Corn gluten meal (CGM) was studied to investigate the effect of plasticizers and water on its melt processing, and how this melting affects its mechanical properties. CGM containing varying amounts of water were mixed with 23% (w/w) plasticizers; (glycerol, triethylene glycol (TEG), dibutyl tartrate, and octanoic acid in a Haake bowl mixer at 80°C. The amount of water in the CGM affected the amount of torque produced in the Haake mixer. This increase in torque was correlated with how well the CGM melted in the mixer. SEM images of CGM melted in the mixer showed a more uniform homogenous structure when processed at its optimum moisture content. Glycerol, TEG, and dibutyl tartrate produced the greatest torque when the CGM contained <1% water. Octanoic acid produced the greatest torque when the CGM was processed at 8% moisture. CGM plasticized with TEG and octanoic acid were mixed at either their optimum moisture or at 9.6% moisture and then compression molded into tensile bars. The tensile strengths of the bars that were mixed at their optimum moisture content were significantly greater than the bars mixed at 9.6% moisture. The tensile properties of the CGM samples were affected by relative humidity (rh). The tensile strength decreased and elongation increased as relative humidity increased. CGM plasticized with TEG saw a greater changes in its tensile properties due to relative humidity than did octanoic acid plasticized CGM.

New uses need to be investigated for the co-products produced from the bio-ethanol industries. These co-products have traditionally found outlets in the livestock feeding industry. The increasing supply of co-products is becoming available at the same time that traditional consumption in livestock feed is diminishing. One possible use for protein co-products is to extract and purify zein from them. Traditionally, zein has been extracted from corn gluten meal (CGM). Zein has a long history of uses and its industrial uses predates synthetics (Lawton 2002). Currently, the cost of zein excludes its use as a plastic. CGM is rich in protein (15% to 20% db), it is also low in fiber and oil and contains 70% starch. The high protein and low fiber content of CGM, it is an excellent candidate for a thermoplastic. Di Gioia et al (1999) produced thermoplastic resins of CGM using glycerol, polyethylene glycol, and urea in a heated bath mixer. Later, Di Gioia and Guilbert (1999) showed that the amphiphilic plasticizer, octanoic acid, can also be processed in a heated bath mixer to produce a thermoplastic resin. The mechanical properties of compression-molded CGM plasticized with glycerol or octanoic acid was studied by Di Gioia et al (2000). Composites of CGM and wood fiber also have been studied recently (Wu et al 2003; Beg et al 2005). The mechanical properties of thermoplastic CGM resins need to be improved for these materials to be used in commercial markets. This study was done to assess the melting characteristics of CGM and how its melting affects its mechanical properties.

MATERIALS AND METHODS

Wet CGM was donated by Aventine Renewable Energy (Pekin, IL). Triethylene glycol (TEG), dibutyl tartrate, octanoic acid, and dithiobis (DTT) were purchased from Sigma-Aldrich (St. Louis, MO). Glycerol was purchased from Fisher Scientific (Pittsburgh, PA). The wet CGM was dried in a laboratory hood at room temperature (23°C) and ground through a pin mill (Alpine). The CGM had a nitrogen content of 11.2% db (70% protein) and a moisture content of 9.6%.

CGM and the plasticizers were mixed in a torque rheometer (Rheocord 90, Haake, Paramus, NJ). CGM was mixed with either water or 70% (v/v) aqueous ethanol as a 50/50 blend. DTT was added to the blends in the solvents at 0.5% (g/v). CGM adjusted to the correct moisture content was added to the torque rheometer along with the plasticizer. CGM was plasticized at ratios of 0.3 g of plasticizer to 1 g of CGM, making the CGM composite 23% plasticizer on a dry basis. The torque produced during the mixing was recorded. Temperature during mixing was set at 80°C.

To produce compression-molded tensile bars, plasticized CGM was removed from the torque rheometer just as maximum torque began falling. The mixture was taken out of the torque rheometer and allowed to cool overnight. The cooled samples were cut into smaller pieces and frozen in liquid nitrogen. These frozen pieces were ground through a Wiley mill (Thomas Scientific) using a 1-mm screen. Approximately 2.2 g of plasticized CGM was put into each cavity of a four cavity D639 type V compression mold. The mold was preheated along with the Carver press (Wabash, IN) to 100°C and subsequently pressed at 3,500 lb at 100°C for 30 min. The mold was then removed from the press and allowed to cool. Tensile bars were conditioned before testing for seven days in either a 50% rh room or in constant humidity chambers (Hotpack, Philadelphia, PA) at 20 and 70% rh. The temperature during conditioning was maintained at 25°C. Tensile tests were performed using an Instron 4201 tester with Series IX software (Canton, MA), and a 1 kN load cell. Thickness of each specimen was measured before testing with a micrometer (Testing Machines, Amityville, NY). The grip distance and gauge length were 50 mm and 7.62 mm respectively. The crosshead speed was 10 mm/min. At least four specimens were tested for each sample. Moisture content of the samples was determined using a modification of Approved Method 41-15A (AACC International 2000): 2 g of tested samples that had been cut into pieces was dried in a forced air oven at 105°C for 2 hr.

The fracture surfaces of tensile bars and the fracture surface of freeze-fractured samples from the torque rheometer were sputter-coated with Au/Pd and observed with a JEOL 6400V scanning electron microscope (Peabody, MA). Transition electron microscopy (TEM) was performed at Purdue University, courtesy of B. R. Hamaker. The fixing, embed-
ding, sectioning, staining, and scanning were performed as described in Batterman-Azcona and Hamaker (1998).

RESULTS AND DISCUSSION

The morphology of corn gluten meal consists of small particles (Fig. 1A). These particles are probably mostly protein, but CGM also contains starch, which would be in the granular state as well. A TEM micrograph of CGM shows that the protein bodies of corn survive the wet-milling process (Fig. 2A). The black specks seen in the micrograph are rabbit antibodies to α-zein. Batterman-Azcona and Hamaker (1998) used these same antibodies to identify zein, proving that the similar particles seen in corn flour were indeed protein bodies. For CGM to be melted, the particles in Fig. 1A need to be broken apart and melted while the protein bodies in Fig. 2A need to be ruptured and the zein within released to participate in the melt.

Solvents for zein are good candidates for dissolving and disrupting the protein bodies, thereby releasing the zein. Figure 3 shows the Haake torque rheometer curves of CGM being mixed with either water or aqueous ethanol (70%, v/v). There was an increase in the torque when CGM was mixed with the aqueous ethanol as opposed to mixing in water. The increase in torque is thought to be achieved by rupturing the protein bodies, which

Fig. 1. SEM of CGM. A, CGM before mixing with 70% aqueous ethanol. B, CGM after mixing with aqueous ethanol. Bars = 10 μm.

Fig. 2. TEM of CGM. A, CGM before mixing with 70% aqueous ethanol. B, CGM after mixing with aqueous ethanol. Black specks are rabbit antibodies to α-zein. Bars = 0.5 μm.

Fig. 3. Torque rheometer curves for CGM mixtures. CGM was mixed with 70% (v/v) aqueous ethanol, aqueous ethanol containing DTT, water and water containing DTT. CGM was mixed with 50% (w/w) solvent.
allows for the release of zein. Figure 2B shows that mixing CGM with aqueous ethanol does disrupt the protein bodies, as indicated by their absence after mixing. DTT was added to the aqueous ethanol to aid in the disruption of protein bodies. The torque curve is slightly lower when DTT is added to the aqueous ethanol, likely because the DTT reduces the size of the zein molecules. Zein with a smaller overall size would be expected to produce a lower torque. The use of aqueous ethanol did disrupt the protein bodies and produced an increased torque in the torque rheometer, but its use as an industrial solvent-plasticizer would be limited because of its volatility. While aqueous ethanol may be a good candidate for CGM processing, it would not perform well as a plasticizer. Because of its volatility, ethanol would be lost to evaporation, thus changing the physical properties of the final product.

Figure 1B shows the morphology of the CGM after mixing with aqueous ethanol. The particles appear to have been partially melted and fused together, but not completely melted and disrupted into a homogenous morphology. Because of the high amount of solvent used during the mixing, the total shear developed in the mixing bowl was probably too low to completely disrupt the particles. The amount of aqueous ethanol was most likely effective in dissolving zein in the protein bodies but provided too much lubrication in the mixer to thoroughly shear and break down the particles.

![Fig. 4](image-url)

**Fig. 4.** Tensile properties of compressing molded plasticized CGM resin. CGM containing 9.6% water was plasticized with either 23% TEG or 23% octanoic acid.

Other traditional zein plasticizers were tried to see whether they could melt and disrupt the protein bodies during mixing. Lower amounts of the plasticizers were used during mixing. It is thought that too much solvent or plasticizer will over lubricate the particles and mixer. The result would be reduced shear during mixing, as in the CGM aqueous ethanol mixture. Shear is thought to be needed to help rupture and break down the particles.

Triethylene glycol has long been used as a plasticizer for zein (Lawton 2002) and octanoic acid has produced a melt when mixed with CGM in a Brabender torque rheometer (Di Gioia and Guilbert 1999). Both TEG and octanoic acid were mixed at 23% (w/w) with CGM, producing a torque curve similar to that seen when aqueous ethanol was used. However, the torque developed during mixing of the CGM was much greater than that seen with aqueous ethanol (data not shown). The tensile properties of these melts were studied by removing the melt from the torque rheometer after 5 min of mixing and compression molding into tensile bars. The tensile properties of the compression-molded bars are shown in Fig. 4. The bars made with 23% octanoic acid had greater tensile strength and lower elongation than the bars made with 23% TEG. The difference may be because TEG is a better plasticizer for CGM. Di Gioia and Guilbert (1999) showed that dry CGM containing 23% octanoic acid had a $T_g$ at $50^\circ C$, whereas Lawton (2004) showed that dry zein containing 23% TEG had a $T_g$ at $40^\circ C$. The tensile bars stored at 50% rh had approximately the same moisture content: 9.3% moisture for bars containing octanoic acid and 8.7% moisture for bars containing TEG. The stress-strain curve (data not shown) of the two indicates that the CGM plasticized with octanoic acid is more brittle and probably below its $T_g$ when stored at 50% rh and 23°C. Water content of the tensile bars definitely affected the tensile properties of the plasticized CGM. When stored at 20% rh, the CGM containing both plasticizers were brittle and their tensile properties were similar. When the bars were stored at 70% rh, both sets of bars were rubbery. They exhibited lower tensile strength and greater elongation when compared with bars stored at 20 and 50% rh. TEG-plasticized CGM had lower tensile strength and much greater elongation when stored at 70% rh than did CGM plasticized with octanoic acid. The difference can be explained by the greater water absorption of the TEG-plasticized CGM. CGM plasticized with TEG at 70% rh had a water content of 14%, whereas CGM plasticized with octanoic acid had a moisture content of only 10% when stored at 70% rh. TEG is a hygroscopic plasticizer and will absorb more water than a more hydrophobic plasticizer (Lawton 2004).

The SEM image (Fig. 5) of both plasticized CGM tensile bars shows granular structures at the fracture surface. Some granular structure is to be expected because the temperature used during mixing in the torque rheometer was not high enough to melt.

![Fig. 5](image-url)

**Fig. 5.** SEM of the fracture surface of the compression molded tensile bars. A, CGM plasticized with 23% TEG. B, CGM plasticized with 23% octanoic acid.
octanoic acid. During mixing in the torque rheometer, water content in the CGM may be interfering with this process by over lubricating the particles. To study the effect of water content in CGM on the amount of torque produced during mixing in the torque rheometer, water content in the CGM was varied from 0.5 to 20% while keeping plasticizer content at 23%. Plasticizers studied were glycerol, TEG, dibutyl tartrate, and octanoic acid.

Figure 6 shows a Haake mixing graph for CGM plasticized with 23% TEG and varying water content. Haake mixing graphs for CGM plasticized with glycerol or dibutyl tartrate look similar to those of CGM mixed with TEG and were not shown. The two polar plasticizers (glycerol and TEG) and the amphiphilic plasticizer (dibutyl tartrate) had the greatest torque with the driest CGM. All three plasticizers showed decreasing torque as water content in the CGM increased (Fig. 7). Dry CGM plasticized with glycerol produced the greatest torque, followed by TEG, and dibutyl tartrate. The absolute torque produced during mixing of the plasticizers is probably a reflection of their molecular weight. Glycerol, which produced the greatest torque, had the lowest molecular weight, whereas dibutyl tartrate, which produced the lowest torque had the highest molecular weight. The lower molecular weight plasticizers would have a greater number of molecules plasticizing the CGM, thus accounting for their better plasticizing effect. Plasticizing effects of CGM containing 20% water and 23% plasticizer produced about the same amount of torque in the rheometer, regardless of plasticizer.

CGM is unlike traditional plastics which are easy to melt. CGM particles contain protein bodies that contain zein and other proteins, mainly glutenins, starch, and other components. The protein bodies need to be ripped apart so the zein can be liberated and exposed to the plasticizer and other components for a melt to occur. Breaking down the other particles will also expose the glutenins to plasticizers, possibly allowing them to melt. Reducing the particle sizes of the remaining particles that do not melt will make them more effective fillers. Starch that is contained in the CGM will not melt at the temperatures used during mixing. Higher torques seen in the torque rheometer when mixing CGM with lower water content is an indication of greater melt and greater shear taking place. Increasing the amount of water during mixing of CGM is probably reducing the shear taking place in the mixer by over lubricating the CGM particles, the mixer walls, and blades. Reducing shear on the particles would reduce the ability of the mixing action in the torque rheometer to break down the particles. The high torque seen with the mixing curves of CGM in the torque rheometer does appear to be associated with melting and breaking down of the CGM particles (Fig. 8). CGM plasticized with TEG and containing 0.5% water showed the best particle disruption and melt. Fewer particles are seen in the CGM melt containing 0.5% water compared with the other CGM containing a greater water content. The particles that are visible in the CGM melt containing 0.5% water are most likely starch granules. As water content increases in the CGM, less particle reduction and melt is seen in the SEM images, which corresponds to the reduction in torque. It is thought that the increased water reduces the amount of shear taking place in the mixer, which reduces the amount of ruptured particles and melt, which shows itself as a reduced torque during mixing. CGM plasticized with glycerol and dibutyl tartrate showed similar melt morphology as TEG plasticized CGM so those SEM images were not shown.

The octanoic acid was affected differently by water than the more hydrophilic plasticizers (Fig. 7). Octanoic acid needed some water before a high torque could be produced. However, there is an optimal amount of water to produce a high torque, that being 8%. Too much water reduced the amount of torque produced in the torque rheometer, just as the more hydrophilic plasticizers did. As described earlier, it may be that too much water will hinder the melting by reducing the amount of shear taking place. Too little water also produced much lower torque. It may be that octanoic acid could not plasticize the CGM particles alone but needed some water to help it penetrate the particle.

SEM images (Fig. 9) of CGM plasticized with octanic acid showed the same trend as seen with TEG-plasticized CGM. Mixings of octanoic acid with CGM at its optimal water content of 8% exhibited the greatest melting and particle disruption. Mixing octanoic acid with CGM that contains lesser or greater amounts of water did not thoroughly melt and form a homogenous morphology.

To determine whether greater particle disruption during mixing would confer greater tensile properties to CGM tensile bars, CGM was mixed with either TEG or octanoic acid at its optimal water content. Figure 10 shows the tensile properties of the CGM.

![Fig. 6. Torque rheometer curves for CGM at various moistures mixing with 23% TEG.](image)

![Fig. 7. Plot of torque produced after 5 min of mixing of plasticizers and CGM vs. moisture content of the CGM.](image)
The tensile strengths of CGM plasticized with octanoic acid at 8% moisture are significantly different than CGM processed at moisture contents of 9.6%, regardless of the relative humidity during storage. There were no differences seen in elongations of the CGM plasticized with octanoic acid processed at the two different moisture levels. The difference in tensile strength of the samples is believed to be due to processing CGM at its optimum moisture content. Figure 11 shows that the CGM processed at 8% moisture had a better melt and less granular structure than the sample processed at 9.6% moisture. The greater tensile strength of the CGM processed at 8% moisture is thought to be due to its better melt morphology and not because it contains less water. The moisture content between the two samples is about the same. The octanoic acid plasticized CGM had moisture contents of 7.7, 8.51, and 9.4% when processed at 8% moisture, whereas the CGM processed at 9.6% moisture had moisture contents of 5.2, 9.3, and 10% when stored at 20, 50, and 70% rh, respectively. Whereas the sample containing less water would be expected to have greater tensile strength, it would also be expected to have lower elongation. However, there is no difference in the elongation between the two samples.

TEG mixed with CGM at the optimum moisture content showed the same trend as CGM mixed with octanoic acid. The tensile strengths were greater for samples mixed at 1.2% moisture than for CGM samples mixed at 9.6% moisture, regardless of the relative humidity. Again, the moisture content of the test samples is not thought to be the reason for the greater tensile strengths exhibited by the samples processed at 1.2% moisture. The TEG plasticized CGM had moisture contents of 6.1, 7.2, and 15.7%, when processed at 1.2% moisture, whereas the CGM processed at 9.6% moisture had moisture contents of 6.4, 8.7, and 14.7% when stored at 20, 50, and 70% rh, respectively. The TEG-plasticized CGM sample processed at 1.2% moisture had greater elongation when stored at 70% rh than the sample processed at 9.6%. This difference can probably be explained by the fact that the samples processed at 1.2% moisture contained 1% more moisture. The sample with greater moisture would be expected to have greater elongation but also have lower tensile strength. This is not what we found. The sample that was processed at 1.2% moisture had greater tensile strength even though it contained more water. This sample melted better and, therefore, had a more uniform morphology and would thus be expected to have a greater elongation because it would have fewer flaws.

The tensile properties of the CGM composites are thought to be controlled by the melted zein so they would be expected to have properties similar to zein films. Tensile properties of zein films as seen in the literature are similar when tested at similar plasticizer content. Lawton (2004) found similar tensile strength for cast zein films at =10 and 5 MPa when conditioned at 50 and 70% rh, respectively, when using TEG as the plasticizer. When conditioned at 20% rh, the zein cast films had tensile strength of =20 and 5 MPa greater than the compression-molded zein composites. Tillerkeratne and Easteal (2000) had tensile strengths of 16 and 23 MPa for the cast films containing 30% polyethylene glycol (PEG) 400 and PEG 1000, respectively, when conditioned at 50% rh. The greater tensile strength for films containing PEG 1000 may be due to the fact that TEG is a better plasticizer for zein. This is also reflected in the differences in the elongation between the two films. Cast films containing PEG 100 had elongations of only 1–3%, while compression-molded CGM films containing

![Fig. 8. SEM of TEG plasticized CGM melts produced in a torque rheometry at different CGM moistures. Bars = 10 μm.](image-url)
TEG had elongations of ≈50%. Tensile properties of zein sheets prepared by a dough process containing 50% oleic acid (Santosa and Padua 1999) were 9.4 MPa for the tensile strength and 5.9% for elongation when conditioned at 50% rh. This is comparable to the tensile strength an elongation obtained for CGM plasticized with octanoic acid. However, ≈50% octanoic acid is need to achieved the same results.

Both the CGM plasticized with octanoic acid and the TEG-plasticized zein are sensitive to relative humidity. As with all biomaterials, these samples exhibit change in their tensile properties depending on the relative humidity in which they were stored. As relative humidity increased, tensile strength decreased, and elongation increased. CGM plasticized with TEG was more sensitive to relative humidity and showed greater changes in its tensile

Fig. 9. SEM of octanoic acid plasticized CGM melts produced in a torque rheometry at different CGM moistures. Bars = 10 μm.

Fig. 10. Tensile properties of compressing molded plasticized CGM resin. A, Tensile bars containing 23% octanoic acid. CGM was processed at either 9.6% moisture or 8.0% moisture. B, Tensile bars containing 23% TEG. CGM was processed at either 9.6% moisture or 1.2% moisture.
properties with changes in relative humidity. This is probably because TEG is hygroscopic and also absorbs water from the atmosphere. Moisture of tested samples was greater for the TEG-plasticized CGM than for the octanoic plastic CGM at each relative humidity level. Lawton (2004) showed that TEG-plasticized zein films absorbed more at high relative humidity than did other less hygroscopic plasticizers.

CONCLUSIONS

Zein protein bodies in corn gluten meal survive the wet-milling process. These protein bodies and particles can be melted in a Haake batch mixer. The degree of melt is influenced by the moisture content of the CGM. There is an optimum moisture for melting to take place and the optimal moisture depends on the type of plasticizer used. Polar plasticizers melted CGM more thoroughly when it contained low moisture while octanoic acid needed about 8% water for optimum melting. More thorough melting, as would be expected, produced better tensile properties for the CGM samples. The relative humidity in which the samples were stored affected the tensile properties of the CGM samples. Tensile strength decreased and elongation increased as relative humidity increased. TEG plasticized samples were more sensitive to relative humidity changes than were samples plasticized with octanoic acid. CGM composites have tensile properties similar to those of materials made from extracted zein. In the production of thermoplastic material, CGM would be less expensive to use than zein. CGM sells for $0.22 to $0.44/kg, while zein sells for >$20/kg. This difference in price could make CGM more desirable to industry markets. CGM is also less expensive than commodity plastics such as polystyrene and polyethylene. The difference in price would need to go toward improving the properties of CGM to more closely match those of plastics.

ACKNOWLEDGMENTS

We gratefully acknowledge the technical assistance of Paulette Smith and Gary Kuzinar, and Arthur Thompson for the SEM.

LITERATURE CITED


[Received December 18, 2006. Accepted September 18, 2007.]