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The effect of fructose and water on the glass transition of amylopectin

Monica T. Kalichevsky & John M.V. Blanshard

Department of Applied Biochemistry and Food Science, University of Nottingham, Sutton Bonington Campus, Loughborough, UK, LE12 5RD

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Mechanical methods (dynamic mechanical thermal analysis and three-point bend tests) and differential scanning calorimetry have been used to study the effect of variations in the amylopectin:fructose ratio on properties in the region of the glass transition temperature (T_g). The effects of 0–50% (dry basis) fructose content have been studied over a range of water contents between 7 and 27% (of total weight). At and below 20% fructose, the T_g is reduced in excess of the predictions of a three-component Couchman–Karasz equation, whereas, at higher fructose contents, the sugar glass transition (at that water content) begins to dominate the mechanical properties.

INTRODUCTION

The significance of the glass transition temperature (T_g) in determining the stability and mechanical properties of food products has recently received increasing recognition (e.g. Levine & Slade, 1986; Roos & Karel, 1991). Wheat starch is an important component in many food products and its glass transition has been studied by differential scanning calorimetry (DSC) by Zeleznak and Hoseney (1987). The T_g of the constituent polysaccharide amylopectin and the effects of various sugars have previously been studied in this laboratory (Kalichevsky *et al.* 1992*a*, in press). We have now extended these studies to investigate the effect of changing the amylopectin:fructose ratio at different water contents.

Low molecular weight additives decrease the T_g of polymers by increasing the free volume available to the polymer. The requirement for a miscible system is that all components should experience the same average free volume, but it has recently been pointed out (Miller *et al.*, 1990) that this does not necessarily imply that all components will exhibit the same T_g. It is well known (Ferry, 1970) that the fractional free volume at which the glass transition occurs varies between polymers, and low molecular weight diluents would certainly be expected to require less free volume for diffusion and to have considerable mobility below the T_g of the polymer.

Diffusion studies have shown substantial translational movement of probe molecules below the T_g of the polymer, depending on the probe size, with no discontinuity at the T_g of the polymer (Ehrlich & Silescu, 1990). Low-temperature mechanical relaxations somewhat above, or in the region of, the T_g of the diluent have frequently been observed in compatible polymer–diluent mixtures (Janacek & Kolarik, 1967; Kolarik, 1982; Kambour *et al.*, 1991). Thus the observation of such transitions does not necessarily imply phase separation. In fact, if the diluent substantially reduces the T_g of the polymer, significant phase separation is clearly not occurring. It is likely that the amylopectin: fructose 2:1 sample studied in the previous paper (Kalichevsky *et al.*, in press) is partially phase separated, as the T_g of amylopectin is not reduced as much as might be expected, but phase separation is not necessarily occurring in all samples where a low-temperature transition is observed in the region of the diluent T_g.

THEORY

Data on three-component systems may be compared with theoretical predictions of T_g using an extended form of the Couchman–Karasz equation (Couchman & Karasz, 1978). This may be expressed as follows:

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$$T_g = \frac{W_1 \Delta C_{p1} T_{g1} + W_2 \Delta C_{p2} T_{g2} + W_3 \Delta C_{p3} T_{g3}}{W_1 \Delta C_{p1} + W_2 \Delta C_{p2} + W_3 \Delta C_{p3}}$$

where W_1 is the weight fraction of component 1, ΔC_{p1} is the change in heat capacity at T_g for component 1 and T_{g1} is the glass transition of pure component 1. The subscript 1 refers to water, 2 to fructose and 3 to amylopectin.

The values of ΔC_p and T_g of water have been the subject of considerable debate, especially the former. There are also various values for T_g and ΔC_p of fructose (e.g. Finegold *et al*., 1989; Orford *et al*., 1990), although these do not vary to such a great extent. We have found that, if combinations of these values which give a good fit to T_g as a function of water content (using a particular ΔC_p value for water) to both the experimental results for the T_g of amylopectin (Kalichevsky *et al*., 1992) and of fructose (Arvanitoyannis, I., unpublished), then the predictions obtained for the three-component system are almost identical. That is, if the values of 134 K and 1·94 J g^{-1} K^{-1} for T_g and ΔC_p of water (Sugisaki *et al*., 1968) and 280 K and 0·83 J g^{-1} K^{-1} for the corresponding values of fructose (Orford *et al*., 1990) are used, a good fit to DSC data on fructose obtained in this department (Arvanitoyannis, I., unpublished) is achieved; using the same values for the T_g and ΔC_p of water, the corresponding best-fit values to data on hydrated amylopectin are 502 K and 0·41 J g^{-1} K^{-1}. These values were used in the equation above to obtain predictions for the three-component systems studied in this paper; however, as the ΔC_p value used for water is open to debate we have investigated what effect using a smaller value has on the predictions.

A smaller value for ΔC_p of water (1·04 J g^{-1} K^{-1}) may be used to fit the amylopectin data if 0·22 J g^{-1} K^{-1} is used for the ΔC_p of amylopectin (which is the value generally observed in the presence of water although there is a large scatter in the data). If the alternative values for T_g and ΔC_p of fructose (Finegold *et al*., 1989) are used (286 K and 0·46 J g^{-1} K^{-1}) with the latter value of ΔC_p of water, then a reasonable fit to the DSC data on fructose (Arvanitoyannis, I., unpublished) is also obtained. On using the equation above, similar predictions for the three-component system are obtained as when using the previously quoted values.

We believe that it is unrealistic to use the recently reported (Hallbrucker *et al*., 1989) values of the ΔC_p of water, i.e. 0·089 or 0·105 J g^{-1} K^{-1} in the Couchman-Karasz equation, as this would result in a gross underestimate of the plasticizing effect of water on sugars and polymers. We have discussed this in considerable detail in a previous paper (Kalichevsky *et al*., 1992*b*). In the light of these considerations, the first set of T_g and ΔC_p values for amylopectin, water and fructose given above was used to obtain the theoretical curves employed in this study.

EXPERIMENTAL

Sample preparation

Amylopectin was supplied as pregelatinized waxy maize starch by National Starch and Chemical Corp., Manchester. Fructose solutions of the appropriate concentration were ground in liquid nitrogen. Pregelatinized waxy maize starch was then added and mixed with the frozen powdered solutions. The nitrogen was allowed to evaporate. The samples were pressed under a pressure of 3·1 × 10^8 Pa at a temperature of 90–100°C for 5–10 min, to a thickness of 1–2 mm. They were subsequently cut into bars of approximately 3 × 0·8 cm and hydrated over various saturated salt solutions of specified relative humidity (RH). The water contents were established by oven drying at 105°C.

DSC measurements

Calorimetric measurements were carried out using a Perkin-Elmer DSC-2. The glass transition was determined from the midpoint of the heat capacity change observed at a heating rate of 10°C min^{-1}. If observable, the T_g was determined from the second heating scan after cooling at 10°C min^{-1}, in order to eliminate previous differences in the thermal treatment of samples. ($T_{g_{DSC}}$ was not observed for all samples, as in some cases low enough temperatures were not attained and heterogeneity in mixed systems can make reliable DSC measurements difficult.)

DMTA measurements

The Polymer Laboratories dynamic mechanical thermal analyser (DMTA) Mark I was used in the single cantilever bending mode at a frequency of 1 Hz and strain × 1 (corresponding to a nominal peak-to-peak displacement of 16 μm). Samples were heated at 2°C min^{-1}. Sample dimensions were typically 1·5 × 8 × 16 mm.

We originally defined T_g as the region between the onset of the fall in elastic modulus ($\Delta E'$) and the peak in $\tan\delta$ ($= E''/E'$), which occurs 20–50°C higher (Kalichevsky *et al*., 1992*a*, in press). The midpoint of the DSC transition generally falls between these two temperatures. More recently we have also taken the peak in the loss modulus (E'') into account, as in single-component systems we have found that (for a heating rate of 2°C min^{-1} and at 1 Hz) it corresponds closely to the DSC midpoint obtained at a heating rate of 10 K min^{-1} (Kalichevsky *et al*., 1992*b*). In these systems this peak may be quite broad, but is still a useful indicator of the midpoint of the glass transition

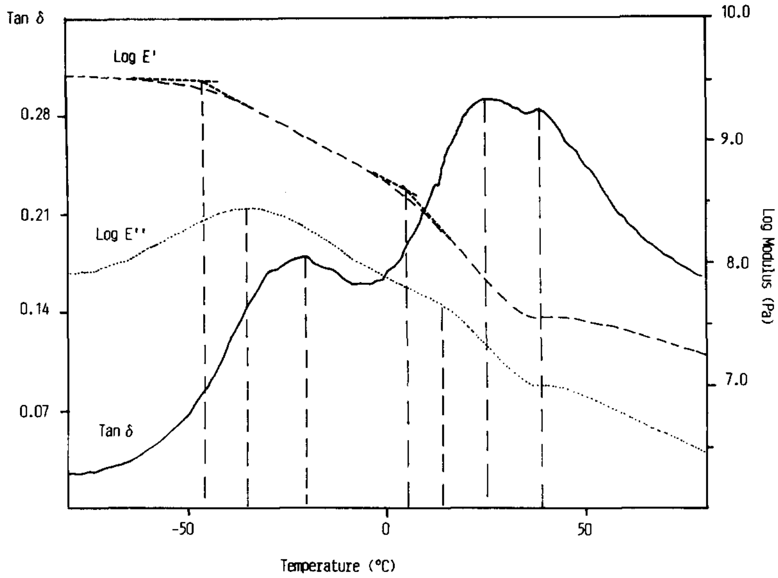

Fig. 1. DMTA tan δ, log E' and log E'' as a function of temperature for a sample of amylopectin + 25% fructose stored at 85% RH (18·6% aq.).

observed mechanically. The transitions recorded for an amylopectin sugar mixture are shown for one sample in Fig. 1.

The reproducibility of transition temperatures monitored by DMTA decreased as the transitions became broader. At low sugar contents, values were generally reproducible to within 4°C. The average of runs of 2–4 samples was taken (it was not possible to repeat runs on the same sample due to water loss during the experiment).

The three-point bend test

A Stable Micro Systems Texture Analyser (TA-XT2) was used at a depression rate of 0·5 mm s^{-1}. The samples were identical to those used for DMTA although the length had to be greater than 25 mm due to the separation of the stationary supporting beams. The Young's modulus was calculated from the initial slope of force against deformation. The peak force and water content at which the sample began to snap were also recorded.

X-ray diffraction

Wide angle X-ray scattering was used to test for sugar or starch recrystallization. The equipment consisted of a Philips APD 15 system, modified by addition of a BBC/Torch microcomputer for the analysis and storage of data. Data were collected over an angular range of $2\theta = 4$–64° at 0·05° 2θ steps. If sugar recrystallization had occurred, pronounced sharp peaks would be noted. These were not observed in any of the samples used, nor was there any visual evidence of recrystallization. In the case of starch, retrogradation could be detected as broad peaks on the amorphous background. The sample crystallinity was estimated from the ratio of the crystalline area to the total area of the diffractogram.

RESULTS AND DISCUSSION

Studies have already been carried out on amylopectin: fructose ratios of 2:1 and 10:1 (Kalichevsky *et al.*, in press). These studies have been extended to cover the ratios 1:1, 3:2, 3:1 and 4:1. In each case the samples were studied at three water contents (stored at 85, 65 and 12% RH). This enabled samples of the same water content and different sugar contents to be compared by interpolation. (Particularly at higher RH values, the water content of the samples increases with increasing sugar content.)

The various transitions recorded from a DMTA trace are illustrated in Fig. 1 for a sample of amylopectin + fructose in the ratio 3:1 stored at 85% RH. In this case two transitions are clearly observed, one in the region of the T_g of fructose and the other closer to that of amylopectin. The average of two or three sets of data at three water contents is plotted with the DSC data in Fig. 2. The more prominent transitions are shown by larger symbols. The log E'' peaks and DSC transition temperatures fall between the drop in E' and the tan δ peak temperature as observed previously (Kalichevsky *et al.*, 1992*a*, in press). The theoretical curves fitting the DSC data for the T_g of fructose and amylopectin (using the first set of T_g and ΔC_p values described in the Introduction) are plotted with the theoretical T_g (by DSC) of the mixed system. This corresponds well to the

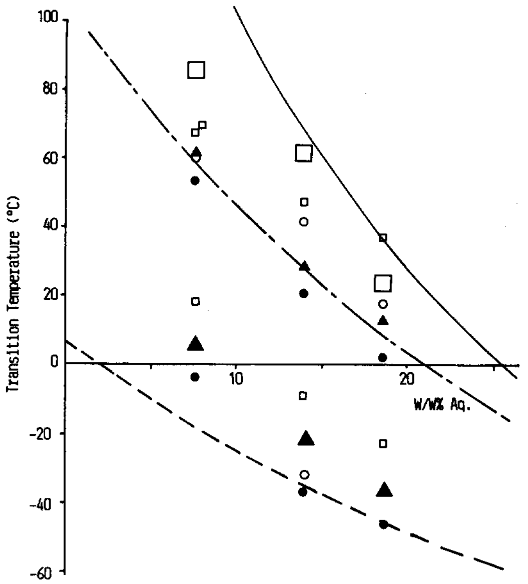

Fig. 2. Summary of DMTA data (tan δ peaks: □ (major), ▫ (minor); drop in E' temperature: ●; peaks in log E'': ▲ (major), ▴ (minor)) and DSC T_g (○) as a function of water content for amylopectin + 25% fructose. Theoretical curves for amylopectin (———), fructose (---) and the three-component system (— — —) are plotted for comparison.

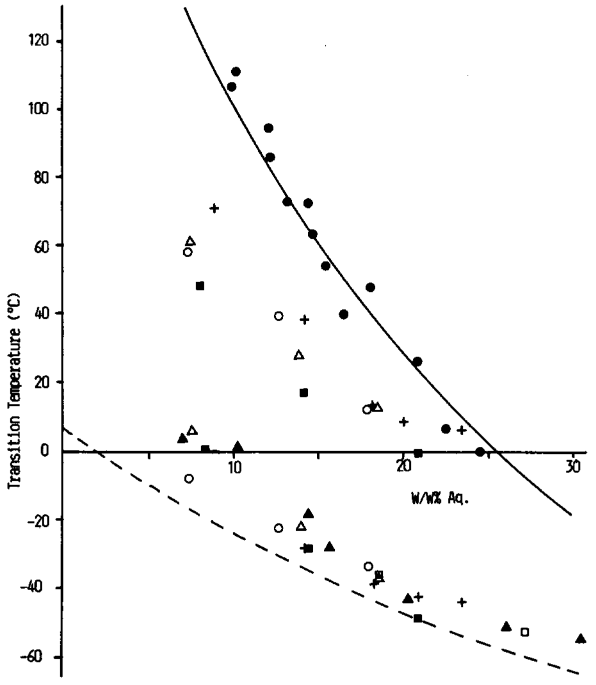

Fig. 3. Summary of log E'' peak data for amylopectin (●), and amylopectin + 9·1 (+), 20 (○), 25 (△), 33 (▲), 40 (■) and 50% (□) fructose. ———, Best-fit curve to $T_{g_{DSC}}$ of amylopectin and ---, T_g of fructose (using Couchman–Karasz equation).

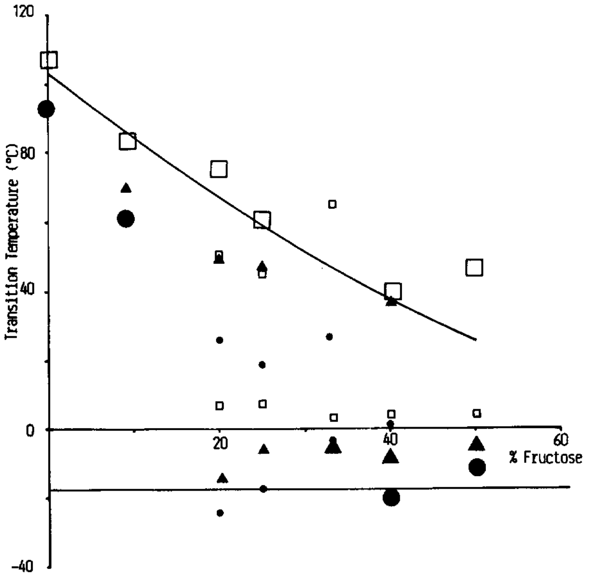

Fig. 4. DMTA transition temperatures as a function of fructose content, at 10% aq. (symbols as used in Fig. 2, with ● and • being the major and minor drop in E' temperatures respectively).

log E'' peak values. Unfortunately, it is difficult to obtain reliable determinations of T_g by DSC for many of these samples, due to a combination of heterogeneity and the low temperatures involved in some cases, but log E'' peak temperatures occur at a similar temperature, at least for amylopectin alone. The lower temperature transition appears to occur 10–23°C above the T_g of fructose, if the log E'' values are used.

The average log E'' peak temperatures obtained for all the samples are plotted in Fig. 3. In most cases (with the exception of amylopectin:fructose 10:1 at low water contents) a low temperature transition is observed 0–25°C above the T_g of fructose at that water content. The position of this transition does not appear to depend on fructose content, whereas the upper transition decreases in temperature with increasing fructose content, especially at lower water contents. As the fructose content is increased, the magnitude of the lower temperature transition increases and for the sample containing 50% fructose (dry basis) no higher temperature transition is observable in log E''.

Summary of the effect of fructose at 10% aq.

The interpolated DMTA results at various fructose contents obtained at 10% aq. are plotted in Fig. 4. The T_g of fructose at that water content is plotted as a straight line and the theoretical effect of fructose as determined by a three-component Couchman–Karasz equation is also plotted for comparison. Generally the upper peak in log E'' (which is expected to approximate to the DSC midpoint at the heating rate used) occurs 12–17°C below the theoretical (DSC) curve, only occurring at the predicted temperature at 40% fructose. At fructose contents above 25% the mechanical properties are increasingly dominated by the lower temperature transition. At 9·1% fructose no low-temperature transition is observed at this water content and at up to 25% fructose the plasticizing effect of fructose on amylopectin is greater than predicted. There is an indication that as the fructose content is increased its plasticizing effect does not increase correspondingly, which may be due to phase separation. The low-temperature transition falls 3–13°C above the T_g of fructose at this water content, suggesting that the amylopectin is having some antiplasticizing effect on the T_g of fructose.

Tan δ is plotted in Fig. 5 for samples of various fructose contents stored at 12% RH. These contain between 7·3 and 9·9% water and are therefore comparable with the results above. This plot clearly shows the reduction in temperature of the higher temperature transition and the increasing magnitude of the lower temperature transition with increasing fructose content. It is also interesting to note the increased breadth of the transition, indicating a broader distribution of relaxation times (and explaining the difficulty in observing a reproducible transition by DSC), as well as the increase in the height of the tan δ peak in the presence of fructose. This generally implies that the volume of the relaxing phase is increased (Wetton, 1986), indicating that the fructose is also involved in the higher temperature transition, or may be increasing the mobility of the amylopectin.

Summary of the effect of fructose at 18% aq.

The interpolated DMTA results for samples containing various fractions of fructose (as a percentage of the dry weight) at 18% aq. are plotted in Fig. 6. It is apparent that both the predicted and actual results show a reduced plasticizing effect at this higher water content, when compared with Fig. 4. Again, when compared with the theoretical (DSC) curve, the results show greater plasticization at lower fructose contents and, more clearly, reduced plasticization at higher sugar contents. The increase in the upper transition temperature at higher fructose contents is probably at least partially due to retrogradation in the samples stored at 85% RH, which is greatest for the samples containing the most fructose (the maximum crystallinity detected by X-ray was 9·7%, but most samples contained much less than 5%, which may result in an increase in T_g of about 10–15°C at the higher water contents (Kalichevsky *et al.*, 1992*a*); the samples stored at 12% RH were amorphous at all fructose contents).

At this water content a lower temperature transition is observed at all fructose contents, which becomes the dominating transition at about 25–33% fructose. Again, the temperature of the low-temperature transition does not change with fructose content and appears only 1–7°C higher than might be expected for fructose at this water content.

Three-point bend test

We have previously studied amylopectin and amylopectin + fructose in the ratio 2:1 by the three-point bend test method (Kalichevsky *et al.*, in press). We here extend this to a sample containing 50% fructose (dry basis) and the moduli obtained are plotted in Fig. 7, with the results obtained previously for comparison. A glassy plateau modulus is not obtained at room temperature for the samples containing 50% fructose, although these samples begin to snap sharply at 12% RH (8·5% aq.). The modulus of this sample is clearly much lower than for the other samples, except at the higher water contents. Above 17% aq. these

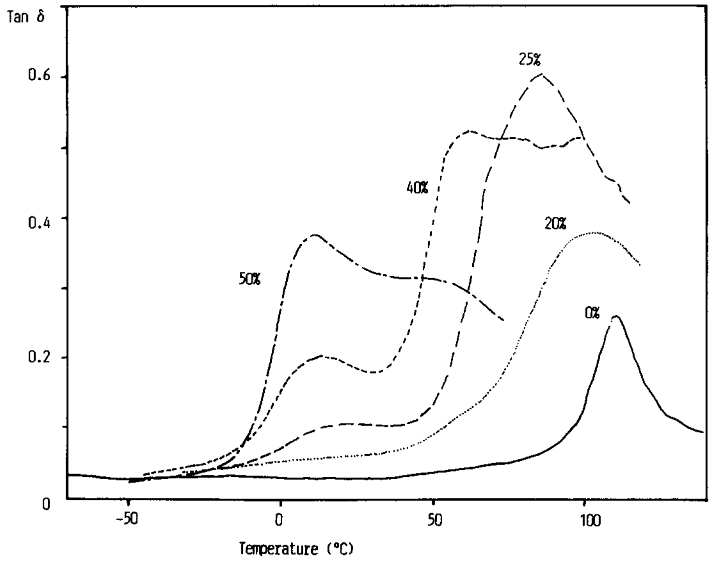

Fig. 5. DMTA tan δ as a function of temperature, for samples containing 0–50% fructose, stored at 12% RH (containing 7–10% water).

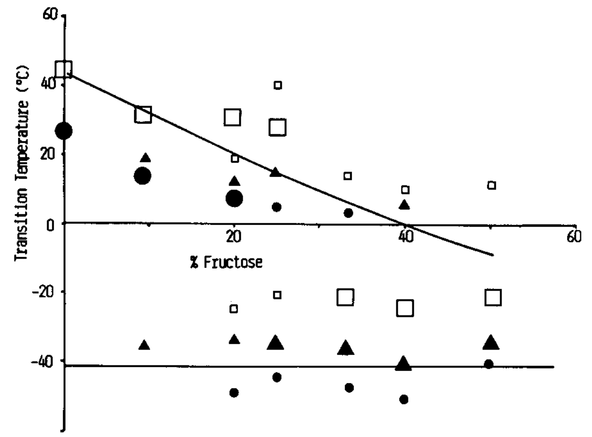

Fig. 6. DMTA transition temperatures as a function of fructose content at 18% aq. (symbols as used in Fig. 2).

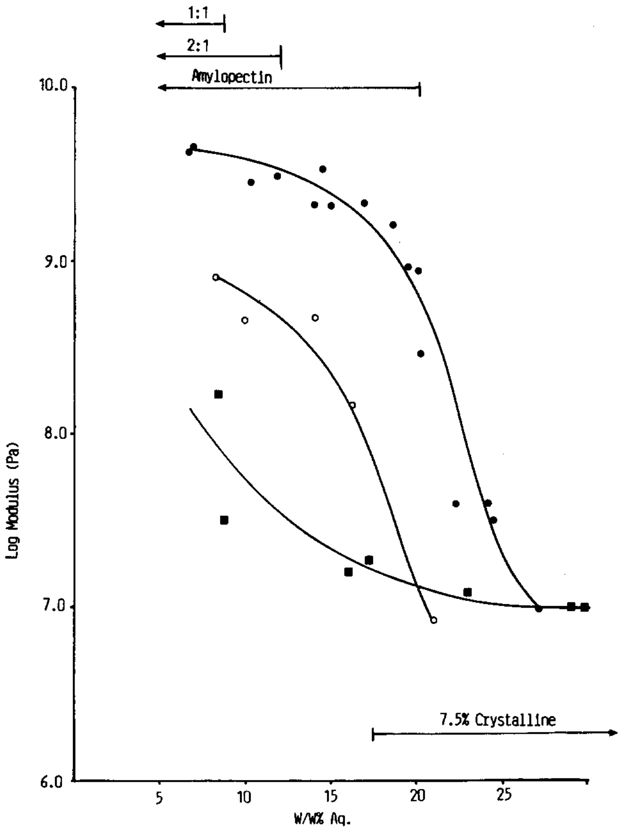

Fig. 7. Three-point bend test modulus data for amylopectin (●), amylopectin + 33% fructose (○) and amylopectin + 50% fructose (■). The arrows indicate the water contents below which the samples break rather than bend. (The former two sets of data were published previously in Kalichevsky *et al.*, in press.)

samples were approximately 7·5% crystalline by X-ray, due to retrogradation of the amylopectin component on storage, which is the reason for the enhanced rubbery modulus. At the lowest water contents the samples were amorphous. The water content at which the samples snap rather than bend is indicated for the three samples (occurring at and below 92% RH for amylopectin and 43% RH for amylopectin + fructose 2:1). This is clearly also dependent on fructose content (being related to T_g). The maximum force to breaking or yielding was much greater for amylopectin alone than in the presence of sugars, which appear to make the samples more brittle.

Do these results imply phase separation?

It could be argued that the presence of a transition in the region of the T_g of fructose as well as a higher temperature transition implies phase separation of the fructose. As discussed in the Introduction, we believe that this is not necessarily the case. Clearly, the broadening of the transition shown in Fig. 5 indicates some degree of sample heterogeneity, which is probably due to the limitations of the sample preparation method. However, the high degree of plasticization of amylopectin by fructose observed does indicate a high degree of compatibility. If the predictions of the Couchman-Karasz equation are to be relied on, it could be argued that, where these predictions fail, some degree of phase separation is occurring, so that not all the fructose present is having a plasticizing effect on the starch.

CONCLUSION

In general, the effect of fructose on the T_g of amylopectin is greatest at lower water contents, as predicted, due to the greater volume fraction of fructose at reduced water content. Due to its low molecular weight, the plasticizing effect of water dominates the effect of fructose as the water content is increased. A mechanical relaxation, observed somewhat above the T_g of fructose in most of the samples, is not necessarily thought to imply phase separation of fructose and amylopectin, although phase separation may be occurring in some samples. As the fructose content is increased the mechanical behaviour becomes dominated by the lower temperature glass transition of the fructose. This is also shown by a three-point bend test.

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