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1995

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Cherian, George; Gennadios, Aristippos; Weller, Curtis L.; and Chinachoti, Pavinee, "Thermomechanical Behavior of Wheat Gluten Films: Effect of Sucrose, Glycerin, and Sorbitol" (1995). *Biological Systems Engineering: Papers and Publications*. 103.

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## Thermomechanical Behavior of Wheat Gluten Films: Effect of Sucrose, Glycerin, and Sorbitol<sup>1</sup>

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### ABSTRACT

Cereal Chem. 72(1):1-6

Glass transition temperature ( $T_g$ ) and mechanical and water vapor barrier properties of wheat gluten films containing glycerin, sucrose, glycerin-sucrose, and glycerin-sorbitol were studied. Glycerin and sucrose were immiscible; the wheat gluten film containing both solutes showed two separate thermal transitions ( $-58^\circ\text{C}$  and  $-5^\circ\text{C}$ , respectively). The low temperature (low- $T$ ) transition ( $-58^\circ\text{C}$ ) was due to a glycerin-rich region. The low- $T$   $\tan \delta$  peak height influenced the tensile strength and elongation linearly and the water vapor permeability (WVP) curvilinearly.

However, the  $T_g$  failed to change with solute composition and exhibited low correlation with barrier and mechanical properties. Initial addition of glycerin increased the WVP dramatically. Sucrose decreased the WVP (only slightly), but resulted in a rigid and fragile film. The gluten-glycerin-sorbitol film at a ratio of 15:3:3 (w/w), 16.7% moisture (wb), showed a single effective  $T_g$  ( $-42^\circ\text{C}$ ) and intermediate values for tensile strength, percent elongation, and WVP, which were between those of the 15:6:0 and 15:4:2 gluten-glycerin-sucrose films.

Research interest in the development of edible films and coatings for use in food packaging and preservation has recently increased. The obvious appealing characteristics of edible films include the renewable nature of their ingredients; the films' ability to function as carriers of food additives (e.g., antioxidants, flavors); and the potential use of such films in the interior of heterogeneous food systems as selective barriers to the transport of vapors, gases, and solutes. An additional anticipated benefit from the wide commercialization of edible films is the further utilization of several commodities employed as sources of film-forming materials.

Comprehensive reviews on the film-forming properties of protein, polysaccharide, and lipid materials have been published (Guilbert 1986, Kester and Fennema 1986, Krochta 1992). Protein films in particular have been discussed in detail by Gennadios et al (1994). Some commercialization of protein films has been realized in collagen sausage casings (Hood 1987); gelatin pharmaceutical capsules (Rose 1987); and corn zein-based protective coatings for nutmeats and candy (Alikonis 1979, Andres 1984). The formation and property evaluation of wheat gluten films has been dealt with in several studies (Wall and Beckwith 1969; Anker et al 1972; Okamoto 1978; Park and Chinnan 1990; Aydt et al 1991; Gontard et al 1992, 1993; Gennadios et al 1993a-d). In all these studies, films were produced by drying cast aqueous ethanol solutions of wheat gluten. A plasticizer, usually glycerin, was added to reduce film brittleness and ensure the formation of free-standing films. Wheat gluten films in a dry state were very effective oxygen barriers (Gennadios et al 1993b). However, wheat gluten films, and protein films in general, are poor water vapor barriers because of the inherent hydrophilicity of the proteins (Krochta 1992). The incorporation of waxes, fatty acids, surfactants, sugars, etc., to carbohydrate and protein films, either by mixing or as a separate layer, may help in limiting the moisture migration (Kester and Fennema 1986, Kester and Fennema 1989, Rico-Pena and Torres 1990). Use of glycerin as a plasticizer not only increases flexibility, but also gives a very high water permeability. Modification of the amount of glycerin and the pH has decreased permeability, but not to a desirable level (Gontard et al 1993). Because plasticization increases diffusion through the film, it is possible that replacing glycerin with a larger molecular weight solute such as sucrose may help retard diffusion (given

that the rheological properties are acceptable). One of the objectives of this study was to investigate this possibility.

Glass transition temperature ( $T_g$ ) has been an important parameter in the study of synthetic polymers. Above the  $T_g$ , polymeric materials exist in a soft, rubbery state, whereas below the  $T_g$ , polymers assume a glassy state (Ferry 1980). The value of  $T_g$  is governed primarily by chemical composition and the presence of added plasticizers and, secondarily, by structural features, such as chain branching, cross-linking, and crystallinity (Rogers 1985). In the case of hydrophilic synthetic and natural polymers, water functions as a plasticizer depressing the  $T_g$  (Slade and Levine 1988, Slade et al 1989). Thermal analysis techniques such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), are employed for measurement of  $T_g$ . The mechanical and barrier properties of polymers at any particular temperature are affected by the value of  $T_g$  (Oadian 1991). For example, it is expected that the permeation of gas and vapor molecules through a film is higher above  $T_g$  where polymer chains are more mobile (Rogers 1985).

The application of the glass transition concept can be a valuable aid in edible film research. In the only relevant study available, Koelsch and Labuza (1992), using DSC, determined the  $T_g$  of edible emulsion films made from methyl cellulose and fatty acids. They reported that their films, analyzed at ambient condition, were in the rubbery state since recorded  $T_g$  values were in the approximate range of  $-11$  to  $53^\circ\text{C}$ . Thus, they reasoned the higher permeance of the film may be due to the rubbery state. Glass transition behavior of wheat gluten and its glutenin and gliadin fractions has been reported (Hoseney et al 1986, Cocero and Kokini 1991, de Graaf et al 1993). Kalichevsky et al (1992) determined the effect of sucrose and glycerin on the  $T_g$  of wheat gluten. There has been no work done, however, to relate these effects to the physical properties of edible gluten barriers, such as water vapor permeability and mechanical properties.

The  $T_g$  of glycerin-plasticized wheat gluten films is expected to increase when glycerin is partially replaced with sucrose (Kalichevsky et al 1992). Most likely, such an increase in  $T_g$  will be accompanied by an improvement of the water vapor barrier characteristics of the film. Evidence for this assertion comes from a study of a starch-sucrose system where water diffusivity decreased with the addition of sucrose (Chinachoti and Stengle 1990). Diffusion is a very important (often governing) step in the whole permeation process, and substituting sucrose is expected to affect it.

The objectives of the present study were to examine the effect of sucrose on the  $T_g$ , water vapor permeability, and selected mechanical properties of wheat gluten films and to investigate the effects of using sorbitol in the film formulation.

<sup>1</sup>Journal series 10601, Agricultural Research Division, Institute of Agriculture and Natural Resources, University of Nebraska-Lincoln. University of Massachusetts Agricultural Experiment Station, Project MAS 000623.

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## MATERIALS AND METHODS

### Reagents

Vital wheat gluten (Whetpro-80) with ~82% (db) protein content ( $N \times 6.25$ ; value provided by the manufacturer) was donated by Ogilvie Mills Ltd., Quebec, Canada. Glycerin and sucrose, both of ACS grade, were purchased from Fisher Scientific, Pittsburgh, PA. Ammonium hydroxide (4.96*N* solution in water) and D-sorbitol (>99% purity) were purchased from Aldrich Chemical Co., Milwaukee, WI.

### Preparation of Film-Forming Solutions

Wheat gluten (15 g) was mixed and stirred with 95% ethanol (72 ml) and glycerin (6, 4, 3, or 0 g) or sorbitol (3 g) (Table I) before the obtained mixtures were homogenized (Virtishear, Virtis Co., Gardiner, NY) for 5 min at 5,000 rpm. Subsequently, mixtures were heated and stirred on a magnetic stirrer hot plate (model PC-320, Corning, Inc., New York, NY) while slowly adding 14 ml of ammonium hydroxide (4.96*N*) to provide an alkaline condition to disperse the proteins, and warm distilled water (48 ml) in which sucrose (0, 2, 3, or 6 g) was previously dissolved. The dispersion of protein was noted by an apparent decrease in solution viscosity, at which point the solution had a temperature of 75–77°C. After removal from the hot plate, the solutions were kept at ambient conditions (25°C) for 2–3 min to allow bubbling to stop before casting.

### Casting and Drying

Film-forming solutions were cast onto flat glass plates using a thin-layer chromatography spreader bar (Desaga, Brinkmann Co., New York, NY) and placed in an air-circulating oven

TABLE I  
Weight Ratios of Glycerin, Sucrose, and Sorbitol Added per 15 g of Wheat Gluten in Gluten-Based Films

Film	Ratio (w/w)	Glycerol (g)	Sucrose (g)	Sorbitol (g)
Gluten-glycerin-sucrose	15:6:0	6	0	NA <sup>a</sup>
Gluten-glycerin-sucrose	15:4:2	4	2	NA
Gluten-glycerin-sucrose	15:3:3	3	3	NA
Gluten-glycerin-sucrose	15:0:6	0	6	NA
Gluten-glycerin-sorbitol	15:3:3	3	NA	3

<sup>a</sup>Not applicable.

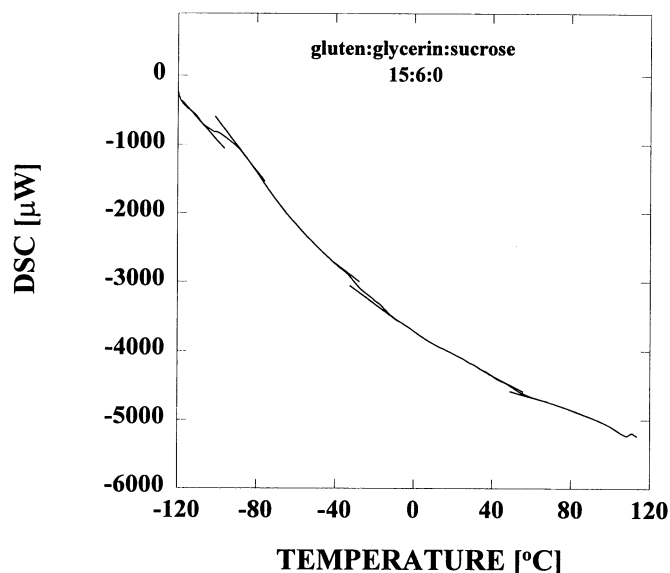


Fig. 1. Differential scanning calorimetry (DSC) thermogram of wheat gluten-glycerin-sucrose film at a ratio of 15:6:0 (w/w) showing a series of decreases in the baseline upon heating and indicating a change in heat capacity.

(Isotemp, model 738F, Fisher Scientific, Pittsburgh, PA) set at 45°C. Films were peeled off the plates after drying for 12 hr.

### $T_g$ Measurements

A differential scanning calorimeter (DSC model 100, Seiko Instruments, Torrance, CA) and a dynamic mechanical analyzer (DMA model 110, Seiko) were used to determine the  $T_g$  of the conditioned films (25°C, 50% rh, two days).

For DSC analysis, ~10–20 mg of the conditioned samples was placed in an hermetically sealed sample pan. The reference was an empty pan. Both were heated from –120 to 150°C at 5°C/min. The instrument was calibrated using mercury and indium as standards.  $T_g$  for each type of film was determined in duplicate and was identified as the midpoint temperature of shift in the baseline due to change in heat capacity upon glass transition (Fig. 1).

The film for DMA analysis was cut into 12- × 50-mm strips. Three strips were pressed together manually and then clamped into the DMA furnace at both ends. The sample was heated from –120 to 200°C at 2°C/min. Simultaneously, a sinusoidal force was applied to the center of the strip (three-point bending or flexure mode) at 1 Hz frequency with strain in the 10- $\mu$ m range. Storage modulus ( $E'$ ), loss modulus ( $E''$ ) and loss angle ( $\tan \delta$ ) were recorded and plotted against temperature for further evaluation of thermal transitions. Typical plots are presented in Figure 2. The measurements were done in triplicate with the  $T_g$  values measured as the peak temperature of  $\tan \delta$ , and were within 3% experimental error.

### Tensile Testing

Rectangular strips 100 mm long and 25.4 mm wide were cut for the tensile test. The film thickness measurements of the tensile test specimens were taken to the nearest 2.54  $\mu$ m (0.1 mil) with a hand-held micrometer (B.C. Ames, Waltham, MA). Thickness of the individual specimens was determined as a means of five measurements taken over the length of the strip. It was then used to estimate the cross-sectional area. Before testing, film specimens were conditioned for two days in a chamber set at 25°C and 50% rh. Tensile testing was performed with a universal testing instrument (UTM) (model TM, Instron Engineering Corp., Canton, MA). The initial grip separation was set at 50 mm. Cross-head speed and chart recorder were both set at 500 mm/min. Tensile strength (TS) was calculated by dividing the maximum (peak) load developed during the test with the cross-sectional area of the specimen. Percentage elongation at break (E) was calculated by dividing film extension at the moment of rupture by 50 mm (initial gauge length of specimen) and multiplying by 100. TS and E for each type of film were determined in triplicate with individually prepared and cast films as the replicated experimental units and eight subsamples (strips) tested from each film replicate.

### Water Vapor Permeability Measurement

Film specimens (7 × 7 cm) were cut from oven-dried films. Five thickness measurements were taken on each specimen, one at the center and four around the perimeter. The mean was used as the specimen thickness in water vapor permeability (WVP) calculations. Before testing, all film specimens were conditioned for two days in a chamber maintained at 25°C and 50% rh. WVP of films was determined gravimetrically using a modification of the ASTM standard method E96-80, known as the "cup method". Cups used for testing were similar to those described by Gennadios et al (1994). Conditions of testing were 25°C and 50% rh gradient (100% rh inside cups; 50% rh outside cups). Water vapor transmission data were corrected to account for the resistance of the air gap (1 cm) between the underside of the film and the water surface in the cup (Gennadios et al 1994). WVP for each type of film was determined in triplicate with individually prepared and cast films as the replicated experimental units and three subsamples (specimens) tested from each film replicate.

## Statistical Analyses

Calculation of mean TS, E, WVP,  $T_g$ , and peak heights ( $\tan \delta$ ) of transition values for each type of film, and comparisons among them, were made using the general linear models procedure (SAS Institute Inc., Cary, NC). Within each property, significant calculated mean values were compared using Duncan's new multiple-range test (Steel and Torrie 1980) at the  $\alpha = 0.05$  level of significance.

## RESULTS AND DISCUSSION

The DSC thermogram for gluten-glycerin-sucrose film at 15:6:0 (18.7% moisture) is shown in Figure 1. A shift in the baseline

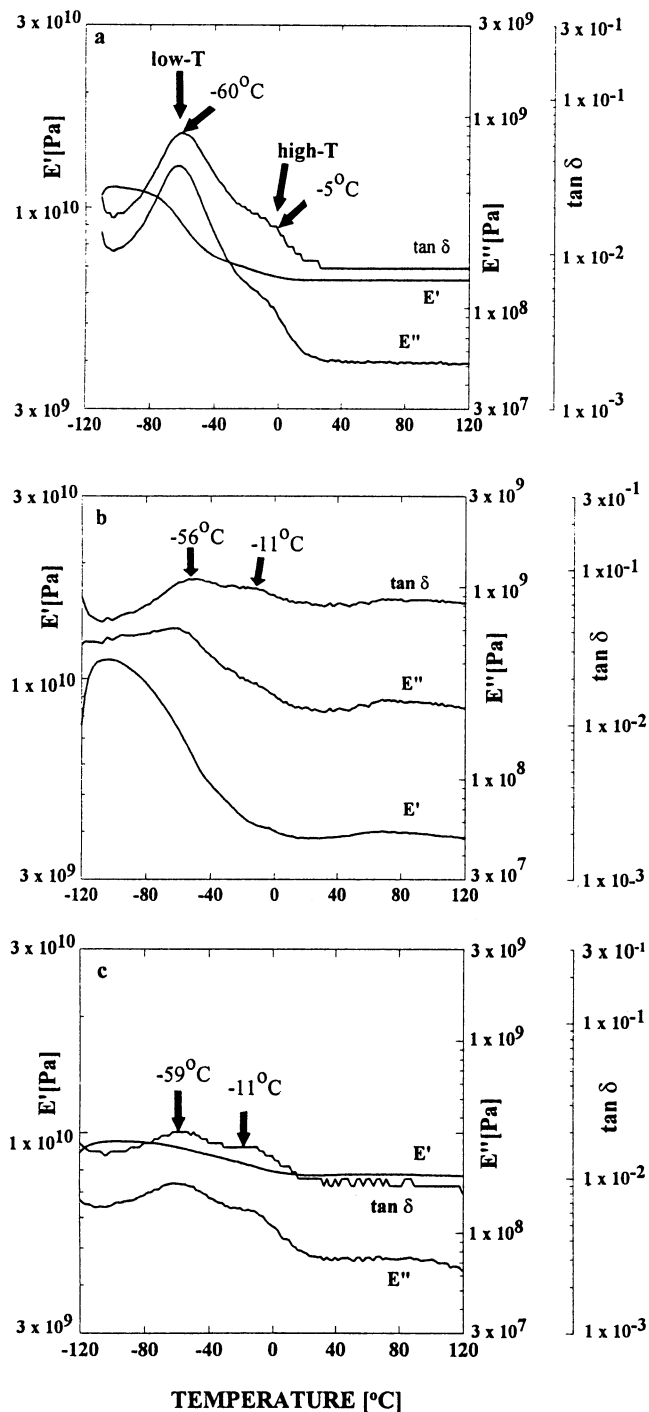


Fig. 2. Dynamic mechanical analysis thermograms for wheat gluten-glycerin-sucrose films at various ratios (w/w) and moisture contents (% wb). a, 15:6:0 (18.7%). b, 15:4:2 (14.4%). c, 15:3:3 (9.6%) conditioned at 50% rh and 25°C for two days. Storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss angle ( $\tan \delta$ ) were recorded and plotted against temperature.

upon heating can be observed, indicating that a change in heat capacity is likely to be caused by glass transitions. All other samples showed multiple transitions that could not be accurately measured by DSC because of very small changes in heat capacity. Thus, only the  $T_g$  values obtained by DMA are reported here. From the DSC data, none of the films showed any ice melting endotherms.

### $T_g$ for Gluten-Glycerin Films

DMA thermograms of various films are shown in Figure 2. The plots of  $\tan \delta$ ,  $E'$ , and  $E''$  against temperature showed changes in these parameters as the films underwent thermal transitions. Upon transition, there was an exponential drop in  $E'$ , and peaking in  $E''$  and  $\tan \delta$ . In gluten-glycerin films (Fig. 2a), a main low temperature (low- $T$ ) transition occurred at  $-62^\circ\text{C}$  (initial and final temperatures,  $T_i$  and  $T_f$ , respectively, are presented in Table II) and a slight shoulder, possibly indicating a separate transition, called a high temperature (high- $T$ ) transition. The  $T_g$  temperature at  $-62^\circ\text{C}$  was higher than the reported value of  $-93^\circ\text{C}$  for pure glycerin (Davies and Jones 1953). The higher values were probably caused by gluten domains that were miscible with glycerin, resulting in an increased  $T_g$  due to an increase in the average molecular weight (Aklonis and MacKnight 1983). This value is supported by other studies of glycerin-containing systems (Hallberg and Chinachoti 1992, Kalichevsky et al 1992).

### $T_g$ for Gluten-Glycerin-Sucrose and Gluten-Sucrose Films

Films in which a portion of the glycerin was replaced with sucrose (gluten-glycerin-sucrose ratios of 15:4:2, 15:3:3, and 15:0:6) were studied using DMA (Figs. 2b, 2c, and 3a, respectively). The low- $T$  and high- $T$  transitions observed in Figure 2a also appear in Figures 2b and 2c. The low- $T$  transition occurred at approximately  $-58^\circ\text{C}$  as observed from the  $\tan \delta$  peak (temperature range  $-55$  to  $-62^\circ\text{C}$ ), and decreased in amplitude with a decreasing glycerin and increasing sucrose content. The high- $T$  transition occurred at approximately  $-5$  to  $-12^\circ\text{C}$  ( $T_i$  and  $T_f$  are listed in Table II). This high- $T$   $\tan \delta$  peak height increased with sucrose content (Figs. 2 and 3a). In Figure 3a (gluten-glycerin-sucrose 15:0:6), substitution of all of the glycerin with sucrose resulted in the disappearance of the low- $T$  peak completely, indicating that the low- $T$  transition was associated with the presence of glycerin.

The effect of glucose, fructose, and sucrose on gluten was reported by Kalichevsky et al (1992). They noted that broader transitions were observed in the presence of these sugars, indi-

TABLE II  
Glass Transition Temperature ( $T_g$ ) of Wheat Gluten Film with Glycerin, Sucrose, Glycerin-Sucrose, and Glycerin-Sorbitol<sup>a</sup>

Film (w/w) [% wb]	Temperature <sup>b</sup>	Low- $T$ ( $^\circ\text{C}$ )	High- $T$ ( $^\circ\text{C}$ )
Gluten-glycerin-sucrose	15:6:0 [18.7%]	$T_i$	$-104.1 \pm 0.4$
		$T_g$	$-61.8 \pm 0.1$
		$T_f$	$-28.3 \pm 5.0$
	15:4:2 [14.4%]	$T_i$	$-85.4 \pm 0.6$
		$T_g$	$-55.7 \pm 0.1$
		$T_f$	$-33.8 \pm 0.6$
	15:3:3 [9.6%]	$T_i$	$-111.2 \pm 0.7$
		$T_g$	$-57.6 \pm 2.3$
		$T_f$	$-33.1 \pm 0.5$
15:0:6 [9.3%]	$T_i$	NO <sup>c</sup>	
	$T_g$	$-5.0 \pm 0.0$	
	$T_f$	$48.7 \pm 0.2$	
Gluten-glycerin-sorbitol	15:3:3 [16.7%]	$T_i$	$-88.8 \pm 3.0$
		$T_g$	$-41.8 \pm 1.2$
		$T_f$	$-2.5 \pm 2.4$

<sup>a</sup> Determination made by dynamic mechanical analysis.

<sup>b</sup>  $T_i$  = initial temperature,  $T_f$  = final temperature,  $T_g$  = peak  $\tan \delta$  temperature.

<sup>c</sup> Not observed.

cating a possible phase separation in gluten. In our study, data in Table II shows that this could happen; however the results were not consistent.

It is interesting to note that for gluten-glycerin-sucrose film at 15:0:6, the DMA thermogram (Fig. 3a) not only shows a single  $\tan \delta$  peak, but also an unusual change in  $E'$ . After the glass transition at  $-5^\circ\text{C}$ ,  $E'$  increased quite significantly. This may indicate a hardening effect, and it occurred specifically for samples within the 5–13% (wb) moisture range. In this range, it was speculated that sucrose crystallized as the mobility of the system increased upon passing through the glass transition region, thereby hardening the sample. However, the DSC data (Fig. 3b) showed little or no exothermic crystallization peak upon heating at  $2^\circ\text{C}/\text{min}$ . Additionally, heating the sample to  $120^\circ\text{C}$  ( $2^\circ\text{C}/\text{min}$ ), quench cooling, and then reheating ( $2^\circ\text{C}/\text{min}$ ) failed to show any exothermic peak. So this possibility was ruled out. Another possibility would be that a particular sample might have lost some small amount of moisture as the material was undergoing glassy-rubbery transition (i.e., increase in diffusion through the polymer network). This loss of moisture would result in a more glassy material, consequently increasing  $E'$ . It is not quite certain what other mechanism could have caused such an increase in  $E'$ , but it is also possible that some cross-linking or other changes occurred in the sample promoted by sucrose in this moisture range.

#### $T_g$ for Gluten-Glycerin-Sorbitol Film

The replacement of some glycerin by sorbitol (maintaining the gluten-glycerin ratio at 15:3) resulted in a single transition at approximately  $-42^\circ\text{C}$  (Fig. 4). Considering that the  $T_g$  reported for sorbitol is  $0^\circ\text{C}$  (Oxford et al 1990) and for glycerin is  $-93^\circ\text{C}$  (Davies and Jones 1953), the gluten-glycerin-sorbitol film gave an intermediate value of  $-42^\circ\text{C}$ . Figure 4b shows only one  $\tan \delta$  peak in the DMA thermogram for gluten-glycerin-sorbitol film at 15:3:3, as compared to two for the gluten-glycerin-sucrose film at 15:6:0 in Figure 2a. Comparing sorbitol and sucrose, both at the 15:3:3 combination, Figures 4a and 4b show that sorbitol was more compatible with glycerin and gluten (one  $T_g$ ) than it was with sucrose, which resulted in a phase separation (two  $T_g$ ). Thus, in this regard, the contribution of sorbitol is more advantageous than sucrose, since the material has only one  $\tan \delta$  peak.

All  $T_g$ , including the initial and final temperatures for films conditioned at 50% rh and  $25^\circ\text{C}$  for two days are presented in Table II. The data from DSC showed results similar to that from DMA (data not shown). Moisture content varied greatly among the different films, depending on the types of solute present. Even though the moisture content of the film decreased with added sucrose, the low- $T$   $T_g$  did not change significantly. The high- $T$  transition did vary only slightly with sucrose content;  $T_g$  was

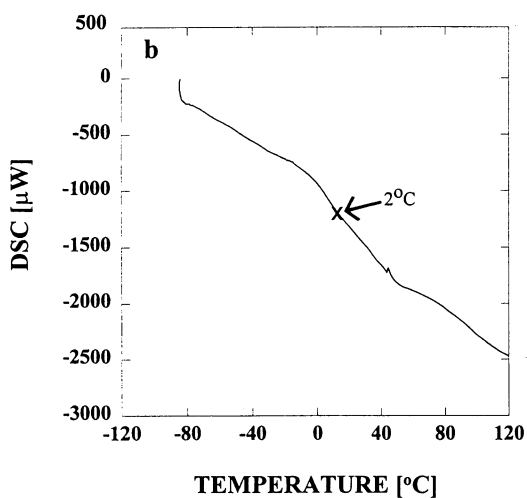
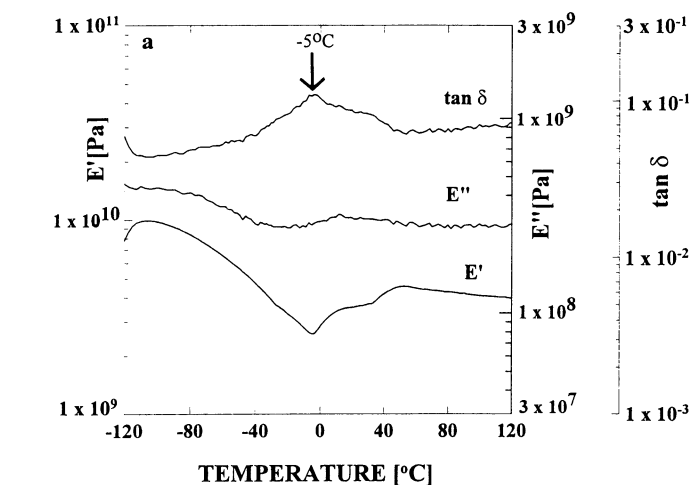


Fig. 3. Thermograms for wheat gluten-glycerin-sucrose film at a ratio of 15:0:6 (w/w), conditioned at 50% rh and  $25^\circ\text{C}$ , moisture content 9.3% (wb). Dynamic mechanical analysis (a) records storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss angle ( $\tan \delta$ ) plotted against temperature. Differential scanning calorimetry (b) shows no ice melting peak.

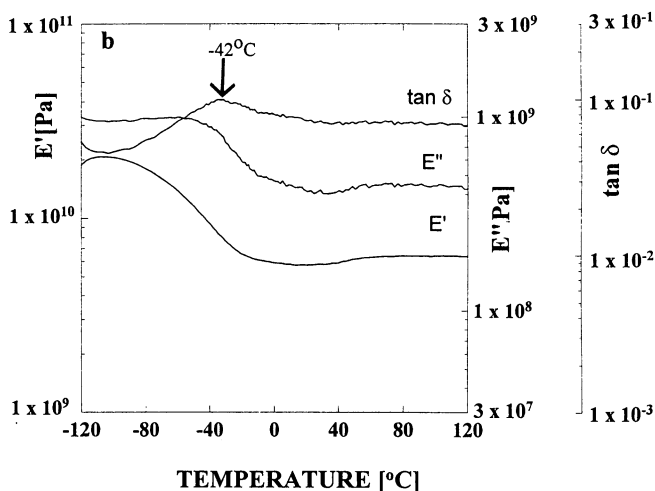
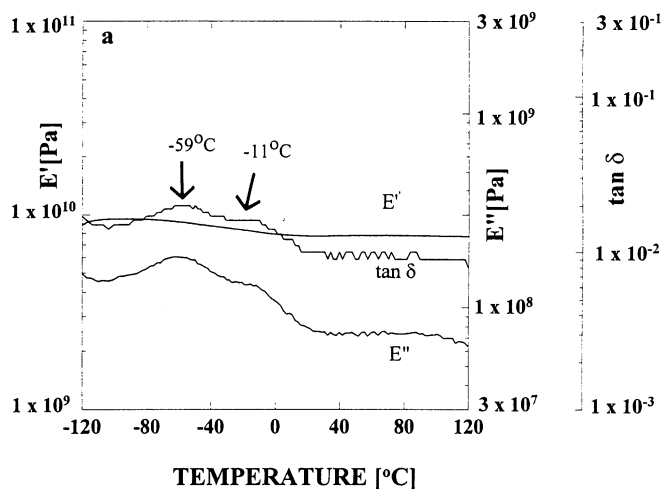


Fig. 4. Dynamic mechanical analysis thermograms comparing 15:3:3 (w/w) wheat gluten-glycerin films containing sucrose (a) or sorbitol (b). Moisture contents (wb): 9.6 and 16.7%, respectively. Storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss angle ( $\tan \delta$ ) were recorded and plotted against temperature.

**TABLE III**  
**Tensile Strength (TS), Percent Elongation at Break (E), Water Vapor Permeability (WVP),**  
**Glass Transition Temperature ( $T_g$ ), and  $\tan \delta$  Peak Heights of Wheat Gluten Films<sup>a</sup>**

Film <sup>b</sup> (w/w)	TS (MPa)	E (%)	WVP <sup>c</sup> ( $\times 10^{-9}$ g/m.s.Pa)	$T_g$ ( $^{\circ}$ C)		$\tan \delta$ Peak Height	
				Low- $T$	High- $T$	Low- $T$ ( $\times 10^{-2}$ )	High- $T$ ( $\times 10^{-2}$ )
Gluten-glycerine-sucrose							
15:6:0	4.2 $\pm$ 0.4 a	89.0 $\pm$ 18.9 a	1.41 $\pm$ 0.02 a	-61.8 $\pm$ 0.1 a	-4.6 $\pm$ 2.5 a	4.0 $\pm$ 0.3 a	1.0 $\pm$ 0.0 a
15:4:2	5.6 $\pm$ 0.2 b	39.0 $\pm$ 5.0 b	1.15 $\pm$ 0.03 c	-55.7 $\pm$ 0.1 b	-11.5 $\pm$ 2.3 b	1.2 $\pm$ 0.0 b	0.9 $\pm$ 0.0 b
15:3:3	6.0 $\pm$ 0.9 b	11.0 $\pm$ 1.8 c	0.95 $\pm$ 0.03 d	-57.6 $\pm$ 2.3 b	-10.5 $\pm$ 1.5 b	0.7 $\pm$ 0.1 c	0.7 $\pm$ 0.0 c
15:0:6	3.8 $\pm$ 0.8 a <sup>d</sup>	3.2 $\pm$ 0.6 c	0.18 $\pm$ 0.04 e	NO <sup>e</sup>	-5.0 $\pm$ 0.0 a	NO	1.5 $\pm$ 0.4 d
Gluten-glycerine-sorbitol							
15:3:3	5.7 $\pm$ 0.2 b	57.2 $\pm$ 4.4 b	1.22 $\pm$ 0.03 b	-41.8 $\pm$ 1.2		5.9 $\pm$ 0.1	

<sup>a</sup>Reported property values for each film are means of three replicates  $\pm$  standard deviation. Means followed by the same letter are not significantly ( $P < 0.05$ ) different according to Duncan's multiple range test.

<sup>b</sup>Mean thickness =  $87 \pm 9 \mu\text{m}$ .

<sup>c</sup>Measured after conditioning at 25 $^{\circ}$ C and 50% rh gradient (100/50%) for two days.

<sup>d</sup>Sample was fragile and cracked.

<sup>e</sup>Not observed.

within the  $-5^{\circ}\text{C}$  to  $-12^{\circ}\text{C}$  range. For the gluten-glycerin-sucrose (15:0:6) film, a single transition was observed at  $-5^{\circ}\text{C}$  that corresponded to the same range as the high- $T$  transition.

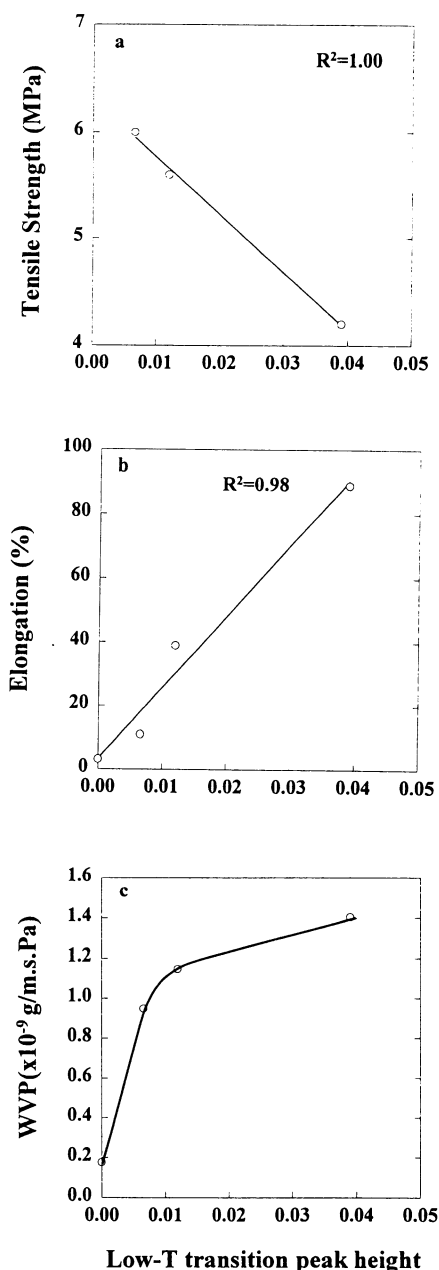
### Correlation of Mechanical and Barrier Properties with $\tan \delta$ Peak Height

Table III compares the change in TS, E, WVP,  $T_g$ , and  $\tan \delta$  peak heights for the wheat gluten films. Changing the film composition by decreasing glycerin content (or correspondingly increasing the sucrose content) of the films resulted in an increase in the TS, and a decrease in E, WVP, and the low- $T$   $\tan \delta$  peak height, except for the low TS observed for the gluten-glycerin-sucrose (15:0:6) film, which was fragile and cracked. However, for the high- $T$  transition, within experimental error, the amplitude did not change appreciably with changing solute compositions (Figs. 2 and 3a).

Visual correlations of the low- $T$   $\tan \delta$  peak heights with TS, E, and WVP are shown in Figure 5. TS and E (Figs. 5a and 5b) changed linearly with peak height and showed a higher linear correlation ( $R^2 = 1.00$  and  $0.98$ , respectively). This may indicate that the low- $T$  transition (associated with glycerin plasticization) was directly related to changes in the films' mechanical properties.

Figure 5c shows WVP as correlated with low- $T$   $\tan \delta$  height; the relationship was curvilinear. Thus, glycerin plasticization (directly proportional to  $\tan \delta$  peak height) had a significant effect on the WVP of the film. It is interesting to note that WVP is highly sensitive to the initial increase in low- $T$  peak height (Fig. 5c). This corresponded to samples with little or no glycerin added initially. Because this low- $T$  transition is associated with glycerin, a possible hypothesis is that the gluten matrix plasticized by glycerin resulted in changes in its network (creating highly mobile channels) that allowed moisture to penetrate easily at room temperature. Therefore, we conclude that the changes in mechanical and water barrier properties are related to the low- $T$  transition. The low- $T$  transition promoted by glycerin and water is most likely associated with the changes in the structure of hydrophilic regions of film that influence the water movement through the film.

In contrast to its excellent plasticizing property, glycerin is a poor candidate for improving WVP. Substitution of glycerin with sucrose decreased the water mobility through the film (WVP decreased from  $1.41 \times 10^{-9}$  g/m.s.Pa to  $0.18 \times 10^{-9}$  g/m.s.Pa, for gluten-glycerin-sucrose films of 15:6:0 and 15:0:6). Unfortunately, this improvement in the WVP due to sucrose cannot be fully utilized because of the poor mechanical properties of sucrose-plasticized films. In addition, sucrose readily takes up water when relative humidity is high, causing loss of film integrity. On the other hand, sorbitol shows a profound effect on the mechanical and barrier properties of the film. Sorbitol-containing films, with a lower  $T_g$ , have reduced WVP while maintaining good mechanical properties. However, from a practical stand-



**Fig. 5.** Plots of tensile strength, percent elongation, and water vapor permeability (a-c) with low-temperature transition peak height (approximately  $-58^{\circ}\text{C}$ ).

point, the sorbitol-containing films still exhibited high WVP. Sorbitol has a higher plasticizing ability than sucrose and thus depresses the  $T_g$  of the system significantly more than sucrose. This lowering of the  $T_g$  improves mechanical properties of sorbitol-containing films as compared to those of sucrose.

## CONCLUSION

The plasticizing effect of sucrose, glycerin, and sorbitol on wheat gluten films was studied. Sorbitol showed good miscibility with glycerin and gluten, resulting in a single transition peak, intermediate to the transition of glycerin and sorbitol. However, sucrose was incompatible with the film components, resulting in phase separation. Two transitions were observed: a low- $T$  transition at approximately  $-58^\circ\text{C}$ , and a high- $T$  transition at  $-5^\circ\text{C}$ . Increasing glycerin increased the low- $T$  peak amplitude, which indicated a strong association with glycerin or glycerin-plasticizing matrix. Mechanical properties and WVP correlated very well with the low- $T$  transition  $\tan \delta$  peak height (but not with  $T_g$ ). The low- $T$  temperature associated with glycerin was related to the opening up of the hydrophilic protein matrix, allowing water to diffuse, and at the same time plasticizing the film. Because of its high miscibility with glycerin and gluten, sorbitol reduced WVP somewhat. However, the resulting  $T_g$  of sorbitol was very low, and WVP was still high from a practical standpoint.

## ACKNOWLEDGMENTS

This work was supported by the The Sugar Association, Inc., Washington, DC. We acknowledge support of author Gennadios through an AACC-administered National Starch and Chemical Company Graduate Fellowship.

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[Received November 19, 1993. Accepted August 25, 1994.]