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# Influence of chitosan concentration on mechanical and barrier properties of corn starch/chitosan films

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ABSTRACT

The active packaging films based on corn starch and chitosan were prepared through mixing the starch solution and the chitosan solution (1:1) by casting. The aim of this work was to characterize and analyze the effects of the chitosan concentrations (0, 21, 41, 61 and 81 wt% of starch) on physicochemical, mechanical and water vapor barrier properties as well as morphological characteristics of the corn starch/chitosan (CS/CH) films. Starch molecules and chitosan could interact through hydrogen bonding as confirmed from the shift of the main peaks to higher wavenumbers in FTIR and the reduction of crystallinity in XRD. Results showed that the incorporation of chitosan resulted in an increase in film solubility, total color differences, tensile strength and elongation at break and a decrease in Young's modulus and water vapor permeability (WVP). Elongation at break of the CS/CH films increased with increasing of chitosan concentration, and reached a maximum at 41 wt%, then declined at higher chitosan concentration. The WVP of CS/CH films increased with an increase of chitosan concentration and the same tendency observed for the moisture content. The results suggest that this biodegradable CS/CH films could potentially be used as active packaging films for food and pharmaceutical applications.



## 1. Introduction

Active packaging has attracted significant interest in food packaging industry since last decade because of its ability to extend shelf life or improve safety or sensory properties while maintaining the quality of the food though incorporating active compounds and ingredients into packaging materials [1,2]. The main active packaging systems, which can be broadly classified into absorbing and releasing systems, involve moisture or liquid absorbing, oxygen scavenging, carbon dioxide emitting/absorbing, ethylene scavenging/emitting, flavour and odour absorbing or releasing, and antimicrobial systems [3–5]. Antimicrobial packaging, a promising version of active packaging, has received attention as a potential pathogen intervention strategy for various foods, which is able to kill or inhibit spoilage and pathogenic microorganisms that are contaminating foods [6,7]. The incorporation of antimicrobial agents in the packaging system or using polymers which are inherently antimicrobial to control the growth of microorganism in food could have a significant impact on shelf-life extension and food quality. Most of the active packaging available in the market is developed from synthetic traditional polymers. Consumer health and environmental concerns caused by the solid waste after use of degradable petrochemical-based packaging materials have attracted increasing interest in the active food packaging materials based on biodegradable and natural polymers.

Starch is one of the most abundant natural polymers and a promising material for food packaging and preservation because of its renewability, biodegradability, edibility and low cost. Starch can be processed with existing plastic processing technologies though disrupting the starch granular structure by mechanical and thermal energy in the presence of water or other plasticizers. Although starch based materials are known to have excellent oxygen barrier properties [8], its applications are limited due to its poor moisture barrier properties, brittleness and low tensile strength. A commonly used approach to overcome these drawbacks and provide further functional properties is to blend starch with other natural biopolymers to form composite materials [9,10].

Chitosan, a deacetylated derivative of chitin, is the second most abundant polysaccharide found in the nature after cellulose and is available mainly from shellfish processing waste. Due to its good film forming ability, excellent biocompatibility and proven antimicrobial activity, chitosan has been previously added into

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starch matrix from different origins, such as potato [11–13], wheat [14], tapioca [15], corn [16–18], cassava [19–22] and kudzu [23] to prepare starch based active packaging displaying antimicrobial properties. The advantage of adding chitosan into starch is not only to reduce water sensitivity but also improve mechanical and barrier properties of starch film [13,14,16,22,24,25]. The effect of the ratio of chitosan and starch on the properties of the starch/chitosan films had been investigated by blending different weight percentages (*x* wt%) of starch and (100-*x*) wt% of chitosan [18] or varying the concentration of starch solutions, such as 1, 2, 3 and 4% [13,16,25], 3.5, 5 and 6% [24]. It was found that water vapor transmission rates decreased with increasing starch to chitosan ratios, as well as tensile strengths and elongation at breaks of the composite films first increased and then decreased, and starch to chitosan ratio of 1:1 was the critical value for the tensile value of the composite films [13,16]. In addition, the effects of glycerol concentration (0%, 2.5%, 5% and 10%, w/w) on the mechanical and thermal properties and molecular level interactions in starch-chitosan (1:1) films were comprehensively studied [17]. The addition of glycerol increase elongation at break and decrease tensile strength of the films due to the interactions among chitosan, starch and glycerol through hydrogen bonding which facilitated the sliding of chain and thus help to improve the overall flexibility and the chain mobility. Dang and Yoksan [19,20] reported blown film extrusion processability and properties of thermoplastic starch (TPS) film by incorporating plasticized chitosan, with a content of 0.37, 0.73, 1.09 and 1.45%. Although the incorporation of chitosan caused decreased extensibility and melt flow ability, as well as increased yellowness and opacity, the films possessed better extrusion processability, improved water vapor and oxygen barrier properties, increased tensile strength, rigidity, thermal stability and UV absorption, as well as reduced water absorption and surface stickiness [20].

However, the effect of chitosan concentration on the properties of starch/chitosan films using a solution casting technique was not taken into consideration in the mentioned study. Therefore, the present work aims to prepare and characterize blend films based on corn starch (CS) and chitosan (CH), analyzing the influence of the chitosan concentration on film morphological characteristics and functional properties such as physicochemical, mechanical and barrier properties, which are relevant for active packaging in food preservation and packaging industry.

## 2. Materials and methods

### 2.1. Materials

Corn starch was supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China). Its moisture content was 12.8%, and the amylose/amylopectin ratio was 28/72. Chitosan with degree of deacetylation of 88.0% was supplied by Sinopharm Chemical Reagent Co. Ltd. No.20120330 (China). Glycerol, anhydrous $CaCl_2$, acetic acid (36%) and $KNO_3$ were obtained from Beijing Beihua Fine Chemicals Co. Ltd. (Beijing, China). All these materials were used as received without further purification.

### 2.2. Film preparation

Chitosan solution was prepared by dissolving chitosan powder (1, 2, 3 and 4 g) in 100 mL of 0.2 M acetic acid aqueous solution at 60 °C with stirring of 600 rpm. Starch solution (5 g/100 mL) was prepared by dispersing corn starch in deionized water at 95 °C and stirring with 600 rpm for 60 min to accomplish a complete starch gelatinization. Glycerol, as a plasticizer, was added to the chitosan solution and starch solution at concentration of 20 wt% of the chitosan and starch, respectively. Based on preliminary experiments, the corn starch/chitosan (CS/CH) film solutions were prepared by mixing the starch solution (5 g/100 mL) and the chitosan solution (1, 2, 3 and 4 g/100 mL) at weight ratio of 1:1 to fabricate the CS/CH films, i.e. CS/CH21, CS/CH41, CS/CH61 and CS/CH81, containing concentrations of 21, 41, 61 and 81% dry weight of chitosan per dry weight of corn starch, respectively. After stirred with 600 rpm for 60 min at 60 °C and degassed, desired amount of film solution was distributed into Petri dishes for casting and dried at 40 °C and 30% relative humidity for 30 h. The peeled films were kept in a chamber at room temperature and 75% RH for 48 h prior to experimental use.

### 2.3. Attenuated total reflectance-Fourier transform infrared analysis (ATR-FTIR)

ATR-FTIR spectra of the obtained CS/CH films were measured by using a Nexus 670 FTIR Spectrometer with an ATR attachment (Nicolet, USA) to investigate the interactions of chitosan and starch in the films. The measuring probe directly touched the surface of the films. A spectral resolution of 4 $cm^{-1}$ was employed and 64 scans were acquired for each spectrum in the range of 4000–700 $cm^{-1}$.

### 2.4. Physicochemical properties

The CS/CH film density was determined from the specimen weight and volume. The specimen volume was calculated from specimen area and thickness. Thickness of the blend films was measured by using a hand-held digital micrometer (Mitutoyo Absolute, Tester Sangyo Co. Ltd., Tokyo, Japan) with a precision of 0.001 mm at five different positions in each specimen and the average values were taken. (These values were used for mechanical properties and water vapor permeability.) All the tests were conducted in triplicate and the means were reported.

Solubility of the blend films in water (WS) was defined as the percentage of the water-soluble dry matter of film that is dissolved after immersion in distilled water and measured according to the method described by Zamudio-Flores et al. [26]. The films were cut to 20 mm × 25 mm strips and were stored in a desiccator (ca. 0% RH) to constant weight. The strips were weighed to determine the initial dry weight and placed in glass vessels with 50 mL of deionized water. The samples were maintained with constant agitation for 2 h at 80 °C and were dried at 105 °C until a constant weight was obtained. The reported results corresponded to the mean of two replicate assays. The percentage of the soluble total material was calculated as follows:

$$WS(\%) = [(\text{Initial dry weight} - \text{Final dry weight}) \times 100]/\text{Initial dry weight}.$$

HunterLab ColorFlex (Xinlian Creation Electronic Co. Ltd., Shanghai, China) was used to determine the change of the blend films color. The color values of L* (luminosity), a* (negative-green; positive-red) and b* (negative-blue; positive-yellow) were measured. A standard plate CX 2064 was used as standard. The color parameter values of the standard plate are L* = 94.52, a* = −0.86, and b* = 0.68. Five measurements were taken on each sample, one at the center and four around the perimeter. The total color difference (ΔE*) and color intensity (C*) were calculated as follows:

$$\Delta E = (\Delta a^2 + \Delta b^2 + \Delta L^2)^{1/2}$$

$$C = [(a*)^2 + (b*)^2]^{1/2}$$

Where $\Delta L = L^*_{standard} - L^*_{sample}$, $\Delta a = a^*_{standard} - a^*_{sample}$, $\Delta b = b^*_{standard} - b^*_{sample}$.