle Size		at least 98% through 355 µm
			at least 80% through 250 µm
5.	(a) Appearance		cream to light brown powder
	(b) Powder Colour		not less than 38
6.	Ash (on dried solids basis)		18-27%
7.	Lead (Pb)		not greater than 5 mg/kg (ppm)
8.	Arsenic (As)		not greater than 3 mg/kg (ppm)
9.	Copper (Cu)		not greater than 10 mg/kg (ppm)
10.	Zinc (Zn)		not greater than 10 mg/kg (ppm)
11.	Mercury (Hg)		not greater than 0.5 mg/kg(ppm)
12.	Cadmium (Cd)		not greater than 0.5 mg/kg(ppm)
13.	Microbiological Limits		
	Bacteria (Total viable mesophilic aerobic count)		not greater than 5000 cfu/g
	Yeast & Mould		not greater than 300 cfu/g
	Coliform		negative by MPN
	E. coli		absent in 25 g
	Salmonella		absent in 25 g

INGREDIENTS

Sodium alginate E401 CAS: 9005-38-3

REGULATORY COMPLIANCE

Complies with Purity Criteria in current EC Directives
Kosher Approved
Food Chemicals Codex
Generally recognised as safe (GRAS) in accordance with 21 CFR 184.1724

QUALITY SYSTEM

MANUGEL GMB is manufactured according to a Quality System registered to ISO9002.

PACKAGING

MANUGEL GMB is packaged in 25 kg multi-ply paper sacks fitted with polyethylene liner or equivalent. All packaging materials comply with relevant UK, EC and United States food contact legislation.

STORAGE

Packages should be kept sealed and stored in a cool, dry place.

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METHODS OF TESTING (Full details of test methods are available on request)

1. **Viscosity (1% Solution)**
Pour 450 g distilled water into a 600 ml glass beaker. Add 5.00 g product slowly while stirring the solution with an electric stirrer fitted with a propeller-type metal paddle. Adjust the weight of solution to 500 g with additional distilled water, rinsing the walls of the beaker. Stir for two hours at 800 rpm, then adjust the temperature to 20 degrees C, stirring by hand to eliminate any layering effects. Measure the viscosity immediately using an LV model of the Brookfield[1] viscometer at 60 rpm, with spindle 2, at 20 degrees C.

2. **pH (1% Solution)**
Measure the pH of a 1% solution at 20 degrees C using a pH meter.

3. **Loss on Drying**
Spread 5-10 g product evenly on a predried tared watch glass and weigh accurately. Dry in an oven at 105 $\pm$ 1 degrees C for four hours. Cool in a desiccator and re-weigh.

4. **Particle Size**
Sieve 10 g product on the specified British Standard Screens (200 mm diameter) for three minutes each screen using an Alpine[2] Air Jet Sieve. Use the finest mesh sieve first and progress to the coarsest mesh. Record the weight of product remaining on each screen and calculate the percentage which passes through each specified screen.

5. **Powder Colour**
Place powder in an optically flat Photovolt cuvette to a depth of 2 cm. Do not shake or tap. Using a green tristimulus filter, measure the powder colour on a Photovolt[3] reflectometer standardised against a white enamel standard of 75% reflectance.

6. **Ash**
Use the procedure given in the current edition of the Food Chemicals Codex.

7-12. **Lead, Arsenic, Copper, Zinc, Mercury and Cadmium**
These metals may be determined by atomic absorption techniques.

13. **Microbiological Limits**
For bacteria (TVMAC), E coli, salmonella, yeast and mould, follow the procedures as given for microbial limit tests in the current edition of the United States Pharmacopoeia. Method for coliform is available on request. For bacteria, plate out 1 ml of 1% solution and incubate for 48 hours at 30-35 degrees C. For yeast and mould plate out 1 ml of 1% solution on acidified potato dextrose agar and incubate for 5 days at 20-25 degrees C. Express results as colony forming units (c.f.u.) per gram.

SUPPLIERS OF TESTING EQUIPMENT

[1] Brookfield Engineering Laboratories, Stoughton, Massachusetts
[2] Hosakawa Micron Ltd, Augsburg, Germany
[3] Photovolt Corporation, Indianapolis, Indiana

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Product Specification Bulletin

FMC BioPolymer

Not Just Products. Partners.

Protanal® LF 120 alginate - 2205500

SPECIFICATIONS:

Purity	fulfills the requirements of FAO/WHO, FCC and Commission Directive 98/86/EC
Appearance	white to yellowish brown free-flowing powder almost odorless and without taste
Viscosity (in 1% aq.sol.)	200 to 400 mPa•s
pH (in 1% aq.sol.)	6.0 to 8.0
Particle size	minimum of 99% through 120 mesh BS
Loss on drying	maximum 15%
Water insolubles	maximum 2% on anhydrous basis
Arsenic	maximum 3 mg/kg
Lead	maximum 5 mg/kg
Heavy metals	maximum 20 mg/kg

MICROBIOLOGY:

Total count	maximum 5,000 cfu/gram
Mold and yeast	maximum 500 cfu/gram
Coliforms	negative by test
Salmonella	negative by test

PRODUCT INGREDIENT: sodium alginate (E-401)

STORAGE CONDITIONS: Store in a cool, dry location

APPLICATION:

- Recommended for use in fruit preparations

Methods of Analysis are available on request.

TECHNICAL SERVICE CENTERS:
FMC BioPolymer

The Americas:
1735 Market Street
Philadelphia, PA 19103
Phone: 1-800-526-3649
1-215-299-6234
Fax: 1-215-299-5809

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13025-151, Campinas, SP, Brazil
Phone: 55-19-255-5222
Fax: 55-19-255-1954

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Colonia Electricistas
Del. Azcapotzalco
C.P. 02060, Mexico, D.F.
Phone: 52-5-352-3589
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1050 Brussels, Belgium
Phone: 32-2-645-9526
Fax: 32-2-645-9434

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N-3002 Drammen, Norway
Phone: 47-32-20-3500
Fax: 47-32-20-3510

Asia Pacific:
85 Science Park Drive
#02-08 The Cavendish
Singapore 118259
Phone: 65 872-2920
Fax: 65 872-2927

REGULATORY STATUS:
In the United States, alginic acid, sodium alginate, calcium alginate, potassium alginate, and ammonium alginate are affirmed as Generally Recognized as Safe when used as a stabilizer or thickener within the limitations specified in the regulations. Propylene glycol alginate is regulated as a food additive in 21 CFR 172.858.

Within the European Union, alginic acid (E 400), sodium alginate (E 401), potassium alginate (E 402), ammonium alginate (E 403), calcium alginate (E 404), and propane 1,2 diol alginate (E 405) are included the Miscellaneous Additive Directives. Refer to the Miscellaneous Additives Directive for the specific conditions of use for these additives.

Alginic acid (INS 400), sodium alginate (INS 401), potassium alginate (INS 402), ammonium alginate (INS 403), calcium alginate (INS 404), and propane 1,2 diol alginate (INS 405) have been evaluated by the Joint FAO/WHO Expert Committee on Food Additives and are permitted for use in food, as specified in the evaluation(s).

PATENTS:
FMC Corporation does not warrant against infringement of patents of third parties by reason of any uses made of the product in combination with other material or in the operation of any process; purchasers assume all risks of patent infringement by reason of any such use, combination, or operation.

WARRANTY:
Because of the numerous factors affecting results, FMC BioPolymer ingredients are sold on the understanding that purchasers will make their own test to determine the suitability of these products for their particular purpose. The several uses suggested by FMC BioPolymer are presented only to assist our customers in exploring possible applications. All information and data presented are believed to be accurate and reliable, but are presented without the assumption of any liability by FMC BioPolymer.

TECHNICAL SERVICE:
The information contained in this bulletin is intended to be general in nature. Techniques and data pertaining to specific uses for FMC ingredients and new developments will be published periodically in the form of supplemental application bulletins.

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ADM
4666 Faries Parkway
Decatur, Illinois 62526
800-637-5843

NovaXan™80

For clear results

NF/FCC Grade Xanthan Gum

Thickener and Stabilizer, for Excipient/Food Use

DESCRIPTION:

ADM NovaXan ™ 80 is an off-white to light tan colored, free-flowing granular powder that meets the specifications of the National Formulary, the Food Chemicals Codex and the J.E.C.F.A.

GENERAL CHARACTERISTICS:

Viscosity (1.0% in 1.0% KCl)	1200 - 1600 cP
Particle Size	100% through USS 60 mesh, 250 μ
	95% minimum through USS 80 mesh, 177 μ
Powder Color	Not less than 60
pH (1.0% Solution)	5.5 to 8.1

STANDARD SPECIFICATIONS:

Identification	Meets NF/FCC tests
Assay	Meets NF/FCC tests
Loss on Drying	6 - 14%
Viscosity	Meets NF/FCC tests
Ash	Between 6.5% and 16%
Arsenic	Not more than 3 ppm
Lead	Not more than 2 ppm
Heavy Metals (as Pb)	Not more than 20 ppm
Isopropyl Alcohol	Not more than 750 ppm
	Not more than 500 ppm (Europe & Japan)
Pyruvic Acid	Not less than 1.5%
Nitrogen	Not more than 1.5%

MICROBIOLOGICAL:

Total Plate Count	Not more than 2000/g
Yeast and Molds	Not more than 100/g
Salmonella	Meets NF test
Escherichia coli	Meets NF test

Shelf life:

36 months from the certificate of analysis test date

PACKAGING:

25 kg boxes, product and package code 174910-2L

The information contained herein is correct as of the date of this document to the best of our knowledge. The recommendations or suggestions contained herein are made without guarantee or representation as to results and are subject to change without notice. We suggest that you evaluate these recommendations and suggestions independently. Our responsibility for claims arising from breach of warranty, negligence or otherwise shall not include consequential or incidental damages, including lost profits, and is limited to the purchase price of material purchased for ADM. Freedom to use any patent owned by ADM or others is not to be inferred from any statement contained herein.

6228799 6222720 25 kg 39.50 /kg