Carbohydrate Polymers 174 (2017) 456–463

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

The effect of temperature on the colligative properties of food-grade konjac gum in water solutions

Joanna Kruk, Kacper Kaczmarczyk, Anna Ptaszek*, Urszula Goik, Paweł Ptaszek

Faculty of Food Technology, ul. Balicka 122, 30-149 Kraków, Poland

ARTICLE INFO

Article history:
Received 17 March 2017
Received in revised form 27 June 2017
Accepted 29 June 2017
Available online 30 June 2017

Keywords:
Konjac gum
Colligative properties
Osmotic pressure
Light scattering
Relaxation time
Intrinsic viscosity

ABSTRACT

This research paper presents the results of tests on the colligative properties of konjac gum chains in water solutions. For this purpose, the measurements of osmotic pressure and intrinsic viscosity of aqueous solutions, in the function of konjac gum concentration and temperature were carried out. The applied methods allowed for the determination of the second osmotic virial coefficients B_2, which raised with the increase of temperature. It indicate that increase of temperature causes higher affinity of polysaccharide's chains to water. It was determined, that the osmotic average molecular mass of the konjac gum in non-purified solutions increases with temperature (1.07×10^5–3.80×10^5 g × mol^{-1}). Values of the reduced viscosity linearly increased in range 18–29 dL × g for all temperatures. Received values of the Huggins constant (0.81–1.72) lead that water is poor solvent for konjac gum. The theta (θ) conditions were extrapolated for non-purified solutions – 325 K (52 °C), and interpolated for purified solutions – 307 K (34 °C). Based on the results of tests using the dynamic light scattering, the values of two main relaxation times (fast – 0.4–1.8 ms and slow components – 4300–5500 ms) were determined (the Kohlrausch-Williams-Watts). The obtained autocorrelation functions were characteristic for sol type systems or these which indicate a gel-like structure.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Konjac, a plant from the genus *Amorphophallus,* is a perennial plant native to subtropical highlands, mainly of Southeast Asia (Zhang, Xie, & Gan, 2005; Li & Xie, 2006). The main components of the konjac corm are carbohydrates, most notably konjac glucomannan. The concentration levels of this polysaccharide differ depending on the variety (Chua, Baldwin, Hocking, & Chan, 2010). The konjac glucomannan (KGM) is a neutral heteropolysaccharide, with the main chain composed of D-mannose and D-glucose units, linked by a β-(1 → 4)-glycosidic bond (Katsuraya, 2003). These units occur in the molar ratio of 1.6:1.0, respectively. In the main chain the acetyl groups, 1 for 19 glucose units, are located at carbon C-6, and the substitution level is at 5–10% (Tatirat, Charoenrein, & Kerr, 2012; Ratcliffe, Williams, English, & Meadows, 2013). The presence of branching and acetyl groups affects the solubility of KGM (Ratcliffe et al., 2013). An increased deacetylation of the KGM chain causes a decreased solubility of the KGM, which is a result of reduced formation of intra- and inter-molecular hydrogen bonds between KGM's chains (Chen, Li, & Li, 2011). This polysaccharide exhibits very high ability to absorb water, around 100 g of water/1 g KGM. The polymerisation of KGM, using acrylic acid and acrylamide or kaolin, leads to the creation of superabsorbents, with absorption capabilities significantly increased compared to the originating polysaccharide (Li, Ji, Xia, & Li, 2012).

Konjac glucomannan is allowed for use in the food industry in Europe and USA (Tester & Al-Ghazzewi, 2013). It is used as a food additive, where it acts as a thickening and stabilising agent, and is also used as dietary fibre. It is also utilised in the production of low- calorie foods, such as solid beverages, noodles, tofu, jellies and snacks, as well as dietary supplements (Zhao et al., 2015).

The physico-chemical characteristics of the KGM solutions haven't been fully described, mainly due to the difficulty in obtaining easily soluble and well-purified samples (Yoshimura & Nishinari, 1999). The research on this subject covered the production of KGM samples, by means of extraction from konjac flour (Tatirat & Charoenrein, 2011; Chua et al., 2012). The studies of the physico-chemical characteristics of native KGM solutions include the determining of the weight average molecular masses using methods such as gel permeation chromatography (GPC), dynamic light scattering (DLS), as well as intrinsic viscosity (Kishida, Okimasu, & Kamata, 1978; Nishinari, Williams, & Phillips, 1992; Qi, Li, & Zong, 2003; Ratcliffe, Williams, Viebke, & Meadows, 2005). Additionally, the values of critical overlap concentration c^* for KGM solutions have also been described. For the extracts

* Corresponding author.
E-mail addresses: a.ptaszek@ur.krakow.pl, anna.w.ptaszek@gmail.com (A. Ptaszek).

http://dx.doi.org/10.1016/j.carbpol.2017.06.116
0144-8617/© 2017 Elsevier Ltd. All rights reserved.

of konjac flour the concentration was 0.29 g × dL^{-1} (Murakami & Motozato, 1992), while for commercial KGM samples it was 0.08 g × dL^{-1} (Ratcliffe et al., 2005).

The use of light scattering methods in the study of molecular parameters is based on the interpretation of results of measurements carried out in a wide range of biopolymer concentrations, and the angles in which the intensity of light scattered by the biopolymer coils is defined. The test results allow for the determination of the weight average M_w, number average M_n molecular mass, virial coefficients (B_2), and the gyration radius R_g, and hydrodynamic radius R_h. The literature data indicates that the majority of results obtained for the konjac gum solutions fall outside the scope of the linear correlation between the intensity of light scattered and the value of the scattering vector. This is due to the nature of interactions between the chains and the water solvent. The study by Ratcliffe et al. (2005) presented a comparison of the values of M_w, M_n, and R_g, estimated with the use of non-linear models. Li & Xie (2006) researched the geometry of the konjac gum chains in a water solution with an initial concentration of 1% (w/w), with the addition of 0.2 mol × L^{-1} NaCl. Their studies also covered the influence of average molecular mass on the conformational properties, and to that effect the konjac gum sample was subjected to controlled hydrolysis. The authors interpreted the results using linear extrapolation in the Zimm plot. They estimated the values of mass average molecular mass (native KGM 1.036×10^5 g × mol^{-1}), the second virial coefficient, and the radius of gyration R_g (105 nm) from the linear regression. The determined value $A_2 = -1.587 \times 10^{-3}$ mol × mL × g^{-2} is negative, and, as the authors suggested, requires further studies. The authors observed, that the molecular chains were extending, semi-flexible and a little rigid (Li & Xie, 2006). The biopolymer concentration used in the study was close to overlap c^*, which explains the complex behaviour of chains in the solution. Jian, Siu, and Wu (2015), in turn, focused on the influence of pH on the conformational properties of the konjac gum chains. The solution's pH was controlled using an addition of NaOH or HCl (pH = 4, 7, 9, 10), and the authors presented test results for two concentrations of KGM (0.02 g × dL^{-1} and 0.05 g × dL^{-1}, c^* = 0.08 g × dL^{-1}). In the case of the g × dL^{-1} solution, the pH increase resulted in a rise of the average molecular mass from 1.318×10^6 g × mol^{-1} to 2.035×10^6 g × mol^{-1} and a slight increase of R_g (123.6–129.9 nm). For the solution of 0.05 g × dL^{-1} the values of B_2 have been determined to be positive, apart from the value of B_2 for the pH = 10. The authors concluded that KGM remained in random coil conformation in all pH conditions.

It follows from the above analysis, that the interpretation of measurement results obtained with the use of DLS/SLS remains open, and could be supplemented by the analysis of classic colligative properties, represented by the osmotic pressure. In research literature, there is an apparent lack of studies concerning osmotic characteristics of the KGM solutions. Moreover, there aren't many reports on the use of DLS in the studies of hydrodynamic properties of these solutions in the wide range of temperatures and concentrations. The results of osmotic, as well as hydrodynamic studies, can provide valuable data on the properties of KGM chains in water solutions.

The aim of this work was to evaluate the impact of temperature on interactions between konjac gum chains and solvent in dilute aqueous solutions using colligative and hydrodynamic methods.

2. Materials and methods

2.1. Materials

In this study, a commercial sample of konjac gum was used as research material (AGRO-SMAK, Dębe Kolonia, Poland).

2.2. Protein content analysis

The protein content in the food-grade konjac gum was determined by the Kjeldahl method, was (1.02 ± 0.01)% (ISO 1871:2009).

2.3. Solutions preparation

Aqueous solutions of the konjac gum were prepared in concentrations of 0.0025–0.0200 g × dL^{-1}. Such range of concentration was chosen because authors want to analyse interactions in dilute solutions (below overlap concentration c^*). The samples were prepared in distilled and degassed water, and then shaken at 40 °C for 4 h. After this time, to prevent the development of microorganisms, a solution of 0.01% (w/w) sodium azide was added to the samples. The prepared solutions were left for 24 h. After that time, the solutions were centrifuged (5000 rpm (2683 × g), time 10 min, temp. 23 °C), in order to separate the non-soluble fractions of the research material. The prepared solutions were then used to study the colligative properties, intrinsic viscosity, and DLS measurements (day-1). Additionally, after subsequent 24 (day-2) and 48 h (day-4) storage of the solutions in 23 °C temperature, they were again used in DLS and osmotic measurements.

2.4. Purification of konjac gum solutions (deproteinization)

The konjac gum solutions were deproteinised with the use of the Carrez I and Carrez II solutions (Goycoolea & Chronakis, 1998; Borromei et al., 2009; Culhaoglu, Zheng, Méchin, & Baumberger, 2011). For this purpose, samples with concentration levels 10 times higher than unpurified solutions were prepared, according to the procedure described above. After 24 h, and centrifuging of the undissolved fractions, the following methodology was applied: 25 mL of the solution and 25 mL of distilled water were measured into a 250 mL volumetric flask, then 2.5 mL of the Carrez I solution was added, the flask contents were mixed and set aside for 5 min. After that time 2 mL of the Carrez II solution were mixed in, and filled up with distilled water to the volume of 250 mL. After 15 min, the solution was filtered through a fluted filter into a dry container.

2.5. Molecular characteristic of the konjac gum – determination of the molecular mass distribution

The measurements of the distribution of molecular masses were performed by means of gel permeation chromatography (GPC), using a system of two columns: Ultrahydrogel-2000 and Ultrahydrogel-500 (Waters, USA), connected in a series with an RI detector (Knauer, Germany). A solution of 0.1 mol × L^{-1} $NaNO_3$ and 0.02% NaN_3 in water was applied as an eluent. Flow rate was set to 0.6 mL × min^{-1} and a sample volume of 100 mL was injected. The sample concentration was ca. 5 mg × mL^{-1}. Calibration was performed using pullulan standards (Shodex, Japan) (Lukasiewicz, Bednarz, & Ptaszek, 2011). The following values were obtained for the konjac gum chains: weighted molecular mass $M_w = 9.9 \times 10^5$ g × mol^{-1}, number molecular mass $M_n = 6.2 \times 10^5$ g × mol^{-1}, polydispersity 1.6.

2.6. Measurements of osmotic pressure (π)

All the prepared solutions were subjected to the measurements of osmotic pressure at temperatures ranging from 303 K (30 °C) to 313 K (40 °C), at temperature increase intervals of 2 K. The temperature control accuracy for the osmotic pressure was 0.1 K. The measurements were carried out using a membrane osmometer OSMOMAT 090 (Gonotec, Berlin, Germany) utilising a membrane with cut-off value of 10 000 g × mol^{-1}. For all tested samples the measurements were done in four repetitions. The obtained results

Download English Version:

https://daneshyari.com/en/article/5156830

Download Persian Version:

https://daneshyari.com/article/5156830

Daneshyari.com