Food Chemistry 216 (2017) 209–216

Contents lists available at ScienceDirect

Food Chemistry

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

Mechanical properties and solubility in water of corn starch-collagen composite films: Effect of starch type and concentrations

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ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form 12 August 2016
Accepted 17 August 2016
Available online 17 August 2016

Keywords:
Collagen
Starch
Amylose
Composite film
Gelatinization

ABSTRACT

This study investigated the possibility of enhancing the properties of collagen with three different maize starches: waxy maize starch, normal starch, and high amylose starch. Scanning electron microscopy images revealed that starch-collagen films had a rougher surface compared to pure collagen films which became smoother upon heating. Amylose starch and normal starch increased the tensile strength of unheated collagen films in both dry and wet states, while all starches increased tensile strength of collagen film by heating. Depending upon the amylose content and starch concentrations, film solubility in water decreased with the addition of starch. DSC thermograms demonstrated that addition of all starches improved the thermal stability of the collagen film. Moreover, X-ray diffraction results indicated that except for high amylose starch, the crystallinity of both starch and collagen was significantly decreased when subject to heating. FTIR spectra indicated that intermolecular interactions between starch and collagen were enhanced upon heating.

1. Introduction

Collagen film, widely used as artificial sausage casing in the food industry, was successfully commercialized during the 1980s (Wang, Zhang, Ye, & Ni, 2015). Collagen casing has uniform size, insolubility property, perfect strength and elasticity, which are essential to maintain the meat and bear various processing conditions (Harper, Barbut, Lim, & Marcone, 2012; Simelane & Ustunol, 2005).

Collagen possesses a highly ordered structure and is the main component of connective tissue in vertebrates, accounting for 25–35% of total body protein content. Indeed, more than 27 forms of collagen have been identified in mammalian tissues (Depalle, Qin, Shefelbine, & Buehler, 2014). Among these forms, type I collagen is the most abundant and widely distributed within animals and is composed of three types of polypeptide chains (two α_1 and one α_2) arranged into fibrils. Collagen fibrils overlap and form larger fibers, which constitute the main building blocks of many structural tissues, such as skin, bones, ligaments, and tendons. Collagen insolubility and fibrous structure, which is stabilized by several post translational modifications allowing the formation of intermolecular and interfibrillar cross-links, contributes to the high strength and durable nature of structures composed of collagen. Films containing collagen fibers demonstrate good mechanical properties and have been thoroughly studied in bioengineering and biomedicine fields (Depalle et al., 2014). With the recent development of edible and biodegradable packaging in the food processing industry, collagen films have received increasing interest with a focus on their scientific evaluation (Harper et al., 2012), film design (Wolf, Sobral, & Telis, 2009), and enhancement (Oechsle, Häupler, Gibis, Kohlus, & Weiss, 2015; Oechsle, Wittmann, Gibis, Kohlus, & Weiss, 2014).

In order to extend its practical applications, it is of importance for collagen film to meet two critical requirements: (1) insoluble in water and (2) ability to maintain mechanical integrity during batter stuffing and cooking in hot water. Although collagen film is relatively strong compared to other protein films, films will gradually disintegrate in water and lose their original strength. In order to survive harsh processing conditions of sausage casing, chemicals such as aldehydes (mainly glutaraldehyde) are used as crosslinking agents in collagen casing preparation. However, due to the increas-

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http://dx.doi.org/10.1016/j.foodchem.2016.08.048
0308-8146/

ing food safety concerns, the development of newer, safer alternatives is much needed. Wang et al. (2015) reported that ultraviolet irradiation and dehydrothermal treatment may be potentially used as a safer alternative for chemical crosslinking in collagen casing. It has also been demonstrated that collagen is able to mix with heterogeneous fillers such as chitosan (Adzaly, Jackson, Villalobos-Carvajal, Kang, & Almenar, 2015), improving product safety and quality. Additionally, some co-gelling proteins such as blood plasma protein, soy protein isolate, whey protein isolate, and gluten, provided a suitable method to modify collagen strength (Oechsle et al., 2015).

Starch, well-known for its excellent film-forming and oxygen barrier properties, is a promising alternative for synthetic polymers in food packaging. It consists of two major fractions, namely linear amylose and branched amylopectin. Although both are composed of glucose residues, they present different physicochemical properties due to their different structures. Amylopectin is a highly branched polymer constituted of short α-1,4 chains linked by α-1,6 bonds with a high molecular weight (1×10^8 g/mol), whereas amylose has mainly linear molecules composed of hydroglucose units connected through α-1,4 linkages, with an average molecular weight of 1×10^6 g/mol (Li et al., 2011). Sheets and films based on high-amylose starch normally exhibit excellent mechanical performance (Chaudhary, Torley, Halley, Mccaffery, & Chaudhary, 2009), as amylose has stronger gelling properties than amylopectin and linear chains of amylose interact through hydrogen bonds to a higher extent than the branched amylopectin chains (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). Starch has been previously studied as a filler in food packaging (Pankaj et al., 2015). Herein we want to extend the study by introducing starch granules in collagen film. Gels of collagen are able to undergo crosslinking with gelatinized starch by the formation of a network via inter-chain hydrogen bends (Langmaier, Mokrejs, & Mladek, 2010). Upon gelatinization, film properties can be improved via H-bonds between functional groups such as –OH in starch polymer chains (amylose and amylopectin) and carbonyl acids/amines in polypeptides chains of collagen (Shin, Spinks, Shin, Kim, & Kim, 2009). Moreover, Strong interactions between gelatin and polysaccharide were also reported in some protein-predominated starch-gelatin composite systems (Acosta, Jiménez, Cháfer, González-Martínez, & Chiralt, 2015).

The goal of the present work is to introduce raw starch granules as a reinforcing agent in collagen matrix for the improvement of the mechanical properties of collagen film and satisfying the requirement of batter stuffing. In this work, we discovered that crystallinity and forming strong interactions between collagen and starch molecules improved not only the mechanical strength but also the water resistance of the resultant composite films. Specifically, three different types of corn starches were added to collagen syrup at variable concentrations for preparing the starch-collagen composite films. Properties including micromorphology, water solubility, mechanical strength, and thermal stability of the resultant composite films were studied in details.

2. Materials and methods

2.1. Materials

Bovine skin splits, pretreated with 10 wt% lime (based on the wet skin) for 30 days were donated by Longbao Collagen Casing Co., Ltd. (Zibo, China). High amylose corn starch (Al) was donated by National Starch Co. (Shanghai, China). Waxy corn starch (Ap) was obtained from Chemical Industry Co. (Tokyo, Japan). Normal corn starch (Ns) was purchased from Aladin Industrial Corporation (Shanghai, China). The amylose contents of the aforementioned starches were 72%, 0%, and 27%, respectively (pre-determined by suppliers). All commercial chemicals were of analytical grade and used without further purification.

2.2. Film preparation

Collagen fibers were extracted from limed skin splits by extensively washing with distilled water until the pH value was near to 7. The washed skin was treated with 0.05 N HCl solution at the ratio of skin to acid (1:3; W:V) at 20 °C for 24 h. The intact collagen fibers were torn down carefully from the total swelled skin by a rake tweezers and dispersed in deionized water to form a 1.5 wt % collagen slurry. The collagen slurry with 30 wt% of glycerol (on the basis of the dry collagen fiber) was mixed with high amylose corn starch, waxy corn starch, and normal corn starch, each at the concentrations of 10 wt%, 50 wt%, and 0 wt% (i.e. neat collagen film as the control). After mixing, 65 ml of the dispersion (pH = 2) were quickly cast onto a pre-leveled polyacrylic plate (12 × 12 cm) and then air-dried in a ventilation hood at room temperature for 24 h. The newly formed film was peeled off from the plate and kept in a desiccator at 25 °C and 52% relative humidity (RH) for 48 h. In order to study the affect of heat on film performance, some films were firstly heated in a water bath at 80 °C for 30 min then air-dried at room temperature. All experiments were carried out immediately after removal from the chamber in order to avoid variation caused by moisture.

2.3. Film thickness

The thickness of film was measured using a hand-held micrometer (Mitutoyo No. 293-766, Tokyo, Japan, 0.001 mm accuracy). Thickness was determined by the average of ten random measurements on each film sample.

2.4. Optical properties

The light barrier properties of the films was evaluated by exposing films to light absorption at a wavelength of 600 nm in an UV–Vis spectrophotometer as described previously (Condés, Añón, Mauri, & Dufresne, 2015). Samples were cut into rectangular pieces and placed directly in a spectrophotometer test cell for capturing the absorbance spectrum. Measurements were performed using air as the reference value. The transparency value of each film was calculated using the following equation:

$$T = A_{600}/M$$

where A_{600} is the absorbance at 600 (nm), M is the thickness of films (mm). According to this equation, a higher value of T indicates a less degree of transparency.

2.5. Scanning electron microscope (SEM)

Film micromorphology was featured by SEM (SU1510, Hitachi of Japan) following a previously reported method (Ye, Ran, Luo, & Ning, 2014). Film samples were fixed on a SEM holder with a conductive adhesive, sputter-coated with a thin layer of gold, and then observed at an acceleration voltage of 20 kV.

2.6. Mechanical properties

The mechanical characteristics including tensile stress (TS) and elongation at break (E%) of film samples were evaluated as described in the literature (Xuan et al., 2015) using a Texture Analyzer (Stable Micro Systems Ltd, UK) at a crosshead speed of 3 mm/s and an initial grip separation of 30 mm. Film samples were cut into 20 cm × 70 cm pieces which were then clamped and stretched