

Plasticizers for Zein: Their Effect on Tensile Properties and Water Absorption of Zein Films

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ABSTRACT

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Cast zein films are brittle at room conditions, so plasticizers are added to make them more flexible. The tensile properties of these films are known to be affected by the relative humidity (RH) of the ambient air. However, little is known about how the plasticizers are affected by RH. Cast zein films were plasticized with either glycerol (GLY), triethylene glycol (TEG), dibutyl tartrate (DBT), levulinic acid (LA), polyethylene glycol 300 (PEG), or oleic acid (OA). Mechanical properties and moisture content (MC) of the films were measured after one week of storage at 3, 20, 50, 70, 81, and 93% RH. The relative humidity of the films' storage had a great effect on the films' tensile properties. All the films' tensile strength and Young's modulus values decreased as RH increased. Films containing DBT, TEG, LA, or PEG showed an increase in the percent elongation with increasing RH. Films containing GLY, OA, or no plasticizer did not show any increase in percent elongation as RH increased.

The changes seen in tensile properties with increasing RH are because of zein's hygroscopic nature. The absorbed water will further plasticize the zein. The type of plasticizer used determined the extent of the changes seen in the tensile properties of films stored at different RH values. Depending on the plasticizers used in the film, there were large differences in the amount of water absorbed. Films increasingly absorbed water depending on the plasticizer they contained in the order GLY > TEG > LA > PEG > NONE > DBT > OA. Films containing hygroscopic plasticizers like TEG absorbed too much water at high RH and became weak, but they absorbed enough water at lower RH values to not be brittle. While films containing the more hydrophobic plasticizer DBT were brittle at intermediate RH values, they had good mechanical properties at high RH values.

Zein has been commercially manufactured in the United States since the late 1930's. During this time, it was used as an ingredient in a number of materials including adhesives, coatings, fibers, and films (Lawton 2002). In the late 1950's, zein started losing markets to petroleum-derived materials, and today the only use is as coatings in the pharmaceutical and food industries. Currently, there is a great deal of interest in using agriculturally derived alternatives to petroleum-derived products. In the decade of the 1990's, there was considerable work done using zein as an ingredient in the manufacture of films. Many studies have reported on the mechanical and barrier properties of zein films (Ayd et al 1991; Gennadios et al 1993a,b). Zein films prepared without a plasticizer are brittle. As early as 1938, Hansen published a list of likely zein plasticizers and classified them by type. More recently, zein films have been prepared using mixed plasticizer systems and yielding good mechanical properties (Park et al 1994; Parris and Coffin 1997). Gennadios and Weller (1994) showed that zein films absorb water as water activity increases. Beck et al (1996) showed that compression molded zein samples containing different plasticizers absorbed water to differing degrees depending on the type of plasticizer in the sample. This water, absorbed by both the zein and its plasticizers, will likely affect the tensile strength of zein films because water is a very good plasticizer for zein (Lawton 1992; Kokini et al 1995).

In this study, film blends containing various plasticizers were prepared and subjected to various levels of relative humidity and subsequently evaluated for water absorption and tensile properties. The object of this research was to find the relationship between plasticizer type and water absorption in the film and how this influences the tensile properties.

MATERIALS AND METHODS

Materials

Commercial zein was purchased from Freeman Industries (Tuckahoe, NY). Water content of the zein was 4.7% as received. All plasticizers and salts were reagent-grade and purchased from Sigma-Aldrich (St. Louis, MO).

Film Preparations

Plasticized zein films were made with the following plasticizers: dibutyl tartrate (DBT), triethylene glycol (TEG), polyethylene glycol (300) (PEG), levulinic acid (LA), glycerol (GLY), and oleic acid (OA). Plasticizer levels in the films were 30% based on zein weight. Zein was dissolved in 90% aqueous ethanol (w/w) at room temperature. Enough zein was added to the aqueous ethanol to make a 15% (w/v) solution. The solution was stirred with a magnetic stirrer for 30 min. A plasticizer was added to the solution and the solution was stirred for an additional 30 min. After stirring, the solutions were cast at 1.25 mm (50-mil) wet thickness onto glass plates and air-dried overnight in a laboratory hood.

Mechanical Testing

Ultimate tensile strength (UTS), Young's modulus, and percent elongation at break (%E) were evaluated for each film using an Instron Universal Testing Machine (UTM). Four dumbbell-shaped specimens (ASTM D412-68, type C) were cut from each film. The films were cast in duplicate and the reported data are the means of eight specimens. Specimens had a width of 6.35 mm. Each piece was measured for thickness in three places along the test length using a Mini Test 3000 (Elektro-Physik, Cologne, Germany). The gauge length and the grip distance were both 50.8 mm. Crosshead speed of the UTM was 50 mm/min. Tests were conducted at 23°C and 50% relative humidity (RH).

Young's modulus, UTS, and %E of each film were evaluated after storage at different RH values for seven days. Constant RH values were obtained by using saturated salt solutions of sodium sulfate (\approx 93% RH), ammonium sulfate (\approx 81% RH), and potassium acetate (\approx 20% RH); humidity cabinet set at 70% RH and 23°C; constant humidity testing room set at 50% RH; and dry phosphorus pentoxide (\approx 3% RH). Films were stored in desiccator chambers over the salt solutions or phosphorus pentoxide at 23°C in the constant humidity testing room. Moisture levels of the films were determined after mechanical testing by weighing 2 g of film

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into aluminum pans and drying at 110°C for 2 hr. Moisture content of the films was determined by weight loss. Before testing, the films were taken out of the storage chambers and placed into zip-lock bags. Films were taken out of the bags and tested on the UTM. After testing, the films were placed back into the zip-lock bag. Moisture content of the films was determined the same day they were tested to minimize moisture changes in the film samples.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on commercial zein samples containing the plasticizers listed previously at levels of 5–40% to determine the glass transition temperature (T_g) using a DSC-7 instrument (Perkin-Elmer, Norwalk, CT). The plasticized zein scanned was either dried (<1% moisture) or contained 5% moisture (as is). Zein was ground to 0.5–0.125 mm

with an IKA A10 grinder. Dry zein was obtained by drying the zein in a forced-air oven at 105°C for 48 hr. Plasticizers were mixed with dry zein in a low humidity glove box (0.3–0.7 RH), and undried zein was mixed with plasticizers at the lab bench. Plasticized zein formulations were made by adding the desired amount of plasticizers to a weighed amount of zein. The mixture was stirred and blended twice in a mortar and pestle to ensure uniform mixing and allowed to equilibrate for 48 hr before running the DSC. Samples containing low amounts of plasticizers were scanned at –30°C to 180°C. Zein samples containing greater amounts of plasticizers gradually ended the scanning lower than 180°C to save time. All samples were scanned at a heating and cooling rate of 10°C/min and then rescanned at the same heating rate. The T_g of plasticized zein was determined by analysis of the second scan using thermal analysis software (Perkin-Elmer TAS-7).

RESULTS

The relative humidity at which the films were stored had great effect on the films' tensile properties (Figs. 1 and 2). All the films underwent decreases in UTS and Young's modulus values as the RH level increased. The %E of the films plasticized with DBT, TEG, LA, or PEG increased with increasing RH (Fig. 3). Films containing no plasticizer, OA, or GLY did not show any increase in %E as RH increased except for the films containing OA when stored at 93% RH (Fig. 3). This effect of RH on the tensile properties of the zein films is to be expected because zein will gain or lose water to achieve equilibrium with the ambient air (Gennadios and Weller 1994; Wei and Baianu 1999) and water is a good plasticizer for zein (Lawton 1992; Kokini et al 1995; Madeka and Kokini 1996). The decrease in UTS and Young's modulus of the films along with the increase in %E is consistent for polymers with increased plasticizer levels (Sear and Touchette 1989). Previous reports have shown similar changes in zein's tensile properties with increasing RH (Gennadios et al 1993, Tillekeratne and Easteal 2000).

The type of plasticizer contained in the films had great effect on the water absorption of the films (Fig. 4). The extent of the water absorption can be seen in the changes in tensile properties of the films (Figs. 1–3). Films containing hygroscopic plasticizers TEG, GYL, and LA exhibited larger decreases in UTS and Young's

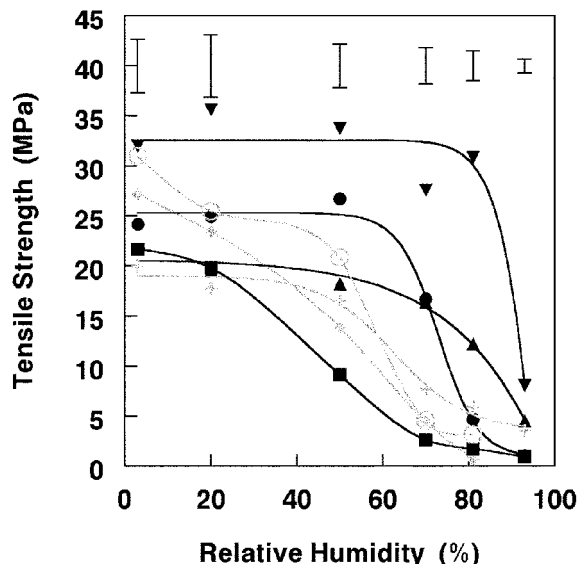


Fig. 1. Tensile strength of zein films containing plasticizers stored at varying levels of relative humidity. Plasticizers are DBT (●); TEG (■); LA (◆); GLY (⊕); OA (▲); PEG (○); none (▼). Bars indicate mean \pm average standard deviation.

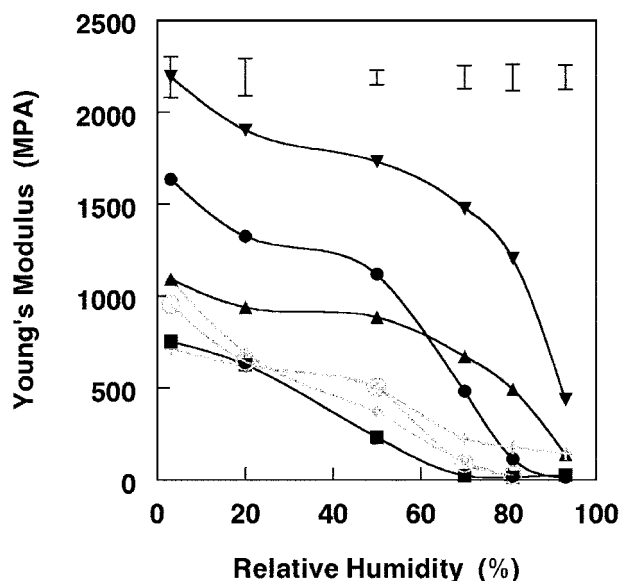


Fig. 2. Modulus of zein films containing plasticizers stored at varying levels of relative humidity. Plasticizers are DBT (●); TEG (■); LA (◆); GLY (⊕); OA (▲); PEG (○); none (▼). Bars indicate mean \pm average standard deviation.

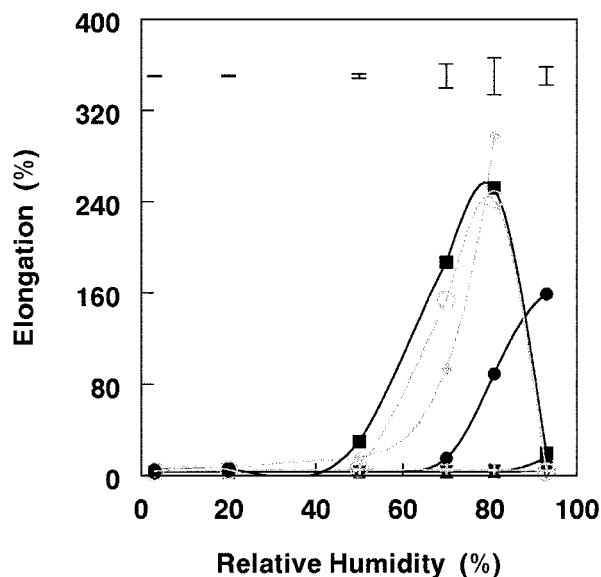


Fig. 3. Percent elongation of zein films containing plasticizers stored at varying relative humidities. Plasticizers are DBT (●); TEG (■); LA (◆); GLY (⊕); OA (▲); PEG (○); none (▼). Bars indicate mean \pm average standard deviation.

modulus with increasing RH values than did films containing other plasticizers. The plasticizers with greater water absorption probably cause this rapid decrease in UTS and Young's modulus. There were large differences in the amount of water absorbed depending on the plasticizer contained in the films. At 3% RH, all films contained low amounts of water. Films containing no plasticizer contained 2.4% water, while films with DBT and TEG contained 3.1 and 4.8%, respectively. When the RH was increased to 50%, the water content of the films with no plasticizer and films containing DBT and TEG increased to 7.1, 4.1, and 8.1%, respectively. At high 93% RH, the absorbed water in films containing no plasticizers was 20.5%, and 16 and 40% for films containing DBT and TEG. Films containing hygroscopic plasticizers such as GLY, TEG, and LA absorbed more water, particularly at higher RH values than did films containing no plasticizers, but films containing these plasticizers also contained more water at lower RH values.

The amount of water absorbed by the films at each RH level was ranked and the average rank for which the plasticized films absorbed water was GLY > TEG > LA > PEG > NONE > DBT > OA. Beck et al (1996) found similar zein absorption results with compression molded zein samples. Films containing GLY had more water at most RH values tested, however, at 93% RH, TEG contained more water. The greater absorptions of films containing hygroscopic plasticizers have conflicting consequences. At low RH, the capacity of these plasticizers to absorb water from the air allows for more flexible films at lower RH values. However, this same capacity to absorb water from the air can be a disadvantage at high RH values. Films containing TEG became so weak at 93% RH that they could no longer be extended. Films containing LA absorbed so much water that on storage at 93% RH, they were no longer solid and their mechanical properties could not be tested. Films containing more hydrophobic plasticizers (DBT and OA) absorbed considerably lower water at high RH values than did the hygroscopic plasticizers. In fact, these films absorbed less water than the films that contained no plasticizers. Films containing DBT were very brittle at low RH values and were not very flexible or extensible, as shown by their high Young's modulus value and low %E value. This is probably due to the low amount of water in the films. At higher RH, the films containing DBT started to absorb enough water to become flexible. Films containing OA did

not absorb as much water as those with the hygroscopic plasticizers. However, their tensile properties were very poor. This was unexpected, as OA has been reported in the past to be a good plasticizer for zein (Santosa and Padua 2000). This is probably due to the method of preparing the films. In the cast films, the OA was melted and added to the zein solutions, which were subsequently cast onto glass plates. There was probably an incompatibility problem between the aqueous ethanol solvent and OA during the drying of the film. Lai and Padua (1997) previously showed that OA and zein are incompatible in cast films but were compatible in films that were compression molded.

Differential Scanning Calorimetry

Scanning calorimetry was done on dry zein ($\approx 0.6\%$ moisture content) containing the six plasticizers to determine the plasticizers' effect on the T_g of zein. The more hygroscopic plasticizers (GLY, TEG, LA) had the most acute effect, with only a small amount lowering zein T_g greatly (Fig. 5). However, once GLY addition reached 20%, greater amounts did not greatly lower T_g . Zein T_g was lowered below room temperature (23°C) when TEG or LA was added to zein at $>30\%$. The two hydrophobic plasticizers (DBT, OA) also lowered zein T_g but not to the extent of the hygroscopic plasticizers. Neither DBT nor OA lowered zein T_g below room temperature, even at 40% addition. Initially, the addition of OA to zein lowered T_g , but adding $>10\%$ OA to zein did not depress T_g further. A compatible mixture of OA and zein was not formed by simple mixing of OA and zein as confirmed by the increased melting peaks of OA seen in Fig. 6.

Of the plasticizers tested, TEG was the most effective plasticizer on a weight basis. However, when the plasticizer content was plotted against T_g on a molar basis, the more hydrophobic plasticizers were more effective (Fig. 7). The plasticizing efficiency increased with the molecular weight of the plasticizer in the order PEG > DBT > TEG > LA > GLY (300, 262, 150, 116, and 92 g/mol, respectively). Similar results were seen by di Gioia et al (1998) for plasticized corn gluten meal.

OA was not included in this plot because of its incompatibility with zein under these conditions. PEG effectiveness in reducing zein T_g exceeds that of TEG, indicating that molecular size of the plasticizer is important for T_g reduction even when molecules are similar.

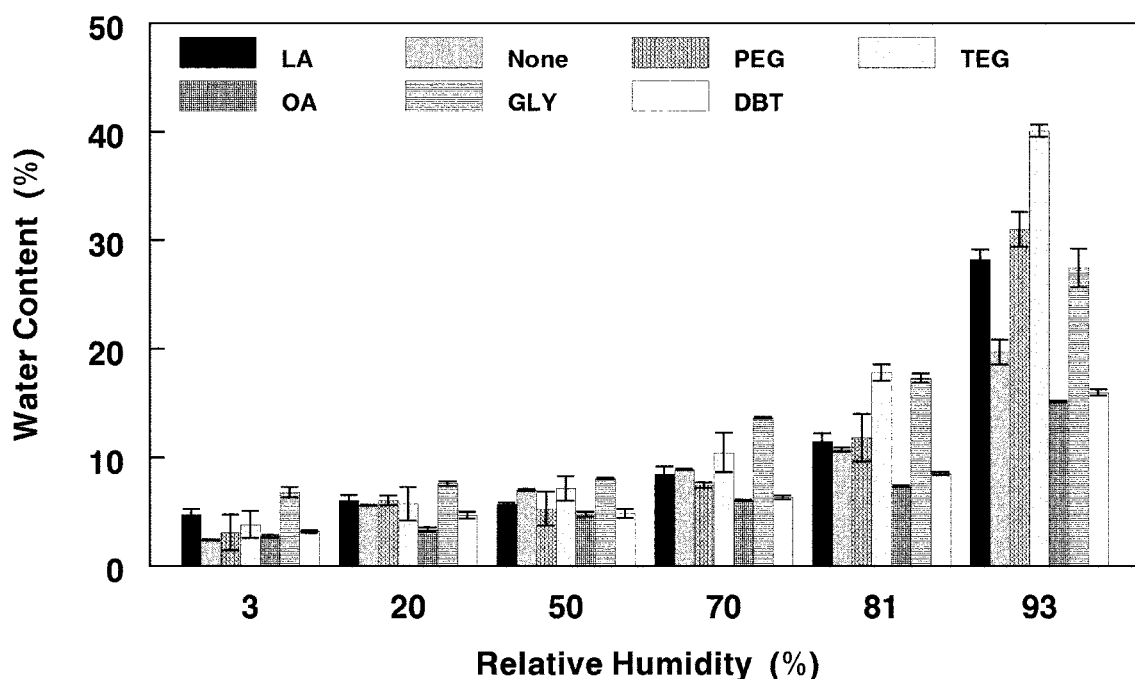


Fig. 4. Percent water contained in zein films plasticized with various plasticizers and stored at varying levels of relative humidity.

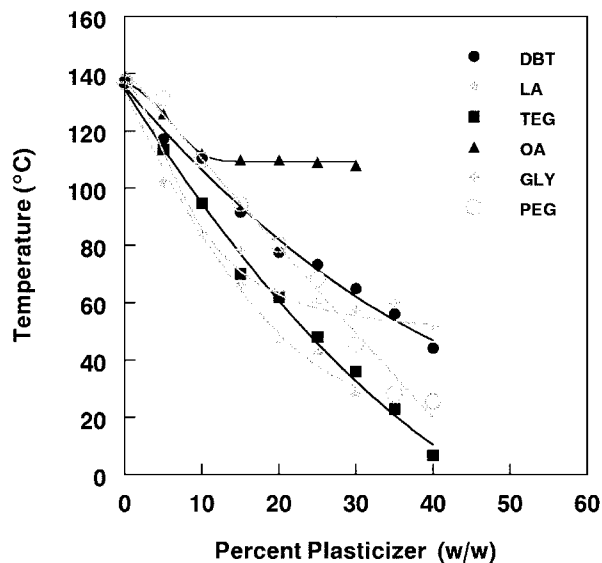


Fig. 5. Glass transition temperature of dry zein as a function of various plasticizers.

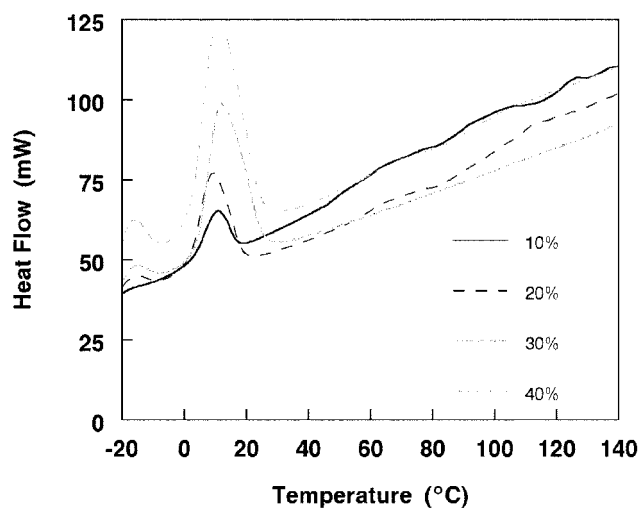


Fig. 6. Differential scanning calorimetry scans of zein containing oleic acid (OA).

Because of the considerable effectiveness of water on the T_g of zein, DSC scans were run on zein containing 5% water and the six plasticizers (Fig. 8). Water influences the T_g of the zein, no matter what plasticizer the zein contains. The addition of 5% plasticizer already containing 5% water lowered the T_g substantially when compared with the T_g of dry zein containing only 10% of the same plasticizer. This is understandable, as water is a good plasticizer for zein. For all plasticizers except GLY and OA, the addition of greater amounts of plasticizers further decreased zein T_g . For hygroscopic plasticizers, water initially had a substantial effect on zein T_g . At low plasticizer contents, the water-plasticizer combination lowered T_g more than the plasticizer did alone. At greater plasticizer content, the additional water was not effective in further decreasing zein T_g (Fig. 9A and B). An additional 5% water did not further decrease the T_g of films containing 30–40% plasticizer, indicating that water and these more polar plasticizers are competing for plasticization of zein. The water and DBT combination behaved differently than water and the polar plasticizers (Fig. 9C). After the initial drop in zein T_g seen for dry zein, the two curves were almost parallel, indicating that the two plasticizers are not competing in the plasticization of zein but are possibly plasticizing different parts of zein. The additional 5%

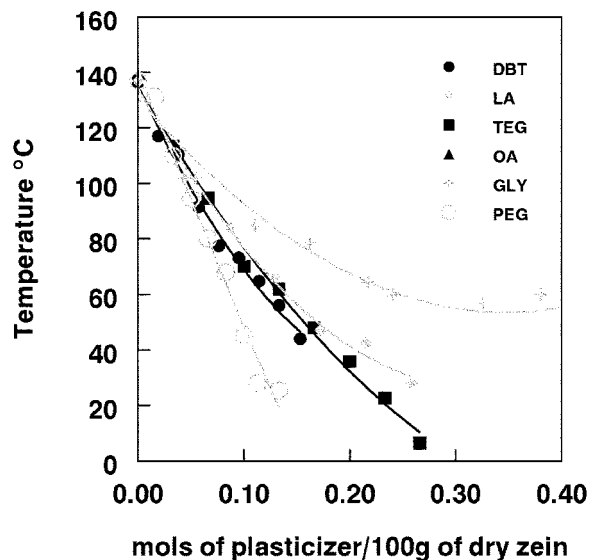


Fig. 7. Glass transition temperature of dry zein as a function of plasticizer content on a molar basis.

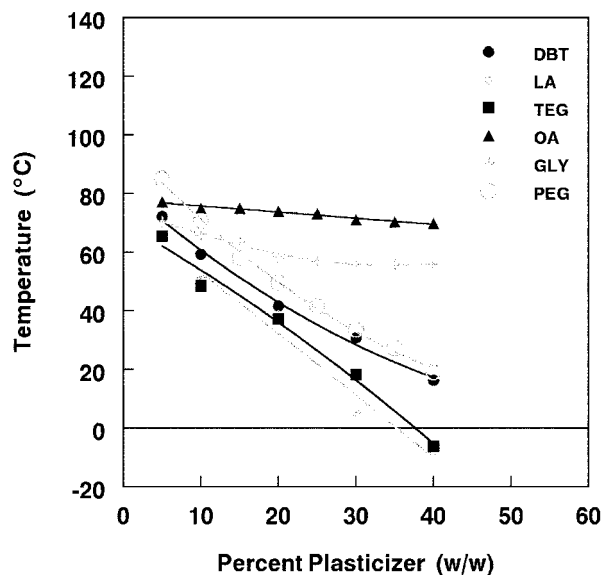


Fig. 8. Glass transition temperature of zein containing 5% water as a function of various plasticizers.

water along with DBT lowered zein T_g below room temperature when the total plasticizer content was 45%.

After the initial lowering of zein T_g , subsequent addition of GLY or OA did not cause additional reductions in T_g . As stated earlier, the lack of zein T_g reduction when using OA may be due to the incompatibility with zein under these test conditions. The total failure of GLY to reduce the T_g of zein containing 5% water is somewhat surprising, even though GLY has been tried in the past as a plasticizer for zein and was inadequate. (Aydt et al 1991; Gennadios et al 1993). GLY does have some ability to plasticize dry zein with contents of 20% (Fig. 5), lowering zein T_g to $\approx 60^\circ\text{C}$. However, further addition of GLY up to 40% only lowered zein T_g another 10°C . Similar results were found by di Gioia and Guilbert (1999) with corn gluten meal; they showed that 30% GLY addition to corn gluten meal lowered T_g to $\approx 60^\circ\text{C}$. When water is present, GLY does not seem to plasticize zein. This is apparent from looking at Fig. 8, which shows that adding additional GLY to zein containing 5% water does not decrease zein T_g . Figure 3 also shows that films containing 30% GLY had no better elongation than did films containing no plasticizers other than water. Swallen and Danehy (1946) claimed that GLY alone was completely incom-

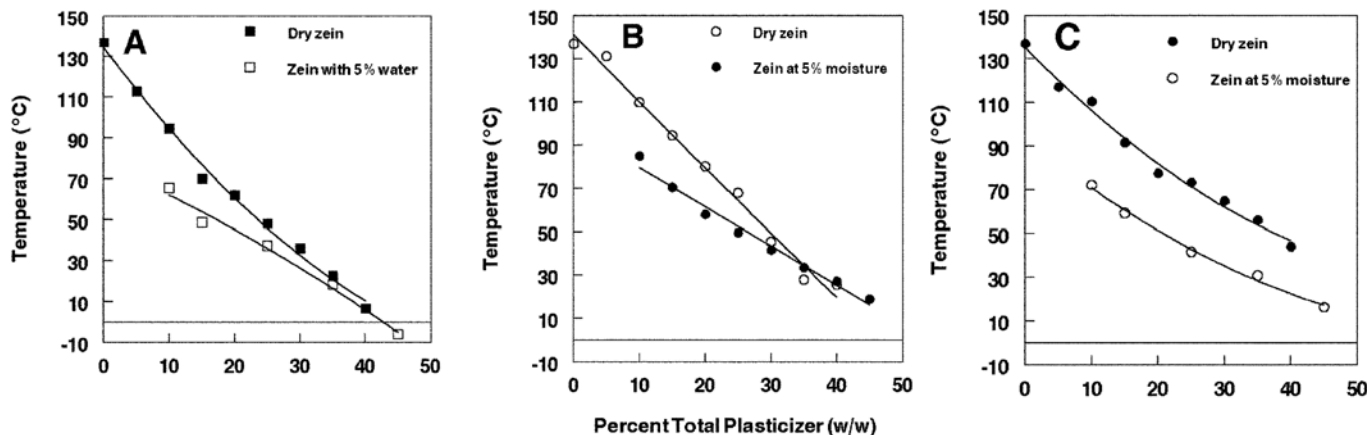


Fig. 9. Comparison of glass transition temperatures of dry zein and zein with 5% water containing triethylene glycol (TEG) (A); polyethylene glycol 300 (PEG) (B); and dibutyl tartrate (DBT) (C) as plasticizers.

patible with zein. Product literature from Corn Products Sales Co. (1949) stated that GLY could not be used alone as a plasticizer for zein but may contribute to a mixed plasticizing system. Park et al (1994) and Parris and Coffin (1997) confirmed that a mixture of GLY and polyethylene glycol were more effective plasticizers together than GLY alone.

CONCLUSIONS

Relative humidity affected the tensile properties of zein plasticized films. Increases in RH lead to corresponding decreases in UTS and Young's modulus of zein films. The magnitude of these decreases were brought about by the nature of the plasticizer the film contained. Plasticizers that were more hygroscopic absorbed more water, and films that contained these plasticizers had greater declines in the tensile properties as RH increased. Films that contained 30% TEG had excellent tensile properties at moderate RH values, but the films were far too weak at high RH values. DBT did a good job of controlling water in the films and did not get weak at high RH levels. Unfortunately, films prepared with DBT were brittle at moderate RH levels. The order of water absorbance in the films was GLY > TEG > LA > PEG > NONE > DGT > OA. Because of the relationship between plasticizers and water absorption, water needs to be accounted for in the zein when plasticizers and the tensile properties of zein are evaluated. Oleic acid did not work well as a plasticizer in cast zein films. This was probably because of the incompatibility of the OA and the aqueous ethanol. Films containing OA did, however, have low water absorption. So, for zein films not prepared by casting, OA may be an appropriate plasticizer to control water. Glycerol is not a good plasticizer for zein. The addition of GLY up to 40% to zein only reduced zein T_g to $\approx 50^\circ\text{C}$, which is far too great a temperature for GLY to be an effective plasticizer for a film.

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