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Physical properties of sodium alginate solutions and edible wet calcium alginate coatings

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ABSTRACT

Calcium alginate structures are of interest to the meat industry as replacers for natural casings. This paper focuses on the study of the physical properties of sodium alginate solutions and wet calcium alginate films at 12 °C for their assessment as fermented sausage coatings. Six different commercial sodium alginates were dissolved at different concentrations (0.02, 0.03 and 0.04 kg/kg solution). The viscosity of the sodium alginate solution provided information about the maximum force and tensile strength of the calcium alginate films, depending on the alginate type and concentration of the solution. The required time for the conversion of sodium alginate solution to calcium alginate gel was higher at a higher alginate concentration, and the method used for its determination was appropriate and simple. No significant differences in colour, moisture, water activity and permeance of the wet films made from the different sodium alginate types were found. The results of the mechanical properties and permeance indicate that alginate coatings could be appropriate as a substitute for natural casings.

1. Introduction

Natural casings from animals have been used for many centuries in sausage production. During the last century, casings made of collagen, cellulose or plastic appeared on the market to replace the traditional ones. A more recent innovation in meat industries is the use of edible coatings obtained by a co-extrusion process as a substitute for casings. Co-extrusion process is a technology which has been developed to manufacture sausages under a continuous production system. This process is based on coating a large strand of meat batter with a coating paste forming a thin layer on the surface of the sausage (Frye, 1996). The coatings most commonly used are composed of sodium alginate alone, or blended with other food additives such as proteins, pectin or cellulose derivatives (Bontjer, Meggelaars, Thoonsen, & Van Den Berg, 2006; Gennadios, Hanna, & Kurth, 1997; Harper, Barbut, Lim, & Marcone, 2013; Holzschuh, Buch, Weiland, & Metzger, 2003; Liu, Kerry, & Kerry, 2007; Nielsen & Wells, 2009).

Alginates are polysaccharides obtained from brown seaweeds. They are composed of β-D-mannuronic acid (M) and α-L-guluronic acid (G). Alginates have the ability to form uniform, transparent, water-insoluble and thermo-irreversible gels at room temperature, by cross-linking with di- or tri-valent ions. The most commonly used are calcium chloride solutions (Helgerud, Gåserød, Fjæreide, Andersen, & Larsen, 2009). Other properties of alginates are their high availability, biodegradability and low price compared to natural casings (Frye, 1996).

The physicochemical and mechanical properties of calcium alginate gels are affected by the composition and formation process (Fabra, Talens, & Chiralt, 2010; Galus & Lenart, 2012; LeRoux, Guilak, & Setton, 1999; Liu, Kerry, & Kerry, 2005; Olivas & Barbosa-Cánovas, 2008; Rhim, 2004; Sriamornsak & Kennedy, 2006). Therefore, the understanding of the factors affecting the above mentioned properties is essential to develop proper coatings for co-extrusion applications on meat products. The properties of alginate gels and dry alginate films have been extensively studied. However these formats are not suitable to predict the behaviour of alginate casings used to coat meat batters, which are wet films.

The objective of this study was to study physical properties of sodium alginate solutions and wet calcium alginate films for assessment as fermented sausage coatings, considering six different commercial sodium alginates dissolved at different concentrations (0.02, 0.03 and 0.04 kg/kg solution).

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2. Materials and methods

2.1. Preparation procedures

2.1.1. Materials

Six commercial sodium alginates, variable in viscosity and chemical composition, were supplied by Cargill Inc. (Minneapolis, MN, USA) and FMC Biopolymer A/S (Drammen, Norway) (Table 1). Food grade anhydrous calcium chloride was purchased from Cargill Inc. (Minneapolis, MN, USA).

2.1.2. Sodium alginate solutions

Solutions of 0.02, 0.03 and 0.04 kg/kg solution of each sodium alginate type were prepared in deionised water using a Thermomix blender (Vorwerk, Wuppertal, Germany). Independent batches were prepared for each concentration and alginate type. The solutions were stirred for 30 min at 500 rpm. The alginate solutions were then stored for 24 h at 12 °C in order to stabilise the temperature and to facilitate de-aeration.

2.1.3. Calcium alginate films

Several alginate films were prepared per batch with a hand-operated Thin Layer Chromatography Plate Coater (CAMAG, Muttenz, Switzerland). The gate for layer thickness was adjusted to 0.5 mm. A 0.1 kg/kg solution $CaCl_2$ solution was also prepared and kept at 12 °C prior to being used as a gelling-agent. The plates coated with sodium alginate solution were soaked in a $CaCl_2$ brine bath for 30 s at 12 °C for crosslinking. They were then covered with a high density polyethylene sheet (Bacaicoa Industrias Plásticas, S.A., Oricain, Spain) of 0.08 mm thickness and 0.94 kg/m^3 density to prevent dehydration until the film analyses were performed.

2.2. Characterisation of sodium alginates

2.2.1. Mineral and sugar analysis

Several minerals from sodium alginates were analysed according to Regulation (CE) No 152/2009. Ash: Gravimetric. Calcium, Sodium, Potassium and Magnesium were determined after sample humid digestion by Flame Atomic Absorption Spectrometry. Chloride: Volumetric Carpentier-Vohlard. Phosphor: Espectrofotometry. Sugar: Volumetric Luff-Schoorl. The analytical error of these methods was 3% of the measure except for ash which was 1%. The estimation of the ionic strength of the sodium alginate solutions was calculated according to Lange (1999).

2.2.2. M/G analysis by ^{1}H NMR

Twenty three mg of each sodium alginate type were dissolved in 1 ml of deuterium oxide (0.9998 kg/kg solution D_2O). Sonication was applied to the solution for 1.5 h, with vigorous shaking every 20–30 min. Following the homogenisation, the sample was maintained at 65 °C for 1 h to achieve a lower viscosity to facilitate its transfer to an NMR Bruker Avance 600 MHz tube. The sample required a few hours until it reached the bottom of the tube.

The chemical composition and sequence of the sample of sodium alginate was obtained by acquiring the ^{1}H NMR spectrum at 65 °C (ASTM International Standard F 2259-03, 2003; Santi, Coppetta, & Santoro, 2008).

The data processing carried out using the software Mestrenova v. 8.1.2 (Mestrenova, 2013). The data was processed with a line broadening function of 1 Hz, the baseline was adjusted automatically with a Whittaker Smoother function and the results of the integrations were obtained through a de-convolution of the peaks.

2.3. Measurements on sodium alginate solutions

2.3.1. Viscosity

The viscosity of the alginate solutions was measured using a rotational viscometer Viscostar Plus (Fungilab, Barcelona, Spain). Spindle R3 was used for alginate solutions at 0.02 and 0.03 kg/kg solution, at 20 rpm and 4 rpm respectively. Spindle R5 at 6 rpm was used for alginate solutions at 0.04 kg/kg solution concentration. The viscosity was measured for 10 min at 12 °C; the values were recorded every 30 s and were averaged excluding the first five values. Each sample was measured in duplicate. Three batches for each alginate solution were analysed.

The logarithm of viscosity was related to the logarithm of concentration according to a linear regression model (Walstra, 2003) (Equation (1)).

$$Log_{10}\ Viscosity = a + b \cdot Log_{10}\ Concentration \quad (1)$$

Intercept (a) and slope (b) were calculated for each alginate.

2.3.2. Gelation front

The penetration of the gelation front into a sodium alginate solution was determined as an estimation of the gelation speed using a transparent cuvette of 45 mm long and 10 mm wide. The cuvette was filled with alginate solution and the open end was wrapped with filter paper that once inverted maintained in contact with 0.01 kg $CaCl_2$/kg solution. Images were taken throughout the gelation process. A change of colour of the sodium alginate solution was observed when the solution gelled, which was identified as the gelation front. The distance between the gelation front and the filter paper in contact with the $CaCl_2$ solution was monitored.

Two batches for each alginate solution were analysed. Two replicates per batch were measured.

2.4. Characterisation of calcium alginate films

2.4.1. Film thickness

The thickness of alginate films was measured in triplicate using a digital micrometer (Mitutoyo, Tokyo, Japan). In order to minimise the compressive effect generated by the micrometer, the film was placed between two methacrylate plates.

Table 1
Technical information of commercial sodium alginates obtained from the product datasheet.

Alginate type[a]	Commercial reference	Viscosity (0.01 kg/kg, 20 °C) in mPa s	pH (0.01 kg/kg, 20 °C)	M:G ratio	Supplier
A1	Algogel 3001	30–60	6.0–8.5	0.60–0.75	Cargill Inc. (Minneapolis, MN, USA)
A2	Protanal GP 3350	100–200	6.0–8.0	0.80–1.20	FMC Biopolymer A/S (Drammen, Norway)
A3	Algogel 6021	150–300	6.0–8.5	0.45–0.60	Cargill Inc. (Minneapolis, MN, USA)
A4	Algogel 5541	300–500	6.0–8.5	0.60–0.75	Cargill Inc. (Minneapolis, MN, USA)
A5	Protanal SF 120 RB	400–600	6.0–8.0	0.80–1.20	FMC Biopolymer A/S (Drammen, Norway)
A6	Protanal RF 6650	400–600	6.0–8.0	0.45–0.65	FMC Biopolymer A/S (Drammen, Norway)

[a] The code was assigned to each commercial alginate during this study according to the viscosity range.