Food Hydrocolloids 87 (2019) 436–447

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Effect of aging treatment on the physicochemical properties of collagen films

Donghui Shi[a,b,1], Fei Liu[a,b,1], Zhe Yu[a,b], Bingyu Chang[a,b], H. Douglas Goff[c], Fang Zhong[a,b,*]

[a] State Key Laboratory of Food Science and Technology, Jiangnan University, Wuxi, 214122, China
[b] School of Food Science and Technology, Jiangnan University, Wuxi, 214122, China
[c] Department of Food Science, University of Guelph, Guelph, ON, N1G 2W1, Canada

ARTICLE INFO

Keywords:
Collagen films
Aging treatment
Mechanical properties
Thermal properties
Triple helix structures

ABSTRACT

Aging treatment was used as a safe and green physical crosslinking method to successfully improve the physicochemical properties of collagen casing films. The aging treatment increased the Young's modulus (YM) of dry, wet, and boiled collagen films, as well as the tensile strength (TS) of wet and boiled collagen films to some extent. However, the highest aging temperature (80 °C) together with the higher relative humidity (RH) values (70% and 80%) led to the decreases in YM and TS and increases in elongation at break (EB). The aging treatment also improved the cooking performance of collagen films, like water absorption and shrinkage in boiling water, where the water absorption decreased to the range of 185%–102% and the shrinkage decreased to the range of 41.5%–21.5%. Collagen films after aging treatment had higher moisture contents than that of control film, and their moisture contents increased with increasing aging time and RH value. The thermal properties of collagen films was improved only at lower temperatures (< 130 °C) by aging treatment as shown from the thermogravimetric analysis results. Furthermore, the aging treatment did not significantly affect the chemical composition of collagen films but caused the denaturation of collagen triple helix structures at different degrees according to fourier transformation infrared spectroscopy, x-ray diffraction pattern, and differential scanning calorimetry analyses.

1. Introduction

Sausage casings include natural casings and artificial casings. Natural casing are tough and transparent films obtained from animal gastrointestinal tracts (pig, cattle and sheep) after removing the unwanted contents and fatty outer covering. However, natural casings are in short supply due to their limited resource, inefficient production and high cost. With the increasing demand for sausages, researchers turned their attention to the development of artificial casings (Burke, 1975). Artificial casings, like plastic casings, cellulose casings and collagen casings, have been developed. Among them, only collagen casings were edible..

Collagen casings can not only block oxygen and water vapor from direct contact with sausages, but also reduce exudation of meat juice, maintain color and resist oxidation during storage (Walz et al., 2018). As a food adhesive material, collagen can also be made into fiber membrane for meat, fish and other packaging (Amin & Ustunol, 2007; Conte, Marino, Della Malva, Sevi, & Del Nobile, 2012; Farouk, Price, & Salih, 1990). However, collagen casings still have various problems in the production process. Their low mechanical strength often leads to ruptures during stuffing. Then collagen casings will be stretched too much due to the effect of gravity during the next drying process. Moreover, the excess shrinking of collagen casings will also cause ruptures during cooking (Khor, 1997; Thiemig & Kordel, 1997; Walls, Cooke, Benedict, & Buchanan, 1993). Crosslinking or aging treatments can be used to solve these problems of collagen casings.

Crosslinking has received high attention in food industry due to its improvement in physicochemical properties of collagen casings (Motte & Kaufman, 2013), as well as other edible collagen-based films (Oechsle, Wittmann, Gibis, Kohlus, & Weiss, 2014; Uriarte-Montoya et al., 2010). Generally, various synthetic crosslinkers, such as formaldehyde, carbodiimide, hexamethylene-1,6-diaminocarboxysulphonate and glutaraldehyde, have been developed for the crosslinking of collagen (Drexler & Powell, 2010; Erdem et al., 2018; Nagai et al., 2010). Although these synthetic crosslinkers have stable and efficient cross-linking characteristics (Khor, 1997; Nimni, Ertl, Villanueva, & Nimni, 1990) and collagen casings or films crosslinked by them have superior physicochemical properties, their potential cytotoxicity should not be underestimated (He et al., 2011; Mattson et al., 1993). Recently, a natural crosslinker, genipin, provides a potential

* Corresponding author. State Key Laboratory of Food Science and Technology, Jiangnan University, Wuxi, 214122, China.
E-mail address: fzhong@jiangnan.edu.cn (F. Zhong).

[1] These two authors contributed equally to this work.

https://doi.org/10.1016/j.foodhyd.2018.08.016
Received 6 May 2018; Received in revised form 7 August 2018; Accepted 7 August 2018
Available online 09 August 2018

alternative to synthetic crosslinkers. But the high price limits its application in food industry. Also, it has been reported to have similar cytotoxicity as glutaraldehyde (Bigi, Cojazzi, Panzavolta, Roveri, & Rubini, 2002).

Aging is usually believed to be a safe and green physical cross-linking method. Aging treatment has been widely used to enhance the properties of some food materials, like sweet potato starch, sorghum starch, barley kernel starch and chestnut starch (Sun, Han, Wang, & Xiong, 2014; Yadav, Guleria, & Yadav, 2013; Zavareze & Guerra Dias, 2011), by controlling temperature, humidity and time. It also has a positive effect on the sensory characteristics and physicochemical properties of black tea (Jia et al., 2016). Gennadios, Park, and Weller (1993) investigated the effects of relative humidity and temperature on the tensile strength of two types of protein-based (corn zein and wheat gluten) and two types of cellulose-based (methylcellulose and hydroxypropyl cellulose) edible films. They found that the tensile strength increased with increasing temperature for all types of films. Zhang, Kim, Yokoyama, and Kim (2018) further found that moisture content markedly affected the properties of edible films, where low moisture content led to higher tensile strength and thermal stability.

Although a great deal of research has been devoted to study the cross-linking of collagen, comprehensive information with regards to the effects of aging conditions on the cross-linking of collagen casing is rather limited in the literature (Harper, Barbut, Lim, & Marcone, 2012; Oechsle et al., 2014). The comprehensive influences of relative humidity, temperature and time on the physicochemical properties of collagen casings are still not clear. In this study, collagen casings were prepared in the form of films. Aging method was used to improve the properties of collagen films and different combinations of temperature, relative humidity (RH) and time were investigated. The mechanical properties of collagen films were evaluated by analyzing Young's modulus, tensile strength and elongation at break under dry and wet conditions, respectively. The basic properties, like moisture content, water absorption, and shrinkage of collagen films were also measured. The thermal properties were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The collagen films were also characterized by fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

2. Materials and methods

2.1. Materials

Bovine skin was obtained from China Beijing Qiushi Agriculture Development Co., Ltd. (Beijing, China). Cellulose was purchased from Du Pont China Holding Co., Ltd. (Shanghai, China). All other chemicals of analytical grade were obtained from Sigma–Aldrich Co., Ltd. (Shanghai, China).

2.2. Preparation of collagen films

Bovine skin was repeatedly washed with ammonium sulfate solution and sodium citrate solution until the pH was 4.6. The washed skin was ground with ice at the ratio of 1/1 (w/w) at room temperature. The skin slurries were then mixed with 15% (w/w) hydrochloric acid, 20% (w/w) cellulose and 30% (w/w) glycerol, and then stirred to form homogenous 4% (w/w) collagen pastes using IKA RW20 digital cantilever stirrer (IKA Works Inc., Wilmington, USA). The collagen films were prepared by casting method at 35 °C after neutralizing the weighted collagen pastes (10 g) in sodium hydroxide solution. The average thickness of collagen films after drying was basically the same at about 0.05 mm.

2.3. Film aging treatment

Collagen films were stored at different aging conditions and times using a constant temperature and humidity chamber (Boxun Instrument HC BXS150S, China). Experiments of three factors and three levels were designed by Box-Behnken test design with Minitab (Version 17, Minitab, Inc., State College, Pa., U.S.A.), where temperature, relative humidity (RH) and time were chosen as independent variables. The levels and codes of independent variables are shown in Table 1.

Table 1
The temperature, relative humidity and time levels used for film aging treatment, and the sample codes.

Samples	Temperature (°C)	Relative Humidity (%)	Time (d[a])
60-60-2	60	60	2
60-70-1	60	70	1
60-70-3	60	70	3
60-80-2	60	80	2
70-60-1	70	60	1
70-60-3	70	60	3
70-70-2	70	70	2
70-70-2	70	70	2
70-70-2	70	70	2
70-80-3	70	80	3
70-80-1	70	80	1
80-60-2	80	60	2
80-70-3	80	70	3
80-70-1	80	70	1
80-80-2	80	80	2

[a] The letter “d” represents days.

2.4. Mechanical properties

Tensile strength (TS), elongation at break (EB) and Young's modulus (YM) were determined according to the ASTM standard method D882 (ASTM, 2001) with modifications using a texture analyzer (TA. XT2i, Lloyd instruments, U.K.) equipped with a tension grip system A/TG at room temperature. Films immersed in room temperature water for 30 s (wet film) and in boiling water for 1 min (boiled film), as well as the initial dry films were all measured. Film strips of 2 × 5 cm were initially cut and tested using initial grip separation and crosshead speed at 50 mm and 0.5 mm/s, respectively. The curves of force (N) as a function of deformation (mm) were recorded using Texture Expert Exceed software (Version 2.64, Stable Micro Systems LTD., Godalming, UK). TS (MPa), EB (%) and YM (MPa) were calculated using the following equations (1)–(3):

$$TS = \frac{\text{Maximum force (N)}}{\text{Thickness (mm)} \times \text{Width (mm)}} \tag{1}$$

$$EB = \frac{L - L_0}{L_0} \times 100\% \tag{2}$$

$$YM = \frac{F/A}{\Delta L/L_0} = \frac{FL_0}{A\Delta L} \tag{3}$$

where L_0 is the initial length of film and L is the length of film when it breaks. F is the force exerted on the film under tension. A is the actual cross-sectional area, which equals the area of the cross-section perpendicular to the applied force. ΔL is the amount by which the length of film changes.

2.5. Moisture content

Moisture content of films after aging was immediately determined by measuring the weight loss of samples (2 cm × 5 cm) after drying in an oven at 105 ± 1 °C until constant weight (about 24 h). Films were analyzed at least in triplicate and results were expressed as a percentage of total weight.