

Effect of Hydrophilic Plasticizers on Thermomechanical Properties of Corn Gluten Meal

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ABSTRACT

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The glass transition temperature and rheological moduli of plasticized corn gluten meal (CGM) were determined with dynamic mechanical thermal analysis (DMTA). The tested plasticizers were water, glycerol, polyethylene glycols (PEG) 300 and 600, glucose, urea, diethanolamine, and triethanolamine, at concentrations of 10–30% (dwb). The glass transition temperature (T_g) of CGM, measured at 188°C when unplasticized, was lowered by >100°C at 30% plasticizer content, except by PEG 600 and

glucose, which showed limited compatibility with CGM proteins. The highest plasticizing efficiency, on a molar basis, was measured with PEG 300 and was attributed to the large number of hydrophilic groups and the high miscibility of this compound with CGM proteins. The change in T_g due to the plasticizing effect was modeled with the Gordon and Taylor equation, but a better fit of the experimental data was obtained with the Kwei equation.

For the last 20 years, many studies have shown that various agricultural raw materials could be used as biopolymers for the manufacture of biodegradable products (Guilbert 1986, Gontard and Guilbert 1994, Nawrath et al 1995, Cuq et al 1997a). Among natural biopolymers, plant proteins may constitute a viable source of biodegradable materials, because they are inexpensive, renewable, and abundant (Cuq et al 1997a, Lai et al 1997). Proteins are thermoplastic heteropolymers of polar and nonpolar amino acids that are able to form numerous intermolecular linkages and interactions, offering a wide range of potential functional properties (Graillie and Guilbert 1994, Cuq et al 1995, Marquié et al 1995). For instance, thermoplastic properties of wheat gluten proteins could be exploited to make biopackagings (Guilbert and Gontard 1995). Before the emergence of synthetic polymers, the plastics industry also largely used zein as a thermoplastic resin (Walsh 1934; International Patents Development Company 1937a,b; Sturken 1944; Navikas 1945; Pinner 1946).

Zein is a thermoplastic protein with a hydrophobic nature, related to its high content of nonpolar amino acids (Reiners et al 1973, Lai et al 1997). Corn gluten meal (CGM), an abundant coproduct of corn wet-milling (May 1987), is mainly used as animal feed (Wright 1987). The different protein fractions consist of ≈65% prolamines (zein), 30% glutelins, and 4% globulins (Watson and Yahl 1967, Neumann and Wall 1984). Although rich in proteins (65–70% dwb) and with a cost as low as thermoplastic starch, CGM has not yet been considered as a raw agricultural feedstock for biodegradable materials.

The thermoplastic forming of proteins requires knowledge of the glass transition temperature (T_g) (Guilbert and Gontard 1995). Two techniques have been mainly used for studying the glass transition phenomenon of proteins: differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Studies of the glass transition in corn proteins have, for the most part, used DSC (Lawton 1992, Madeka and Kokini 1996). For proteins, the glass transition is broad, and the change in heat capacity is small. DMTA is thus more appropriate than DSC (Cherian and Chinachoti 1996). However, it is important to note that the “softening temperature” measured by DMTA corresponds to the frequency-dependent main α -relaxation temperature (T_α) in polymers (Ferry 1980). It is generally considered that T_α is equivalent to the calorimetrically measured T_g for a 1 Hz frequency and 5°C/min heating rate (Perez et al 1990).

Thermoplastic forming of proteins involves incorporation of plasticizers. Plasticizers decrease the T_g , thus avoiding blushing and thermal degradation. In addition, they reduce brittleness of the formed material. Water is the most ubiquitous plasticizer of natural polymers (Slade and Levine 1993). For instance, the T_g of anhydrous purified zein dropped from ≈160°C to ≈20°C at 20% moisture content (Lawton 1992, Kokini et al 1995). Useful plasticizers of zein include glycols such as di- and triethylene glycol, fatty acids (oleic, palmitic, or stearic acids), glycol and glyceryl monoesters (glycol phthalate), and acetylated monoglycerides (Reiners et al 1973, Lai et al 1997). Clark and Gralow (1949) reported that polyethylene glycols, diethanolamine, triethanolamine, urea, glycerol, and sorbitol are good plasticizers of zein. Swallen (1941) noted that high molecular weight unsaturated fatty acids (soybean fatty acids), esters of hydroxy acids (dibutyl tartrate), or substituted sulfonamides also plasticize zein.

In the present study, thermoplastic properties of plasticized CGM were investigated using DMTA. All plasticizers were hydrophilic substances containing hydroxyl or amino functions (water, glycerol, polyethylene glycols [PEG] 300 and 600, glucose, diethanolamine, triethanolamine, and urea). The effect of plasticizer type and content on T_g and rheological moduli was determined and modeled.

MATERIALS AND METHODS

Materials and Reagents

Commercial CGM (Glutalys) (composition [dwb]: 70.3% proteins, 16.3% starch, 5.7% lipids, 3.9% fibers and 0.8% ash) was provided by Roquette Frères (Lestrem, France) and ground to produce a homogeneous granulation (<160 μ m) with a Cyclotec 1093 sample miller (Tecator, Sweden). The final moisture content was determined in triplicate after 24 hr drying in an oven at 103°C. Other ingredients included anhydrous glycerol (Prolabo, Vaulx-en-Velin, France); poly(ethylene glycol) (M_r 6000 g/mol), diethanolamine, triethanolamine, anhydrous urea, and D-glucose (Sigma-Aldrich Chimie, St. Quentin Fallavier, France); and poly(ethylene glycol) (M_r 3000 g/mol) (Merck, Hohenbrunn bei München, Germany).

Preparation of CGM-Plasticizer Blends

Homogeneous blends of CGM and plasticizer were obtained by carefully kneading in a mortar the CGM, plasticizer (10, 20, or 30 g/100 g of dry CGM) and distilled water (100 g/100 g of dry CGM). Blends were freeze-dried after 1 hr of resting.

Homogeneous blends were formed into tablets of cylindrical shape (5 mm diameter and 10 mm height) with a pharmaceutical tableting machine (Frogerais, Vitry-sur-Seine, France) using a pressure between 10 and 30 kN/cm². Tablets were dried in a ventilated desiccator containing P₂O₅ to constant weight (generally one week).

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The adjustment of water content was achieved by equilibration of CGM tablets at 25°C over saturated salt solutions (LiCl, CH₃COOK, MgCl₂, K₂CO₃, NaBr, SrCl₂, NaCl, KCl, BaCl₂, K₂SO₄) for one week. The water content of the tablets was determined after 24 hr of drying at 103°C.

Thermomechanical Properties

DMTA analysis of CGM-based tablets was conducted with a dynamic mechanical thermal analyser (MK III, Rheometric Scientific, Piscataway, NJ). A variable-amplitude, sinusoidal mechanical stress was applied to the sample (1 Hz) to produce a sinusoidal strain of preselected amplitude (16 µm peak-to-peak). The compression mode of deformation was chosen for use with the sample geometry. Temperature scans (from -100°C to 260°C) were performed at a heating rate of 3°C/min. In the case of multiple scans (heating-cooling-heating), the first heating was operated from -100°C to a temperature 10°C higher than T_{α} (determined from the main tan δ peak), followed by cooling to 0°C (at 3°C/min), and finally a second heating from 0°C to 260°C (at 3°C/min). The furnace temperature was calibrated with indium (mp 156.6°C, Rheometric Scientific standard), and the furnace was flushed with dry nitrogen during analysis to avoid rehydration of the tablets. Three samples were tested for each formulation. During analysis, the stored values were the storage modulus (E' = dynamic elastic Young's modulus in compression deformation) and the loss tangent (tan δ).

Location of the α -relaxation temperature was determined from the onset of the storage modulus E' or the maximum of the tan δ peak observed in the DMTA scans. The T_g was correlated to the temperature of the onset of the drop in E' .

Thermal Gravimetric Analyses

To follow plasticizer loss during heating under conditions close to those of the DMTA experiments, thermal gravimetric analyses (TGA) were conducted (DuPont 2000 Thermal Analysis TGA). Approximately 15 mg of the plasticized CGM, prepared as previously described (20 g/100 g of CGM) and dried to constant weight in a ventilated desiccator containing P₂O₅, were subjected to heating from 50°C to 300°C at 5°C/min under a nitrogen atmosphere. The mass of the substance was measured as a function of temperature.

RESULTS AND DISCUSSION

Thermomechanical Properties of CGM-Plasticizer Blends

The DMTA scans of CGM as a function of water content are given in Fig. 1. Drastic changes in storage modulus and loss tangent are evident >180°C. This transition zone from glasslike to rubberlike consistency, characterized by the sudden decrease in storage modulus from 10^{8.4} to 10^{7.1} Pa (onset at 188°C) and the tan δ peak (at 207°C), was attributed to the α -relaxation associated with the calorimetric glass transition of dry corn proteins. This relaxation is observed for any initial water content because of the drying effect of the heating during the scan. Similar variations for dry biopolymers were previously observed at the T_g (Kalichevsky et al 1992, Slade and Levine 1993, Gontard and Ring 1996, Cuq et al 1997b). This transition is in the temperature range of those recently observed for dry proteins, and more particularly, is in agreement with the softening temperature of dry zein (180–200°C) (Clark and Gralow 1949), but is slightly higher than the value of 165°C reported for purified dry zein (Kokini et al 1995). The mechanical α -relaxation measured by DMTA corresponds to an increase in the molecular motion of the structural units of the mixture, which are mainly zein proteins. The difference could result from the contribution of nonzein corn proteins to the overall transition.

A tan δ peak and a small decrease in storage modulus are located between 15 and 80°C (Fig. 1). Those variations are enhanced and shifted to lower temperatures with increasing water content, and thus are attributed to the glass transition of water-plasticized proteins. The T_g values were estimated from the onset of the drop

in E' at 8, 28, and 41°C, respectively, for 28.4, 18.1, and 9.9% water content (w/w), and the associated tan δ peaks were at temperatures 40°C higher (Fig. 1).

An increase in E' value is also observed above T_g and enhanced by higher water content. A subsequent increase in E' is observed at >100°C for 0% water content. A decrease of the tan δ peak height at 207°C (relaxation of dry CGM) is also observed when the initial water content increased (Fig. 1b). It is important to note that the application of DMTA for hydrated materials is difficult to interpret because the atmosphere around samples cannot be controlled. The drying phenomenon is significant beyond room temperature and very important above the tan δ peak temperature. Thus, it can generally explain the increases in storage modulus at those temperatures (Kalichevsky et al 1993a). But with CGM tablets, a packing effect of the powder under heat and stress treatment could also be considered, as well as crosslinking reactions of CGM components, enhanced by higher water content. Attenburrow et al (1990) explain a similar increase in storage modulus for wheat gluten containing 55% water (v/w), by the gelatinization of residual starch at 60°C and particularly by crosslinking of proteins near 70–90°C. Madeka and Kokini (1996), using a special pressure rheometer that prevented loss of water, associated an increase in storage modulus between 65 and 160°C for zein proteins, when moisture content was higher than 25%, with networking reactions of the proteins.

A low-temperature transition is observed near 0°C for the highest water content (28.4%, Fig. 1b) and is generally associated with the melting of freezable water (Kalichevsky et al 1993b).

The final drop-off in storage modulus near 240°C could be attributed to thermal degradation of CGM proteins and minor constituents (T_g of dry starch was reported at 243°C by Roos and Karel [1991]). This was confirmed by TGA, which showed an important loss of volatile compounds at temperatures >240°C (Fig. 2).

CGM was plasticized with low molecular weight molecules containing hydroxyl or amino groups (glycerol, diethanolamine, triethanolamine, and urea). The DMTA scans are modified in a similar manner (Figs. 3 and 4) for glycerol- and urea-plasticized materials,

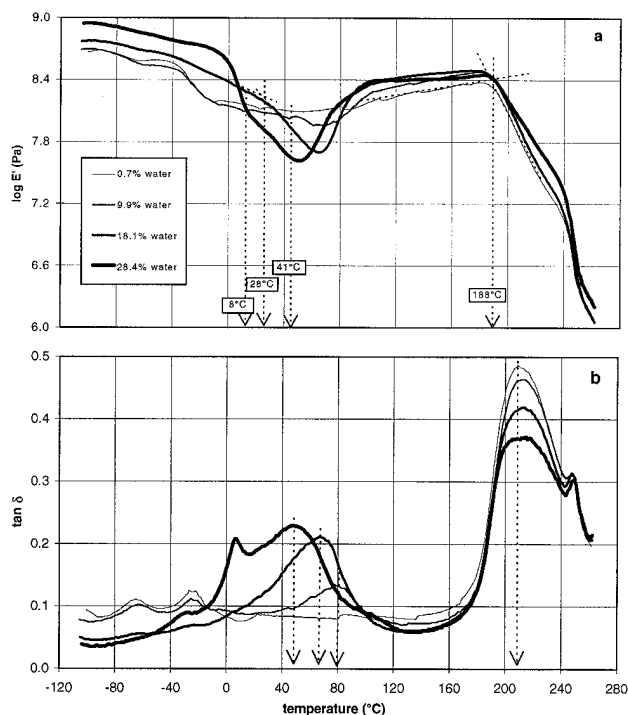


Fig. 1. Thermograms from dynamic mechanical thermal analysis for corn gluten meal as a function of water content. **a**, Storage modulus (E'). **b**, Loss tangent (tan δ).

respectively. Increasing plasticizer content decreases the rubbery storage modulus. The onset of the drop in E' and the $\tan \delta$ peak associated with the α -relaxation of dry proteins are shifted to lower temperatures. An important increase in height for this $\tan \delta$ peak is also induced by an increase in plasticizer content, and is generally

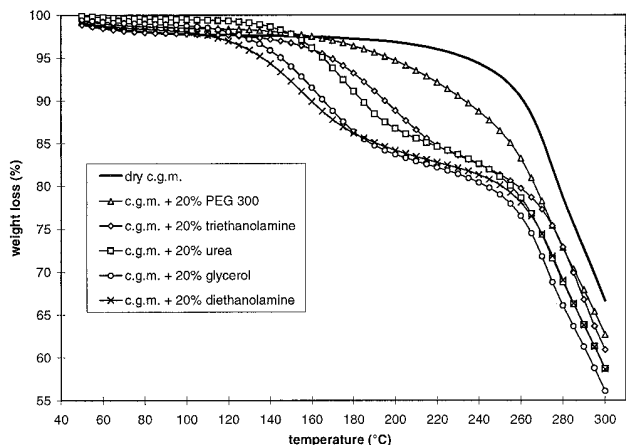


Fig. 2. Thermogravimetric analysis thermogram of corn gluten meal (CGM) blended with different plasticizers (20% dwb).

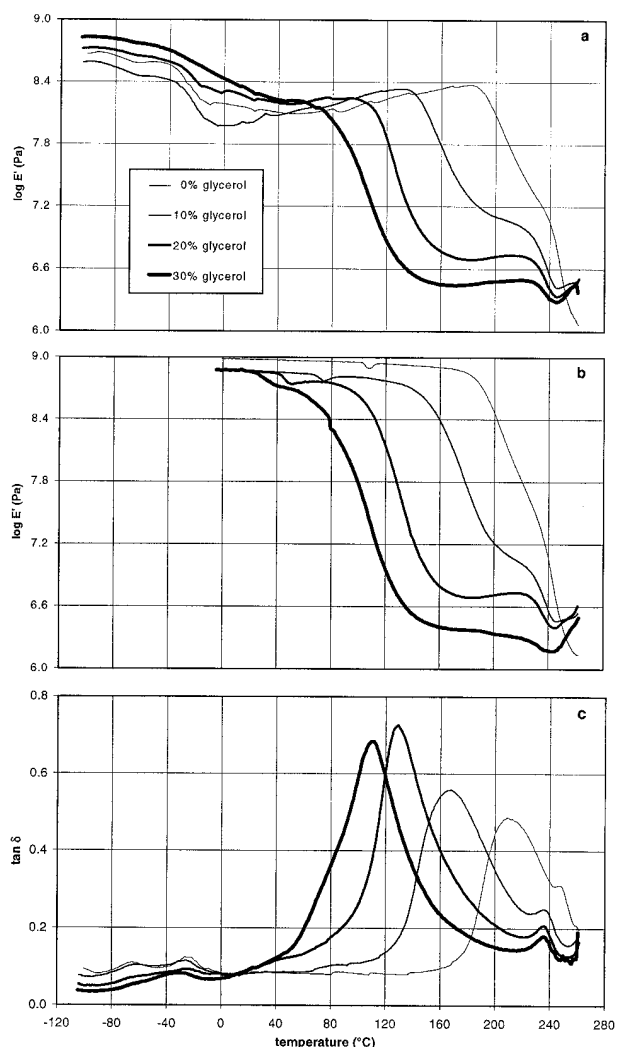


Fig. 3. Thermograms from dynamic mechanical thermal analysis for corn gluten meal as a function of glycerol content. **a**, Storage modulus (E') in single heating scan. **b**, Storage modulus (E') in second heating scan. **c**, Loss tangent ($\tan \delta$) in single heating scan.

attributed, in the case of biopolymers, to a reduction in cross-linkage, hydrogen bonding or hydrophobic interactions (Kalichevsky et al 1993b).

Second heating scans showed that the α -relaxation of CGM proteins is almost reversible. A slight shift of the onset of the drop in E' to higher temperatures (Fig. 3a,b and 4a,b) was observed during the second heating. This shift can be explained by some loss of plasticizer, due to volatilization or thermal degradation during the first heating. The loss of diethanolamine, glycerol, urea, and triethanolamine was confirmed by TGA experiments (Fig. 2), which showed an onset of weight loss at 130, 135, 150, and 160°C, respectively. Willett et al (1994) have indicated that the plasticizing effectiveness of urea in starch-urea blends is diminished during extrusion at 150–160°C due to hydrolysis to CO_2 and NH_3 .

It is important to note that the glycerol loss observed by TGA (Fig. 2) did not induce any increase in E' in the rubbery zone (Fig. 3a,b). But an increase in storage modulus was observed for all amine-containing plasticizers which were similarly lost at high temperature. This increase is located at $>175^\circ\text{C}$ for urea (Fig. 4a,b) and at $>195^\circ\text{C}$ for di- and triethanolamine. Thermal condensation and *trans*-amidification reactions of proteins with amines (Mandal and Chandrasekaran 1986, Somanathan et al 1992) could explain this increase in elasticity.

The rubbery storage modulus (corresponding to the rubbery plateau, $T > T_\alpha$) in the second heating scan was similar to the E'

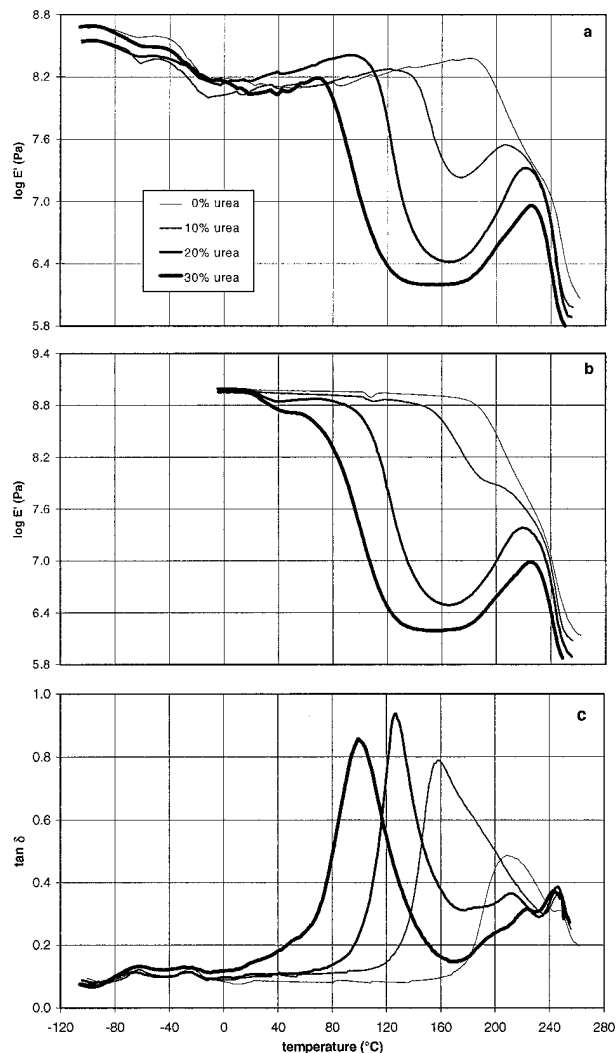


Fig. 4. Thermograms from dynamic mechanical thermal analysis for corn gluten meal, as a function of urea content. **a**, Storage modulus (E') in single heating scan. **b**, Storage modulus (E') in second heating scan. **c**, Loss tangent ($\tan \delta$) in single heating scan.

measured with a single heating, but the glassy storage modulus (corresponding to the glassy region, $T < T_g$) was significantly higher (Fig. 3a,b and 4a,b). This probably results from the transformation of the initial compacted CGM powder (tablet) into an isotropic, dense glassy material, because the glass transition is passed. During the second heating, the glassy storage modulus reaches a stable value (10^9 Pa) similar to those observed for most biopolymers (Attenburrow et al 1990, Kalichevsky et al 1993b). The drop in E' at T_g (glassy storage modulus minus rubbery storage modulus), which varies from $10^{1.1}$ to $10^{2.7}$ Pa depending on plasticizer type and content, is smaller than the expected value of 10^3 Pa for a typical amorphous polymer (Kalichevsky et al 1993b). In the case of CGM, which is a blend of many biopolymeric components, the change in E' is due to the major fraction of the component that undergoes the relaxation (the proteins), and to its morphology in the composite material. The greatest drop in storage modulus during the second heating was observed in urea at 30% dwb (Fig. 4b). Concentrated urea solutions are excellent denaturing agents for proteins, producing an unfolding of polypeptide chains (Xiong and Kinsella 1990) that could enhance molecular mobility at T_g .

High and intermediate molecular weight molecules containing hydroxyl groups (PEG 300, PEG 600, and glucose) were tested as plasticizers for CGM. DMTA scans are presented in Figs. 5 and 6 for PEG 600 and glucose, respectively (results for PEG 300 are not presented). Incorporation of PEG in CGM induced a broadening of the α -relaxation, and the $\tan \delta$ peak was lower than without that plasticizer (Fig. 5). This could be related to the dispersity of plasticizer molecular weight (285–315 g/mol for PEG 300; not available for PEG 600). With glucose and PEG 600, the slight shift of the α -relaxation zone to lower temperatures (Fig. 6) indicates that the plasticizing effect of glucose and PEG 600 on CGM is limited.

A dramatic increase of the storage modulus is located at $>170^\circ\text{C}$ and is enhanced with increasing glucose content. Reactions of proteins with reducing sugars (Maillard reactions) are heat-catalyzed and involve covalent attachment of sugars to NH_2 groups of proteins to form glycosylated proteins (Friedman 1996). This loss of glucose by grafting could explain the apparent antiplasticization effect.

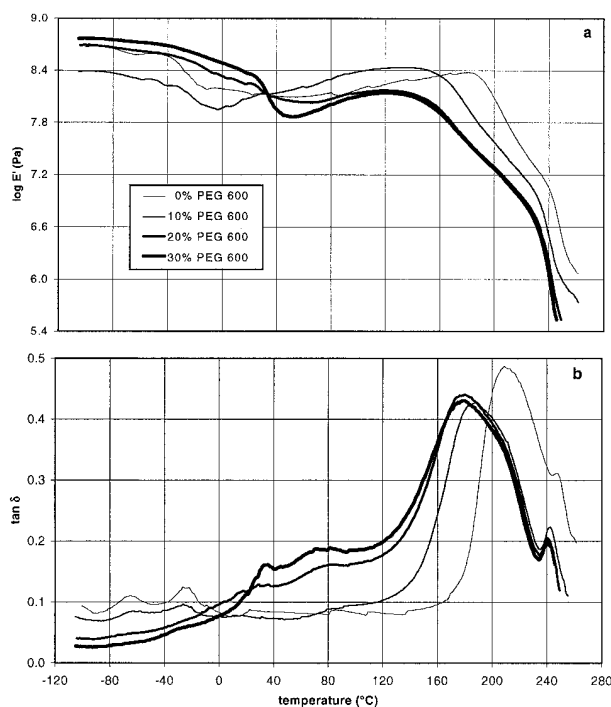


Fig. 5. Thermograms from dynamic mechanical thermal analysis for corn gluten meal as a function of polyethylene glycol (PEG) 600 content. **a**, Storage modulus (E'). **b**, Loss tangent ($\tan \delta$).

At $>20\%$ PEG 600 or glucose content, some shoulders or peaks in the $\tan \delta$ curves and possibly some small decreases in storage modulus were observed before the α -relaxation. Those phenomena could be attributed to the melting of PEG 600 near 25°C (Fig. 5), and to the main relaxation of glucose near 60°C (Fig. 6), associated with the glass transition of this sugar ($\approx 36^\circ\text{C}$) (Roos 1995). This suggests a phase separation in those blends.

Finally, it is interesting to note that two “small” $\tan \delta$ peaks, associated with a “small” decrease in storage modulus, were observed near -65 and -25°C for plasticized and unplasticized CGM (Fig. 1, 3-6). Those phenomena were diminished by an increase in plasticizer content. Maxima of small magnitude in $\tan \delta$ curves (on the order of 0.1) are often designated as secondary transitions, arising from local mode relaxations of main chains or rotations of terminal groups or other side chains (Ferry 1980). Such transitions have been studied in the context of starch antiplasticization (Lourdin et al 1997a). Such secondary transitions in proteins have been reviewed by Kalichevsky et al (1993b), who observed that some low-temperature relaxations gradually decrease in magnitude with increasing low molecular weight additives.

T_g of CGM as a Function of Plasticizer Type and Content

The decrease of T_g , as a function of plasticizer, is shown in Fig. 7, where plasticizer content was expressed on a molar basis. Except with PEG 600 and glucose, for which the drop in T_g was $<50^\circ\text{C}$, an important decrease ($>100^\circ\text{C}$) was obtained for all plasticizers. The plasticizing efficiency increased with increasing molecular weight: PEG 300 $>$ triethanolamine $>$ diethanolamine $>$ glycerol $>$ urea ($M_r = 300, 149, 105, 92,$ and 60 g/mol, respectively). Only small differences were observed with diethanolamine, triethanolamine, and glycerol, even though those substances have large structural differences (secondary amine group, tertiary amine group or no amine). Those observations suggest that among hydrophilic plasticizers, the molecular weight (size and shape) is one important characteristic related to the plasticizing effect on CGM proteins. It is generally considered that whatever the molecular weight and number of polar groups, hydrophilic plasticizers have very similar

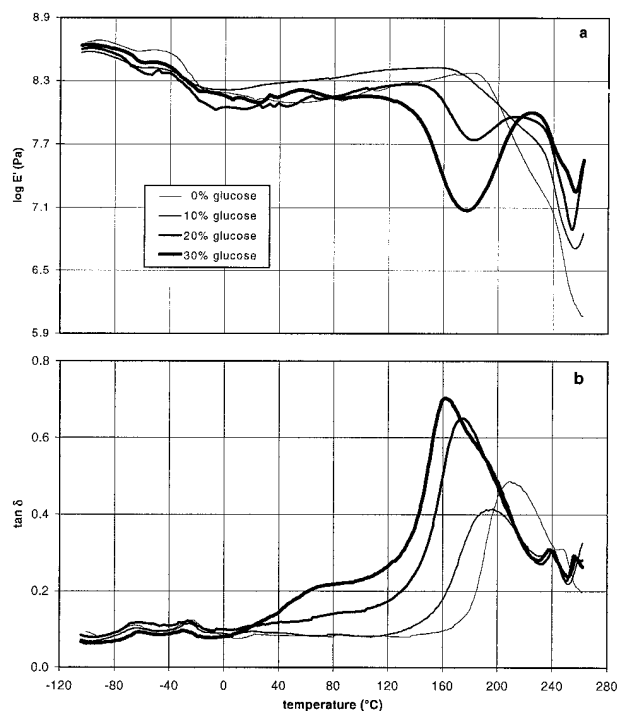


Fig. 6. Thermograms from dynamic mechanical thermal analysis for corn gluten meal as a function of glucose content. **a**, Storage modulus (E'). **b**, Loss tangent ($\tan \delta$).

efficiency when considered on a molar basis. This was established for glycerol, sorbitol or sucrose incorporated in fish myofibrillar proteins (Cuq et al 1997c), water, glycerol or sorbitol in wheat gluten proteins (Pouplin et al, *in press*), and for fructose, sucrose, or glucose in wheat gluten (Kalitchevsky et al 1992). The apparent discrepancy with our results, particularly observed for PEG, might be attributed to the combined effects of steric hindrance, high number of hydrophilic groups per molecule, and high miscibility of CGM proteins with PEG, which was listed as a good primary solvent for zein (Reiners et al 1973). On the contrary, the low plasticizing efficiency observed for glucose could be due to its limited compatibility with proteins (Kalitchevsky et al 1992).

Model for Prediction of T_g in Plasticized CGM

Prediction of T_g in binary mixtures (food component and plasticizer) is often obtained from the Gordon and Taylor equation (Eq. 1) (Gordon and Taylor 1952, Roos 1995). Eq. 1 was used to describe the plasticizing effect of various molecules on the CGM fraction which undergoes the transition, where k is a constant proportional to the plasticizing effect, W_1 and W_2 are the weight fractions, and T_{g1} and T_{g2} are the glass transition temperatures of the components ($1 = \text{CGM fraction}$, $2 = \text{plasticizing molecule}$).

$$T_g = (W_1 T_{g1} + k W_2 T_{g2}) / (W_1 + k W_2) \quad (1)$$

The T_{g2} values from the literature are 138, 193, and 309K, respectively, for water, glycerol, and glucose (Wilson and Turner 1988, Roos 1995). The T_{g1} value determined experimentally was 461K. Application of the Gordon and Taylor equation requires optimization of the constant k from experimental data.

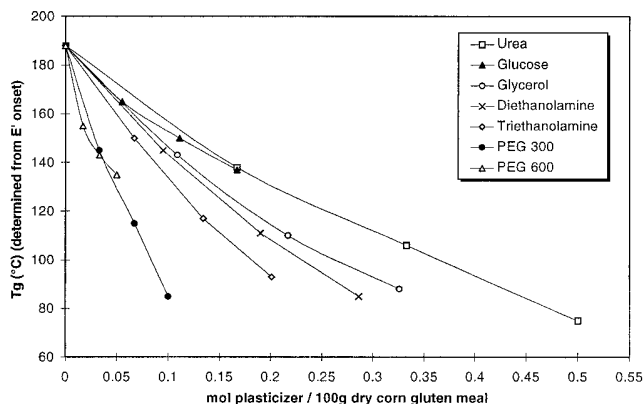


Fig. 7. Glass transition temperatures (T_g) of corn gluten meal as a function of plasticizer molar fraction. PEG = polyethylene glycols.

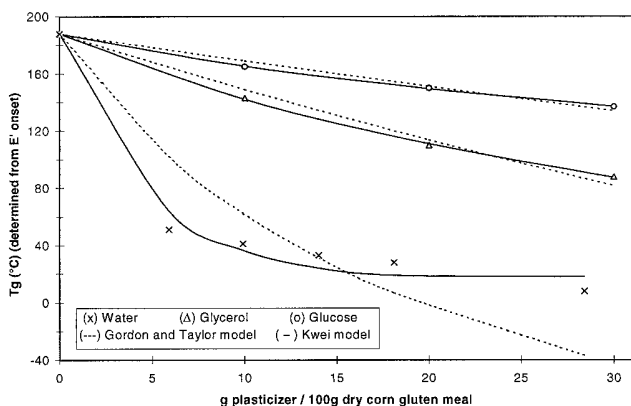


Fig. 8. Glass transition temperatures (T_g) of corn gluten meal as a function of water, glycerol, glucose weight fraction and T_g prediction using the Gordon and Taylor or Kwei models.

Experimental data can be fitted by the Gordon and Taylor semi-empirical equation (Fig. 8), but T_g values are underestimated at low plasticizer content and overestimated at high plasticizer content. The optimized k values (5.78 for water-CGM, 1.53 for glycerol-CGM, and 1.28 for glucose-CGM) are of the same order of magnitude as the value for water-plasticized zein ($k = 6.24$) reported by Madeka and Kokini (1996), for water ($k = 4.85$) and glycerol ($k = 2.2$) plasticized wheat gluten reported by Pouplin et al (*in press*), and for gliadin ($k = 3.6$) and glutenin ($k = 6.3$) plasticized by water (de Graaf et al 1993).

The Kwei equation (Eq. 2) (Lin et al 1989, Roos 1995) is an empirical modification of the Gordon and Taylor equation that can also be applied to binary systems with k , W_1 , W_2 , T_{g1} , and T_{g2} as previously defined, and q as another constant that can be optimized from experimental data. In the case of miscible polymer blends, the term qW_1W_2 represents the deviation of the T_g of the blend from the weighted mean of T_{g1} and T_{g2} (Lin et al 1989). When $q > 0$, there is an excess stabilization energy between components, leading to a higher glass transition temperature for the blend.

$$T_g = [(W_1 T_{g1} + k W_2 T_{g2}) / (W_1 + k W_2)] + q W_1 W_2 \quad (2)$$

With all plasticizers, and at any content, data were fitted with the Kwei equation (Fig. 8). The optimized k and q values were 14.28 and 515, respectively, for water-CGM; 3.04 and 244, respectively, for glycerol-CGM; and 2.90 and 159, respectively, for glucose-CGM. In our experimental system, where component 2 is a plasticizer (a small molecule), at high plasticizer content, positive values of q can also indicate a phase separation in the blend into a polymer-rich phase and a plasticizer-rich phase. This is in agreement with Lourdin et al (1997b), who described three stages in starch plasticization, related to the increase in plasticizer content: 1) strong hydrogen-bonding interactions between plasticizer and polymer that could result in a more compact system than the polymer-polymer system; 2) a homogeneous blend formed where all macromolecules are surrounded by plasticizer molecules; 3) phase separation of plasticizer and macromolecules. Differences in q values could indicate that the stabilization energy is higher for water ($q = 515$) than for glycerol ($q = 244$) or glucose ($q = 159$), because water has a very small size and can interact well with protein chains (Slade and Levine 1993).

CONCLUSION

The plasticizing effect of low and intermediate molecular weight molecules, containing hydroxyl or amino functions, on CGM was compared. The T_g was lowered by more than 100°C in the presence of only 0.1 mol of PEG 300 (or 30 g) per 100 g of dry CGM. Glycerol, diethanolamine, and triethanolamine also showed a high plasticizing effect. With PEG 600 and glucose, a phase separation was observed and related to the high molecular weight or limited compatibility with CGM. The steric hindrance and miscibility of plasticizers, through their polar functions, were the two most important characteristics that could be related to their efficiency. The addition of the term qW_1W_2 in the Gordon and Taylor equation (Kwei model) allowed us to take into account such phenomena as high polymer-plasticizer interactions and phase separation that can occur in blends made from a protein biopolymer and a plasticizer.

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