

# Tensile Properties and Water Absorption of Zein Sheets Plasticized with Oleic and Linoleic Acids

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Corn zein has been investigated for fabrication of biodegradable packaging materials. Our objective was to investigate the effect of added plasticizers, oleic and linoleic acids, on tensile properties and water absorption of zein sheets. Moldable resins were precipitated from aqueous ethanol dispersions of zein and fatty acids and rolled into sheets of ~0.5 mm in thickness. To increase plasticization effects, zein–oleic acid sheets were replasticized by heating them in fatty acid baths. Plasticization resulted in flexible sheets of high clarity, low modulus, and high elongation and toughness, although low tensile strength. Water absorption of zein sheets was lowered by plasticization, attributed in part to reduced mass fraction of zein. Polymerization of linoleic acid may have sealed off pores on sheet surfaces, thus slowing water absorption.

**Keywords:** *Zein; plasticization; oleic acid; linoleic acid; biodegradable*

## INTRODUCTION

Plastic waste accounts for 20 vol % of the ~100 million metric tons of waste handled annually in the United States (Osborne and Jenkins, 1992). Replacing conventional synthetic packaging with biodegradable polymers, in certain applications, can reduce usage of nonrenewable resources and decrease waste through biological recycling to the biosystem (Fishman, 1997).

Zein, the prolamine of corn, has been investigated for the fabrication of biodegradable packaging materials (Lai et al., 1997). Zein is a relatively hydrophobic thermoplastic material that has excellent film-forming properties (Gennadios and Weller, 1990; Krochta, 1996). According to Gennadios et al. (1994), zein films form through development of hydrophobic, hydrogen, and limited disulfide bonds between zein chains. Zein has been used commercially in the formulation of edible and nonedible coatings. Films, however, are brittle and require plasticizers to induce softness and permanent flexibility (Reiners et al., 1973; Mendoza, 1975; Andres, 1984; Wright, 1987; Aydt et al., 1991; Trezza and Vergano, 1994).

Plasticizers are low molecular mass organic compounds added to soften rigid polymers (Ward and Hadley, 1993). They act by reducing the glass transition temperature of polymers, reducing their crystallinity, or their melting temperature (Sperling, 1992). Plasticizers dissolve in the polymer separating chains from each other and thus facilitating molecular movement. They are applied to increase workability, flexibility, and extensibility of polymers (Ferry, 1980). Plasticizers act as internal lubricants by reducing frictional forces between polymer chains (Briston and Katan, 1974), and their action may cause dramatic changes in mechanical properties of polymers (Chatfield, 1953; Roos, 1995). Plasticizers cover a wide range of chemical compounds including esters, hydrocarbons, water, alcohols, glycols,

phenols, ketones, and ethers (Chatfield, 1953; Briston and Katan, 1974). Ideal plasticizers are miscible and compatible in all proportions with plastic components. However, compatibility and permanence follow opposite trends; thus, the more compatible and efficient is a plasticizer, the more rapidly it can diffuse out of the polymer (Chatfield, 1953). Plasticizers may be added to polymers in solution (dispersion techniques) or after solvents have been removed (absorption techniques).

Water plasticization of biopolymers, particularly food solids, has been extensively studied (Roos, 1995). Levine and Slade (1990) mentioned that water is a strong plasticizer for food solids including starch and gluten, although not necessarily a good solvent. The mechanism of water plasticization is governed by the free volume concept (Ferry, 1980). Water, a low molecular weight compound, increases polymer free volume, allowing an increase in the segmental mobility of the backbone chain (Ellis, 1988; Levine and Slade, 1990). The effect of water plasticization is observed from the  $T_g$  depression of food solids with increasing water content (Roos, 1995). Atkins (1987) observed that water plasticization of most biological materials caused  $T_g$  depression from ~200 °C, for anhydrous high molecular weight polymers such as starch and gluten, to -10 °C (30% moisture content). Levine and Slade (1987) stated that water plasticization at temperatures above  $T_g$  influences viscoelastic, thermomechanical, electrical, guest and host diffusion, and gas permeability properties of completely amorphous and partially crystalline polymer systems. Plasticization by water is affected by evaporation. Thus, hydrophilic substances are required as stabilizers, although their use results in higher water absorption of biopolymer films. The tendency of zein films, similar to that of other protein films, to absorb water from the environment dictates the selection of plasticizers (Andres, 1984; Wright, 1987; Aydt et al., 1991; Krochta, 1992; Trezza and Vergano, 1994; Lai et al., 1997). Plasticization of

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**Table 1. Effect of Plasticization Level on Tensile Properties of Zein–OA Sheets<sup>a,b</sup>**

OA/zein mass ratio (g/g)	TS (MPa)	E (%)	YM (MPa)	T (MPa)	EBP (J)
plasticized					
0.5	9.4 ± 0.8 a	5.9 ± 2.4 e	557.3 ± 97.0 a	0.47 ± 0.19 fg	0.22 ± 0.09 ef
0.6	5.9 ± 0.2 b	43.6 ± 8.2 d	307.1 ± 10.5 b	2.38 ± 0.43 cd	1.12 ± 0.18 c
0.7	4.2 ± 0.5 d	46.9 ± 24.1 d	202.1 ± 13.8 d	1.68 ± 0.58 e	0.98 ± 0.49 c
0.8	3.4 ± 0.2 e	17.7 ± 3.6 e	189.7 ± 17.9 d	0.57 ± 0.13 fg	0.36 ± 0.07 def
0.9	2.0 ± 0.2 hi	11.0 ± 3.1 e	136.0 ± 22.8 ef	0.21 ± 0.05 g	0.14 ± 0.04 f
1.0	2.2 ± 0.3 hg	7.5 ± 1.5 e	163.1 ± 20.7 de	0.16 ± 0.04 g	0.10 ± 0.03 f
replasticized					
0.5	5.4 ± 0.6 c	62.3 ± 17.4 c	252.6 ± 69.1 c	2.72 ± 0.81 bc	1.44 ± 0.44 b
0.6	3.3 ± 0.2 e	153.6 ± 26.4 a	129.3 ± 13.2 ef	3.72 ± 0.85 a	1.99 ± 0.45 a
0.7	2.3 ± 0.3 fg	165.0 ± 32.5 a	113.0 ± 10.4 ef	3.24 ± 0.75 ab	1.91 ± 0.34 a
0.8	3.1 ± 0.1 ef	88.8 ± 8.4 b	122.4 ± 8.9 ef	2.08 ± 0.18 de	1.46 ± 0.14 b
0.9	1.9 ± 0.2 i	48.7 ± 9.1 cd	79.0 ± 5.1 gh	0.75 ± 0.17 f	0.49 ± 0.14 de
1.0	1.6 ± 0.3 i	66.5 ± 18.9 c	49.9 ± 12.4 h	0.73 ± 0.37 f	0.58 ± 0.24 d

<sup>a</sup> TS, tensile strength; E, elongation; YM, Young's modulus; T, toughness; EBP, energy-to-break-point. <sup>b</sup> Lower case letters indicate significant differences in LSD test ( $\alpha = 0.05$ ).

zein with fatty acids is expected to endure low relative humidity and improve water vapor barrier properties of films.

Fatty acids have received substantial attention as plasticizers. Unsaturated fatty acids are useful in paint technology due to their compatibility with coating resin components (Eisenhard, 1968) and their ability to form "dry" films through air oxidation (Fulmer, 1968). The type and amount of fatty acids employed affect film properties including hardness, color retention, and durability, as well as speed of cross-linking. Oleic acid was used to plasticize zein-based films (Kanig and Goodman, 1962; Reiners et al., 1973; Masco-Arriola, 1996; Lai and Padua, 1997). Kanig and Goodman (1962) evaluated plasticizing effects of oleic acid on properties of resulting zein films. They observed that water vapor transmission of zein films was lower than that of ethyl- and methylcellulose films. Zein films, however, were not stable upon storage. They showed discoloration, oxidation, increased brittleness, and softening after 1 week at 93% relative humidity. Our objective was to investigate the plasticizing effects of oleic and linoleic acids on tensile properties and water absorption of zein sheets.

## MATERIALS AND METHODS

Materials included regular grade com-zein, 90–96% protein (F 4000, Freeman Industries, Inc., Tuckahoe, NY) and oleic and linoleic acids (technical grade, Aldrich Chemical Co., Inc., Milwaukee, WI). Oleic acid (OA), analyzed by gas chromatography, contained 92% oleic acid, 5% linoleic, 3% stearic, and 0.5% palmitic acids. Linoleic acid (LA) contained 61% linoleic, 24% oleic, 8% linolenic, 5% palmitic, and 1.5% stearic acids. Isopropyl alcohol (technical grade, Aldrich Chemical Co.) was diluted with water to obtain 80% aqueous alcohol.

**Preparation of Plasticized Zein Sheets.** Zein solutions (400 g of zein/2 L of 80% isopropyl alcohol) were stirred, at 60 °C for 10 min, with OA or LA to form zein–fatty acid dispersions containing 0.5, 0.6, 0.7, 0.8, 0.9, or 1.0 g of OA/g of zein or 0.6, 0.7, or 0.8 g of LA/g of zein. Cold water was added to dispersions to form zein–fatty acid aggregates that were recovered as soft solid compounds. They were soaked in water at 4 °C overnight and subsequently kneaded in a Farinograph mixer (Brabender Corp., Type FT3, Rochelle Park, NJ) for 20 min to obtain cohesive moldable resins. Wet resins were rolled into sheets (~0.5 mm thick) using a pasta roller (model 150, Atlas, Italy). Sheets were dried at room conditions for 48 h and hot pressed (150 °C) by hand between two metal surfaces to produce flat samples.

**Replasticization of Zein Sheets.** OA plasticized sheets of 0.5–1.0 g/g of zein and LA plasticized sheets of 0.6–0.8 g/g of zein were subjected to replasticization. Sheets were im-

mersed in OA or LA baths and heated in an oven for 2 h at 120 °C. Also, samples plasticized with OA at 0.7 g/g of zein were heated in air or vacuum ovens for 2, 4, or 6 h at temperatures of 100, 120, or 140 °C.

**Tensile Properties.** Tensile properties were determined using ASTM Standard Test Method D 882-91 (ASTM, 1994a) on specimens 13 mm × 120 mm. All samples were conditioned at 25 °C and 50% relative humidity for 48 h in a desiccator containing saturated calcium nitrate. An Instron Testing Machine (model 1011, Instron Corp., Canton, MA) was employed to measure tensile strength (TS), percentage elongation at break (E), Young's modulus (YM), energy to break point (area under stress and strain curve, EBP), and toughness (EBP/specimen volume, T). Initial grip separation was set at 60 mm and cross-head speed at 25.4 mm/min. Experimental design for OA-containing samples was a factorial of 2 (plasticization methods) × 6 (plasticizer levels) × 6 (replicates). For LA-containing samples the design was a factorial of 2 × 3 × 6. Statistical analysis was performed using the SAS System (SAS System for Windows 3.95, release 6.08, copyright 1992, SAS Institute Inc., Cary, NC).

**Water Absorption.** Water absorption (WA) properties were determined according to ASTM Standard Test Method D 570-81 (ASTM, 1994b). Specimens, 76.2 mm × 25.4 mm, were conditioned in an oven at 50 °C for 24 h, cooled in a desiccator, and weighed. Conditioned specimens were entirely immersed in distilled water at 25 °C. At prescribed time intervals specimens were removed from the soaking water, surface water was wiped off with a dry cloth, and the specimens were weighed. Water absorption (percent) was calculated as (wet weight – conditioned weight) × 100/conditioned weight. Reported values represent averages of three determinations.

**OA Uptake.** OA absorption upon replasticization was determined following a modified version of ASTM Standard Test Method D 570-81 (ASTM, 1994b) for water absorption. Specimens, 15 cm × 20 cm, were conditioned in an oven at 50 °C for 24 h, cooled in a desiccator, and weighed. Conditioned specimens were entirely immersed in OA and placed in an air or vacuum oven for the time–temperature schedules prescribed for replasticization. Specimens were then removed from the OA bath, surface OA was wiped off with a dry cloth, and the specimens were weighed. OA uptake was calculated as follows: OA uptake (%) = (replasticized weight – conditioned weight)/conditioned weight. Reported values represent averages of three determinations.

## RESULTS AND DISCUSSION

**Plasticization of Zein.** Tensile properties of zein sheets were affected by plasticization (Tables 1 and 2). TS of OA plasticized sheets decreased from 9.4 to 2.2 MPa as plasticizer level increased from 0.5 to 0.9 g of OA/g of zein. LA-containing sheets also decreased in TS when plasticizer increased from 0.6 to 0.7 g/g of zein.

**Table 2. Effect of Plasticization Level on Tensile Properties of Zein-LA Sheets<sup>a,b</sup>**

LA/zein mass ratio (g/g)	TS (MPa)	<i>E</i> (%)	YM (MPa)	<i>T</i> (MPa)	EBP (J)
plasticized					
0.6	5.9 ± 0.2 a	14.5 ± 2.8 b	270.3 ± 8.0 a	0.70 ± 0.12 b	0.37 ± 0.07 cd
0.7	4.7 ± 0.6 b	27.6 ± 4.1 b	209.7 ± 10.2 b	1.00 ± 0.16 b	0.55 ± 0.08 c
0.8	4.6 ± 0.3 b	12.3 ± 2.8 b	211.3 ± 18.3 b	0.48 ± 0.09 b	0.22 ± 0.04 d
replasticized					
0.6	3.2 ± 0.1 c	144.7 ± 32.7 a	141.7 ± 5.2 c	3.39 ± 0.28 a	2.25 ± 0.23 a
0.7	2.8 ± 0.3 d	140.1 ± 23.4 a	101.3 ± 16.6 d	3.39 ± 0.98 a	1.66 ± 0.40 b
0.8	3.1 ± 0.3 c	125.9 ± 27.4 a	140.3 ± 25.4 c	3.35 ± 0.52 a	1.44 ± 0.35 b

<sup>a</sup> TS, tensile strength; *E*, elongation; YM, Young's modulus; *T*, toughness; EBP, energy to break point. <sup>b</sup> Lower case letters indicate significant differences in LSD test ( $\alpha = 0.05$ ).

In general, TS of polymeric materials decreases with plasticization. TS is affected by the extent of polymer chain associations in the sheet matrix. Plasticizers reduce such associations and decrease TS. Park et al. (1994) added saturated fatty acids (lauric acid, palmitic acid, and stearic-palmitic acid blends) to zein films and observed a decrease in TS but an increase in elongation of laminated methyl cellulose/corn zein-fatty acid edible films. Lai et al. (1997), however, observed an increase in TS of zein sheets plasticized with palmitic acid, up to 0.5 g/g of zein. Gedde (1995) referred to this behavior as antiplasticization and explained it in terms of strong intermolecular interactions between polymer and plasticizers. Addition of OA beyond 0.9 g/g of zein or of LA above 0.7 g/g of zein (Tables 1 and 2) did not affect TS any further, suggesting a limited capacity of the zein structure to absorb fatty acids.

Lai et al. (1999) proposed a structural model for zein-OA films based on X-ray scattering measurements. They interpreted X-ray spacings in terms of the rod-shaped molecular conformation of zein proposed by Tatham et al. (1993) and Matsushima et al. (1997). The model for zein-OA films consisted of a layered arrangement of zein planes separated by double layers of OA molecules. The model suggests that plasticization of zein with OA involves dispersion of rod-shaped zein molecules in aqueous alcohol and adsorption of fatty acids to hydrophilic regions of the zein surface. Addition of cold water during resin precipitation resulted in hydrophobic aggregation of zein-OA units to form a moldable solid. We observed that excessive heat treatment or excessive stirring during initial dispersion of zein and fatty acids promoted gelation, which prevented resin formation. Gelation may have involved zein molecular unfolding resulting in protein-solvent associations rather than protein-fatty acid associations. Solvated proteins readily formed three-dimensional networks leading to gel formation. Once solvation occurred, protein-fatty acid associations were not likely formed.

Elongation of zein sheets increased by the use of plasticizers (Tables 1 and 2) with respect to the value of 0.5% for unplasticized zein sheets reported by Lai et al. (1997). Plasticizer levels of 0.6–0.7 g of OA/g of zein affected elongation, toughness, and energy to break point of sheets. A maximum *E* of ~45% was observed at 0.6–0.7 g of OA/g of zein and a maximum value for toughness (2.4 MPa) at 0.6 g/g of zein. Addition of OA up to those levels may have facilitated structural mobility, which resulted in increased elongation and flow. However, excess OA weakened the structure, lowering elongation, toughness, and energy to break point. Young's modulus showed an overall decreasing trend with increasing OA mass fraction. Plasticizers, added to plastics to increase flexibility, act similarly to solvents, lowering resin viscosity and allowing slip to

occur between polymer molecules. Lai et al. (1997) reported modulus of unplasticized zein sheets at 1475 MPa. Data in Tables 1 and 2 show that both OA and LA lowered the modulus of zein sheets. Addition of LA lowered Young's modulus and increased elongation with respect to unplasticized sheets. However, increasing plasticizer level did not significantly affect tensile properties.

**Effects of Replasticization.** Replasticization or absorption of fatty acids by already plasticized zein sheets was intended to increase plasticization. Replasticization produced clear, glossy, tough, and flexible sheets. Clearness is indicative of miscibility and increased interactions between polymer and fatty acids (Chatfield, 1953).

Replasticization increased elongation, toughness, and energy to break point of sheets (Tables 1 and 2). It decreased Young's modulus, TS of samples containing LA, and TS of samples plasticized with OA at 0.5–0.7 g/g of zein.

According to a structural model for zein films plasticized with OA proposed by Lai et al. (1999), OA forms bilayer leaflets that interdigitate with zein sheets formed by rod- or bar-shaped molecules aligned side by side and joined by hydrophobic bonds. In this model excess OA would form domains separated from the OA bound to zein and would contribute little to the tensile properties of the sheet. In replasticized sheets, we think that heat treatments applied during replasticization destabilized and unfolded zein rods, allowing them to bind extra amounts of OA. Higher amounts of plasticizer increased chain mobility, facilitating elongation and flow.

Elongation, toughness, and energy to break point were highest for samples originally plasticized at 0.6–0.7 g of OA/g of zein. We considered that for sheets of 0.6–0.7 g of OA/g of zein, OA was evenly distributed and bound to the zein surface. When the OA to zein ratio of plasticized sheets was lower than 0.6, zein-to-zein interactions possibly prevented the matrix from swelling, thus limiting absorption of fatty acids during replasticization. Replasticization of sheets of >0.7 g of OA/g of zein resulted in decreased elongation, toughness, and energy to break point. We thought that excessive amounts of OA promoted plasticizer migration out of the sheets followed by formation of zein-to-zein interactions, which prevented higher elongation.

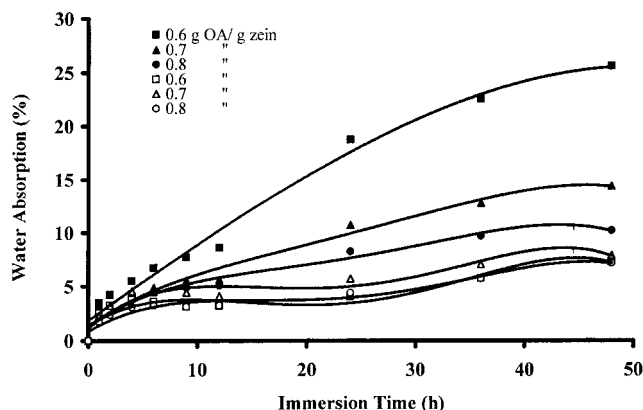
OA uptake during replasticization was affected by heat treatment (Table 3). Vacuum heating increased OA uptake over air oven heating when treatment was at or above 120 °C for 4 h or longer. We speculated that heating above 120 °C melted the sheets, facilitating diffusion and uptake of OA. Application of vacuum eliminated gas bubbles from sheets, which contributed to fatty acid absorption. TS of vacuum oven heated



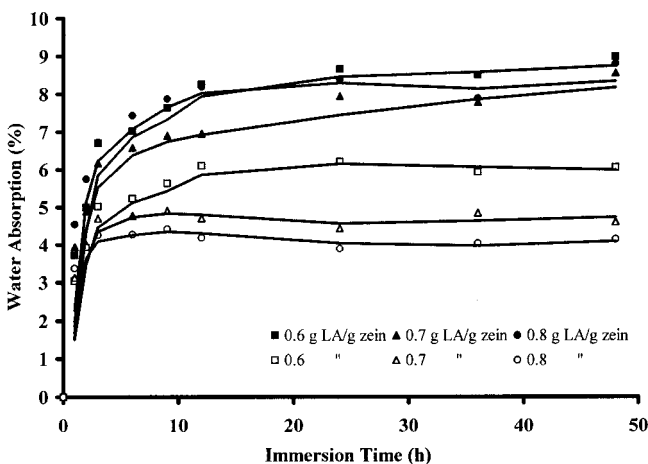
**Table 3. Effect of Replasticization Heat Treatment on Tensile Properties of Zein-OA Sheets<sup>a,b</sup>**

time (h)	air oven heating			vacuum oven heating		
	TS (MPa)	E (%)	OU (%)	TS (MPa)	E (%)	OU (%)
<i>T<sub>H</sub></i> = 100 °C						
2	2.6 ± 0.3 ef	111.7 ± 41.1 e	22.1 ± 3.0 ef	4.8 ± 0.4 a	28.9 ± 6.2 ij	17.7 ± 2.6 f
4	2.6 ± 0.2 ef	138.1 ± 19.2 dc	24.7 ± 5.8 de	2.8 ± 0.2 d, e	78.8 ± 13.6 f	28.9 ± 5.4 cd
6	2.8 ± 0.2 de	164.7 ± 11.4 a,	33.5 ± 1.1 bc	2.5 ± 0.2 f	67.6 ± 15.9 fg	36.4 ± 4.6 b
<i>T<sub>H</sub></i> = 120 °C						
2	2.3 ± 0.3 g	165.3 ± 32.5 ab	24.8 ± 0.8 de	3.6 ± 0.2 c	144.2 ± 20.0 bc	26.5 ± 6.6 de
4	3.0 ± 0.4 d	52.4 ± 11.0 ghi	28.9 ± 2.0 cd	2.2 ± 0.1 g	158.4 ± 17.3 abc	48.3 ± 1.1 a
6	4.0 ± 0.3 b	34.1 ± 7.2 jhi	34.1 ± 1.1 bc	2.2 ± 0.3 g	178.2 ± 24.6 a	53.0 ± 4.9 a
<i>T<sub>H</sub></i> = 140 °C						
2	2.8 ± 0.1 de	54.8 ± 15.1 gh	26.6 ± 2.1 de	3.0 ± 0.1 d	115.7 ± 17.8 de	27.0 ± 2.8 de
4	2.0 ± 0.2 g	45.9 ± 10.4 ghi	33.6 ± 2.6 b, c	2.1 ± 0.4 g	118.2 ± 34.6 de	50.1 ± 2.2 a
6	1.7 ± 0.1 h	11.3 ± 2.0 j	35.5 ± 2.4 b	1.9 ± 0.1 gh	105.2 ± 26.4 e	51.2 ± 4.4 a

<sup>a</sup> *T<sub>H</sub>*, temperature of heating; TS, tensile strength; E, elongation; OU, oleic acid uptake during replasticization. <sup>b</sup> Lower case letters indicate significant differences in LSD test ( $\alpha = 0.05$ ).



**Figure 1.** Variation of WA of zein-OA sheets with immersion time. Lines represent polynomial curve fitting. Symbols represent data points (solid for plasticized samples and open for replasticized sheets).



**Figure 2.** Variation of WA of zein-LA sheets with immersion time. Lines represent polynomial curve fitting. Symbols represent data points (solid for plasticized samples and void for replasticized sheets).

sheets was inversely correlated with OA uptake ( $R^2 = 0.8$ ), consistent with the discussion in the above section.

**Water Absorption.** Plasticization with OA and LA affected water absorption of zein sheets (Figures 1 and 2). Lai et al. (1997) applied first-order kinetics to water absorption data from zein sheets immersed for 2 h at 25 °C. They reported pseudo-saturation values of 110 g of water/100 g of solids for unplasticized zein sheets and 15.5 for sheets plasticized with palmitic acid at 1.0 g/g of zein. Figure 2 shows apparent saturation values of

9% for LA plasticized samples, indicating that LA was more effective than palmitic acid at limiting water absorption of zein. Replasticization lowered apparent saturation to 4–6%, which was largely attributed to a reduced mass fraction of zein after replasticization. Soaked sheets swelled and softened but did not disintegrate after 48 h of immersion. For OA plasticized samples, apparent saturation decreased with increasing plasticizer level (Figure 1). However, after replasticization, the effect of the original amount of OA in the resin was less pronounced (mean values presented in Figures 1 and 2 had an overall coefficient of variation of 13.2% calculated from 324 observations). WA rate of sheets with LA was slower than that of OA-containing samples at long immersion periods. LA polymerization during sheet preparation may have contributed to slow water uptake by sealing off pores on sheet surfaces and preventing swelling.

**Conclusions.** Plasticization with OA and LA increased elongation percent, decreased Young's modulus, and decreased water absorption of zein sheets. Elongation was affected by plasticizer level, and maximum elongation occurred at fatty acid mass ratios of 0.7 g/g of zein. Lower amounts of fatty acids were not as effective, and higher amounts may have led to excessive plasticizer migration out of the sheets. Fatty acid separation caused zein aggregation, resulting in loss of flexibility and increased water absorption. LA was more effective than OA at reducing water absorption of sheets, possibly due to LA polymerization, which may have filled pores and gaps in the structure preventing it from swelling. Replasticization treatment improved toughness and water resistance of sheets. Vacuum oven heating at high temperature increased the amount of OA absorbed during replasticization. It melted the sheets and possibly eliminated trapped gas bubbles from the zein melt, thus reducing pores and gaps in the structure. Plasticization of zein with OA resulted in relatively tough and water-resistant sheets that may find application in thermoformed packaging trays.

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