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Properties of Zein Films Coated with Drying Oils

QIN WANG AND GRACIELA W. PADUA*

Department of Food Science and Human Nutrition, University of Illinois, 382/D AESB, 1304 West Pennsylvania Avenue, Urbana, Illinois 61801

Zein films prepared by resin were coated with either flax oil or tung oil and cured by UV- or γ-radiation. Coated zein films were then evaluated for tensile and water barrier properties. Film microstructure was examined by transmitted light microscope. Tensile strength, elongation, and toughness of oil-coated samples increased substantially with respect to uncoated films. Flax oil coated samples showed an increase in elongation of 300%. It was suggested that oil coatings fill in pinholes and cracks existing in zein films, affecting their mechanical properties. Water vapor permeability also decreased statistically for coated film (except for tung oil coated−UV treated films), suggesting water vapor transfer was controlled by film hydrophobicity and microstructure. Moreover, the liquid water transmission rate of coated films was at least 10 times slower than for control films. Examination of film microstructure revealed that flax oil coatings had uniform coverage and smooth finish, which explained their high elongation, low water vapor permeability. Tung oil coatings cured under UV light showed patterns of intertwined dark and light regions, which may be caused by cross-linking and drying at different times. The oriented structures were found when tung oil coatings were cured by γ-radiation.

KEYWORDS: Zein; protein films; linseed oil; tung oil; biodegradable plastics; water vapor permeability

INTRODUCTION

Biobased biodegradable plastic films can be prepared from zein, a major protein in corn endosperm. Considerable research on the formulation and processing of zein-based plastic films has been reported (*1*−*3*). According to those reports zein forms reasonably strong and elastic films. However, although water barrier properties of zein films are superior to other protein films (*4*), they are inferior to those of synthetic plastics (*5*, *6*), especially when in contact with liquid water. Zein films are well-suited for food service applications where short service life is expected. However, longer or controlled time serviceability, for example, food packaging, horticultural covers, and consumer products, require further development.

Drying oils can be defined as liquid vegetable oils that when applied in thin layers to a nonabsorbent substrate, will dry in air to form a solid film. Drying is the result of polymerization brought about by a series of chemical reactions triggered by light and aided by atmospheric oxygen (autoxidation). The resulting film is typically hard, nonmelting, and usually insoluble in water. Two common drying oils are linseed oil and tung oil, which are extracted from flaxseed and the seed kernels of tung trees, respectively. Increasing production and availability make them practical for use in coating formulations even though their price is higher than that of soybean oil. Linseed oil contains triglycerides with nonconjugated fatty acids whose double bonds are separated by at least two single bonds. Tung oil contains triglycerides with conjugated fatty acids whose double bonds are partly or fully conjugated. Conjugated double bonds, being considerably more reactive than the nonconjugated, favor polymerization, and oils with conjugation dry more rapidly than nonconjugated oils (*7*). Resultant films offer increased resistance to water and alkalis. It was reported that zein films coated with tung oil finish or linseed oil finish exhibited higher resistance to water vapor (*8*−*9*). Also Kraft paper coated with oxidatively polymerized linseed oil had higher tensile strength and could be used as mulch for preventing weed growth (*10*). In the paint industry, drying oils are often pretreated by adding driers, applying heat, or blowing air while applying heat to promote oxidation and fasten the polymerization process. However, driers may be toxic; for example, cobalt and manganese salts (*11*) or high thermal treatments may generate toxic compounds (*12*). Coatings from drying oils without pretreatment usually take several days to dry in air. Therefore, finding safe and effective ways to cure oil coatings is of practical importance. UV radiation was reported as an accelerator of linseed oil curing (*13*). It is also well-known that γ-radiation promotes lipid oxidation in foods by generating free radicals (*14*). Therefore, it could be expected to speed up the initial step of polymerization of drying oils. In this work, zein films were coated with flax and tung oils and treated with UV- or γ-radiation to promote curing. The effect of coating on tensile and water barrier properties of zein films was evaluated.

MATERIALS AND METHODS

Chemicals. Zein was regular grade F4000 (lot no. F4000318C, Freeman Industries, Inc., Tuckahoe, NY). The reported protein content was 90−96% (dry base). The lipid content was 1.18%. Other chemicals

* To whom correspondence should be addressed. Telephone: (217) 333-9336. Fax: (217) 333-9329. E-mail: gwpadua@uiuc.edu.

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Table 1. Tensile Properties of Coated Zein Films*

sample	thickness (μm)	tensile strength (MPa)	elongation (%)	Young's modulus (MPa)	toughness (MPa)
uncoated	76.7 ± 9.1^{a}	3.72 ± 0.83^{a}	29.5 ± 1.19^{a}	157 ± 36.5^{a}	0.94 ± 0.17^{a}
coated with flax oil	81.0 ± 9.8^{a}	3.32 ± 1.06^{a}	89.3 ± 30.7^{b}	112 ± 19.0^{b}	2.95 ± 1.92^{b}
coated with tung oil	97.6 ± 9.5^{b}	5.19 ± 0.84^{b}	54.3 ± 10.8^{a}	62.5 ± 8.67^{c}	1.92 ± 0.73^{ab}

* Same letter means they are not significantly different ($P > 0.05$).

Table 2. Water Vapor Permeability of Coated Zein Films*

	water vapor permeability (pg/(Pa·s·m))		
film treatment	0–51% RH	0–100% RH	increment (%)
control zein film	40.86 ± 4.40^{b}	50.58 ± 4.51^{a}	23.8
UV treated zein film	35.18 ± 1.27^{cd}	42.71 ± 1.97^{b}	21.4
γ-radiated zein film	36.34 ± 5.88^{c}	51.85 ± 2.66^{a}	42.7
flax oil coated, UV treated zein film	30.79 ± 1.97^{de}	34.61 ± 1.62^{cd}	12.4
flax oil coated, γ-radiated zein film	24.19 ± 0.34^{f}	24.89 ± 0.93^{f}	2.9
tung oil coated, UV treated zein film	44.10 ± 0.12^{b}	50.81 ± 1.04^{a}	15.2
tung oil coated, γ-radiated zein film	27.66 ± 1.16^{ef}	28.47 ± 0.81^{ef}	2.9

* Same letter means they are not significantly different ($P > 0.05$).

used were oleic acid (C18, 90%, technical grade, Aldrich Co., Inc., Milwaukee, WI), ethyl alcohol (Midwest Grain Products, Pekin, IL), flax oil (cold-pressed unbleached, Bioriginal Food & Science Corp, Saskatchewan, Canada), tung oil (Industrial Oil Products Inc., Arro Corp., Hodgkins, IL), and calcium nitrate (Certified ACS, Fisher Scientific, Pittsburgh, PA).

Zein Film Preparation. Zein films were formed using the method described by Lai et al. (*2*). Zein was dissolved in 75% ethanol (v/v) to a concentration of 16% (w/v). Zein solutions were stirred and heated to 60−65 °C. At this time, oleic acid was gradually added at the ratio of 0.8 g of fatty acid/(g of zein) with continued heating for 8 min. Resulting emulsions were degassed for a half-hour to remove air bubbles. Zein-fatty acid dough-like resins were obtained by precipitating the above emulsions in 20-fold volumes of cold water (3−5 °C). Resins were kneaded by hand for 1 h. Resins thus formed were stretched over the rim of plastic cups to form thin films. Film thickness was measured with a dial gauge micrometer (B. C. Ames Co., Waltham, MA) to the nearest 0.001 mm.

Film Coating. Zein films were coated with either flax oil or tung oil after zein films were dried in air. Coatings were applied by rolling drops of oil over the film surfaces. Several drops of oil were placed on the films and rolled by uneven leveling of the surface.

UV Treatment. Both coated and uncoated zein films were placed under UV light (15 W) at a distance of 18 cm for 8 h.

γ-Radiation Treatment. Both coated and uncoated zein films were irradiated at ambient temperature with a ^{60}Co source at doses of 75 or 100 KGy. The dose rate was around 0.24 KGy/min. The radiation was performed with a Gammacell 220 Excell cobalt irradiator (MDS Nordion 447, Ontario, Canada, K2K 1 × 8) located in the Nuclear Engineering Laboratory at the University of Illinois. It was loaded in October of 2002 with 24 000 Ci of cobalt-60. The irradiation chamber is a cylinder with dimensions of 203 mm height and 152 mm diameter. Precise dose distribution in the irradiation chamber was measured through the use of Gafchromic MD-55 (ISP Technologies Inc., Wayne, NJ) and Radiachromic FWT-60 film dosimeters (Far West Technologies Inc., Goleta, CA), which were calibrated in the National Institute of Standards and Technology. In order for film samples to receive uniform radiation, samples were placed at the location in the chamber where a nearly uniform field distribution was found with the Gafchromic MD-55 and Radiachromic FWT-60 films.

Mechanical Properties. Tensile strength (TS), elongation (*E*), Young's modulus (YM), and toughness (*T*) were measured with an Instron Model 1011 testing system (Instron Engineering Corp., Canton, MA). Zein films were cut into dumbbell shape specimens (ASTM Standard D638-86, type I). Samples were preconditioned at relative humidity (RH) of 50% for at least 48 h. Tensile tests were performed according to ASTM Standard Method D638-91 (*15*). Groups of resin films were produced in random order to eliminate systematic error. Film strips were placed in pneumatic grips on the testing machine. Initial grip separation was 100 mm. The instrument was operated at a cross-head speed of 5 mm/min. For each treatment 10 or more specimens were tested. Tensile strength, elongation, Young's modulus, and toughness were computed by the instrument software. Tensile strength of samples was obtained by dividing the maximum load in newtons by the original minimum cross-sectional area of the specimen in square meters. Elongation was calculated by reading the extension at the moment the samples break, dividing that extension by the original gage length, and multiplying by 100. Young's modulus was obtained by extending the initial portion of the load-extension curve and dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain. Toughness was obtained by calculating the area under the stress−strain curve.

Moisture Barrier Properties. Moisture barrier properties of films were determined gravimetrically according to the ASTM E 96-95 desiccant method (*16*). The method involves sealing a known open area of an impermeable container with the film being tested. Anhydrous calcium sulfate was used to maintain a 0% atmosphere inside the cells. Saturated solutions of calcium nitrate or distilled water, placed in sorbostats, were used to maintain 51 or 100% RH outside the cells, respectively. Test cells were placed in the sorbostats and stored under controlled temperature at 25 °C. Weight gain was 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 WVT. Water vapor permeability (WVP) was calculated as follows (*16*): $\mathrm{WVP} = (\mathrm{WVT})L/S(R_1 - R_2)$, where L is film thickness, S is water vapor pressure, R_1 is RH at the source expressed as a fraction, and R_2 is RH at the vapor sink expressed as a fraction. Both flax oil and tung oil coated samples were placed with coated sides facing sorbostats, uncoated sides facing inward.

Microscopic Morphology. Film morphology was observed under a transmitted light microscope (Zeiss Axiovert 135, Carl Zeiss Inc., New York). Images were captured with a black−white Hamamatsu digital camera (C4742-95, Melville, NY). A 2 cm × 4 cm piece of the film was placed on a microscope glass slide and was covered by a glass cover slide. The observations were performed at 50× or 100× magnification levels.

Liquid Water Transmission. Jet-printer ink on white paper was used as an indicator for liquid water transmission tests. Film samples were placed over printed sheets of paper, and distilled water (5 mL total) was dropped on each film. Each film was covered with a glass cup in order to minimize water evaporation, and water was periodically replenished to offset evaporation. Ink stains on the paper sheets were taken as indication of water permeation through the films. Pictures of the setup were taken periodically to estimate the time taken by the water to penetrate films.

RESULTS AND DISCUSSION

Tensile Properties. Thickness, tensile strength, elongation, Young's modulus, and toughness of uncoated zein films and films coated with drying oils cured under UV light are reported in **Table 1**. The thickness of flax oil coated samples was the same as uncoated samples statistically. Tung oil coated samples had larger thickness than uncoated samples. Flax and tung oils had different effects on tensile properties of films. Elongation and toughness of flax oil treated films increased 300%, while

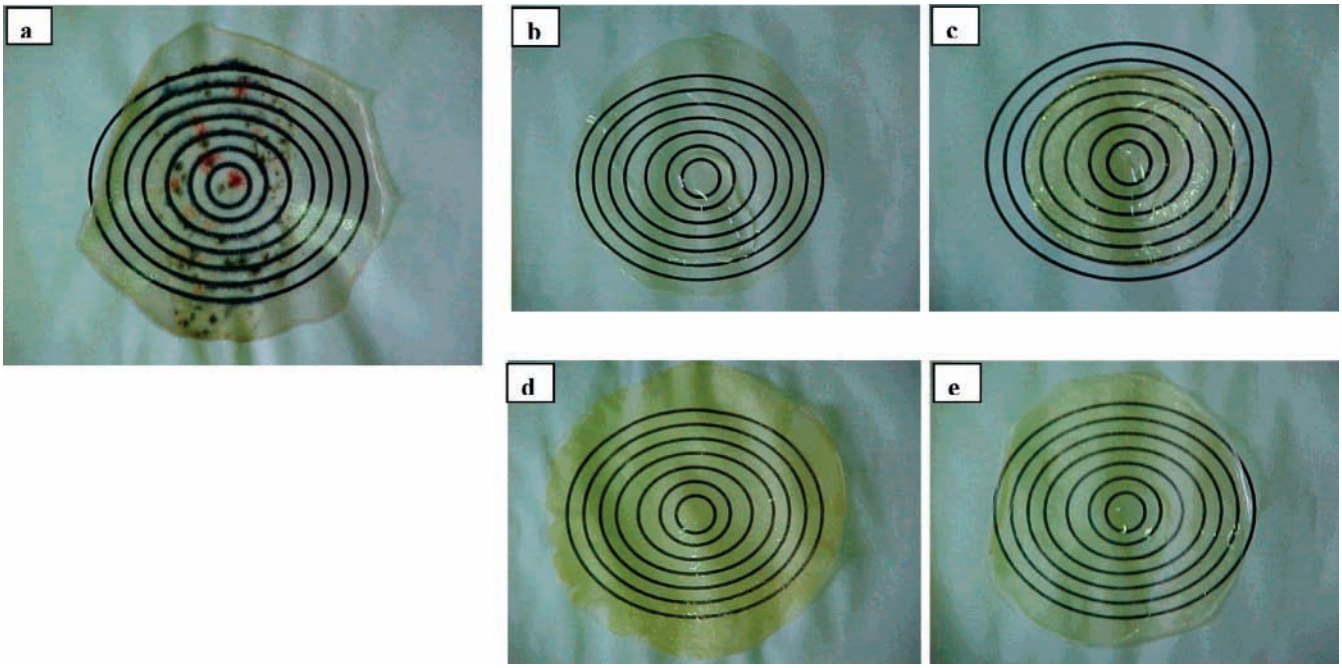

Figure 1. Water permeation through zein films: (**a**) uncoated zein film; (**b**) film coated with flax oil and cured under UV; (**c**) film coated with flax oil, cured under γ-radiation; (**d**) film coated with tung oil and cured under γ-radiation.

tensile strength and Young's modulus remained at the same level. Fracture of zein films often starts at a defect or a crack from where it propagates across the film. In the case of flax oil coated films, it was noticed that the stress−strain curve was not as stable as that of uncoated films. This may be caused by an early failure of the zein−oleic acid film while elongation of the coating layer still proceeded. Increased elongation of flax oil coated films could be due to crazes in the polymerized coating layer, which absorbed energy before failure of films. Crazes effectively increase toughness and affect strength of materials (*17*). Also, flax oil may be absorbed into the film matrix, contributing to plasticization and increasing elongation. Tensile strength of tung oil coated films increased from 3.8 to 5.2 MPa, while Young's modulus was reduced and toughness was enhanced indicating that tung oil coated films were stronger and more flexible. Overall, coating zein films with drying oils and curing the coating layer under UV light delayed mechanical failure. Flax and tung oils have long been used in the paint and varnish industries because they dry in air to form tough insoluble coatings. The basic mechanism of coating formation involves polymerization of unsaturated fatty acids in the presence of oxygen. Polymerized coatings are flexible and elastic, which might have contributed to increased elongation and toughness of coated films **(***18*).

Moisture Barrier Properties. Water vapor permeability measurements on coated and uncoated zein films are reported in **Table 2**. Overall, coated films showed statistically lower permeability than uncoated films, except for films coated with tung oil and treated by UV. Permeability is influenced by the hydrophobic or hydrophilic nature of the material (*19*), by the presence of voids or cracks (*20*), and by stearic hindrance and tortuosity in the structure (*21*). Drying oil coatings presented a highly hydrophobic surface, which prevented films from wetting, thus decreasing the rate of water vapor permeating through the films. In general, lipid-based films have low affinity for water and low moisture permeability (*18*). Water vapor permeability increased when relative humidity increased from 51 to 100% for both coated and uncoated films driven by increasing vapor pressure differences between the two sides of the films. Water sorption by biopolymers often results in swelling and conformational changes (*2*). Absorbed water plasticizes the film matrix, leading to a less dense structure where chain ends are more mobile, thus increasing permeability (*22*, *23*). However, it is interesting to find that WVP of coated samples increased relatively less than that of uncoated samples with similar relative humidity changes (51−100%). For example, WVP of uncoated zein films increased 24%, while that of flax oil coated, γ-radiated films increased only by 3%, suggesting that coating was effective even at high relative humidity. This effect may be attributed to lesser water adsorption on coating layers leading to less swelling of coated films with respect to uncoated films. Coating layers may have prevented zein films from swelling, thus maintaining their integrity.

Liquid Water Permeation. A qualitative estimation of the barrier properties of films to liquid water permeation was obtained from the development of ink stains on printed paper covered with test films when water was poured over them. The test was based on the staining of jet-ink printed lines when coming in contact with liquid water. This test was thought to be useful to compare the water barrier ability of coated vs noncoated films. Zein films placed on top of paper sheets with ink-jet printed rings were photographed on a daily basis as water was poured on them. Selected images are presented in **Figure 1**. **Figure 1a** shows water penetration through uncoated films after 1 day. Mold growth was observed at later days, indicating high moisture permeation through zein films. However, the paper under coated films showed no signs of being wet after 10 days of exposure to liquid water (**Figure 1b**−**e**). This observation is consistent with WVP measurements which indicated that coatings were effective at high relative humidity. Coating layers of flax oil and tung oil were effective in preventing water permeation through zein films. This property may be useful in applications requiring long exposure to liquid water.

Film Structure. Flax oil and tung oil coatings solidified after UV radiation for 8 h or γ-radiation at 75 KGy. All samples were examined under a transmitted light microscope. Images were recorded with a digital camera (**Figure 2**). Uncoated zein

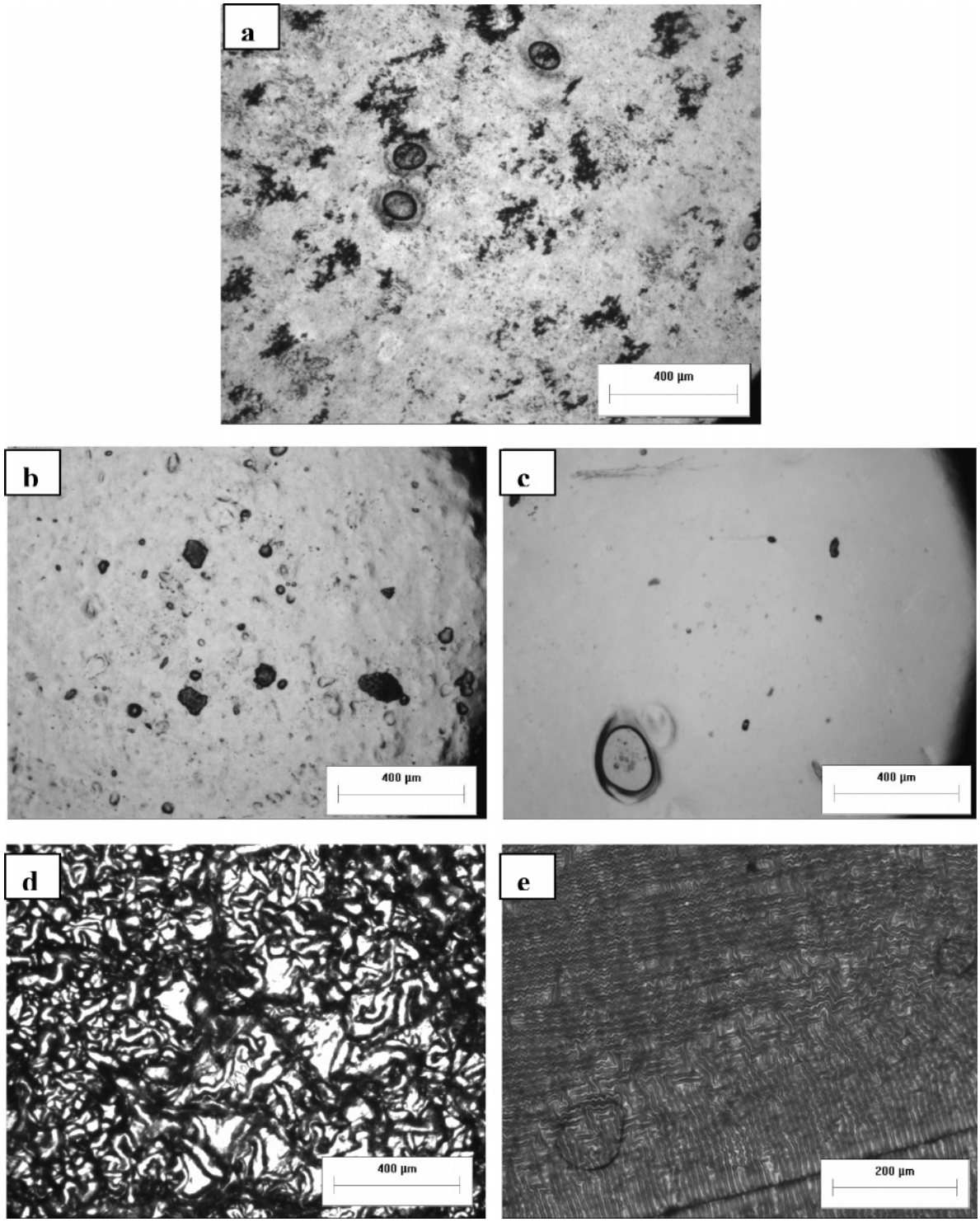

Figure 2. Morphology of zein films: (**a**) uncoated zein film; (**b**) film coated with flax oil and cured under UV; (**c**) film coated with flax oil, cured under γ-radiation; (**d**) film coated with tung oil and cured under UV; (**e**) film coated with tung oil and cured under γ-radiation.

films containing translucent regions as well as dark regions are shown in **Figure 2a**. Translucent regions suggested a well-plasticized material, while dark regions suggested zein aggregation.

Flax oil coatings were transparent, glossy, and slightly sticky. The stickiness may come from low-molecular-weight compounds, which usually exist in young paint films (*24*). Images of flax oil coated, UV treated, and $\gamma-$irradiated films are shown in **Figure 2b,c**, respectively. Black edges seen in **Figure 2b,c** may be caused by the field aperture not being set to a small value or when a very low numerical aperture lens was used. Films coated with flax oil seem to have less dark regions and brighter appearance than uncoated films. Flax oil may have permeated into the zein film structure making it translucent. Flax oil permeation may have contributed to higher elongation values of flax oil coated samples compared to uncoated samples.

Tung oil coatings were opaque, matte, and nonsticky. Films were continuous, smooth, and translucent. Tung oil coated films showed a different structure. UV treated films showed patterns of intertwined dark and light regions under the transmitted light microscope (**Figure 2d**). This suggested that during the curing process tung oil molecules cross-linked and aggregated into

dense structures. Aggregation may have caused shrinking of the top surface which left film regions uncoated. This structure could explain why films treated this way had WVP values similar to those of uncoated zein films. Interestingly, tung oil coatings cured under γ-radiation show a different structure (**Figure 2e**). Regular patterns were observed at the surface showing structure orientation at the micrometer level. This development of an oriented structure might be related to a substantial decrease in WVP observed for those samples.

γ-radiation has a higher penetration than UV light. Therefore, it may have caused a simultaneous polymerization of coating layers, preventing differential shrinking and uneven cover density of resulting coatings. Ring-shaped features appearing in **Figure 2 a,c,e** were thought to be air bubbles present in zein films.

Therefore, it could be concluded that both drying oil type and curing method have effects on the film structures and thus change the film properties accordingly. Further research on the relationships of film structure and film functionality need to be studied systematically.

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LITERATURE CITED

(1) Gennadios, A.; Weller, C. L. Edible films and coatings from wheat and corn proteins. *Food Technol*. **1990**, *44*, 63−69.
(2) Lai, H.-M.; Padua, G. W.; Wei, L. S. Properties and microstructure of zein sheets plasticized with palmitic and stearic acids. *Cereal Chem.* **1997**, *74*, 83−90.
(3) Wang, Y.; Padua, G. W. Tensile properties of extruded zein sheets and extrusion blown films. *Macromol. Mater. Eng.* **2003**, *288*, 886−893.
(4) Guilbert, S. Technology and application of edible protective films. In *Food Packaging and Preservation*; Mathlouthi, M., Ed.; Elsevier Applied Science: London, 1986; pp 371−394.
(5) Smith, S. A. Polyethylene, low density. In *The Wiley Encyclopedia of Packaging Technology*: Brody, A. L., Marsh, K. S., Eds.; John Wiley & Sons: New York, 1986; pp 514−523.
(6) Foster, R. Ethylene-Vinyl alcohol copolymers (EVOH). In *The Wiley Encyclopedia of Packaging Technology*; Bakker, M., Ed; John Wiley & Sons: New York, 1986; pp 270−275.
(7) Payne, H. F. Oils, resins, varnishes and polymers. *Organic Coating Technology*; John Wiley & Sons: New York, 1965; pp 42−132.
(8) Lai, H.-M.; Padua, G. W. Water vapor barrier properties of zein films plasticized with oleic acid. *Cereal Chem.* **1930**, *75*, 194−199.
(9) Rakotomirainy, A. M.; Padua, G. W. Effects of lamination and coating with drying oil on tensile and barrier properties of zein films. *J. Agric. Food Chem.* **2001**, *49*, 2860−2863.
(10) Shogren, R. L. Preparation and characterization of a biodegradable mulch: Paper coated with polymerized vegetable oils. *J. Appl. Polym. Sci.* **1999**, *73*, 2159.
(11) Klebsattel, C. A. Driers in lectures of the 1950 short course on drying oils. *J. Am. Oil Chem. Soc*. **1950**, *27*, 500−504.
(12) Wheeler, D. H. The chemistry of drying oil in lectures of the 1950 short course on drying oils. *J. Am. Oil Chem. Soc*. **1950**, *27*, 440−445.
(13) Boyatzis, S.; Ioakimoglou, E.; Argitis, P. UV exposure and temperature effects on curing mechanisms in thin linseed oil films: Spectroscopic and chromatographic studies. *J. Appl. Polym. Sci.* **2002**, *84*, 936−949.
(14) Urbain, W. M. Radiation chemistry of food components and of foods. *Food Irradiation*; Academic Press: Orlando, FL, 1986; pp 37−82.
(15) ASTM. Standard test methods for tensile strength of plastic sheets. *Annual Book of ASTM Standards*, Vol. 04.06, No. D638-91; American Society for Testing and Materials: Philadelphia, PA, 1994; pp 65−70.
(16) ASTM. Standard test methods for water vapor transmission of materials. *Annual Book of ASTM Standards*, Vol. 08.01, No. E96-95; American Society for Testing and Materials: Philadelphia, PA, 1994; pp 65−70.
(17) Birley, A. W.; Howorth, B.; Batchelor, J. Crazing and shear yielding in *Physics of Plastics*; Oxford University Press: New York, 1991; pp 286−287.
(18) Lazari, M.; Chiantore, O. Drying and oxidative degradation of linseed oil. *Polym. Degrad. Stab.* **1999**, *65*, 303−313.
(19) Gennadios, A.; Weller, C. L. Moisture adsorption by grain protein films. *Trans. ASAE* **1994**, *37*, 535−539.
(20) Torres, J. A. Edible films and coatings from proteins. In *Protein Functionality in Food Systems*; Hettiarachchy, N. S., Ziegler, G. R., Eds.; Marcel Dekker: New York, 1994; pp 467−507.
(21) Hanlon, J. F. Moisture-barrier properties of flexible materials. *Handbook of Packaging Engineering*; Technomic Publishing: Lancaster, PA, 1992; pp 4−12.
(22) Morillon, V.; Debeaufort, F.; Blond, G.; Capelle, M.; Voilley, A. Factors affecting the moisture permeability of lipid-based edible films: A review. *Crit. Rev. Food Sci. Nutr.* **2002**, *42*, 67−89.
(23) Park, H. J.; Bunn, J. M.; Weller, C. L.; Vergano, P. J.; Testin, R. F. Water vapor permeability and mechanical properties of grain protein-based films as affected by mixtures of polyethylene glycol and glycerin plasticizers. *Trans. ASAE* **1994**, *37*, 1281−1285.
(24) van den Berg, J. D. J.; van den Berg, K. J.; Booh, J. J. Identification of non-cross-linked compounds in methanolic extracts of cured and aged linseed oil-based paint films using gas chromatography−mass spectrometry. *J. Chromatogr. A* **2002**, *950*, 195−211.

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