Glass Transition of Wheat Gluten Plasticized with Water, Glycerol, or Sorbitol

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The glass transition temperature of wheat gluten, plasticized with water, glycerol, or sorbitol, has been studied using dynamical mechanical thermal analysis. For the three plasticizers studied, the general behavior of the glass transition temperature broadly followed the Couchman–Karasz relation using a wheat gluten ΔC_p of 0.4 J g^{-1} K^{-1}. Compared on such a fractional weight basis, it could be concluded that the plasticizing effect of glycerol and sorbitol on wheat gluten proteins is less important than the plasticizing effect of water. A continuous curve was obtained with the three plasticizers when the evolution of the glass transition temperature was presented on a fractional molecular basis. This was related to the similar chemical structure of these three components containing hydroxyl groups.

Keywords: *Wheat gluten; proteins; glass transition; plasticizers; thermodynamic model*

INTRODUCTION

The glass transition temperature (T_g) is an important and well-known parameter of many synthetic polymers (McKenna, 1990). Above the T_g, polymeric materials are in a soft, rubbery state, whereas below the T_g, polymers are in a metastable glassy state (Ferry, 1980). This transition corresponds to a general increase in disorder, free volume, and mobility of macromolecules. Theoretically, the addition of plasticizers under isothermal conditions has the same effect as increasing temperature on molecular mobility.

Extrusion is the most commonly used process to shape petrochemical origin plastics. This technique is based on the thermoplastic properties of synthetic polymers, which are generally structurally and chemically well-defined. Knowledge of T_g is important to adjust extrusion parameters such as temperature and plasticizer content.

There is a growing concern around the world over nondegradable petroleum-derived plastics. The renewable and biodegradable nature of agricultural origin polymers (agropolymers) renders them appealing for innovative uses in the field of packaging. Study of the thermoplastic properties of such polymers is necessary to consider a profitable industrial scale production of agropolymer-based materials. The glass transition behavior of agropolymers, including proteins and polysaccharides, has thus received increasing attention (Di Gioia et al., 1998; Cuq et al., 1997; Lourdin et al., 1997; Cherian and Chinachoti, 1996).

The glass transition temperature is usually measured by differential scanning calorimetry (DSC), but dynamic mechanical thermal analysis (DMTA) is more sensitive to the changes in molecular motions and interactions occurring over the transition region. When the transition is broad and the heat capacity is small, as for most agropolymers, DMTA may allow measurements of T_g when it is not possible by DSC (Kalichevsky et al., 1993a; Wetton, 1984).

Despite their wide variety of structure, reflecting the diversity of amino acids from which they are built, it is well established that most proteins undergo a glass transition (Slade, 1984; Slade et al., 1989). Plasticization by water, polyols, or mono-, di-, or oligosaccharides affects the T_g of amorphous or partially amorphous proteins such as caseine (Kalichevsky et al., 1993b), gelatin (Yannas, 1972; Marshall and Petrie, 1980), collagen (Batzer and Kreibich, 1981), or elastin (Kakivaya and Hoeve, 1975; Scandola et al., 1981), resulting in a drop of T_g. A variety of techniques have been used to show that wheat gluten is a highly amorphous multipolymer system that is water plasticizable but not water soluble (Hoseney et al., 1986; Slade, 1984; Slade et al., 1989; Cocero and Kokini, 1991; Kalichevsky et al., 1992). Gluten and gluten/sugar mixtures have been studied (Kalichevsky et al., 1992), and small quantities of sugar (10%) did not appear to affect the T_g of gluten, whereas similar amounts of glycerol did have a plasticizing effect, due to the lower molecular weight and glass transition temperature of glycerol.

In previous investigations (Gontard, 1991, 1992), the film-forming properties of wheat gluten were studied, a laboratory scale method using solvents was developed, and wheat gluten based films with interesting functional properties were obtained. To consider extrusion for processing wheat gluten based materials, the present study was undertaken. The objective was to gain a better understanding and control of wheat gluten's glass transition and plasticization by the most commonly used plasticizers for proteins. The effects of water, glycerol, and sorbitol on the glass transition temperature of wheat gluten proteins were studied by DMTA and tentatively described using a thermodynamic model.

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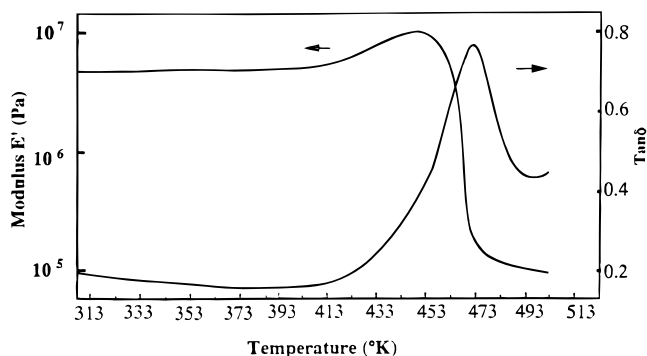[†] CIRAD/ENSIA.
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Figure 1. Typical DMTA plot of dry wheat gluten proteins.

MATERIALS AND METHODS

Wheat Gluten/Plasticizer Mixtures Preparation. Wheat gluten/water mixtures were prepared using vital wheat gluten (Amylum Aquitaine, Bordeaux, France), which was equilibrated for 10 days at 25 °C over saturated salt solutions. The salts used (with their corresponding relative humidities at 25 °C) were P_2O_5 (0%), NaBr (57.7%), $SrCl_2$ (70.2%), KCl (84.3%), and $BaCl_2$ (90.3%) (Stamp et al., 1984; Spiess and Wolf, 1987). The moisture content of each sample was determined after 24 h of drying at 105 °C.

To obtain homogeneous wheat gluten/glycerol or /sorbitol mixtures, the following procedure was used: Glycerol or sorbitol was homogeneously mixed with a 50% water content wheat gluten paste in a mixer (Moulinex M331, Paris, France). The samples were then subsequently frozen in liquid nitrogen, lyophilized for 24 h at 0.2 mbar (RP2V, Serail, Argenteuil, France), and finally crushed in a mortar. The water content after lyophilization (determined after 24 h of drying at 105 °C) was <3% dm.

All samples were stored in hermetic pans at 4 °C until DMTA analysis.

DMTA Measurements. DMTA measurements were carried out with a Perkin-Elmer apparatus DMA-7 (Norwalk, CT) according to a protocol established by Cuq et al. (1997).

A small oscillating uniaxial mechanical strain (frequency = 1 Hz) is impressed on powder samples (disposed in an 18 mm diameter stainless steel cup) by parallel plate probes (15 mm diameter disk). The deformation amplitude is defined with regard to the sample length (0.15% of the sample length). Temperature scans (from 0 to 250 °C) were performed at a heating rate of 5 °C min^{-1}. The Perkin-Elmer DMA-7 is equipped with a cooler system (Intracooler, FTS Systems, Stone Bridge, USA). The system was calibrated (furnace calibration), using Perkin-Elmer calibration software, with indium (mp 156.6 °C, Perkin-Elmer standard) and distilled water (mp 0 °C) samples.

For each analysis, the DMTA stored values were storage modulus (E'), tan δ, and sample height.

The T_g was defined by the tan δ peak and the beginning of the drop in E'. The drop in the elastic modulus was determined from the intercept of the extrapolated glassy modulus and the extrapolation of the slope at the inflection point in the drop in E'.

Samples were run in triplicate. Multiple scans were performed with water-plasticized samples: a first scan was run up to 393 K, and then the sample was removed and reequilibrated over the corresponding saturated salt solution until constant weight and rescanned. To avoid sample dehydration problems, no T_g value >373 K was used in the results of water plasticization.

RESULTS AND DISCUSSION

DMTA Plot of Dry Wheat Gluten Proteins. A typical DMTA graph of dry wheat gluten proteins showing E' (storage modulus) and tan δ (loss modulus/storage modulus) as a function of temperature is presented in Figure 1.

Wheat gluten clearly displays the behavior of an amorphous polymer: with increasing temperature, these amorphous proteins go through the glassy region, the transition region (tan δ peak and E' modulus drop), and a rubbery plateau. The size of the tan δ peak, which is thought to reflect the volume fraction of the material undergoing the transition (Wetton, 1986), is similar to the typical tan δ peak of other totally amorphous biopolymers, such as elastin (Lillie and Gosline, 1993), gelatin, amylopectin, casein (Kalichevsky et al., 1993a), or native wheat gluten (Kalichevsky et al., 1992).

A significant increase in the storage modulus E' can be observed in the temperature range from 413 to 453 K. Similar observations have been made by Cuq et al. (1997) and di Gioia et al. (1998) when studying the glass transition of myofibrillar proteins or corn gluten meal in powder form. These changes were attributed to a drying of samples at very high temperature, but a packing effect of the powder under heat and stress treatment as well as cross-linking reactions of proteins could also be considered.

The small drop in E' (from 10^7 to 10^5 Pa) compared to that in synthetic polymers [from $10^{9.5}$ to $10^{6.5}$ Pa (Kalichevsky et al., 1993a] and the absence of a flow region preclude the presence of intermolecular covalent bonds, such as disulfides bonds, or important and strong physical junctions between high molecular weight polymeric chains. Gluten was described as an extremely high molecular weight polymer (Wrigley, 1996; Sutton, 1996), in which glutenin subunits (the higher molecular weight components of gluten) are linked by interchain disulfide bonding of cysteine residues (Graveland et al., 1985; Blanshard, 1988). This probable molecular organization should be responsible for the lack of "flow region" on thermomechanical scans.

The decrease in storage modulus and the tan δ peak for wheat gluten proteins occurred over a relatively large temperature range. This great glass transition breadth (~20 °C) may reflect a wide variety of degrees of order within wheat gluten proteins. This broadening may be due to sample inhomogeneity, as has already been observed for casein (Kalichevsky et al., 1993a), reflecting the high heterogeneity of gluten protein molecular weights ranging from 30000 to millions (Graveland et al., 1985; Bietz and Wall, 1972).

The T_g value obtained with tan δ for dry gluten (187 °C) is a little higher than the reported litterature value of 162 °C (Kalichevsky et al., 1992). The T_g value of dry gluten can be compared to the values reported for other biopolymers such as collagene [200 °C (Batzer and Kreibich, 1981)], gelatin [190−210 °C (Marshall and Petrie, 1980)], starch [143−250 °C (Roos and Karel, 1991; Biliaderis et al., 1986)], or myofibrillar proteins [253 °C (Cuq et al., 1997)]. These very high glass transition temperatures in the absence of plasticizers could be explained by the presence of a significant amount of polymer−polymer interactions, by a high density of hydrogen bonding, or by ionic or hydrophobic interactions.

Effect of Water on the T_g of Wheat Gluten Proteins. The effect of water on the depression of native wheat gluten T_g was studied, and the temperature at the peak in tan δ ($T_{g(tan\delta)}$) and the drop in E' ($T_{g(E')}$) were recorded for each run (Figure 2).

To confirm the value of T_g of water-plasticized samples, the reversibility of the glass transition was studied. A wheat gluten sample equilibrated over NaBr
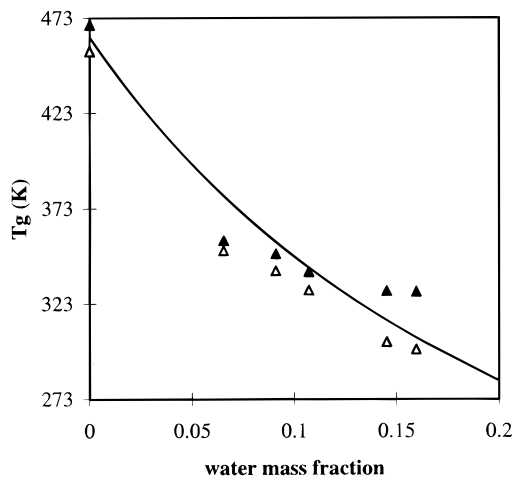
Figure 2. T_g of wheat gluten proteins as a function of water mass fraction with DMTA tan δ peak (▲), drop in log E' (■), and Couchman–Karasz best fit curve (−). $r^2 = 0.980$ and 0.914 for E' and tan δ value fitting, respectively.

Table 1. Variation of DMTA tan δ Peak Height of Wheat Gluten as a Function of Water Mass Fraction and Scanning Repetition

water mass fraction	tan δ peak height	scanning repetition[a]
0	0.75	
0.07	0.11	
0.1	0.27	first
0.1	0.22	second
0.1	0.18	third
0.1	0.16	fourth
0.12	0.41	
0.17	0.68	
0.19	0.72	

[a] Thermal scanning to 393 K.

at 25 °C (with 10 ± 0.3% water content) was scanned on DMTA up to 120 °C. The same sample was removed from the oven, re-equilibrated over NaBr salt solution at 25 °C until constant weight, and rescanned. The procedure was repeated four times. Results of these multiple scans are sumarized in Table 1. The temperature of the tan δ peak is very stable ($\Delta T_g = 5\%$). However, the peak height decreases with scanning repetition (Table 1). Similar results have been observed by De Koning (1994) when studying the effect of storage time on tan δ peak height of polyhydroxybutyrate. It was attributed to a partial crystallization phenomenon. For wheat gluten proteins it can be suggested that this phenomenon was related to a modification of wheat gluten protein structure, probably through the formation of covalent cross-bonds, following successive thermal treatments. This result of the reversibility study illustrates the importance of sample history in these systems.

It was also interesting to note that rubber state E' values decrease and tan δ peak sizes (Table 1) increase with water content. As the size of the tan δ peak is thought to reflect the volume fraction of the material undergoing the transition (Wetton, 1986), it can be suggested that wheat gluten proteins undergo glass transition phenomenon to a greater extent when the water content increase. Similar behavior was already observed in many biopolymers systems, such as polysaccharides and proteins (Kalichevsky et al., 1993a), and also in ionic and polar synthetic polymers (Yeo and Eisenberg, 1977). This behavior can be related either to a partial solvent evaporation or to the plasticizer
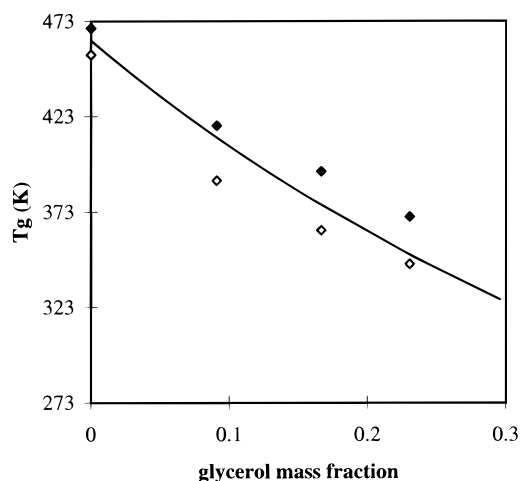

Figure 3. T_g of wheat gluten proteins as a function of glycerol mass fraction with DMTA tan δ peak (▲), drop in log E' (■), and Couchman–Karasz best fit curve (−). $r^2 = 0.974$ and 0.990 for E' and tan δ value fitting, respectively.

effect, which was suspected to reduce effective cross-linking, as the magnitude of the rubbery modulus and tan δ peak is proportional to the effective cross-link density (Barton, 1979). In the case of biopolymers, it was suggested by Kalichevsky et al. (1993a) that the effect of a plasticizer depends on how it affects hydrogen bonding or hydrophobic interactions. Concerning wheat gluten proteins, increasing water content could increase polymer–water interactions to the detriment of polymer–polymer interactions, thus reducing density and intensity of physical junctions (containing hydrogen bondings and/or hydrophobic interactions) and improving the glass transition extent inside the protein chain network. However, this hypothesis cannot explain the high glass transition extent (high tan δ peak) of dry gluten.

Figure 2 shows that the T_g decreased when the water content of wheat gluten proteins increased, showing the plasticizing effect of water on gluten. With increasing water content, the T_g drops at first rapidly (12 °C/1% water for 0–0.1 water mass fraction) and then more slowly (4 °C/1% water for 0.1–0.2 water mass fraction), indicating a large plasticizing effect of water on wheat gluten proteins. The sensitivity of T_g to polar diluent, such as water, makes it very likely that this transformation involves the region that contains numerous polar amino acid residues such as glutamine, asparagine, arginine, and lysine. This lowering of the T_g is similar to the value observed for glutenin (~9 °C/1% water for <0.14 water mass fraction; Cocero and Kokini, 1991), starch (~5 °C/1% water; Orford et al., 1989), elastin (15 °C/1% water for low water content and 5 °C/1% water for 0.1–0.2 water mass fraction; Kakivaya and Hoeve, 1975), or other biopolymers (generally 5–10 °C/1% water; Slade et al., 1989).

T_g of Glycerol and Sorbitol Mixtures. The polyols studied were glycerol and sorbitol in the ratio of gluten to polyol of 10:0, 10:1, 10:2, and 10:3.

The presence of glycerol or sorbitol had a significant plasticizing effect on gluten (Figures 3 and 4) by reducing the temperature of tan δ and E' drop. The strong plasticizing effect and the observation of a single transition (in the range of temperature studied) reflect a good compatibility of polyols and gluten proteins. This plasticizing effect could be attributed to their low molecular weight and hydroxyl groups leading to the
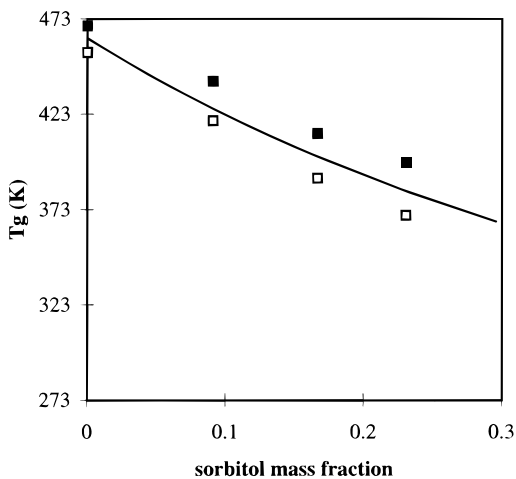
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Figure 4. T_g of wheat gluten as a function of sorbitol mass fraction with DMTA tan δ peak (▲), drop in log E' (■), and Couchman−Karasz best fit curve (−). $r^2 = 0.997$ and 0.995 for E' and tan δ value fitting, respectively.

formation of polymer−plasticizer interactions to the detriment of polymer−polymer interactions.

Contrary to water plasticization, no modification of tan δ peak size and E' drop scale was observed by adding glycerol and sorbitol to wheat gluten, whatever the plasticizer content. Tan δ peak size and E' drop scale were always similar to those of dry wheat gluten. Glycerol and sorbitol have higher molecular weights and lower evaporation rates than water. Their accessibility to high-density junction zones could thus be limited compared to that of smaller molecules such as water.

It was interesting to note that after T_g, E' of gluten/sorbitol or /glycerol mixtures increased quite significantly when temperatures reach ∼175 °C. This phenomenon (increase in E' above T_g) was also observed by Cherian et al. (1995) in gluten/sucrose mixtures and by Rials and Glasser (1988) in hydroxypropylcellulose films at 40 °C. This may indicate a hardening effect of gluten proteins related to cross-linking or other chemical changes in the sample, but polyol or residual water evaporation is also possible.

The plasticizing effect of glycerol and sorbitol on the T_g of gluten (Figures 3 and 4) is more important than the plasticizing effect of fructose on sodium caseinate (Kalichevsky et al., 1993b) or of fructose, sucrose, or glucose on wheat gluten (Kalichevsky et al., 1992).

Modeling. The depression of T_g by the addition of a diluent or plasticizer may be described by a number of theoretical approaches, such as free volume or thermodynamic theories (Gordon and Taylor, 1952; Couchman and Karasz, 1978). These theoretical models relate the T_g of a homogeneous blend of several elements to their fractional concentrations and thermodynamic characteristics of the pure compounds (T_g and ΔC_p, the specific heat capacity change at T_g).

In this study, the Couchman−Karasz equation was used, because it was successfully used to fit data of varous biopolymers, such as starch, wheat gluten, and myofibrilliar proteins (Roos and Karel, 1991; Lourdin et al., 1997; Kalichevsky et al., 1992; Gontard and Ring, 1996; Cuq et al., 1997). The Couchman−Karasz theory leads to the following equation for a two-component mixture:

$$T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \qquad (1)$$

In eq 1, T_g is the glass transition temperature of the plasticized polymer, T_{gi} and ΔC_{pi} are the glass transition temperatures and the specific heat capacity changes at T_g of the pure components, and w_i are the mass fractions of the components. Subscript "1" stands for wheat gluten and subscript "2" for the plasticizer.

The thermodynamic characteristics of the plasticizers were obtained from the literature ($T_{g2} = 136$, 180, and 270 K and $\Delta C_{p2} = 1.94$, 0.88, and 0.96 J g^{-1} K^{-1} for water, glycerol, and sorbitol, respectively; Donth et al., 1992; Orford et al., 1989). The glass transition temperature of dry gluten, T_{g1}, was experimentally determined in the present study ($T_{g1} = 460$ K).

The DMTA data have been calculated according to the Couchman−Karasz equation for the three plasticizers with ΔC_{p1} as the only variable. The best results (i.e., least mean square error between experimental and fitted values for tan δ peak as well as for E') were obtained with a ΔC_{p1} value of 0.4 J g^{-1} K^{-1}.

This value was in close agreement with the 0.39 J g^{-1} K^{-1} ΔC_p value obtained by Kalichevsky et al. (1992) using the same experimental approach (DMTA measurements of T_g and determination of ΔC_{p1} with Couchman−Karasz fit). Noël et al. (1995) found ΔC_p values of gluten subfractions ranging from 0.37 to 0.47 for HMW glutenin and ω gliadin, respectively, using DSC measurements.

As a conclusion it appears that in the range of relatively low fractional weight of plasticizers studied, the Couchman−Karasz model can be applied quite successfully, classifying the efficiency of plasticizers (water > glycerol > sorbitol) according to their thermodynamical characteristics (i.e., T_{gi} and ΔC_{pi}).

However, a simple comparison of T_g curves obtained on a fractional weight basis (Figure 2−4) leads also to the conclusion that the plasticizing effect of glycerol and sorbitol on wheat gluten proteins is less important than the plasticizing effect of water. At a plasticizer fractional weight content of 0.1, the T_g of wheat gluten plasticized with water, glycerol, or sorbitol is about 66, 145, and 165 °C, respectively (tan δ peak values).

These differences in plasticizing effect could be explained by the plasticizer chemical structure and molecular mass (18, 92, and 182 g/mol for water, glycerol, and sorbitol, respectively). To evaluate the effect of the plasticizer's molecular weight, the evolution of T_g was evaluated on a fractional molecular basis (Figure 5). A continuous curve between T_g and molecular fraction was obtained when using a mean molecular mass of 432 g/mol for the functional unit of gluten. The continuity of the curve means that no difference of plasticizing efficiency among these three components can be concluded. One mole of glycerol, sorbitol, or water has the same effect on the depression of wheat gluten T_g. Such a behavior could be explained through the similarity of chemical structure of these three components. Each of these three molecules contains hydroxyl groups that interact with amino acids of wheat gluten proteins through hydrogen bonds. The plasticizers' efficiency appears to be independent of their number of hydroxyl groups per mole (three for glycerol and six for sorbitol).

Thus, it could be interesting to propose a new model predicting plasticizer effect on proteins. This model could be based on the molecular fraction of plasticizer
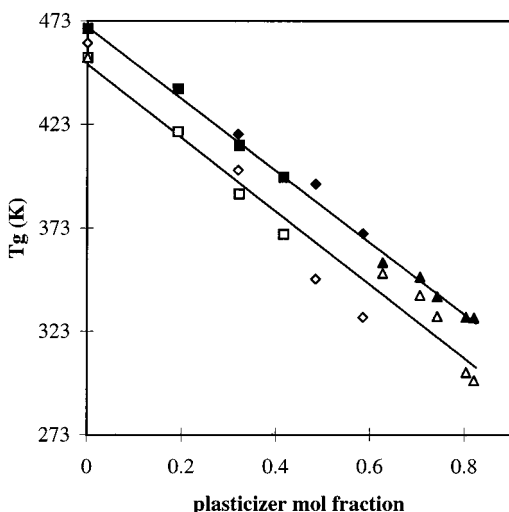
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Figure 5. T_g of wheat gluten proteins as a function of water ($\blacktriangle$, $\triangle$), glycerol ($\blacklozenge$, $\lozenge$), and sorbitol ($\blacksquare$, $\square$) mole fraction. Solid symbols are DMTA tan δ peak, open symbols are drop in log E', and continuous curves are linear regression ($y = -174x + 471$ with $r^2 = 0.996$ and $y = -178x + 453$ with $r^2 = 0.982$ for tan δ and E' value fitting, respectively).

and should take into account the chemical structure of the plasticizer molecules and potential sites of molecular interactions between plasticizer and lateral groups of amino acids. Insolubility of proteins, such as wheat gluten in the plasticizer (i.e., water), for high plasticizer contents leading to a phase separation and to a limit of the T_g (Gontard and Ring, 1997; Cuq et al., 1997) could also be taken into account.

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