Plasticizing–Antiplasticizing Effects of Water on Physical Properties of Tapioca Starch Films in the Glassy State

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ABSTRACT: The effects of moisture sorption on physical properties of native and cross-linked starch films in the glassy state were studied. Water played a dual role as a plasticizer or an antiplasticizer, depending on the physical property measured. Plasticizing effects were clearly evident in the case of the calorimetric glass transition temperature (T_g), tensile modulus, linear expansion, and water vapor permeability. In contrast, antiplasticization by water resulted in maxima in tensile strength, strain-at-break, and toughness of films that were observed at an intermediate moisture content ranging from 4% to 8% (RVP 0.1 to 0.4). The seemingly contradictory effects of water on mechanical properties associated with lower and higher deformation of starch films were reconciled by assigning different roles to water operating primarily via opposite entropic/free volume effects. Relationships, if any, between DSC thermal events and mechanical antiplasticization were not apparent.
　Key Words: antiplasticization, plasticization, glass transition, starch films, water

Introduction

WATER IN FOODS HAS GENERALLY BEEN REGARDED as the universal plasticizer (Levine and Slade 1988; Slade and Levine 1991), implying that it serves always to soften or make less brittle a food material. It has been observed, however, that changes in mechanical properties, similar to antiplasticization of synthetic polymers by certain diluents, were discernible when certain foods and other biomaterials were humidified from the dry state (Seow and others 1995, 1999). It was hypothesized that water in food polymer systems may be able to act as either plasticizer or antiplasticizer, thereby giving rise to intriguing effects on food properties over the low-to-intermediate moisture range. The concept of antiplasticization–plasticization in polymer science is strictly applicable to changes in mechanical properties. However, it may be reasonably and usefully extended to other physical properties.

　In light of the recent polymer science-based interpretations, the effects of water on physical and textural properties of reduced-moisture food polymeric systems require closer scrutiny. Thus far, attention has been focused on the role of water as a "universal plasticizer." Our main objective was to gain a better understanding of the effects of water, acting either as plasticizer or antiplasticizer, on physical properties of reduced-moisture systems. For this purpose, we chose as model systems films derived from native and cross-linked tapioca starch. The latter was used to provide supportive evidence and to aid interpretation. The properties of biodegradable or edible films are known to be profoundly influenced by water acting as a plasticizer (Lieberman 1973; Gontard and others 1993; Debeaufort and others 1994; Lai and Padua 1998). However, antiplasticizing effects of water, if any, on the properties of such films have received scant attention. This study also provided some insight into possible relationships between different physical properties.

Results and Discussion

Adsorption isotherms

　The sigmoid-shaped moisture adsorption isotherms for native and cross-linked starch films at 30°C (Fig. 1) were similar to those obtained for high amylose corn starch films (Bader and Göritz 1994), with a fraction of the water being more "tightly bound" up to an RVP of about 0.2. Modification of starch by cross-linking did not appear to affect the sorption properties of
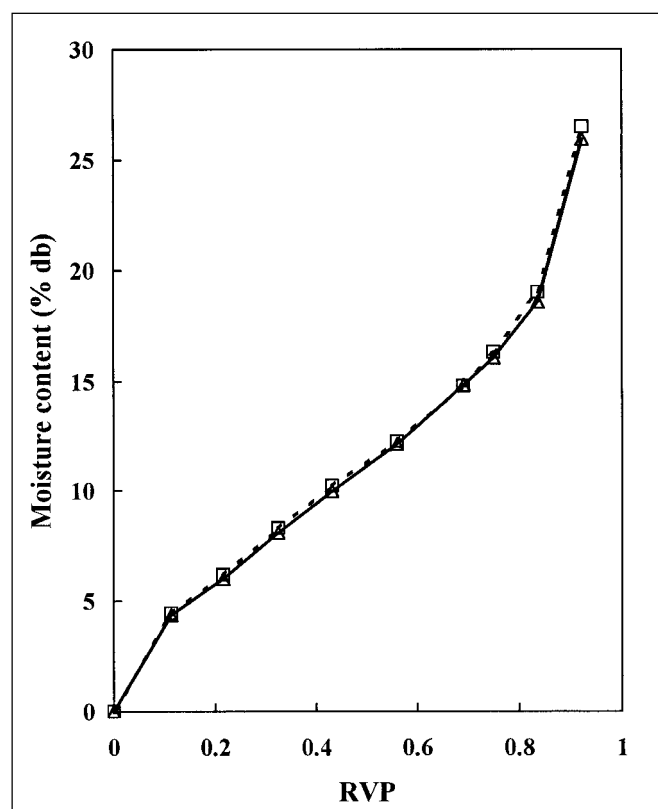
Fig. 1—Water adsorption isotherms of native (◻) and cross-linked (△) tapioca starch films at 30°C

the films. Most cross-linking reactions produce a relatively low degree of cross-linking sufficient to strengthen the outer envelope of the starch granules. This amount of cross-linking, although probably having a substantial effect on certain properties (for example, granule swelling, paste viscosity, and retrogradation), may actually contribute little to water sorption properties, as has been previously reported for potato starches (Chilton and Collison 1974).

Thermal properties

The DSC thermal profile of native or cross-linked starch films exhibited a glass transition and a crystallite melting endotherm typical of a partially crystalline polymeric system (Fig. 2). Recrystallization of amylose and, to a lesser extent, amylopectin, would have taken place during the film-forming process. A small endothermic event, centered at about 60°C, was also observed for samples at intermediate moisture levels. The existence of such an event, the origin and significance of which are not clear, appears to be characteristic of low-moisture polysaccharide systems (Kalichevsky and others 1992; Shogren 1992;

Appelqvist and others 1993; Cooke and others 1996). The water in samples with # 27% moisture was nonfreezing, as indicated by the absence of an ice melting endotherm in the DSC thermograms. Freezing water was, however, observed when the moisture content was raised to about 35% (results not shown).

As expected, the glass transition temperature (T_g) was progressively lowered with increasing moisture content (Fig. 3), an effect generally perceived to arise from plasticization of the amorphous regions of partially crystalline polymeric systems (Slade and others 1989). The T_g – moisture content curves of the 2 types of films appeared to parallel each other, suggesting that cross-linking of starch did not substantially affect T_g. Hydration of the films to a moisture content $ 27% would be expected to lower the calorimetric T_g to # 30°C. Thus, films with a moisture content below 27% would be in the glassy state at 30°C, the temperature at which sorption and mechanical properties of the films were determined in this study. However, note that the glass transition was extended over a range of temperature, and transition effects may, therefore, be perceived at much lower moisture levels.

The enthalpy (**DH**) associated with melting of the crystalline phase increased with increasing moisture content (Table 1). Such an effect was similarly observed by Cooke and others (1996) for low-moisture gel-derived agar and attributed to enthalpic association of water molecules with the helix structure of the polysaccharide. Cross-linked starch film gave **DH** values that were slightly but consistently higher than those of native starch film. However, transition temperatures (onset, T_o; peak, T_p; and conclusion, T_c) did not appear to be affected by cross-linking or moisture content (Table 1).

Mechanical properties

Modulus of elasticity, as an index for "stiffness" for both types of films, showed a general decrease with increasing mois-
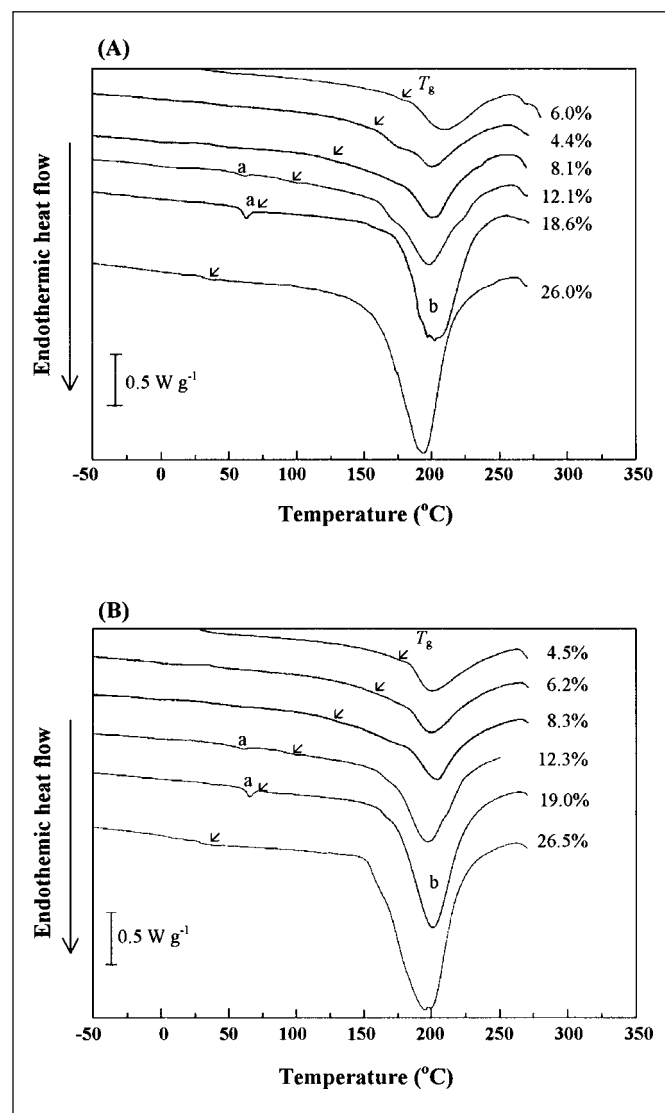

Fig. 2—DSC thermograms of (A) native and (B) cross-linked tapioca starch films at various moisture contents [a = sub-T_g endothermic event, b = melting endotherm]
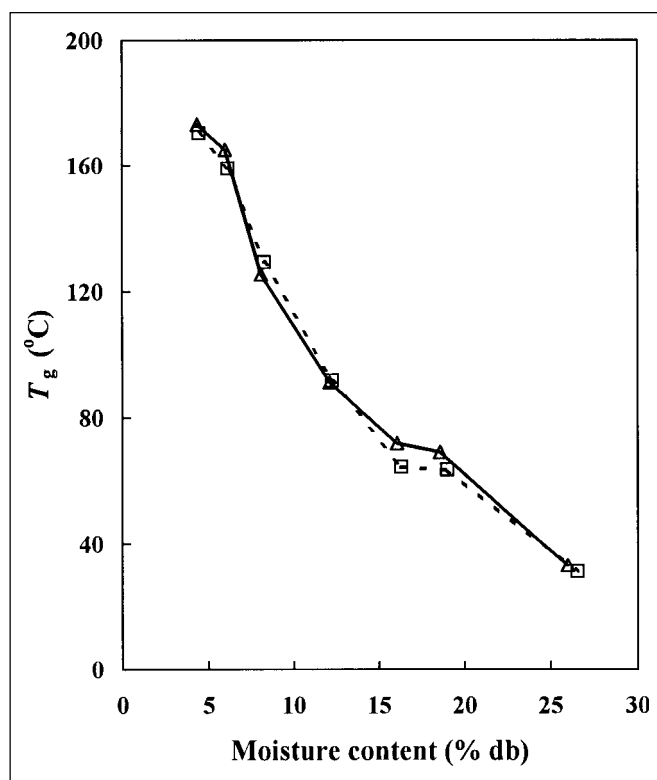

Fig. 3—Glass transition temperature of native (D) and cross-linked (G) starch films as a function of moisture content

Table 1—DSC transition temperatures and enthalpy (DH) associated with crystalline phase melting in starch films as a function of moisture content

Material content (% db)	Moisture	Transition temperature(°C)			DH (J g⁻¹)
		T_o	T_p	T_c	
Native starch film	4.4	168.1	197.5	241.0	98
	6.0	166.7	200.6	239.5	153
	8.1	174.1	205.9	238.5	158
	12.1	165.3	198.5	231.0	194
	16.1	180.2	201.1	227.5	216
	18.6	177.8	201.4	232.5	260
	26.0	159.7	193.4	221.0	359
Cross-linked starch film	4.5	166.8	203.2	250.0	147
	6.2	168.6	201.5	246.0	159
	8.3	160.2	198.1	235.0	203
	12.3	173.7	202.5	237.0	203
	16.3	172.7	205.6	238.5	224
	19.0	171.3	201.4	231.5	277
	26.5	154.4	182.9	221.0	398

ture content (Fig. 4), a behavior expected for a plasticized material. However, tensile strength increased with an increase in moisture content, reaching a maximum value at a moisture content of about 5% for both types of films, before decreasing with further increase in moisture content (Fig. 5). Tensile strength of starch film-water blends was notably higher than that of the completely dry polymeric systems up to a hydration level of 14% to17%, suggesting a mechanical antiplasticizing effect exerted by water. On further hydration beyond this "antiplasticization range" of moisture content or "plasticizer threshold," water appeared to exert a plasticizing effect on the polymeric glass, thereby reducing the tensile strength of the films below that of
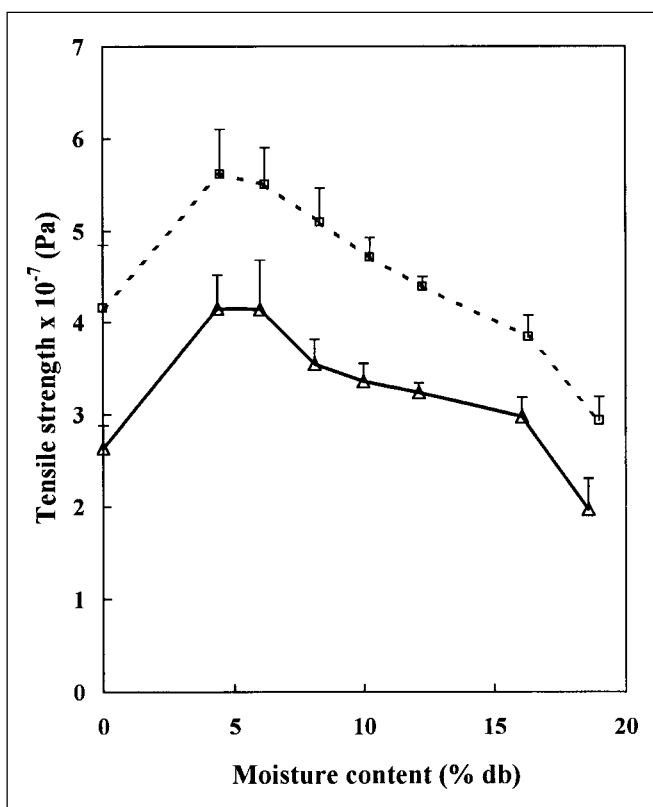
Fig. 5—Tensile strength of native (D) and cross-linked (G) starch films as a function of moisture content [vertical bar represents plus one standard deviation from the mean.]
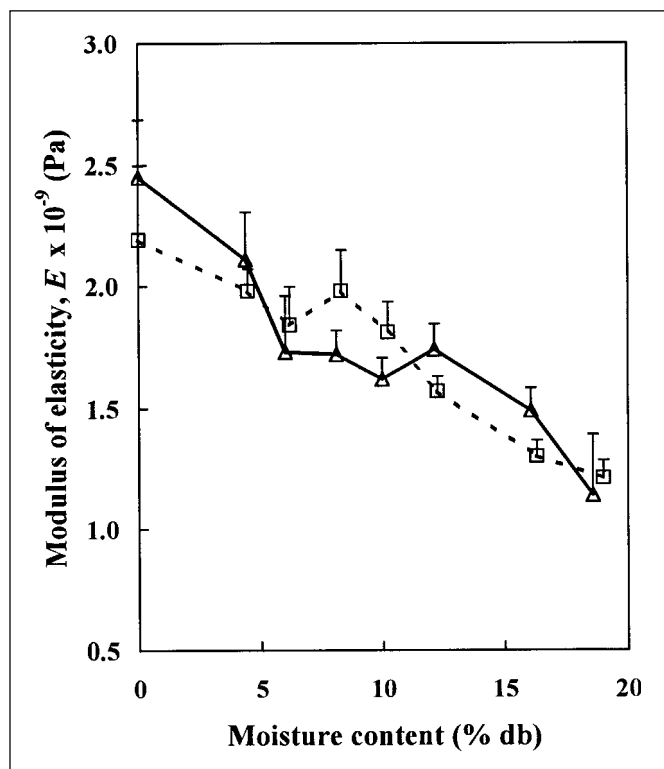
Fig. 4—Modulus of elasticity of native (D) and cross-linked (G) starch films as a function of moisture content [vertical bar represents plus one standard deviation from the mean.]
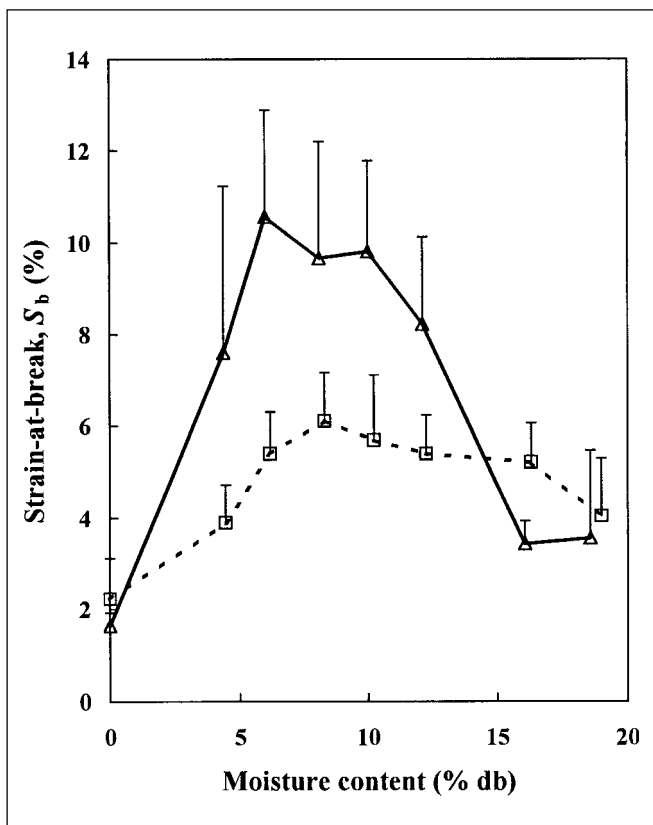
Fig. 6—Strain-at-break of native (D) and cross-linked (G) starch films as a function of moisture content [vertical bar represents plus one standard deviation from the mean.]

the completely dry film. Film samples conditioned at an RVP of 0.92 (about 27% moisture) became somewhat soggy, deformed, and could not be tested for mechanical properties as they were already in the rubbery state at the test temperature.

Both types of starch films exhibited strain-moisture content and toughness-moisture content relationships (Fig. 6 and 7, respectively), which were qualitatively similar to tensile strength-moisture content relationships. Maximum values for strain and toughness were observed at 6% to 8% moisture (0.2 to 0.3 RVP). The mechanical antiplasticizing effect of water was observed up to a moisture content of about 17%. Similar strain–moisture content relationships have also been reported for zein films (Lai and others 1997; Lai and Padua 1998) and extruded starch bars (Nicholls and others 1995).

The effects of water on mechanical properties of glassy starch films measured at lower (for example, modulus) and higher (for example, tensile strength, strain, and toughness) deformation appear to be contradictory. Such disparate responses of mechanical properties to moisture sorption have been similarly observed in some cereal products (Attenburrow and Davies 1993; Harris and Peleg 1996), extruded starch bars (Nicholls and others 1995), and zein films (Lai and Padua 1998). Harris and Peleg (1996) hypothesized that initial loss of brittleness in puffed cereals when compressed enabled a higher deformation or strain to be sustained because of the reduced ability of failure to propagate, consequently increasing stress and toughness. The partially plasticized matrix would be expected to become more cohesive at intermediate moisture levels, thereby resulting in greater resistance and higher apparent stiffness. We hypothesize that the peak in tensile strength could be due to antiplasticization by water. It is plausible that higher deformation could induce much greater bond breaking/forming, enhance orienta-

tion of polymer chains, and increase free volume by creating "holes" in the polymeric system. Diluent (water) molecules, added in small amounts to the base polymer, would facilitate polymer orientation as well as fill "holes" created under high stress/deformation. This would reduce "hole free volume" and further increase structural order, which would be macroscopically manifested by increased tensile strength, strain-at-break, and toughness of the films. Free volume reduction through "hole filling" is a hypothesis for antiplasticization of synthetic polymers by diluents favored by several researchers (Vrentas and others 1988; Anderson and others 1995). Mechanical antiplasticization would thus occur on hydration of starch films from the dry state until maximal effects were attained. Addition of water beyond the point where all "holes" created on stretching were fully filled with diluent molecules and maximal compactness or structural order was achieved would lead to a decrease in mechanical parameters measured at higher deformation. At low deformation, however, there would be much less increase in volume, bond breaking/forming, and orientation of polymer chains. Under such conditions, diluent molecules may serve mainly to increase free volume and/or to lubricate, thereby reducing the modulus or stiffness of the films. This is a classic example of plasticization. We propose a mechanism where water, at low concentrations, may act as a plasticizer under low deformation conditions and as an antiplasticizer under high deformation conditions, acting primarily via opposite entropic/ free volume effects.

The fact that the same antiplasticization effects were observed for the same mechanical properties in both types of films excludes the possibility that they were experimental artifacts. The tensile strength of cross-linked starch films was, however, generally higher than that of the native starch films at corresponding moisture contents. The reverse was true for strain and toughness. These effects are to be expected since chemical cross-linking of polymer chains would probably induce a more highly organized structure and increase structural integrity (Wurzburg 1986), thereby reducing extensibility of the films. The moduli of elasticity of both films were, however, generally of the same order over the whole range of moisture content studied. This implies that cross-linking, at least to the extent achieved in the present study, did not affect the stiffness of starch films.

The relationship between thermal and mechanical property changes in the glassy state induced by moisture sorption remains unclear. It is possible that the increased magnitude of the unusual sub-T_g endothermic event at about 60°C with increasing moisture content could be related to water plasticization of the glass, enhanced local motions, and a continuous decline in modulus. Using dynamic mechanical thermal analysis (DMTA), Appelqvist and others (1993) detected mechanical softening of low-moisture polysaccharide systems, as indicated by a slight fall in the elastic storage modulus (E') in the same temperature region as the endothermic event. This event, however, apparently bears no direct relationship to the discontinuous mechanical property changes of starch films measured at high deformation over the intermediate moisture range. Similarly, the apparent development of crystallinity, when films were hydrated from the dry state, cannot account for the mechanical antiplasticization effects observed.

Degree of expansion/contraction

The progressive expansion of starch films on hydration from 0% to about 19% moisture (Fig. 8) is indicative of water plasticization. However, there was a notable shift from expansion to contraction as moisture content was further increased to about 26% for both types of films. The films also became somewhat
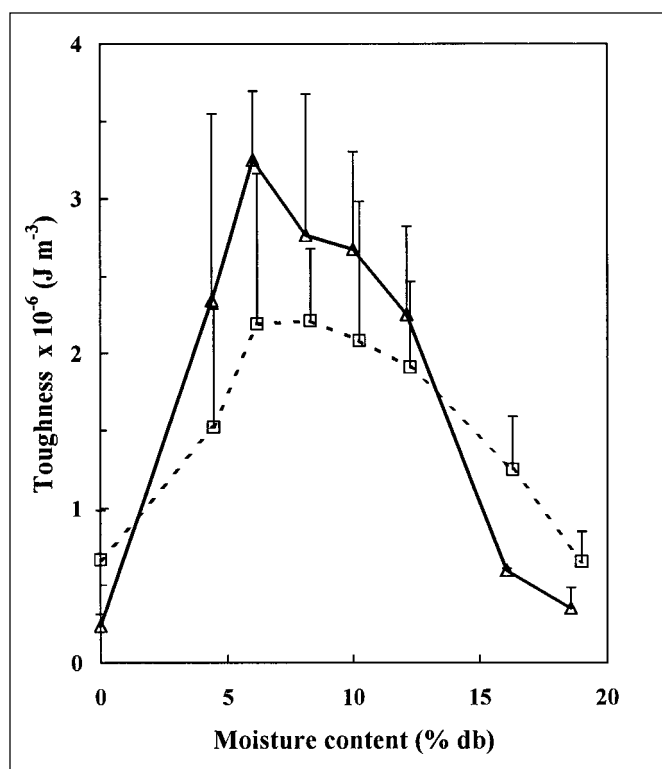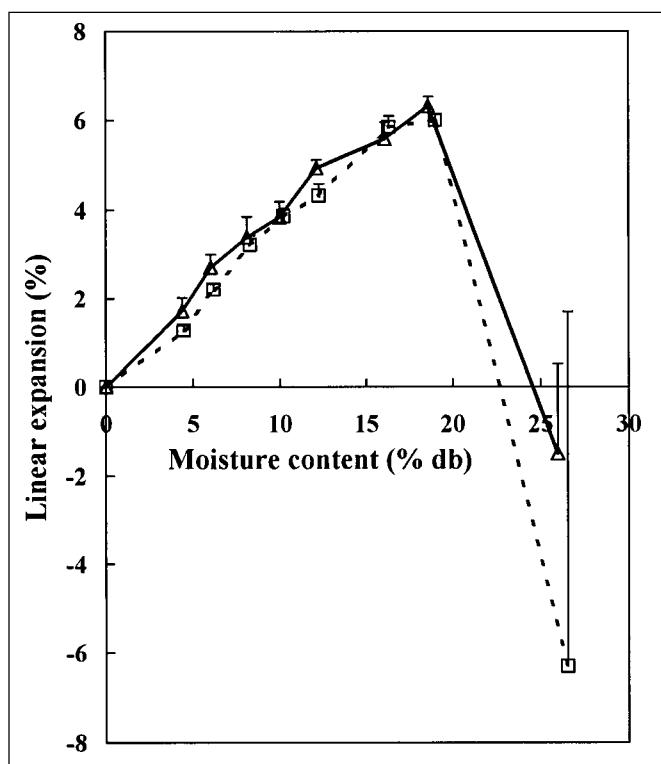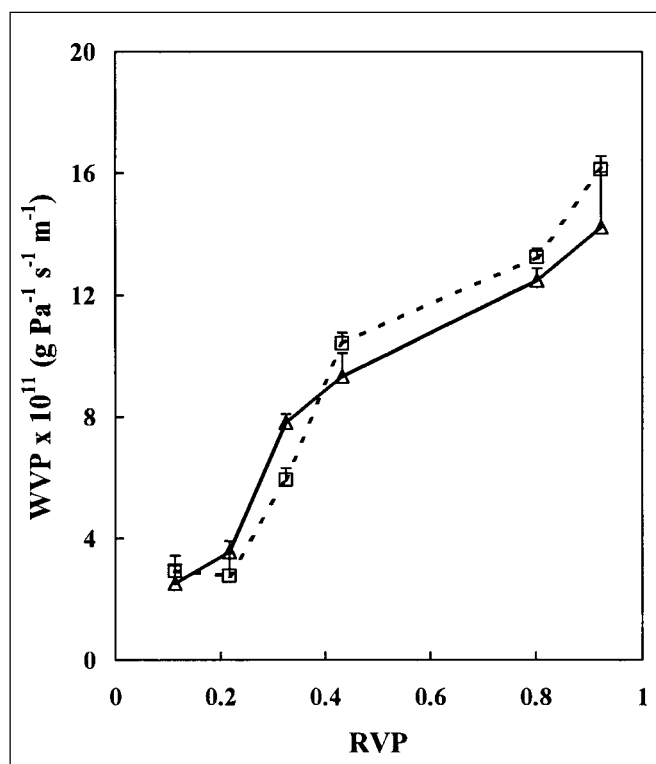
Fig. 7—Toughness of native (□) and cross-linked (○) starch films as a function of moisture content [vertical bar represents plus one standard deviation from the mean.]

Fig. 8—Linear expansion/contraction of native (D) and cross-linked (G) starch films as a function of moisture content [vertical bar represents plus one standard deviation from the mean.]

Fig. 9—Water vapor permeability of native (D) and cross-linked (G) starch films as a function of relative vapor pressure [vertical bar represents plus one standard deviation from the mean.]

soggy. The degree of shrinkage was highly variable as shown by the large error bars. Shrinkage of films at this high hydration level may be attributed to the fact that such films were in the rubbery state. Transformation from glassy to rubbery state would initiate translational molecular mobility. In the rubbery state, the relatively mobile amylopectin chain ends would undergo a random coil-to-helix transition (Keetels and others 1996) followed by association of the double helices. Polymer-polymer interactions and water-water interactions would then become greater than polymer-water interactions. This "retrogradation" or "recrystallization" process would lead to irregular shrinkage of the films. A concomitant effect would be syneresis or capillary condensation of water (entrapped in the polymer network) that would eventually cause the films to become soggy. Cross-linking of the starch polymers did not appear to have any substantial effect on the expansion/contraction behavior of starch films.

Water Vapor Permeability

Water vapor permeability (WVP) increased with increasing RVP for both types of films (Fig. 9). Similar effects were reported by other researchers for different types of biopolymeric films (Banker 1966; Lieberman 1973; Parris and Coffin 1997). This behavior is typical of films derived from hydrophilic polymers that can interact strongly with water molecules. As RVP on both sides of the film was increased, with the differential relative humidity maintained at about 10%, the equilibrium RVP within the film matrix was elevated. The corresponding rise in the amount of sorbed moisture had a plasticizing effect that tended to increase the diffusion constant for water vapor, and hence the WVP (since permeability is defined as the product of the dif-

fusion constant and the solubility coefficient). Furthermore, swelling of the hydrocolloid components, which generally accompanies moisture sorption, would probably affect the structural integrity and barrier properties of the film. Antiplasticization, involving a reduction of free volume of polymer glasses by low diluent concentrations that was expected to reduce gas sorption and permeation rates, was not observed. Both types of films did not differ much in terms of water vapor permeability.

Conclusions

Antiplasticization of starch films by water, in terms of mechanical properties such as tensile strength, toughness, and strain-at-break, was prevalent over the range of moisture content where such films existed in the glassy state at temperatures # 30°C. The conventional plasticizing effects of water on these mechanical properties could only be observed with further hydration beyond the limit imposed by the antiplasticization range. In contrast, immediate hydration from the dry state resulted in plasticizing effects on T_g, modulus of elasticity, linear expansion, and water vapor permeability. It is intriguing that mechanical properties measured at smaller (for example, modulus) and larger (for example, tensile strength) deformation can respond in such contrasting fashion to moisture sorption by partially amorphous starch films. Further investigations are warranted. However, it can be surmised that water, when present at low concentrations in food systems, is intrinsically neither an antiplasticizer nor a plasticizer. Within the glass, its role must be viewed in relation to specific physical properties and probably also the system studied. It is clear that variations in certain physical properties of glassy biomaterials resulting from moisture changes may not be governed by or related to T_g.

Materials and Methods

Samples

Tapioca starch ("Kapal ABC" brand) was imported from Thailand and had a moisture content of about 14% (db), determined in triplicate by vacuum-drying at 70 °C and < 1 mm Hg pressure for 24 h.

Preparation of cross-linked starch

Cross-linked starch was prepared following the method described by Cooreman and others (1995). Tapioca starch (300 g, dry weight) was suspended in 0.082M NaOH (450 ml) and epichlorohydrin (0.24 ml) was added. This level of epichlorohydrin was within the range usually applied in the cross-linking process (Jane and others 1992; Cooreman and others 1995). The suspension was continuously shaken at about 28°C for 48 h. After neutralization to pH 6.5 using 6M HCl, the suspension was filtered through Whatman filter paper No.3 and washed 3 times with water (450 ml each time). The resulting cross-linked starch was vacuum-dried at 25°C to 28°C and < 1 mm Hg pressure for 16 to18 h to a moisture content of 13% to 14% (db).

Preparation of films

Starch films were prepared by casting following the procedures described by Hari and Bhalla (1986), with some modifications. A 2% (w/w) starch slurry in water was prepared and allowed to stand for 1 h with manual shaking every 15 min. It was then heated to 95°C in a water bath and maintained at 95°C for 30 min with regular shaking. After cooling to room temperature, a certain amount of the paste was poured and spread onto a level, square (16 x 16 cm) perspex plate. The quantity poured onto the plate was calculated to obtain 6.6 mg starch cm^{-2}. The solution was allowed to dry at room temperature (about 28°C) for 20 h. Translucent films were obtained.

Film thickness measurements

Thickness of films was measured at 9 different positions and to the nearest 0.0001 mm using a micrometer Model No. 49-61 (Testing Machines Inc, Amityville, N.Y., U.S.A.) with 16 mm dia contact faces.

Measurements of adsorption isotherms

Adsorption isotherms of starch films were determined at 30°C according to the procedure described by Spiess and Wolf (1983), with some modifications. Samples of starch films, cut into small square (3 x 3 mm) pieces, were dried in a vacuum desiccator over P_2O_5 for 7 to 10 d. The dried samples (200 mg each) were weighed to the nearest 0.0001 g into pre-weighed weighing bottles. The dried samples, in triplicate, were equilibrated in air-tight 1-litre Kilner jars containing different saturated salt solutions of known relative vapor pressures (RVP) ranging from 0.11 to 0.92 at 30°C (Greenspan 1977). "Equilibrium" moisture content (% db) was calculated from the gain in weight. Equilibrium was assumed to have been achieved when the change in weight did not exceed 0.1% for 3 consecutive weighings.

Differential scanning calorimetry (DSC)

A DuPont 2910 differential scanning calorimeter (E.I. duPont de Nemours & Co., Inc., Wilmington, Del., U.S.A.), equipped with a standard DSC cell and a Thermal Analyst 2000 Controller, was used. Small pieces of samples (about 8 mg, weighed to 0.01 mg), which had been equilibrated for approximately 14 d at different RVP over saturated salt solutions using the same procedure described for determination of adsorption isotherm, were sealed in hermetic aluminum DSC pans. Each pan was then placed in the DSC cell, quench-cooled to –80°C using liquid nitrogen, and then heated to 270°C at 10°C/min with a constant purge of nitrogen gas. An empty aluminum pan with 2 lids was used as the reference pan to balance the heat capacity of the sample pan. All measurements were performed in duplicate.

Heat flow was calibrated using pure indium, while temperature was calibrated using pure indium and pure mercury. Analysis was carried out using the DuPont DSC Standard Data Analysis Program Software (Version 4.0). The glass transition temperature (T_g) was determined as a single temperature point from the peak of the derivative heat-flow curve (not shown).

Mechanical properties

Tensile tests were conducted using a Lloyd Instrument 1000S Tensile Tester (Lloyd Instrument Ltd, Segensworth Fareham, U.K.). Films were cut into 10 x 1.5 cm strips and dried over P_2O_5 under vacuum for at least 7 d. The dried samples were then equilibrated over saturated salt solutions of known RVP ranging from 0.10 to 0.82 at 30 °C, for at least 4 d. Tensile tests were performed according to ASTM (1981a) Method D882-80a. Pieces of tapes (2.5 H 2.5 cm) were affixed to both ends of a test strip to hold it in place and to keep the pneumatic grips of the testing machine from cutting the film. Each test strip was placed in pneumatic grips (25 psi) on the testing machine. Initial grip separation was 50 mm and cross-head speed was 20 mm/min^{-1}. Tensile properties for different types of films and treatments were determined with 2 individually prepared films as the replicated experimental units and 5 or 6 sub-samples tested from each film. At each RVP, the moisture content of the samples was determined from the adsorption isotherms.

Tensile strength was calculated on the basis of the original cross-sectional area of the test specimen using the equation F = F/A, where F is the tensile strength (Pa), F is the force (N) at maximum load, and A is the initial cross-sectional area (m^2). The percentage elongation- or strain-at-break (%S_b) was calculated by dividing the extension-at-break of the specimen by the initial gauge length and multiplying by 100. Modulus of elasticity (E, Pa) was calculated from the initial slope of the stress-strain curve. The tensile energy (J m^{-3}), which is a measure of toughness, was the total energy absorbed (determined from the area under the stress-strain curve) per unit volume of the specimen up to the point of rupture.

Linear expansion/contraction

Circles of about 50 mm dia were drawn on each film. Four lines were then drawn diametrically across each circle before it was cut out. The circular pieces of films were equilibrated under vacuum over P_2O_5 for at least 7 d at room temperature before the initial lengths of the 4 diametric lines were measured to the nearest 0.5 mm with the aid of a thread and a measuring tape. Then the dried circular samples were equilibrated under vacuum over different saturated salt solutions of known RVP's for 4 d at 30 ºC before the lengths of the lines were measured once again. Percent linear expansion or contraction (%j) = 100 (L_t – L_o) L_o^{-1}, where L_o and L_t are the total

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lengths (cm) of the lines before and after equilibration over the different saturated salt solutions. A positive value of %j indicates expansion of the films, whereas a negative value indicates shrinkage. The degree of expansion/contraction for each type of film and treatment was determined with 2 individually prepared films as the replicated experimental units and 3 sub-samples tested from each film.

Water vapor permeability

Water vapor permeability tests were conducted using ASTM (1981b) Method E96-80, with some modifications. Each film sample was sealed as a patch over a circular opening (with an area of 13.2 cm^2) cut into a heavy-duty aluminum foil. The foil was, in turn, sealed to the ledge part of a cup with dimensions of 4.1 cm (i.d.), 4.6 cm (o.d.), and 3.0 cm (depth). The permeation cells were stored at 30°C in desiccators, each maintained at a constant RVP with a preselected saturated salt solution. Appropriate saturated salt solutions and silica gel were selected to maintain a constant RVP gradient of 0.1 ± 0.02 across the film. The RVP inside the cell was always lower than that outside. The dull side of the cast film was oriented toward the higher RVP compartment, and water vapor transport was determined from the weight gain of the cell. Sufficient time (12 to 20 h) was allowed to ensure a stable equilibrium water vapor transmission rate. After steady state conditions were reached, weighings were made daily over a 6 d period. Changes in weight of the permeation cell were recorded to the nearest 0.0001g and plotted as a function of time. Straight lines with r^2 values $0.99 were obtained. The slope of each curve was calculated by linear regression. The water vapor transmission rate (WVTR) was calculated from the slope of the straight line divided by the test area. After the permeation tests, film thickness was measured with a micrometer. WVTR ($g\ s^{-1}\ m^{-2}$) for each type of film was determined with 2 individually prepared films as the replicated experimental units and 3 sub-samples tested from each film. Water vapor permeability (WVP, $g\ Pa^{-1}\ s^{-1}\ m^{-1}$) was calculated as WVP = [WVTR/S (R_1-R_2)] x d, where S = saturation vapor pressure (Pa) of water at test temperature, R_1 = RVP in the desiccator, R_2 = RVP in the permeation cell, and d = film thickness (m).

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