Performance of high amylose starch-composited gelatin films influenced by gelatinization and concentration

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ABSTRACT

In order to study the impact of starch in film performance, high amylose corn starch was composited in gelatin films under different gelatinization conditions and, in high and low concentrations (10 and 50 wt.%). It was found that hot water gelatinized starch (Gel-Shw) increased film mechanical strength and was dependent upon the starch concentration. The addition of an alkali component to the starch significantly enhanced the swelling of the starch granules and expedited the gelatinization process. Incorporation of starch, especially the alkalized starch (Sha), into the gelatin films decreased film solubility which improved its water resistance and water vapor permeability (WVP). Multiple techniques (DSC, TGA, FT-IR, and XRD) were used to characterize the process and results, including the crosslinking of the dissolved starch molecules and the particles formed from gelatinized starch during retrogradation process, which played an important role in improving the thermal stability of the composited gelatin films. Overall, the starch-gelatin composition provides a potential approach to improve gelatin film performance and benefit its applications in the food industry.

1. Introduction

In recent decades, the extensive use of plastic packaging has led to increased concerns surrounding the plastic waste generated in daily life due to its non-biodegradable and non-renewable nature [1]. For this reason, a variety of bio-based materials, including gelatin, have been developed as environmentally friendly alternatives [2]. Although gelatin has been used in even edible film format and varied applications due to its renewable character, and good film-forming abilities [3,4], its applications are limited in some certain areas due to its brittleness and high moisture absorption [5]. In order to address these challenges and expand its applicability, different materials have been formulated as filler in gelatin film fabrication including high molecular weight carbohydrates such as starch and chitosan [6,7], organic acids [8], several inorganic substances [9], and bio-nanomaterials [1].

Among these, starch, especially high amylose starch, has drawn significant attention because of the semi-crystal nature that amylose imparts due to its good mechanical and vapor/oxygen barrier properties [10]. For example, Ryu et al. explored the physical properties of composite films using high-amylose corn starch and corn zein as filler [11]. Muscat et al. studied the film forming behavior of low and high amylose starches [12]. In many of these studies, the functional properties of high amylose starch were obtained via the gelatinization of the starch dispersion, normally conducted in heated water [13]. In some cases, gelatinization of the starch dispersion also occurred at room temperature with the aid of certain chemicals such as electrolytes [14], dimethyl sulfoxide (DMSO) [15], urea [16], and most recently sodium hydroxide (NaOH) [17].

The objective of this work was to use high amylose corn starch as a filler to enhance gelatin film, with a focus on the impact of gelatinization degree and addition dosage of starch on film properties. Critical gelatinization conditions, such as heating and sodium hydroxide media, were also studied in terms of their impact on the degree of starch gelatinization. Native (Sn), hot water gelatinized (Shw), and hot alkaline (Sha) high amylose starch dispersion/solutions at low and high concentrations (10 wt.% vs. 50 wt.%) were used to fabricate gelatin films Gel-Sn, Gel-Shw, and Gel-Sha, respectively. Film morphology together with water

resistance, optical and mechanical properties was studied using multiple analytical techniques. The role of crosslinking and the crystallinity of the amylose component on the thermal stability of these composite films were also extensively studied.

2. Materials and methods

2.1. Materials

Bovine-hide gelatin, type A (Bloom 220, was purchased from Aladdin Industrial Corporation (Shanghai, China). High amylose corn starch (72% amylose content) was donated by the National Starch Co. (Shanghai, China). All other reagents and solvents were of analytical grade and used as received, without any further purification.

2.2. Film preparation

Firstly, 0.15 g of high amylose starch was added to 20 ml of a 0.1 M NaOH solution. It was then heated to 125 °C for 80 min to obtain a yellow, viscous, and gelatinized starch solution named Sha (low concentration, 10 wt.%). A white, less viscous Shw solution (10 wt.%) was obtained by stirring a mixture of 0.15 g of high amylose starch in 20 ml of deionized water at 125 °C for 80 min. A white dispersion referred to as Sn was obtained by mixing 0.15 g of high amylose starch in 20 ml of deionized water at room temperature. Similarly, a high concentration starch solution/dispersion (50 wt.%) was obtained by adding 0.75 g of high amylose starch to each media, followed with the same stirring and heating process for gelatinization, except for Sn. The pH values of all starch samples (Sn, Shw, and Shw) were measured using an acidometer before and after gelatinization. Finally, in order to prepare the starch-gelatin composited films (Gel-Sn, Gel-Shw, and Gel-Sha), a gelatin stock solution was made by adding 1.5 g of gelatin powder and 0.45 g of glycerol to 10 ml of deionized water, which was then stirred at 45 °C for 2 h. Then, the gelatin stock solution was mixed with 20 ml of each gelatinized starch solution or dispersion to form approximately 30 ml of each mixture. The mixtures were stirred for 2 min and quickly individually cast onto pre-levelled 11 cm x 11 cm polyacrylic plates and gently air-blown for 5 h at 25 °C. The dried films were peeled off of the plates and conditioned in a desiccator at 25 °C, 52% relative humidity (RH) for 48 h. A neat gelatin film (Gel) was formed by directly casting the gelatin stock solution mixed with 20 ml deionized water. All film characterization was carried out immediately after chamber film removal.

2.3. Film thickness

The film thickness was measured using a hand-held micrometer (Mitutoyo No. 293–766, Tokyo, Japan, 0.001 mm accuracy). Ten random measurements on each film were taken to obtain a statistically relevant average.

2.4. Optical properties

Colors (L*, a* and b*) were determined using a Konica Minolta colorimeter CM-700d (Osaka, Japan) in accordance with a previously described method [18]. The total difference in color (ΔE) was calculated by the following equation:

$$\Delta E = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2}$$

where $\Delta L*$, $\Delta a*$ and $\Delta b*$ are the differences between the corresponding color parameter of each sample and the standard of white paper (L* = 89.99, a* = −0.23, b* = −8.94).

The light absorbance of each film was determined at 600 nm using a UV–vis spectrophotometer (Model G10S UV–vis, Genesys, Madison, USA) according to the following equation [19]:

$$T = \frac{A_{600}}{M}$$

where A_{600} is the absorbance at 600 nm and M is the film thickness (mm). Higher transparency values represent lower film transparency.

2.5. Scanning electron microscopy

Film morphology was assessed under scanning electron microscopy (SEM) (SU1510, Hitachi of Japan). SEM images were taken at 800x and 1000x magnifications. For cross section analysis, cryo-fractured films were sputtered with gold and then photographed [20].

2.6. Mechanical properties

The cast film tensile strength and elongation at break (E) (20 mm × 70 mm) were measured in ambient conditions in accordance with ASTM D882-97 using a Texture Analyzer (Stable Micro Systems Ltd, UK) (crosshead speed of 3 mm/s and an initial grip separation of 30 mm). Tensile strength (MPa) and E (%) were calculated using the following equations:

$$TS = \frac{T_m}{A}$$

$$E = \frac{L_1 - L_0}{L_0}$$

where T_m is the maximum load (N) needed to stretch the sample to break; A is the cross-sectional area (m^2) of the composite film. L_0 (mm) is the initial length of the film and L_1 (mm) is its length at break.

2.7. Water solubility

Film water solubility was measured as described in the literature [21] with some modifications. A pre-dried cast film sample (4.0 cm × 4.0 cm) was weighed and immersed in 50 ml of deionized water at room temperature for 24 h. Undissolved film residues were filtered out and dried in an oven at 105 °C for 24 h to obtain the dry, insoluble sample debris. Film solubility (%) was defined as $(W_b - W_a)/W_b \times 100\%$, where W_b is the weight of the sample before water immersion and W_a is the dry weight of the insoluble component after immersion.

2.8. Water vapor permeability

The water vapor permeability (WVP) of the cast film samples was measured according to a previously reported method [22] with minor modifications. Briefly, a film sample (6 cm in diameter) was prepared on the top of a substrate dish in which 7 g of anhydrous calcium sulfate was stored. The film sample was then conditioned at 38 °C, 90% RH and recorded at 6 h, 12 h, 24 h, 48 h, and 96 h. According to ASTM E96-00 (ASTM, 2000), WVP can be calculated as follows:

$$WVP = \frac{GL}{At\Delta p}$$

where G is the weight gain of the dish (g) during the test, L is the film thickness (m), A is the total test area (5.72×10^{-4} m^2 in this study), t is the conditioning time (s), and Δp is the pressure difference between the inside and outside of the dish (Pa).