



## Effect of multiple extrusion passes on zein<sup>☆</sup>

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### ABSTRACT

Zein was processed up to seven times using a single screw extruder at a temperature of 145 °C and at approximately 15 g per minute to determine the extent of degradation that occurs with multiple extrusion passes. SDS-PAGE shows that with the second pass, and each additional pass, the amount of high molecular weight material increases. Given that a reducing agent reduces the molecular weight of the protein, then this increased molecular weight is predominantly due to disulfide bond formation between proteins. Examination of the secondary structure of the protein using far-UV CD illustrated that after the third pass there was a significant reduction in the amount of  $\alpha$ -helix and  $\beta$ -sheet content. Examining the near-UV CD spectra, which reflects changes in protein tertiary structure, illustrates significant changes in structure after the first and second pass through the extruder. IR and NMR spectroscopy revealed small differences with multiple passes through the extruder. Examining color using the  $\delta E$  scale displays a change in color after four extrusion passes. The physical properties of compression molded samples from each pass are similar with statistical differences being observed only in modulus. While some changes in zein properties can be observed with multiple extrusion passes, if physical properties are of the highest importance, then zein can be processed at least seven times and still provide a quality material.

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### 1. Introduction

The main techniques for the industrial processing of corn are dry milling and wet milling [1]. Dry milling is mainly used to produce ethanol. Wet milling is used to produce corn starch which can either be the final product or further converted into ethanol. In both of these processes, the proteinaceous components are not used in producing the main product of interest. These materials must be fully utilized to maximize revenue. Zein (corn protein) is one of the main components in the co-products from either process [2]. Zein was successfully used in the textile fibers market from the 1940's through 1960's [3,4]. These fibers were made using wet-spinning techniques, where the chemically modified zein solution was extruded into a non-solvent which results in the production of solvent resistant fiber being formed after fiber drawing. While wet-spinning can produce valuable fibers, the current standard for fiber production uses extrusion techniques [5]. The advantage that extrusion techniques bring to a process arises from the elimination

of solvent. This results in significant cost reductions as waste treatment and/or solvent recovery can be avoided. However, extrusion imparts a great deal of heat and shear into a polymer which may result in degradation which can have a negative impact on the properties of the final product [6,7]. Zein has been processed using extrusion techniques [8–14]. The amount of degradation that occurs when extruding zein at different temperatures has been investigated, where the degree of degradation was monitored using various techniques (circular dichroism, infrared spectroscopy) as well as by measuring physical properties [14]. These studies were conducted after processing zein through the extruder one time at various temperatures. Given that one of the advantages that thermoplastic materials have is that they can be recycled using extrusion techniques, it is important to understand how multiple passes through an extruder impacts the properties of the polymer. With that, research has been conducted examining how multiple passes through an extruder can impact properties on other bio-based and petroleum based polymers [15–17]. While a commercial application of zein is not in hand using extrusion processes, developing information on the affects extrusion recycling has on zein will contribute to the development of a successful zein based melt process. It has been shown that at extrusion temperatures above or between 140 and 160 °C, physical properties begin to deteriorate [14], therefore 145 °C was chosen as the temperature to evaluate

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the effect of multiple extrusion passes on zein. We report herein our results on how multiple passes through an extruder effects the chemical and physical properties of zein.

## 2. Experimental

### 2.1. Materials and equipment

Zein was obtained from Flo Chemical (Ashburnham, MA), Lot #40008064 (14.6% Nitrogen, 4.2% moisture, 1.3% ash). Deionized water was used to adjust moisture content to the desired level. Triethylene glycol (TEG) was used as received from Aldrich Chemical Company (Milwaukee, WI). A single screw extruder, Model PL2000 (C.W. Brabender, South Hackensack, NJ), with a 30:1 L/D screw with a 3:1 metered ratio was used [14]. The compression zone of the screw begins 43.2 cm down its length. The transition section of the screw is 1.5 cm long. A rod die having an opening of 1.14 cm and a length of 9.5 cm long was used for all items. Pictures of the extrudate exiting the extruder were taken using a Canon PowerShot A60. For the first pass, TEG was added to zein and mixed in a mixer for 10 min before feeding. For subsequent extrusion passes, the extrudate from the previous run was ground in a Wiley Mill (Thomas Scientific, Swedesboro, NJ) using a 5 mm screen to provide feed for the next extrusion pass. The portion of extrudate that was destined for analytical testing was further milled using a 2 mm screen. A Carver Model C press (Carver Inc., 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 where the ' $L$ ' represents white/black ( $L = 100$  pure white), ' $a$ ' represents red/green (positive is red and negative is green), and ' $b$ ' represents yellow/blue (positive is yellow and negative is blue). Color is also expressed using the  $\delta E$  scale, which is equal to the square root of the sum of the squares of  $\delta L$ ,  $\delta a$ , and  $\delta b$ . Sample thicknesses of compression molded samples were measured at five different locations using a micrometer (Model No. 49–63, Testing Machines Inc., Amityville, NY). Constant relative humidity (50% RH) at 25 °C was obtained by storing in a constant temperature and humidity room. Moisture contents were measured gravimetrically after drying for 3 h at 105 °C. Tensile strength (TS), Young's modulus (YM), and elongation to break (Elo) were evaluated for each sample using an Instron Universal Testing Machine Model 4201. Physical properties were determined with a crosshead speed of 50 mm/min, a gauge length of 7.62 mm, and a 1 kg load cell. NuPAGE Novex 10% Bis-Tris gels, lithium dodecyl and sulfate sample buffer were obtained from Invitrogen (Carlsbad, CA) and protein molecular weight standards (Lonza, Allendale, NJ) were used for performing sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) [18]. Infrared (IR) spectra were obtained on a Thermo Nicolet Avatar 370 FTIR (Thermo Scientific, West Palm Beach, FL) spectrophotometer in transmission mode under nitrogen following preparation of a potassium bromide (KBr, Thermo Spectratech IR grade, Waltham, MA, 250 mg) pellet produced after grinding with a Wig-L Bug (Thermo-Fisher Scientific, Newington, NH) and pressed into a pellet using a Carver Model 4350.L Press (Carver Inc., Wabash, IN). Zein far-UV and near-UV circular dichroism (CD) spectra were collected on an AVIV Model 215 Circular Dichroism Spectrometer in 90% ethanol/10% water (Aviv Biomedical, Inc., Lakewood, NJ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were run on a Bruker 500 MHz NMR (Billerica, MA) in dimethylsulfoxide- $d_6$  (Cambridge Isotope, Andover, MA) at room temperature.

### 2.2. Sample preparation

For the production of zein extrudate, ten percent TEG (20 g) was added to the zein (180 g) mixing at low speed in a Hobart mixer

(Troy, OH). After 10 min of mixing the mixture was then added to the extruder. Extrusion temperatures were set to 105, 132, 145, and 145 °C going from the feed zone to the die. Other extrusion conditions are detailed in Table 1. Screw rpm was set to achieve approximately the same throughput (residence time) for each item in the extruder. After each pass the extrudate was collected and ground on a Wiley mill using a 5 mm screen to provide the feed for the next pass. A total of seven batches using this formulation were processed, the first using fresh material and subsequent passes using ground extrudate from the previous extrusion pass. The torque produced by the extruder and the extrudate pressure on exiting the extruder increases with each pass suggesting increased melt viscosity. After the initial pass, the relationship between torque and extrudate pressure is linear (pressure = 0.35\*torque – 7.7  $R^2 = 0.96$ ).

Compression molding was carried out using a mold that could produce four test samples at a time. The appropriate amount of powder (1.5 g) was placed into each pocket of the mold to obtain a well formed sample. Samples were subjected to sufficient heat using a 5 min preheat, followed by compression at 29.1 MPa for 20 min at the desired temperature. Mold temperatures were 93 °C for pass 1, 110 °C for pass 2, 121 °C for pass 3, and 127 °C for passes 4 through 7. Molding conditions were selected to provide quality tensile test samples. It is recognized that testing the samples after different molding conditions brings an additional variable into the experiment; however, quality samples were required for testing.

### 2.3. Sample evaluation

Tensile property samples were stored at 23 °C and 50% for five days before testing physical properties. TS, YM and Elo data are presented as the calculated value and one standard deviation for a minimum of five samples. CD evaluations were carried out in solution in a manner described previously [19]. Color was measured on compression molded samples after storage at 50% relative humidity; three measurements were made and averaged to provide the results given. For color measurements, the sample standard deviations were less than 0.5%, therefore only the sample average colors are reported. SDS-PAGE is a standard protein technique where the protein is dissolved in a suitable solvent system where the proteins are typically denatured (loss of secondary and tertiary structure) and bind the surfactant (SDS) to the extent that when they are placed in a cross-linked polyacrylamide gel, they move through the gel at a rate proportional to their molecular volume [20]. The proteins can be visualized by staining the protein with a dye. When run in conjunction with proteins of known molecular weight, the relative molecular weight of the protein can be determined. For this study, SDS-PAGE was carried out after dissolving the ground extrudate in DMF utilizing a known procedure [18]. In the SDS-PAGE tests dithiothreitol (DTT) is a reagent that cleaves disulfide bonds. These bonds may be intramolecular or

**Table 1**  
Screw rpm and average throughput for processing zein + 10% TEG.

Pass	Screw rpm	Average throughput (gr/min)	Average torque (MPa)	Torque $\sigma$ (MPa)	Average pressure (MPa)	Pressure $\sigma$ (MPa)
1	115	14.5	7.3	3.7	0.2	0.2
2	15	14.2	26.2	2.4	1.1	0.5
3	12	15.6	29.5	2.5	2.4	0.3
4	13	16.0	28.5	2.4	2.8	0.1
5	12	15.2	34.4	2.1	3.9	0.1
6	12	14.1	36.9	2.1	5.1	0.1
7	12	14.9	38.9	1.1	5.9	0.2

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