

Properties of Films from Corn Zein Reacted with Glutaraldehyde

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ABSTRACT: To improve the mechanical properties of zein films, a commercial white zein was reacted in glacial acetic acid (HAc) with glutaraldehyde (GDA) from 0.5 to 16% by weight based on the weight of zein. Amounts of 4% or higher GDA-modified zein, when cured in a closed system, generated a gel. That gel was insoluble in organic solvents known to solubilize zein. Zein solutions cast within a silicon rubber gasket sealed onto Teflon-coated plates, when air dried, generated 0.7–0.9-mm thick films. Those films from 8% GDA-modified zein had a water vapor permeability of 5.9×10^{-8} g cm/Pa s m². Overall, results indicate that our thicker films gave higher water vapor permeability than values reported in the literature. To achieve consistent and comparable results with differential scanning calorimetry (DSC) and dynamic mechanical analyses (DMA), film samples had to be heated to remove residual HAc. An increase in the glass transition temperatures for those films from GDA-modification of zein, observed with both DSC and DMA, was attributed to the

crosslinking of zein. Physical testing of tensile bars cut from GDA-modified zein films showed minor enhancement of tensile strength, percent elongation, and Young's modulus in the 0.5% GDA-modified zein films, which increased and leveled off with 4% or higher amounts of GDA for the modifications. When the 4 to 16% GDA results are averaged, the tensile strength for the modified zein films increased 1.8-fold when compared with unmodified zein control films. On the same note, percent elongation showed a 1.8-fold increase and Young's modulus showed a 1.5-fold increase. GDA reaction with zein generated films with improved tensile strength, ductility, and stiffness when compared with respective zein control films that retained their integrity when subjected to either boiling water or extensive soaking. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2877–2883, 2007

Key words: proteins; modification; films; thermal properties; mechanical properties

INTRODUCTION

Corn is an abundant renewable resource that was used to produce 4.5 billion gallons of ethanol in 2006 from over one billion bushels of corn. To make ethanol production economically feasible with less reliance on government subsidy, it is imperative that the coproducts of its manufacture be better utilized. Zein, a valuable coproduct from ethanol production and a predominant corn protein has many uses including its excellent film forming capabilities.^{1,2} Plasticizers such as triethylene glycol and water have been used to alleviate brittleness in zein films.^{3,4} However, those

plasticizers impacted negatively on the mechanical properties of zein films causing diminished tensile strength, increased elongation percent, and decreased Young's modulus. An alternative approach to increasing tensile strength as well as elongation of zein films is to either chain extend or mildly crosslink zein.⁵ Those authors modified zein with carbodiimide to generate films that possessed a 1.3-fold increase in tensile strength and a 1.6-fold increase in elongation when compared with films from unmodified zein.

Glutaraldehyde (GDA), a dialdehyde, is known to promote inter- and intramolecular crosslinking of proteins.^{6–8} The predominant reaction product of GDA with protein is the conjugated Schiff base with the ϵ -amino group of lysine.⁹ Because zein lacks lysine and possesses three sulfhydryl groups,¹⁰ the only other nucleophilic functional groups that may be available for reaction with GDA are the α -NH₂ group of N-terminal, the imidazole ring of histidine and the phenolic group of tyrosine.⁶ Films from zein proteins crosslinked with GDA were prepared either in aqueous ethanol or aqueous acetone.¹¹ Mechanical proper-

*Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the stand of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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ties of those films differed greatly with the solvent used where those GDA-modified zein films prepared in 70% aqueous ethanol possessed a tensile strength of 21.4 MPa, elongation percent of 4.1, and Young's modulus of 1085 MPa. Whereas, those GDA-modified zein films prepared in 70% aqueous acetone had a tensile strength of 7.6 MPa, elongation percent of 2.6, and Young's modulus of 668 MPa. Zein films prepared and cast with either aqueous acetone or aqueous ethanol, when assessed by Fourier transformation scanning electron microscopy, showed separation of the zein as small globules observed on the surface of the film.¹² The small globules observed on the surface of those films cast in either aqueous ethanol or aqueous acetone resulted from poor solubility of zein upon evaporation of those solvents. The film-forming solvent will influence characteristics of the finished film, whereby, maximum solvation markedly influences cohesive film structure.¹³

Water, aqueous alcohols, and acetone generally have been used as solvents for generating protein-based films and coatings.¹⁴ Because GDA may react with alcohol to form a hemiacetal,¹⁵ alcoholic solvents may impede the crosslinking reaction. Either acid or base will catalyze the crosslinking of protein with GDA.^{16–18} The process for the formation of a plasticized proteinaceous material can be selectively matched with a solvent that acts as a plasticizer component to form a blend.¹⁹ The solubility parameters for a protein are the sum of the solubility parameter values contributed by dispersive forces, hydrogen bonding forces, and polar forces. Because glacial acetic acid (HAc) matches the solubility parameters of zein, the secondary forces between zein segments and acetic acid molecules are strong and therefore the zein molecules will assume a dispersed conformation in solution as well as in the finished film. The use of HAc for casting kafirin films proved advantageous in producing films of more consistent quality than did films cast with binary solvents.²⁰ On the basis of this premise and the fact that acid will catalyze the GDA crosslinking of proteins, we used HAc as the solvent in our current investigation to characterize the mechanical properties of zein films from zein chemically modified with GDA. To better understand the changes in film mechanical properties when zein films were chemically modified, we investigated structure property correlations of those films by their respective thermal and rheological properties.

MATERIALS AND METHODS

Materials

The commercial zein used in this investigation was Japanese white zein (Showa Sangyo, Tokyo, Japan), designated JZ, which had a crude protein 91.82%,

crude fat 0.44%, crude fiber 0.26%, ash 0.74%, and moisture 6.94%. GDA was Grade 1, 50% in water, and specially purified for sophisticated use was purchased from Sigma, St. Louis, MO. HAc, reagent grade, was obtained from EM Science, Gibbstown, NJ. All other chemicals and reagents used in this study were of reagent grade.

Film and gel preparation

Zein formulations for films consisted of dissolving zein in HAc at 25% by weight of solids to solvent volume (i.e., 25g zein/100 mL) by stirring at room temperature with a magnetic stirrer. Appropriate amounts of GDA were added to each solution so that the final concentration of GDA was 0.5, 1, 2, 4, 8, 10, 12, and 16% based on the weight of zein. These solutions, along with a control with no GDA added, were each stirred for 2 h at room temperature and then sonicated for 30 min with a Branson 2510 (Process Equipment and Supply, Cleveland, OH) sonicating bath prior to pouring onto Teflon-coated glass plates bordered with a 3-mm silicon gasket stuck on with a glue stick. These plates were placed in a hood at room temperature.

The air-dried films, while still attached to the gasket on the glass plate, were twice washed with 500-mL batches of absolute ethanol to remove HAc residues. Upon the removal of films from the gaskets, test strips were cut for either dynamic mechanical analysis (DMA) or physical properties testing using an Instron. Stored strips were equilibrated for 1 week at either 50 or 70% relative humidity at 21°C. Because test strips of control films with no GDA tended to shrivel upon removal of the gasket, those films were heated while still attached to the gasket for 24 h in a hot air oven at 60°C to remove some of the residual HAc. Test strips were kept flat by either sandwiching between two Teflon-coated glass plates until evaluated for mechanical properties with an Instron or two stainless steel plates for DMA analysis.

Gels were prepared from 25% solutions of JZ, dissolved in HAc, to which 0.5, 1, 2, 4, or 8% GDA was added. After stirring for 2 h and sonicating for 30 min, the resulting solutions were poured into molds consisting of a 3-mm thick silicon rubber gasket sandwiched between two Teflon-coated glass plates. The molds remained clamped shut for 1 week at room temperature to allow for a completed crosslinking reaction.

Permeability of zein films

A Payne permeability cup was used to determine the water vapor transmission (WVT) and the permeance of zein films based on ASTM E96–00.²¹ Each film was cut into three circular pieces with a diameter larger

than the opening of the cup, 3.5 cm. The circular pieces were equilibrated in an environmental stability chamber (Model 417532, Hotpack, Philadelphia, PA), maintained at $(25 \pm 0.5)^\circ\text{C}$ and $(50 \pm 2)\%$ relative humidity, for at least a week. Each piece was measured and weighed prior to the experiment. The thickness of the samples ranged from 0.7 to 0.9 mm. Each testing cup was filled with 10 mL of distilled water and one sample was placed on the top of each cup. The sample was then topped with a retaining ring and tightly clamped to the testing cup. The initial mass of the entire apparatus and the start time were recorded. The mass of each apparatus was measured at the same time every weekday for 8 weeks. At the end of the experiment, the film samples were removed from the chamber, weighed, measured, and dried in a desiccator for at least 1 week to determine their moisture content.

The mass of the entire apparatus was plotted versus time, and the slope of the line was determined using least squares. The WVT for each sample was calculated by dividing the slope of this line by the test area, as in the following equation:

$$\text{WVT} = G/tA - (G/t)/A$$

where G is the weight change from the straight line, t the time, G/t the slope of the straight line, and A the test area (cup mouth area).

The permeance of each sample was then calculated by dividing the WVT by the vapor pressure difference across the film, using the following equation:

$$\text{Permeance} = \text{WVT}/\Delta p = \text{WVT}/S(R_1 - R_2)$$

where WVT is the water vapor transmission, Δp the vapor pressure difference, S the saturation vapor pressure at test temperature, R_1 the relative humidity at the source (in the dish) expressed as a fraction, and R_2 the relative humidity at the vapor sink (in the chamber) expressed as a fraction.

DMA analysis

Rectangular test strips with dimensions 15-mm long, 9-mm wide, and 0.8-mm thick cut from the air-dried films were evaluated by DMA. The magnitude and shape of the storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$) were measured with an ARES LS2 controlled strain rheometer (TA Instruments) equipped with a torsion rectangular fixture. Measurements of G' , G'' , and $\tan \delta$ were conducted at a frequency of 1.0 rad/s and a strain of 0.05%. Each sample was heated twice with a forced air oven at a rate of $2^\circ\text{C}/\text{min}$. The samples were first heated from 20 to 100°C (for the control sample) or 160°C (for the GDA-modified sample), and held at this temperature for

1 h. The samples were then cooled to 20°C , and heated again until microbubbles were formed and the sample became distorted.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed either on powdered samples or film segments packed into either aluminum pans or stainless steel high pressure pans, hermetically sealed, using a DSC 2920 (TA Instruments) that was calibrated against an indium standard. Samples and empty aluminum or stainless steel pans, as reference, were heated from 15 up to 210°C at a scan rate of $5^\circ\text{C}/\text{min}$, for two cycles. The glass transition temperature, T_g , the midpoint between the onset temperature (T_i), and the final temperature (T_f) were measured on the second heating cycle.

Mechanical property measurement

Films from zein formulations either with or without GDA modification were cut with a die to produce dumbbell-shaped test specimens with gauge length 7.62 mm and a width of 3.18 mm. Two or more replicate films with five test specimens for each treatment were exposed to relative humidities of 50 and 70% for 7 days. Five thickness measurements across the gauge length of each specimen were taken using a Mini test 2500 (Electro Physik, Cologne, Germany) and averaged. Testing was performed using an Instron Universal Testing Machine (Model 4201, Canton, MA) in a constant relative humidity room (50%) at 23°C where Series 1X software handled data recording and manipulation. For those specimens, a cross-head speed of 10.00 mm/min was used with grip distance set at 50.00 mm. Tensile strength (MPa), elongation (%), and Young's modulus (MPa) were compared between GDA-modified zein films versus control films with no GDA.

Moisture evaluations were calculated by taking the difference in weight of the test strips before and after heating in a hot air oven at 105°C for 24 h and dividing that difference by the wet weight.

Tensile bars of 8% GDA-modified zein films were either subjected to soaking in water for 24 h or boiled for 10 min then blotted dry with filter paper prior to physical testing on an Instron.

RESULTS AND DISCUSSION

GDA-modified zein gels

HAc solutions of JZ and zein reacted with 0.5, 1, 2, 4, and 8% GDA (w/w of protein) were each poured into a mold confined with a 3-mm silicon gasket glued onto a Teflon-coated glass plate sealed with a second

TABLE I
Comparison of Permeabilities for Glutaraldehyde-Modified Japanese Zein (JZ) Films with Other Plant Polymers

Polymer	Permeability $\times 10^8$ (g cm/Pa s m ²)	Reference
JZ:glutaraldehyde (3.75:1)	5.93	–
Zein/acetone	1.60	11
Zein/acetone/15% glycerol	2.81	11
Zein/ethanol	1.72	11
Zein/20% dialdehyde starch/ethanol	1.48	11
Zein/70% ethanol (cast 70°C)	0.67	20
Kafirin/70% ethanol (cast 70°C)	1.19	20
Kafirin/glacial acetic acid (cast 40°C)	1.14	20
Kafirin/glacial acetic acid (cast 25°C)	1.22	20
Zein/95% ethanol/glycerin/citric acid	1.16	22
Wheat gluten/57% ethanol/glycerin/NH ₄ OH	6.16	22

coated glass plate. When those sealed systems were cured at room temperature for 1 week, the unmodified zein and zeins modified with 0.5, 1, and 2% GDA remained fluid, whereas those systems modified with 4 and 8% gelled. In those systems, where zein was modified with 0.5, 1, and 2% GDA, crosslinking was too minimal to generate gel formation under the conditions used. Zein gels formed by modification with 4 and 8% GDA were insoluble in solvents common for zein including aqueous ethanols of 60 and 80% (w/v), HAC, dimethyl formamide, and methyl cellosolve. Gel formation indicates that zein was crosslinked with either 4 or 8% GDA. In a good solvent, such as HAC for zein, crosslinked polymers will form a gel but will not dissolve to form a solution. The liquid prevents the polymerized network from collapsing into a compact mass and the network in turn retains the liquid.

According to Habeeb et al.⁶, the nucleophilic functional groups available for reaction with GDA are the α -NH₂ group of the N-terminal, the ϵ -NH₂ group of lysine, the SH group of cysteine, the imidazole ring of histidine, and the phenolic group of tyrosine. A high purity α -zein contains one α -NH₂ group of the N-terminal, three cysteines, one histidine, and eight tyrosines.¹⁰ Based on a molecular mass of 24,535 Da, for a high purity α -zein¹⁰ and availability of those reactive sites, an estimated 1887 equivalents, calculated by dividing 24,535 by 13, the stoichiometric ratio between two aldehyde groups in the GDA and those active amino acid sites equates to a volume of 2.6% GDA.

Permeability of GDA-modified zein films

Film formation occurred when either zein or zein modified with GDA are poured within the confines of the 3-mm gasket and left open to the atmosphere. JZ modified with 8% GDA generated films that possessed a WVT of 4.17 ± 0.18 g/h m², a permeance of $7.30 \text{ E-}07 \pm 3.14 \text{ E-}08$ g/Pa s m² and a permeability of $5.93 \text{ E-}08 \pm 2.23 \text{ E-}09$ g cm/Pa s m² where each value

was based on the means from three replicates. A comparison of our data for water vapor permeability of GDA-modified zein films with permeabilities for unmodified zein and other plant polymers reported in the literature is shown in Table I.

The tabulated data for the films in some instances vary significantly where solvent, plasticizer, and casting temperature play a major role in film permeabilities.^{11,20} Permeability of our GDA-modified zein film, substantially higher than the unmodified zein films quoted from the literature values cited, may be caused by HAC residues entrapped within the film matrix (see Thermal and rheological properties of zein films section).

The GDA-modified zein films in this investigation ranged in thickness from 0.7 to 0.9 mm, which is about 10-fold thicker than the cast protein films quoted from the literature.^{11,20,22} Park and Chinnan²² report that increased film thickness caused increased water permeability of their zein and wheat gluten films. Those investigators attributed increased water permeability with increased film thickness as due to changes in the structure of the film where increased thickness and swelling of hydrophobic films alter film structure.

Park and Chinnan²² state that passage of water vapor through the thickened film may cause bands of aggregated protein strands within the film, thereby, resulting in larger pore openings that then would allow ready passage of water vapor. Those researchers²² speculate the packing structure of zein molecules in the thicker films may be more "loosely entangled" than in the thinner films. Morphological and surface investigations are needed to prove those points.

Thermal and rheological properties of zein films

DSC scans of the powdered JZ starting material subjected to vacuum drying at 105°C to a constant weight gave a T_g of 158.0°C (Table II and Fig. A.1).

TABLE II
DSC of JZ and JZ Films^a

Sample ^b	T_g (°C) ^c	T_i (°C) ^c	T_f (°C) ^c	ΔCp (J/g) (°C)
JZ control (powder)	158.0	152.0	164.0	0.565
JZ film	135.4	122.6	148.3	0.813
JZ film (8% GDA-modified) ^d	147.0	137.6	156.3	0.451

^a DSC scans from second heating cycle of each sample are shown in Figure A.1.
^b All samples were vacuum-dried at 105°C to constant weight.
^c Data for each sample resulted from second heating cycle from 15 to 200°C.
^d Film generated from 8% (w/w of zein) glutaraldehyde-modified zein.

This T_g is about 6°C lower than the literature values for anhydrous zein.^{23,24} DSC scans of JZ film and film samples from 8% GDA-modified JZ yielded T_g s that were 22.6 and 11.0°C lower than the JZ control powder. Even with vacuum drying those samples to constant weight at 105°C residual amounts of HAc still remained. The 11.6°C differential between the film from GDA-modified zein and the control film is reproducible within a range of 10.0–11.6°C and is deemed to have resulted from the GDA modification. T_g is known to increase with crosslinking because chain mobility is lowered.²³

DMA complements DSC, particularly for studying molecular motions that give rise to the glass transition temperatures.²³ The results for the storage and loss moduli, as well as the loss tangent ($\tan \delta = G''/G'$), are shown in Figure 1 for the control sample and in Figure 2 for the GDA-modified sample.

For the control films, we did not scan above 140°C, and for the GDA-modified, we did not scan above 179°C because microbubbles, indicative of phase separation, were formed. Holding the samples for longer

than 1 h, at those elevated temperatures, did not affect the results of the second temperature scan. In both Figures 1 and 2, the results for the first temperature scan are shown with open symbols, and the results after being held at an elevated temperature for 1 h are shown with closed symbols. The level of the storage modulus, G' , indicates the strength of the sample. Both samples initially have similar G' values, which decrease slightly as the temperature is increased. However, the control sample softens rapidly as the temperature is increased above 50°C. The storage modulus for the GDA-modified sample continues to decrease at the initial rate until 100°C when it also begins to soften more rapidly. After being held at an elevated temperature, the G' value in the second scan remains high until the sample is heated beyond 90°C (control) or 130°C (GDA-modified), and then drops sharply. The softening observed in each case is typical of a sample being heated through a glass transition temperature. Rheological measurements are often used to identify a glass transition temperature

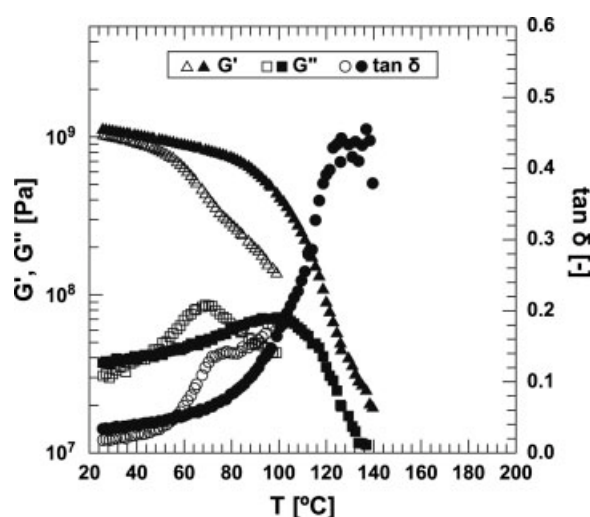


Figure 1 Mechanical properties of the Japanese zein control film. Measurements for the first temperature scan are shown with open symbols, and the results after holding at 100°C for 1 h are shown with closed symbols.

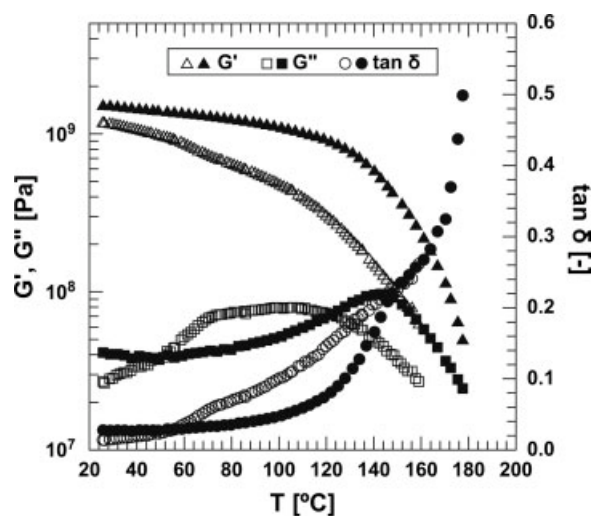


Figure 2 Mechanical properties of the film from Japanese zein modified with 8% GDA. Measurements for the first temperature scan are shown with open symbols, and the results after holding at 160°C for 1 h are shown with closed symbols.

TABLE III
Mechanical Properties of Films from Glutaraldehyde (GDA)-Modified JZ Stored at 50 and 70% Relative Humidity^a

% GDA (w/w % based on zein)	Tensile strength (MPa)		Elongation (%)		Young's modulus (MPa)	
	50% RH	70% RH	50% RH	70% RH	50% RH	70% RH
0	28.9 (5.6)	23.4 (4.2)	12.7 (1.6)	13.3 (1.9)	309.7 (47.6)	270.1 (43.4)
0.5	36.5 (4.8)	29.7 (5.6)	13.3 (1.5)	11.0 (2.5)	362.9 (56.1)	319.4 (48.3)
1	35.3 (4.9)	24.9 (5.5)	13.4 (2.2)	9.2 (2.1)	341.9 (27.8)	299.7 (17.0)
2	33.8 (4.1)	33.5 (2.7)	30.8 (3.7)	28.7 (1.3)	313.7 (36.9)	296.5 (36.2)
4	49.1 (4.6)	44.7 (3.1)	30.8 (4.5)	28.4 (3.2)	510.0 (78.2)	463.7 (30.9)
8	49.4 (6.1)	42.8 (5.2)	30.3 (2.2)	34.7 (3.2)	435.8 (80.8)	377.3 (72.9)
10	51.3 (4.8)	45.4 (5.0)	14.7 (1.7)	14.2 (1.7)	456.2 (57.2)	427.4 (60.4)
12	50.1 (6.2)	45.8 (1.6)	20.8 (3.7)	34.3 (2.1)	442.0 (36.0)	373.1 (30.6)
16	53.8 (5.7)	47.1 (2.7)	16.4 (1.3)	20.8 (3.9)	469.7 (42.7)	458.1 (29.5)

^a Data sets from average of three replicates with five tensile bars for each replicate stored for one week at either 50 or 70% relative humidity (RH) where standard deviation is given inside parentheses.

through a peak in the loss tangent versus temperature plot. A weak glass transition in the control film (Fig. 1) yielded a peak in the loss tangent measurement at about 136°C, which coincides with the T_g of 135.4°C (Table II). However, with the film test strip from GDA-modified zein (Fig. 2), a peak in the loss tangent measurement was not evident because of bubble formation. With that film strip, a clearer indication of the glass transition can be seen in the loss modulus, G'' , which has a broad peak for that sample that shifts to a higher temperature of 148°C after heating. That temperature equates well with the T_g of 147.0°C (Table II) observed by DSC analysis. The results for measurements of G' , G'' , and $\tan \delta$ from the first temperature scans as shown with open symbols in Figures 1 and 2 and the results from heating film strips of the control film at 100°C and the 8% GDA-modified zein film strips at 160°C each for 1 h can be explained by a loss of residual solvent from the samples when held at those elevated temperatures. The presence of solvent resulted in a lower glass transition temperature and greater softening of the samples. Significant broadening of the glass transition defined by the loss modulus, G'' , in the GDA-modified zein film as compared with the control film reflects different types of intermolecular interactions between protein chains.²⁵

Mechanical properties

Data for the mechanical property measurements of zein control film and films from zein modified with 0.5 to 16% GDA are shown in Table III. The moistures of tensile bars stored for 1 week at 50% moisture ranged from 6.7 to 7.2%, whereas tensile bars stored for the same period of time at 70% moisture ranged from 8.6 to 10.5%. Because the higher moisture contents of tensile bars stored at 70% RH, the tensile strengths, as expected, are either equal or slightly less than those tensile bars stored at 50% RH.

Elongation at break, measured as a percentage, increased significantly when 2.0–8.0% GDA, either stored at 50 or 70% RH, was used to modify the zein. However, when 10, 12, and 16% GDA were used to modify zein, the resulting films tended to become less ductile. The reason for the observed drop in elongation percent at those GDA concentrations demonstrates that a higher degree of crosslinking must have occurred with those films modified with those higher amounts of GDA. Hernández-Muñoz et al.²⁶ reported similar results in their investigation of glutenin-rich films crosslinked with formaldehyde, GDA, and glyoxal where they attributed the decrease in film elongation with degree of crosslinking as caused by the development of a more rigid structure.

TABLE IV
Mechanical Properties of Processed Films from 8% Glutaraldehyde-Modified JZ

Process ^a	Moisture (%)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
None	7.2	49.4 ± 6.1	30.3 ± 2.2	435.8 ± 80.8
Soaked	25.0	15.2 ± 2.6	83.8 ± 10.2	113.4 ± 22.3
Boiled	21.3	9 ± 1.2	55.9 ± 8.3	78.3 ± 16.3

^a None, stored at 50% RH for 1 week; soaked, 24 h in water prior to testing; boiled, 10 min in water prior to testing.

Films from zein modified with 4–16% GDA yielded Young's moduli that were significantly higher in value than with either no treatment or those modifications with 0.5, 1.0, and 2.0% GDA. Again, the GDA modifications of zein are within the same population whether stored at 50 or 70% RH.

When the 4–16% GDA-modified zein results are averaged, the tensile strength for the modified zein increased 1.8-fold when compared with unmodified zein control films. On the same note, percent elongation showed 1.8-fold increase and Young's modulus showed a 1.5-fold increase.

Tensile bars of 8% GDA-modified zein film subjected to soaking in water for 24 h or boiling for 10 min, each blotted dry prior to mechanical testing with the Instron, retained their respective structural integrities. Films, so treated, swelled with consequent weakening of tensile strength, and Young's modulus along with increases in elongation percent (Table IV).

Water is acting as a plasticizer, where, on a molecular level water plasticization of the zein film led to increased free volume within the film along with decreased local viscosity and increased back-bone chain segmental mobility.²⁷

CONCLUSION

HAc is an excellent solvent for zein that can be used to generate smooth-surfaced, transparent, and amber-colored films. HAc residues entrapped within the matrix of the control and GDA-modified zein films have a plasticizing effect that causes an increase in elongation percent of tensile bars subjected to analysis on Instron. DMA of zein films, either with or without GDA modification, show that the main relaxation temperature, associated with the glass transition, shifts to higher temperatures with decreasing weight fraction of solvent when samples are heated above 100°C. GDA modification of zein in HAc confers an integrity to those films when they are subjected to boiling in water for 10 min or soaking in water for 24 h prior to testing on Instron. Despite their swollen state, the tensile bars retain a moderate tensile strength and Young's modulus along with an elevated elongation percent. GDA reaction with zeins generates films with significantly increased strength, ductility, and stiffness when compared with untreated zein films.

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APPENDIX

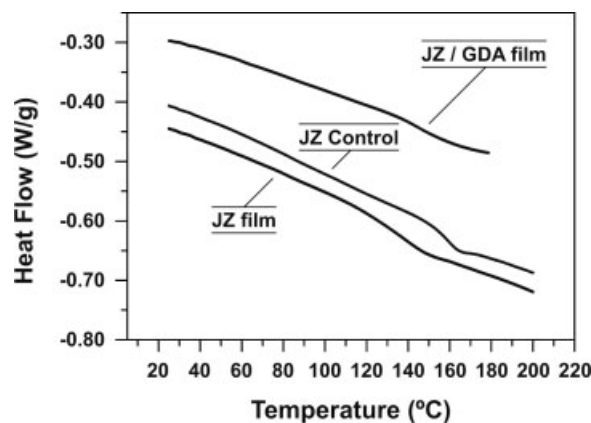


Figure A.1 DSC scans from JZ samples (See Table II) from second heating cycle.

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