Competitive Plasticization in Ternary Plasticized Starch Biopolymer System

Deeptangshu S. Chaudhary

Department of Chemical Engineering, Curtin University of Technology, Perth 6845, WA, Australia

ABSTRACT: Two plasticizers namely, glycerol and xylitol, based on their similar molecular diameter ($\sim$ 6.3 Å) but different molecular weights (glycerol-92; xylitol-152) were selected were selected for studying the plasticization of starch biopolymer containing 70% amylopectin structure via glass transition measurements carried over a wide range of water activity. A standard calorimetry was used to determine the onset temperature of polymeric viscous flow. For both glycerol and xylitol, typical antiplasticization was evident at low plasticizer concentrations, whereas at higher concentration, there was significant reduction in glass transition temperature. Water activity isotherms showed that equilibrium moisture content of the starch biopolymer (no plasticizer) steadily increases up to 11%, however, for plasticized biopolymer, the moisture content was nearly double than that of biopolymer. We used a modified Gordon-Taylor model, using a new interaction parameter, to understand the competitive plasticization of glycerol and xylitol in presence of water, and determined 8 wt % water as a threshold amount of matrix water for strong three-way interactions: starch-plasticizer, plasticizer-plasticizer/water and starch-water. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 486–495, 2010

Key words: water-soluble polymers; glass transition; modelling; structure-property relations

INTRODUCTION

The well known hydrophilicity of starch biopolymers[1] makes it inferior in certain packaging applications even though it has excellent film forming abilities and optical clarity, apart from being biodegradable. Further, its high glass transition temperature, T_g, and its moisture sensitivity can render the biopolymer films to become brittle in dry environments.[2] The brittleness is typically reduced by the addition of plasticizer/s, which tend to lower the glass transition temperature and increase the optical clarity of the biopolymeric films. To be of any use, starch needs gelatinisation (a process of opening up the amylose and amylopectin chains with water which creates greater free volume within the matrix). Introducing plasticizers into the water-starch system can (1) add starch-plasticizer interaction instead of starch-water interactions and (2) reduce the biopolymeric intermolecular entanglements[3,4] by the localised hydrophilic interactions between the plasticizers and the biopolymers.[5] Plasticizers such as glycerol and sorbitol are excellent candidates for starch-based polymer because apparently they maintain biopolymeric flexibility relatively independent of the matrix water content.[1,6–8]

As mentioned earlier, gelatinisation is a thermodynamic process of unravelling the starch biopolymer by addition of water. It is typically found that this process involves increasing starch-water interactions that strongly depends on the amylose content.[5,9] These interactions are primarily hydrogen bonding, and addition of plasticizers competes with water for these interactions. The interaction levels are critical to macroscopic properties (strength, elongation, etc), glass transition behavior and gelatinisation. For example, we have shown recently that macroscopic properties of starch biopolymer can be influenced by different additives and the extent of their interactions.[10] Interestingly, the quantities also dominate these interactions and typically hydrophilic biopolymers can have three-way interactions (starch-plasticizer, starch-starch, plasticizer-water). Well known cases where complex interactions lead to reduced flexibility include glycerol, sorbitol (at low concentrations) that act to increase the antiplasticization behaviour[11] by bonding greater fraction of plasticizer-biopolymer entities, which significantly reduces matrix flexibility and increases T_g. It is further known that structural similarity between plasticizer and biopolymers molecules facilitates interaction,[8,9,12] and the extent interaction varies depending upon the plasticizer type,[10,13] for example, the plasticization threshold for glycerol is $\sim$ 14%, but for sorbitol, it is $\sim$ 25%, or nearly double.

Plasticizer	WLA	GLA5	XLA5	GLA10	XLA10	GLA15	XLA15	GLA20	XLA20
Water	11%								
Glycerol		5%		10%		15%		20%	
Xylitol			5%		10%		15%		20%

The typical route for investigating starch-water or starch-plasticizer interactions has been water absorption-isotherm of starch-based polymer[14,15] to understand how the interaction of free water with starch influences the polymer crystallinity, and therefore, extrapolate this understanding to determine how viscous flow maybe affected. However, direct experimental evidence of starch biopolymer viscous flow data due to interaction of plasticizer-water is limited in literature and moreover, variation in starch types adds complexity to the scenario. This study focuses on two aspects; the water activities of the plasticized starch biopolymers with glycerol and xylitol (currently, such data is nonexistent in open literature), and the bulk viscous flow behavior of plasticized amylopectin. The latter is especially important because flexibility is directly related to the onset temperature of bulk viscous flow behavior. This would indicate the interaction levels of these two plasticizers due to their varying concentrations and varying free water content in the polymer. To understand the plasticizer-starch and/or plasticizer-water interactions, Gordon-Taylor (GT) equation is modified with an interaction parameter (discussed later in "Gordon-Taylor Model" section) and the analysis of the GT parameter (K_{gt}) is based on earlier developments by Goldstein[16] and Kwei.[17] GT model is typically reserved for binary systems with one plasticizer, where the K_{gt} underlines the plasticizer's efficacy in the chosen matrix, and the numerical value can be considered as an arbitrary, but unified value of the intermolecular interactions between starch and plasticizers.[18]

Even though any application of starch biopolymeric material would typically involve more than two plasticizers, there is little work carried out on analysis of a ternary starch biopolymeric system. This could be due to the fact that the study of starch ternary system is complex as water content at a given relative humidity results from the combined affinities of the macromolecular network and the characteristics of plasticizers as pointed out previously.[13] Moreover, in literature, most experiments used the GT model for data-fitting without a significant attempt to understand how the parameters link to the different plasticizer characteristics and the T_g obtained from experiments is used to determine the GT constants. The current model allowed the use of K_{gt} from the GT model for starch-water system to be used for a semi-empirical model involving a parameter for interaction, n, defined as the ratio of interaction between starch plasticizer and starch-water. We have determined the glass transition behavior using high-speed DSC as reported earlier[19] and the higher heating rates allow us to capture small transitional endotherm.

MATERIALS AND METHODS

Sample preparation and procedures

Tables I and II gives the details of materials used for this investigation. The pure starch were obtained from Timstock. Australia. Pure starch was labeled LA based on their dominant amylopectin content (65–70%). In Table I, WLA, GLA, and XLA refers to water + LA starch, glycerol + LA starch, and xylitol + LA starch, respectively. The reason LA starch was chosen here is because amylopectin has a relatively stable crystalline domain and we can investigate the effect of equilibrium water activities on the bulk viscous behavior of the plasticized biopolymers. Further, this allowed for the investigation of the networking ability of amylopectin in presence of plasticizers. As shown here later, with careful preparation of samples and storage, the variation in crystallinity for different plasticizers content is statistically insignificant.

The glycerol and xylitol were obtained from Consolidated Chemicals, Vic, Australia. All materials were added on dry basis for sample preparation. For example, GLA10 contained 10 g of glycerol with 90 g of LA starch on dry basis. These mixtures were first dry mixed using Hobart planetary mixture (model no: N50-619, Hobart Australia) while the overall moisture content of the mixture was maintained at 40% for 1 h. Different formulations based on their respective wt % were then stored at controlled humidify environment of 50% RH for 24 h.

TABLE II
Characteristics of Plasticizers

Property	Glycerol	Xylitol
Carbon number	3	5
Molecular weight	92	152
Melting point (°C)	18	94
Hygroscopy	High	High
T_g (°C)	−90	−20

Parameters	Processing conditions
Screw speed (rpm)	120–135
Highest temperature (°C)	110
Water content (%)	22–28
Residence time (sec)	240–275

These samples were then kept in hermetically sealed polyethylene bags before extruding them in a counter-rotating twin-screw extruder (Brabender, Duisburg, Germany) following processing information for starch systems already published by us.[8] Briefly, the temperature of the inlet, mid and end temperatures were maintained at 95, 125, and 105–110°C, respectively and other details are mentioned in Table III. Extruded samples were mixed with dry ice in a ball mill to be ground to fine powder, whilst their structure is frozen. All samples were sealed in hermetically sealed polyethylene bags before subjecting them to controlled RH conditions, as described in "Equilibrium moisture content and matrix crystallinity" section X-ray diffraction (XRD) technique was predominantly used to monitor the crystallinity of the sample. The XRD measurement were performed on the plasticized starch powder samples using a Bruker D8 Diffractometer operating at 20 KV, 40 mA Cu Kα radiation monochromatised with a graphite sample monochromator. A diffractogram was recorded between 2Θ angles or 5° and 45° at a fixed time of o.1s per step of 0.05°.

Equilibrium moisture content and matrix crystallinity

Triplicate 2 g of samples were placed in open perforated plastic containers in various controlled humidity chambers. The relative humidity of the chambers was controlled from 0 (Magnesium Perchlorate) to 93% (Potassium sulphate) using saturated salt solution. The protocol recommended by COST-90[20,21] was used to prepare the standard salt solution, the humidity chamber and also the weighing protocols. We used powder rather than film because excess moisture can be collected over the film and this would modify the temperature reading during the thermo-mechanical analysis. Thin layer of the above powders were equilibrated for 3–4 weeks to allow sufficient time for the powders to reach equilibrium. Once the samples reached equilibrium, they were taken out and their total moisture content was determined using a 120°C infra-red heated balance (Kern moisture analyzer, Germany). The water activity of the samples was also cross-checked with Novasina water activity meter (Novasina, Switzerland). The

equilibrium moisture values were plotted against the free water content of each sample, at a constant temperature, known as the moisture sorption isotherm. Triplicate measurements were carried out for all tests and the average values for the bulk behavior are reported here.

Thermal analysis

Thermal analysis was done using a Perkin–Elmer calorimeter (DSC 6000) from 0 to 200°C with 10 mg of sample. Tests were conducted in high pressure stainless steel crucibles with gold seals (max pressure rating − 10 bar) using dry argon as purge gas (30 mL/min flowrate) and nitrogen as environment gas (100 mL/min flowrate) with at least two specimens for each sample to ensure sample run repeatability. The heating and cooling were constant at 30°C/min. The higher than usual heating rate ensures that small fluctuations in heat capacity are correctly measured. The results were analyzed from the second heating and cooling curves. The stability of any particular plasticizer–polymer system was determined after comparing the crystallization enthalpy and the temperatures of the first and second cooling curves. Enthalpies of melting and crystallization, along with the respective temperatures, were obtained by using the peak integration method. In fact, DSC measurements with traditional heating rates of 10–20°C/min generally fail to highlight the small change in heat capacity, and only recently glass transition behavior of corn starch was investigated using hyper DSC technique (heating rate of 50–100°C/min).[19]

GT model

Water activity measurements are able to relate the matrix free water content to the equilibrium moisture content and for a hydrophilic matrix such as starch, its second order phase transition (a kinetic and relaxation process) at its characteristic temperature is a function of moisture content.[22] Glass transition behavior is a powerful tool for understanding the quantification of water mobility in products. The modified GT model used here has two levels of analysis. For the first part of the modelling, starch-water is lumped as one system (based on the assumption that starch-water interaction is the strongest) and this system is investigated in the absence of plasticizers to obtain the K_{gt} value, as shown in eq. (1). This K_{gt} value indicates the plasticizing ability of the water. In the second part, the ternary system is considered; starch, water and plasticizer are mixed together where water and plasticizers compete for polymer interactions. For the model data, T_g of pure starch is 170°C and the T_g of

glycerol, xylitol and water is $-90°C$, $-20°C$ and $-135°C$.[23,24] Plasticizer interaction and effectiveness can be related to the overall matrix by assuming additive law of volume of the repeating monomer units, and related free volume of polymeric matrix,[25] as mentioned in original treatise by Gordon and Taylor.[26] This assumes that the transition from a glass to a viscous liquid requires a certain degree of molecular mobility. Here we determine K_p [eq. (2)] as the strength of starch-plasticizer interaction and any changes in K_p can be related to the plasticizing ability of the plasticizers. Considering that K_{gt} is a relationship factor for the continuity of the enthalpy of mixing, we then determine n from eq. (3), which is a second order equation in concentration to account for the interaction effect as recommended in literature.[16,27]

$$K_{gt} = (1/Xs - 1) * [(Tw - Ts)/(Tgw - Ts)] \quad (1)$$

$$K_p = (1/Xs - 1) * [(Tp - Ts)/(Tgp - Ts)] \quad (2)$$

$$n^2(XwTwXp) + n(XpTp + XsXwTw + XpTg)$$
$$+ Xs(Ts - Tg) = 0; \ n = K_p/K_{gt} \quad (3)$$

where X and T represent the mass fraction and glass-transition temperature in Kelvin for pure components, and s, w, and p denotes the starch, water and plasticizer component, respectively. T_{gw} and T_{gp} refer to the glass transition temperatures of pure starch-water and pure starch-plasticizer system, respectively. T_g refers to the experimental glass transition temperature of the ternary mixture (starch-water-plasticizer). The "n" is the plasticizer interaction parameter, defined as the ratio of interaction between starch-plasticizer and starch-water. The values of the mass fraction of water, glycerol and starch are calculated from the moisture content of the samples from the water isotherm experiments. Graphs of K_{gt} and "n" against the free water content of the matrix were plotted to understand the starch-water interaction and the competitive interaction of plasticizers and water, respectively.

RESULTS AND DISCUSSION

Matrix crystallinity and water-plasticizers interactions

In presence of water, the plasticizer effectiveness is related to its relative concentration to that of the water, as it interacts with both water and biopolymer. In amylopectin biopolymer, the interaction of polymer-plasticizer is dominant in comparison to that of plasticizer-water, as all of the water is "locked" via starch-water interactions. It is well known that the overall matrix crystallinity is primarily due to the starch-starch and starch-water interac-

tions.[28] In such cases, the only way to reduce strong starch-water and starch–starch interactions is by adding excess plasticizers.

As seen in Figure 1(A), neither plasticizers changes starch crystallinity significantly. Further, when excess water is present, plasticizer-water interaction can become significant and this can result in slight reduction in overall crystallinity, but again, for this to happen, the plasticizer needs to be in excess. Figure 1(B) shows that at high water activities, there is little change in the overall crystallinity of the samples. Finally, xylitol samples also show sharp peaks for 20 wt % samples, and this refer to the strong localised starch-water domains due to phase separated water-xylitol interaction. Similar evidence of complex water and plasticizer interactions were reported for sorbitol.[29] In terms of a different starch matrix, Table IV data is reproduced from Chang et al.[30] and further highlights the interaction between water and glycerol plasticizer for tapioca starch. It can be seen that for 20% glycerol samples, increasing water activity from 0.11 to 0.56 decreases the observed glass transition temperature by 50%. However, reducing the glycerol to 10% while increasing the water activity from 0.32 to 0.56 still shows a small increase in the glass transition temperature.

Water activity measurements and equilibrium moisture content

Figures 2 and 3 shows the moisture sorption isotherms for two plasticizers, glycerol, and xylitol. Both figures indicate the strong hydrophilic interaction of plasticizers. At higher water activities (A_w), the water content in the starch matrix was due to the hydrophilicity of the plasticizers and they typically absorbed large amount of water,[3,4] as compared to the pure starch samples. Each data point in Figures 2 and 3 is equilibrium moisture content for a particular water activity.

Comparing Figures 2 and 3, glycerol samples showed increased moisture content compared to xylitol samples for identical water activities. Several reasons attribute to this behavior; firstly, with a lower molecular weight and greater affinity to moisture, samples with glycerol exhibit greater interaction with water molecules[31] as compared to xylitol, and secondly, xylitol has greater hydroxyl groups, possibly enabling greater starch-xylitol interactions. So, even though free water content depends on the nature and amount of plasticizer,[2] it was found that water sorption does not provide straightforward relationship between the moisture content and the number of hydrophilic sites on the plasticizer. A key observation can be made by comparing Figures 2 and 3 for water activity between 0.11 and 0.55. Twenty percent plasticized samples (both glycerol
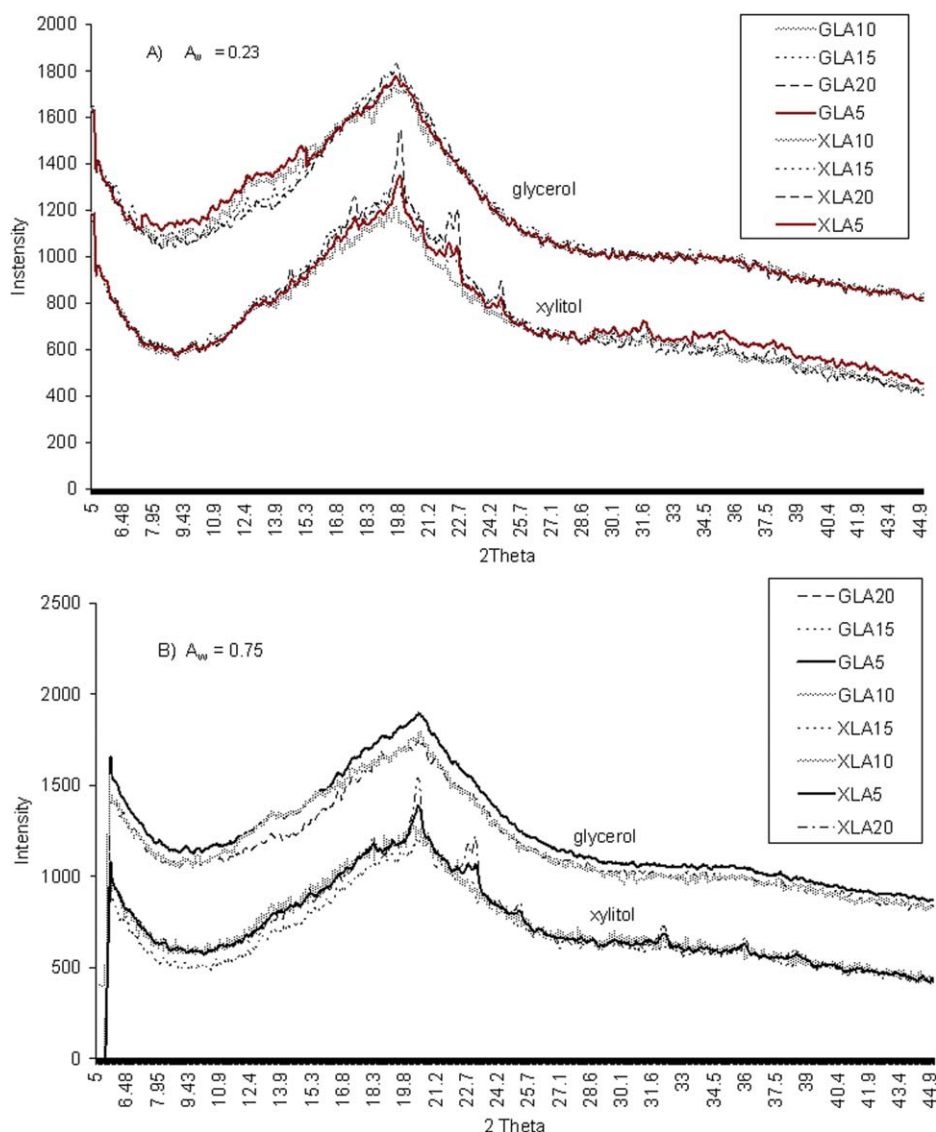
Figure 1 XRD plots of starch plasticized samples for two water activities. A) represents the lower water activity (0.23) plots and B) represents the higher water activity (0.75) plots for both plasticizers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and xylitol) have lower equilibrium moisture content as compared to 5–15% plasticized samples. In fact, for xylitol samples, water activity of 0.7 is required for the 20% sample to surpass the lower concentrations in terms of its equilibrium moisture content. From literature, we note that the stronger starch-plasticizer interaction[3] corroborate such observed starch-xylitol interactions.

By comparing Figures 2 and 3, for water activity >0.6, the GLA samples show greater overall moisture content compared to XLA samples. One reason for such behavior has been proposed earlier by Mali et al.[8] as the excellent hydrophilicity of glycerol, and similar behavior has been reported for other varieties of starches with glycerol and water.[32] The figures are presented with overlaying best-fit lines (with no scientific meaning) to highlight the transi-

tion points in equilibrium moisture content. This analysis combined with the analysis of Table IV data can suggest that there is a threshold amount of free water within the matrix, which can strongly

TABLE IV
Experimental Glass Transition Temperature of 35% Amylose Starch at Different Water Activities with Only One Plasticizer[30]

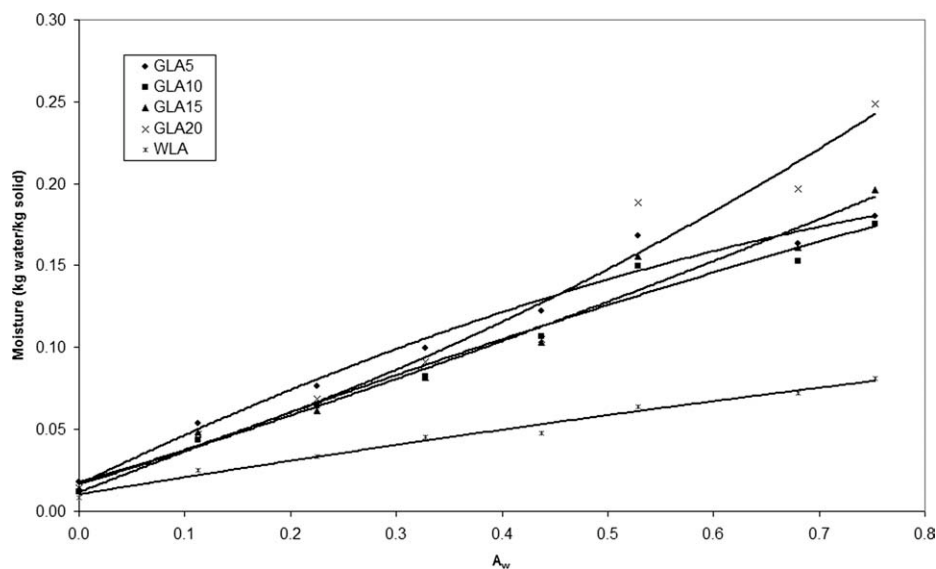| A_w	Moisture content (wt %)	Glycerol content (wt %)	T_g (°C)
0.11	6.41	0	165.7
0.11	5.81	10	117.2
0.11	5.76	20	86.5
0.56	10.62	0	91.2
0.56	9.83	10	72.1
0.56	11.23	20	37.6

Figure 2 Glycerol with starch – water sorption isotherm.

influence the overall plasticization ability. If that amount of water is available in the starch matrix, apparently the polymer chains have increased competition between the additional plasticizers and water. Does the starch-water (WLA) sorption curve in Figures 2 or 3 reflect anything about this threshold water content? In the following sections, we will further analyse this using modified GT model.

Glass transition and viscous flow behavior of starch-water-plasticizer systems

The samples were tested for any variation in water activities to ensure that the free water content of the sample was representative. In Figure 4, all glycerol plasticized starch samples show a reduction in the onset temperature for viscous flow after $A_w \sim 0.23$ as compared to pure starch sample, while before $A_w \sim 0.23$, the 5 and 10% glycerol samples had insignificant change to their onset temperatures. Starch with no glycerol had a glass transition onset temperature at $\sim 170°C$ and this value converged to 20°C as the equilibrium moisture content within the starch matrix increased, similar to previous studies on wheat starches.[33] Both Figures 4 (glycerol samples) and 5 (xylitol samples) show typical antiplasticization behavior due to plasticizer content at very low A_w. Xylitol samples tend to have greater antiplasticization tendencies and this is possibly due to greater number of hydroxyl groups.

In terms of molecular diameter, both glycerol and xylitol have similar sizes, and the greater number of
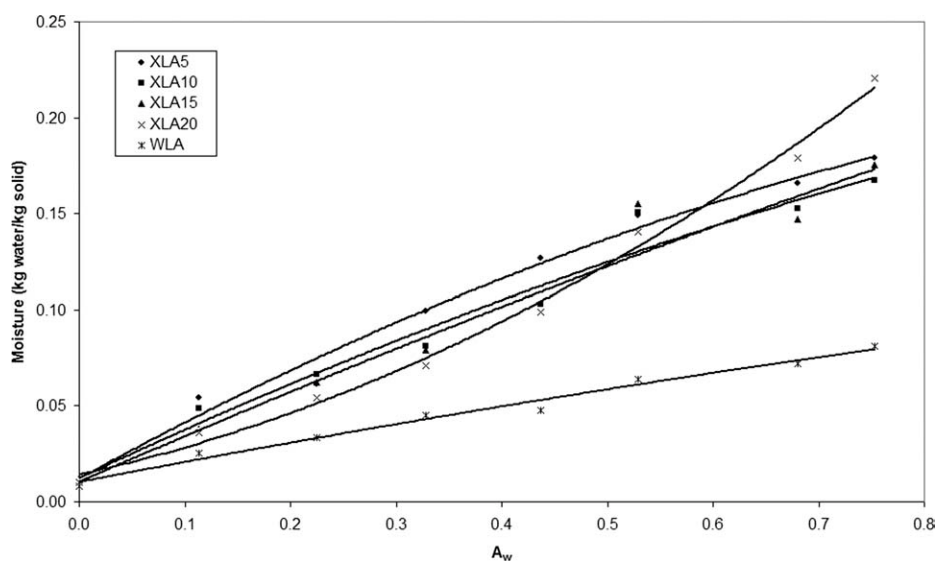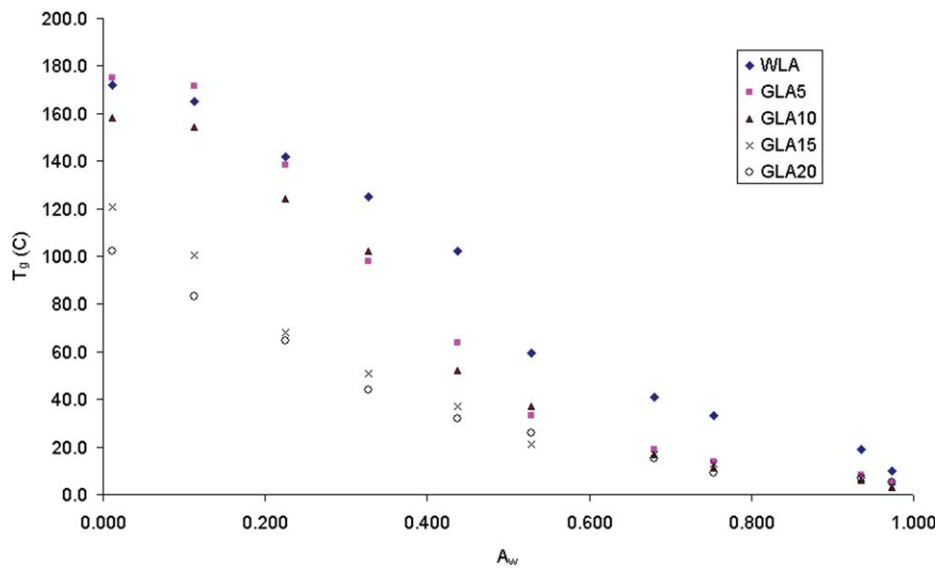

**Figure 3** Xylitol with starch – water sorption isotherm.

Figure 4 Bulk viscous flow temperature with increasing water activity for different glycerol concentration (Standard deviation for all samples was <0.55°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydroxyl groups allow xylitol to increase starch-xylitol-starch type of interactions (increased networking) and increase molecular entanglement and reduce free volume.[6] However, smaller molecules such as water can preferentially occupy starch free volume and then the plasticizers primarily reduce the molecular entanglements. A recent study suggests that glycerol and sorbitol bind with starch at low concentrations to increase chain coalescence; leading to increased starch matrix T_g,[4] but in presence of excess water in the starch matrix, starch and plasticizers and plasticizers and water preferentially interact, as recently shown by molecular modelling.[34]

Typical antiplasticization is seen in Figure 4 with 5% glycerol sample; and similar behavior was reported earlier with the likely reasoning that there is increased association of starch and glycerol and starch with starch, via hydroxyl linkages that causes interlocking.[35,36] We have used 170°C as the T_g of amylopectin dominant starch[37] for the GT model analysis. Further, when the our maize sample glass transition values in Figure 3 are compared with the Chang et al. Tapioca data[30] (reproduced in Table IV), we see similar values for 20% glycerol content, but for 10% glycerol, there are significant differences (at $A_w \sim 0.11$, our T_g is 30°C higher, but at $A_w \sim 0.5$,
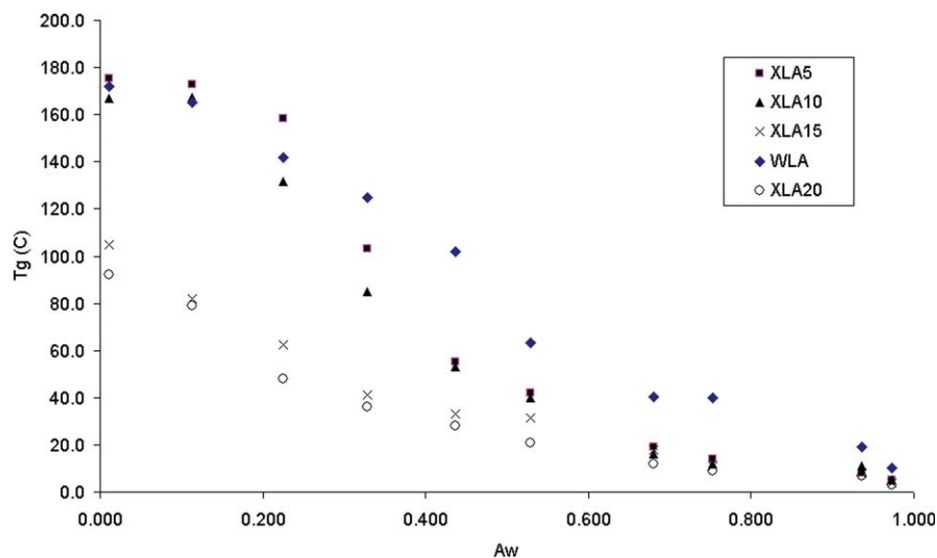
Figure 5 Glass transition (bulk viscous flow) temperature with increasing xylitol concentration at various water activity values (Standard deviation for all samples was <0.55°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
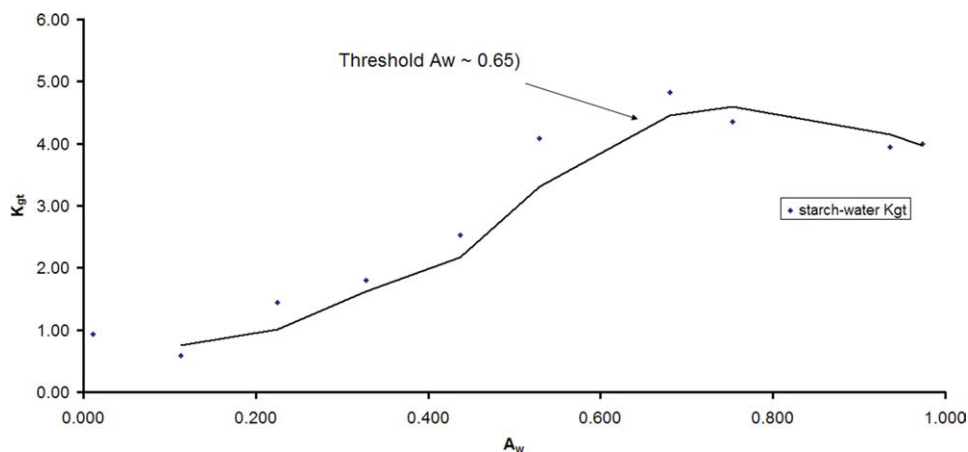
Figure 6 Variation of K_{gt} parameter of starch-water with increasing free water content in starch matrix. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

our T_g is 30 lower). This is primarily due to the influence of starch composition (amylopectin amount), which is masked at higher plasticizer content. Comparing the effect of glycerol concentration on the glass transition temperatures, we see relatively small change for $A_w > 0.6$. Such behavior is dominated by water-starch interactions, and possibly the excess plasticizers primarily interacts with the free water rather than the polymer matrix—such as starch-water and plasticizer-water, instead of starch-plasticizers. Similar behavior on the strong water-starch interaction has been mentioned before[4,36] and we suspect it is due to "threshold" free water content. Figure 4 data on starch-glycerol is similar to previously reported analysis[37,38] including the anti-plasticization behavior. To understand the threshold water content that could dominates starch-plasticizer interactions, we can see that till $A_w \sim 0.45$, doubling glycerol wt % in starch polymer results in an average drop in viscous flow temperature of 50°C, but above A_w of 0.6, glycerol plasticized samples show reduced impact of the additional plasticizers on the glass transition temperature.

In Figure 5, we note that as A_w is increased from 0.11 to 0.23, the onset temperature for bulk flow for 10% xylitol samples drops by about 40°C. However, xylitol plasticized samples show greater antiplasticization behavior than glycerol (XLA5 T_g remains significantly higher than WLA T_g till $A_w \sim 0.23$), and this suggests stronger starch-xylitol-water interactions in absence of water as compared to starch-glycerol-water interactions. From a free volume concept for bulk motion, as described earlier by Seow et al.,[3] the reduction in T_g value is related to both the plasticizer concentration and the free water content of the matrix. We find that unlike xylitol, with glycerol samples, antiplasticization is limited to $A_w < 0.23$, indicating glycerol imparts better matrix plasticization when water content is low. In Figures 4 and 5,

the impact of excess plasticizer in reducing bulk viscous behavior can be seen for A_w values of 0.11 to 0.23; as compared to 5 or 10% wt, 15 and 20% wt plasticized samples showed nearly 50% reduction in T_g values. This reflects that these plasticizers can replace water to interact with the starch polymer at the molecular level to significant reduce matrix T_g. However, with increasing equilibrium water content ($A_w > 0.6$), we note that excess plasticizers have little effect and this could be attributed to excessive plasticizer-water interaction (or phase separation of plasticizers) and unchanged matrix free volume due to presence of plasticizers, as mentioned earlier.[39,40] We also believe that key solubility index for plasticizers are influenced by the water content and corroborating experimental evidence and validating molecular modelling needs to be done to confirm this.

Evaluation of interaction parameters for starch-plasticizer-water system

The GT model is based on the concept of increasing free volume due to plasticizers and the resulting reduction in the fundamental T_g. This is highlighted in Figure 6 as shown by the increase of the K_{gt} value of the starch-water sample. The increase in K_{gt} is an indication of the increase in plasticization, as evidenced by the reduced T_g value with addition of water, and similar findings have been reported earlier on different starch samples.[14]

From Figure 6, based on the enthalpic contribution or the volume expansion effect as discussed by Goldstein,[16] the starch-water interaction based on K_{gt} increases linearly until a particular free water concentration, indicating that presence of water reduces starch-starch interaction till such value where excess of water has no longer any effect on the starch-starch interactions. Arvanitoyannis and Biliaderis also confirmed that for plasticized starch mixtures,
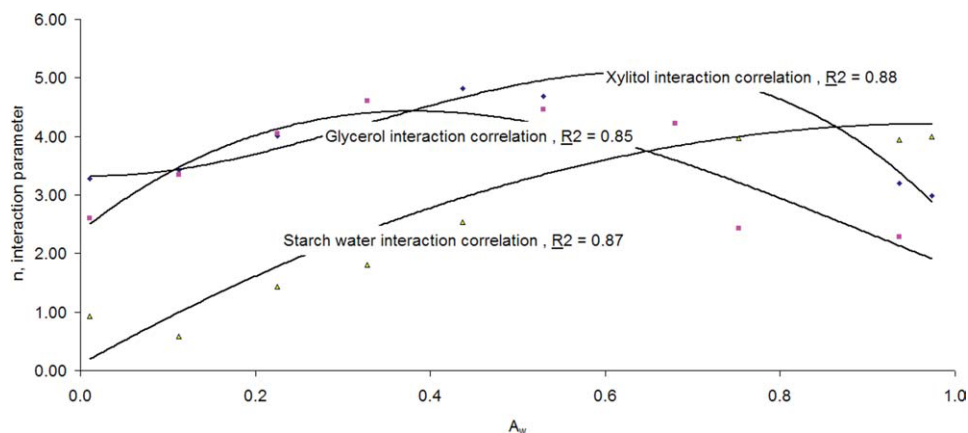
Figure 7 Parameter n variation for all plasticizers with starch (averaged over the respective concentration range) with increasing A_w (the curves through the data points are for representation purposes of respective trends). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the larger the GT parameter, the greater the plasticization effect.[41] However, after a certain A_w (identified as the threshold $A_w \sim 0.65$), the increase in free water within starch matrix does not increase the influence of K_{gt} on T_g - meaning that at this matrix moisture content, additional plasticizers (both water and others) would have little influence on overall plasticization. From Figure 2, $A_w \sim 0.65$ corresponds to a moisture content of 7.5–8% wt. This is the threshold moisture range beyond which the starch matrix preferentially interacts with excess of water reducing the influence of plasticizers. This is highlighted by the higher n parameter values for plasticized samples in Figure 7.

Finally, to understand the extent of competition between water and plasticizer in the ternary starch plasticizer mixture, we used the fitting parameter for starch-water, K_{gt}, to calculate interaction parameter, n [eqs. (1)–(3)]. Figure 7 shows the variation of K_{gt} of starch-water (fitted using the WLA T_g data) and n for plasticised starch (averaged over the concentration range for glycerol and xylitol) with increasing free water content in the starch matrix. Figure 7 was produced from eq. (3) by using the experimental data reported in Figures 4 and 5.

From Figure 7, we see that as the plasticizers are introduced to the starch system, the interaction of starch-water is not dominant and further, the increasing trend for water and both plasticizers indicate reduced starch-starch interactions (plasticisation effect)[41] and the interaction of plasticizer and the starch dominates, as recently reported.[42] In presence of plasticizers, the interaction between starch-plasticizer takes precedence when the free water content is comparatively lower till the "threshold" value, as discussed earlier. Further, it can also be seen that both plasticizer-starch interaction parameters show a decreasing trend as starch-water interaction increases. This is the strongest evidence of competitive

plasticization within starch polymers due to water and plasticizers. Further, Figure 7 also suggests that the plasticizers behave differently if in presence of an excess of water in terms of the ternary starch-water-plasticizer interaction. It can be hypothesized that xylitol interacts both with starch and water at the same time due to its higher degree of hydroxyl functionality[23,24] resulting in a reduced antiplasticization effect. This can also explain why xylitol plasticised samples need higher water activity to achieve similar moisture content as compared to the glycerol plasticized starch.

Significance of findings

The threshold water activity (~ 0.65 and corresponding moisture content as 7.5–8% wt) is a key finding because below this particular water concentration, application of plasticizers is likely to enhance the starch-plasticizer interaction and matrix flexibility. For the formulation engineer, this is the moisture range optimum for working with plasticizers. Also, equally important is the concentration of the plasticizers to achieve similar flexibility in starch biopolymers; xylitol at higher water activity region (higher humidity regions) would be able to provide better structural flexibility than glycerol, but would need higher concentration than glycerol.

CONCLUSIONS

An effort has been made to combine data of water activity and glass transition temperature of amylopectin starch polymer and to understand and predict the glass transition temperature of the polymer on addition of varying concentration of glycerol and xylitol. This investigation found a complex relationship between plasticizer and water in starch. Xylitol and glycerol behave differently in presence of

different amounts of free water content, and this difference could be attributed to their different number of hydroxyl groups. Glycerol is a better plasticizer than xylitol at lower A_w; however, at higher plasticizer concentrations, xylitol has better plasticization ability. Both plasticizers also showed typical antiplasticization behavior at lower water contents, and a modified GT model indicated the presence of threshold water content within the starch matrix and this value was determined to be $\sim$ 8% wt ($A_w \sim 0.6$). The modified model also determined that both starch-water and starch-water-glycerol interaction parameter n had a maximum value of $\sim$ 4, but for glycerol samples, the maximum occurred at $A_w \sim 0.33$ as compared to $A_w \sim 0.65$ for starch-water samples. Xylitol samples had the largest value of interaction parameter n occurring at $A_w \sim 0.6$. Once the water activity increased to 0.7, the efficacy of the plasticizer is reduced by preferential plasticizer-water interactions. The modified model helps to understand the effect of water and plasticizers on starch polymer structure modification from glass transition measurements carried over a wide range water activity.

References

1. Myllärinen, P.; Partanen, R.; Seppälä, J.; Forsella, P. Carb Polym 2002, 50, 355.
2. Han, J. H. Innovations in Food Packaging; Academic Press: UK, 2005.
3. Seow, C. C.; Cheah, P. B.; Chang, Y. P. J Food Sci 1999, 64, 576.
4. Cheng, L. H.; Abd Karim, A.; Seow, C. C. J Food Sci 2006, 71, 62.
5. Pittia, P.; Sacchetti, G. Food Chem 2008, 106, 1417.
6. Herbert, G.; Bader, D. G. Starch – Stärke 1994, 46, 249.
7. Park, H. J.; Chinnan, M. S. J Food Engg 1995, 25, 497.
8. Mali, S.; Sakanaka, S.; Yamashita, F.; Grossmann, M. V. E. Carb Polym 2005, 60, 283.
9. Chaudhary, D. S. J Polym Sci: Polym Phys 2008, 46, 979.
10. Chaudhary, D. S.; Adhikari, B. P. J Appl Polym Sci 2009, in press.
11. Smits, A. L. M.; Kruiskamp, P. H.; Soest, J. J. G.; Vliegenthart, J. F. G. Carb Polym 2003, 53, 409.
12. Alves, V. D.; Mali, S.; Beléia, A.; Grossmann, M. V. E. J Food Eng 2007, 78, 280.
13. Mehyar, G. F.; Han, J. H. J Food Sci 2004, 72, 293.
14. Lourdin, D.; Cheah, B. P. J Appl Polym Sci 1997, 63, 1047.
15. Müller, C. M. O.; Yamashita, F.; Borges, L. J Carb Polym 2008, 72, 82.
16. Goldstein, M. Macromolecules 1985, 18, 277.
17. Kwei, T. J Appl Polym Sci 1984, 22, 307.
18. Schellenberg, J.; Vogel, J. J Polym Sci Part B: Polym Phys 1994, 32, 1969.
19. Liu, P.; Yu, L.; Liu, H.; Chen, L. L.i Carb Polym 2009, 77, 250.
20. Wolf, W.; Spiess, W. E. L.; Jung, G. Properties of Water in Foods, Simatos, D.; Multon, J. L., Eds.; Martinus Nijhoff Publishers: Boston, 1985.
21. Spiess, W. E. L.; Wolf, W. Water Activity: Theory and Applications to Food, Rockland, L. B.; Beuchat, L. R., Eds.; Marcel Dekker: New York, 1987.
22. Slade, L.; Levine, H. Crit Rev Food Sci Nut 1991, 30, 115.
23. Mathew, A. P.; Dufresne, A. Biomacromolecules 2002, 3, 1101.
24. Enrione, J. I.; Hill, S. E.; Mitchell, J. R. Starch– Stärke 2007, 59, 1.
25. Constantino, H. R.; Pikal, M. J., Eds. Lyophilization of Biopharmaceuticals; AAPS Press: Virginia, 2004; 367–422.
26. Gordon, M.; Taylor, J. S. J Appl Chem 1952, 2, 493.
27. Owusu-Apenten, R. K. Food Protein Analysis; CRC press: California, 2002.
28. Gidley, M. J. Carbohydr Res 1987, 161, 301.
29. Riku, A.; Talja, M. P.; Ritva, S.; Kirsi, J. Biomacromolecules 2008, 9, 658.
30. Chang, Y. P.; Abd Karim, A.; Seow, C. C. Food Hydrocolloids 2006, 20, 1.
31. Leung, H. K. Water Activity and Other Colligative Properties of Food; American Society of Agricultural Engineers: Michigan, 1986.
32. Godbillot, L. P. D.; Joly, C.; Rogé, B.; Mathlouthi, M. Food Chem 2006, 96, 380.
33. Zeleznak, K. J.; Hoseney, R. C. Starch-Starke 1987, 39, 231.
34. Ubbink, J.; Giardello, M. l; Limbach, H. J. Biomacromolecules 2007, 8, 2862.
35. Bizot, H.; Leroux, D.; Davy, B. J.; Roger, P.; Buleon, A. Carb Polym 1997, 32, 33.
36. Biliaderis, C. G.; Lazaridou, A.; Arvanitoyannis, I. Carb Polym 1999, 40, 29.
37. De Graaf, R. A.; Karman, A. P.; Janssen, P. B. M. Starch– Stärke 2003, 55, 80.
38. Westling, A. R.; Stading, M.; Gatenholm, P. Biomacromolecules 2002, 3, 84.
39. Sala, R.; Tomka, I. The Glassy State in Foods, Blanshard, J. M. V., Lillford, P. J., Eds. Nottingham University Press: Nottingham, 1993; 483–489.
40. Levine, H.; Slade, L. Water Sci Reviews, Franks, F., Ed. 1988; 3, pp 79–185.
41. Arvanitoyannis, I.; Biliaderis, C. Food Chem 1998, 62, 333.
42. Chen, C. H.; Lai, L. S. Food Hydrocolloids 2008, 22, 1584.