

Characteristics of Different Molecular Weight Chitosan Films Affected by the Type of Organic Solvents

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ABSTRACT: Chitosan films were prepared using 3 chitosan molecular weights and 4 organic acid solvents without plasticizer. Tensile strength (TS) and elongation (E) ranged from 6.7 to 150.2 MPa, and from 4.1 to 117.8%, respectively. Water vapor permeability (WVP) and oxygen permeability (OP) ranged from 0.3 to 0.7 ng·m/m²·s·Pa and OP from 0.4 to 5.8 × 10⁻⁸ cc/m²·day·atm, respectively. TS increased with chitosan molecular weight. Acetic acid resulted in the toughest films followed by malic, lactic, and citric acid, respectively. Films prepared with citric acid had the highest E values. WVP was not influenced significantly by the molecular weight of chitosan. OP of films prepared with malic acid was the lowest, followed by acetic, lactic, and citric acid.

Keywords: Chitosan films, molecular weight, organic acids, tensile strength, elongation, Water Vapor Permeability, Oxygen Permeability

Introduction

CHITOSAN, A LINEAR POLYAMINE COPOLYMER OF β-(1-4)-D-glucosamine and acetyl-β-(1-4)-D-glucosamine, is obtained by alkaline N-deacetylation of chitin, the 2nd most abundant polysaccharide on the earth (Gudmund and others 1989; Muzzarelli 1977). Chitosan is commercially available from plentiful, renewable sources, primarily waste from the shellfish industry (Li and others 1992). Chitosan is not soluble in pure water or organic solvents, but is soluble in aqueous solutions of organic acid and mineral acids at specific conditions. Most of the applications of chitosan are based on the polyelectrolytic nature and chelating ability of the amine groups of the macromolecule. In an acidic solution, amine groups of chitosan are protonated to NH³⁺, and thus polyelectrolytic and chelating properties of chitosan are mainly governed by the acidity of the -NH³⁺ (Park and others 1983). Though chitosan is allowed for food use in some countries, such as Japan and Korea, it is not allowed for food use in the U.S.A., which does, however, allow its use for animal feed.

Chitosan forms viscous solutions in various organic acids. These viscous solutions have been used to make functional films. Kienzle-Sterzer and others (1982) evaluated the effect of concentration of chitosan and type of aqueous solvent (acetic or propionic acid) on the mechanical properties such as the elasticity and relaxation response of chitosan films. Butler and others (1996) determined basic barrier and mechanical properties of chitosan film prepared with 1% acetic acid. Preservative (sorbic or benzoic acid) impregnated chitosan films were developed and tested for their efficacy as a potential active packaging material (Labuza and Breene 1989). The uses for unmodified chitosan films are limited because of their high moisture permeability and brittleness; however, the properties of chitosan films can be modified to improve barrier and mechanical properties. Wong and others (1992) reported the use of chitosan-lipid composite films to improve the moisture barrier properties of chitosan film. Hosokawa and others (1990) reported that chitosan films had a low permeability for O₂ and CO₂. Hoagland and Parris (1996) developed a chitosan/pectin-laminated film to alter

water vapor permeability and water solubility of the film.

Most of the previous works on chitosan films (Park and others 1999; Rhim and others 1998; Caner and others 1998; Butler and others 1996) have been done with plasticized chitosan films, but basic data on the effect of solvent acid and molecular weight of chitosan on barrier and mechanical properties are not available for unplasticized chitosan films.

The main objective of the present study was to prepare chitosan films using different molecular weight of chitosan and different organic acids without plasticizer, and to investigate their effects on mechanical and barrier properties of the films.

Materials and Methods

Materials

Three chitosan samples from red crab shell with different viscosities (10, 30, and 50 cP) with degree of deacetylation above 95%, were obtained from the Biotech Co., Inc. (Mokpo, Korea). They were designated as CH-10, CH-30, and CH-50, respectively, and the maker claimed their molecular weights determined by the method of Hirai and others (1981) were 37000, 79000, and 92000 Daltons, respectively. Acetic acid was purchased from Aldrich Chemicals (Milwaukee, Wis., U.S.A.); citric acid and lactic acid were purchased from Fisher Chemical Co. (Fair Lawn, N.J., U.S.A.); malic acid was purchased from Sigma Chemical Co. (St. Louis, Mo., U.S.A.). All reagents and chemicals were of analytical grade or better.

Preparation of films

For each molecular weight chitosan, 2% (W/V) chitosan solutions were prepared by dissolving chitosan in 2% of acetic acid, malic acid, lactic acid, and 4% citric acid solutions based on the criterion of solubility for chitosan in acidic solutions (Hon 1997). The pH of acidic solutions were 3.07, 2.26, 2.42, and 2.57 for acetic, citric, lactic, and malic acid, respectively. After dissolving chitosan, the pH of the solution increased to 3.87, 2.82, 3.24, and 3.16, respectively.

Dissolved solution was filtered through a filter paper

(Whatman, No. 4) to remove foam and any undissolved impurities, and then poured onto a framed and leveled Teflon-coated glass plate (30 cm × 30 cm) which had been previously cleaned with ethyl alcohol.

Film thickness was controlled by consistently casting the same amount (250 ml) of film-forming solution. The solution was cast in a circular area in the center of the plates, and then spread by manually rotating the plates. Films were allowed to dry at ambient conditions for about 48 h. Dried films were peeled from the plate and cut for property testing. Samples for tensile strength (TS) testing were cut into 2.54 cm by 10 cm rectangular strips. Water vapor permeability (WVP) and oxygen permeability (OP) testing samples were 10 cm and 3.5 cm squares, respectively.

Thickness

Film thickness was measured with a hand-held micrometer (B.C. Ames Co., Waltham, Mass., U.S.A.). Five thickness measurements were taken on each tensile testing sample along the length of the strip, with the mean used in TS calculations. Similarly, 5 measurements were taken on each WVP and OP sample, 1 at the center and 4 around the perimeter, and the mean values were used in WVP and OP calculations.

Conditioning

All chitosan films for TS, WVP, and OP test were conditioned in an environmental chamber (Model 317322, Hot-pack Corp., Philadelphia, Pa., U.S.A.) set at 25 °C and 50% RH for 48 h before testing.

Tensile strength and percentage elongation at break

TS and elongation at break (E) were evaluated with an Instron Universal Testing Machine (Model 4201, Instron Engineering Corp., Canton, Mass., U.S.A.). Initial grip separation was set at 50 mm and crosshead speed was set at 500 mm/min. TS was calculated by dividing the maximum (peak) load for breaking film by the cross-sectional area of the film. E was calculated as the percentage of change by dividing film elongation at the moment of rupture by the initial gauge length (50 mm). TS and E measurements for each type of film were replicated 3 times with individually prepared films as the replicated experimental units, and each replicate being the mean of fifteen tested sampling units taken from the same film.

Oxygen permeability

An OX-TRAN 1000 Oxygen Permeability Tester (MOCON, Inc., Minneapolis, Minn., U.S.A.) was used to determine oxygen transmission rate of the chitosan film samples. The oxygen permeability tester was operated according to ASTM standard Method D 3985-81 (ASTM 1989). Film samples were conditioned in a desiccator containing calcium sulfate (0% RH) for 48 h prior to testing, then placed between 2 aluminum masks with a circular area of 50 mm². Testing conditions were 25 °C and 0% RH. OP values were calculated from oxygen transmission rate divided by film thickness and oxygen partial pressure difference across the films (Gennadios and others 1993).

Water vapor permeability

The water vapor permeability (ng·m/m²·s·Pa) of film was calculated as follows:

$$WVP = (WVTR \cdot L) / \Delta P$$

where WVTR was measured water vapor transmission rate

(g/m²·s) through a film, L was mean film thickness (m), and ΔP was partial water vapor pressure difference (Pa) across the 2 sides of the film. WVTR was determined gravimetrically using a modified ASTM Method E 96-95 (ASTM 1995). Film specimens were mounted on poly (methyl methacrylate) cups filled with 18 ml of distilled water up to 0.9 cm from the film underside. The cups were placed in an environmental chamber set at 25 °C and 50% RH. Weights of the cups were recorded every 2 h for a period of 10 h. A steady state weight loss was reached after 2 h. Slopes of the steady state (linear) portion of weight loss compared with time curves were determined by linear regression to estimate WVTR. Coefficient of determination (R²) for all reported data was 0.99 or greater. In calculating WVP, the effect of resistance of the stagnant air layer between the film undersides and the surface of water in the cups was corrected (McHugh and others 1993; Gennadios and others 1994). For each type of film, WVP measurements were replicated three times.

Statistical analysis

Measurements of each property were measured in triplicate for TS, E, WVP, and OP with individually prepared and cast films as the replicated experimental units. Statistics on a completely randomized design were determined using the General Linear Model procedure in the SAS statistical analysis program (SAS Institute, Inc. Cary, N.C. 1988). Analysis of variance (ANOVA) of the data was conducted and mean property values were separated ($p < 0.05$) with Duncan's multiple range test for the property values which indicated significantly different ($p < 0.05$) between treatment groups.

Results and Discussion

Tensile strength

TS values of chitosan films prepared with three different molecular weight of chitosan and four different organic acid solutions are shown in Table 1. All means were compared against each other because the results of ANOVA indicated a significant ($p < 0.05$) interaction between the molecular weight of chitosan and the type of acid solvent for TS of chitosan films. TS of chitosan films varied widely ranging from 7 to 150 Mpa, depending on both the molecular weight of chitosan and the type of acid used. TS of the films increased significantly ($p < 0.05$) with increasing molecular weight of chitosan for all the types of acid used. Muzzarelli and others (1977) suggested that TS of chitosan film increased with increasing molecular weight of chitosan. Chitosan forms hydrogen bonds between hydroxyl groups and amino groups in chitosan film (Uragami and others 1994). During the film formation, hydrogen bonding in the chitosan films increased with the increasing amount of amino and hydroxyl groups, due to the increase in concentration of chitosan.

In addition, the intermolecular arrangement of chitosan in an aqueous solution is influenced by the peculiarity of acid solutions such as ionic strength and the degree of dissociation. Kienzle-Sterzer and others (1982) reported that the mechanical properties of chitosan films change with the type of acid solvent. They estimated that acid type or concentration of chitosan used in preparing film might affect both junction density and topological limitations in the film. This may be due to the different interaction between chitosan and acid solution. The different interactions are represented by the spatial configuration of the chitosan molecules during film formation.

Among the acids tested, acetic acid resulted in the toughest films or films with the greatest TS, followed by malic, lac-

Table 1—Effect of solvent system on tensile strength (TS) of different molecular weight chitosan films¹

Solvents	TS (Mpa)		
	CH-10 ²	CH-30	CH-50
Acetic Acid	68.8 ± 31.5 ^d	143.2 ± 14.6 ^e	150.2 ± 15.8 ^e
Citric Acid	6.7 ± 1.6 ^a	14.0 ± 2.9 ^a	17.4 ± 5.9 ^{ab}
Lactic Acid	17.1 ± 3.2 ^{ab}	50.8 ± 7.9 ^c	62.6 ± 11.3 ^{cd}
Malic Acid	27.4 ± 3.6 ^b	56.3 ± 6.9 ^{cd}	62.4 ± 10.6 ^c

Means of 3 replicate ± SD; any 2 means followed by the same letter are not significantly ($p > 0.05$) different by Duncan's multifactor range test.

²CH-10, CH-30, CH-50 are chitosans with viscosity of 10, 30, and 50cP, respectively.

Table 2—Effect of solvent system on elongation at break (E) of different molecular weight chitosan films¹

Solvents	Elongation (%)		
	CH-10 ²	CH-30	CH-50
Acetic Acid	4.1 ± 1.2 ^a	5.5 ± 1.1 ^a	7.6 ± 2.6 ^a
Citric Acid	117.8 ± 19.5 ^e	61.7 ± 14.4 ^d	41.9 ± 12.0 ^c
Lactic Acid	31.1 ± 7.8 ^{bc}	21.7 ± 11.8 ^{ab}	19.6 ± 9.5 ^{ab}
Malic Acid	18.2 ± 4.3 ^{ab}	17.8 ± 4.2 ^{ab}	29.9 ± 6.8 ^{abc}

Means of 3 replicate ± SD; any two means followed by the same letter are not significantly ($p \geq 0.05$) different by Duncan's multifactor range test.

²CH-10, CH-30, CH-50 are chitosans with viscosity of 10, 30, and 50cP, respectively.

tic, and citric acid, respectively. Citric acid formed significantly ($p < 0.05$) weaker films than the other acids, which might be caused by dissolving higher concentration of the acid (4%) compared with other acids (2%). This result agrees with that of Rhim and others (1998), who found acetic acid made tougher chitosan films than malic, lactic, or citric acid. Park and others (1998, 2000) explained the relationship between film properties and the organic acid solution properties such as molecular weight and molecular dimension of chitosan measured by light scattering method. They showed that molecular weight of chitosan dissolved in acetic acid was larger than that dissolved in the other three acid solutions. In acetic acid solution, chitosan forms dimers indicating that the intermolecular interaction is relatively strong, which suggests that the chitosan films prepared with acetic acid had tighter structure than those prepared with other acid solutions. Even though some chitosan films had extremely high physical strength, such as the films prepared with acetic acid and CH-50 chitosan, they were too brittle to be used as an ordinary film.

Park and others (1999) reported TS of 15 cP unplasticized chitosan films prepared from acetic acid and malic acid were 65.96 and 12.72 MPa, respectively. Rhim and others (1998) reported 41.6 ± 5.9 , 25.9 ± 2.4 , 26.7 ± 2.8 , and 27.3 ± 0.9 MPa for TS of chitosan films with 1% of acetic, citric, lactic, and malic acid, respectively. Butler and others (1996) also reported 15 to 35 Mpa for TS of the films with 1% acetic acid. The reported values are lower than those of the films prepared with same acid (acetic acid) solution in the present study. The difference may be attributed to the fact that they used different types of chitosan and added plasticizer for preparing the films. Plasticizers are known to make film more flexible with reduced toughness (Banker 1966). Plasticizers function by weakening intermolecular forces between adjacent polymer chains resulting in decreased tensile strength and increased film flexibility.

Elongation at break

E (a measure of a film's ability to stretch) of chitosan films also varied according to the type of acid and molecular weight of chitosan used as shown in Table 2. There was a significant ($p < 0.05$) interaction between molecular weight of chitosans and acid types for E of the films. Mean E values of chitosan films varied widely from 4.1 to 117.8%. Films prepared with acetic acid were the toughest (lowest E values) and films prepared with citric acid were the most resilient (greatest E values) among the films tested. Generally, it is known that there is an inverse relationship between TS and E of biopolymer films (Rhim and others 2000); that is, extensibility of films reduced (lower E) as strength of films increased (greater TS).

Butler and others (1996) reported E of 14.6 to 18.7% for chitosan films prepared with 3% chitosan solution in 1% ace-

tic acid. Park and others (1999) determined E of chitosan films prepared with acetic, citric, or lactic acid solutions and reported E of chitosan film with lactic acid showed the highest value of 31.9 to 104.9%. Rhim and others (1998) demonstrated that E of chitosan also varied according to the type of acid solution used. They reported mean values of E of chitosan films prepared with acetic, citric, lactic, or malic acid were 42.4, 25.2, 58.3, and 42.6%, respectively. These values are higher than those of the present study, which can be explained by their use of a significant amount of plasticizer (0.75 g of glycerol per g of chitosan) for preparing film.

Though E values of chitosan films were much lower than those of commercial high density polyethylene (HDPE) or low density polyethylene (LDPE) films, their mechanical properties with higher TS and reasonable E values suggest a high potential for film use in packaging and other applications.

Water vapor permeability

WVP of chitosan films prepared using different organic acid and different molecular weight of chitosan ranged from 0.26 to 0.69 ng·m/m²·s·Pa (Table 3). ANOVA test results indicated that both the effect of molecular weight of chitosan and the effect of interaction between molecular weight of chitosans and solvent acids on WVP of the films were not significant ($p > 0.05$). WVP values of chitosan films prepared with acetic acid showed slightly higher water vapor barrier (lower WVP values) properties, while those with lactic acid showed slightly lower barrier (higher WVP values) properties. Chitosan films prepared with citric and lactic acid exhibited small increases of WVP values with increasing molecular weight of chitosan.

Butler and others (1996) determined WVP of chitosan films prepared with 1% acetic acid and 0.25% glycerol using a Permatran-W600 Water Vapor Permeability Tester equipped with an infrared detector. They reported WVP values at 25 °C and 11% RH of 0.25 ± 0.14 ng·m/m²·s·Pa. Park and others (1999) reported WVP of 0.34 to 0.60 ng·m/m²·s·Pa for chitosan-based films (viscosity; 15 cP, 50 cP, and 400 cP) prepared without plasticizer. Rhim and others (1998) tested the effect on WVP values of the films prepared from commercial chitosan cast from 8 different organic acid solvents. They reported mean WVP values ranging from 0.83 to 1.79 ng·m/m²·s·Pa, depending on the organic acid used. These WVP values differ from those of the present study. This discrepancy may be attributed to the preparation conditions for films such as molecular weight of chitosan, types of solvent and their concentration, and addition of plasticizers. For example, Rhim and others (1998) added glycerol in preparation of chitosan films resulting in higher WVP values due to enhanced segmental mobility caused by the plasticizer. Actually, WVP values reported in the literature must be compared with caution as WVP values of hydrophilic films are known to be affected by

Table 3—Effect of solvent system on water vapor permeability (WVP) of different molecular weight chitosan films¹

Solvents	WVP (ng × m/m ² × s × Pa)		
	CH-10 ²	CH-30	CH-50
Acetic Acid	0.32 ± 0.04 ^a	0.31 ± 0.04	0.32 ± 0.02 ^a
Citric Acid	0.40 ± 0.04 ^a	0.49 ± 0.03 ^b	0.51 ± 0.04 ^{ab}
Lactic Acid	0.47 ± 0.09 ^a	0.53 ± 0.02 ^b	0.69 ± 0.06 ^b
Malic Acid	0.41 ± 0.02 ^a	0.26 ± 0.02 ^a	0.26 ± 0.02 ^a

¹Means of 3 replicate ± SD; any 2 means in the same column followed by the same letter are not significantly ($p \geq 0.05$) different by Duncan's multifactor range test.

²CH-10, CH-30, CH-50 are chitosans with viscosity of 10, 30, and 50cP, respectively.

Table 4—Effect of solvent system on oxygen permeability (OP) of different molecular weight chitosan films¹

Solvents	OP (×10 ⁻⁸ cc/m × day × atm)		
	CH-10	CH-30	CH-50
Acetic Acid	1.4 ± 1.4 ^{ab}	1.7 ± 1.4 ^a	5.8 ± 2.9 ^b
Citric Acid	3.3 ± 1.5 ^b	4.9 ± 2.9 ^b	3.0 ± 1.9 ^a
Lactic Acid	2.7 ± 1.3 ^b	3.0 ± 2.0 ^{ab}	2.7 ± 1.3 ^a
Malic Acid	0.8 ± 0.4 ^a	0.4 ± 0.3 ^a	1.9 ± 0.3 ^a

¹Means of 3 replicate ± SD; any two means in the same column followed by the same letter are not significantly ($p \geq 0.05$) different by Duncan's multifactor range test.

²CH-10, CH-30, CH-50 are chitosans with viscosity of 10, 30, and 50cP, respectively.

various factors such as measuring method, measuring conditions such as the RH gradient and temperature, correction of air gap effect, and film thickness (Rhim and others 1998).

Oxygen permeability

ANOVA results indicated that there was significant ($p < 0.05$) effect of solvent acids on OP of the films with significant ($p < 0.05$) interaction between molecular weight of chitosans and solvent acids. OP of chitosan films varied from 0.4 to 5.89 × 10⁻⁸ cc / m²·day·atm, depending on the type of acid and the molecular weight of chitosan used (Table 4). These values agree well with 7.2 × 10⁻⁸ cc / m²·day·atm reported by Muzzarelli and others (1974) and 1.2 to 4.5 × 10⁻⁸ cc / m²·day·atm reported by Butler and others (1996). No distinct correlation occurred between OP values of chitosan films and molecular weight of chitosan. However, OP values of chitosan films were affected by different acid solutions. The oxygen barrier of chitosan films prepared with malic acid was the greatest with (lowest) OP of 0.4 to 1.9 × 10⁻⁸ cc / m²·day·atm among the acid solutions tested. OP values of chitosan films prepared with citric acid appeared the highest (3.3 to 4.9 × 10⁻⁸ cc / m²·day·atm) of the films tested.

The OP test of chitosan films casted from acetic acid was complicated by brittleness of the films under the experimental condition of 0% RH. The OP of 5.8 × 10⁻⁸ cc / m²·day·atm for CH-50 film prepared with acetic acid is questionable because the film was extremely brittle and might have formed cracks in the film, resulting in a higher value. Generally, OP value of low molecular weight (10 cP) chitosan film was lower than that of chitosan films prepared with high molecular weight chitosan (50 cP).

As indicated by Butler and others (1996), OP values of chitosan films are comparable with commercial polyvinylidene chloride (PVDC) or ethylene vinyl alcohol copolymer films. Low oxygen permeability of chitosan films can be exploited for food and medical packaging applications.

Conclusions

MECHANICAL AND BARRIER PROPERTIES OF CHITOSAN FILMS can be controlled through choosing appropriate molecular weight of chitosan and solvent system. The chitosan films with tailored properties can be useful in the food and medical packaging and applications.

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