Carbohydrate Polymers 148 (2016) 309–317

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Evaluation of different methods to prepare superabsorbent hydrogels based on deacetylated gellan

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ARTICLE INFO

Article history:
Received 17 December 2015
Received in revised form 4 April 2016
Accepted 6 April 2016
Available online 7 April 2016

Keywords:
Deacetylated gellan
Superabsorbent
pH
Temperature
Swelling degree
Thermal resistance

ABSTRACT

This study stands out for analyzing distinct ways of preparing hydrogels from deacetylated gellan gum that have high swelling capacity and good thermal resistance. We carried out a thorough investigation, applying various combinations of different experimental parameters. Two preparation methods were evaluated, in which the pH was adjusted before or after thermal treatment of the gellan solution, with subsequent addition of the crosslinking agent, to assess the influence of preparation method on the conformation of the gellan chains regarding formation of double helices. The pH range tested varied from acid (2, 3 or 4) to basic (8, 9 or 10). Gellan solution was prepared in different concentrations. Both pure gellan and hydrogel samples were characterized by Fourier-transform infrared spectroscopy and thermogravimetry. Pure gellan was also characterized by atomic absorption spectroscopy. The swelling degree of the hydrogels was analyzed. The results showed that all the hydrogels had high swelling capacity (>400%), so they can be considered superabsorbent materials. Hydrogels prepared with acid pH in general had lower thermal resistance than samples prepared in alkaline pH, regardless of the preparation method. Samples prepared with alkaline pH tended to have initial decomposition temperature similar to that of pure gellan.

1. Introduction

Hydrogels make up a promising class of polymer materials that are able to absorb large quantities of water. They are composed of one or more three-dimensional polymer networks, formed by macromolecular chains linked by covalent bonds (crosslinks) or physical interactions (Aouada, Muniz & Mattoso, 2009; Coutinho et al., 2010; Bortolin, Aouada & Mattoso, 2012). Due to these characteristics, hydrogels present high hydrophilicity and insolubility. The hydrophilicity can be controlled by the nature of the groups present in their chains, such as —OH, —COOH, among others. In turn, the insolubility is directly affected by the entanglement degree (physical interactions or crosslinks) of the chain forming the hydrogels (Aouada et al., 2009). Hydrogels can be synthesized from natural or synthetic materials.

Gellan gum is an anionic polysaccharide whose molecular structure is based on repeated units of (β-1,3 D-glucose, β-1,4 D-glucoronic acid, β-1,3 D-glucose, α-1,4-L-rhamnose) and two acetyl groups, acetate and glycerate, linked to glucose residue adjacent to the glucoronic acid. It is sold in two forms: native and deacetylated form, in the second case where the two acetyl groups have been completely removed (Supplementary material 1). The presence of the acetyl group has a strong influence on the gel's characteristics. The deacetylation of native gellan gum results in the change from soft, elastic and dull gels into firm, hard and shiny gels with high thermal stability (Bajaj, Survase, Saudgar & Singhal, 2007; Matricardi, Cencetti, Ria, Alhaique & Coviello, 2009; Coutinho et al., 2010; Manjanna, Kumar & Shivakumar, 2010; Morris, Nishinari & Rinauto, 2012; Prajapati, Jani, Zala & Khutliwala, 2013; Osmalek, Froelich & Tasarek, 2014). Under suitable conditions, gellan gum can form thermoreversible gels and highly viscous aqueous solu-

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http://dx.doi.org/10.1016/j.carbpol.2016.04.019
0144-8617/

tions. The best known properties of gellan gum are its gelling action, malleability, excellent stability and flexible processing conditions, enabling the production of products with different textures and high efficiency (Bajaj et al., 2007; Morris et al., 2012; Hasheminya & Dehghannya, 2013).

Picone and Cunha (2011) studied the influence of different pH values (3.5, 5.3 and 7.0) on the formation of gels containing deacetylated gellan gum by uniaxial compression measurements and scanning electron microscopy and concluded that all the gels formed were thermoreversible, independent of the pH value. However, the mechanism by which gels form and their mechanical properties are directly related to the pH of the solution.

Norton, Cox and Spyropoulos (2011) investigated the behavior of gels obtained from deacetylated gellan gum in an acid medium by analysis of texture and measurement of Young's modulus. It was observed that the gels' structures depended both on the pH value and the polysaccharide concentration.

Other studies have been published on the preparation of gels from deacetylated gellan gum, but our study stands out for analyzing distinct ways of preparing hydrogels from deacetylated gellan gum that have high swelling capacity and good thermal resistance. We carried out a thorough investigation, applying various combinations of different experimental parameters. All told, we evaluated two methods to prepare hydrogels, with different concentrations of the aqueous gellan solution, absence or presence of $CaCl_2$ as a crosslinking agent, different temperatures and different pH vales of the medium, with adjustment of the pH before or after the heating of the gellan solution.

2. Experimental part

2.1. Materials

The deacetylated gellan gum was kindly supplied by CPKelco Brasil S.A. (Kelcogel F) and was used as received. The crosslinking agent, $CaCl_2$ dihydrate, was acquired from Vetec Química Fina Ltda, with P.A. purity grade, and was used to prepare a solution containing 10 mM Ca^{2+}. The pH was measured using a pHmeter made by Tecnopon, model MPA 210, and it was adjusted by use of solutions of HCl and NaOH 0.1 M, prepared from P.A. reagents purchased from Vetec Química Fina Ltda.

2.2. Preparation of the hydrogels

Two methods of preparing the hydrogels were used, as described below:

2.2.1. Method I—control of pH before heating the gellan solution

In this case, aqueous gellan solutions were prepared at different concentrations (0.25%, 0.5% and 1.0% wt/v). The gellan was dissolved in deionized water under magnetic stirring at 25 °C for 24. The solutions' pH was adjusted by adding different quantities of HCl 0.1 M and NaOH 0.1 M, so that the final pH was either 2, 3 or 4 (acid range) or 8, 9 or 10 (alkaline range). Then the solutions were left at rest for 24 to evaluate the gel formation. If the sample still was liquid (not gelled), it was heated to 90 °C for 30 min, followed by a new 24-h rest period to evaluate gel formation. If the sample still was liquid, $CaCl_2$ (10 mM Ca^{2+}) was added to promote crosslinking. Then the samples were placed in a freezer for 48 and lyophilized for subsequent characterization studies.

2.2.2. Method II – control of pH after heating the gellan solution

The gellan solutions were prepared in the same way as in Method I. However, here the gellan solution was first heated to 60 °C and the pH was controlled at this temperature. Then the temperature was raised to 90 °C and kept there for 30 min. The solution was then cooled to 25 °C and left at rest for 24 h. If the sample remained liquid, $CaCl_2$ (10 mM Ca^{2+}) was added to promote crosslinking. Next, the samples were placed in a freezer for 48 h and lyophilized for subsequent characterization studies.

2.3. Characterization of the samples

The pure gellan gum was characterized regarding metals content by atomic absorption spectroscopy, using a Perkin Elmer Analyst 300 spectrometer.

The chemical composition of the hydrogel samples was characterized by Fourier-transform infrared spectroscopy (FTIR) using a Perkin-Elmer Spectrum One spectrometer, with a germanium crystal ATR accessory. The spectrum was varied from 4000 to 400 cm^{-1} with resolution of 16 cm^{-1}.

The thermal stability was evaluated with a TA Instruments Q50 V6.4 Build 193 thermogravimetric analyzer (TGA). About 10 mg of sample was placed in a platinum capsule, which was then heated in a nitrogen atmosphere with a flow of 100 mL/min., from 10 °C to 600 °C, at heating rate of 20 °C/min. The starting temperature (T_{onset}) of the principal thermal degradation stage of the gellan chains was obtained from the intersection between the baseline and the tangent of the inflection point of the TG curve.

The hydrophilic properties of the hydrogels were studied by measuring the swelling degree (Q) in function of time in a specific swelling medium (deionized water). The average mass of the dry hydrogel samples used in this study was approximately 150 mg. For determination of the Q values, the dry hydrogels were weighed on an analytic balance and then placed in 30 mL of water. After different time intervals ("t"), the samples were removed from the water and carefully dried to remove any excess water on the surface, after which they were weighed again. The Q values of the different hydrogels were calculated by using Eq. (1) (Aouada et al., 2009):

$$Q = \frac{M_2 - M_1}{M_1} \times 100 \quad (1)$$

where M_2 is the mass of the hydrogel after swelling for time "t" and M_1 is the mass of the dry hydrogel.

3. Results and discussion

The pure gellan gum sample was characterized regarding the content of metals by atomic absorption spectroscopy. The results obtained were: K^+: 2.6%, Ca^{+2}: 2.0% and Mg^{+2}: 0.44%. The aim of this characterization was to evaluate the concentrations of monovalent and divalent cations present in the gum.

3.1. Fourier-transform infrared spectroscopy (FTIR) of the pure gellan and hydrogels

The FTIR spectrum of pure gellan is presented in Fig. 1. It contains the main bands of deacetylated gellan gum: an O—H axial stretching band of the glucopyranose unit at 3313 cm^{-1}; bands at 1600 and 1425 cm^{-1}, attributed to the asymmetric and symmetric axial deformations of the carboxyl groups, a band near 2920 cm^{-1}, related to the axial vibration of the $-CH_2$ groups, a band at 1023 cm^{-1}, related to the angular deformation of the C—O bond, and a band near 887 cm^{-1}, attributed to the angular vibration of the C—H bond (Smith, 1999; Agnihotri, Jawalkar & Aminabhavi, 2006; Pandey, Verma, Yadav & Behari, 2014; Novac, Lisa, Profire, Tuchilus & Popa, 2014; Karthika & Vishalakshi, 2014; Verma, Pandey & Behari, 2015).