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Gelation and structural characteristics of deacetylated salep glucomannan

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ABSTRACT

Controlled deacetylation of salep glucomannan (SGM) was performed in this study for the first time. SGM, with different degrees of deacetylation (DD), were prepared with the control sample. The rheological properties of SGM were affected by the deacetylation process. Deacetylated samples showed lower apparent viscosities and pseudoplastic characteristics. The gelation of SGM occurred at 90 and 100% DD for 0.75% and 1% SGM concentrations, and increasing the concentration from 0.5% to 1% increased the gelation kinetics of the samples. The whiteness index and strength of salep gel increased as the DD and concentration increased. The remarkable decrease in absorption bands at approximately 1736 cm^{-1} with deacetylation was detected with an FTIR experiment. The SEM images showed that deacetylation resulted in a smooth surface. Removing acetyl groups with the aid of alkali weakened the solubility but improved the thermal stability of SGM, which was determined with DSC and TGA experiments.

1. Introduction

Salep glucomannan is found in the tuber of the *Orchidaceae* family. The structure of glucomannan consists of a linear backbone connected with β-(1 → 4) glycosidic bonds, which are composed of glucose and mannose units. Glucomannan is the main constituent present in the tubers. The high molecular weight and water-soluble neutral characteristics made this polysaccharide useful for different applications, such as in traditional beverages and as a stabilizer for ice cream, drinks and medicines (Du, Li, Chen, & Li, 2012; Farhoosh & Riazi, 2007; Kurt & Kahyaoglu, 2014; Kurt, Cengiz, & Kahyaoglu, 2016).

The acetyl group contents of salep glucomannan were not determined previously. However, the deacetylation of konjac glucomannan (KGM) was extensively studied in food processing with regard to the gelation and water solubility of differently deacetylated KGM (Gao & Nishinari, 2004a, 2004b; Herranz, Tovar, Solo-de-Zaldivar, & Borderias, 2012; Huang, Takahashi, Kobayashi, Kawase, & Nishinari, 2002; Li et al., 2014; Luo, He, & Lin, 2013; Solo-de-Zaldívar, Tovar, Borderías, & Herranz, 2014; H.; Zhang et al., 2001). KGM includes acetyl groups in the glucomannan backbone as attached to the saccharide units, which are scattered randomly along the molecule with an occurrence of approximately 1 per 19 unit of sugar residue at a C-6 position (Du et al., 2012). Acetyl group contents were reported in KGM with varied range of 1.1%–25% (Campestrini, Silveira, Duarte, Koop, & Noseda, 2013) and 5–10% (Gao & Nishinari, 2004a), which can be attributed to the different type, source, period and climatic conditions.

Before the deacetylation, the first step should be purification of glucomannan from the salep because the tubers also contain starch (36.31%); protein (4.60%); and ash (2.07%) (Kurt & Kahyaoglu, 2015), which are considered impurities. We increased the glucomannan content of salep powder from 56% to 90–95%, which is the accepted limit for referring to a substance as purified (Chua et al., 2012). While we were studying the effect of pH on the rheological properties of purified salep, we observed that the solution changed from a sol to gel state at pH 9 due to the alkali effect, which is the well-known method of removing the acetyl group. The gelation of konjac glucomannan in the range of pH 9–10 was also reported previously (Herranz, Tovar, et al., 2012). The deacetylated KGM can form a thermoirreversible gel (Li et al., 2014). Removing acetyl groups with the aid of alkalis causes the aggregation of

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glucomannan chains through linkages such as hydrogen bonding and hydrophobic interaction (Du et al., 2012; Nishinari & Zhang, 2004). Therefore, we want to determine the effect of deacetylation on salep.

In addition to the first attempt to remove the acetyl group from SGM, we also applied a controlled deacetylation process to generate samples. It is widely accepted that the presence of acetyl ensures the water solubility of glucomannan. The solubility of glucomannan was reduced with deacetylation. It was very difficult to dissolve deacetylated KGM in water due to the interaction between glucomannan chains. Therefore, the researcher suggested different solvents for the dissolution of deacetylated KGM, such as urea and thiocyanate, to observe their characteristics (Wang et al., 2014). However, in this study, deacetylation was conducted on glucomannan, which (i) dissolved in water (homogenous systems) and (ii) dispersed in an ethanol-water system (heterogenous system) by using NaOH. In the first condition, the gel behaviour of salep was determined, and in the other method, characterization studies were applied to dried ethanol-water system products.

The objective of this study was to examine the influence of deacetylation on the gelation behaviour on the deacetylation degree and concentration of SGM in addition to the effect on its structural and thermal properties. This study may be useful for fundamental research and the industrial application of SGM.

2. Materials and methods

The native salep powders were purchased from a supplier in Kastamonu. The glucomannan of salep was purified by mixing the sample with distilled water at room temperature to extract the glucomannan, followed by centrifugation to remove the insoluble materials. The glucomannan was then precipitated with ethanol. The M_w and PDI values of purified glucomannan were determined to be 1.03×10^6 g/mol and 1.78, respectively, via high performance size-exclusion chromatography. Dried and milled SGM was used for the deacetylation process. All chemicals used in this study were of analytical grade. The ethanol and sodium hydroxide were purchased from Sigma Chemical Co. (St. Louis, MO, USA).

2.1. Preparation of differently deacetylated salep glucomannan solutions

The degree of acetylation of the glucomannan backbone was determined to be 2.2% by using the reported back-titration method (Xiao et al., 2015). The solutions included glucomannan at different concentrations with varied degrees of deacetylation using sodium hydroxide. The solutions were prepared using the following equation (Liu, Luo, & Lin, 2010):

$$DD\ (\%) = \frac{W_2 \times 43}{40 \times W_1 \times 0.022} \times 100 \quad (1)$$

where W_1 and W_2 were the weight of SGM and NaOH in g, respectively. SGM was dissolved in distilled water at an ambient temperature. The addition of NaOH, which was determined with Eq. (1), was done at 65 °C by mixing for 15 min. A small amount of the sample was used for rheological measurements.

2.1.1. Rheological properties of solutions

The rheological properties of samples were determined by using a rheometer (HAAKE Mars III; Thermo Scientific, Germany) that was equipped with a Peltier heating system with a cone and plate configuration (diameter: 35 mm, cone angle: 2°, gap size: 0.150 mm).

One percent SGM solutions were prepared with different degrees of acetylation (DD): 0%, 40%, 80%, 90% and 100%. The samples were designated as 0DD, 40DD, 80DD, 90DD and 100DD. The rheological analysis was applied in two groups regardless of the occurrence of gelation following storage at 4 °C overnight. Laboratory experiments revealed that the samples of 90DD and 100DD exhibited a gel structure after storage. Therefore, these samples were evaluated to determine its gel properties, which were listed as the followed steps (2.1.2–2.1.4). The SGM solutions (1%) that could not ensure gel formation (0DD, 40DD and 80DD) were exposed to steady flow and frequency sweep tests.

Samples were sheared continuously at a rate ranging from 0 to 100 s^{-1} for 3 min at 4 °C to fit the data to the Ostwald-de Waele model (Eq. (2)):

$$\tau = K \cdot \dot{\gamma}^n \quad (2)$$

whereτ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency coefficient ($Pa.s^n$), and n is the flow behaviour index (dimensionless).

The stress sweep measurements in the stress control were carried out in the range of 0.01–50 Pa at 4 °C and at a 1 Hz frequency to determine the linear viscoelastic range (LVR). A frequency sweep test was performed at 0.1 Pa (within the LVR) over a frequency range of 0.1–10 Hz. The storage (G′) and loss (G″) moduli values at the crossover point were determined at 4 °C.

2.1.2. Determination of gelation temperature and time

The temperature sweep measurements were carried out at a constant stress and frequency of 0.1 Pa and 1 Hz, respectively, over a temperature range of 25–0 °C. To observe the effects of concentration on gelation properties of 100 DD glucomannan, the solutions were prepared at 0.5%, 0.75% and 1.00% SGM concentrations.

2.1.3. Determination of gel colour

The SGM gel samples were subjected to colour measurement using a Colorflex, EZ (Hunter associates laboratory, USA). Before use, the colorimeter was standardized using a white calibration plate. The L*-value (lightness), a*-value (redness/greenness) and b*-values (yellowness/blueness) were determined to calculate the whiteness index (WI) of the salep gel as follows (T. Zhang, Xue, Li, Wang, & Xue, 2015):

$$WI = 100 - \sqrt{(100 - L^*)^2 + (a^*)^2 + (b^*)^2} \quad (3)$$

2.1.4. Determination of gel strength

A texture analysis was carried out using Texture Analyzer (TA-XT2 Stable Micro Systems Co., Ltd., Surrey, UK) to determine the gel strength of the samples. For each sample, three measurements with two replicates were performed using a cylindrical probe (5 mm diameter) attached to a 30 kg load cell. The penetration depth at the geometrical centre of the samples was 10 mm, and the penetration speed was set at 1.0 mm s^{-1}. Differently deacetylated glucomannan solutions were stored in containers (35 mm diameter and 20 mm height) to obtain gel at +4 °C for 24 h. The gel strength expressed as stress was calculated as follows:

$$\sigma = \frac{F}{\pi \times r^2} \quad (4)$$

where σ, F and r are the stress (kN/m^2), the maximum force (N) and the radius of the cylindrical probe (m), respectively.