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The effects of sugars on moisture sorption isotherm and functional properties of cold water fish gelatin films

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ABSTRACT

Sugars were incorporated into CWFG solutions at different ratios (0%, 2%, 4%, and 6% w/w). Functional properties of the modified films were characterized following American standard test methods, and moisture sorption isotherm was characterized by polynomial and GAB models. Permeation to water vapor and oxygen of the modified films decreased compared to that of the control CWFG films. Moisture content, solubility, and monolayer water content of CWFG films decreased with the increase of sugar content. The addition of sugars significantly increased the Tensile strength of CWFG films from 30 to 40 MPa for ribose, and 30 to 35 MPa for fructose whereas elongation at the breaks decreased from 60% to 30% for ribose, and from 60% to 45% for that which incorporated fructose sugars. Moisture sorption isotherm curve significantly shifted to lower moisture content in $a_w < 0.6$. In $a_w > 0.6$, ribose-incorporated CWFG films, had similar function to hydrogel materials. In all the characterizations, the effects of ribose were significantly higher than those of fructose. Results of this research can be explored for commercial use, depending on the application for either packaging purposes or in the cosmetics industries.

1. Introduction

Replacement of bovine gelatin has attracted a great deal of research attention in recent years. This study compared the effects of ribose and fructose on the moisture sorption isotherm, and barrier, physical, and mechanical properties of cold water fish gelatin (CWFG) films. Demand for environmentally friendly polymers has grown in the recent decade and has been the focus of many research efforts [1]. Biopolymers have advantages over synthetic polymers; biopolymers are biodegradable and renewable materials [2]. Permeability inhibition of gases by biopolymers increases the shelf life of fresh products, such as fruits and vegetables. Proteins, lipids, polysaccharides, and their derivatives are some examples of these polymer substances, which are used to produce edible films [3–5]. Among the various types of films investigated and developed, protein-based biopolymer films had very good mechanical properties. Formation of side chains via cross-linking of proteins can improve the mechanical properties of the films [6]. Gelatin is a protein obtained from the hydrolysis of collagen. The skin, bone, cartilage, and tendon of animals such as cows, pigs, and fish are some of the sources of gelatin extraction [3,7–9]. For reasons such as biodegradability, renewability [10,11], high productivity with low cost [12], and improvement of elasticity, consistency, and stability [9,13,14], gelatin has wide applications in the pharmaceutical and food industries [12].

Fish gelatin is an inexpensive material made from the residual of fish skin and bones [15]. Fish gelatin gained importance in recent years mainly because of religious sentiments (e.g., Islam and Judaism forbid the use of pig gelatin, while Hindus do not use gelatin produced from cows), low production cost, and easy availability worldwide [16].

Although protein-based films are claimed to have wide applicability in the food industry, poor water vapor resistance and lower mechanical strength in comparison with synthetic polymers have limited their applications [17]. Most of previous studies have focused on warm water fish gelatins. The main difference between warm and cold water and fish gelatin is their gelation temperature. Cold water fish gelatin has much lower gelation temperature than those of other species. This is due to fish gelatin having lower proline and hydroxyproline content [18]. To overcome this problem, researchers have tested physical (e.g., radiation treatments, ultrasound) and chemical (e.g., aldehydes, especially glutaraldehyde, calcium salts) treatments along with the use of natural plant products like phenolic compounds (e.g., tannic acid, caffeic acid) [19,20] for their ability to improve the cross-linking properties of films.

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Some sugars, especially ribose, induce Maillard cross-linking after mild heat treatments and are able to cross-link proteins [21,22].

The main objective of this research is to compare the changes induced in cold water fish gelatin (CWFG) films (via possible improvement in cross-linking) by the addition of different ribose (an aldopentose monosaccharide in linear form) and fructose (a 6-carbon poly hydroxyl ketone) contents. Physical, mechanical, and barrier properties, as well as equilibrium moisture sorption isotherm of the films were characterized to provide fundamental data for their application in food and other industries.

2. Materials and methods

2.1. Materials

CWFG was obtained from Sigma-Aldrich (St. Louis, MO, USA). Food-grade glycerol and liquid sorbitol were prepared in the analytical grade. Ribose and fructose sugars were purchased from R & M Marketing (Essex, UK).

2.2. Film preparation

Sugars were dissolved in water at different concentrations [0% (control), 2%, 4%, and 6%; w/w based total CWFG dried mater], and stirred for 30 min. The solutions were used to prepare the aqueous CWFG dispersion at 8% (w/w). Plasticizer in accordance with Abdorreza et al. [23] was added at 25% ratio to the CWFG. To produce a clear sol, the CWFG dispersions were then heated to 70 ± 2 °C. The CWFG solutions were cooled to 40 °C, and the bubbles were removed by degassing via an ultrasonic process (42 kHz, 135 W; Branson ultrasonic corporation, USA). A portion (46 g) of the dispersion was cast on Perspex plates (20 × 20 cm^2) fitted with rims around the edge to yield a 16 × 16 cm^2 film-forming area. The films were dried under controlled conditions in a humidity chamber [25 ± 2 °C and 45 ± 5% relative humidity (RH)]. Dried films were peeled and stored at 25 °C and 50% RH until characterization (up to 30 days). The thickness of each film was measured at eight different locations and to the nearest 0.01 mm with a hand-held micrometer (Mitutoyo, Tokyo, Japan). All the films were prepared in four replicates.

2.3. Physical properties

2.3.1. Moisture content

Moisture content of the samples was determined using thermogravimetry analysis (TGA) (Pyris1 TGA, Perkin-Elmer, Massachusetts, USA). First, the films were conditioned at 55% RH and 30 °C prior to analysis. The TGA temperature was increased from 30 °C to 130 °C at a rate of 3 °C/min, and then held at 130 °C for 90 min. The change in weight (mass) of the samples was measured accurate to $\pm 10^{-3}$ mg. Moisture content was calculated by converting the mass loss obtained after ensuring that the residual mass of the sample was constant [1].

2.3.2. Solubility in water

Solubility of the CWFG films in water was determined following the method described by Sadegh-Hassani and Mohammadi Nafchi [24]. Pieces of film (2 × 3 cm ≈ 500 mg) were cut from each film and were stored in a desiccators with P_2O_5 (0% RH) for 7 days. Samples were weighed to the nearest 0.0001 g and placed into beakers with 80 mL deionized water (18 MΩ). The samples were stirred with constant agitation for 1 h at room temperature. The remaining pieces of film after soaking were filtered through filter paper (Whatman no. 1), followed by oven drying at 60 °C to constant weight. Samples were measured in triplicates and the percentage of total soluble matter (% solubility) was calculated as follow:

$$\text{Solubility}\,(\%) = \frac{(\text{Initial dried weight of film} - \text{Final dried weight of film})}{\text{Initial dried weight of film}} \times 100$$

2.3.3. Water absorption capacity

Water absorption capacity (WAC) of the films was measured with a method adapted from Kiatkamjornwong et al. [25] with some modifications. CWFG films were first dried over P_2O_5 for 7 days, and then 50 mg of dried films was kept for more than 24 h over a 100% RH and allowed to equilibrate after swelling. The swollen film samples were weighed. The WAC of the films was calculated as the amount of water retained by the films per dried weight.

2.4. Moisture sorption isotherm

The equilibrium moisture sorption isotherm of the samples at 30 °C was evaluated using the method following Mohammadi Nafchi et al. [26]. Equilibrium moisture content at 30 °C (g absorbed water/g dry film) was measured for each water activity. Experimental data were modeled using the GAB equation [27]:

$$W = \frac{w_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$$

where W is the moisture content (dry basis), K and C are thermodynamic constants of the GAB model, w_m is the monolayer water content of the films, and a_w is the water activity. Mean relative deviation modulus (E%) was calculated to evaluate the accuracy of the GAB model for experimental sorption isotherm of gelatin films. The formula is as follows:

$$E = \frac{100}{N} \sum_{i=1}^{N} \frac{|m_i - m_{pi}|}{m_i}$$

where E is the mean relative deviation modulus, N is the number of experimental data points, and m_{pi} and m_i are the experimental and predicted values, respectively. A modulus (E) value below 10% indicates a good fit [28].

The fourth-degree of the polynomial model for moisture sorption isotherm also fitted with the practical data.

$$W = A a_w^4 + B a_w^3 + C a_w^2 + D a_w$$

where A, B, C, and D, are the constants, and W and a_w are the moisture content (dry basis) and water activity, respectively.

2.5. Mechanical properties

Mechanical properties of the CWFG films were estimated according to ASTM D882-10 [29] under standard conditions. Film strips 120 mm long and 25 mm wide were cut and conditioned for 48 h in 30 ± 2 °C and 55 ± 5% RH. Texture analyzer (TA.XT2, Stable Micro System, Surrey, UK) was used to measure the mechanical properties of the film strips. The initial grip separation was 60 mm, and the crosshead speed was 30 mm/min.

2.6. Barrier properties

2.6.1. Water vapor permeability

Water vapor permeability (WVP) of the film samples was estimated according to the method described by Nouri and Mohammadi Nafchi [30]. The films were sealed using parafilm in permeation cups filled with a suitable amount of distilled water