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Influence of processing conditions on the properties of alginate solutions and wet edible calcium alginate coatings

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ABSTRACT

Two alginates with different viscosities (η-low and η-high) were used to study the effects of processing conditions (pH, addition of sodium chloride, addition of $CaCl_2$, mixing speed, mixing temperature, gelation time, gelation temperature) on the viscosity of sodium alginate solutions and the properties of wet calcium alginate films. No differences in the monomeric fractions proportion (M/R ratio) between alginates were observed. η-high presented higher values of estimated average length of G- and MG-blocks than η-low alginate. The viscosity of the alginate solution was increased in the presence of calcium traces. The impact of $CaCl_2$ addition on alginate viscosity was much stronger for η-low alginate. However, no improvement of the mechanical properties was observed. The presence of NaCl in alginate solutions also increased the viscosity and had a negative impact on the puncture properties of calcium alginate films. On the contrary, the use of high mixing speeds resulted in less viscous sodium alginate solutions and stronger films. Finally, the use of neutral pH values and refrigeration temperatures during the co-extrusion process would be advisable in order to prevent a detrimental effect on the mechanical properties of alginate films.

1. Introduction

During the last century, casings made of collagen, cellulose or plastic appeared on the market as an alternative to traditional natural casings. A more recent innovation in meat industries is the use of edible coatings obtained by a co-extrusion process as a substitute for casings. The co-extrusion process is a processing technology that allows the manufacturing of sausages under a continuous production system. This process consists in coating a large strand of meat batter with a coating solution in order to form a thin cover layer on the surface of the sausage (Frye, 1996). The coatings most commonly used are composed of calcium alginate or composites of alginate with other food additives such as proteins, pectin or cellulose derivatives (Gennadios, Hanna, & Kurth, 1997; Harper, Barbut, Lim, & Marcone, 2013; Liu, Kerry, & Kerry, 2005; Olivas & Barbosa-Cánovas, 2008; Rhim, 2004).

Alginate is of interest as a potential biopolymer film or coating component because of its unique colloidal properties such as thickening, film forming, gel producing, and emulsion stabilizing agent (Draget, Smidsrod, & Skjak-Braek, 2005; King, 1983). Alginates are polysaccharides obtained from brown seaweeds. They are composed of β-D-mannuronic acid (M) and α-L-guluronic acid (G) in varying proportions, sequence, and molecular weight. Alginate gellation takes place when divalent or multivalent ions (usually Ca^{2+}) interact ionically with blocks of guluronic acid residues from two different chains resulting in a three-dimensional network (Braccini & Pérez, 2001; King, 1983; Stabler, Wilks, Sambanis, & Constantinidis, 2001).

The physical properties of alginate gels vary widely depending on their chemical composition, i.e., the proportion of guluronic (G) to mannuronic (M) acid residues, the sequential order of these residues, the length of G-blocks, and the overall molecular weight of the polymer (Draget, Østgaard, & Smidsrød, 1990; Klöck et al., 1997; Stabler et al., 2001). 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 (Comaposada, Gou, Marcos, & Arnau, 2015). Although co-extruded casings are used by several North American and European companies, little is known about these casings and there is

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little information in the literature on wet films for its use (Harper, Barbut, Smith, & Marcone, 2015).

In a previous study Comaposada et al. (2015) reported the influence of different types of sodium alginates and concentrations on the properties of sodium alginate solutions and wet calcium alginate films. Two alginates from this study were selected (a low and a high viscosity alginates) to further study the effects of processing conditions on the viscosity of sodium alginate solutions and the properties of wet calcium alginate films.

2. Materials and methods

2.1. Materials

Sodium alginates with different viscosities (low and high) were selected for the experiment: Protanal GP 3350 (η-low) and Protanal SF 120 RB (η-high) were supplied by FMC BioPolymer (Drammen, Norway). Table 1 shows the technical information. Food grade anhydrous calcium chloride was purchased from Cargill Inc. (Minneapolis, MN, USA).

2.2. Preparation of sodium alginate solutions and calcium alginate films

Solutions of 0.02 kg/kg of each sodium alginate were prepared in deionised water using a Thermomix blender (Vorwerk, Wuppertal, Germany). The standard solutions were stirred at 20 °C for 30 min at 500 rpm. The pH of the solution was 6.70 ± 0.01. The obtained alginate solutions (standard) were stored for 24 h at 12 °C in order to stabilize the temperature and to facilitate deaeration.

Alginate films were obtained using a hand-operated Thin Layer Chromatography Plate Coater (CAMAG, Muttenz, Switzerland). The gate for layer thickness was adjusted to 0.5 mm. Sodium alginate solutions were crosslinked by immersion in a 0.1 kg/kg $CaCl_2$ solution in water (pH = 6.7) for 30 s at 12 °C. The obtained films (standard) were covered with a high density polyethylene film to prevent dehydration until analysis.

The effect of varying processing conditions on the properties of alginate solutions and calcium alginate films was studied. A range of alginate solutions and gels were prepared by varying the standard processing conditions: i) addition of sodium chloride to alginate solutions (15, 30 g/kg NaCl); ii) addition of $CaCl_2$ to alginate solutions (0.05, 0.5 g/kg); iii) mixing speed (2000, 5100 rpm); iv) temperature during mixing of alginate solutions (37, 70 °C); v) pH of alginate solution (4, 5); vi) concentration of $CaCl_2$ solution (0.05, 0.2 kg/kg); vii) pH of $CaCl_2$ solution (2); viii) gelation time (15, 60 s); ix) gelation temperature (4, 25 °C). Three independent batches for each alginate solution were prepared.

Table 1
Chemical composition and technical information of sodium alginates.

	Alginate	
	η-low	η-high
Viscosity[a] (mPa·s)	100–200	400–600
pH[a]	6.0–8.0	6.0–8.0
M:G ratio[a]	0.80–1.20	0.80–1.20
Mn (g/mol)	1.58×10^5	2.38×10^5
Rn (nm)	17.39	41.09
F_G[b]	0.42	0.39
F_M[b]	0.58	0.61
F_{GG}[c]	0.25	0.23
F_{MM}[c]	0.42	0.44
$F_{GM,MG}$[c]	0.16	0.16
F_{GGG}[d]	0.22	0.22
F_{MGM4}[d]	0.13	0.16
$F_{GGM,MMG}$[d]	0.03	0.01
M/G (%)	1.41	1.55
$N_{G>1}$	9.7	23.0
F_{MGM}/F_{GGM}	1.41	16.0
Ca (g/kg)	2.1	1.6
Na (g/kg)	97.0	91.6
K (g/kg)	0.16	1.7
NaCl (g/kg)	3.4	4.6
P (g/kg)	0.89	1.2
Mg (mg/kg)	8.0	8.1
Sugar (g/kg)	<5.0	<5.0
Ash (g/kg)	267.2	218.4
Ionic Strength[e]	0.069	0.067

η-low: Protanal GP 3350; η-high: Protanal SF 120 RB.
[a] Technical information obtained from the product datasheet for solutions at 1% (w/w), 20 °C; Mn: molecular weight; Rn: radius of gyration.
[b] Monomeric fractions of alginates.
[c] Diadic fractions of alginates.
[d] G-centered triadic fractions of alginates; $N_{G>1}$: average length of G-blocks; F_{MGM}/F_{GGM}: average length of MG-blocks according to Donati and Paoletti (2009).
[e] Calculated according to Dean (1999) considering a 3% sodium alginate solution.

2.3. Characterization of sodium alginates

2.3.1. Mineral and sugar analysis

Mineral content of sodium alginates were analysed according to the Regulation (CE) No 152/2009. Ash was determined with a gravimetric method. Calcium, sodium, potassium and magnesium were determined by flame atomic absorption spectrometry after sample digestion. Determination of chloride ion was measured by titration according to the Carpentier-Volhard method. Total phosphorus was determined by spectrophotometry. Determination of total sugars was performed following the Luff-Schoorl method. The estimation of the ionic strength of the sodium alginate solutions was calculated according to Dean (1999).

One batch for each alginate solution was analysed. The measurements were done in duplicate. The analytical error of these methods was 3% of the measure except for ash which was 1%.

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

Twenty three mg of each sodium alginate were dissolved in 1 mL of deuterium oxide (99.98% D_2O). Sonication was applied to the solution for 1.5 h, with vigorous shaking every 20–30 min. After the homogenisation, the sample was kept at 65 °C for 1 h in order to achieve a lower viscosity to facilitate its transfer to the tube of the NMR Bruker Avance 600 MHz (Billerica, Massachusetts, USA). 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, 2003; Santi, Coppetta, & Santoro, 2008). Data was processed with Mestrenova v. 8.1.2 software. 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 deconvolution of the peaks. The measurements were done in duplicate.

2.3.3. Asymmetric flow-field flow fractionation (AF4)

Experimental solutions of 1 mg/mL in NaCl 0.1 mol/L of η-low and η-high alginates were obtained and stored to 4 °C prior to analysis.

Experiments were carried out with an AF4 system (AF2000 Focus, PostNova Analytics, Landsberg am Lech, Germany) coupled online to seven-angle laser light scattering (PostNova Analyitics) and differential refractive index detector (DRI, PN3150). System control as well as data collection and treatment were performed using the AF2000 Control software (version 2.0.1.5, PostNova Analytics). The spacer nominal thickness was 350 μm.

The carrier solution was NaCl 0.1 mol/L in milliQ water filtered on a 0.1 μm pore size teflon filter.