Physicochemical, mechanical and thermal properties of chitosan films with and without sorbitol

Mei Liu, Yibin Zhou*, Yang Zhang, Chen Yu, Shengnan Cao

School of Tea and Food Technology, Anhui Agricultural University, 130 Chang Jiang West Road, Hefei 230036, China

ABSTRACT

The effect of sorbitol on the physicochemical, mechanical and thermal properties of chitosan films with different degrees of deacetylation (DD; i.e., DD85% and DD95%) was investigated. The thickness, moisture content (MC), water solubility (WS) and water–vapor permeability (WVP) of the films were evaluated. Sorbitol addition reduced MC, increased WS and significantly ($p < 0.01$) reduced WVP of both film types. DD95% films had lower MC and WVP, and higher WS than DD85% films. Static (thermomechanical analysis) and dynamic (dynamic mechanical analysis) tests indicated that sorbitol increased the strain and decreased stress for both DD films, but DD95% could sustain higher strain and DD85% could sustain higher stress. Thermogravimetrics analysis and differential scanning calorimetry showed that sorbitol elicited a lower degradation temperature for both films, and that DD95% films exhibited higher thermal stability than DD85% films.

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1. Introduction

In recent years, exploring the possibility of using biopolymer-based films as packaging materials has garnered interest because of their biocompatibility, biodegradation, non-toxic nature, antimicrobial activity and other environmentally friendly properties [1,2]. Chitosan, obtained by the partial *N*-deacetylation of chitin [3], is a candidate material for packaging films because of its film-forming property.

However, films formed of pure chitosan are fragile and brittle, which limits their application [4]. The addition of polyols could improve the related properties of chitosan by reducing the frictional forces among polymer chains [5–7]. According to one report, the properties of chitosan films are dependent on the type and quantity of plasticizer [8] and vary with the nature of plasticizer used [9]. Sorbitol has better physicochemical and mechanical properties than other polyols [10,11].

In our previous study, the mechanism of film formation of chitosan films as well as the structure of different degrees of deacetylation of chitosan with and without sorbitol were investigated and characterized [12]. Differences in the molecular structure of a compound usually result in different properties. Thus,

discussion of the properties of different chitosan films with different components is important and necessary to further illustrate the relationship between films various properties and their structure.

The objective of the present work was to analyze the different physicochemical (thickness, moisture content [MC], water solubility [WS] and water vapor permeability [WVP]), mechanical (thermomechanical analysis [TMA] and dynamic mechanical analysis [DMA]) and thermal (thermogravimetric analysis [TGA] and differential scanning calorimetry [DSC]) properties of various films. This was carried out to (i) further clarify the influence of chitosan formation on the various properties of its films and (ii) to shed light on the effect of sorbitol and different degrees of deacetylation on the properties of chitosan films. Ultimately, these results will provide information for the better choice of suitable formation in eventually various applications of chitosan films as biodegradable packaging materials.

2. Materials and methods

2.1. Materials

Chitosan with different degrees of deacetylation, i.e., 85%DD (molecular weight [MW] = 343.75 kDa) and 95%DD (MW = 312.5 kDa), were purchased from Zhejiang Golden-shell Biochemical Co. Ltd. (Zhejiang, China). The MC of the 85%DD and 95%DD chitosan were $11.92\% \pm 0.032\%$ and $12.97\% \pm 0.042\%$, respectively. Sorbitol was purchased from Sigma–Aldrich (St Louis,

MO, USA). All of the other chemicals used were of analytical grade and available commercially.

2.2. Preparation of film-forming solutions and film casting

Samples of chitosan with different degrees of deacetylation (2%, w/v), with and without sorbitol (2%, w/v), were dissolved in 2% (v/v) acetic acid solution. The different solutions were used to prepare films via a previously described film-casting method with some modification [13]. The detailed processing methodology can be found in our previous publication [12]. Unspiked chitosan films and those spiked with sorbitol as a plasticizer were abbreviated to "CHF" and "CHFP", respectively.

2.3. Measurement of physicochemical properties

2.3.1. Thickness

Film thickness was measured using a CHY-C$_2$ Thickness Gauge (Lab Think Co., Jinan, China). Samples were tested at 10 random points, and the mean value was calculated.

2.3.2. MC

About 10 mg of each sample was balanced in a drying vessel until a constant weight M_1 was achieved. Then, it was dried in an oven at 105 °C for 24 h, and a constant weight, M_2, was reached. The MC was calculated as the percentage of water removed from the system using the following formula:

$$MC \ \ (\%) = M_1 - \frac{M_2}{M_1} \times 100\% \qquad (1)$$

2.3.3. WS

Films were cut into strips (4 cm × 2 cm). The initial dry weight was determined by drying the strips in an oven at 105 °C to constant weight (Wi), and then immersed them in 50 mL distilled water with stirring at 100 rpm. After 24 h, the strips were removed and dried at 105 °C until a constant weight (Wf) was achieved. WS was calculated using the following formula:

$$WS \ \ (\%) = Wi - \frac{Wf}{Wi} \times 100\% \qquad (2)$$

2.3.4. WVP

The WVP of the films was measured on a TSY-TI Water Permeability Tester (Lab Think Co. Jinan, China) according to GB1037-88 in a similar way to the ASTM E96 method [14]. Approximately the same thickness of each film with the diameter of 10 cm was tested. All samples were dried for 4 h before testing, and then the tested film was sealed on the top of a permeation cell containing distilled water, placed in the tester at 20 °C with a relative humidity of 57% with silica gel. The preheating time was 4 h and then the loss of water weight over 24 h was measured. The instrument was adjusted with a 200-g weight before each examination. The WVP of films was determined using the following formula:

$$WVP = WVTR \times \frac{L}{\Delta p} \qquad (3)$$

where WVTR is the measured rate of transmission of water vapor (g/(m^2 s)) through the film, L is the mean thickness of the film (mm), and Δp is the difference in the partial pressure of water vapor (kPa) across the two sides of the film [15].

2.4. Static and dynamic mechanical analyses

Static and dynamic mechanical properties of the films were evaluated on a Dynamic Thermal Mechanical Analyzer (DMTA Q800; TA Instruments, New Castle, DE, USA). Each sample of identical thickness was cut to the same width; the length was measured automatically by the instrument. Conditions for static mechanical test were an applied force from 0 N to 18 N with a speed of 0.25 N/min under a constant temperature of 25 °C. For the dynamic mechanical test, samples were tested at a frequency of 10 Hz, temperature was in the range −100 °C to 200 °C with a heating rate of 5 °C/min and displacement amplitude of 30 μm. Values of storage modulus, loss modulus and loss tangent (tan σ) were obtained as a function of temperature.

2.5. Thermal analyses

2.5.1. TGA

A Thermogravimetric Analyzer (TGAQ5000, TA Instruments) was utilized to determine the variations in quality and thermal degradation during heating. Temperature scans were carried out from room temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Approximately 5 mg of each sample was placed in an alumina pan (A1203) with an empty pan used as a reference. The starting, conclusion and peak temperature (T_p) and percentage weight loss at each stage were obtained from the derivative (DrTGA) curves.

2.5.2. DSC

DSC was undertaken with a Perkin Elmer DSC-8000 system (Perkin Elmer, Waltham, MA, USA) calibrated with indium as the standard. Approximately 6 mg of each sample was placed in an aluminum pan (A1203) and sealed hermetically with an empty pan of the same type (used as a reference). Measurements between 30 °C and 350 °C were made at a heating rate of 10 °C/min under a nitrogen atmosphere. Data were analyzed using Pyris Manager version 8.0 (Perkin Elmer). The onset, peak and conclusion of melting temperatures in the endothermic and exothermic phases were utilized as the onset temperature (T_o), peak melting temperature (T_m) and conclusion temperature (T_c). Melting enthalpy (ΔH) was employed as a criterion for comparison of the thermal stability of the film during the two-phase transition.

2.6. Statistical analyses

Differences between factors and levels were evaluated by one-way analysis of variance (ANOVA) using SPSS version 20 (SPSS, Chicago, IL, USA). Tukey's test was employed to compare the means in order to identify groups that were significantly different from other groups at a confidence level of 95%. The results were expressed as the mean and SD.

3. Results and discussion

3.1. Physicochemical properties of different chitosan films

3.1.1. Thickness

The thickness of the different films is presented in Table 1. The thickness of the sorbitol-spiked and sorbitol-unspiked films was similar ($p > 0.05$). This observation suggested that sorbitol did not influence the thickness of films, a finding that was in accordance with that of Piermaria et al. [16].

3.1.2. MC

The MC of different films is summarized in Table 1. DD95% films (spiked and unspiked with sorbitol) did not display significantly ($p > 0.05$) lower MC than those of the corresponding DD85% films. This result suggested that deacetylation degree of 85%, 95% presented little difference on chitosan films moisture content. The little variation might be ascribed to the higher crystallinity of the DD95% films elaborated in our previous work [12] which decreased