Melt-processed blends of zein with polyvinylpyrrolidone

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ARTICLE INFO

Article history:
Received 30 June 2010
Received in revised form 25 August 2010
Accepted 26 August 2010

Keywords:
Zein
Polyvinylpyrrolidone
Melt-processing
Compatible blend

ABSTRACT

Melt-processed blends of zein and polyvinylpyrrolidone (PVP) of varying molecular weights (55K, 360K and 1.3M) were compared based on mechanical and thermal properties. Generally, all samples stored at 50% RH exhibited a slight improvement in tensile strength, with the PVP360K samples showing the greatest improvement. At the higher levels of PVP, samples stored at 70% RH showed a decrease in tensile strength. Elongation was also more significantly impacted at higher humidity, with the higher levels of PVP causing greater elongation increases. Differential scanning calorimetry data for the blends showed single Tg values intermediate between the zein and PVP controls. Kinetic thermogravimetric data suggested a multi-step degradation interaction for the zein/PVP blends. Scanning electron microscope imaging of compression molded samples showed homogeneous surface contours for even the 20% PVP1.3M blend. Melt-processed blends of zein with polyvinylpyrrolidone of various molecular weights appear to be compatible. This work represents the first melt-processed blend of zein with PVP to generate a compatible blend.

1. Introduction

With the Energy Independence and Security Act of 2007, Congress mandated the production of 36 billion gallons of bio-fuels by 2022. Ethanol from corn is projected to make up nearly half of that total. To make ethanol production from corn more economically feasible without government subsidy, it is imperative that the co-products of that industry be better utilized. Zein, the predominant prolamin found in corn, is a major co-product of corn gluten meal (wet milling) and distillers dried grains (dry milling). Thanks to a renewed interest in bio-based products stemming from rising crude oil prices, zein is gaining popularity because of its numerous potential industrial applications in the production of bio-plastics, paper coatings and packaging materials.

According to an excerpt from a Freedonia Marketing Report, the demand for extruded plastics in the U.S. will grow 2.6% annually to 34 billion pounds in 2013. Significant trends driving this growth are bio-plastics for eco-friendly packaging and green products. Zein is a potentially attractive component of bio-based plastics. The vast amount of waste generated through the use of traditional petroleum-based plastics has become a burden on landfills. Plastics manufacturers and consumers alike are increasingly interested in the use of renewable resources to replace or partially replace petroleum-based plastics. Melt extrusion, based on its cost efficiency, processing ease, and high throughput capabilities, is the method of choice to meet the increasing demand for thermoplas-
2. Experimental

2.1. Materials

Zein was used without modification and was grade F4000 (Lot F400008064C, 14.48% nitrogen, 4.79% water, 1.53% fat, 0.07% fiber, 1.01% ash) obtained from Freeman Industries LLC (Tuckahoe, NY). Polyvinylpyrrolidone (PVP) of three different molecular weights was purchased from Sigma Aldrich (St. Louis, MO). The PVPs had average molecular weights of 55,000 (PVP55K), 360,000 (PVP360K) and 1,300,000 (PVP1.3M) based on viscosity average measurements.

2.2. Melt-processing of blends

Zein powder was blended with PVP at the desired ratios. Distilled water was then added to adjust the total moisture content of all samples to 8.5%. These powder mixtures were then sealed and allowed to equilibrate for 48 h. Zein/PVP blends and controls were processed at 60 rpm on a Brabender single screw extruder, Model PL2000 (C.W. Brabender, South Hackensack, NJ), with a 30:1 L/D screw with a 2:1 compression ratio. The barrel temperature conditions for sample production were as follows: zone 1, 60 °C; zone 2, 90 °C; zone 3, 120 °C; die, 130 °C. The zone temperatures were based on the temperatures needed to plasticize the zein control with no PVP and just water as a plasticizer. For the extruded rope, a die was used with a single circular opening with diameter of 6.39 mm and land length of 20 mm. Under this set of conditions, those zein blends with PVPs demonstrated extensive die swell. Upon cooling to solidify the plasticized blend after one pass on the extruder, the sample was ground on a Wiley mill through a 2 mm screen and extruded for a second pass under the same conditions. The die swell was minimal on the second passage through the extruder.

2.3. Tensile property analysis

The melt-processed blends were ground on a Wiley mill through a 1 mm screen. The finely ground sample was then compression molded into tensile bars in accordance with the ASTM D-638-V standard. The mold could produce six test samples at a time. Sufficient powder (1.5 g) was placed into each of the six molds to obtain a well-formed sample. Molding conditions were selected to provide a tensile test sample that appeared fully melted in the interior of the bar based on visual lack of graininess. The mold was heated in a Carver press at 125–150 °C under a pressure of 12,500 psi for 20 min. Control samples required the highest molding temperature, while blends with higher amounts of PVP required temperatures at the lower end of the range. The mold was removed from the press and allowed to cool at room temperature. Samples were stored in humidity chambers, each set at 23 °C and 50% and 70% relative humidity, respectively, for five days before testing physical properties. Sample thicknesses were measured at three different locations in the testing region using a micrometer (Model No. 49-63, Testing Machines, Amityville, NY). Data values reported are the average of at least four tested bars. Tensile strength (TS), elongation to break (Eb) and Young's modulus (YM) were evaluated for each sample using a Instron® Universal Testing Machine Model 4201 and are presented as the calculated value ±1 standard deviation. 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.

2.4. Differential scanning calorimetry (DSC)

DSC experiments were performed using TZero aluminum pans on an indium-calibrated Q2000 with an RCS90 cooling unit (TA Instruments, New Castle, DE). Samples were heated from 35 °C to 120 °C, cooled to 35 °C to eliminate prior thermal history, and then heated again to 200 °C. These temperature ranges from 35 °C to 200 °C were based on previously reported research performed at our center (Sessa et al., 2008). All samples were heated/cooled at 5 °C/min in a nitrogen atmosphere with a flow rate of 50 ml/min. All reported data is from the second heating cycle.

2.5. Thermogravimetric analysis (TGA)

TGA experiments were performed on a 2050 TGA (TA Instruments, New Castle, DE). Samples were run at a heating rate of 10 °C/min from 25 °C to 800 °C. All samples were run in a nitrogen atmosphere with a flow rate of 90 ml/min. For TGA kinetics, each sample was run at three different heating rates: 5 °C, 10 °C and 15 °C/min. The kinetic data was then analyzed using the TA Specialty Library software (Version 1.4, TA Instruments, New Castle, DE).

2.6. Scanning electron microscopy (SEM)

Specimens for SEM analysis were the fractured surface of compression molded bars broken under liquid nitrogen. SEM was performed after sputter coating the fibers with Au–Pd and then examination by a JEOL 6400 V (JEOL USA, Inc., Peabody, MA). Images were taken at 2000× magnification and represent a surface area of 24 μm × 24 μm.

3. Results and discussion

3.1. Differential scanning calorimetry

DSC was performed on the zein control, zein/PVP blends and each of the three PVP powders. Glass transition (Tg) values for the zein control and all blends are reported in Table 1 and are the
Table 1
Glass transition data for zein/PVP blends obtained by DSC.

<table>
<thead>
<tr>
<th>Blend</th>
<th>( T_g )</th>
</tr>
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<tbody>
<tr>
<td>Zein control</td>
<td>154.3 ± 2.1</td>
</tr>
<tr>
<td>2.5% PVP55K</td>
<td>154.0 ± 1.8</td>
</tr>
<tr>
<td>20% PVP55K</td>
<td>153.9 ± 1.0</td>
</tr>
<tr>
<td>PVP55K</td>
<td>158.3 ± 3.4</td>
</tr>
<tr>
<td>2.5% PVP360K</td>
<td>152.8 ± 0.8</td>
</tr>
<tr>
<td>20% PVP360K</td>
<td>158.5 ± 0.3</td>
</tr>
<tr>
<td>PVP360K</td>
<td>180.8 ± 0.0</td>
</tr>
<tr>
<td>2.5% PVP1.3M</td>
<td>154.3 ± 0.6</td>
</tr>
<tr>
<td>20% PVP1.3M</td>
<td>160.4 ± 0.7</td>
</tr>
<tr>
<td>PVP1.3M</td>
<td>180.6 ± 0.2</td>
</tr>
</tbody>
</table>

The average of three runs ± 1 standard deviation. All reported data is taken from the second heating cycle. Representative DSC data for blends containing zein and PVP360K are shown in Fig. 1. The \( T_g \) of the zein control (A) was 154.3 °C. This value is much higher than the \( T_g \) reported for the zein control in a previous zein/PVP study (Woods et al., 2009). The zein/PVP blends in that work contained 10% triethylene glycol, a plasticizer which significantly reduces the glass transition temperature of zein (Lawton, 2004). The \( T_g \) of pure PVP360K was significantly higher at 180.8 °C. Zein/PVP360K blends exhibited a single \( T_g \) that shifted higher with more added PVP. While the \( T_g \) of the 2.5% PVP360K blend was not much different from the zein control (154.0 °C), the \( T_g \) of the 20% PVP360K blend shifted to 158.5 °C. The same trend was seen in the DSC data from the zein/PVP1.3M blends (Table 1). In that case, the \( T_g \) of the blend with 20% PVP1.3M was shifted to 160.4 °C. The DSC temperature range for the 2.5% and 20% zein/PVP55K blends were less than those of the other PVP blends because the \( T_g \) of pure PVP55K is much lower (158.9 °C). The \( T_g \)s of the 2.5% and 20% PVP55K blends were not significantly different from the control samples based on the standard deviations of each of the data sets. Predicted values for \( T_g \)s for the 20% PVP blends, based on the Fox equation (Leisz et al., 1980), were 155.3 °C for PVP55K, 159.0 °C for PVP360K, and 158.9 °C for PVP1.3M. These values are in line with the observed values given in Table 1. This finding indicates that melt-processing of zein with PVP generates a compatible blend.

Regardless of PVP molecular weight, the addition of 2.5% PVP had little effect on the \( T_g \) of the blend. With 20% added PVP, though, there was a clear \( T_g \) increase of ~6 °C for the zein/PVP360K and zein/PVP1.3M blends. This increase in \( T_g \) may indicate that the ordered association of zein molecules was increased by the presence of PVP. The presence in these blends of a single \( T_g \), independent of the glass transitions of the zein and PVP controls, suggests the presence of a compatible blend. These results correspond well with previous research that suggested the compatibility of zein and PVP in solution-cast films (Woods et al., 2009).

3.2. Thermogravimetric analysis

TGA data for the blends of zein with PVP360K are plotted as the temperature versus derivative weight (Fig. 2). While only the PVP360K blend is represented, the blends of zein with PVP55K and PVP1.3M show the same trends. The zein control film exhibited a single dominant peak at 320 °C, representing the temperature at the greatest rate of mass loss. The PVP360K control sample degraded at a significantly higher temperature (439 °C), which corresponds with previous studies on PVP thermal stability (Moore and Kaur, 1998; Cranford et al., 1999; Kim et al., 2002; El-Hag Ali et al., 2003; Devi et al., 2006; Lu et al., 2007). Thermal degradation of the zein/PVP blends occurs through a two step route in which the first step corresponds to degradation of zein and the second step is attributed to the decomposition of a PVP/zein complex with the PVP360K/zein blend exhibiting a degradation at 428 °C. While the temperature of the zein degradation peak remained consistent for the zein control and zein/PVP blends (319–320 °C), the PVP degradation peak shifted lower with increasing PVP. The sample containing 2.5% PVP360K displayed the PVP peak at 433 °C, while the 20% PVP360K peak was at 428 °C. Regarding total decomposition, the zein control sample retained 14.6% of its weight upon heating to 800 °C. The PVP360K decomposed more completely, with only 1.8% remaining. As expected, the amount of total decomposition of the zein/PVP blends increased with increasing PVP concentration, with 13.3% and 11.3% sample remaining for the 2.5% and 20% PVP360K blends, respectively. If the blends were immiscible and the presence of the zein did not influence the degradation of the other PVP in the polymer blend, poor interfacial compatibility of the polymer components would lead to de-bonding of the phases upon thermal decomposition to yield decomposition values identical to those of the individual zein and PVP controls. Such was not the case. The zein/PVP blends showed some interaction during the degradation process. The extent of interaction is a function of the miscibility of the blends. Mohamed et al. (2007) observed similar trends in melt-processed polyactic acid/polystyrene blends.
Kinetic TGA data was also collected. An analysis of the activation energy ($E_a$) at 50% conversion is shown in Fig. 3. The $E_a$ of the PVP control samples was an average of 64% higher than that of the zein control. For the zein/PVP55K samples, the 2.5% blend had a lower $E_a$ (160 kJ/mol) than the zein control (199 kJ/mol), while the 20% blend (202 kJ/mol) was essentially the same as the zein. For the PVP360K blends, the 20% blend had an $E_a$ (227 kJ/mol) between the zein and PVP controls, while the 2.5% blend was the same as the zein control. Both of the PVP1.3M blends exhibited an $E_a$ between that of the two controls, with the 20% blend having the higher $E_a$ of the two.

A more detailed analysis of the kinetic data reveals the complex relationship between PVP molecular weight and concentration. Fig. 4 shows the plots of $E_a$ vs. % conversion for all of the blends. For the PVP55K blends, the plots of % conversion vs. $E_a$ are generally straight between 20% and 70% conversion, following the same pattern as the zein control. This is indicative of a one-step kinetic mechanism or pathway. For PVP360K and 1.3M, the plots are more complicated. While the 2.5% PVP blends are not significantly different than the zein control, the 20% blends deviated from the control after about the point of 70% conversion. For PVP360K, the $E_a$ of the 20% blend began to increase rapidly after 60% conversion, and was eventually 43% higher than the PVP control at 80% conversion. For the 20% PVP1.3M blend, the $E_a$ was slightly higher than that.
of the PVP control at 70% conversion, but dropped significantly to below the zein control at 80% conversion. As the 20% PVP samples became more fully degraded, the $E_s$ generally shifted toward the $E_s$ of the PVP control. The exception to this was the 20% PVP1.3M blend, which exhibited the sharp decrease in $E_s$ from 70% to 80% conversion. A more extensive analysis, including the testing of more intermediate blends, will be required to fully explore the complex kinetics of the high molecular weight PVP blends.

3.3. Scanning electron microscopy

SEM analysis was conducted on the fractured surface of compression moulded tensile bars. Resulting images at 2000× magnification for the zein control (A) and 20% PVP1.3M blend (B) are shown in Fig. 5. Except for cavities caused by trapped bubbles, surfaces of both the control and zein/PVP blend exhibited no distinguishing features or obvious phase separation to suggest the incompatibility of zein and PVP. It was expected that if the zein/PVP blends were not compatible, the sample containing 20% of the highest molecular weight PVP would reveal clear surface inconsistencies. The lack of such features further supports the conclusion that at the concentrations tested, zein and PVP form compatible blends.

3.4. Mechanical property analysis

Mechanical property data for the zein/PVP blends is shown in Table 2. The percent moisture of compression moulded zein control bars was 4.8% when stored at 50% RH, and 7.5% when stored at 70% RH. The percent moisture of zein/PVP bars ranged from 5.2% to 6.0% at 50% RH, and from 7.8% to 9.2% when stored at 70% RH. Samples with higher amounts of PVP took on moisture more readily than samples with little PVP.

3.4.1. Mechanical property analysis at 50% RH

The tensile strength (TS) of the zein control bars was 38.4 MPa. There were few significant changes in the tensile properties of the blends. The greatest TS increase was for the 2.5% PVP55K sample at 44.0 MPa, (15% improvement), while blends with higher amounts of PVP55K showed less improvement. Blends of zein with PVP1.3M exhibited a small level of improvement for the 2.5% and 5% blends (8% and 9% improvement, respectively). Although the PVP360K blends had consistently higher TS than the control, the large standard deviations in all but the 20% blend prevent any conclusive analysis. Those samples with high standard deviations may result from the cavities caused by trapped air bubbles observed in the edges of the tensile bar break (see SEM analysis, Fig. 5). The same trend applies to the elongation (%E) of the samples. Except for the 20% PVP55K/zein blend, there was little change in the %E for the PVP55K samples. The PVP360K and PVP1.3M blends showed modest improvement. For all PVPs, the %E of the 20% PVP blends is not statistically different from either the zein control or the %E of the 2.5% PVP blend (based on differences of least squares means with $p = 0.0001$).

While this data suggests that PVP does not significantly improve the mechanical properties of melt-processed zein, it does support the assertion that the melt-processed blends are compatible. If zein and PVP were not compatible, the addition of high concentrations of PVP to a melt-processed zein sample should have a detrimental effect on mechanical properties. Since even the addition of 20% high molecular weight PVP does not negatively affect mechanical properties, the data suggests that melt-processed blends of zein and PVP are compatible. This again supports the previous work showing the compatibility of zein/PVP in solution-cast films (Woods et al., 2009).

3.4.2. Mechanical property analysis at 70% RH

While few significant differences were found in the tensile property data at 50% RH, higher humidity levels caused a greater effect on properties. For samples stored at 70% RH, the tensile strength decreased with increasing PVP concentration (Table 3). The zein/20% PVP55K exhibits a TS of 30.0 MPa, 23% lower than the control. The addition of 2%–5% PVP55K had no effect on TS properties at higher humidity. The addition of 10% PVP360K caused a 9% decrease in TS, while 20% PVP360K reduced the TS by 30%. For PVP1.3M, the addition of as little as 5% PVP caused a TS reduction of 18%. Increasing the amount of PVP1.3M to 20% caused no further decrease in TS. Therefore, the higher the molecular weight of the PVP, the less PVP was required to cause a significant tensile strength reduction.

Elongation was also more affected at higher humidity (Table 3). The only sample with a statistically different elongation than control was the 20% PVP1.3M, with a 25% increase. Other blends, though, exhibited small %E increases of 6–10%, including 5–15% PVP360K and 10% PVP55K. As seen with previously zein/PVP films, samples with higher levels of higher molecular weight PVPs are more affected by moisture. These humidity effects may be attributed to a greater interaction between zein and PVP facilitated by the increased free volume of zein at elevated humidity (Lawton, 2004).

Table 2

<table>
<thead>
<tr>
<th>50% RH</th>
<th>70% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zein control</strong></td>
<td><strong>Zein control</strong></td>
</tr>
<tr>
<td>TS (MPa)</td>
<td>%E</td>
</tr>
<tr>
<td>38.4 ± 1.0</td>
<td>8.6 ± 0.9</td>
</tr>
<tr>
<td>PVP55K – 2.5%</td>
<td>44.0 ± 3.8</td>
</tr>
<tr>
<td>5%</td>
<td>39.8 ± 5.8</td>
</tr>
<tr>
<td>10%</td>
<td>38.5 ± 3.0</td>
</tr>
<tr>
<td>20%</td>
<td>41.7 ± 3.1</td>
</tr>
<tr>
<td>PVP360K – 2.5%</td>
<td>42.0 ± 2.6</td>
</tr>
<tr>
<td>5%</td>
<td>43.3 ± 3.6</td>
</tr>
<tr>
<td>10%</td>
<td>41.6 ± 5.8</td>
</tr>
<tr>
<td>20%</td>
<td>42.2 ± 0.9</td>
</tr>
<tr>
<td>PVP1.3M – 2.5%</td>
<td>40.6 ± 3.8</td>
</tr>
<tr>
<td>5%</td>
<td>41.7 ± 0.6</td>
</tr>
<tr>
<td>10%</td>
<td>38.5 ± 0.7</td>
</tr>
<tr>
<td>20%</td>
<td>39.7 ± 3.5</td>
</tr>
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</table>
4. Conclusions

We describe here the first melt-processed compatible blend of zein with the synthetic polymer, PVP. Melt-processed blends of zein with three different PVPs were analyzed by several methods, including tensile property testing, DSC, TGA and SEM. While tensile property improvements were modest, the fact that 20% added PVP did not significantly reduce tensile strength suggests the presence of a compatible blend. Zein/PVP blends exhibited single glass transitions without evidence of the component zein and PVP peaks. Kinetic TGA data showed a greater effect on activation energy of the blends with increasing PVP concentration. SEM analysis showed no inhomogeneities in the blends compared to the zein control. The current work supports the conclusion that melt-processing zein with PVP produced compatible blends over a range of PVP concentrations and molecular weights.

Acknowledgements

We thank the Biotechnology Research and Development Corporation (BRDC) and Global Protein Products, Inc. for funding this research. We thank Jason Adkins for performing the TGA analysis, Art Thompson for performing the SEM analysis, and Kathy Hornback and Gary Kuzniar for assistance with extrusion.

References


