Carbohydrate Polymers 142 (2016) 293–299

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Rheological properties and formation mechanism of DC electric fields induced konjac glucomannan-tungsten gels

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ARTICLE INFO

Article history:
Received 2 September 2015
Received in revised form 6 January 2016
Accepted 27 January 2016
Available online 30 January 2016

Keywords:
Konjac glucomannan
Electrogel
Rheological properties
Formation mechanism
DC electric fields

ABSTRACT

Konjac glucomannan-tungsten (KGM-T) hydrogel of electrochemical reversibility was successfully produced under DC electric fields in the presence of sodium tungstate. The structure and the effects of sodium tungstate concentration, KGM concentration, voltage and electric processing time on the rheological properties of the gels were investigated. pH experiments showed that KGM sol containing $Na_2WO_4{\cdot}2H_2O$ in the vicinity of the positive electrode became acidic and the negative electrode basic after the application of DC electric fields. Under acid conditions, WO_4^{2-} ions transformed into isopoly-tungstic acid ions. FTIR and Raman studies indicated that isopoly-tungstic acid ions absorbed on KGM molecular chain and cross-linked with —OH groups at C-6 position on sugar units of KGM. Frequency sweep data showed with increasing sodium tungstate concentration, voltage, and electric processing time, the viscoelastic moduli, i.e., the storage and the loss moduli of the gel increased, whereas an increase in KGM concentration led to a decrease in gel viscoelastic moduli. The temperature sweep measurements indicated the obtained gel exhibited high thermal stability. Finally, the mechanism of gel formation was proposed. Our work may pave the way to use DC electric fields for the design and development of KGM gels as well as polysaccharide gels.

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1. Introduction

Gels are one of the most common forms of food, endowing foods with unique structure and mouthfeel. Polysaccharides have become attractive as important food materials due to their special gel performance that plays a major role in improving food texture (Roman-Leshkov, Barrett, Liu, & Dumesic, 2007). However, polysaccharide gels are found to be metastable, particularly thermally unstable. Therefore, methods to improve the thermal stability of polysaccharide gels have become one of the key scientific issues in food industry. The development of thermal irreversible polysaccharide gels is the most effective way to solve this problem. However, there is still a lack of holistic and deep understanding of such type of gels.

Konjac glucomannan (KGM) is a neutral polysaccharide extracted from the tuber of *Amorphophallus konjac C.* plant, which has been known for its excellent gelling properties and is widely used in food and medical industries (Abhyankar, Mulvihill, Chaurin, & Auty, 2011; Liu et al., 2012). There are mainly three different types of konjac glucomannan gels—thermally irreversible gels prepared in the presence of an alkaline coagulant (Du, Li, Chen, & Li, 2012), thermally reversible gels prepared with boron (Gao, Guo, Wu, & Wang, 2008; Jian, Zeng, Xiong, & Pang, 2011; Ratcliffe, Williams, English, & Meadows, 2013), and synergistic reversible gels prepared from gums such as xanthan, carrageenan (Fan, Wang, Liu, & He, 2008; Sun, Ye, & Pang, 2009), etc. However, they all have limitations. For example, more than 90% of konjac glucomannan gels, prepared in the presence of an alkaline coagulant, exhibit multiple issues, such as high syneresis rate, poor taste and color uptake, strong alkaline taste, etc. (Herranz, Tovar, Solo-de-Zaldivar, & Javier Borderias, 2012), causing billions of dollars loss each year. In order to get rid of the strong alkaline taste, gels are washed with water or acid repeatedly, which affects product quality. In addition, alkaline gel products are preserved in alkaline solutions, causing inconvenience in transportation and storage. It also results in unnecessary consumption of manpower and materials. For KGM-borax gels, boron ions that are toxic and non-food grade seems to greatly limit their

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http://dx.doi.org/10.1016/j.carbpol.2016.01.060
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practical applications. While, synergistic gels, prepared with other polysaccharides, undergo syneresis more easily and exhibit poor thermal stability, which is a severe challenge for traditional foods needed to be steamed or cooked. Owing to these limitations, synergistic gels are mainly used for jelly processing and products that require shaping. In conclusion, new alternatives or techniques for preparing KGM gels is one of the important ways to overcome these limitations.

The environmental stimuli, such as pH, temperature, light, chemicals, electrical and magnetic field, etc., may affect the network structure and permeation properties of gel (Filipcsei, Fehér, & Zrínyi, 2000). Among these factors, electric field is often utilized due to its easy manipulation and control. However, such studies mainly focus on the stimulation response of smart gels under electric field, rather than the formation of gels induced by electric field. The goal of using electric field to induce biopolymer self-assembly is to design and control structures of substances that are used in food, biology, and pharmaceuticals fields, etc. (Kojic et al., 2012). Recently an electrically mediated hydrogel (e-gel) from silk fibroin has been reported (Leisk, Lo, Yucel, Lu, & Kaplan, 2010; Lu et al., 2011; Yucel, Kojic, Leisk, Lo, & Kaplan, 2010).

To the best of our knowledge, there are no studies available on electric field induced self-assembly of polysaccharides till date. KGM is a type of natural polysaccharide containing readily dissociated acetyl groups and glycosidic bonds that are sensitive to electric field (Yao et al., 2011). Furthermore, the hydroxyl-rich structure can interact with many metal ions (Wang, Jiang, Lin, Zhong, & Pang, 2014; Wang et al., 2013). Thus, we can speculate that the structure and conformation of KGM may change under the condition of electric field and metal ions, resulting in the change of rheological and gelling properties. So, the aim of this study was to use DC electric field to induce KGM self-assemble into three dimensional gel network and investigate the rheological properties and possible formation mechanism of the gel. This work provides a theoretical understanding as well as a new method for the preparation of new types of KGM gels.

2. Materials and methods

2.1. Materials

KGM with 91.4% glucomannan content was purchased from San Ai Konjac Food Co. (Zhaotong, China) and used without further purification. Sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) was of analytical grade and purchased from Cuilin Chemical Industry Co. (Zhangzhou, China).

2.2. Preparation of konjac glucomannan-tungsten (KGM-T) gels under DC electric fields

KGM powder was precisely weighed and dispersed in distilled water at room temperature to prepare 0.3–1.1% KGM sol under magnetic stirring for 1 h, and the sols were stored overnight at 4 °C to ensure complete hydration, swelling, and dispersion. Subsequently, 0.1–0.5% sodium tungstate was added into the sols. The carbon electrodes were immersed in the mixture and 10–40 V d.c. was applied to a pair of conductive electrodes for 3–15 min. The distance between two electrodes was about 3.5 cm. A visible gel formed at the positive electrode within seconds of the application of the voltage.

2.3. FTIR spectroscopy

KGM-T gels were taken down from the carbon electrode, and freeze dried. The Fourier transform infrared (FTIR) spectra were measured on a Nicolet iS10 FTIR spectrometer (Nicolet iS10, USA) in the range of 400–4000 cm^{-1}. The samples were mixed with AR-grade KBr at a 1:100 mass ratio and pressed into pellets. The measurements were conducted at a resolution of 0.4 cm^{-1} with 64 scans per sample, referenced against a blank KBr pellet.

2.4. Raman spectroscopy

Raman spectra were recorded with a Labram Aramis confocal microprobe analyzer (Horiba Jobin-Yvon, FRA) equipped with an Olympus microscope and a CCD cooled. We used the 633 nm laser line (0.7 mW power) with a spectrum resolution of 1 cm^{-1}.

2.5. Rheological measurements

Oscillatory shear measurements were done with an advanced rheological expansion system (ARES-LS, Rheometric Scientific) using a plate – plate geometry (diameter 25 mm, gap 1 mm). The temperature was controlled by a Peltier system and the geometry was covered with paraffin oil to prevent water evaporation. The linear viscoelastic region (LVR) for gel samples was determined by performing an amplitude sweep measurements (0.01–10%) at constant frequency (1 Hz) and 25 °C. Frequency sweep tests at a constant strain in the LVE region were carried out to determine the viscoelastic nature of KGM-T gel. In this test a strain of 0.1% was applied. Under this strain limit, the macromolecular structure will not be destroyed by the measurements. The mechanical spectra were characterized by values of G', G''(Pa) as a function of frequency in the range of 0.1–100 rad/s and 25 °C. The storage modulus (G') can be used as a measure of the elastic component of the sample and similarly, the loss modulus (G'') – the viscous component of the sample. The temperature sweep measurements were performed at the constant strain of 0.1%, which was well within the linear viscoelastic region, while the frequency was fixed at 1.0 Hz. Temperature increased from 20 °C to 80 °C (heating), using a rate of 5 °C/min.

3. Results and discussion

3.1. Preparation of KGM-T gel under DC electric fields

While using DC on a certain volume of 0.5% KGM sol, it was noticed that bubbles produced on the electrodes due to the production of H^+ and OH^- during water electrolysis, releasing hydrogen and oxygen gases on the respective electrodes. The gel formation did not occur even with an electric treatment of 45 min. However, a white gel produced at the positive electrode when DC was utilized to process 0.5% KGM sol containing a certain amount of sodium tungstate. And heat released during electric processing.

A series of control experiments have been done to explore the possible mechanism of KGM electro-gel formation. In detail, 0.5% KGM containing a certain amount of sodium tungstate was exposed to 20–60 °C water bath or constant incubator, yet no gel was observed, which can exclude the possibility that gel was induced by temperature. To discuss the effect of pH on the gel formation, 0.1% HCl or NaOH were titrated into 0.5% KGM sol containing sodium tungstate to adjust the pH to be around 4.0–12.0, but no gel was observed, which indicated that H^+ or OH^- produced by water electrolysis were not the cause for gel formation. In addition, to further discuss the effect of ion species on the gel formation, we also used DC for processing 0.5% KGM sol containing NaCl or KCl, similarly no gel was observed.

Combining with the fact that gels formed at the positive electrode, it was deduced that WO_4^{2-} ions promoted KGM gel formation under a DC electric field. Furthermore, we also found that if the electrode polarity is reversed and low voltage reapplied,

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