Sample preparation and testing methods affect the physical properties and evaluation of plasticized zein

Gordon W. Selling*, David J. Sessa

Plant Polymer Research; National Center for Agricultural Utilization Research, USDA-ARS, Peoria, IL 61604, USA

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Abstract

The objective of this research was to generate zein ribbons on an extruder in which physical property analyses can be performed to determine whether physical properties were dependent on the testing direction. The extruded zein ribbon samples had between 10 and 15% triethylene glycol (TEG) and were conditioned at relative humidities between 23 and 70% before testing to determine the impact of sample testing direction on physical properties. Tensile strengths in the machine direction were between 18 and 64% higher than in the transverse direction. Elongations in the machine direction were between 33 and 291% higher than in the transverse direction. The magnitude of the difference between the machine and transverse direction was dependent on relative humidity and formulation. The impact of relative humidity was larger when the samples were tested in the machine direction; for example, tensile strength was reduced by 36% in the transverse direction and by 49% in the machine direction for the 15% TEG formulation when relative humidity was increased from 23 to 70%. With increased amounts of TEG, the magnitude of these differences was increased. The transverse direction tensile strength was reduced by 22% for a 10% TEG formulation, and by 36% for a 15% TEG formulation when relative humidity was increased from 23 to 70%. Polarized IR spectra of zein ribbons displayed differences between the spectra taken in the machine direction versus that taken in the transverse direction. Examination of the ribbons using polarizing light microscopy demonstrated that the ribbon was birefringent ($\Delta n = 0.0004$). These results demonstrate that molecular orientation occurred during extrusion and that orientation impacts physical properties.

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Keywords: Zein; Extrusion; Physical properties; Orientation effects; Film; Triethylene glycol

1. Introduction

With the growing importance of the bioethanol industry, new coproduct markets must be developed for the underutilized materials generated by this industry.

Zein, the predominant protein in corn, is a significant fraction of the underutilized part of corn. Research has been reported to reduce the cost for isolating the zein to allow it to be more competitive with petroleum based products. Procedures being evaluated to make the zein more accessible include utilizing improved extraction techniques of corn gluten meal (Shukla et al., 2000). Numerous reports exist in producing zein-based films via extrusion or casting techniques (Parris and Coffin, 1997; Pol et al., 2000; Paramawati et al., 2001; Padua and Wang, 2002; Yoshino et al., 2002; Padua et al., 2003; Wang and Padua, 2003; Padua and Santosa, 2004; Wang et al., 2005). Of the many

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* Corresponding author. Tel.: +1 309 681 6338; fax: +1 309 681 6681.
E-mail address: sellingg@ncaur.usda.gov (G.W. Selling).
goals that were being pursued in these efforts, one of the most important was improving the physical properties of zein-based films. Films produced by extrusion have inherent economic advantages over films produced using other techniques, one of the most important being avoidance of solvents (Park and Mount, 1987).

One disadvantage of extrusion generated films that have not been further treated to impart biaxial orientation is their inherent directionality of physical properties (Park and Mount, 1987). Property dependency on directionality is a very important parameter and is readily observed in other polymers such as nylon (Rhee and White, 2002) and polyethylene (Zhang et al., 2004). IR spectroscopy demonstrates that zein films prepared by rolling undergo orientation as evidenced by shifts in the location of the amide I band from 1658 to 1670 cm\(^{-1}\), and in the amide II band that shifts from 1538 to 1520 cm\(^{-1}\) when measured parallel to the direction of shear (Kretschmer, 1957). Differences were also observed in the amount of transmission for the amide I and II bands. The physical properties of these films were not measured.

When a series of zein samples having varying degrees of mechanical mixing (as is zein powder, cast zein films, hand stretched zein films, extruded zein ribbons, and blown zein films) were examined by wide angle X-ray scattering (WAXS), it was observed that the inter-prism packing of zein samples was being disrupted (Wang et al., 2005). Small angle X-ray scattering (SAXS) experiments carried out on these same samples demonstrated that increased mechanical mixing results in increased long-range periodic structures. The zein formulations used in these evaluations had high amounts of plasticizer (35–43%). Physical property testing of these samples was not described.

For studying the physical properties of extruded ribbons or films, the testing directions have been designated as the machine direction (MD) and the transverse direction (TD) (Park and Mount, 1987). The impact on physical properties of how the stress is applied to uniaxially oriented zein articles has not been reported. Measurements indicate that thermo-mechanical treatments change the structure of zein (Kretschmer, 1957; Wang et al., 2005). In order to develop new markets for zein, such as zein-based films, we generated samples of zein ribbons on an extruder in order to determine whether physical properties were dependent on the testing direction. These efforts will be carried out using a ribbon die that will allow property measurements to be taken in variable directions as well as to facilitate sample preparation.

### 2. Experimental

#### 2.1. Materials

Zein was used without modification and was grade F4000 (Lot F400002371C, 14.41% nitrogen, 3.47% water, 1.90% fat, 0.11% fiber, 1.53% ash) obtained from Freeman Industries LLC (Tuckahoe, NY). Distilled water was used to adjust moisture content to the desired level. Triethylene glycol (TEG) was used as received from Aldrich Chemical Company (Milwaukee, WI).

#### 2.2. Equipment

A single screw extruder, Model PL2000 (C.W. Brabender, South Hackensack, NJ), with a 30:1 L/D screw with a 3:1 compression ratio was used. For the extruded rope, a die was used with a single circular opening that was 2 mm wide and 7 mm deep. For the ribbon, a slit die with a 5.08 cm width and 0.5 mm height was used. A conveyor belt was used to take up the ribbon at the same speed as the ribbon was being produced. Samples were cut from ribbons using a press (MS Instrument Inc., Castleton on Hudson, NY) using a dog bone die having an overall length of 8 cm long, 13 mm wide at the widest point, and 4 mm wide at the narrowest point (consistent with ASTM D412) (Allen, 1999). Sample thicknesses were measured at five different locations with a micrometer (Model No. 49–63, Testing Machines Inc., Amityville, NY). Tensile strength (TS), Young’s modulus (YM), and elongation to break (Elo) were evaluated for each sample using the Instron Universal Testing Machine Model 4201 (Instron Corporation, Canton, MA). Physical properties tests were measured with a crosshead speed of 50 mm/min, a gauge length of 2.54 cm, and a 1 kg load cell. Optical microscopy, using plain or polarizing light, was performed using an Olympus CX31-P microscope (Center Valley, PA) fitted with a 10× eyepiece, using 4, 10, 20, and 40× strain-free objectives and a polarizing intermediate attachment. Microscope pictures were taken using an Olympus DP12 camera (Center Valley, PA).

#### 2.3. Sample preparation

For the production of zein rope on the extruder, the initial blend was prepared following the procedure described. The zein in a Hobart mixer (Troy, OH) was treated with the desired amounts of TEG and water were slowly added, followed by 10 min of mixing at low speed. TEG and water were both found to be effective plasticizers for zein (Lawton, 2004; Selling et al., 2004). The
Table 1
Extruder conditions for zein rope and ribbon production

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zone 1 (°C)</th>
<th>Zone 2 (°C)</th>
<th>Zone 3 (°C)</th>
<th>Die (°C)</th>
<th>Screw rpm</th>
<th>Throughput (g per min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rope A</td>
<td>65</td>
<td>90</td>
<td>90</td>
<td>80</td>
<td>60</td>
<td>16.5</td>
</tr>
<tr>
<td>Rope B</td>
<td>65</td>
<td>90</td>
<td>90</td>
<td>80</td>
<td>60</td>
<td>19.9</td>
</tr>
<tr>
<td>Rope C</td>
<td>65</td>
<td>85</td>
<td>85</td>
<td>90</td>
<td>15</td>
<td>10.9</td>
</tr>
<tr>
<td>Ribbon A</td>
<td>65</td>
<td>85</td>
<td>85</td>
<td>95</td>
<td>11</td>
<td>11.7</td>
</tr>
<tr>
<td>Ribbon B</td>
<td>65</td>
<td>85</td>
<td>85</td>
<td>100</td>
<td>9</td>
<td>13.5</td>
</tr>
<tr>
<td>Ribbon C</td>
<td>65</td>
<td>85</td>
<td>85</td>
<td>100</td>
<td>9</td>
<td>13.5</td>
</tr>
</tbody>
</table>

water content of the zein was such that 7% additional water (dry basis) was added. TEG at 10, 12.5, or 15% was added. Samples A through C all used 518 g zein (500 g dry basis) and 35 g of water (7%). For sample A, 50 g of TEG (10%) was added. For sample B, 62.5 g of TEG (12.5%) was added. For sample C, 75 g of TEG (15%) was added. Rope samples were then produced on the extruder where each of the three zones and the die were heated to different temperatures (Table 1). For all rope and ribbon production, the extruder was filled at a rate that the material was processing at a consistent rate. With the higher amount of plasticizer, the melt viscosity is reduced (Selling et al., 2004) that would lead to reduced pressure drop, and therefore higher throughput. The degree to which the viscosity is reduced was not large enough to cause slippage to occur. After extrusion, the rope was allowed to cool and then converted into pellets shorter than 1 cm using a Killion chopper (Cedar Grove, NJ). These pellets were then used as the feed for producing the ribbon. For ribbon production, the extruder conditions were not the same for each ribbon, as they were selected to provide ribbons that had few visible defects during production (Table 1). As was detailed for pellet production, the throughput for producing ribbons had a positive correlation with the level of TEG.  

2.4. Sample characterization

For the physical property measurements with the samples cut perpendicular from the ribbon, the ribbon width was not sufficiently wide enough to accommodate the entire dog bone shaped die; however, sufficient space at both ends of the sample was present to allow mounting in the Instron in an arrangement so that the part of the samples bearing the load was the same for both the perpendicular and parallel samples. Samples were stored for a minimum of one week at the desired relative humidity (RH). The moisture content in percent for samples after storage at these conditions were measured by heating the samples in an oven at 105 °C for 1 h. Constant RH values at: 23% was obtained by storage over a saturated potassium acetate solution, 50% by storing samples in a constant humidity testing room, and 70% by using a Hotpack humidity chamber (Warminster, PA). For all samples, tensile runs were performed on either three or four samples with values reported as means.

Infrared spectroscopy were performed by MTEC Photoacoustics, Inc. (Ames, IA) using a Digilab FTS7000 spectrometer (Randolph, MD), with an MTEC PAC300 photoacoustic detector (Ames, IA) and an IR polarizer (Specac, Woodstock, GA). Spectra and second derivative spectra were generated using Win-IR Pro (Digilab, Randolph, MD). The surface layer of the zein ribbon was removed (∼90 μm) using a 320 grit emery paper.

2.5. Statistical analysis

Single-factor fixed effects analyses of variance (ANOVA) were performed comparing direction differences in ELO, TS, and YM data at each of 9 RH-%TEG combinations (3 RH levels *3% TEG levels). If \( P < .05 \) from an ANOVA \( F \)-test, the directions MD and TD were considered to be significantly different from one another.

3. Results and discussion

3.1. Physical property comparisons

Pellets and ribbons were satisfactorily produced from compositions of sample A, B, or C. Samples had similar moisture content at each of the various relative humidities (Table 2). The tensile properties of the ribbons were measured in both the MD and TD after storing the rib-
Table 3
Impact of direction (machine direction, MD; and transverse direction, TD) of applied stress on tensile strength (TS, MPa), Young’s modulus (YM, MPa) and elongation (Elo, %) at different relative humidities with F-test P-values from ANOVA analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>RH (%)</th>
<th>TEG (%)</th>
<th>Dir</th>
<th>TS Mean ± S.D.</th>
<th>F-Test P-value</th>
<th>Elo mean ± S.D.</th>
<th>F-test P-value</th>
<th>YM mean ± S.D.</th>
<th>F-Test P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>23</td>
<td>10.0</td>
<td>MD</td>
<td>39.28 ± 6.18</td>
<td>.0026</td>
<td>5.10 ± 0.66</td>
<td>.0012</td>
<td>1.29 ± 0.09</td>
<td>.0025</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>23.92 ± 0.51</td>
<td></td>
<td>3.12 ± 0.19</td>
<td></td>
<td>1.52 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>23</td>
<td>12.5</td>
<td>MD</td>
<td>37.52 ± 3.36</td>
<td>.0013</td>
<td>4.90 ± 0.14</td>
<td>.0002</td>
<td>1.28 ± 0.14</td>
<td>.1336</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>25.81 ± 2.37</td>
<td></td>
<td>3.65 ± 0.29</td>
<td></td>
<td>1.47 ± 0.17</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>23</td>
<td>15.0</td>
<td>MD</td>
<td>34.28 ± 0.99</td>
<td>.0004</td>
<td>9.68 ± 3.35</td>
<td>.0086</td>
<td>1.07 ± 0.05</td>
<td>.0005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>22.72 ± 3.17</td>
<td></td>
<td>3.15 ± 0.58</td>
<td></td>
<td>1.49 ± 0.12</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>50</td>
<td>10.0</td>
<td>MD</td>
<td>40.35 ± 1.83</td>
<td>.0001</td>
<td>5.62 ± 0.97</td>
<td>.0438</td>
<td>1.27 ± 0.05</td>
<td>.0238</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>25.99 ± 1.93</td>
<td></td>
<td>4.18 ± 0.60</td>
<td></td>
<td>1.46 ± 0.11</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>50</td>
<td>12.5</td>
<td>MD</td>
<td>34.20 ± 3.96</td>
<td>.0035</td>
<td>4.62 ± 0.25</td>
<td>.0006</td>
<td>1.23 ± 0.11</td>
<td>.0130</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>24.47 ± 1.37</td>
<td></td>
<td>3.30 ± 0.32</td>
<td></td>
<td>1.48 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>50</td>
<td>15.0</td>
<td>MD</td>
<td>34.68 ± 2.87</td>
<td>.0003</td>
<td>5.55 ± 0.65</td>
<td>.0002</td>
<td>1.16 ± 0.07</td>
<td>.0747</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>21.25 ± 2.05</td>
<td></td>
<td>2.82 ± 0.21</td>
<td></td>
<td>1.42 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>70</td>
<td>10.0</td>
<td>MD</td>
<td>27.95 ± 1.68</td>
<td>.0002</td>
<td>6.78 ± 0.95</td>
<td>.0006</td>
<td>0.82 ± 0.08</td>
<td>.0055</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>18.69 ± 1.70</td>
<td></td>
<td>3.50 ± 0.27</td>
<td></td>
<td>1.03 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>70</td>
<td>12.5</td>
<td>MD</td>
<td>24.62 ± 2.14</td>
<td>.0266</td>
<td>9.72 ± 2.46</td>
<td>.0168</td>
<td>0.72 ± 0.09</td>
<td>.7535</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>18.08 ± 3.94</td>
<td></td>
<td>5.18 ± 1.27</td>
<td></td>
<td>0.74 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>70</td>
<td>15.0</td>
<td>MD</td>
<td>15.22 ± 2.66</td>
<td>.7372</td>
<td>24.32 ± 3.81</td>
<td>.0002</td>
<td>0.49 ± 0.15</td>
<td>.6688</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TD</td>
<td>14.63 ± 2.10</td>
<td></td>
<td>6.88 ± 2.04</td>
<td></td>
<td>0.45 ± 0.12</td>
<td></td>
</tr>
</tbody>
</table>

bons at various relative humidities (Table 3). A typical stress–strain curve is detailed in Fig. 1, which displayed no unusual features. Microscopic analysis displayed no differences between the ribbon samples.

Physical properties are reported in Table 3. Results for each sample are grouped by RH. When measuring physical properties in a given direction, there were no statistically significant trends in tensile properties with increasing TEG at all relative humidities in a given direction. Samples A, B and C had tensile strengths of 40.3, 34.2 and 34.7 MPa, respectively at 50% RH in the MD. The tensile strength when measured in the MD is higher that that in the TD, except for sample C at 70% RH. With thermo-mechanical shear, the zein molecules or zein domains will begin to flow in the direction of the induced shear. The differences in physical properties observed between the MD and TD may be due to some form of orientation taking place during extrusion. This orientation may be due to the formation of long-range periodic structures that have been observed previously during zein ribbon formation made with high amounts (37–47%) of plasticizer (Wang et al., 2005). Zein has also been shown to undergo molecular orientation when rolled into a film (Kretschmer, 1957). For polymers that have been subjected to thermo-mechanical shear, physical property differences were observed that were dependent on which direction the force is being applied (Stell et al., 1976). The results detailed in Table 3 are consistent with results obtained in other polymer systems where properties were superior in the MD (Park and Mount, 1987; Rhee and White, 2002, Zhang et al., 2004). When orientation is present, more of the force will be borne by the strong

Fig. 1. Stress–strain curves in MD (—–) and TD (—) for composition having 10% TEG and stored at 23% RH.
covalent bonds present along the protein chain when the load is being applied in the same direction as the orientation (the MD) (Park and Mount, 1987). When the load is applied in the perpendicular direction (the TD) to the direction of orientation, more of the load will be borne by the weaker van der Waals interactions (Park and Mount, 1987).

The tensile properties of the ribbons, independent of direction of applied stress and formulation, at 23 and 50% RH were comparable. All of the samples experienced a large reduction in tensile strength and modulus and an increase in elongation when stored at 70% RH. For sample C at 70% RH, the S.D. for the two TS were large enough and the respective means close enough, that they were not statistically different. sample A consistently had the highest tensile strength in the MD direction.

The magnitude of the difference between MD and TD tensile strengths decreased significantly at higher humidities. For example, the difference in MD and TD tensile strength for sample B is about 12 MPa at 23% RH and it is about 5 MPa at 70% RH. This reduced difference between the TS in the TD and MD is due to a larger reduction in the TS in the MD. For RH increase (23–70% RH), the TS of sample A decreased from 39.3 to 27.9 MPa in the MD, whereas it went from 23.9 to 18.7 MPa in the TD. This equates to a reduction in TS of 29% in the MD and 22% in the TD. Similar analysis of sample B shows larger changes with the TS in the MD decreasing by 39% (37.5–23.0 MPa) and in the TD decreasing 30% (25.8–18.1 MPa). Finally, a similar analysis of sample C shows larger changes with the TS in the MD decreasing by 49% (34.2–17.3 MPa) and in the TD decreasing 36% (22.7–14.6 MPa). When the %TS lost is plotted versus %TEG, a linear relationship was obtained (Fig. 2). With increased levels of TEG, a hydrophilic plasticizer, the impact that moisture has on physical properties increases.

These results are consistent with some form of orientation taking place in the protein. Water is a known plasticizer for zein and it will increase the free volume of the protein and reduce tensile strength (Lawton, 2004). This increased free volume will increase molecular motion and the polymer chains will be able to move more freely. At higher humidities, where the amount of moisture retained increases (Table 2), with increased molecular motion, zein molecules will be able to slip past each other more freely. With this increased motion, a load applied in the MD will now be borne to some extent by the weaker van der Waals interactions. The TS in the MD will be reduced by both the effect of the higher amount of plasticizer (water, due to storage at higher RH) and to a change in the how the stress is being borne by the polymer. The TS measured in the TD will be reduced mainly by the higher amount of plasticizer only, as van der Waals interactions already bear a larger amount of the stress in this direction.

Elongation is always higher in the MD direction, whereas the modulus is typically lower in the MD direction (Table 3). This is consistent with some form of orientation where the ability to bear the load on the strong covalent bonds of the main polymer chain will allow for higher elongation. This higher elongation will decrease the slope of the stress–strain curve, thus giving reduced modulus. With increasing relative humidity, elongation increases and modulus decreases. The increased free volume will allow greater chain mobility giving higher elongation and the higher elongation will decrease modulus.

3.2. Infrared spectroscopy

Microscopy and spectroscopy have been used to determine whether orientation is present in an extruded sample. SEM examination of extruded ribbons did not display any structure that could be attributed to orientation. Infrared (IR) spectroscopy did provide some insight into the structure of the ribbons. IR spectra were obtained using polarized infrared light in both the MD and TD of the extruded ribbon having the composition of sample C. When the normal spectra were examined closely, only small differences were observed between the two spectra. When significant amounts of molecular orientation
are present, then larger changes in either peak position and/or intensity would be observed (Kretschmer, 1957; Tsuboi et al., 2004). When smaller amounts of orientation are present, then these changes may not be easily discerned in the normal spectra. In these situations, second derivative plots have been used by others to discern small differences in the IR spectra of zein (Forato et al., 2003; Forato et al., 2004). When the second derivative plots were generated of the ribbon from sample C, small reproducible differences were obtained. Differences in the carbonyl region of the second derivative IR spectra are detailed in Fig. 3. Based on earlier work utilizing zein, it is expected that differences can be found in the carbonyl region if orientation is taking place (Kretschmer, 1957). When approximately 90 μm of material was removed from the ribbon surface, these small differences are removed and the spectra overlapped (Fig. 4). This result is consistent with small amounts of orientation taking place during extrusion. It would be expected that greater amounts of orientation would be present at the surface of the ribbon because the surface of the ribbon experiences the greatest shear stress during processing that would impart the highest amount of orientation. However, because the differences were small, the physical property differences may be caused by the long-range periodic structures and not molecular orientation as was observed in earlier work (Wang et al., 2005). The physical property differences observed between the MD and TD directions may be due to either long-range periodic structure or small amounts of molecular orientation developing in the shear direction during extrusion.

Fig. 3. Second derivative of polarized infrared spectra of zein ribbon surface taken in the MD (thin line) and TD (heavy line) directions.

Fig. 4. Second derivative of polarized infrared spectra of zein ribbon after removal of 90 μm from surface, taken in the MD (thin line) and TD (heavy line) directions—note lines overlap.

Fig. 5. Sample C pictures taken using polarized light using 10× objective and 10× eye piece using cross polarizing filters 45° from extinction (a) and at extinction (b).
3.3. Birefringence

The use of polarized light to determine whether orientation is present, through the manifestation of birefringence, is a classic method of determining whether molecular orientation is present (White and Mukerrem, 1987). If a polymer film or fiber is birefringent, then molecular orientation is present. A standard method for measuring birefringence is to use a polarizing microscope having two polarizing filters. The light generated by the microscope is passed through a first polarizing filter (termed a polarizer) to produce plane polarized light. This light then passes through the sample of interest and then through a second polarizing filter (termed an analyzer). If the polarizer and analyzer are crossed, orthogonal to each other, the background will be black. If the sample being studied is the same color as the background then it is not anisotropic. If under these conditions the sample appears to be white or some other color, then the sample is anisotropic and has at least two principal refractive indices and is termed birefringent (McCrone et al., 2003). When ribbon sample C was analyzed with the filters crossed it was a light gray color, and the ribbon is birefringent (Fig. 5a). When the analyzer was rotated by 45° the sample darkened (Fig. 5b). The birefringence of the sample can be calculated by using the Michel-Levy Chart (McCrone et al., 2003) using the formula in Eq. (1). The average thickness of the sample was 0.41 mm (410000 nm) and the color of the sample was such that the retardation was 158 nm. These values give an average birefringence (dn) value of 0.0004. Poured films are not birefringent. This is the first observation of orientation taking place in a non-crosslinked extruded zein article with less than 20% plasticizer.

\[
\delta n = \frac{\text{Retardation (nm)}}{\text{Sample thickness (nm)}} \tag{1}
\]

4. Conclusion

As observed with other polymers, extruded zein articles will have different physical properties dependent on how the sample is mounted in the physical testing device. In general, the physical properties in the machine direction were superior to those in the transverse direction for extruded ribbons. These behaviors are consistent with other polymer systems where they are attributed to molecular orientation. With increased relative humidity, the tensile strength is reduced in both directions; however, the machine direction tensile strength is reduced to a larger extent. Based on work by other researchers, it is likely that long-range periodic structures are being formed during the extrusion of zein ribbons. The amount of molecular orientation would be low because the IR spectra utilizing polarized light taken in the transverse direction and machine direction did not display differences large enough to be evident in the normal spectra. However, the second derivative spectra did show differences that were removed when the surface of the sample, where the higher amount of orientation would be present, was removed. Utilization of polarizing light microscopy clearly showed birefringence confirming that the ribbon produced underwent molecular orientation during processing.

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References


