Food Hydrocolloids 35 (2014) 59–68

Contents lists available at SciVerse ScienceDirect

Food Hydrocolloids

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

Effect of deacetylation on the glucomannan gelation process for making restructured seafood products

B. Solo-de-Zaldívar [a,*], C.A. Tovar [b], A.J. Borderías [a], B. Herranz [a]

[a] Department of Products, Instituto de Ciencia y Tecnología de los Alimentos y Nutrición (ICTAN-CSIC), c/José Antonio Nováis 10, 28040 Madrid, Spain
[b] Department of Applied Physics, Faculty of Sciences, University of Vigo, As Lagoas, 32004 Ourense, Spain

ARTICLE INFO

Article history:
Received 18 January 2013
Accepted 8 April 2013

Keywords:
FT-IR
Deacetylation ratio
Restructured seafood products
Glucomannan gels

ABSTRACT

This paper focuses on the relationship between network structure and physicochemical and rheological properties of aqueous glucomannan dispersions (AGD) as a function of pH, to establish optimal conditions of glucomannan gelation for making restructured seafood products. Various lots of AGD were prepared from 3% (L1) and 5% (L2) konjac glucomannan adding different amounts (0.5–5%) of 0.6 N KOH to obtain samples with successively increasing degrees of alkalinity, from pH = 8.9 to = 11.9 (samples L1.1–L1.6 for 3% AGD) and from pH = 7 to 11.4 (samples L2.1–L2.6 for 5% AGD). The spectra of the different AGDs were obtained by Fourier Transform Infrared spectroscopy (FT-IR) to quantify the deacetylation ratio, whose effect on the physicochemical, mechanical (puncture), viscoelastic (at both small and large time scales) and structural characteristics (scanning electron microscopy (SEM)) was analysed. A linear dependence was found between the relative area of acetyl bands of AGD and pH, showing a discontinuous region in the function or gap zone between pHs 9.3 (L1.2) and 9.8 (L1.3) for 3% AGD and between 9.2 (L2.3) and 10.7 (L2.4) for 5% AGD. Samples before the gap zone (L1.2 and L2.3) were gels of varying degrees of weakness, becoming strong gels thereafter. The gelation conditions were best at pH ~ 10.7 for both 3 and 5% AGDs, corresponding to high and moderate deacetylation ratio, respectively. The resulting gels possessed elastic, cohesive and time-stable networks and thus formed basic structures able to contain several ingredients for making restructured seafood products. The SEM photographs corroborated the physicochemical and rheological characteristics.

1. Introduction

Restructured seafood products offer a means of using muscle by-products and developing new products that have different textures and can also contain functional ingredients. These structures are usually formed by thermostable protein gelation, but such gelation is not possible when the muscle has been previously processed and the protein is degraded. In previous works (Herranz, Borderias, Solo-de-Zaldívar, Solas, & Tovar, 2012; Herranz, Tovar, Solo-de-Zaldivar, & Borderias, 2012, 2013), the authors proposed the use of Konjac glucomannan (KGM) as a thermostable gelling agent for restructuring. For that purpose an aqueous glucomannan dispersion (AGD) could be mixed with minced muscle after alkaline deacetylation to obtain thermostable gels with a texture and flavour similar to those of seafood muscle. This kind of thermostable gel is a three dimensional network, with different physical gel characteristics depending on the kind of processing. For instance, it is accepted (Maekaji, 1974; Williams et al., 2000) that the addition of alkali strongly diminishes steric hindrance caused by the acetyl groups, causing the formation of non covalent cross-links among junction zones. The number, size and position of junctions can fluctuate with time and temperature, producing transient networks (Herranz, Borderias, Solas, & Tovar, 2012; Ross-Murphy, 1995) involving non-covalent bonds such as hydrogen bonds, hydrophobic interactions, ionic bonds, etc., which under specific conditions may behave as permanent cross-links (Lapasin & Pricl, 1999, chap. 4). Hydrogen bonds in particular are considered the main interactions responsible for gel formation, although hydrophobic interactions, which gain in importance with increasing deacetylation, also seem to play an important role (Chen, Li, & Li, 2011). Moreover, when pH increases, the resulting anionic groups can form KGM chains that can change the structural function of water within the network, modifying the final properties of KGM gels. Specifically, Herranz et al. (2012) reported differences among electrostatic interactions such as ion-dipole, depending on the type and concentration of alkali, e.g. among cations (Na^+ and K^+) with

* Corresponding author. Tel.: +34 91 549 2300; fax: +34 91 549 3627.
E-mail address: beatriz.solodezaldivar@ictan.csic.es (B. Solo-de-Zaldívar).

0268-005X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodhyd.2013.04.009

OH groups of KGM chains, and with water molecules, on mechanical and viscoelastic properties of KGM gels. The authors found that 0.6 N KOH was the most suitable alkali to deacetylate KGM, thus producing KGM gels with more elastic and time-stable networks. However, the effect of pH on the deacetylation ratio and its influence on the physical properties of resulting samples has not yet been studied. This aspect is of paramount importance for designing gels with adequate textural characteristics for the particular technological purpose. In the present paper, the authors propose that strong gels capable of retaining a non-functional minced muscle as a filler and with a texture and appearance as similar as possible to real seafood muscle, which can also be heated, would be a real solution to upgrading many different muscle by-products remaining after processes that render the muscle remain non-functional.

The objective of this study was to evaluate the effect of the percentage of acetyl groups released from KGM chains, as measured by FT-IR, on the physicochemical, mechanical, viscoelastic and the microstructural characteristics of KGM gels. The practical aim was to optimize KGM gelation conditions in line with KGM concentration, for use in the manufacture of restructured seafood products.

2. Materials and methods

2.1. Preparation of samples

3 and 5% (w/v) aqueous glucomannan dispersions (AGD) from konjac glucomannan (Glucomannan purity 100%, Guinama, Valencia, Spain) were prepared according to the methodology previously described in Herranz et al. (2012). For KGM gelification, 0.6 N KOH (Panreac Química, S. A., Barcelona, Spain) was the alkali used to raise the pH of AGD from around 6 to around 11.9 (3% AGD) and 11.4 (5% AGD). After setting for 1 h at 30 °C and 5 h at 5 °C, they were removed from cylindrical containers (diameter 3 cm × height 3.5 cm) and Petri dishes, and placed in citrate–phosphate buffer at pH 5 (the gel:buffer proportion was 1:10) for 20 h at 5 °C in order to bring the pH of the gels down to 6.5–6.8.

The different lots of gels were prepared with 3 and 5% AGD (L1 and L2 respectively) and increasing amounts of 0.6 N KOH (from 0.5 to 6%) to reach a set of pH values for both lots, which were designated as shown in Table 1.

An aliquot of each sample was frozen (−80 °C) and freeze dried using a VirTis Benchtop-6KB freezer (Gardiner, NY,USA), for further analysis by *FT-IR* spectroscopy analysis.

2.2. Analyses

2.2.1. pH and moisture

The pH was measured using a model 9165BNWP pH probe (Analítica Instrumental, S.A., Barcelona) inserted in the gel. The pHmeter was an Orion model 720A (Analítica Instrumental, S.A., Barcelona). The pH was measured after homogenization of AGD for 3 min immediately after addition of the necessary amount of 0.6 N KOH.

Water content was determined by drying the sample to constant weight at 110 °C. The results are expressed as a percentage (AOAC, 2000).

Both analyses were done in triplicate.

Table 1
Nomenclature of samples containing 3 and 5% glucomannan at different pHs.

pH			
GM 3%		GM 5%	
L1.0	5.8	L2.0	5.5
L1.1	8.9	L2.1	7
L1.2	9.3	L2.2	8.1
L1.3	9.8	L2.3	9.2
L1.4	10.8	L2.4	10.7
L1.5	11.4	L2.5	11
L1.6	11.9	L2.6	11.4

2.2.2. Fourier Transform IR spectra measurement or FT-IR spectroscopy analysis

AGD (3% and 5%) was mixed with different proportions of a solution of 0.6 N KOH (0, 0.5, 1, 2, 3 and 4 (w/v)) to achieve different pHs and analysed by FT-IR. This range of pH values for KGM gelation was based on the reports by Thomas (1997) (pH values of 9–10), and Kohyama and Nishinari (1990) (pH values of 11.3–12.6). In this case other lower pHs were assayed to observe the acetyl band in FT-IR spectra and its gradual disappearance with increasing pH (or alkaline addition). The freeze-dried samples were dispersed in the agate mortar. Fluorolube was used as a matrix for dispersion of samples; this only fits absorption bands in frequency range above 1360 cm^{-1} except at 2321.9 cm^{-1}, and therefore it does not interfere in the observation of the bands that were of relevance to this study. Once a very homogeneous paste had been obtained, a small quantity was placed between CaF_2 crystals; these were mounted on the supports and transmission measured in the FTIR. Prior to sample measurement, spectrophotometry was prepared by running a "background" air absorption spectrum and a Fluorolube IR spectrum, which were later subtracted from the samples to avoid potential interference.

In all cases, IR spectra were recorded by accumulation of at least 32 scans, with a resolution of 2 cm^{-1} in a frequency range of about 4000 to 100 cm^{-1} (mid-infrared spectroscopy). Measurements were carried out in triplicate. The spectral data were processed with the Grams/AI (Thermo Electron Corporation, Waltham, MA) software, which includes baseline correction, smoothing (with a nine-point Savitsky–Golay function) to reduce the noise, and band area measurement.

Because the intensity of the absorption is proportional to the concentration of the adsorbing species, quantitative analysis is possible by FT-IR spectroscopy (Wilson, Slack, Appleton, Sun, & Belton, 1993). The area under the acetyl band was measured relative to the area of the CH band. In this way, the pH of the sample was associated with the relative intensity of the acetyl bands and hence with the percentage of acetyl in the KGM chains.

Three independent spectra were taken from each sample and the area of interest was measured. The spectral data were processed with the Grams/AI (Thermo Electron Corporation, Waltham, MA) software and smoothed using the Savitsky–Golay algorithm with nine points to reduce the noise. Baseline corrections were done with a non-automatic function (multipoint correction) and smoothing with a nine-point Savitsky–Golay function to reduce the noise. Carbonyl stretching vibration (C=O) in Acetyl groups at ~1730 cm^{-1}, and –CH stretching vibration at ~2920 cm^{-1} bands area, were measured for each spectrum. The average relative areas and the mean value were then obtained and plotted versus pH by linear regression to each AGD concentration.

2.2.3. Water binding capacity (WBC)

Neutralized gels were cut into small pieces (2 g) and placed in a centrifuge tube (diameter 10 mm) with a filter paper (2 filters Whatman no. 1, diameter 90 mm). The samples were then centrifuged in a Heraeus Multifuge 3L-R (Kendro Laboratory Products, Germany) for 10 min at 3000 g and room temperature. WBC was expressed as percent water retained per 100 g water in the sample prior to centrifuging. Measurements were carried out in triplicate.