

Melt Reaction of Zein with Glyoxal to Improve Tensile Strength and Reduce Solubility

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ABSTRACT: Glyoxal, in the presence of base, has been used to crosslink zein in a melt process involving reaction in a melt state combined with compression molding. The resulting zein articles had improved tensile strength, increasing from 34.3 to 40.6 MPa, when the amount of glyoxal was 6% by zein weight. Reduced solubility in solvents, such as acetic acid, was achieved with glyoxal amounts as low as 1%. Derivatization of zein by glyoxal required the presence of base. As little as 0.00019 mmol of NaOH per

gram of zein when using 6% glyoxal gave reduced solubility. Other bases such as KOH and $\text{Ca}(\text{OH})_2$ also gave reduced solubility. However, these bases did not yield improvements in tensile strength. Decreases in melt temperature and processing time caused a corresponding decrease in tensile strength, but had little effect on solubility. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2375–2383, 2008

Key words: zein; glyoxal; crosslinking; extrusion; melt

INTRODUCTION

With increased production of bio-ethanol, development of products utilizing the potential coproducts of this industry is becoming increasingly important. Zein, the dominant prolamine found in corn, is the main component in corn gluten meal (obtained from wet milling ethanol processes) and a major component of distillers dried grains (obtained from dry milling ethanol processes).¹ Historically, zein was mainly used in the textile fibers market.¹ To be suitable for this market the zein had to be crosslinked with formaldehyde in solution.^{2–5} The resulting solution was then wet spun to give fibers.^{3,6} After fiber formation additional formaldehyde treatments could be used. Recently, dry spinning techniques have been used to produce zein fibers. However, in these experiments zein was once again dissolved in a suitable solvent before spinning and the fibers were post treated with formaldehyde.⁷

Zein fibers used in the textile market will typically be dyed using various techniques, such as acid dyes, that may affect the properties of the zein fiber.^{8,9}

Improved resistance of zein fibers to acid solutions will improve the suitability of zein based fibers in this market. Improved solvent resistance (historically imparted by crosslinking with formaldehyde) to solvents found in commercial textile operations or in residential use, such as vinegar, alcohol or water, will also improve the suitability of zein based articles in new markets.

Many synthetic polymers, such as nylon and polyester, are melt spun using extrusion processes.¹⁰ Extrusion processes bring many valuable economic advantages relative to solution processes, one of the key factors being elimination of the need for solvent recovery. Zein has been processed using extrusion techniques; however, the resulting articles required post treatment with formaldehyde.¹¹ Crosslinking zein in the melt state has not been reported. Crosslinking other polymers in the melt state has provided advantageous properties.^{12–15}

To improve the suitability of zein in the fiber and other markets, crosslinking with formaldehyde was formerly the method of choice. However, commercial use of a suspected human carcinogen requires significant investment to be performed safely. Other chemistries are being explored as an alternative to formaldehyde to improve the properties of zein based materials for various markets.^{16–21} These routes utilize chemicals of similar toxicity to formaldehyde and have not been shown to derivatize zein in the melt state. Glyoxal has previously been shown to crosslink zein in solution.^{20,22} To obtain the economic advantages of melt processing, the crosslinking of zein in the melt state would have significant

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard 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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value. We report here our efforts to crosslink zein with glyoxal in the melt state to provide zein articles with improved physical properties and reduced solubility and to reap the economic advantages of melt processing.

MATERIALS AND METHODS

Materials and equipment

Zein was obtained from Freeman Industries (Tuckahoe, NY), Lot no. 40004081 (14.1% Nitrogen, 5.0% moisture, 0.57% ash). Glyoxal (40% w/w aqueous solution), NaOH, KOH, Ca(OH)₂ and solvents were obtained from Sigma-Aldrich (St. Louis, MO).

A Haake Fisons Rheocord 90 torque rheometer, using the 600 mixing bowl and high shear roller rotors (Thermo Electron, Madison, WI), was used to process the zein melts and make the torque measurements on the blends. Torque curves presented have been smoothed using one and one half minute moving averages. Individual torque values presented are one and one half minute averages. The temperature of the blend while being sheared was not controlled.

A Carver Model C press (Wabash, IN) was used to make compression molded tensile bars in accordance with ASTM D-638-V Standard. Sample thicknesses were measured at three different locations in the testing region using a micrometer (Model No. 49-63, Testing Machines, Amityville, NY). Constant relative humidity (RH) at 25°C was obtained using Hotpack humidity chambers (Warminster, PA). Moisture contents were measured on an Ohaus moisture meter MB45 (Pine Brook, NJ). Tensile strength (TS), Young's modulus (YM), and elongation to break (%E) were evaluated for each sample using an Instron[®] Universal Testing Machine Model 4201. Physical properties were determined with a crosshead speed of 10 mm/min, a gauge length of 7.62 mm, and a 1 kg load cell.

Blend preparation and melt processing

Reagents were added to 45 g of zein and the blend was initially stirred with a spatula to provide a crude blend. This blend could be added to the Haake rheometer in ~ 30 s. The start time ($T = 0$) for all tests is 30 s after the start of sample addition. Glyoxal was evaluated as a crosslinking reagent in the range of 1–6% (w/w dry-basis zein). Sodium hydroxide (NaOH) solutions used in this study were in the range of 0.001–1.5M. The amount of NaOH that was delivered to the blend was in the range from 0.00019 to 0.279 mmol/g zein. Potassium hydroxide (KOH) was used as a 1M solution and was used at 0.186 mmol KOH/g zein. Calcium hydroxide (Ca(OH)₂) was used as a 0.5M solution and was used at 0.093 mmol Ca(OH)₂/g zein. Initial tempera-

ture of the chamber walls of the torque rheometer was varied between 40 and 90°C, and the roller rotors were run at 50 rpm. The melt was allowed to mix for between 2 and 10 min. The majority of samples were processed at 80°C for 10 min. These conditions should be assumed unless noted otherwise.

Tensile property testing

For the production of compression molded samples, the dough produced from the Haake was frozen with liquid nitrogen and then ground to a powder. The mold could produce four test samples at a time. Sufficient powder (1.5 g) was placed into each mold to obtain a well formed sample. Molding conditions were selected to provide a tensile test sample that did not have visible remnants of the starting powder. The mold was heated at 127°C and a pressure of 28 MPa for 20 min. The mold was removed from the press and then allowed to cool at room temperature. Samples were stored at 23°C and 50% relative humidity for five days before testing physical properties. Data values reported are the average of five tested bars. TS and %E data are presented as the calculated value ± 1 standard deviation.

Percent loss/swelling ratio testing

After cooling, the samples were tested for resistance to dissolution in acetic acid (AcOH) or other solvents by placing ~ 0.5 g of a molded bar in 10 g of solvent. It should be assumed that AcOH was used for solubility testing unless noted otherwise. The sample remained in the AcOH for 16 h, then the swelled bar was removed and gently blotted dry to obtain the wet weight (W_w). Wet samples were placed in a fume hood for 8 h and then dried in a 130°C oven for 24 h before weighing to obtain the dry weight (W_d). Percent loss was calculated by comparing the final dry weight to the original sample weight. Swelling ratio was calculated using eq. (1).

$$\text{Swelling ratio (Q)} = \frac{(W_w - W_d)}{W_d} \quad (1)$$

A swelling ratio of 1.0 describes a sample that has swelled 100% (doubling its mass when wet) compared with the dry bar. It is therefore possible to have a swelling ratio of less than 1.0, describing a sample that has swelled, but at less than a 100% change.

RESULTS AND DISCUSSION

Processing of control samples

When a zein formulation is melt processed in the presence of water and varying levels of base, the

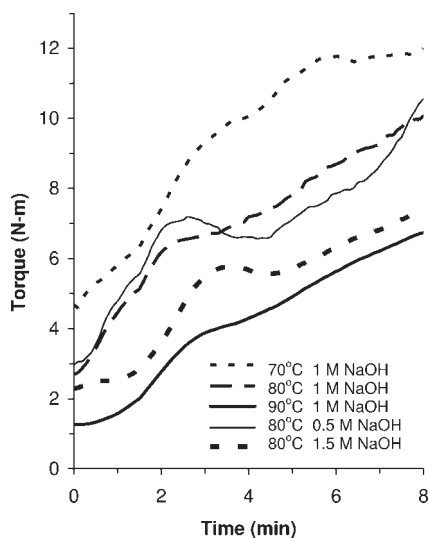


Figure 1 Torque traces of zein samples with varying base concentration and processing temperature, 50 rpm roller rotors.

torque does not undergo significant increases indicative of rapid aggregation. Figure 1 shows the torque traces of five samples with various base concentrations and rheometer temperatures. There is no significant difference among the traces, indicating that variations in base concentration and Haake temperatures alone do not cause significant changes in dough processing. The shape of the curve is similar to that observed previously when using water alone as the plasticizer.²³

When the resulting doughs were ground and compression molded, the samples completely dissolved in AcOH. Any sample prepared without glyoxal, regardless of temperature or base concentration, gave compression molded bars that were not solvent resistant. Table I shows the solubility data for the control sample prepared at 80°C and 0.186 mmol NaOH/g zein (0% glyoxal sample). A value of 100% loss indicates a sample that completely dissolved when placed in AcOH for 16 h.

Impact of glyoxal concentration

When glyoxal is added to the formulation, there is no significant change in the shape of the torque curves (Fig. 2) compared with the control samples in Figure 1. This would suggest that little crosslinking occurred during melt processing, since if significant crosslinking had taken place, it would be expected that viscosity would dramatically increase leading to much higher torque. Solubility data for the glyoxal samples after compression molding are presented in Table I. All of these samples contained 0.186 mmol NaOH/g zein. Samples containing at least 1.5% glyoxal showed a measurable decrease in solubility

TABLE I
Effect of Glyoxal on Solvent Resistance

% Glyoxal	% Loss	Swelling ratio
0	100	N/A
1	>50	N/A
1.5	27.2	3.1
2	18.0	3.1
3	4.0	1.8
6	4.7	1.6

compared with control. Although the sample without glyoxal dissolved completely in AcOH, the 1.5% glyoxal sample exhibited only a 27.2% loss. Increasing concentrations of glyoxal provided further decreases in solubility, with roughly 4% loss being the lowest level achieved. Even if complete crosslinking was achieved, 0% loss is not possible due to water loss and leaching of corn oil out of the molded bars. NMR analysis of the solution extracted from the molded bars showed the presence of corn oil and zein (data not shown).

The 1% glyoxal sample was determined to undergo greater than 50% mass loss. An exact value could not be calculated because the sample did not swell, but rather became sticky and partially fell apart after 16 h in AcOH. If left in AcOH for longer periods of time, the 1% glyoxal sample would eventually completely dissolve. So while the 1% sample did provide a small amount of solvent resistance compared with control, extended soaking in AcOH eventually led to a 100% loss.

As Table I shows, swelling ratios decreased as the glyoxal concentration increased. This result was expected because as the glyoxal level is increased, more crosslinks between zein and glyoxal will lead to a network with higher crosslink density and, therefore, a sample more resistant to swelling. The

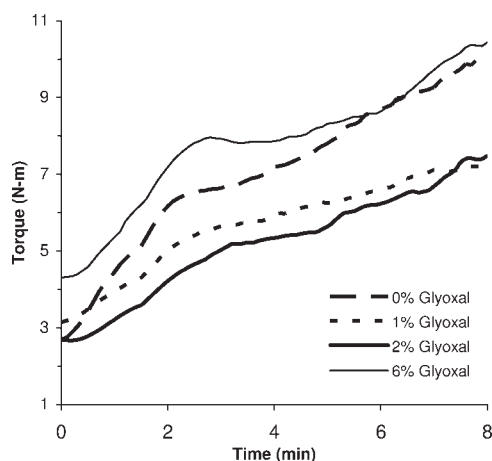


Figure 2 Effect of glyoxal on torque, 0.186 mmol NaOH/g zein, 80°C initial temperature and 50 rpm roller rotors.

TABLE II
Effect of Glyoxal on Tensile Properties

% Glyoxal	TS	%E	YM	% Moisture
0	34.3 ± 2.3	9.9 ± 0.9	451 ± 23	3.8
1	32.3 ± 4.7	9.6 ± 1.2	460 ± 55	2.7
3	39.8 ± 2.6	16.1 ± 5.3	416 ± 27	3.1
6	40.6 ± 5.6	14.1 ± 3.3	391 ± 24	3.6

ability of glyoxal to improve the solvent resistance of zein when processed in a melt state is similar to that observed when the chemistry was performed in solution.²²

Tensile property data are presented in Table II. A typical stress-strain curve, detailed in Figure 3, displayed no unusual features. The 3% glyoxal sample exhibited a tensile strength of 39.8 MPa, an improvement of 16% compared with control. The sample containing 6% glyoxal gave a further improvement to 40.6 MPa. The 1% glyoxal sample showed no change compared with control (within error). In addition to higher tensile strength, the 3 and 6% glyoxal samples also exhibited an increase in elongation. Again, these results are comparable with those seen previously with cast zein/glyoxal films.²²

The torque traces of the glyoxal samples suggested that significant crosslinking was not occurring during melt processing in the rheometer. Crosslinking did eventually occur, as evidenced by the decrease in solubility and improved tensile strength of molded bars. Crosslinking must be occurring during the high temperature/high pressure molding step. Given the volatility of glyoxal, it is expected that no free crosslinker will remain after melt processing. Therefore, an initial reaction must be taking place during melt processing that allows for crosslinking to occur during the later compression molding step. In addition to the torque traces, further evidence of this is that the dough, before being ground and compression molded, exhibits reduced solvent resistance when exposed to AcOH. Doughs containing the highest levels of glyoxal and base are somewhat solvent resistant, with a percent loss of about 50% (data not shown). Except for these specific formulations, though, the melt processed doughs slowly dissolve in AcOH, leading to an eventual 100% loss. Although some minimal reaction is occurring during melt processing, samples prepared in the rheometer require additional processing to be rendered solvent resistant.

Attempts to provide direct evidence of crosslinking were not successful. IR analysis of compression molded glyoxal-reacted zein bars showed no differences between control bars and those containing 6% glyoxal. Previous solution work has shown, though, that reaction of zein with glyoxal under basic condi-

tions produces higher molecular weight material, illustrated by SDS-PAGE of the reaction solution.²² This SDS-PAGE result, coupled with the reduced solubility and improved tensile properties of both cast films²² and compression molded bars, provides evidence that crosslinking is occurring.

Impact of NaOH concentration

The crosslinking of zein with glyoxal was conducted under basic conditions because it has been reported that glyoxal is preferentially active at alkaline pH.²⁴ It has also been observed that the presence of NaOH in zein films increased the elongation and reduced the modulus of zein at when stored at elevated humidity.²² To investigate how base affects the tensile strength and solvent resistance of compression molded bars, a series of formulations were prepared and tested (Table III). All of these samples contained 6% glyoxal. The torque trace of the items having the highest amount of base is similar to that of the other items (Fig. 4). It is clear that as the amount of base is increased, samples exhibited improved solvent resistance. A sample containing 6% glyoxal, but without NaOH, falls apart after 16 h in AcOH. This percent loss value is recorded as greater than 50% because the soaked sample did not simply swell, but fell apart and became sticky so that an intact sample could not be collected. However, even with an NaOH concentration as low as 0.00019 mmol/g zein, the solubility of the molded bar is reduced to 25.7%. As the NaOH concentration is further increased, the percent loss plateaus at ~ 4% with the addition of at least 0.046 mmol NaOH/g zein. As mentioned previously, the percent loss will never be zero due to loss of water and oil from the molded zein bars.

Swelling ratios generally decreased along with the percent loss as NaOH concentration increased. For a given solvent, it is expected that the percent loss will

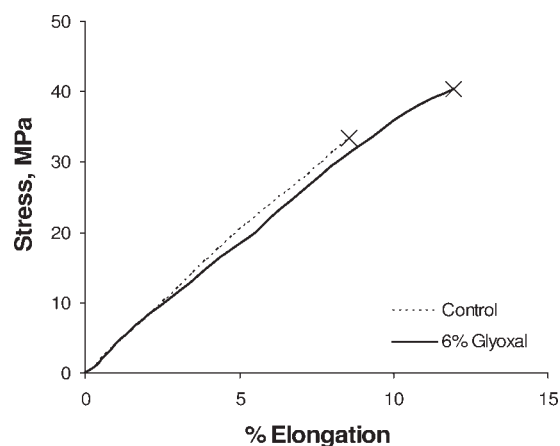


Figure 3 Stress-Strain Curve. The breakage point is designated by the X.

TABLE III
Effect of Base Concentration on Tensile Properties and Solubility of Zein Samples Modified with 6% Glyoxal

mmoles NaOH per gram zein	TS	% E	YM	% Moisture	% Loss	Swelling ratio
0	29.9 ± 2.2	10.1 ± 0.5	402 ± 30	5.3	>50	N/A
0.00019	29.7 ± 1.2	10.2 ± 0.8	408 ± 20	4.9	25.7	3.3
0.00093	^a	^a	^a	^a	10.1	2.1
0.0093	^a	^a	^a	^a	8.5	1.5
0.019	^a	^a	^a	^a	8.8	1.1
0.046	30.7 ± 3.8	8.7 ± 0.6	437 ± 30	4.1	4.1	0.8
0.093	33.1 ± 4.1	10.1 ± 2.0	444 ± 22	4.0	4.0	1.2
0.186	40.6 ± 5.6	14.1 ± 3.3	391 ± 24	4.6	4.7	1.6
0.279	36.0 ± 2.5	12.8 ± 2.3	391 ± 29	4.1	4.6	1.2

^a Not tested.

decrease as the swelling ratio decreases due to increasing crosslink density, leading to more and more of the protein being incorporated into the insoluble network. There was some unexpected variability in the swelling ratio of the samples with higher levels of base. Much of this variation is probably due to the error in weighing the wet bars after swelling in AcOH. Bars were removed from the solvent and placed on a paper towel, then gently dabbed to remove excess AcOH. Although all samples were treated in the same way, it is possible that some samples were dried more or less than others. So, while the swelling ratio data did not exactly follow the expected trend, the overall swelling data are consistent with the percent loss data.

Varying amounts of base also had an effect on physical properties (Table III). Only the two highest levels of NaOH (0.186 and 0.279 mmol/g zein) yielded samples with improved tensile strength. Higher levels of base were not tested due to the fact that high amounts of NaOH may lead to hydrolysis

of the zein.²⁵ Samples containing 0.093 mmol/g zein or lower exhibited a tensile strength similar to control. Many of the samples with the lowest NaOH concentrations were not tested for tensile strength. It was assumed that since the sample with 0.046 mmol NaOH/g zein had a comparable tensile strength to the sample containing 0.00019 mmol NaOH/g zein, intermediate levels of base would exhibit similar properties. These results show that while very low levels of NaOH can render the samples solvent resistant, at least 0.093 mmol NaOH/g zein are required to give any improvement in tensile strength.

Impact of base selection

To determine if bases other than NaOH can be used, KOH and Ca(OH)₂ were used at equimolar amounts based on hydroxide. The torque traces when using KOH and Ca(OH)₂ are similar to that obtained when using NaOH (Fig. 5). Although these other bases do impart solvent resistance, they are not as effective as

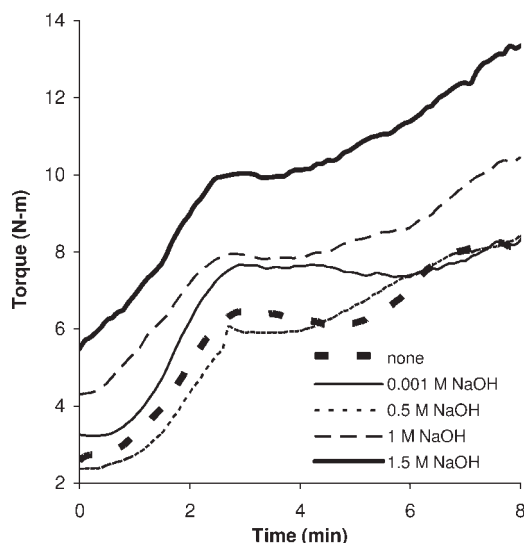


Figure 4 Effect of base concentration on torque, 6% glyoxal, 80°C initial temperature and 50 rpm roller rotors.

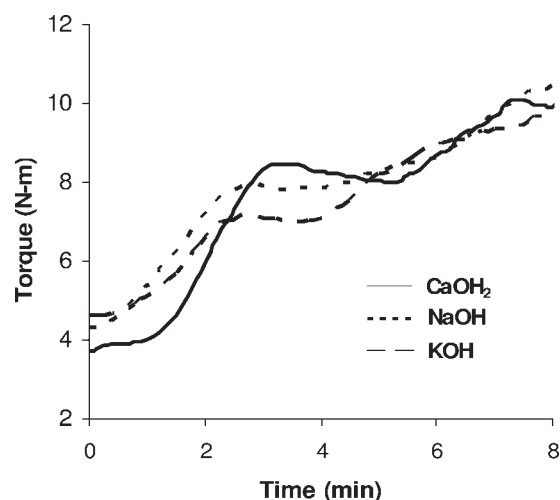


Figure 5 Effect of base selection on torque, 0.186 mmol HO⁻/g zein, 6% glyoxal, 80°C initial temperature and 50 rpm roller rotors.

TABLE IV
Effect of Base Selection on Tensile Properties and Solubility

Base used	mmoles HO ⁻ per gram zein	TS	%E	YM	% Moisture	% Loss	Swelling ratio
NaOH	0.186	40.6 ± 5.6	14.1 ± 3.3	391 ± 24	4.6	4.7	1.6
KOH	0.186	29.3 ± 2.8	10.0 ± 1.2	407 ± 8	5.1	7.9	1.2
Ca(OH) ₂	0.186	28.9 ± 2.0	10.2 ± 1.2	379 ± 30	5.1	7.6	1.2

NaOH in reducing solubility (Table IV). All samples in Table IV contained 6% glyoxal. The amount of hydroxide ion in the Ca(OH)₂ and KOH items was 0.186 mmol/g zein, which yielded bars with % loss values of 7.6 and 7.9, respectively. To achieve a comparable improvement in solvent resistance, the required amount of NaOH is much less at 0.0093 mmol/g zein (8.5% loss). Swelling ratios were similar among the three samples, with the NaOH sample swelling slightly more than the other bases. The effect of KOH and Ca(OH)₂ on physical properties is detailed in Table IV. Neither KOH nor Ca(OH)₂ yielded samples with improved tensile strength. The significant differences observed when changing the base warrant additional work.

Impact of rheometer temperature and processing time

Several experiments were carried out to determine if temperature and time of melt processing affected the solubility or tensile properties of the zein-glyoxal samples. All samples in Table V contained 6% glyoxal and 0.186 mmol NaOH/g zein, but with varying mixing times and temperatures. All of the samples, regardless of temperature, produced doughs that were thoroughly mixed. The torque traces for these items *versus* time are shown in Figure 6(A). The traces show that as the rheometer mixing temperature was increased, the torque values decreased as expected, since higher temperatures will reduce melt viscosity and drive torque to lower values.

On examination of the curves, there appears to be a shift in how the torque varies over time between samples at different temperatures. At 40, 50 and 60°C the torque stays relatively flat or decreases slightly with time. At temperatures of 70, 80 and 90°C, the torque undergoes a more rapid increase

followed by a relatively constant torque value. When the initial torque values are plotted *versus* temperature, there appears to be a discontinuity in the results, occurring between 60 and 70°C, which can be seen when the data is fitted with either linear or exponential fits [Fig. 6(B)]. When all of the data is used, a linear fit provides a line with a relatively good correlation of 0.9788. When the two upper temperatures, 80 and 90°C, are dropped, the fit is improved giving a correlation of 0.9925. Similarly, when all of the initial torque values are fitted using an exponential relationship, a reasonable fit is obtained with a correlation value of 0.9736. However, when the two lowest temperatures are dropped, the fit is improved giving a correlation of 0.9982.

The energy of activation (E_{act}) of flow is used to describe the rate at which the viscosity of a polymer melt changes with temperature. This value is determined by plotting the natural logarithm of torque *versus* $1/T$ over the temperature (degrees Kelvin) where the slope of this line is the E_{act} of flow after correcting for units and multiplying by -1 . Higher values describe a sample where the melt viscosity undergoes large changes in viscosity with changes in temperature. When the initial torque values for the entire temperature series are plotted, the E_{act} of flow was determined to be 40 kJ/mol [Fig. 7(A)]. This result is in good agreement with other polymer systems.^{23,26,27} On examination of the resulting plot, it can be seen that the discontinuity described above is also seen here. The initial torque values for the higher temperatures provided a better exponential fit than those values taken at lower temperatures. If the initial torque values for only the 60–90°C samples are used, the resulting fit is improved (correlation value of 0.9994) and the slope of the resulting line provides an E_{act} of flow of 53 kJ/mol [Fig. 7(B)].

TABLE V
Effect of Processing Temperature/Time on Tensile Properties and Solubility

Temp. (°C)	Time (min)	TS	%E	YM	% Moisture	% Loss	Swelling ratio
90	10	31.7 ± 2.5	9.7 ± 0.6	421 ± 14	4.7	4.1	1.1
80	10	40.6 ± 5.6	14.1 ± 3.3	391 ± 24	4.6	4.7	1.6
70	10	39.7 ± 6.8	12.6 ± 2.3	393 ± 23	4.2	4.3	1.2
60	10	33.1 ± 5.0	11.4 ± 2.4	394 ± 11	5.4	8.8	1.7
40	10	33.5 ± 6.0	12.4 ± 2.8	382 ± 15	5.2	9.3	1.3
80	2	29.3 ± 3.7	9.4 ± 1.1	422 ± 44	4.6	6.9	1.6

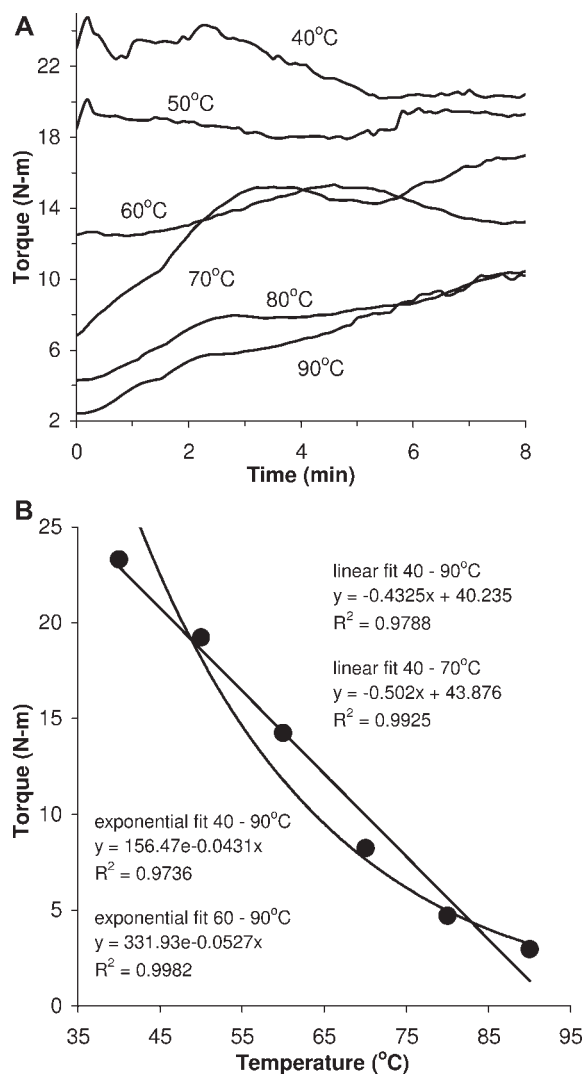


Figure 6 Effect of processing temperature on torque, 6% glyoxal, 0.186 mmol NaOH/g zein, and 50 rpm roller rotors. (A) Torque trace with time. (B) Initial torque *versus* temperature having both linear and exponential fitted lines.

These results suggest that the structure of the zein melt undergoes a significant change at temperatures above 50–60°C. It has been shown that when torque increases with time (as with the higher temperature samples in [Fig. 6(A)]), the cause may be an increase in the molecular weight of zein during melt processing.²⁸ This increased molecular weight could be due to protein aggregation or disulfide bond formation, or more likely in this case where a crosslinking reagent is present, a small amount of protein crosslinking. This suggests that when the zein melt is processed at temperatures of 40–60°C, there is minimal change in molecular weight, while at higher temperatures the protein crosslinking becomes more significant. Previous work showed a requirement for temperatures above 50°C for the zein/glyoxal reaction

to take place in a basic solution.²² Therefore, it is not surprising that melt processing at higher temperatures leads to increased molecular weight of zein in the presence of glyoxal and base.

Solubility results are presented in Table V. The percent loss value of the 40°C sample is higher (9.3%), but still relatively low, compared with the percent loss at the standard mixing temperature of 80°C (4.7%). So, even a small amount of heat added during mixing achieved a significant reduction in solubility of the molded bars. This suggests that as long as the dough is thoroughly mixed during processing, even at a low temperature, the sample can still be rendered solvent resistant after compression molding. Processing time also had little effect on the percent loss value. The sample processed at 80°C for 2 min rather than 10 min exhibited a low loss of 6.9%. The 2 min experiment was conducted to more closely represent the processing time of extrusion processing. The reduced solubility of this sample illustrates that the shorter time required for an extrusion reaction is enough to achieve improved solvent resistance.

Although the 2 min sample exhibited a low percent loss, it failed to show an improvement in tensile strength. The only temperatures that yielded samples with improved tensile strength were 70 and 80°C. It was assumed that at the lower temperatures, the glyoxal/zein reaction was not extensive enough to achieve increased tensile strength when compression molded. The sample processed at 90°C gave a lower tensile strength than expected. This may be due to the fact that although the wall temperature of the rheometer was set to 90°C, the actual processing temperature could have exceeded 100°C. At this increased temperature, glyoxal may have left the sample before a sufficient reaction could take place to provide improved tensile strength. These results show that while processing conditions have little effect on solvent resistance, they can significantly affect tensile properties.

Effect of combined formulation changes

To test the combined effect of glyoxal level, base concentration, processing time and temperature, a sample was prepared with lower levels of each of these components. The dough was prepared with 3% glyoxal and 0.046 mmol NaOH/g zein, and was processed at 70°C for 2 min in the torque rheometer. The dough was ground and compression molded under the same conditions as previous samples. The tensile strength of this sample was not improved compared with control, but it did exhibit reduced solubility (15.6% loss). These results show that more than one processing component can be changed

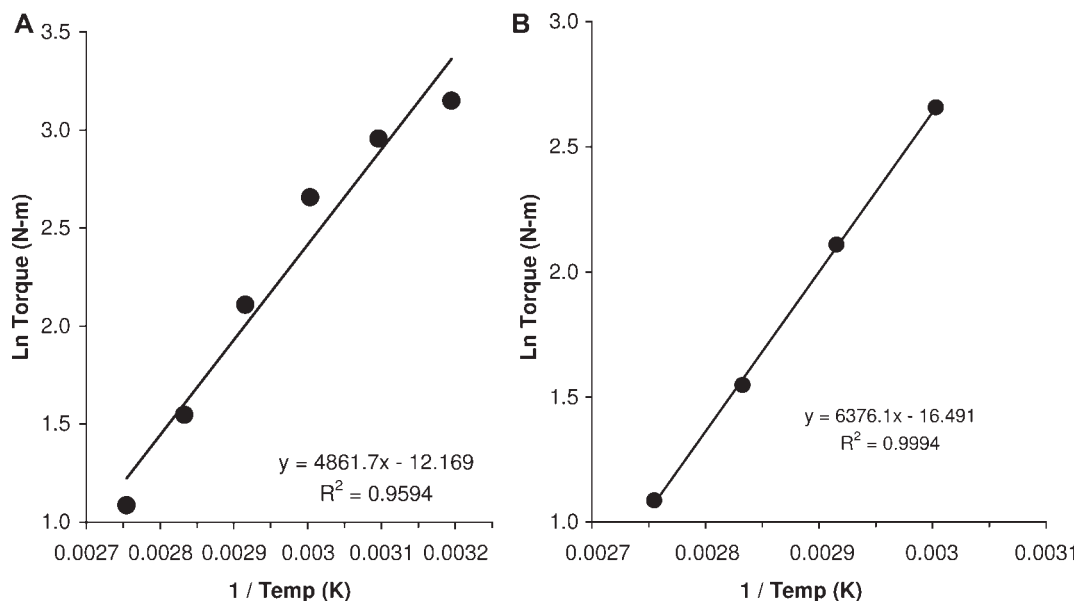


Figure 7 Determination of E_{act} of flow, plot of $1/\text{temperature}$ ($^{\circ}\text{K}$) versus the natural logarithm of the initial torque, for zein samples having 6% glyoxal, 0.186 mmol NaOH/g zein, and 50 rpm roller rotors for the temperature range of 40–90°C (A) and 60–90°C (B).

without compromising the solvent resistance of the molded bar.

Impact of different solvents on solubility

Although AcOH was used as the standard solvent for solubility testing, other solvents were also tested for their ability to dissolve the compression molded samples. The results are presented in Table VI. All samples contained 6% glyoxal and 0.186 mmol NaOH/g zein. Solvents tested were 80% aqueous ethanol (EtOH), *N,N*-dimethylformamide (DMF), 10% hydrochloric acid (HCl), 10% NaOH, acetone, toluene, tetrahydrofuran (THF), acetonitrile and AcOH. Of the samples that swelled, the sample exposed to 80% aqueous EtOH had the highest percent loss (10.7%), followed closely by 10% HCl, toluene and THF (all 9.9%), acetonitrile (9.8%) and acetone (9.5%). DMF exhibited a loss value (5.6%) closest to that of the AcOH sample (4.7%). The sample exposed to 10% NaOH completely dissolved after soaking for 16 h. Concentrated base has been shown to degrade zein.²⁵

The DMF sample had the highest swelling ratio, followed by AcOH and 80% EtOH. The same trend in swelling ratio (DMF > AcOH > 80% EtOH) was seen previously in cast zein/glyoxal films.²² The remaining solvents yielded samples with very low swelling ratios, with no visible swelling after soaking for 16 h.

Percent loss values did not directly correlate with swelling ratio data. The 80% aqueous EtOH sample, for example, had the highest percent loss but a fairly

low swelling ratio. Conversely, DMF had a low percent loss and the highest swelling ratio. Acetone and 10% HCl had negligible swelling but relatively high percent loss values. The use of concentrated base (10% NaOH) resulted in hydrolysis of the protein. The ability of a given solvent to swell a polymer depends on a number of factors.²⁹ These findings show that the swelling ratio for a given solvent cannot be inferred from the percent loss data.

CONCLUSIONS

The effect of varying glyoxal, base concentration, and processing conditions on compression molded zein bars produced from melt processed zein was explored. To improve solvent resistance, the zein required two processing steps. Melt processing was utilized to provide a homogenous blend, followed by compression molding to impart solvent resistance

TABLE VI
Impact of Various Solvents on Solubility of Compression Molded Bars

Solvent	% Loss	Swelling ratio
AcOH	4.7	1.6
80% aqueous EtOH	10.7	0.6
DMF	5.6	2.3
10% HCl	9.9	0.3
10% NaOH	100	N/A
Acetone	9.5	0.1
Toluene	9.9	0.1
THF	9.9	0.1
Acetonitrile	9.8	0.1

to samples produced using appropriate formulations. Samples containing 6% glyoxal with at least 0.00019 mmol NaOH/g zein, and those including at least 1.5% glyoxal with 0.186 mmol NaOH/g zein, exhibited increased solvent resistance compared with control bars. Improved tensile strength was obtained at glyoxal levels of at least 3%. Although the low levels of NaOH tested provided solvent resistance, the amount of NaOH had to be greater than 0.186 mmol/g zein to provide improved tensile strength. Other inorganic bases provided some reduction in solubility; however, tensile strength was not improved. Modification of processing conditions during the initial melt processing step had a minimal effect on the solubility of the compression molded bar. These same modifications, including varying temperature and processing time, had a significant effect on tensile properties.

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