P-017	**Gellan microgels obtained from atomization followed by ionotropic gelation**	

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INTRODUCTION AND OBJECTIVE

Micrometer-sized gel particles, the microgels, are of great interest for food, pharmaceutical and cosmetic industries, because they can be used as encapsulation matrix of bioactive compounds or as texture agents. These particles show similar macrogel characteristics, as good mechanical properties, high water content and biocompatibility, associated with additional properties such as increased surface area (Oh 2009).

The use of polysaccharides to produce the microgels allows their incorporation into foods without risk to health, since most of these materials are recognized as safe for use in foods. Gellan gum is an anionic polysaccharide, widely used in the food industry, which shows the ability to form gels at low concentrations in the presence of mono or divalent cations (Sanderson 1990).

Depending on the size and stability of the microgels, their incorporation into the products may cause undesirable changes of sensorial properties or even destabilize the system (Burey 2008). In this work the production of gellan microgels by atomization process followed by ionotropic gelation induced by salt solutions (KCl and $CaCl_2$) was studied, as well as the properties (size distribution and stability) of the obtained microgels.

MATERIALS AND METHODS

Materials

Gellan gum gently supplied by Kelco Biopolymers (San Diego, CA) was used without further purification. The salts (KCl and $CaCl_2$) were of analytical grade.

Preparation and characterization of gellan solutions

The gellan solutions (0.4, 0.6, 0.8, 1 and 1.2% w/w) were prepared by the dispersion of gellan powder in deionized water followed by a heat treatment at 70ºC for 30 min. After that the solutions were cooled to 25ºC using a water bath. The density of gellan solutions were measured in a Digital Density Meter (Anton Paar, Austria). The rheological properties of the solutions were obtained by an up-down-up steps program in a Physica MCR301 Rheometer (Anton Paar, Austria). All measurements were done at 25°C in triplicate.

Phase Diagram

Gellan/$CaCl_2$ and gellan/KCl phase diagrams were constructed in order to establish the appropriate concentration of salts and biopolymer for gel formation.

The gellan solution (0.4, 0.6, 0.8, 1 and 1.2% w/w) was dripped into the salt solutions through a hypodermic needle of 0.8 mm diameter. The collecting distance (10 cm) and the hardening time (30 min) were kept fixed. The drip process was used in order to obtain macroscopic ($d \cong$ 3mm) beads. The beads were subjected to uniaxial compression measurements using a TA-XT Plus Texture Analyser (Stable Micro Systems, UK). The maximum force was obtained by compressing the beads to 80% of their original height at 25°C, using a cross-head speed of 0.5 mm/s.

Microgels production

In order to produce the microgels, gellan solutions (25°C) were extruded from an atomizer nozzle (0.7 mm diameter) into a 1.1% (w/v) $CaCl_2$ or 2.28% (w/v) KCl solution (determined through the phase diagrams). Experiments were done to evaluate the influence of the pressure air and collecting distance in the size of the particles obtained. In this case the gellan concentration was fixed in 1% w/w and only $CaCl_2$ was used. After that the effect of gellan concentration and kind of salt used was evaluated using collecting distance (20 cm), hardening time (30 min), feed flow rate (0.0002 m^3/h) and atomization air pressure fixed (1 bar) fixed. The salt solutions containing the microgels were immediately evaluated by laser diffraction analysis in a Mastersizer 2000 (Malvern, UK). The size distribution and the Sauter Mean Diameter ($D_{3,2}$) were measured. Solutions were also filtered through a sieve with opening of 0.037 mm, and the morphology of the microgels was evaluated by optical microscopy using a Scope A1 microscope (Carl Zeiss, Germany). The microgels were also subjected to stability analysis, evaluated after storage at 10ºC of a suspension containing 10% w/w of particles in distilled water.

RESULTS AND DISCUSSION

Gellan solutions characterization

Table 1 shows the values obtained for density and apparent viscosity of the gellan solutions. All gellan solutions showed non-Newtonian shear thinning behavior, except the 0.4% solution, which showed Newtonian behavior. The increase on gellan concentration led to an increase in both properties. The viscosity was evaluated at the maximum shear rate possible for each solution, in order to being closer the shear rate used in the atomization process ($\sim 10^4\ s^{-1}$).

Table 1 : Gellan solutions properties at 25°C

Gellan (% w/w)	Viscosity (mPa.s)	Density (g/cm³)
0.4	9.51	0.9987
0.6	16.03 (4000 s^{-1})	0.9996
0.8	20.1 (4000 s^{-1})	1.0004
1	25.06 (4000 s^{-1})	1.0012
1.2	29.1 (4000 s^{-1})	1.0024

Phase Diagram

The increase on gellan concentration led to an increase of the maximum force up to 1% w/w gellan gum, but a higher gum concentration (1.2%) led to a decrease of this property (data not shown). Thus it was considered the limit concentration of polysaccharide. From the phase diagram using $CaCl_2$ (Fig. 1) an intermediate salt concentration (1.1% w/v) was chosen for the microgels production. The concentration of KCl was fixed in 2.28% (w/v), which resulted in the same ionic strength (0.3 M) of the 1.1% $CaCl_2$ solution.

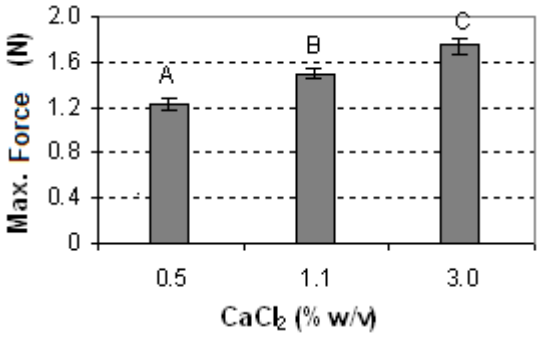

Figure 1 : Maximum force of the beads obtained under drip of 1% w/w gellan solution.

The effect of air pressure on the size of the particles

The effect of the atomization air pressure (1, 1.25, 1.5, 1.75 and 2 bar) on the particles was evaluated. Figure 2 shows the results for the extreme values. It was observed a slight decrease of particle size distribution within the range of pressure studied.

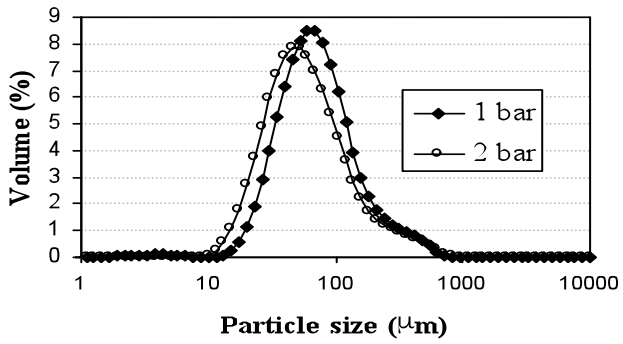

Figure 2 : Effect of atomization air pressure on the gellan/$CaCl_2$ microgel.

The effect of the collecting distance on the size of the particles

The effect of the collecting distance (15, 20, 25, 30 and 35 cm) on the particles properties was evaluated. Above 20 cm an increase of the particle size could be observed and the size distribution showed that the smaller particles tended to disappear. These results can be explained by the possible agglomeration of the particles in the path between the nozzle and the hardening bath.

The effect of gellan concentration on the microgels

Figure 3 shows the effect of the gellan concentration on the microgels obtained using $CaCl_2$-induced gelation. In general, the microgels became more spherical with the increase of gellan concentration, and with the lowest content (0.4% w/w) there was no particle formation, only filamentous structures can be seen (Fig. 3A). The same tendency was observed for the KCl-induced microgels.

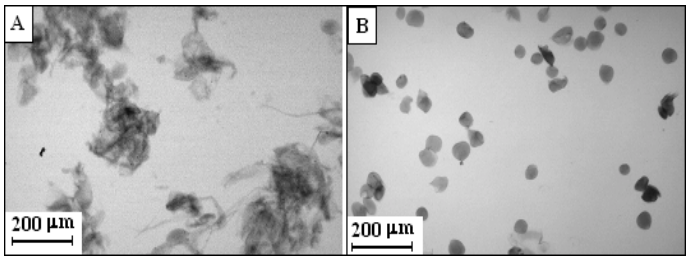

Figure 3 : Micrographs of gellan/$CaCl_2$ microgels with 0.4% w/w (A) and 1% w/w (B) gellan gum.

The great difference between KCl and $CaCl_2$ microgels was their stability in water. The gellan (1% w/w)-$CaCl_2$ particles showed a $D_{3,2}$ of 68 μm, with no significant particle size change even after 15 days of storage. On the other hand, the KCl microgels were less stable and presented more agglomeration of the particles during storage.

CONCLUSIONS

The results showed that the gellan microgels production by atomization process was possible at mild conditions (*i.e.* room temperature and low polysaccharide concentration). Mainly gellan particles induced by $CaCl_2$ was particularly stable in water showing a great potential for use in food products as encapsulation matrix for bioactive compounds.

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