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Effects of polyols on gelation kinetics, gel hardness, and drying properties of alginates subjected to internal gelation

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ABSTRACT

This study investigates the influence of polyols (glycerol, sorbitol, mannitol and isomalt) on thickening of sodium alginate solutions, hardness and drying kinetics of calcium alginate gels and their glass transition temperature (Tg) after drying. Two alginate samples with 30% and 63% guluronate were used to prepare gels by internal gelation based on release of calcium ions from $CaCO_3$ by hydrolysis of glucono-delta-lactone. The lag period, determined from viscosity-time plots, for the low-G alginate was about 13 min less than that for the high-G alginate. Presence of polyols did not influence the lag period values. The hardness value for high-G gels was about 100 g greater than that of low-G gels. Addition of isomalt resulted in gels with higher hardness values compared to other polyols. Presence of polyols had a significant effect on residual moisture and Tg of alginate films. Initial drying rates were the same for all samples but gels containing glycerol had high residual moisture (~3.5 g/100 g) and produced very flexible films, whereas mannitol containing samples had low moisture (~0.2 g/100 g) and produced brittle films. Tg of the films varied from −88 °C to 35 °C and decreased upon polyol addition.

1. Introduction

Alginates are used in diverse industries for various functions ranging from thickening of solutions to encapsulation of sensitive compounds (Draget, Smidsrød, & Skjåk-Bræk, 2005). In food applications, the interaction between guluronate residues of adjacent alginate chains and divalent cations (e.g., Ca^{2+}) is utilized to form gels. Crosslinking of alginate with calcium ions is often achieved by one of two methods: external or internal gelation (Draget et al., 2005). In external gelation, calcium ions diffuse into alginate solution for crosslinking and this sets a reaction front advancing linearly with the square root of time (Ak, Nussinovitch, Campanella, & Peleg, 1989; Potter, Balcom, Carpenter, & Hall, 1994). It has been shown that, in absence of other ions, gels formed by external gelation were inhomogeneous with significant spatial variations in Ca-alginate concentration (Skjåk-Bræk, Grasdalen, & Smidsrød, 1989). Gels with more uniform structures are obtained by using internal gelation. In this method, also applied here, a slowly hydrolyzing glucono-delta-lactone (GDL) lowers pH of the medium which then facilitates release of calcium ions from salts like $CaCO_3$ (Draget, Ostgaard, & Smidsrød, 1991). Internally set gels display a more solid-like behavior than externally set gels despite their similar compositions. This difference in rheological behavior is related to the microstructure of alginate gels produced by these methods (Schuster et al., 2014).

The progressive introduction of calcium ions into alginate solutions under internal gelation conditions means that gelation takes time. Farres and Norton (2014) studied effects of shear rate, alginate concentration and molecular weight on the kinetics of gel formation. They reported that the onset time of gelation has almost tripled when shear rate is increased from 100/s to 600/s. From industrial point of view, solution properties, gelation kinetics and gel characteristics of hydrocolloids are important for controlling the process and properties of final product (Comaposada, Gou, Marcos, & Arnau, 2015). In food applications, alginates often undergo thickening and gelation in presence of other ingredients (e.g., proteins, fruits) (Hughes, Ledward, Mitchell, & Summerlin, 1980; Kaletunç, Nussinovitch, & Peleg, 1990). Polyols have become a common ingredient in food formulations due to their versatile functions such as sucrose replacement (Hao et al., 2016). Rheological and textural properties of neat alginate gels have long been studied (Mitchell & Blanshard, 1976; Zhang, Daubert, & Foegeding, 2005). There is however limited information on gelation of alginates in presence of polyols. Zhang, Daubert, Mulligan, and Foegeding (2008) investigated gelation kinetics of alginate solutions containing dextran or glycerol. They reported that glycerol up to 32 g/100 g did not affect

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gelation of alginate solutions and mechanical properties of resulting gels.

Many reports have been published on properties of edible films containing alginates and polyols (da Silva, Bierhalz & Kieckbusch, 2009; Santana & Kieckbusch, 2013). Santana and Kieckbusch (2013) compared effects of glycerol, mannitol and xylitol on permeability and mechanical properties of Ca-alginate films. After analyzing the effects of each polyol on properties of Ca-alginate films, they concluded that a mixture of glycerol and mannitol works better to optimize mechanical properties of the films. It is therefore important to study how substituting a polyol with another affects different properties of the final product.

Air drying of gels is often applied to obtain alginate films and beads. The effects of drying conditions on physical properties of alginate films plasticized with glycerol have been studied (da Silva, Bierhalz & Kieckbusch, 2012). These authors have reported that a significant loss of glycerol occurs when drying is conducted at temperatures above 40 °C. Sensitivity of alginate gel beads to drying conditions was apparently also considered by Vreeker, Li, Fang, Appelqvist, and Mendes (2008) as they used air at room temperature with low humidity (RH = 11%) to obtain dry beads (without polyols).

Glass transition temperature (**Tg**) is an important parameter that controls changes in food structure and behavior. In general, it is better to keep foods at temperatures below their **Tg** for product stability (Roos, 2003). However, addition of plasticizers, such as polyols, is often required to improve properties critical for processing and handling (Talja, Helén, Roos, & Jouppila, 2007). It is therefore important to understand how addition of different polyols changes **Tg** of alginate-based systems.

Regarding industrial flavor encapsulation, it is particularly useful to understand how incorporation of polyols affects, sequentially, viscosity development in solutions, gel hardness, and drying kinetics of alginate gels. Hence, the objectives of this study were to investigate the influence of four polyols on: a) viscosity growth in alginate solutions, b) hardness of alginate gels, c) drying kinetics of alginate gels, and d) **Tg** of resulting dry alginate films.

2. Materials & methods

2.1. Materials

Two commercial sodium alginates were used in this study: Manugel® DMB with 63% G content (Sriamornsak, Nunthanid, Luangtana-anan, & Puttipipatkhachorn, 2007) and molar mass of 150.000 g/mol (Eriksson, 2011) from FMC Biopolymer (Norway) and Grindsted® Alginate FD 175 with 30% G content and molar mass of 478.000 g/mol (Liu, Becker, & Neufeld, 2005) from DuPont™ Danisco® (Denmark). Alginates were referred to as high-G and low-G based on their guluronic acid content. The polyols tested here included glycerol (Aromsa AS; lot#H60826), sorbitol (Tereos Starch & Sweeteners; lot# F3C349571), mannitol (Cargill, Inc.; lot# 05128691) and isomalt (Beneo; lot# L121490100). Glucono delta-lactone (GDL, Roquette; lot# S4713) and calcium carbonate ($CaCO_3$, Aromsa AS; lot# H59456) were food-grade. Calcium carbonate ($CaCO_3$) was passed through a 200 µm sieve to eliminate large particles. For comparison, additional rheological tests were conducted with $CaCO_3$ particles passing through a 38 µm sieve.

2.2. pH and conductivity measurements

pH and conductivity of distilled water and 5 g/100 g polyol solutions were monitored. To 500 g of distilled water or polyol solution, approximately 0.83 g $CaCO_3$ was added and the dispersion was stirred at 400 rpm for 1 min at room temperature. To this dispersion approximately 2.92 g GDL was added. The mixture was stirred at 400 rpm for 80 min and pH (inoLab® pH 7110, WTW, Germany) and conductivity (Cond 3210 Set1, WTW, Germany) were measured every 10 min.

Dissolution of GDL particles in presence of $CaCO_3$ was observed under a Nikon C-DSS230 light microscope (Nikon Instruments Europe BV, Netherlands) using Clemex Vision PE V6.0 software (Clemex Technologies Inc., Canada).

2.3. Experimental design

A D-Optimal design was used to investigate effects of alginate type (high-G and low-G), polyol type (glycerol, isomalt, mannitol, sorbitol) and concentration (0–5 g/100 g) on the lag period of sodium alginate solutions and hardness of Ca-alginate gels. Totally, 24 experimental runs were generated with 3 factors. The ranges for factors were chosen based on preliminary experiments. Experimental design and data analysis were made with Design-Expert 7 software (Stat-Ease, Inc., USA).

2.4. Preparation of gelling mixtures and rheological tests

Sodium alginate solutions for gelation studies were prepared following the method of Kuo and Ma (2001) with some modifications. Briefly, 1.44 g sodium alginate was dissolved in 100 mL deionized water and left overnight for hydration and de-aeration. For polyol containing mixtures, the same amount of sodium alginate was dissolved in 100 mL of polyol solution of varying concentrations (0, 1.25, 2.50, 3.75, and 5.00 g/100 g) in deionized water. Calcium carbonate was used as the ion source for gelation. Approximately 0.2 g $CaCO_3$ was added to the hydrated alginate solution and stirred at 1300 rpm for 1 min using a magnetic stirrer bar (diameter = 6,1 mm; length = 30 mm). To this dispersion, 20 mL of 3.5 g/100 g fresh aqueous GDL solution was added and mixed at 900 rpm for 5 min to initiate gelation. The order of material additions and details of mixing conditions (e.g., stirrer size) were critical for repeatable results. Hence, they were strictly kept the same in every run.

Gelation mixtures prepared as described above were immediately transferred to the measurement cup of the rheometer (Bohlin Gemini 2, Malvern Instruments, UK). Viscosity measurements were performed at 25 °C and a constant shear rate of 0.1/s with concentric cylinder geometry. It is recognized that sedimentation of $CaCO_3$ particles may occur during the test (Draget et al., 1991). However, since repeatable results were obtained for rheological tests at 0.1/s the sedimentation issue was assumed to influence each measurement equally. Moreover, additional rheological tests performed at 1/s and 10/s produced the same trends for the parameters studied (data not included). Minimum three measurements were made for each experiment and the averages were used in statistical analysis.

Contributions of polyols to viscosity of alginate solutions without $CaCO_3$ and GDL were assessed at a higher shear rate of 100/s to avoid the lower torque limit of the rheometer.

One of the main parameters investigated in this research was called lag period. It was determined from the intersection of two straight lines drawn around turning point in viscosity growth curves (Fig. 1). The coefficient of determination (R^2) for regression lines was greater than 0.96.

2.5. Hardness measurement

Once the gelation was initiated upon addition of $CaCO_3$ and GDL, approximately 8.0 g of gelling mixtures were poured into plastic cups (diameter = 38,5 mm; height = 11 mm), sealed, and stored at room temperature for 24 h. Uniaxial compression test at a crosshead speed of 1 mm/s was conducted to determine hardness (i.e., force at 50% deformation) of the calcium alginate gels with a CT3 Texture Analyzer (Brookfield, USA). The diameter of sample cups was bigger than that of compression probe (38,5 mm vs. 12,7 mm). Ten specimens were tested for each sample and the averages were used in statistical analysis.