Biodegradable plastics based on soy protein were prepared with glycerol as a plasticizer and compounded with different additives such as: polycaprolactone, zinc stearate or heat treated at various temperatures after the injection molding process in order to characterize base material strength and the effect of water absorption. The results indicated that the polycaprolactone and, respectively a medium to high heat treatment enhanced the tensile strength and decreased the water absorption significantly.

Introduction

With an increase in worldwide environmental pollution caused by non-biodegradable polymers, research on the development of biodegradable biorenewable polymers is both necessary and valuable to support global sustainability and to help reduce industry dependence on petroleum and address environmental issue with petrochemicals [1]. Commercially available soy products, such as soy oil, soy protein isolate, soy flour, and soy protein concentrate have attracted much attention because of their abundance, low cost and good biodegradability [2]. Recently, these soy products have been considered environmentally friendly materials for adhesives [3], health care [4,5], plastics [6,7], and various binders [8].

In general proteins are naturally occurring polymers with amino acids as the monomer structures. The structures of these polymers are complex and generally have limited regions of linear polymerization as often seen petroleum based plastics. For example, Figure 1 shows a computer generated image of the S11 protein found in soy beans. It is seen that the structure is complex and the folds onto it self. In order to linearize the structure, it is common to add solvents (water and/or glycerine) and extrude the mixture to promote linearization of the structure to increase the mechanical properties of the based material.

Soy-based adhesives were first developed in 1928 [25], and a patent was granted for a soy-meal-based glue [9]. The use of soy protein as plastics can be traced back to the 1930’s and 1940’s [10]. Soy plastics made from soy products by compression molding and screw extrusion with glycerol or water as a plasticizer exhibit moderate strength and good biodegradable [11,12], but they are brittle and water sensitive [13,14]. To improve the mechanical properties, researchers have blended soy protein isolate with natural or synthetic biodegradable polymers (i.e., starch, water-born polyurethane foams [15], methylene diphenyl diisocyanate modified polycaprolactone [13], and anhydride-grafted polyesters [16]),. In addition, natural polymers have been modified by organic or inorganic agents (i.e., acetic anhydride [17-19] or urea [20]), or crosslinked the base protein molecules with glutaraldehyde to prepare biodegradable plastics with various properties and functions.

The focus of this work was the development of water-resistant soy protein plastics prepared from renewable resources via a fast, convenient, and economical polymer processing techniques. The present study consists of three methods of preparing and treating the soy based plastics in order to improve their mechanical properties. The first method follows Mungara et al. procedure [11,12] , however, after the injection molding standard ASTM samples, various heat treatments were evaluated for decreasing the base material’s water sensitivity. This work (heat treatment) was based on finding by Rouilly et al [22,23], where it was reported water absorption of the sunflower oil cake resulting in a significant improvement by applying a heat treatment to the injection molded samples. In the second method, polycaprolactone and zinc stearate were blended with the soy mixture containing the appropriate compatibilizer (polyvinylpirrolidone).

Experimental

Materials

Soy protein isolate (SPI, Supro 760, ~90% protein) was obtained from Solae Company, St. Louis, MO. Other reagents and salts (glycerol, sodium sulfite, potassium sorbate), were obtained from Fisher Scientific (Pittsburgh, PA) and used as received. Nanoclay (Cloisite 30B), a natural montmorillonite modified with a quaternary ammonium salt composed
by layer silicates was obtained from Southern Clay Products, Gonzales, TX. Polycaprolactone (P767, Dow Chemical Co.), polyvinylpyrrolidone (PVP 360, Sigma Aldrich Inc.), and zinc stearate (CG 221, Chemical Group Inc.) were used as received.

**Sample preparation**

*Processing of the heat treated samples:*

A mixture of soy protein isolate (raw polymer) (100 parts) and nanoclay (Cloisite 30B) (10 parts) was mixed in a high-speed mixer (Henschel Mixers American, Inc., Houston, TX) to uniformly distribute the ingredients. To prevent clumping of the mixture, a solution of water (80 parts), sorbic acid potassium salt (or potassium sorbate 0.5 parts), sodium sulfite (0.5 parts), and glycerin (30 parts) was gradually poured in the high-speed mixer. Compounding extrusion was carried out in a twin-screw, co-rotating extruder equipped with an autofeeder (Leistritz Micro 18, L/D ratio 30, American Leistritz Corp., Sommerville, NJ). The temperature zones were set to: 92, 100, 105, 105, 100, and 85°C from the die to the hopper respectively. The material was extruded through a circular die with a diameter of 3 mm. The extrudant was pelletized using a Brabender pelletizer (Lab. Pelletizer model, C.W. Brabender Instruments, Inc., Hackensack, NJ). The pellets obtained were dried in an oven to the desired moisture content (~10%) and injection molded.

*Processing of the PCL and zinc stearate blended samples:*

A mixture of soy protein isolate (raw polymer) (100 parts), nanoclay (Cloisite 30B) (10 parts), and compatibilizer (polyvinylpyrrolidone) (3 parts) for the PCL blended samples or zinc stearate (2 parts) for the zinc stearate blended samples were mixed in a high-speed mixer (Henschel Mixers American, Inc., Houston, TX) to uniformly distribute the ingredients. To prevent clumping of the mixture, a solution of water (80 parts), sorbic acid potassium salt (or potassium sorbate 0.5 parts), sodium sulfite (0.5 parts), and glycerin (30 parts) was gradually poured in the high-speed mixer. Compounding extrusion was carried out in a twin-screw, co-rotating extruder equipped with an autofeeder (Leistritz Micro 18, L/D ratio 30, American Leistritz Corp., Sommerville, NJ). The temperature zones were set to: 92, 100, 105, 105, 100, and 85°C from the die to the hopper respectively. The material was extruded through a circular die with a diameter of 3 mm. The extrudant was pelletized using a Brabender pelletizer (Lab. Pelletizer model, C.W. Brabender Instruments, Inc., Hackensack, NJ). The pellets were dried to the desired moisture (~10%) and injection molded for the zinc stearate blended samples. For the PCL blended samples, the pellets with 10% moisture were mixed with the polycaprolactone pellets in a 50:50 ratio and extruded again in the same twin-screw, co-rotating extruder. The pellets obtained were dried in an oven to the desired moisture content (<5%) and injection molded.

**Injection molding:**

Pellets were injection molded using an injection-molding machine (Boy 22S, Boy Machine Inc., Berwyn, IL) to produce ASTM tensile bar specimens (total length 165 mm; rectangular portion 54 mm x 12 mm x 3 mm). The barrel temperature from the feeder to the nozzle ranged from 125°C to 150°C. It should be noted that during injection molding process, a lubricant (tallow) was used in order to facilitate demolding.

**Characterization**

**Mechanical properties:**

Tensile strength was determined using an Instron Universal Testing Machine (Model 4502, Instron Corporation, Canton, MA) with a cross head speed of 5 mm/min. Specimens were tested in a dry state for the control samples following the ASTM standard procedure and the wet state for the rest of the samples.

**Water absorption:**

For the water absorption tests, the PCL and zinc stearate samples were initially dried in an oven at 50°C for 24 h, and the heat treated samples at: 80°C, 100°C, and 120°C for 24 h. The glass transition temperature study realized by Chen and Zhang [24] represented a good starting point for our treatment temperatures. After heat treatment, the samples were cooled in a desiccator over anhydrous calcium sulfate, and then weighed. The samples were then submerged in distilled water for times varying between 30 min-24 h. The total time in the water was defined as the submersion time. The excess of water was removed using paper towels, and the samples were weighed. Water absorption was calculated as the weight gain between wet and dry samples and expressed as a percentage. It is important to note that the soluble loss was not taken into account.

**Results and Discussion**

Table 1 details the tensile strength values in the wet state for all the processed samples at different stages of the water submersion. As seen from Figure 2 the tensile strength of the samples is inversely proportional to the submersion time. The trend lines in the graph are added for visualization. For example by increasing the submersion time from 30 min 24 h, the breaking strength decreases from 6.3 MPa to 0.2 MPa for the heat treated samples at 100°C for 24 h. It is believed that the loss of strength is the result of the water molecules penetrating between the intermolecular bonds...
of the soy protein plastics, acting as a solvent. It is also seen, that if the combination of the treatment temperature and time is too high, such as 120ºC for 24h, the breaking strength decreases from 0.9 MPa to 0.1 MPa for submersion times from 30 minutes to 24h. It is believed that this is due to thermal degradation at high temperature and long time exposures. It is important to note that the strength of control group, was approximately 3 MPa and the strength of the control dropped to nearly zero within 60 minutes of exposure to water and thus this data is not included in the graph.

The zinc stearate samples followed a similar trend relative to the exposure to water however that they had a relatively low average tensile strength. It is important to note that it was not possible to measure the tensile strength after 4h of immersion because the samples were extremely fragile and soft. It is believed that the zinc stearate did not promote strong bonds at the intramolecular level during the extrusion and injection molding processes in order to prevent water migration in the samples.

The PCL samples showed a significant enhancement of the tensile strength (~5.5 MPa average) compared to the previous samples. As seen Figure 2 there is a slight decreasing trend with increasing the immersion time, but in general, the tensile strength value remained reasonably constant. The breaking strength value proves a good compatibility between the PCL and the soy protein isolate ensured by the compatibilizer (polyvinylpyrrolidone).

Table 2 details the percentage of water absorption expressed for all samples. For the heat treated samples the water absorption decreases from 120% to 43% with increasing the temperature from 80ºC to 120ºC for 24h immersion time. This may be due to a higher level of denaturation degree of the soy protein after certain temperature and time exposures. As the temperature is increased, a number of bonds in the protein molecule are weakened. The first affected are the long range interactions that are necessary for the presence of tertiary structure. As these bonds are first weakened and are broken, the protein obtains a more flexible structure and the groups are exposed to solvent. If heating ceases at this stage the protein should be able to readily refold to the native structure. As heating continues, some of the cooperative hydrogen bonds that stabilize helical structure will begin to break. As these bonds are broken, water can interact with and form new hydrogen bonds with the amide nitrogen and carbonyl oxygens of the peptide bonds. The presence of water further weakens nearby hydrogen bonds by causing an increase in the effective dielectric constant near them. As the helical structure is broken, hydrophobic groups are exposed to the solvent.

The zinc stearate samples show a significant increase of the water absorption with the submersion times, as seen in Figure 3. The PCL samples follow the same trend: the water absorption increases with the immersion time, but the amount of absorption is insignificant compared to the previous samples: from 2.8% for 30 minutes immersion time to only 16% for 24h submersion time. The good interaction and compatibility between the PCL and the soy protein isolate resulted in a lower water absorption percentage. It is believed that the water insoluble PCL formed a continuums phase within the blend and shrouded the soy plastic from the water. Figure 4 and Figure 5 show optical microscopy images of microtome sample from the PCL/protein blends. The magnification was arbitrary but higher in Figure 5. In these figures the light colored regions are continuous and correspond to PCL and the darker regions (discontinues phase) correspond to the soy plastics.

### Table 1. Tensile strength of all samples

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Tensile Strength (MPa)</th>
<th>0.5h</th>
<th>1.5h</th>
<th>2h</th>
<th>4h</th>
<th>6h</th>
<th>8h</th>
<th>24h</th>
</tr>
</thead>
<tbody>
<tr>
<td>80ºC</td>
<td>1.78</td>
<td>0.65</td>
<td>0.69</td>
<td>0.17</td>
<td>0.16</td>
<td>0.14</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>100ºC</td>
<td>6.38</td>
<td>4.31</td>
<td>3.66</td>
<td>0.64</td>
<td>0.39</td>
<td>0.18</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>120ºC</td>
<td>0.96</td>
<td>1.56</td>
<td>0.72</td>
<td>0.66</td>
<td>0.76</td>
<td>0.25</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Polycaprolactone</td>
<td>6.14</td>
<td>5.87</td>
<td>5.87</td>
<td>5.16</td>
<td>5.08</td>
<td>5.00</td>
<td>5.11</td>
<td></td>
</tr>
<tr>
<td>Zinc stearate</td>
<td>3.7</td>
<td>1.07</td>
<td>0.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** The zinc stearate samples were extremely fragile after 4h of immersion in water.

### Table 2. Water absorption of all samples

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Water absorption (%)</th>
<th>0.5h</th>
<th>1.5h</th>
<th>2h</th>
<th>4h</th>
<th>6h</th>
<th>8h</th>
<th>24h</th>
</tr>
</thead>
<tbody>
<tr>
<td>80ºC</td>
<td>20.6</td>
<td>37.3</td>
<td>39.4</td>
<td>52.0</td>
<td>67.1</td>
<td>80.1</td>
<td>120.6</td>
<td></td>
</tr>
<tr>
<td>100ºC</td>
<td>9.7</td>
<td>22.8</td>
<td>27.2</td>
<td>39.6</td>
<td>49.9</td>
<td>53.0</td>
<td>86.8</td>
<td></td>
</tr>
<tr>
<td>120ºC</td>
<td>6.9</td>
<td>13.0</td>
<td>14.7</td>
<td>23.5</td>
<td>27.7</td>
<td>33.3</td>
<td>43.0</td>
<td></td>
</tr>
<tr>
<td>Polycaprolactone</td>
<td>2.8</td>
<td>3.8</td>
<td>5.3</td>
<td>6.4</td>
<td>8.4</td>
<td>9.2</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td>Zinc stearate</td>
<td>-</td>
<td>38.2</td>
<td>54.8</td>
<td>91.3</td>
<td>112.5</td>
<td>120.9</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Computer image of S11 protein

Figure 2. Breaking strength in the wet state at various time intervals for all samples

Figure 3. Moisture absorption at various time intervals for all samples
Conclusion

Plasticizers such as water, and/or glycerol enhanced the processability of soy protein isolate. Various additives such as: zinc stearate and PCL, and heat treatments were used in order to improve the mechanical properties. Reagents such as: sodium sulfite, sorbic acid, potassium salt and Cloisite 30B (nanoclay) also played a crucial role in processability. The heat treatment to a certain extent achieved higher breaking strength and lower water absorption, but the PCL proved to ensure the highest tensile strength and the lowest water absorption overall.

The soy protein plastics possess suitable properties, which make them prime candidates for applications such as flower pots [23], packaging and disposable food containers, among others [2].

References