

Water Vapor Barrier Properties of Zein Films Plasticized with Oleic Acid

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ABSTRACT

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Water sorption, water vapor permeability, and tensile properties were evaluated for zein films plasticized with oleic acid. The effect of relative humidity on water vapor permeability and tensile properties of films was investigated. Samples were produced by two different methods: casting from a zein solution and stretching from a zein-fatty acid resin. Films were also coated with linseed oil. Results indicated that preparation method affected water sorption and permeability of zein films. Resin films showed lower water sorption than cast films, especially at high A_w values. Water vapor permeability was also lower for resin films. Coating with linseed oil further improved water vapor barrier ability of resin

films. Permeability was affected by environmental relative humidity; higher relative humidity resulted in increased permeability. Environmental relative humidity also affected tensile properties of resin films. Toughness and elongation were improved when relative humidity increased from 50 to 85% rh. Tensile strength showed a maximum at 75% rh. Coating improved elongation and toughness of films. Maximum elongation and toughness were observed for coated samples at 85% rh. Zein resin films showed good tensile and water barrier properties that were maintained through environmental humidity levels from 50 to 98% rh.

Sorption and permeation of fluids, particularly water, are of practical importance in considering materials for packaging uses. The ability to provide a moisture barrier is required in many applications, especially food packaging. Plastic materials exhibit low densities as a result of an open molecular structure that also allows small molecules to pass through the structure without being affected by the diffusion process. Permeation is the rate at which a gas or vapor passes through a polymer. The mechanism by which permeation takes place involves three steps: 1) absorption of the permeating substances into the polymer; 2) diffusion of the permeating species through the polymer, traveling along the concentration gradient; and 3) desorption of the permeating species from the polymer surface and evaporation or removal by other mechanism (Sperling 1992).

Composition and morphology play a significant role in determining the sorption and transport properties of plastics. Factors with the most influence fall into two categories: those relating to the chemical composition and structure of the polymer, such as degree of saturation, presence of side chains, and crosslinking; and those that involve heterogeneities in the polymer such as orientation, crystallinity, and the presence of plasticizers and fillers (Felder and Huvard 1980). Plasticizers are added to polymers to reduce brittleness. They work as spacers between polymer chains decreasing intermolecular forces and thus increase flexibility and extensibility of polymers. However, addition of plasticizers usually increases permeability of gases and water vapor due to an increase in free volume between chains (Gontard et al 1993, Cherian et al 1995). The introduction of a plasticizer into a polymer, either during fabrication or subsequently by permeation, increases the mobility of chain segments and consequently increases the effective diffusion coefficient of permeates. In most cases, the rate of permeation is closely related to the mobility of the polymer chains and free volume of chain segments (Seymour and Carraher 1984).

Permeability (P) is a common measure of the ease a material can be penetrated by the permeates. It is defined by ASTM E 96-95 (ASTM 1995a) as the transfer of an amount (q) of substance through a barrier of thickness (d) and area (A) in time (t) under a driving pressure gradient (Δp). While there are many dimensions and units found in literature for permeability, the preferred current dimensions are (Sperling 1992): $P = (\text{quantity of permeant}) \times (\text{film thickness}) / (\text{area} \times (\text{time}) \times (\text{pressure drop across the film}))$.

Barrier characteristics of plastics may be expressed in reference to three coefficients: 1) S solubility constant, 2) D diffusion coef-

ficient, and 3) P permeability coefficient, related as $P = S \times D$. Permeation is therefore a function of both the solubility of the sorbant gas and its diffusion rate across the barrier (Brown 1993).

The application of protective biopolymer films to maintain or improve food quality, stability, and safety has been reviewed in detail (Guilbert 1986, Kester and Fennema 1986, Gennadios et al 1994, Torres 1994, Krochta and de Mulder-Johnston 1997). Several commercial films are derived from proteins, including collagen for sausage casings, gelatin for pharmaceutical capsules, and zein-based coatings for nuts and candies (Alikonis and Cosler 1961, Andres 1984). However, protein films are generally poor water vapor barriers due to their inherent hydrophilic character (Krochta 1992).

Lipids have been added to biopolymer film-forming formulations to improve barrier performance of films. Kamper and Fennema (1984, 1985) developed a fatty acid-hydroxypropyl methylcellulose (HPMC) film which provided considerable protection against moisture transmission at relative humidities up to $\approx 90\%$ rh. Also, to reduce water permeation, film surfaces were coated with lipid materials (Labuza and Contreras-Medelin 1981). Solid fatty acids such as palmitic and stearic acid have been proposed to form protective layers on casein and cellulose-based films (Park et al 1994a,b; Park et al 1996). Solid fatty acid molecules tend to pack tightly and regularly on film surfaces, thus allowing little water passing through films. However, they are sensitive to temperature, lack supporting strength, and are difficult to apply (O'Donnell 1996). Vegetable oils from linseed, perilla, fish, or soybean can also form resistant coating layers on films. Lai et al (1997) employed heated linseed oil as coating for zein-based sheets. After coating, water absorption of zein sheets was substantially decreased. Microstructure images showed that cracks and pores on sheets were sealed off by the oil coating.

Zein was investigated for its potential use as structural material in packaging applications (Lai and Padua 1997, Lai et al 1997). Film-forming properties of zein have long been recognized (Reiners et al 1973) and they are the basis for its commercial utilization (Winters and Deardorff 1958, Kanig and Goodman 1962, Mendoza 1975, Andres 1984). Recent interest in the development of edible and biodegradable films has driven research on the formation of free-standing zein films for food and packaging applications (Guilbert 1986, Aydt and Weller 1988, Aydt et al 1989, Gennadios and Weller 1990, Gennadios et al 1993, Gennadios and Weller 1994, Wu 1995, Krochta and de Mulder-Johnston 1997). One method employed by researchers for preparing zein films involves casting of zein alcoholic solutions on inert surfaces. Films are formed after solvent is evaporated. Plasticizers are usually added to the solution to increase film flexibility. Commonly used plasticizers are liquid organic compounds such as polyols, mono-, di-, or oligosaccharides, lipids, and lipid derivatives

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(Reiners et al 1973). Oleic acid was used by Kanig and Goodman (1962) to plasticize zein films. Yoshimoto and Sato (1994) considered that the liquid crystalline state of oleic acid at room temperature contributed to the flexibility and fluidity of membrane structure. Lai and Padua (1997) reported a novel method for preparing zein films. They plasticized zein with oleic acid to form an intermediate moldable resin. The moldable resin was stretched over rigid frames to form thin membranes that set into flexible films. Resin films were ductile and tough. The microstructure images showed a high degree of structural development consisting of fibers and ribbon-like protein structures thought to be responsible for the flexibility and toughness of the films.

The objective of this study was to investigate the water sorption and water vapor barrier properties of zein films drawn from zein resins. Films were plasticized with oleic acid, and a subgroup of films was coated with linseed oil. The high content of linolenic acid in linseed oil was expected to polymerize in air and form tough coating layers on films.

MATERIALS AND METHODS

Materials

Zein, regular grade (F4000, lot F4000318C, Freeman Industries, Inc., Tuckahoe, NY) with a moisture content of 5.29% was used. Reported protein content for F4000 zein was 90–96% (dry basis). Other materials included: oleic acid (C_{18:1}), 90% (Aldrich, Milwaukee, WI); calcium nitrate, calcium sulfate, magnesium chloride, magnesium nitrate, sodium chloride, potassium acetate, potassium carbonate, potassium chloride, and potassium sulfate, reagent grade (Fisher Scientific, Fair Lawn, NJ); potassium iodide, reagent grade (EM Science, Gibbstown, NJ); lithium chloride, reagent grade (Mallinckrodt Inc., St. Louis, MO); ethyl alcohol (Midwest Grain Products Co., Pekin, IL); linseed oil (code no. 1601) (Seymour Organic Foods, Seymour, IL).

Film Preparation

Films were prepared by casting zein-oleic acid emulsions or by stretching zein-oleic acid resins. Zein emulsions were prepared by dissolving zein in 75% (v/v) warm ethanolic solutions and stirring in oleic acid to a mass ratio of 0.5 g of fatty acid/g of zein. Emul-

sions were cast on inert surfaces to a thickness of ≈ 1 mm. Films were allowed to dry at room conditions and peeled off after 24 hr. Resin films were prepared by precipitating zein-oleic acid emulsions, prepared as described above, with cold water. The soft precipitated resin was stretched over the rims of containers (16 cm diameter) and allowed to dry at room conditions. A subgroup of the resin films was coated with linseed oil that had been heated to 230°C for 1.5 hr. After cooling the oil to room temperature, film samples were dipped in for coating. Samples were allowed to dry at room temperature. Film thickness was measured with a dial gauge micrometer (B. C. Ames Co., Waltham, MA) to the nearest 0.001 mm. Thickness values for each film represent an average of 10 measurements.

Tensile Tests

Tensile strength, elongation, Young's modulus, and toughness were measured with an Instron testing system (model 1011, Instron Engineering Corp., Canton, MA). Tensile tests were performed according to ASTM Standard Method D 638-91 (ASTM 1994). Sample films were cut in dumbbell shapes and conditioned at 50, 75, 85, and 98% rh and 25°C for 48 hr before tensile tests were performed. Constant relative humidity environments were established inside sorbostats employing saturated salt solutions of calcium nitrate, sodium chloride, and potassium sulfate (Greenspan 1977, Wolf et al 1984, Aydt et al 1991). Film samples were assumed to have an A_w value corresponding to the relative humidity of the sorbostat and to reach an equilibrium moisture content within each sorbostat. Film strips were placed in pneumatic grips on the testing machine. Initial grip separation was 115 mm and crosshead speed was 5 mm/min.

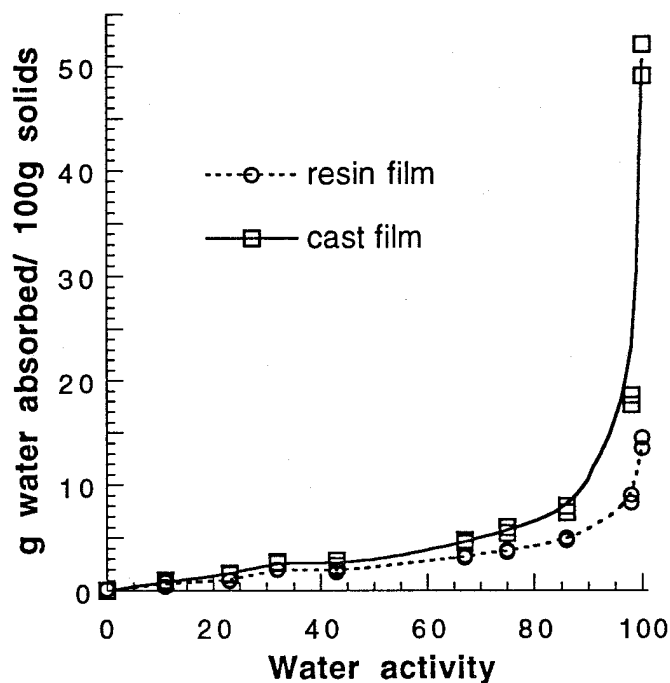


Fig. 1. Moisture sorption isotherms of zein-oleic acid films.

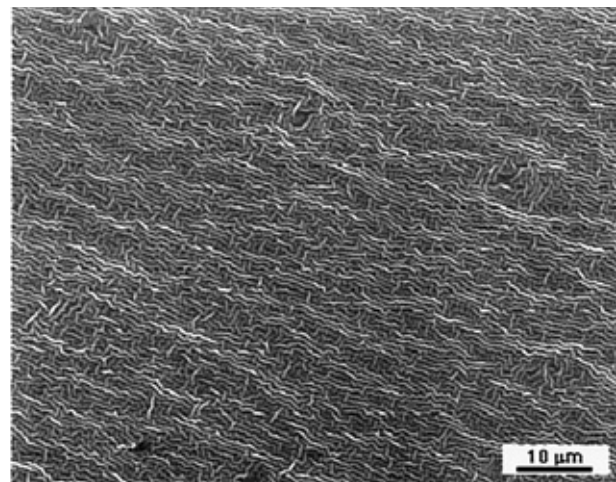


Fig. 2. Scanning electron micrograph of zein-oleic acid resin films showing structural orientation.

TABLE I
Water Vapor Barrier Properties of Zein-Oleic Acid Films Prepared by Different Methods^{a,b}

Preparation Method	Thickness (μm)	Water Vapor Permeability ^c
Casting (smooth) ^d	70.2 (4.93)	23.11a (2.39)
Casting (dull) ^e	63.4 (9.92)	18.26b (3.07)
Resin	36.7 (8.4)	12.20c (0.79)
Coated	47.7 (8.7)	7.86d (0.79)

^a Values in parentheses are standard deviations. Values within columns followed by different letters are significantly different at the 95% confidence level (Duncan's protected least significant difference).

^b Measured at 53% rh and 25°C.

^c Picograms per (Pa \cdot sec \cdot m).

^d Smooth surface of films facing the "wet" side of the testing chamber.

^e Dull surface of films facing the "wet" side of the testing chamber.

Moisture Absorption

Constant relative humidity environments from 0 to 98% rh were established inside sorbostats using saturated salt solutions according to Greenspan (1977) and kept at $20 \pm 1^\circ\text{C}$. Distilled water was used for 100% rh. Film samples were cut into small pieces ($\approx 5 \times 10$ mm) and brought to 0 moisture content by freeze-drying at -75°C and 2.68 Pa (20 milli Torr) for 24 hr (Freezemobile 12, The Virtis Co., Gardiner, NY) before placing them in sorbostats (Gennadios and Weller 1994). Sample weight was recorded to the nearest 0.0001 g after the first two days and every day thereafter until equilibrium. Equilibrium was assumed to have been reached when the change in moisture content of samples was <0.001 g of water/g of dry matter (Labuza 1984). Adsorption tests were done in duplicate for each group.

Water Vapor Barrier Properties

Water vapor barrier properties of zein-fatty acid films were determined gravimetrically according to the desiccant method described by ASTM E 96-95 (ASTM 1995b). The method involves sealing a known open area of an impermeable container with the film being tested. Test cells employed were 6.5 cm (i.d.), 7.0 cm (o.d.), and 3.2 cm in height. Anhydrous calcium sulfate was used to maintain 0% rh inside the cell. Saturated solutions of magnesium nitrate, sodium chloride, and potassium sulfate were placed in sorbostats to maintain relative humidities of 53, 75, and 98% rh, respectively, outside the cells. Test cells were stored in these sorbostats at 25°C . Weight gains were plotted versus time. When a straight line adequately fitted at least six points of the plot, a nominal steady state was assumed. The slope of the straight line divided by test area was the rate of water vapor transmission (WVT). Water vapor permeability (WVP) was calculated from WVT as: $\text{WVP} = [\text{WVT}/S(R_1 - R_2)] \times d$, where S = saturation vapor pressure at test temperature (mmHg or Pa); R_1 = relative humidity in the test chamber; R_2 = relative humidity inside the cell (which equals 0%

TABLE II
Effect of Relative Humidity and Linseed Oil Coating on Water Vapor Permeability (WVP) of Zein-Oleic Acid Films Prepared from Resin Method^{a,b}

Film Treatment	% rh	Thickness (μm)	WVP ^c
Without coating	53	36.7 (8.4)	12.2a (0.79)
	75	27.1 (6.5)	14.3a,b (2.21)
	98	50.2 (9.5)	16.6b (0.81)
With coating	53	31.6 (2.0)	7.86a (0.79)
	75	29.7 (0.9)	13.2b (0.56)
	98	40.2 (7.6)	14.2b (3.16)

^a Values in parentheses are standard deviations. Values within columns followed by different letters are significantly different at the 95% confidence level (Duncan's protected least significant difference).

^b Measured at 25°C .

^c Picograms per ($\text{Pa} \cdot \text{sec} \cdot \text{m}$).

TABLE III
Water Vapor Permeability (WVP) of Selected Film Materials

Materials	Method	WVP	Test Conditions ^a
Zein-oleic acid ^b	Resin stretching	12.2	25°C , 0–50% rh
Amylose ^c	Casting	330	27°C , 1–100% rh
Hydroxymethylcellulose, stearic acid ^d	Emulsion casting	8.0	27°C , 0–85% rh
Wheat gluten, glycerin ^e	Emulsion casting	620	21°C , 0–85% rh
Cellophane ^f	Extrusion	84	38°C , 0–90% rh
Low density polyethylene ^g	Extrusion	0.12	35°C , 0–90% rh

^a Test temperature and relative humidity range.

^b Average of the measurements from two-sided testing (see Table I).

^c Data from Rankin et al (1958). Laboratory-prepared samples.

^d Data from Heagenmaier and Shaw (1990). Laboratory-prepared samples.

^e Data from Park and Chinnan (1990). Laboratory-prepared samples.

^f Data from Taylor (1986). Commercial samples.

^g Data from Hanlon (1992). Commercial samples.

in the desiccant method); and d = film thickness. Storage temperatures of 5, 15, 25, and 35°C were adjusted by incubators to study the effect of temperature on WVP of films. Relative humidity (and saturated water vapor pressure) of a saturated magnesium nitrate solution at those temperatures were 59% (6.54 mmHg), 56% (12.79 mmHg), 53% (23.76 mmHg), and 50% (42.18 mmHg), respectively (Greenspan 1977). A minimum of five replicates at each temperature were tested for WVP.

Scanning Electron Microscopy

Film samples were loaded on aluminum specimen mounts with double-coated carbon conductive tapes (Ted Pella, CA) then coated with 60% gold and 40% palladium with 35 mA current in a sputter coater (Polaron SEM Coating System) for 1 min. Samples were observed by scanning electron microscopy (DSM 960, Zeiss, Germany) using an accelerating voltage of 7 kV.

Statistical Analysis

Statistical analysis was performed using the SAS version 6.09 (SAS Institute Inc., Cary, NC). Curve fitting of data was performed by using KaleidaGraph version 3.0 (Synergy Software, PCS Inc., Reading, PA).

RESULTS AND DISCUSSION

Moisture Sorption Isotherms

Moisture sorption isotherms for cast and resin-formed zein-fatty acid films are shown in Fig. 1. Equilibrium was assumed after a week of storage at 20°C . For cast films, very little moisture was gained until $A_w > 0.6$. In the 0.6–0.85 range, moisture absorption was still limited. At $A_w > 0.9$, moisture sorption increased substantially. Results of moisture sorption of cast films were similar to those reported by Gennadios and Weller (1994) and Wu (1995). In their studies, all grain protein films prepared by casting solutions on flat surfaces absorbed a considerable amount of moisture at $A_w > 0.8$. However, the water sorption isotherm of cast zein-fatty acid films was not the sigmoidal curve typical of food systems. Instead, it resembled the sorption isotherm of crystalline sugars, which also shows very little moisture gain for $A_w < 0.7$ –

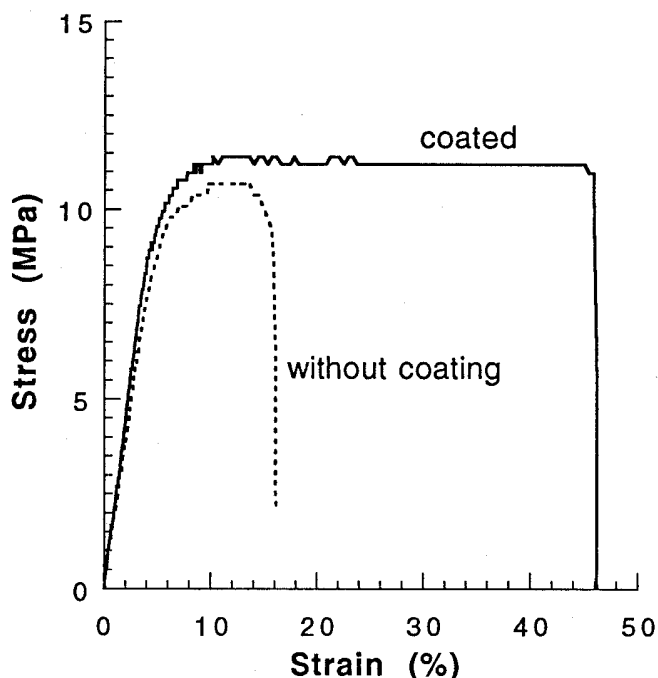


Fig. 3. Typical tensile stress-strain curves of zein-oleic acid resin films with and without coating.

0.8 (Labuza 1984). This behavior was attributed to the hydrophobic character of zein (Gennadios et al 1994) that resulted in lower moisture absorption for zein films than for other hydrophilic films.

Resin films showed similar moisture sorption trends to those of cast-produced films, however, they had lower absorption in the A_w range of 0.75–0.98. Results suggested that besides the chemical nature of the material, preparation method affected moisture sorption of zein films. Sorption phenomenon explains the initial penetration and dispersion of permeate molecules into the polymer matrix and includes both adsorption and absorption. Sorption depends on the relative strength of the interactions between the permeate molecules and the polymer or among the permeate molecules themselves (Robertson 1993). It has been proposed that sorption of permeates is closely related to polymer structure. For polymer materials of crystalline or highly oriented structure, where polymer chains are closely packed, sorption, and dissolution of permeates into the polymer matrix is difficult. Unlike cast-produced films, resin films observed under scanning electron microscopy presented an oriented microstructure consisting of closely packed ribbon-like structures (Fig. 2). Orientation in resin films was thought responsible for the lower water absorption with respect to cast films.

Water Vapor Barrier Properties

Water vapor permeability measurements on cast and resin zein films are reported in Table I. Because cast films presented different surface finishes on each side of the film, permeability through each side was evaluated. Smooth finished surfaces were considered to be formed of protein, while the dull finish side was thought to contain high amounts of lipids (Lai and Padua 1997). When films were placed with the dull side facing the salt solutions (higher relative humidity), the WVP was lower. This behavior was attributed to low water vapor adsorption on the lipid surface. Phase separation of protein-lipid emulsion films was observed by McHugh and Krochta (1994a,b). Casting of unstable solutions resulted in lipid concentration gradients across the film thickness, which caused differences in WVP from one side of the film to the other (Torres 1994).

Resin films showed lower permeability than cast films that was consistent with their lower water absorption. Decreased permeability of resin films with respect to cast samples may have been

the result of microstructure orientation (Fig. 2). Coated films showed better barrier properties than noncoated samples. WVP was decreased considerably after coating. Heated linseed oil may have slowed down water permeability by decreasing the adsorption of water molecules on the film surface.

Effect of Relative Humidity on WVP

The effect of relative humidity on WVP of zein-oleic acid resin films is summarized in Table II. Water vapor permeability increased with relative humidity for coated and noncoated samples likely driven by increasing vapor pressure differences between the two sides of the films. Also, water sorption of biopolymer often results in swelling and conformational changes. Absorbed water plasticizes the film matrix and increases its permeability (Park et al 1994a). Coating with linseed oil reduced permeability over the relative humidity range tested. However, coating was less effective at high relative humidity. This effect was attributed to film swelling upon water absorption. Swelling might have impaired the coating integrity thus exposing the film matrix to the highly moist air. Water vapor permeability of selected film materials is listed in Table III. The WVP of zein-oleic acid resin films was higher than most synthetic polymeric films including low density polyethylene. However, the WVP of resin film was considerably lower than that of many biopolymer-based films, for example, glycerin-plasticized wheat gluten films and amylose films, as indicated in Table III. The WVP of zein-oleic acid resin films was also lower than that of cellophane, a cellulose-derived film commonly used in food packaging.

Effect of Relative Humidity on Tensile Properties

Tensile properties of zein-fatty acid films at different relative humidity conditions are listed in Table IV. Tensile strength of coated and noncoated films increased as relative humidity increased from 50 to 75% rh. Elongation also increased as relative humidity increased from 50 to 84% rh. Young's modulus decreased continuously as relative humidity increased. Toughness showed a maximum at 85% rh for both coated and noncoated samples. Films conditioned at 98% rh became curled at the edges and soggy. In agreement with the study of Gennadios et al (1993), moisture absorption at high relative humidity hydrated the film and caused early failure on tensile tests.

TABLE IV
Tensile Properties of Zein-Oleic Acid Resin Films With and Without Coating at Various Relative Humidity Levels^a

Treatment	% rh	Thickness (μm)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)	Toughness (MPa)
Without coating	50	37.7a (5.9)	8.7d (1.0)	11.9d (3.1)	267.2a (46.4)	0.8e (0.2)
	75	29.0b (4.1)	10.0b,c (1.3)	12.9d (3.6)	232.8b,c (29.3)	1.1e (0.3)
	85	37.1a (3.3)	8.0d (2.1)	32.7b,c (7.4)	179.2d,e (27.3)	2.3c (0.5)
	98	35.1a (7.8)	8.0d (1.38)	28.4c (12.4)	155.7e (27.1)	2.1c,d (0.8)
With coating	50	38.4a (5.8)	9.1c,d (1.9)	15.1d (4.2)	216.4b,c (39.0)	1.3d,e (0.5)
	75	38.9a (6.5)	11.5a (0.9)	41.1b (5.4)	240.1a,b (42.4)	4.7b (1.2)
	85	33.8a (7.8)	10.4a,b (1.1)	67.5a (20.8)	206.1c,d (29.8)	5.9a (1.9)
	98	33.8a (7.1)	10.1b,c (1.9)	35.6b,c (13.3)	170.3e (45.6)	2.7c (0.8)

^a Values in parentheses are standard deviations. Values within columns followed by different letters are significantly different at the 95% confidence level (Duncan's protected least significant difference).

TABLE V
Analysis of Variance for Effects of Coating (COAT) and Relative Humidity (RH) on Tensile Properties of Zein-Oleic Acid Films

Source	Degrees of Freedom	P Values ^a			
		Tensile Strength	Elongation	Young's Modulus	Toughness
COAT ^b	1	0.0001*	0.0001*	0.9484	0.0001*
RH ^c	3	0.0001*	0.0001*	0.0001*	0.0001*
COAT × RH	3	0.0411*	0.0001*	0.0002*	0.0001*

^a * = Significant at 0.05 level.

^b With and without heated flax oil coating.

^c 53, 75, 85, and 98% rh.

TABLE VI
Effect of Temperature on Water Vapor Permeability (WVP) of Zein-Oleic Acid Films Prepared by Resin Method^a

Temperature (°C)	Thickness (μm)	WVP ^b
5	33.4 (4.3)	46.39a (11.4)
15	37.2 (5.1)	29.78b (13.3)
25	38.6 (6.6)	12.20d (0.79)
35	35.5 (5.9)	17.22c (0.98)

^a Values in parentheses are standard deviations. Values within columns followed by different letters are significantly different at the 95% confidence level (Duncan's protected least significant difference).

^b Picograms per (Pa*sec*m).

Tensile strength was higher for coated films at the various levels of relative humidity. Elongation percent, indicative of ductility, was also substantially increased after coating. There was no clear effect of coating on Young's modulus of films. However, the toughness of films was greatly improved by coating. Flax oil has long been used in the paint and varnish industry as drying oil. Drying oils dry in air, forming tough insoluble coatings. The basic mechanism of coating formation involves polymerization of unsaturated fatty acids in the presence of oxygen. Polymerized coatings are elastic and flexible, which might be the reason of increased strain for coated films.

Typical stress-strain diagrams of films with and without coating are shown in Fig. 3. Both plots were essentially linear at low strains and showed elongation with stable stresses. Coated samples showed higher elongation than noncoated samples. The observed instability in the stress-strain curve of the coated film maybe due to an early failure of the zein-oleic film while elongation of the coating still proceeded. The polymeric film from flax oil may have formed crazes that absorbed energy before failure of films. This phenomenon is reported for many highly cross-linked rubber materials. Crazes, in most cases, effectively increase toughness and affect strength of materials (Birley et al 1991).

Analysis of variance on the effect of coating and environmental relative humidity on tensile properties of resin films is presented in Table V. Coating films with linseed oil significantly increased the tensile strength, elongation, and toughness. Coating did not affect film stiffness as indicated by Young's modulus. Tensile properties measured were significantly affected by environmental relative humidity. The interaction between coating and relative humidity was also significant in that coating was more effective at low relative humidity.

Effect of Temperature on WVP

Water vapor permeability measurements on zein resin films were performed at different temperatures. Results are listed in Table VI. WVP was higher at 35°C than it was at room temperature. Polymer films often show an increase in WVP with temperature resulting from a higher coefficient of diffusion due to increased molecular mobility of plasticizers and polymer chains. Kester and Fennema (1989) reported a positive activation energy for water permeation through a lipid-and-cellulose composite film. However, WVP also increased when temperature was lowered to 5°C. This effect may be related to water condensation on the films surface that plasticized the protein and thus increased permeability. Higher WVP of synthetic and biopolymer-based films at low temperature has been reported. Karel et al (1959) studied the effect of temperature on WVP of commonly used food packaging materials and found the WVP of polyethylene was nearly the same at 30°C as at 2°C. Kamper and Fennema (1984) found that the WVP of C₁₈-C₁₆ HPMC films increased six times when temperature decreased from 25 to 5°C. Similar phenomena was observed for C₁₈-C₁₆ MC/HPMC films (Kester and Fennema 1989), which the authors attributed to minor defects in the film due to lipid contraction at low temperatures.

CONCLUSIONS

Preparation method affected water sorption and WVP of zein films. Resin films showed lower water sorption than cast films, especially at high A_w values. Water vapor permeability was also lower for resin films. Increased water barrier properties for resin films were attributed to microfibril formation and orientation. Coating with linseed oil further improved water vapor barrier ability of resin films. Permeability was affected by environmental relative humidity. High relative humidity resulted in increased permeability. Coating delayed water sorption though WVP followed a similar trend with respect to relative humidity to that observed for noncoated samples. Water vapor permeability increased with temperature. How-

ever, high WVP values were observed at refrigeration temperatures, perhaps due to water condensation on the surface of films. Condensed water plasticized the films thus increased permeability.

Environmental relative humidity affected tensile properties of resin films. Toughness and elongation were improved when relative humidity increased from 50 to 85% rh. Tensile strength showed a maximum at 75% rh. Coating improved elongation and toughness of films possibly by absorbing tensile stress and delaying failure. Maximum elongation and toughness were observed for coated samples at 85% rh. Zein resin films maintained good tensile and water barrier properties through environmental humidity levels from 50 to 98% rh. Water barrier properties of zein resin films indicated their potential application as biodegradable packaging materials.

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