Effects of Lamination and Coating with Drying Oils on Tensile and Barrier Properties of Zein Films

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Zein films plasticized with oleic acid have been considered potentially useful for biodegradable packaging applications. However, moisture was found to affect their tensile and gas barrier properties. We investigated the effects of two converting processes, fusion lamination and coating with drying oils, on tensile properties and gas permeability of zein films. Zein films were laminated to 4-ply sheets in a Carver press and coated with tung oil, linseed oil, or a mixture of tung and soybean oils. Tensile properties and permeability to water vapor, oxygen, and carbon dioxide were measured according to ASTM methods. Laminated films were clearer, tougher, and more flexible, and had a smoother finish than nontreated sheets. Lamination decreased O_2 and CO_2 permeability by filling in voids and pinholes in the film structure. Coating increased tensile strength and elongation and decreased water vapor permeability. Coatings acted as a composite layer preventing crack propagation and increasing film strength. They also formed a highly hydrophobic surface that prevented film wetting.

Keywords: *Protein films; zein; oxygen permeability; carbon dioxide permeability; water vapor permeability*

INTRODUCTION

Research on agricultural-based materials has intensified in the past decade, and has been driven by environmental issues and agricultural economics. A number of biopolymers, including starch, cellulose, polylactic acid, polyhydroxy butyrate/valerate, polycaprolactone, casein, corn zein, and soybean proteins were investigated as structural materials (*1*, *2*). They were found potentially useful in packaging applications as films and formed containers. However, challenges remain to their widespread utilization. Biopolymers tend to be brittle and moisture sensitive. Extreme brittleness encumbers processing and prevents film utilization in wrapping applications. Brittleness can be ameliorated by the addition of plasticizers, but the treatment usually increases moisture sensitivity (*3*−*8*). Biopolymers tend to swell in water, thereby losing their dimensional stability and having their mechanical and barrier properties adversely affected.

Zein, a thermoplastic and relatively hydrophobic material, has been proposed for use as a structural material (*9*). Preparation of zein films from a resin containing oleic acid was described by Lai and Padua (*10*). Zein and oleic acid (used as plasticizer) were dissolved in aqueous ethanol where oleic acid adsorbed to the protein. The plasticized zein was later precipitated in a stream of cold water. The recovered material (resin) was stretched over rigid frames forming thin films that were allowed to dry in air. Dry films (∼0.030 mm thick) were translucent, flexible, ductile, and heat sealable. Typical tensile strength (TS), elongation (*E*), and Young's modulus values of zein films (at 25 °C and 50% RH) were 9 MPa, 12%, and 270 MPa, respectively (*10*). For comparison, TS and *E* values of collagen films are 3−11 MPa and 25−50%, respectively (*11*). TS and *E* values for low-density polyethylene (LDPE) films are 9−17 MPa and 500%, respectively (*12*). Tensile properties of zein films, as expected for protein-based films, were affected by moisture. *E* increased from 12 to 30% and Young's modulus decreased from 270 to 150 MPa when relative humidity (RH) increased from 50 to 98% (*13*). Changes were attributed to zein plasticization by moisture. Films kept at 98% RH lost dimensional stability, in agreement with previous reports (*14*, *15*). Structure characterization of zein films drawn from zein and oleic acid resins was reported by Lai et al. (*16*). Small-angle X-ray scattering (SAXS) measurements suggested a layered film structure consisting of staggered zein planes alternating with oleic acid layers. SAXS patterns also suggested the presence of planar voids scattered between layers. Voids were thought to have been formed by evaporation of residual solvent.

Water vapor permeability (WVP) of drawn zein films was relatively low (0.06 g·mm/m^2·h·kPa at 25 °C and 0/98% RH gradient) (*13*) compared to that of hydrophilic biopolymers, such as wheat gluten (2.2 g·mm/m^2·h·kPa at 21 °C and 0/85% RH gradient) (*17*) and cellophane (0.3 g·mm/m^2·h·kPa at 38 °C and 0/90% RH gradient) (*18*). However, it was an order of magnitude higher than that of LDPE films (0.003 g·mm/m^2·h·kPa at 38 °C and 0/90% RH gradient) (*19*). WVP of zein films changed with RH, increasing from 0.04 to 0.06 g·mm/m^2·h·kPa when RH increased from 50 to 98% (*13*). Temperature also affected WVP of zein films. WVP was lower at 25 °C than at 5, 15, or 35 °C (*13*). Polymer films often show an increase in WVP with increased temperature because of a higher diffusion coefficient resulting from increased molecular mobility of plasticizers and polymer chains. WVP of zein films also increased at lower temperatures

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(5 and 15 °C), possibly because of plasticization by water condensed on the film surface (*13*). Zein films, cast from solutions, were coated with waxes and fatty acids in order to increase their water resistance (*20*). Those coatings effectively increased the water resistance of the films, but the waxes and fatty acids were often temperature sensitive.

Oxygen and carbon dioxide permeability values of zein films (*17*, *21*−*23*) were lower than those of common plastic films such as LDPE, high-density polyethylene, polypropylene, polystyrene, and unplasticized poly(vinyl chloride) (*24*). However, RH markedly affected their gas barrier characteristics. Moisture has a plasticizing or swelling effect on hydrophilic polymers that results in increased permeability (*25*). Moisture-sensitive, oxygen-barrier synthetic polymers must be either copolymerized with a hydrophobic polymer, sandwiched between hydrophobic polymer layers, or treated with cross-linking agents to limit their exposure to moisture. The use of plasticizers also affects the gas permeability of films. Increasing plasticizer content in zein films increased oxygen permeability (*8*, *26*).

The manufacture of multilayer flexible packaging is known as converting (*27*). Converting processes include lamination and coating. Lamination is used to improve the performance of polymeric films by combining the properties of several types of films into one sheet, e.g., polyethylene and foil. Lamination may be accomplished by hot-pressing heat-sealable films together or by applying an adhesive to the surface of single layers. Lamination of similar materials may be useful to decrease leakage through film pores. Each film would cover tears, pores, and cracks on the next. Coating with drying oils has been practiced for a long time to protect wooden surfaces from mechanical and water damage. Drying oils (linseed and tung oil, among others) oxidize and polymerize in air to form dry, hard, and water-impermeable coatings. Drying oils are often heat treated and added with metallic catalysts to promote oxidation and hasten the polymerization process.

Our objective was to investigate the effects of processing treatments, fusion lamination, and coating with drying oils, on tensile properties, water vapor permeability, and gas permeability of zein films.

MATERIALS AND METHODS

Materials. Corn zein, regular grade (F4000, Freeman Industries, Inc., Tuckahoe, NY). Oleic acid ($C_{18:1}$) 90% (Aldrich Chemical Co., Milwaukee, WI) was used as plasticizer. The ethyl alcohol used was technical grade. Tung oil finish (Minwax Company Inc., Montvale, NJ), boiled linseed oil (Sunnyside Corporation, Wheeling, IL), and a mixture of tung oil (Aldrich Chemical Co., Milwaukee, WI) and soybean oil (Archer Daniels Midland Co., Decatur, IL) 60/40 (v/v) were used for coatings.

Preparation of Zein Films. Zein-based resins were prepared by dissolving granular zein (16% w/v) in 75% aqueous ethanol. Oleic acid was gradually added at a ratio of 1 g/g of zein. An emulsion was formed by stirring the mixture at 3500 rpm for 10 min in an Omni-Mixer (Servall, Ivan Servall, Inc., Norwalk, CT) at 75−80 °C. A zein−oleic acid dough-like resin was obtained by precipitating the emulsion in chilled water (4 °C). The resin was kneaded for 15 min in a farinograph (C. W. Brabender Co., Hackensack, NJ). Zein films were then obtained by stretching the resin over circular rims (15.5 cm in diameter). Films were let to dry in air for 24 h and later laminated and/or coated with drying oils.

Lamination (fusion type) involved pressing together film stacks, 1 to 4 ply, in a Carver Press (Model C, Carver Laboratory Press, Fred S. Carver Inc., Menomonee Falls, WI) under 5.5 metric tons at 120 °C for 5 min. Coated films were brushed with tung oil finish, boiled linseed oil, or a 60/40 (v/v) mixture of tung oil and soybean oil. Coated films were let to dry at ambient conditions.

Tensile Properties. Tensile strength, elongation, Young's modulus, and toughness were measured with an Instron testing system (model 1011, Instron Engineering Corp., Canton, MA) following the ASTM Standard Method D638-91 (*28*). Zein films were cut into dumbbell-shape specimens of Type I dimensions (*28*), taking one specimen per film. Film thickness was measured with a dial gauge micrometer (B. C. Ames Co., Waltham, MA). Films were preconditioned at 23 °C and 50% RH for 48 h prior to testing. The Instron machine was set to an initial grip separation of 115 mm and an extension rate of 5 mm/min. Five replicates were run for each film treatment.

Density Determination. Density of the zein films was determined from the weight, measured in a nanogram-precision balance, and thickness of samples cut out with a circular punch (1 cm diam).

Water Vapor Permeability. Water vapor permeability of zein films was determined according to the ASTM E 96-95 desiccant method (*29*). Anhydrous calcium sulfate was used to maintain a 0% RH atmosphere inside the cells. A saturated solution of potassium sulfate placed in a sorbostat was used to maintain the relative humidity outside the cells at 97.3 ± 0.5%. Test cells were placed in the sorbostat and kept at 25 °C. Water vapor transmission was monitored by weight. Five replicates of each type of film were tested.

Oxygen and Carbon Dioxide Permeability. Oxygen and carbon dioxide permeability determination was based on the isostatic method ASTM D 3985 (*30*). The experimental setup consisted of two stainless steel chambers (58 cm^3 each) separated by the test film (permeating area of 46.35 cm^2). O_2 or CO_2, at 20 kPa, filled one of the chambers while N_2 was kept at the same pressure in the other chamber. A hermetic closure was kept between the chambers. A dual headspace analyzer (Mocon Pac Check 650, Modern Control, Inc., Minneapolis, MN) was employed to monitor O_2 or CO_2 in the N_2 chamber. O_2 or CO_2 concentrations were plotted against time. Permeability was calculated from the linear data corresponding to the steady-state transfer of permeant gas. The expression used was $p = Q{\cdot}l/A{\cdot}t{\cdot}\Delta P$, where p was O_2 or CO_2 permeability, Q was quantity of permeant, l was film thickness, A was area of permeation, t was permeation time, and ΔP was the partial pressure difference of the permeant across the film. Permeability was expressed in $cm^3{\cdot}cm/cm^2{\cdot}s{\cdot}Pa$.

RESULTS AND DISCUSSION

Effect of Lamination. Fusion-laminated zein films were clearer, tougher, and more flexible, and had a smoother finish than nontreated sheets. Tensile properties of laminated films are shown in Table 1. Results indicated that the heat and pressure treatment applied in the lamination process had a limited effect on tensile properties of films. No significant ($P > 0.05$) differences in tensile strength, elongation, or toughness were found between the original film and the heat-treated ones up to 2-ply sheets. At 3 and 4 ply, significant differences were found in all properties. Tensile strength and elongation increased slightly, toughness increased 3-fold, and Young's modulus decreased by 3-fold. The lamination process apparently induced melting and flow of film material, eliminating pinholes and cracks in the film matrix, and also filling in the planar voids observed by X-ray scattering in the control film (*16*). Elimination of voids and defects possibly contributed to the improvement on tensile properties. It may also have contributed to the increase in film density, shown in Table 2, as the ply number increased.

Gas and water vapor permeability values of laminated zein films are shown in Table 2. O_2 and CO_2 perme-

Table 1. Tensile Properties of Laminated Zein Films[a]

treatment	thickness mm	tensile strength MPa	elongation %	Young's modulus MPa	toughness MPa
no heat treatment	0.035	2.08 ± 0.27 b	15.8 ± 3.11 c	328 ± 90.1 a	0.25 ± 0.04 c
heat treated, 1 sheet	0.030	2.10 ± 0.38 b	16.2 ± 1.89 c	264 ± 33.4 b	0.28 ± 0.08 c
laminated, 2 ply	0.056	2.12 ± 0.37 b	16.2 ± 1.35 c	241 ± 24.2 c,b	0.29 ± 0.05 c
laminated, 3 ply	0.058	2.96 ± 0.36 a	20.3 ± 2.79 b	185 ± 19.0 c	0.49 ± 0.09 b
laminated, 4 ply	0.060	3.17 ± 0.49 a	26.4 ± 4.54 a	104 ± 8.08 d	0.66 ± 0.18 a

[a] Means with the same letter are not significantly different ($P > 0.05$).

Table 2. Density, Oxygen Permeability, Carbon Dioxide Permeability, and Water Vapor Permeability of Laminated Zein Films[a]

treatment	density g/cm^3	O_2 permeability 10^{-14} cm^3·cm/cm^2·s·Pa	CO_2 permeability 10^{-14} cm^3·cm/cm^2·s·Pa	water vapor permeability pg/Pa·s·m
no heat treatment	1.00 c	1167 a	526 a	17.97 a
heat treated, 1 sheet	1.04 b	1056 b	451 a, b	17.89 a
laminated, 2 ply	1.06 b	807 c	391 b	17.88 a
laminated, 3 ply	1.08 b	320 d	190 c	17.50 a
laminated, 4 ply	1.12 a	N.A.	N.A.	16.55 b

[a] Means with the same letter are not significantly different ($P > 0.05$).

Table 3. Tensile Properties and Water Vapor Permeability of Coated Zein Films[a]

coating	tensile strength MPa	elongation %	Young's modulus MPa	toughness MPa	water vapor permeability pg/Pa•s•m
no coating	2.09 ± 0.27 d	15.8 ± 3.11 c	328 ± 90.1 a	0.25 ± 0.04 b	17.97 a
coated w/tung oil	4.10 ± 0.77 b	19.3 ± 5.86 b, c	200 ± 50.6 b	0.70 ± 0.14 b	1.43 d
coated w/linseed oil	2.87 ± 0.56 c	77.5 ± 7.62 a	75 ± 11.2 c	1.97 ± 0.64 a	4.18 c
coated w/tung and soybean oils mixture	5.95 ± 0.48 a	25.2 ± 3.38 b	180 ± 38.9 b	0.68 ± 0.33 b	5.26 b

[a] Means with the same letter are not significantly different ($P > 0.05$).

Table 4. Gas Permeability of Zein Films Coated with Tung Oil[a]

treatment	O_2 permeability 10^{-14} cm^3·cm/cm^2·s·Pa	CO_2 permeability 10^{-14} cm^3·cm/cm^2·s·Pa
no lamination, no coating	1167 a	526 a
no lamination, coated	1002 a	514 a
laminated, no coating	319 b	190 b
laminated, coated	255 b	150 b

[a] Means with the same letter are not significantly different ($P > 0.05$).

ability decreased with the number of sheets laminated together. Elimination of voids and defects during the lamination process may have contributed to the observed decrease in gas permeability. Zein films were more permeable to O_2 than to CO_2, possibly because of the ability of oleic acid to absorb oxygen (*14*). On the other hand, water vapor permeability did not decrease appreciably with lamination. Results suggested that water vapor followed a transmission mechanism different from that of O_2 or CO_2. Regardless of voids and defects, water vapor hydrated the protein and traversed the thickness of film by migrating through the zein layers.

Effect of Coating. Table 3 shows the effect of coating on tensile properties of zein films. Significant ($P < 0.05$) differences were found between noncoated and coated films on most properties for the three types of coatings. Linseed oil had the most pronounced effect on tensile strength, elongation, Young's modulus, and toughness. It was suggested that coatings acted as a composite layer on zein films, preventing crack propagation and increasing film strength. Table 3 also shows the effect of coating on water vapor permeability. All coatings substantially improved water barrier properties of films, with tung oil finish having the most pronounced effect. Coatings provided a highly hydrophobic surface, thus preventing films from wetting. Coatings retarded wetting for from a few hours to 21 days at 98% RH. The results of gas permeability determination on coated zein films are shown in Table 4. Results indicated that coating had no significant ($P > 0.05$) effect on gas permeability. Polymerized drying oils were not effective barriers to gas transport.

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