Reactive Extrusion of Zein with Glyoxal

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ABSTRACT: Cross-linked zein has been produced using glyoxal (GLY) as the cross-linking reagent via reactive extrusion for the first time in a twin screw extruder using dilute sodium hydroxide as catalyst. Tri(ethylene glycol) was used as a plasticizer for various items. The extrudate was then ground and processed using either compression or injection molding. At the highest level of GLY (6%), tri (ethylene glycol) was used at 10% as a plasticizer to allow further processing to take place. With this formulation, samples could be obtained from the injection mold, however, the samples did not hold their molded shape due to the elasticity of the sample at the mold temperature. When lower levels of GLY were used, injection molded sample bars of similar quality to control were obtained. The physical properties of these samples were similar to control. At GLY levels of 1.75% and higher, the samples were resistant to dissolution by acetic acid. © 2009 Wiley Periodicals, Inc.[†] J Appl Polym Sci 113: 1828–1835, 2009

Key words: zein; glyoxal; reactive extrusion; cross-linking; injection molding

INTRODUCTION

As the amount of bio-ethanol being produced from corn increases, it is becoming more important to develop higher value end uses for the coproducts generated. Zein is the dominant protein present in both corn gluten meal, from wet millers, and distillers dried grains, from dry millers.[1] These two materials are some of the main coproducts of the bioethanol industry and are second only to carbon dioxide. Historically, zein was mainly used in the textile fibers market where it had to be cross-linked with formaldehyde to provide a fiber with properties allowing it to be used as a wool replacement.[2–5] With the limited number of lysine residues[6,7] present in the structure of zein, the use of cross-linking reagent capable of reacting with nonamine functional groups is needed. The few cysteines also make the formation of sulfur bridges unlikely.[6,7] These zein fibers were produced using wet spinning techniques. Dry spinning techniques have been developed recently for producing zein fibers, however these fibers also required formaldehyde treatment to have acceptable properties.[8] Both wet and dry spinning require the polymer to be dissolved in a solvent, which then requires significant investment in waste treatment or solvent recovery facilities. Many synthetic polymer fibers, such as those based on nylon and polyester, are produced using melt processing.[9]

Extrusion manufacturing techniques avoid solvent recovery and treatment, which then delivers significant economic advantages. Zein has been processed using extrusion techniques to provide improved properties, however, once again formaldehyde was used to deliver improved properties.[10,11] Commercial use of formaldehyde, a suspected human carcinogen, will require significant investment to be performed safely. In addition, the zein modifications previously described have taken place after the article has been produced. Citric acid and 1,2,3,4-butane tetracarboxylic acid have been used to modify zein in the melt state, however, either physical properties were not measured or the carboxylic acids were not incorporated into the zein structure.[12,13] Other methodologies are being explored to improve the properties of zein; however, these processes were performed in solution.[14–19] Recently, zein has been cross-linked using glyoxal (GLY), where GLY is capable of reacting with functional groups present on arginine, lysine (this residue is not present in zein) and the N-terminal amine, in both solution[20] and in the melt state.[21] By carrying out the reaction in the melt state, the economic advantages of extrusion

may be obtained. Finally, the overall safety of the process will be improved as further treatments after article formation can be avoided.

Reactive extrusion has been shown to provide the continuous production of chemically modified polymers.[22–26] Other workers have used reactive extrusion to produce polymeric systems that may be cross-linked by further treatments.[25–28] Reactive extrusion has also been used to modify soy protein.[29,30] By using the reactive extrusion technique with zein, we hope to develop a continuous means of producing a cross-linked zein extrudate that can be further processed to provide high value articles with improved solvent resistance.

MATERIALS AND METHODS

Materials and equipment

Zein was obtained from Freeman Industries (Tuckahoe, NY), Lot #40007023 (14.6% nitrogen, 5.0% moisture, and 1.3% ash). GLY (40% w/w aqueous solution), NaOH, tri(ethylene glycol) TEG, and solvents were obtained from Sigma-Aldrich (St. Louis, MO).

A Werner and Pfleiderer (Werner and Pfleiderer, Tamm, Germany) corotating ZSK30 twin screw extruder was used for reactive extrusion. The screw configuration is given in Table I. The first digit represents the number of that particular element that was used. The second set of numbers and letters describes the configuration of the conveying or mixing elements. The entire length of the screw was 134 cm. For injection molding of the extrudate from twin screw compounding, an ACT75B injection molder (Cincinnati Milacron, Batavia, OH) was used. A Carver Model C press (Carver, Wabash, IN) was used to make compression molded tensile bars in accordance with the ASTM D-638-V Standard. The color of samples was measured using a Hunter ColorFlex (Hunter Associates Laboratory, Reston, VA) colorimeter with results reported using the L, a, b scale. Sample thicknesses for the physical property samples were measured at three different locations in the testing region using a micrometer (Model No. 49–63, Testing Machines Inc, Amityville, NY). Constant relative humidity (RH) at 25°C was obtained using Hotpack humidity chambers (Hotpack, Warminster, PA). Moisture contents were measured on an Ohaus moisture meter MB45 (Ohaus, Pine Brook, NJ). Infrared spectra were obtained on a Thermo Nicolet Avatar 370 FTIR (Thermo Scientific, Waltham, MA) where the samples were tested in KBr pellets. Tensile strength (TS), Young's modulus (YM), and elongation at break (%E) were evaluated for each sample using

TABLE I
Screw Configuration for Reactive Extrusion of Zein with GLY

Element type	Cumulative length (cm)
42/42 (157×)	63[a]
20/20	65
KB45/5/42	69
KB45/5/28	72
KB45/5/14	73
42/42	78
28/28	80[b]
28/14	82
KB45/5/20	84
KB45/5/14	85
KB90/5/28	88
KB/45/5/14/LH	89
42/42	94
28/28	96
20/20	98
KB45/5/20	100
KB45/5/14	102
KB90/5/28	105
KB/45/5/14/LH	106
42/42	110
28/28(2X)	113
KB45/5/20	115
KB45/5/14	116
KB90/5/28	119
KB/45/5/14/LH	121
42/42	125
28/28 (2X)	130
20/20 (2X)	134

[a] Fifth and sixth injection ports located in these sections.
[b] Ninth injection port located in this section.

an Instron® Universal Testing Machine Model 4201 (Instron, Norwood, MA).

Reactive extrusion

Zein was added to the inlet of the twin screw extruder at 71.25 g/min. Reagents were added at the fifth, sixth, and ninth ports along the extruder barrel. At the fifth injection port (46.2 cm along length of extruder), 1M NaOH/water solution was added at 13.2 g/min. At the sixth injection port (54.6 cm along length of extruder) various amounts of TEG were added. The amount of TEG added was such to deliver 5% (3.6 g/min), 7.5% (5.3 g/min) or 10% (7.1 g/min). At the ninth injection port (80.1 cm along length of extruder) a 40% GLY solution was added to give the desired amount of GLY. The amounts of GLY solution added were such to deliver 1% (1.8 g/min), 1.25% (2.2 g/min), 1.5% (2.7 g/min), 1.75% (3.1 g/min), 2% (3.6 g/min), 3% (5.3 g/min), 4% (7.1 g/min), and 6% (10.7 g/min). The extruder was run at 147 rpm. The first zone of the extruder was set to 37°C with the remaining zones controlled at 80°C. The specific mechanical energy put into the resin was between 194 and 455 J/g. The main contributors

to the SME were the amount of TEG and GLY/ NaOH. Increased levels of TEG decreased SME whereas increased levels of GLY/NaOH increased SME. A die was not used at the end of the extruder as the extrudate was going to be ground using a Wiley Mill (Brabender, Duisburg, Germany) for further processing. The elimination of the die avoided flow irregularities and pressure fluctuations as the extrudate exits the die which may result in pluggage.

Injection molding

The zones in the extruder were varied in the following fashion where the lower temperatures were used for formulations having lower amounts of GLY. Zone temperatures ranged from 71–93°C for Zone 1, 110–138°C for Zone 2, 132–149°C for Zone 3, and 132–149°C for the nozzle. The sprue temperature was between 132 and 149°C, where lower amounts of GLY required lowered temperatures. The injection pressure was between 103 (control, 0% GLY) and 186 MPa (higher levels of GLY). The mold was run between 38°C (control, 0% GLY) and 85°C (higher levels of GLY). After injection and mold release, the part was placed between two metal plates with a 2 kg weight placed on top to help the article cool and ensure a flat configuration. Samples were stored at 23°C and 50% or 70% RH for 5 days before testing physical properties. It has been shown that storing samples for 5 days is sufficient time to equilibrate the samples.[31] Data values reported are the average of five samples. TS, YM, %E data are presented as the calculated value ± one standard deviation. Physical properties were determined with a cross-head speed of 50 mm/min, a gauge length of 7.62 mm, and a 1 kg load cell. Data values reported are the average of five samples.

Compression molding

Extrudate from the twin-screw experiments were ground to a fine powder using a Wiley Mill. 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, and then allowed to cool at room temperature. Samples were stored at 23°C and 50 or 70% RH for 5 days before testing physical properties. TS, YM, and %E data are presented as the calculated value ± one standard deviation.

Percent loss/swelling ratio testing

After cooling, the samples were tested for resistance to dissolution in acetic acid (AcOH) by placing approximately 0.5 g of a molded bar in 10 g of solvent. The sample remained in the AcOH for 4 or 24 h and then the swelled bar was removed and gently blotted dry to obtain the wet weight. 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. Percent loss was calculated by comparing the final dry weight with the original sample weight. Swelling ratio was calculated using eq. (1), where W_w and W_d represent the wet and dry sample masses, respectively. A swelling ratio of 1.0 describes a sample that has swelled 100% (doubling its mass when wet) compared with the dry bar whereas a ratio of 0.5 describes a sample that has swelled 50% (increasing its mass by 50% when wet).

$$\text{Swelling ratio} = (W_w - W_d)/W_d \qquad (1)$$

RESULTS AND DISCUSSION

Color and appearance

Reactive extrusion production of zein with various amounts of GLY was performed on a twin-screw extruder. Various formulations were prepared as detailed in Table II. Item names list the % GLY, followed by the % TEG. The sample containing 4% GLY and 5% TEG, for example, is labeled 4–5. TEG was used as a plasticizer between 0 and 10%. The amount of base used was based on previous work done using GLY in a batch melt process.[21] All

TABLE II
Zein GLY Formulations Produced via Reactive Extrusion

Item	% GLY	% TEG	Injection molded	Compression molded
0–0	0	0		X
0–5	0	5	X	X
0–10	0	10	X	X
1–0	1	0	X	X
1–5	1	5	X	X
1.25–0	1.25	0	X	X
1.5–0	1.5	0	X	X
1.75–0	1.75	0	X	X
2–0	2	0	X	X
2–5	2	5	X	X
2–7.5	2	7.5	X	X
2–10	2	10		X
4–0	4	0	X	X
4–5	4	5	X	X
6–0	6	0		X
6–5	6	5		X
6–10	6	10	X	X

formulations were produced on the twin screw extruder using the same processing conditions.

Visual differences were observed in the extrudate. The control extrudate was a burnt orange in color. As GLY and base are added the color darkens becoming a chestnut color. When either reagent is used alone, the color does not darken to the same extent. The color of the samples were measured using a colorimeter and the resulting $L, a,$ and b values are detailed in Table III. The L value represents the amount of white/black that is present in the sample with a value of 100 being pure white. The a value represents the amount of red/green that is present in the sample with positive values representing higher amounts of red color and negative values representing higher amounts of green color. The b value represents the amount of yellow/blue that is present in the sample with positive values representing higher amounts of yellow color and negative values representing higher amounts of blue color. The ΔE value is a composite of the $L, a,$ and b values and is obtained by taking the square root of the sum of the squares of each of these color values [eq. (2)]. By using ΔE, the absolute color differences between samples can be more easily quantified in examining a single number. It has been determined that if two samples have a difference in ΔE of 1, then the eye can discern these samples as being different in color.[32]

$$\Delta E = \sqrt{L^2 + a^2 + b^2} \qquad (2)$$

As the amount of GLY is increased the color of the sample darkens as evidenced by a decrease in the L value. At levels of GLY above 4%, the bars are
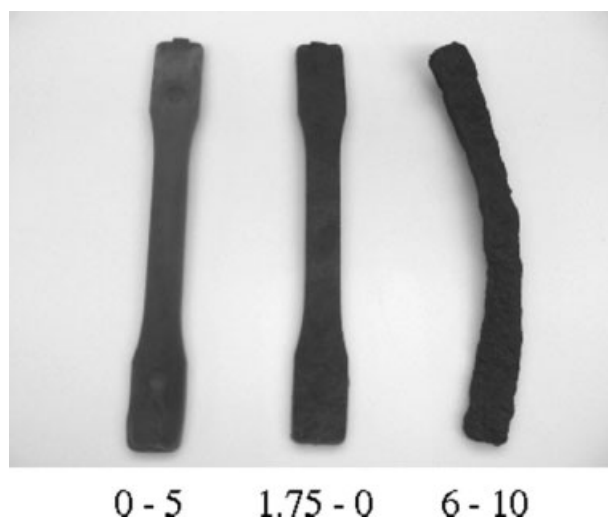

Figure 1 Injection molded zein samples, 0–5, 1.75–0, and 6–10.

a very dark brown. This color change is useful in terms of defining when a transition, for example when going from control to 2% GLY, is complete. Approximately, 2 min after turning off the GLY flow to the extruder, the extrudate color will change from a dark brown to the control color of burnt orange.

Select samples detailed in Table II were processed via injection molding. Elevated amounts of TEG combined with GLY concentrations of 2% led to formulations that could not be injection molded using the extruder and molding conditions used. The material would not flow through the extruder into the mold at a rate required to completely fill the mold. All formulations having 6% GLY could not produce quality injection molded samples. Using this formulation, the bars came out of the mold wrinkled and not straight (Fig. 1). Some surface imperfections were also observed in compression molded samples as well when the amount of GLY was high (Fig. 2). With higher amounts of GLY, leading to higher cross-link density,[21] the samples will have higher elastic modulus[33,34] so that when the mold is released, the samples retract giving ill-formed articles. It is anticipated that further research into injection molding conditions will yield quality injection molded samples. All of these samples were tested for resistance to dissolution by AcOH.

TABLE III
L, a, b Color of Zein-GLY Samples

	L	a	b	ΔE
Injection molded				
0–5	27.7 ± 0.9	9.0 ± 0.3	20.9 ± 1.8	35.8 ± 2.0
2–5	26.8 ± 0.8	6.8 ± 0.3	8.4 ± 0.2	28.9 ± 0.9
4–5	23.8 ± 0.4	0.5 ± 0.1	0.6 ± 0.2	23.8 ± 0.5
6–10	19.7 ± 0.9	0.2 ± 0.1	0.0 ± 0.2	19.7 ± 0.9
Compression molded				
0–0	32.7 ± 0.9	4.4 ± 0.2	15.2 ± 1.7	36.3 ± 1.9
0–5	24.2 ± 0.1	4.8 ± 0.4	9.1 ± 1.4	26.3 ± 1.5
2–0	18.1 ± 1.8	3.2 ± 0.3	3.2 ± 0	18.6 ± 2.0
2–5	16.8 ± 1.5	3.9 ± 0.5	5.5 ± 0.9	18.0 ± 1.8
4–0	19.3 ± 1.3	3.4 ± 0.5	2.9 ± 0.3	19.8 ± 1.4
4–5	19.2 ± 2.0	2.6 ± 0.3	3.9 ± 1.0	19.7 ± 2.3
6–0	16.1 ± 4.0	1.7 ± 0.8	2.9 ± 1.2	16.4 ± 4.3
6–10	20.8 ± 2.4	1.4 ± 0.2	2.2 ± 0.5	21.0 ± 2.4

Values reported are averages $\pm$ 1 standard deviation.

Solvent resistance

It has been shown that GLY can improve the solvent resistance of zein articles when the articles were allowed to soak in AcOH.[20,21] In these studies, the zein-GLY reactions either took place in solution or in a batch melt process. In the batch melt process, the samples were processed for 10 min. When appropriate samples from these trials were soaked
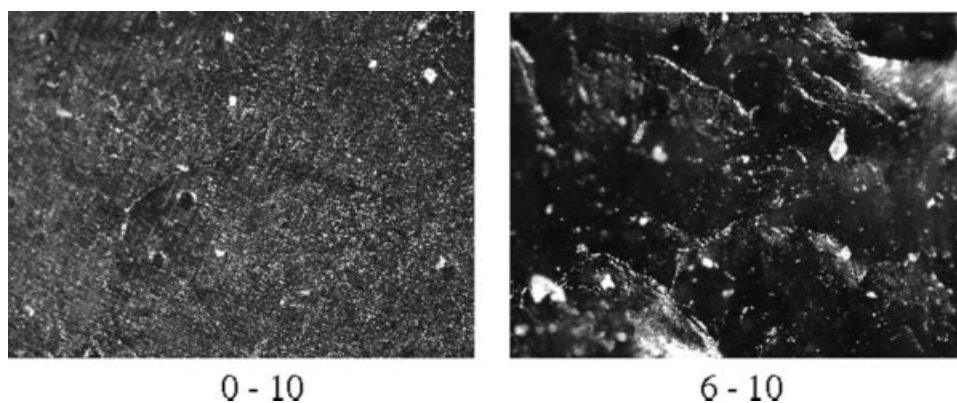
Figure 2 Compression molded bar surface analysis by optical microscope (×100).

in acetic acid, instead of dissolving or disintegrating to give a dispersion, the sample swelled indicating that a cross-linked networked had formed, resulting in increasing rubber-elastic behavior giving ill-formed bars after injection molding. In these studies, when GLY levels were above 1.5% swelling ratios could be obtained. Seen in Table IV are the % loss and swelling values for the reactive extrusion and injection molded samples. When samples were produced at 1 and 2% GLY, there was observed a step change in the amount of material that dissolved. With those results, additional samples were produced to better define where the % loss reached its minimum. At GLY concentrations greater than 1.5% the amount of sample that dissolves in AcOH is reduced. When 1.75% or more GLY is used, the amount of material that dissolves reaches it minimum. When GLY levels of 4 and 6% were used, TEG had to be added to give injection molded samples. Although the samples having 6% GLY were ill formed, they could be tested for dissolution by AcOH. It is surprising that despite the presence of TEG, the amount of sample that is lost on soaking in AcOH is still very low. This may be due to the reduced mobility that is present in a cross-linked system so that diffusion of the plasticizer is greatly

slowed. Similar results are seen when examining the degree of swelling in AcOH. After soaking for 4 h, the swelling ratio increases, reaches a maximum, and then declines. The initial low swelling values are due to the relatively high amount of sample that dissolves. When sufficient GLY is present to provide a cross-linked network of sufficient density, enough sample resists dissolution so that the swelling ratio increases. With increasing amounts of GLY, the cross-link density increases and the swelling ratio then decreases. At levels of at least 1.75%, the article is resistant enough to solvent so that a swelling ratio could be measured after soaking in AcOH for 24 h (at levels below 1.75%, the sample is either too sticky to blot dry or it completely dissolves). At the highest levels of GLY used, TEG was incorporated to assist in production. Given the solubility of TEG in AcOH, both the % loss and swelling ratio will be affected by loss of TEG. This would then be interpreted as a lower degree of cross-linking. Efforts were not

TABLE IV
Swelling Ratio and % Loss Values for Injection molded Samples after Soaking in AcOH for Either 4 or 24 h

Sample	4 h % loss	24 h % loss	4 h swelling ratio	24 h swelling ratio
0–0	39	100	0.3	0.0[a]
1–0	46	100	0.2	0.0[a]
1.25–0	45	100	0.3	0.0[a]
1.5–0	29	70	0.4	0.0[a]
1.75–0	11	12	1.4	1.4
2–0	11	8	1.4	1.4
4–5	9	9	1.1	1
6–10	7	7	0.7	0.7

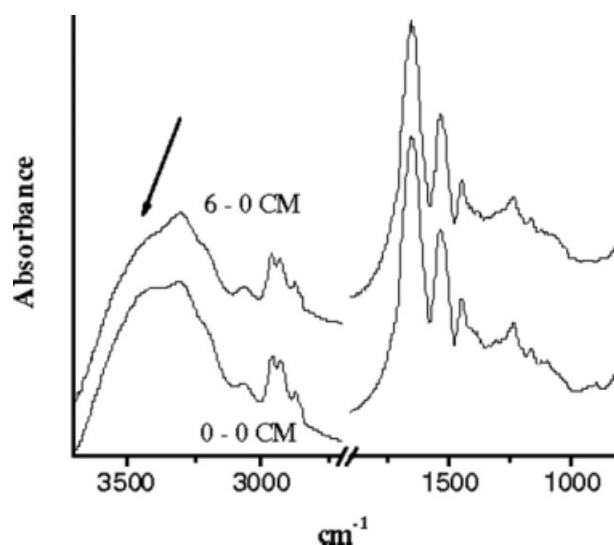[a] Sample dissolved or too sticky to measure.

Figure 3 IR spectra of samples 0-0 cm and 6-0 cm. Absorbance is relative for each region of the spectra displayed. Arrow highlights area of difference.

TABLE V
Physical Properties of Injection Molded Samples after Storage at 50% or 70% RH

Sample	50% RH			70% RH		
	TS (MPa)	Elo (%)	YM (MPa)	TS (MPa)	Elo (%)	YM (MPa)
0–5	35.2 ± 3.3	4.8 ± 0.7	1126 ± 33	26.3 ± 1.5	7.2 ± 0.8	626 ± 35
0–10	33.0 ± 3.0	6.9 ± 0.9	806 ± 32	15.4 ± 0.9	30.6 ± 14.7	305 ± 26
1–0	24.0 ± 10.6	4.0 ± 2.0	1096 ± 131	32.5 ± 2.5	4.9 ± 0.2	999 ± 55
2–0	26.6 ± 2.2	5.1 ± 0.6	948 ± 98	27.2 ± 1.2	6.4 ± 0.7	774 ± 54
2–5	26.0 ± 1.5	4.6 ± 0.3	1084 ± 169	26.2 ± 1.8	5.7 ± 1.2	722 ± 45
4–0	35.2 ± 0.6	6.4 ± 0.6	951 ± 70			

expended in attempting to determine the amount of TEG relative to the amount of zein present in the material that was removed by solvent.

IR spectra

To determine if there are chemical differences that occur when modified with GLY IR spectra were obtained. The spectra were examined in both the absorbance and transmittance modes. As seen in Figure 3 (absorbance), a subtle difference is seen around 3325 cm^{-1}. Given that GLY can react with alcohol group,[35-38] it is not surprising to see subtle changes in the spectra corresponding to the —O—H (3325 cm^{-1}) peak. However, this difference could also be affected by how water in sample interacts with the cross-linked protein relative to starting material. There were no apparent differences in the carbonyl region of the spectra suggesting little change in the secondary structure of the protein.[39,40] Given the structure postulated for zein, where many of the nucleophilic species are located on the periphery of the protein, it is not too surprising that changes in secondary structure were not observed.[41]

Physical properties

The use of GLY has been shown to improve the physical properties of both melt and solution processed articles.[20,21] Injection molded articles of formulations that provided quality injection molded samples had their physical properties evaluated after storage at 50% RH and select samples were tested after storage at 70% RH (Table V). Samples 4–5 and 6–10 (Fig. 1) did not provide quality injection molded samples suitable for physical property testing. The stress–strain curve of both control and GLY samples were similar, displaying brittle failures (Fig. 4). The inability to provide improved TS may be due to reaction time. It has been shown that when this reaction was carried out in a batch melt process using either short reaction times and/or lower reaction temperatures, tensile properties were not improved however solvent resistance was imparted.[21] The TS observed for both control and GLY

modified articles is similar to that of polypropylene so these absolute values may have some usefulness in the marketplace.[42] As was seen in Table IV, the extent of reaction is sufficient to provide solvent resistance. The detrimental effect of elevated levels of TEG on TS when the samples are stored at elevated humidity is readily seen in the control sample. It has been shown that water is a strong plasticizer (not a cross-linking reagent) for zein and will negatively affect TS with samples are stored at elevated humidity.[32,43] However, the sample having 2% GLY does not lose a significant amount of TS after storing at 70% RH.

To better define the impact of using the reactive extrusion technique, samples were prepared using compression molding. If additional time at elevated temperature is required to complete the reaction, which has been observed to change solvent resistance in glutaraldehyde systems,[44] then improvements may be seen after compression molding where the time at temperature is significantly longer.
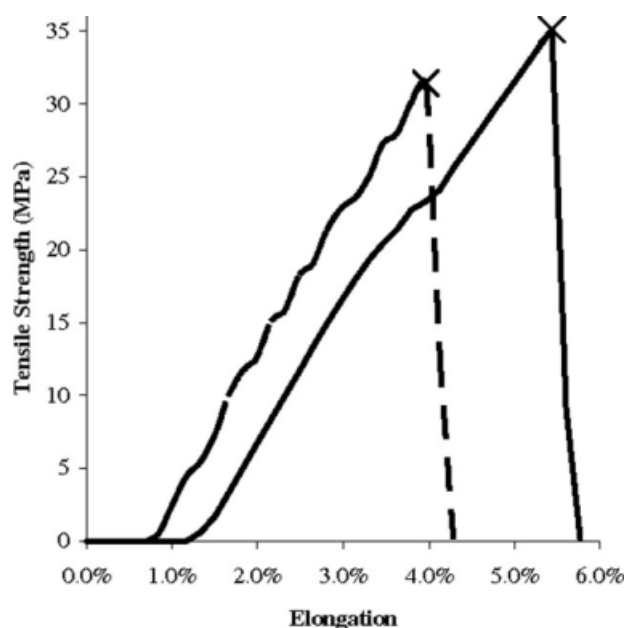

Figure 4 Stress–strain curve of samples 0–0 (– –) and 4–0 (—). The break point is designated by the ×.

TABLE VI
Physical Properties of Compression Molded Samples after Storage at 50 or 70% RH

Sample	50% RH			70% RH		
	TS (MPa)	Elo (%)	YM (MPa)	TS (MPa)	Elo (%)	YM (MPa)
0–0	35.5 ± 1.3	10.5 ± 1.2	457 ± 21	34.3 ± 6.0	12.2 ± 2.8	391 ± 33
1–0	40.3 ± 6.5	13.1 ± 2.6	400 ± 31	44.6 ± 4.6	14.8 ± 2.7	401 ± 12
2–0	40.0 ± 6.3	14.4 ± 2.8	445 ± 20	40.0 ± 4.0	12.8 ± 1.2	431 ± 12
4–0	40.4 ± 8.3	12.3 ± 2.8	416 ± 21	37.3 ± 6.4	13.8 ± 3.3	369 ± 30
6–0	42.9 ± 7.1	14.2 ± 3.9	413 ± 26	38.2 ± 3.3	13.6 ± 1.3	388 ± 21
0–5	39.5 ± 1.0	13.4 ± 0.8	390 ± 35	29.1 ± 1.8	12.9 ± 1.4	316 ± 21
1–5	40.4 ± 4.1	15.0 ± 1.0	356 ± 35			
2–5	38.3 ± 3.3	14.7 ± 2.3	346 ± 15			
4–5	41.1 ± 6.6	15.4 ± 3.1	337 ± 20			
6–5	38.6 ± 3.7	16.1 ± 1.7	304 ± 21			
0–10	38.0 ± 2.5	13.2 ± 0.9	389 ± 26	21.8 ± 1.3	83.3 ± 16.3	205 ± 14
2–7.5	35.6 ± 4.6	12.6 ± 1.6	354 ± 21			
2–10	37.5 ± 3.6	17.0 ± 1.3	297 ± 15	19.1 ± 1.2	65.1 ± 15	162 ± 7
6–10	32.8 ± 2.4	15.1 ± 2.1	290 ± 17			

Values after ± sign represent one standardstandard deviation.

Detailed in Table VI are the physical properties of various formulations after compression molding. Select samples were conditioned at both 50 and 70% RH. The % moisture of the samples stored at 50 or 70% RH ranged from 3.6 to 4.7% and 4.5 to 5.0%, respectively. The incorporation of GLY did not have an impact on % moisture. There are significant differences in physical properties when comparing the results from compression or injection molding. Differences in physical properties between injection molded and compression molded article have been seen in other systems and were attributed to shear effects, cooling rates, or cooling times.[45,46] TS is not improved relative to control with the incorporation of GLY. This result suggests that the necessary chemistry that is required to provide improved TS can not be actuated by additional heating. The deleterious affect of TEG on physical properties after storage at elevated humidity is seen here as well.

CONCLUSIONS

Reactive extrusion has been used to successfully derivatize and cross-link zein. Formulations using 2% or less GLY could be readily injection molded. Other formulations, especially those with elevated amounts of GLY, could not be injection molded using the conditions used. All samples could be compression molded. Samples produced by either injection molding or compression molding were found to be resistant to dissolution by AcOH. As the amount of GLY increased beyond 1.25% the amount of material that was dissolved by AcOH decreased significantly. At GLY levels of at least 1.75%, the samples swell on exposure to AcOH. Samples produced by compression molding had higher TS than those produced by injection molding. Incorporation of GLY did not improve TS relative to control.

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