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Physico-chemical and film-forming properties of bovine-hide and tuna-skin gelatin: A comparative study

J. Gómez-Estaca, P. Montero, F. Fernández-Martín, M.C. Gómez-Guillén *

Instituto del Frío (CSIC), Meat and Fish Science and Technology, José Antonio Novais, 10, 28040 Madrid, Spain

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ABSTRACT

A bovine-hide gelatin and a tuna-skin gelatin, both characterized on the basis of their amino acid composition and molecular weight distribution, were used to prepare edible films by casting with glycerol and sorbitol added as plasticizers. The molecular weight distribution of the tuna-skin gelatin exhibited appreciably higher quantities of β-components (covalently linked α-chain dimers), whereas bovine-hide gelatin showed a certain degradation of α_1-chains being indicative of a greater proteolysis. Intrinsic differences in the gelatin attributes affected in diverse manner some of the physical properties of the films. Thus, water vapour permeability was higher in the bovine-hide gelatin film, whereas deformability was considerably higher (10 times higher) in the tuna-skin gelatin film. In contrast, breaking force and water solubility were basically unaffected by gelatin origin. Analysis of the thermal properties revealed both films to be wholly amorphous with similar glass transition temperature values thanks to the plasticizing effects of the glycerol and sorbitol and the low moisture contents.

1. Introduction

Gelatin is a protein with a wide range of industrial applications employed worldwide. It enhances the functional properties of food products by improving their elasticity, consistency, and stability, and it may also be used as an outer film to protect food against drying, light, and oxygen, especially in those cases where oxidative and microbiological deterioration occurs (Arvanitoyannis, 2002). Gelatin is obtained by hydrolyzing the collagen present in the bones and skin generated as waste during animal slaughtering and processing. Bovine and porcine wastes are the most frequent sources to obtain gelatin of good quality. Other sources of gelatin are becoming increasingly relevant, such as fish bones and skins. The waste produced by fish filleting can account for as much as 75% of the total weight of catches (Shahidi, 1994), and further processing to yield gelatin can help offset harmful environmental effects.

The quality of a fish gelatin is determined mainly by its bloom strength and heat stability (melting and gelling temperatures). Certain uses, however, do not require these physical attributes to be as high as those of mammalian gelatins, e.g., encapsulation. For a long time, marine gelatins have been shown to present inferior rheological properties as compared to mammalian gelatins, which is especially true in the case of gelatins from cold-water fish species (Leuenberger, 1991; Gudmundsson and Hafsteinsson, 1997; Haug et al., 2004). Nevertheless, recent studies showed that certain fish gelatins might have not superior but similar quality characteristics compared to mammalian gelatin, depending on the species gelatin extracted from and the processing conditions (Choi and Regenstein, 2000; Cho et al., 2005; Zhou et al., 2006; Yang et al., 2007). The lower values for the physical properties of gelatins from cold-water fish species have largely been related to the considerably lower number of proline and hydroxyproline-rich regions in the collagen molecule (Ledward, 1986). The different physical properties of gelatins are related not only to the amino acid composition but also to the relative α-chain, β- or γ-component, and higher-molecular-weight aggregate contents and to the presence of lower-molecular-weight protein fragments (Johnston-Banks, 1990). For this reason, the extraction procedure greatly influences the properties of the resulting gelatin. More severe treatment conditions are widely agreed to be detrimental to a gelatin's physical properties. Nevertheless, high heat is commonly used to increase yields of commercial mammalian gelatins. In the case of fish gelatins, the normally lower degree of crosslinking in the native collagen (Montero et al., 1990; Bateman et al., 1996) allows milder acid and heat treatment conditions, thus yielding gelatin preparations of reasonably high quality (Gómez-Guillén et al., 2002).

In view of the growing interest in biodegradable films, any consideration of the quality of a gelatin should take into account not only its gel-forming properties but also its film-forming ability, along with the physical properties of the resulting films. Both the intrinsic differences between mammalian and fish gelatins and the different extraction conditions employed may influence the properties and the potential applications of films made from a given gelatin.

* Corresponding author. Tel.: +34 91 5445607; fax: +34 91 5493627.
E-mail address: cgomez@if.csic.es (M.C. Gómez-Guillén).

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There has been a review on gelatin films (Arvanitoyannis, 2002), and a considerable body of recently published work on the use of gelatin to obtain edible films is available in the literature (Menegalli et al., 1999; Sobral et al., 2001; Simon-Lukasik and Ludescher, 2004; Bertan et al., 2005). However, the bulk of this information concerns commercial mammalian gelatins. Although researchers are now increasingly turning their attention to fish gelatin films (Muyonga et al., 2004; Jongjareonrak et al., 2006a,b; Gómez-Guillén et al., 2007; Carvalho et al., 2008), the list of literature references dealing with these latter films is considerably shorter. The present literature seems to bear out that there are some differences in the physical properties of films obtained from mammalian and fish gelatins, the former being stronger and more permeable to water vapour and the latter more elastic (Sobral et al., 2001; Thomazine et al., 2005; Avena-Bustillos et al., 2006; Gómez-Guillén et al., 2007) although it remains somewhat unclear. Comparability of the data is limited because of the wide range of different experimental conditions employed for film producing, i.e., plasticizer type and concentration, dehydration temperature, film thickness and conditioning, etc. In addition, the recent knowledge about extraction and characterization of gelatin from many fish species, may difficult generalizing about fish gelatin properties.

The purposes of this study were: (i) to characterize the physicochemical attributes of two different origin gelatins (one from tuna-skin, the other from bovine-hide) on the basis of the more distinct parameters: aminoacid composition and molecular weight distribution; as well as thermal and rheological properties in the presence of plasticizers and (ii) to determine how these attributes affected the properties of the resulting films, produced in identical conditions to provide a proper comparison.

2. Materials and methods

2.1. Characterization of the gelatins

The tuna-skin gelatin was prepared in our laboratory according to the method described by Gómez-Guillén and Montero (2001). The bovine-hide gelatin (Bloom 200/220) was commercially obtained from Sancho de Borja S.L. (Saragossa, Spain).

2.2. Amino acid composition

An amount of 1 mg/ml of dry gelatin was dissolved in distilled water, and samples (50 μl) were dried and hydrolyzed in vacuum-sealed glass tubes at 108 °C for 18 h in the presence of continuously boiling 5.7 N HCl containing 0.1% phenol with norleucine as internal standard. After hydrolysis, samples were vacuum-dried, dissolved in application buffer, and injected onto a Biochrom 20 amino acid analyser (Pharmacia, Barcelona, Spain). DL-5-Hydroxylysine hydrochloride and *cis*-4-hydroxy-D-proline (Sigma, St. Louis, MO, USA) were also used as standards to determine the amount of hydroxylysine and hydroxyproline, respectively.

2.3. Molecular weight profile

The molecular weight distribution of the bovine-hide and tuna-skin gelatins was determined by SDS–polyacrylamide gel electrophoresis. Gelatin (5 mg/ml) solutions were mixed with loading buffer (2% SDS, 5% mercaptoethanol, and 0.002% bromophenol blue) in a proportion of 1:4. Samples were heat-denatured at 90 °C for 5 min and analysed according to Laemmli (1970) in a Mini Protean II unit (Bio-Rad Laboratories, Hercules, CA, USA) using 4% stacking gels and 6% resolving gels at 25 mA/gel. Loading volume was 15 μl in all lanes. Protein bands were stained with Coomassie brilliant blue R-250. Type I collagen from foetal calf was used as a marker for α-chain and β-component mobilities. Also a molecular weight standard composed of myosin (212 kDa), α_2-macroglobulin (170 kDa), β-galactosidase (116 kDa), transferrin (76 kDa) and glutamic dehydrogenase (53 kDa) (Amersham Pharmacia biotech, Buckinghamshire, UK) was employed.

2.4. Film-forming solution and film preparation

The film-forming solutions were prepared using gelatin at a concentration of 4 g/100 ml of distilled water. Sorbitol (0.15 g/g gelatin) and glycerol (0.15 g/g gelatin) were employed as plasticizers. The mixtures were warmed and stirred at 40 °C for 15 min to obtain a good blend, and the films were made by casting an amount of 40 ml in square dishes (12 × 12 cm) and drying in a convection oven at 45 °C for 15 h. Prior to determinations the films were conditioned over a saturated solution of NaBr (58% relative humidity) at 22 °C in desiccators for 2 d. The moisture content of films, determined by AOAC method 24003 (AOAC, 1984) after the conditioning period, was 10.23% (±0.30) for the bovine-hide gelatin films and 13.46% (±0.34) for the tuna gelatin films. Film thickness was measured using a digital micrometer (Mitutoyo, model MDC-25M, Kanagawa, Japan), averaging nine different locations.

2.5. Characterization of the film-forming solutions

2.5.1. Dynamic viscoelastic properties

Dynamic viscoelastic analysis of the film-forming solutions was carried out as described in Gómez-Guillén et al. (2007), on a Bohlin CSR-10 rheometer rotary viscometer (Bohlin Instruments Ltd., Gloucestershire, UK) using a cone-plate geometry (cone angle = 4°, gap = 0.15 mm). Cooling and heating from 40 to 6 °C and back to 40 °C took place at a scan rate of 1 °C/min, frequency of 1 Hz, and a target strain of 0.2 mm. The elastic modulus (G′; Pa), viscous modulus (G″; Pa) and phase angle (°) were determined as functions of temperature. Several determinations were performed for each sample, with an experimental error of less than 6% in all cases.

2.5.2. Gel strength

The film-forming solutions were poured into glasses 2.3 cm in diameter and 3.6 cm in height and left to mature in a refrigerator at 2 °C for 16–18 h. Gel strength at 8–9 °C was determined, as described in Gómez-Guillén et al. (2002), on an Instron model 4501 Universal Testing Machine (Instron Co., Canton, MA, USA) with a 100-N load cell, a cross-head speed of 60 mm/min, and a flat-faced cylindrical plunger 1.27 cm in diameter. The maximum force (*g*) was determined when the plunger had penetrated 4 mm into the gelatin gels.

2.6. Characterization of the films

2.6.1. Mechanical properties

A puncture test was performed to determine the breaking force and deformation of films at the breaking point (Gómez-Guillén et al. (2007). Films were placed in a cell 5.6 cm in diameter and perforated to the breaking point using an Instron model 4501 Universal Testing Machine (Instron Co., Canton, MA, USA) with a round-ended stainless-steel plunger (3 mm in diameter) at a cross-head speed of 60 mm/min and a 100-N load-cell. Breaking force was expressed in N and breaking deformation in %, according to Sobral et al. (2001). All determinations are the means of at least five measurements.

2.6.2. Thermal properties

Calorimetric analysis was performed with a model TA-Q1000 differential scanning calorimeter (DSC) (TA Instruments, New Castle, DE, USA) previously calibrated by running high purity indium