Corn Protein-Based Thermoplastic Resins: Effect of Some Polar and Amphiphilic Plasticizers

Lodovico di Gioia and Stéphane Guilbert*

Unité de Technologie des Céréales et des Agro-polymères, ENSA.M/INRA, 2 Place Viala,
34060 Montpellier Cedex 1, France

Homogeneous blends of corn gluten meal (CGM) and "polar" plasticizers (water, glycerol) or "amphiphilic" plasticizers [octanoic and palmitic acids, dibutyl tartrate and phthalate, and diacetyl tartaric acid ester of mono-diglycerides (DATEM)] were obtained by a hot-mixing procedure. The glass transition temperature (T_g) of the blends was measured by modulated differential scanning calorimetry and dynamic mechanical thermal analysis, as a function of plasticizer type and content (0−30%, dwb). The plasticizing efficiency (i.e., decrease of T_g) at equal molar content was found to be proportional to the molecular weight and inversely proportional to the percent of hydrophilic groups of the plasticizer. The migration rate of the plasticizers in the polymer was related to their physicochemical characteristics. It was assumed that polar substances interacted with readily accessible polar amino acids, whereas amphiphilic ones interacted with nonpolar zones, which are buried and accessible with difficulty. The temperature at which a thermoplastic resin of plasticized CGM could be formed was closely connected to the T_g of the blend.

INTRODUCTION

Many plant proteins are interesting raw materials for industrial applications in the nonfood area because of their thermoplastic properties (Guilbert and Graille, 1994; Borcherding and Luck, 1998). In particular, corn gluten meal (CGM) is a low-cost coproduct of corn wet-milling that is rich in proteins (70%, of which 65% is zein) and has been shown to exhibit high thermoplasticity (di Gioia et al., 1998a). For processing materials at low moisture content, those proteins are changed in a reversible way from a rigid state to a soft state through a temperature increase and plasticizer addition (Cuq et al., 1998).

Many theories have been proposed to account for the mechanisms of plasticizer action, which results in a lowering of processing temperature, and are the products of many workers in the first half of this century (Sears and Darby, 1982). In the "lubricity theory", the plasticizer acts as a lubricant to facilitate movements of the macromolecules over each other, whereas the "gel theory" considers the disruption of polymer−polymer interactions (hydrogen bonds and van der Waals or ionic forces). The "free volume theory" states that a study of plasticization is a study of ways to increase free volume and was useful to clarify the lowering of the glass transition temperature (T_g) by a plasticizer. Regardless of which theory is the most appropriate, the action of a plasticizer is to interpose itself between the polymer chains and alter the forces holding the chains together (Entwistle and Rowe, 1978). Because the protein conformation is stabilized to a large extent by hydrogen bonds (H-bonds) and nonpolar interactions, plasticizers must be polar but need not be particularly good solvents

for the protein (Lillie and Gosline, 1993). Entwistle and Rowe (1978) have observed that the plasticizer efficiency in lowering T_g increases with decreasing degree of plasticizer−polymer interactions. The higher plasticizing effect of small molecules, such as glycerol, has been attributed to ease of insertion and positioning within the three-dimensional protein network (Kalichevsky et al., 1992a; Cuq et al., 1997). Generally the interactions between a polypeptide and a plasticizer are still not clearly understood and could be sensitive to size, molecular weight, and number of hydroxyl groups of the plasticizer (Gueguen et al., 1998). Also, questions regarding how the plasticizer molecules become uniformly distributed among the proteins (i.e., the migration kinetic) are generally lacking.

In plastic technology, production of thermoplastic resins requires admixture of polymer and additives such as lubricants and plasticizers. This operation, called "plastic compounding", is achieved with heated rolling mills, kneaders, batch-mixers, or extruders (Woebcken, 1995). Many techniques have been proposed to get a homogeneous blend of corn proteins and plasticizers, for processing biomaterials. They are hand-kneading zein, plasticizer, and hot water (Martin, 1970); melting a mixture of zein and fatty acids with water in a microwave oven and kneading with pasta roller (Lai et al., 1997); and blending zein or CGM with plasticizers in a heated rolling mill (Hasegawa et al., 1994). Other techniques, such as extrusion, have been proposed to achieve protein compounding (Jane and Wang, 1996; Redl et al., 1998).

At the present time, very few data are available in the literature concerning CGM plasticization. Low-cost thermoplastic resins based on plasticized CGM could lead to an interesting valorization of this coproduct in the biomaterial field. Standard plastic-forming techniques could be used to shape all kinds of nondurable

* Author to whom correspondence should be addressed (telephone 04 99 61 24 77; fax 04 67 52 20 94; e-mail guilbert@ensam.inra.fr).

Corn Protein-Based Thermoplastic Resins

J. Agric. Food Chem., Vol. 47, No. 3, 1999 **1255**

Table 1. Amino Acid Composition of CGM, Given by the Supplier

amino acid	content[a]	amino acid	content[a]
Gly	41	Thr	38
Ala	115	Met	22
Val	46	Asx	55
Leu	145	Glx	203
Ile	35	Cys	17
Phe	44	Tyr	34
Pro	96	His	15
Trp	3	Lys	14
Ser	55	Arg	22

[a] Expressed as a number of residues per 1000.

Table 2. Physicochemical Characteristics of the Plasticizers

plasticizer	$M_w{}^a$	$N_{H-b}{}^b$	$\%HG^c$
water	18	4	100.0
gycerol	92	9	55.4
octanoic acid	144	5	22.9
palmitic acid	256	5	12.9
dibutyl tartrate	262	14	37.4
dibutyl phthalate	278	4	23.5
DATEM	630[d]		

[a] Molecular weight. [b] Number of theoretical hydrogen bonds supplied by the molecule. [c] Percentage of total molecular weight of the molecule consisting of hydrophilic groups. [d] Mean molecular weight.

and disposable items. In this study we will consider some largely employed zein plasticizers (Clark and Gralow, 1949; Reiners et al., 1973), of "polar" or "amphiphilic" nature, to form CGM-based thermoplastic resins. Chosen plasticizers include water and glycerol for polar ones, and octanoic and palmitic acids, dibutyl phthalate and tartrate, and diacetyl tartaric acid ester of mono-diglycerides (DATEM) (all consisting of one or more nonpolar hydrocarbon chains of variable length and one or more polar areas formed by hydroxyl, carboxylic, or ester intermediate or final groups) for amphiphilic ones. The efficiency of the plasticizers will be measured by their effect on the T_g of the blend, and formation of homogeneous plasticized CGM resins will be discussed in relation with T_g and migration of the plasticizer in the biopolymer.

MATERIALS AND METHODS

Materials. Commercial CGM [dry weight basis (dwb) composition: 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 get a homogeneous granulation (<160 μm), with a Cyclotec 1093 sample miller (Tecator, Sweden). The amino acid composition of CGM is given in Table 1. The final moisture content (12.5%, dwb) was determined in triplicate after 24 h of drying in an oven at 103 °C. A sample of commercial rigid (unplasticized) poly(vinyl chloride) (PVC) in the form of pellets was purchased by Gazechim (Beziers, France).

Plasticizers. Polar plasticizers were anhydrous glycerol (Prolabo, Vaulx-en-Velin, France) and distilled water. Amphiphilic plasticizers were palmitic acid (Prolabo), octanoic acid, dibutyl tartrate, dibutyl phthalate (Sigma-Aldrich Chimie, St. Quentin Fallavier, France), and DATEM (Danisco Ingredients, Braband, Denmark). Some physicochemical characteristics of the plasticizers are reported in Table 2. The number of theoretical H-bonds supplied by the plasticizer molecule (N_{H-b}) was calculated according to its chemical structure: as acceptors, the nitrogen or oxygen atoms are expected to form, respectively, one or two H-bonds, and as donors of H-bonds are ascribed X–H units, where X is oxygen or nitrogen (Beck et al., 1996). The percentage of hydrophilic

groups (%HG) was obtained by calculating the percentage of the total molecular weight consisting of hydrophilic groups (i.e., –OH, O, or N) (Kalichevsky et al., 1992b) and is very similar to the hydrophilic–lipophilic balance described by Schuster and Adams (1984).
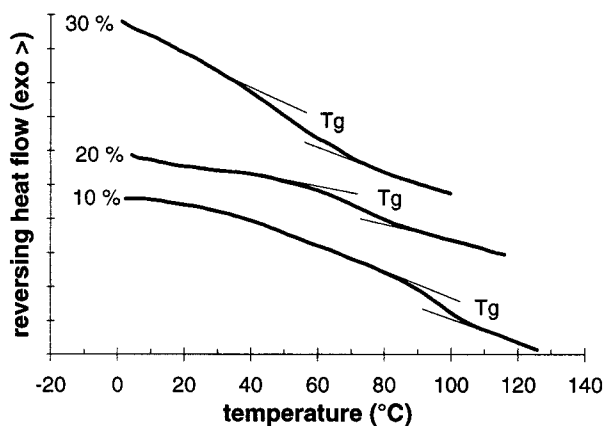
Sample Preparation. Homogeneous blends of plasticizer (5–30%, dwb) and CGM were prepared by introducing subsequently the two components in a Brabender counter-rotating batch mixer (Duisburg, Germany) to achieve a total weight of 40 g and mixing at 25 rpm. The mixing chamber was equipped with an efficient cover to avoid loss of plasticizer, and the chamber wall was thermoregulated at 80 °C (temperature was chosen higher than the melting point of all plasticizers) with circulating water. For studying the effect of temperature in the mixing process, this was varied between 5 and 95 °C. After 6 min, the continuously recorded torque reached a stable value and the mixing process was stopped to avoid sample alteration. A homogeneous plasticized resin was obtained and ground roughly with a laboratory sample miller (Perten Instruments, Huddinge, Sweden) for further processing.

Bars for dynamic mechanical thermal analysis (DMTA) experiments (60 × 5 × 2 mm) were prepared by compression-molding the ground resin for 10 min under 14 bar pressure (14 × 10⁵ Pa) at 110–130 °C and equilibrated at 0% relative humidity in a ventilated desiccator containing P_2O_5 (3 weeks). During compression-molding, an exudation of plasticizer was observed with dibutyl phthalate above 5% content, whereas no exudation was observed with palmitic acid, DATEM, and dibutyl tartrate at 10% and for glycerol and octanoic acid below 30%. Thus, dibutyl phthalate was studied at 5% content; palmitic acid, dibutyl tartrate, and DATEM at 10% content; and water, glycerol, and octanoic acid in the range of 0–30% content. Bars of CGM with no plasticizer were prepared from a resin containing 30% water (dwb) and dried over P_2O_5 after compression-molding. Bars of PVC were prepared similarly with the PVC pellets.

Modulated differential scanning calorimetry (MDSC) measurements were performed on the plasticized resins, finely ground into powder under liquid nitrogen with a ball-grinder, and dried to constant weight in a P_2O_5 atmosphere. The adjustment of water content was achieved by equilibration of the powder at 25 °C over saturated salt solutions (LiCl, CH₃COOK, NaBr, KCl, K_2SO_4) for 2 weeks. The water content was determined concurrently to MDSC measurements by drying 24 h at 103 °C.

Thermomechanical Properties. DMTA analysis of bars was conducted with an MK III dynamic mechanical thermal analyzer (Rheometric Scientific, Piscataway, NJ), equipped with a cryogenic system fed with liquid nitrogen (Air Liquide, Aix-en-Provence, France). A variable-amplitude, sinusoidal tensile stress (frequency = 1 Hz) was applied to the sample to produce a sinusoidal strain of ±16 μm amplitude. Temperature scans (−80 to 240 °C) were performed at a heating rate of 3 °C/min. The furnace temperature was calibrated with indium (mp = 156.6 °C, Rheometric Scientific standard) and was flushed with dry nitrogen gas during analysis to avoid rehydration of the bars. For each material, three samples were tested and the standard deviation was always < ±2 °C. Location of the α-relaxation temperature (T_α) was determined from the onset of the drop of storage modulus (E').

MDSC. Glass transition temperatures were determined using a differential scanning calorimeter equipped with a modulation extension device and a refrigerated cooling system (DSC 2920, TA Instruments, New Castle, USA). The oven was calibrated with indium and purged with nitrogen. A total of 6–8 mg of powdery sample was packed down and sealed into aluminum hermetic pans. The DSC was operated in modulation mode (scan rate = 5 °C/min, sinusoidal temperature oscillation = ±0.796 °C, modulation period = 60 s). For each product, three samples were scanned and the standard deviation was always < ±5 °C. Determinations of baseline changes in the "reversing" heat flow signal, associated with T_g, were obtained using the TA software and characterized by the onset (T_{g_o}), midpoint (T_{g_m}), and end temperatures (T_{g_e}). In this study, the value of T_{g_m} was used for T_g.

**1256** *J. Agric. Food Chem.,* Vol. 47, No. 3, 1999

Di Gioia and Guilbert

Figure 1. MDSC reversing heat flow thermograms for dry CGM, plasticized with 10, 20, or 30% (dwb) octanoic acid.

Thermal Gravimetric Analyses (TGA). Sample degradation and plasticizer loss were followed by TGA (DuPont 2000 Thermal Analysis TGA). Approximately 15 mg of pure or plasticized CGM, prepared as previously described, were subjected to heating from 25 to 300 °C at 5 °C/min under a nitrogen atmosphere, and the mass of the substance was measured concurrently.

RESULTS AND DISCUSSION

Thermal Analysis of Plasticized CGM Resins. DMTA and MDSC are complementary techniques for studying the glass transition. DMTA is very sensitive to the generally weak biopolymer's α-relaxations associated with T_g, and MDSC, a recently developed extension of DSC, allows measurements of T_g with hermetic pans and in a single heating scan, avoiding loss of plasticizer and sample alteration. In this study, water-, glycerol-, and octanoic acid-plasticized CGM resins were analyzed with MDSC and glycerol-, palmitic and octanoic acid-, dibutyl tartrate- and phthalate-, and DATEM-plasticized CGM resins with DMTA.

The reversing heat flow thermograms for CGM containing three concentrations of octanoic acid (Figure 1) show the typical baseline change at the glass transition, as currently observed for synthetic or natural polymers (Bell and Touma, 1996; Coleman and Craig, 1996). The T_g for water-, glycerol-, and octanoic acid-plasticized CGM and the broadness of the transition zone (20−30 °C), defined by T_{g_o} and T_{ge}, are reported in Figure 2. The DMTA scans of CGM as a function of plasticizer type and content are given in Figure 3 (for glycerol and octanoic acid, only 10 and 30% contents are reported, respectively). For dry CGM, a transition from glass-like to rubber-like consistency is evident above 150 °C and was previously attributed to the α-relaxation of CGM proteins (di Gioia et al., 1998a,b). For the plasticized CGM materials, the onset in E' drop is shifted to lower temperatures, and increasing plasticizer content decreases the rubbery storage modulus, whereas the glassy modulus is unaffected. This glassy modulus is similar to that measured for PVC, a thermoplastic synthetic polymer. The drop in E' at T_g, of 2−2.5 decades for plasticized CGM, is smaller compared to the drop of 3 decades for PVC and typical of amorphous polymers (Kalichevsky et al., 1993; Perez et al., 1990). CGM is a blend of many biopolymeric components, and the change in E' is due to the major protein fraction (70%) that undergoes the transition and to its morphology in the composite material (di Gioia et al., 1998a). The higher
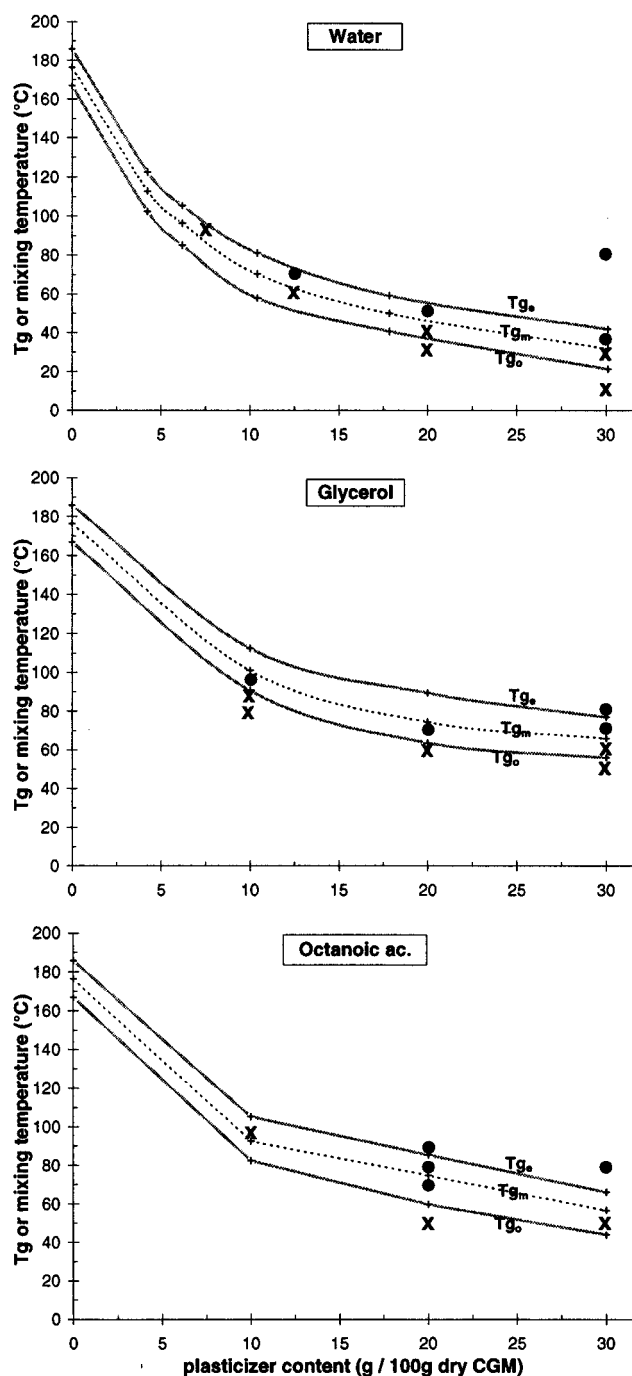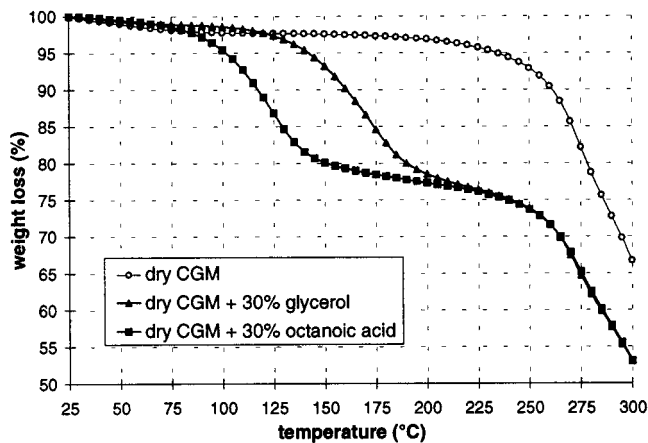

Figure 2. T_g of water-, glycerol-, or octanoic acid-plasticized CGM, determined by MDSC: (●) indicates resin formation and (×) no resin formation in the mixing experiments.

rubbery modulus for CGM can also be attributed to the presence of disulfide cross-linkages, especially in the glutelin fraction of proteins (30%) (Wall et al., 1988). The broadness of the transition zone, which reflects the distribution of relaxation times (Ferry, 1980), is larger for CGM materials (60−90 °C) compared to PVC (30 °C) and may result from a wide variety of components in the biomaterial compared to the pure PVC (Lillie and Gosline, 1993). Also, this transition zone is larger for CGM plasticized with octanoic acid compared to glycerol, and a shoulder is observed at 30% octanoic acid content for temperature >90 °C (Figure 3b). These phenomena are attributed to a loss of this plasticizer above 90 °C, as observed in TGA measurements (Figure 4). The final drop of in E' above 210−230 °C mostly

Corn Protein-Based Thermoplastic Resins

*J. Agric. Food Chem.,* Vol. 47, No. 3, 1999 **1257**
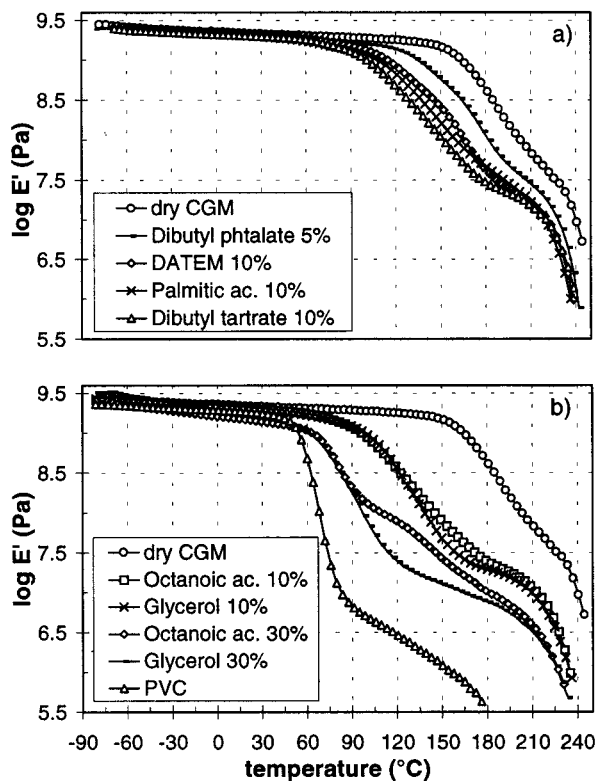
Figure 3. DMTA thermograms for dry CGM alone or plasticized with glycerol, octanoic and palmitic acids, dibutyl tartrate and phthalate, and DATEM, at 5–30% content (dwb).

Figure 4. TGA thermograms of dry CGM alone or blended with 30% (dwb) glycerol or octanoic acid.

results from the thermal degradation of the material, also observed by TGA (Figure 4). Actually, no melting temperature has been observed for zein proteins (Clark and Gralow, 1949; Madeka and Kokini, 1996).

MDSC and DMTA techniques are in good agreement; the mean difference between T_α and T_g is ±6.3 °C with glycerol and ±9.6 °C with octanoic acid. The difference is slightly higher (16.4 °C) at 0% plasticizer content, because T_g was taken from a previous study (di Gioia et al., 1998b) in which the analyses were made with open pans to enable residual water evaporation. This amount of residual water after the samples had been dried in a 0% relative humidity atmosphere, measured to be $\approx0.5\%$, can be neglected in this study because it is similar for all of the samples and very low. The lower sample density of the tablets used for DMTA measurements in our previous studies (di Gioia et al., 1998a,b),
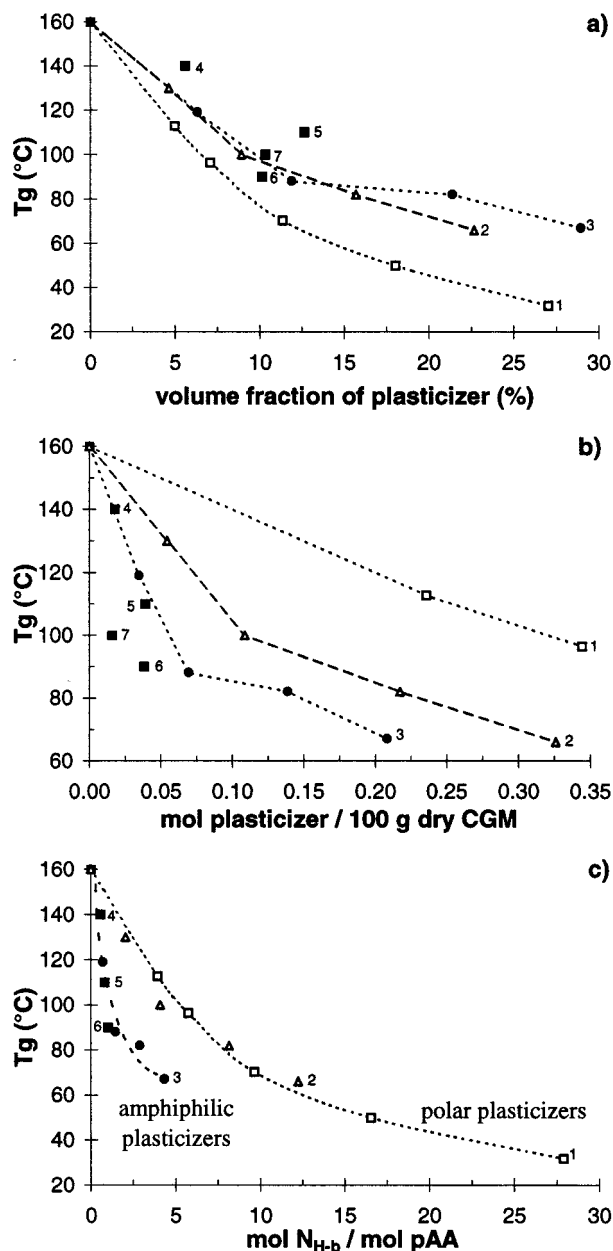
Figure 5. T_g of plasticized CGM as a function of (a) volume fraction of plasticizer, (b) molar plasticizer content, and (c) moles of theoretical H-bonds supplied by the plasticizer per moles of polar amino acids in CGM. Values for water are from MDSC and for other plasticizers from DMTA (1 = water; 2 = glycerol; 3 = octanoic acid; 4 = dibutyl phthalate; 5 = palmitic acid; 6 = dibutyl tartrate; 7 = DATEM).

which delay the heat diffusion, could explain lower values (~30 °C) obtained in this study with isotropic, dense glassy bars.

Plasticization of CGM. The T_g depression of CGM by different plasticizers is reported in Figure 5a as a function of the volume fraction of plasticizer. For a ll plasticizers, the first small amounts are the most effective, and increasing amounts become progressively less so. As expected, lower T_g at equal volume fraction of plasticizer is generally obtained with smaller plasticizer molecules. These two observations are in agreement with the free volume theory of plasticization (Sears and Darby, 1982), which predicts (1) a plasticizer efficiency proportional to the T_g of the plasticized polymer and (2) a smaller oscillation volume for a

smaller molecule, so that greater free volume is available for motion of polymer molecules. In the case of elastin plasticized with various glycols, Lillie and Gosline (1993) also observed that for a similar volume fraction of plasticizer, the α-relaxation occurred at the lowest temperature with the plasticizer of lower molecular weight. However, from Figure 5a, dibutyl tartrate and DATEM decrease T_g equally to octanoic acid at equal volume fraction, despite a much higher molecular weight. Furthermore, T_g for systems containing glycerol and octanoic acid at similar weights or volume fractions are very close (Figures 2 and 5a). Due to the complex structure of the proteins, their plasticization is not a simple process, and other parameters should be taken into account, as discussed subsequently.

The plasticizing efficiency (i.e., T_g depression), on a molar basis, is always higher for "amphiphilic plasticizers" than for "polar plasticizers" (Figure 5b). It is observed that at equal number of molecules, water is the less efficient plasticizer, and dibutyl tartrate and DATEM are the most efficient; glycerol and octanoic acid are intermediate and have similar effects, indicating that molecular steric hindrance is also an important parameter. In Figure 5c, T_g depression is expressed as a function of moles of theoretical H-bonds supplied by the plasticizer molecules (N_{H-b}) per mole of polar amino acids (pAA) in CGM (in this figure DATEM was not reported because the precise chemical structure of this commercial substance was unknown and the calculation could not be done). pAA are those identified by Rothfus (1996) and Phillips et al. (1994) and are calculated in CGM from its average amino acid composition (Table 1). For a given plasticizer, T_g decreases with increasing N_{H-b}/pAA ratio, because plasticizer content is higher. Polar and amphiphilic plasticizers are clearly separated into two distinct curves, indicating similar effects for similar structures. Amphiphilic plasticizers are more efficient than polar ones at equal N_{H-b}/pAA ratio.

To better understand the plasticizer efficiency in relation with its chemical structure, the T_g values of plasticized CGM resins at two different molar contents of plasticizer (0.017 and 0.038 mol/100 g of dry CGM) are plotted against some physicochemical characteristics of the plasticizer, which are molecular weight (Figure 6a) and %HG (i.e., hydrophilicity) (Figure 6b). At the same molarity, the plasticizer efficiency increases with increasing molecular weight (Figure 6a), as observed in a previous study of the effect of hydrophilic plasticizers on CGM (di Gioia et al., 1998a), and it decreases with increasing hydrophilicity (Figure 6b). In Figure 6b DATEM is not reported because the precise chemical structure of the molecule is unknown. For all data, linear relationships are observed, with r^2 values >0.94. An exception is dibutyl tartrate in Figure 6b, which seems to have a much greater plasticizing efficiency regardless of hydrophilicity, compared to other substances.

Effect of Mixing Temperature on the Formation Kinetic of CGM–Plasticizer Resins. CGM–plasticizer blending procedures below and above T_g have been compared. Blends of CGM and glycerol or octanoic acid were prepared by mixing at 80 °C or by hand kneading the two components in a mortar at 20 °C. Blends were then compression-molded at 110 °C. Bars containing glycerol always appeared homogeneous, whereas bars containing hand-kneaded octanoic acid were not homogeneous and partially unmelted. This is confirmed by
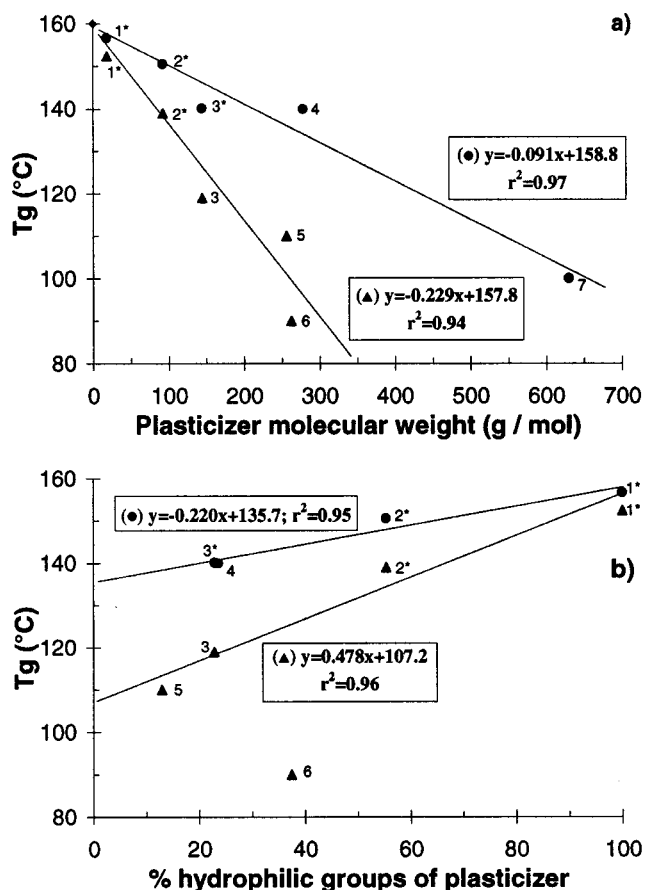
Figure 6. T_g of plasticized CGM as a function of (a) molecular weight and (b) percent hydrophilic groups of plasticizer, at two molar contents: (●) = 0.017 mol of plasticizer/100 g of dry CGM; (▲) = 0.038 mol of plasticizer/100 g of dry CGM (1 = water; 2 = glycerol; 3 = octanoic acid; 4 = dibutyl phthalate; 5 = palmitic acid; 6 = dibutyl tartrate; 7 = DATEM). (*) indicates interpolated values from Figure 5a.
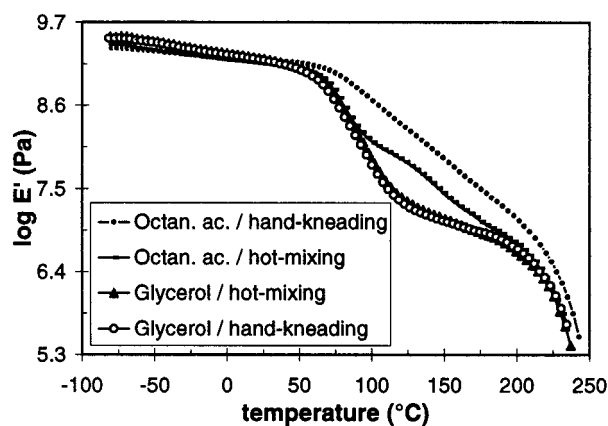
Figure 7. DMTA thermograms of dry CGM, plasticized with 30% (dwb) glycerol or octanoic acid. The blend is hot-mixed or hand-kneaded.

the perfectly superimposed DMTA scans for CGM with glycerol (Figure 7), whereas the α-relaxation is larger and occurs at a higher temperature for the hand-kneaded CGM with octanoic acid sample compared to the hot-mixed sample, indicating no homogeneity and imperfect plasticization (Figure 7).

Mixing experiments have been run using dry CGM (water <1% dwb) to investigate the relationship between the mixing temperature and the formation of a plasticized resin as a function of plasticizer type and

Corn Protein-Based Thermoplastic Resins

J. Agric. Food Chem., Vol. 47, No. 3, 1999 **1259**
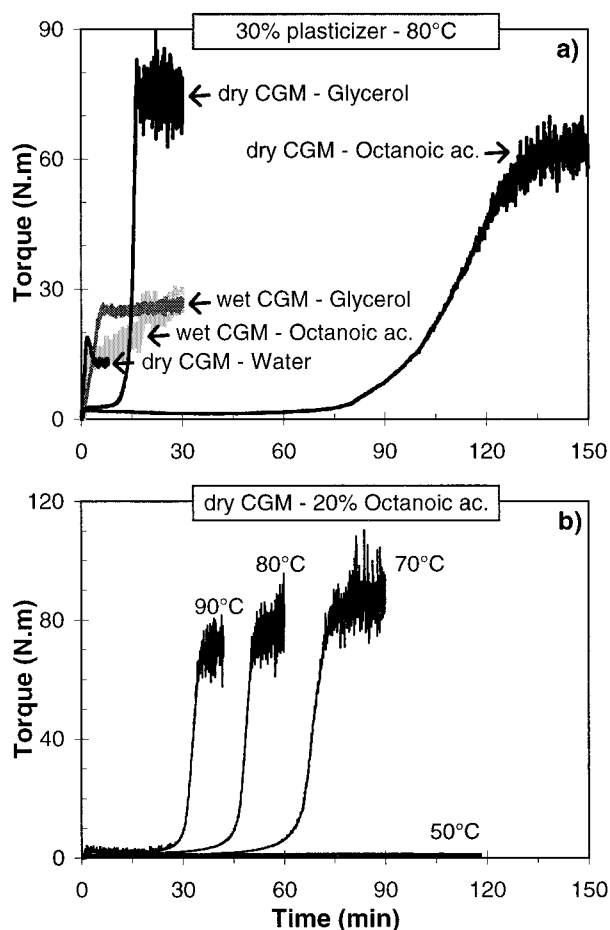
Figure 8. Torque evolution during the mixing process for (a) a blend of dry or wet (12.5% water, dwb) CGM and 30% (dwb) plasticizer (water, glycerol, or octanoic acid) mixed at 80 °C and (b) a blend of dry CGM and 20% (dwb) octanoic acid mixed at different temperatures.

content. When dry CGM is mixed at 80 °C with 30% water, glycerol, or octanoic acid, the evolution of torque is very different (Figure 8a). With water, the torque increases immediately to a maximum (2 min) and decreases to a stable value (5 min). With glycerol, the torque is initially very low and stable (10−12 min), and then it increases very rapidly to a stable value. With octanoic acid, the evolution of the torque is similar, but the lag time before torque development is much longer, ∼75−80 min, and the subsequent increase in torque much more gradual. The final stable value is attained after 140−150 min.

It may be relevant to note that the water−CGM (and to a minor extent the glycerol−CGM) resin is crumbly and not very cohesive, whereas the octanoic acid−CGM resin is a dense, cohesive material. Obviously there are considerable differences in the resin structures. Increasing the temperature of the mixing chamber from 70 to 90 °C for a blend of dry CGM−20% octanoic acid decreases the lag time before torque development (Figure 8b), and when wet CGM (12.5% water, dwb) is mixed at 80 °C with glycerol or octanoic acid, the lag time disappears (Figure 8a). At 50 °C also after 2 h of mixing, no resin is formed. All of the mixing experiments are illustrated in Figure 2, where ● indicates resin formation and × no resin formation. The ability of the blend to form a resin is clearly related to the mixing temperature; the minimal temperature at which a resin can be developed is always located in the glass transition

zone ($T_{g_o} - T_{g_e}$), and a torque will not develop below the T_g of the blend. This is in close agreement with the findings of Lawton (1992), who reported that a zein−starch composite flour could not develop into a dough if mixed below zein's T_g.

General Discussion on the Plasticization of Corn Proteins. A few general comments, based on the mechanisms of plasticizer action, arise from these results. The commonly admitted plasticizer action on a resin is to separate the chains by breaking the attachments (mostly H-bonds and van der Waals or ionic interactions) that hold the polymer chains together and masking the centers of forces through the formation of plasticizer−polymer interactions (Entwistle and Rowe, 1978; Sears and Darby, 1982). Then a plasticizer will have polymer-philic groups to improve its solubility and polymer-phobic groups to improve its effect. Protein macromolecules are primarily stabilized by H-bonds but are also stabilized by nonpolar interactions formed by the nonpolar amino acid side chains (Lillie and Gosline, 1993). From Table 1, we calculated that ∼40% of the amino acids in CGM have nonpolar aliphatic or aromatic side chains. It is probable that a proper balance between the polar and the nonpolar portions of the molecule is necessary to be a good plasticizer of CGM, as observed for zein's solvents (Mossé, 1961). Actually, the particular sequence of zein's amino acids forms a very amphiphilic molecule (Rothfus, 1996) of regularly distributed polar/nonpolar surfaces, resulting in three series of two polar and four nonpolar amino acids for each of the nine repeating units (Argos et al., 1982). Thus, the high plasticizing efficiency of the tested amphiphilic molecules can be related to a good compatibility with CGM through a similar structure. This is particularly the case for dibutyl tartrate, for which the %HG (37.4%) is very close to that of CGM (37.9%, calculated using Table 1). Kalichevsky et al. (1992b) also observed that the greatest depressing effect on the T_g of wheat gluten was obtained with molecules of hydrophilicity similar to that of gluten. In a similar manner, fatty acids with optimal nonpolar chain length are known to dissolve wheat and sorghum glutelins (Kobrehel and Bushuk, 1977; Fliedel and Kobrehel, 1985) by disrupting the important nonpolar protein−protein interactions. These interactions are also very abundant in corn glutelins (Wall et al., 1988), and our recent study (di Gioia et al., 1998b) indicated that the single T_g of CGM mostly resulted from nonpolar interactions between the CGM proteic components. In food systems, it is typically assumed that water is the best plasticizer due to its very low T_g value (Roos, 1995). Despite this strong plasticizing ability of water, its effect on CGM is limited because water cannot interact with the nonpolar protein components responsible for the glass transition. The amphiphilic plasticizers can interact with these regions of the protein and thus have a larger effect on the net T_g of the system. Unfortunately, data were not available in the literature concerning the T_g of the pure amphiphilic plasticizers used in this study. Nevertheless, our results show the very important role of plasticizer−matrix interactions in the case of protein plasticization.

The plasticization of a polymer is a complex step-by-step phenomenon, comprising (1) wetting and adsorption; (2) solvation and/or penetration of the surface; (3) absorption, diffusion; (4) dissolution in the amorphous regions; and (5) structure breakdown (Sears and Darby,

1982). In this study, the lag time differences observed when using plasticizers of different physicochemical characteristics can be attributed to different limiting steps. For polar plasticizers, differences between CGM—glycerol and CGM—water blending kinetics can be explained by longer times for steps 1—3 due to higher viscosity of glycerol compared to water. It is also probable that polar plasticizers would interact with pAA, which are readily accessible, whereas amphiphilic plasticizers (especially with low %HG) would interact with the nonpolar zones, which are buried and accessible with difficulty (Fliedel and Kobrehel, 1985). Steps 2, 3, and particularly 4 are slackened or prevented with octanoic acid, thus explaining the observed large lag time during the hot-mixing procedure and the inhomogeneity of bars made with the hand-kneaded sample. This is confirmed by the reduction or elimination of this lag time, if the molecular mobility is increased by an additional mean, such as heating or adding water to achieve the rubbery state (Figure 8).

Conclusion. In general, compounding of CGM and one or more plasticizers should be carried out above the glass transition temperature of the blend, to form a homogeneous plasticized material. The efficiency of plasticizers was related to many physicochemical characteristics of those molecules. The studied polar plasticizers were efficient because of their low molecular weights, whereas amphiphilic molecules, such as dibutyl tartrate and octanoic acid, could interact efficiently with the proteins, through structure similarities. Probably, those two families of substances interacted with different parts of the proteins (i.e., polar and nonpolar zones), thus explaining the large differences observed in the development of a thermoplastic resin by the hot-mixing procedure. Migration of the plasticizer in the polymer was shown to be an important parameter to take into account in the respective choice of the plasticizer and the admixing procedure. Other important parameters, such as volatility, water resistance, and exudation, should be taken into account in the choice of a good plasticizer. According to these criteria, octanoic acid seems to be a promising molecule to be used with corn proteins. The formed resins were very glassy and dense materials of high thermoplasticity. They could be used as new low-cost biomaterials for applications in the fields of agriculture, packaging, and compostable short-life items.

LITERATURE CITED

Argos, P.; Pedersen, K.; Marks, M. D.; Larkins, B. A. A structural model for maize zein proteins. *J. Biol. Chem.* **1982**, *257*, 9984—9990.

Beck, M. I.; Tomka, I.; Waysek, E. Physico-chemical characterization of zein as a film coating polymer. A direct comparison with ethyl cellulose. *Int. J. Pharm.* **1996**, *141*, 137—150.

Bell, L. N.; Touma, D. E. Glass transition temperatures determined using a temperature-cycling differential scanning calorimeter. *J. Food Sci.* **1996**, *61*, 807—810.

Borcherding, A.; Luck, T. Application of plant proteins as thermoplastics. In *Plant Proteins from European Crops, Food and Non-Food Applications*; Guéguen, J., Popineau, Y., Eds.; Springer-Verlag: Berlin, 1998; pp 313—318.

Clark, R. L.; Gralow, R. C. Zein: versatile packaging resin. *Mod. Packag.* **1949**, *12*, 122—156.

Coleman, N. J.; Craig, D. Q. M. Modulated temperature differential scanning calorimetry: a novel approach to pharmaceutical thermal analysis. *Int. J. Pharm.* **1996**, *135*, 13—29.

Cuq, B.; Gontard, N.; Cuq, J. L.; Guilbert, S. Selected functional properties of fish myofibrillar protein-based films as affected by hydrophilic plasticizers. *J. Agric. Food Chem.* **1997**, *45*, 622—626.

Cuq, B.; Gontard, N.; Guilbert, S. Proteins as agricultural polymers for packaging production. *Cereal Chem.* **1998**, *75*, 1—9.

Di Gioia, L.; Cuq, B.; Guilbert, S. Effect of hydrophilic plasticizers on thermomechanical properties of corn gluten meal. *Cereal Chem.* **1998a**, *75*, 514—519.

Di Gioia, L.; Cuq, B.; Guilbert, S. Thermal properties of corn gluten meal and its proteic components. *Int. J. Biol. Macromol.* **1998b**, in press.

Entwistle, C. A.; Rowe, R. C. Plasticization of cellulose ethers used in the film coating of tablets. *J. Pharm. Pharmacol.* **1978**, *31*, 269—272.

Ferry, J. D. Illustration of viscoelastic behavior of polymeric systems. In *Viscoelastic Properties of Polymers*; Ferry, J. D., Ed.; Wiley: New York, 1980; Chapter 2, pp 33—55.

Fliedel, G.; Kobrehel, K. Studies on sorghum proteins. 1. Solubilization of proteins with soaps. *J. Agric. Food Chem.* **1985**, *33*, 303—308.

Guéguen, J.; Viroben, J.; Barbot, J.; Subirade, M. Comparative properties of pea protein and wheat gluten films. Influence of various plasticizers and aging. In *Plant Proteins from European Crops, Food and Non-Food Applications*; Guéguen, J., Popineau, Y., Eds.; Springer-Verlag: Berlin, 1998; pp 319—323.

Guilbert, S.; Graille, J. Biomatériaux et molécules fonctionnelles. In *Valorisations non alimentaires des grandes productions agricoles. Les colloques no.* 71; Guéguen, J., Ed.; INRA Editions: Paris, 1994; pp 195—206.

Hasegawa, N.; Suzuki, K.; Ishii, T.; Hayashi, M.; Danno, G. Biodegradable thermoplastic composition from corn gluten meal and its preparation. Japanese Patent 6,192,577, 1994.

Jane, J.-L.; Wang, S. Soy protein-based thermoplastic composition for preparing molded articles. U.S. Patent 5,523,293, 1996.

Kalichevsky, M. T.; Jaroszkiewicz, E. M.; Blanshard, J. M. V. Glass transition of gluten. 1: gluten and gluten-sugar mixtures. *Int. J. Biol. Macromol.* **1992a**, *14*, 257—266.

Kalichevsky, M. T.; Jaroszkiewicz, E. M.; Blanshard, J. M. V. Glass transition of gluten. 2: The effect of lipids and emulsifiers. *Int. J. Biol. Macromol.* **1992b**, *14*, 267—273.

Kalichevsky, M. T.; Blanshard, J. M. V.; Marsh, R. D. L. Application of mechanical spectroscopy to the study of glassy biopolymers and related systems. In *The Glassy State in Foods*; Blanshard, J. M. V., Lillford, P. J., Eds.; Nottingham University Press: Nottingham, U.K., 1993; pp 133—156.

Kobrehel, K.; Bushuk, W. Studies of glutenin. X. Effect of fatty acids and their sodium salts on solubility in water. *Cereal Chem.* **1977**, *54*, 833—839.

Lai, H. M.; Padua, G. W.; Wei, L. S. Properties and microstructure of zein sheets plasticized with palmitic and stearic acids. *Cereal Chem.* **1997**, *74*, 83—90.

Lawton, J. W. Viscoelasticity of zein-starch doughs. *Cereal Chem.* **1992**, *69*, 351—355.

Lillie, M. A.; Gosline, J. M. The effect of swelling solvents on the glass transition in elastin and other proteins. In *The Glassy State in Foods*; Blanshard, J. M. V., Lillford, P. J., Eds.; Nottingham University Press: Nottingham, U.K., 1993; pp 281—301.

Madeka, H.; Kokini, J. L. Effect of glass transition and cross-linking on rheological properties of zein: development of a preliminary state diagram. *Cereal Chem.* **1996**, *73*, 433—438.

Corn Protein-Based Thermoplastic Resins

J. Agric. Food Chem., Vol. 47, No. 3, 1999 **1261**

Martin, D. N. Zein-containing plastic composition. U.S. Patent 3,497,369, 1970.

Mossé, J. Monographie sur une protéine du maïs: la zéine. *Ann. Physiol. Veg.* **1961**, *3*, 105−139.

Perez, J.; Cavaillé, J. Y.; Tatibouet, J. La transition vitreuse dans les polymères amorphes. *J. Chim. Phys.* **1990**, *87*, 1923−1967.

Phillips, L. G.; Whitehead, D. M.; Kinsella, J. Chemical nature of proteins and polypeptides. In *Structure−Function Properties of Food Proteins*; Phillips, L. G., Whitehead, D. A., Kinsella, J., Eds.; Academic Press: San Diego, CA, 1994; Chapter 1, pp 3−23.

Redl, A.; Morel, M. H.; Bonicel, J.; Vergnes, B.; Guilbert, S. Extrusion of wheat gluten plasticized with glycerol: influence of process conditions on flow behaviour, rheological properties and molecular size distribution. *Cereal Chem.* **1998**, in press.

Reiners, R. A.; Wall, J. S.; Inglett, G. E. Corn proteins: potential for their industrial use. In *Industrial Uses of Cereals*; Pomeranz, Y., Ed.; Symposium Proceedings of the 58th Annual Meeting of the AACC, St. Louis; AACC: St. Paul, MN, 1973; pp 285−302.

Roos, Y. H. Prediction of the Physical State. In *Phase Transitions in Foods*; Taylor, S. L., Ed.; Academic Press: San Diego, CA, 1995; Chapter 6.

Rothfus, J. A. Potential β-sheet surfaces of corn and wheat proteins. *J. Agric. Food Chem.* **1996**, *44*, 3143−3152.

Schuster, G.; Adams, W. F. Emulsifiers as additives in bread and fine baked products. In *Advances in Cereal Science and Technology*; Pomeranz, Y., Ed.; AACC: St. Paul, MN, 1984; Vol. VI, Chapter 4, pp 139−287.

Sears, J. K.; Darby, J. R. Mechanism of plasticizer action. In *The Technology of Plasticizers*; Sears, J. K., Darby, J. R., Eds.; Wiley-Interscience: New York, 1982; Chapter 2, pp 35−77.

Wall, J. S.; Cooker, L. A.; Bietz, J. A. Structure and origin of maize endosperm alcohol-insoluble glutelin. *J. Agric. Food Chem.* **1988**, *36*, 722−728.

Woebcken, W. Polymer syntheses; Plastics processing and finishing. In *International Plastics Handbook*; Haim, J., Hyatt, D., Eds.; Hanser Publishers: Munich, 1995; Chapter 3, pp 42−164.