Carbohydrate Polymers **18** (1992) 77—88

The glass transition of amylopectin measured by DSC, DMTA and NMR

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(Received 30 October 1990; revised version received 13 July 1991; accepted 15 July 1991)

The glass transition in amorphous amylopectin derived from waxy maize starch, and containing between 10 and 22% water, has been studied using differential scanning calorimetry, dynamic mechanical thermal analysis, the Instron texturometer and nuclear magnetic resonance (both pulsed and solid state NMR). The plasticizing effect of water broadly follows the predictions of the Couchman–Karasz equation. The results of the different techniques are compared and the effect of 2-11% crystallinity on the glass transition is investigated.

INTRODUCTION

Starch is a storage polysaccharide in plants which, in the native form, is ordered in partially crystalline granules (crystallinity ~24% by X-ray in the case of waxy maize starch). Starch usually has two major components, largely linear amylose consisting of α-(1 → 4)-linked D-glucose and amylopectin, having the same backbone as amylose but with myriad α-(1 → 6)-linked branch points. So-called waxy starch, however, consists almost solely of amylopectin.

Over the past two decades, the phase transitions associated with ordering/disordering processes in starch systems, e.g. the gelatinization of the starch granule, have been intensively investigated. More recently, attention has turned to the glass transition. Studies of the glass transition in starch have largely concentrated on the use of differential scanning calorimetry (DSC) which has accompanied a debate centred on the role of the glass transition in native starch, which is a highly non-equilibrium system. Biliaderis *et al.* (1986) have proposed a three-phase model to account for the observed thermal behaviour. These phases are: (i) the amorphous regions, giving rise to a heat capacity change (ΔC_p) at the glass transition temperature (T_g), (ii) the crystalline regions and (iii) the intercrystalline material. The intercrystalline material does not contribute to the ΔC_p observed at T_g as it is motionally restricted by its proximity to crystalline regions. A similar model has been advocated for synthetic polymers (Ellis *et al.*, 1984).

Biliaderis *et al.* (1986) and Slade and Levine (1988) believe that the increased heat capacity observed after starch gelatinization (swelling and melting of crystallites on heating in the presence of water) is due to the glass transition occurring immediately prior to the gelatinization. Zeleznak and Hoseney (1987) have explained the ΔC_p observed as being due to granule swelling and the initiation of crystallite melting, and have reported a glass transition (ΔC_p) at lower temperatures in native wheat starch. This T_g decreases with increasing water content, due to the plasticizing effect of water.

It has also been noted that a commercially pregelatinized wheat starch gave a lower T_g than the native wheat starch, especially at lower water contents. This appeared to be consistent with observations on synthetic polymers in which T_g increases with increasing degree of crystallinity (e.g. Jin *et al.*, 1984).

More recently, Slade and Levine (1988) have studied systems containing at least 50% water. They explained the fact that T_g is not observed in the same place on rescanning after gelatinization, by the redistribution of water that has occurred, so that the T_g of the system falls below 0°C (to T_g', the T_g of the maximally freeze concentrated system). It is apparent that native starch–water systems are complex, multiphase and non-

Carbohydrate Polymers 0144-8617/92/$05.00

equilibrium in nature, and that there could even be two or more T_gs operating in these systems.

Other work on starch-related systems has concentrated on malto-oligosaccharides and by extrapolation has estimated the dry T_g of amylose and amylopectin to be 500 K (227 °C) and the T_g of these materials at 13% water to be 329 K (56 °C) (Orford *et al.*, 1989). That paper also refers to similar extrapolations by other workers.

In this study amylopectin was investigated in the amorphous and partially crystalline states at a variety of water contents by dynamic mechanical thermal analysis (DMTA) and nuclear magnetic resonance (NMR) as well as DSC, with a view to casting further light on the glass transition in starch and relating these measurements to changes in Young's modulus determined by the Instron texturometer.

EXPERIMENTAL

Sample preparation

Amylopectin was supplied either as waxy maize starch or in the pregelatinized form, by National Starch and Chemical Corporation, Manchester, UK. Different methods of preparation were necessary for these two samples. Initially, waxy maize starch was used. Amorphous samples were prepared by gelatinizing a 50% (w/w) water/starch mixture in a boiling water bath. These samples were subsequently dehydrated by microwave heating, pressed to the desired shape at ambient temperature and cut into bars. An improved method of sample preparation was possible using pregelatinized waxy maize starch. The pregelatinized starch was hydrated to 20–25% (w/w) water in liquid nitrogen. The flat samples of low water content were then prepared by pressing at 20 tons psi ($=3{\cdot}1 \times 10^8$ Pa) for 5–10 min at 90–100 °C. Both of these materials were subsequently cut into bars of size approximately 2 mm × 8 mm × 2 cm. Samples were subsequently hydrated over various salt solutions of specified relative humidity and the water content established by drying in the oven at 105 °C to constant weight.

Varying degrees of crystallinity were obtained by allowing the 50% (w/w) aqueous amylopectin gel to retrograde at 1 °C for 1, 5 and 18 h before drying at room temperature overnight. The samples were then left to equilibrate at various relative humidities. The absolute crystallinity of each sample was in each case determined by X-ray diffraction measurements (Marsh & Blanshard, 1988). Samples of 2, 3·9 and 5·5% crystalline amylopectin were obtained by this method.

Further aqueous amylopectin gels (30–35% (w/w) H_2O) were prepared by pressing pregelatinized starch at 90–100 °C. These were allowed to retrograde before drying and storing under various relative humidities. A sample of 11% crystallinity was prepared in this way.

DSC measurements

Calorimetric measurements were carried out using a Perkin Elmer DSC-2. The results were recorded and analysed by a BBC computer. The temperature was calibrated using the melting points of indium (429·8 K) and cyclohexane II (279·7 K). An empty aluminium pan was used in the reference holder.

The glass transition temperature, T_g, by DSC was determined from the midpoint of the heat capacity change observed at a heating rate of 10°/min.

DMTA measurements

The dynamic mechanical thermal analyzer (Polymer Laboratories, Loughborough, UK) (DMTA) Mark I was normally used with the sample presented in the single cantilever bending mode at a frequency of 1 Hz and a strain ×1. This strain corresponds to a nominal peak to peak displacement of 16 μm. This was the smallest available strain and was chosen because some of these samples were brittle and cracked easily. In addition, it was found that the modulus obtained was somewhat strain dependent. The standard heating rate used was 2 °C/min. Occasionally, a heating rate of 5 °C/min was used, and was found to give the same result, within experimental error.

The glass transition was studied by observing the storage modulus E' and tan δ as a function of temperature as shown in Fig. 1; a sharp decrease occurs in E' accompanied by a peak in tan δ. In synthetic polymers the position of the tan δ peak is used as a convenient definition of the glass transition temperature. It normally falls at a slightly higher temperature than the midpoint of the decrease in E'. The height of the tan δ peak relates quantitatively to the volume fraction of the relaxing phase, and the temperature of the peak increases with increasing frequency as is expected for any thermally activated relaxation process (Wetton, 1986).

In this study the temperature of the tan δ peak and that at which the slope in E' changes were recorded for each sample as shown in Fig. 1. The temperature at which the slope in the modulus changed ($\Delta E'$ slope) was determined from the intercept of the extrapolated line of the initial modulus and of the steepest slope as the modulus rapidly descends. Wherever possible the results from at least three runs were averaged at each water content. In the case of partially crystalline samples, the DMTA results were quite scattered.

Low temperature transitions, below T_g, which are not detectable by DSC, may be detected by DMTA. These may be due to the onset of short range motions, whereas the glass transition is the onset of main chain motion.

Measurements were also made at a variety of frequencies from 1 to 30 Hz by DMTA and on the same

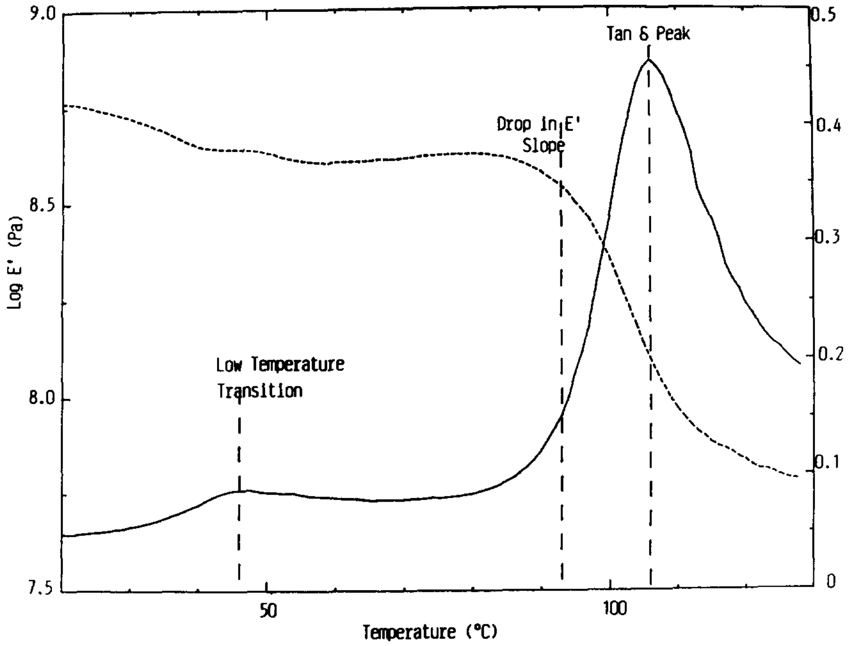

Fig. 1. A typical DMTA T_g plot for amorphous amylopectin.

sample using DETA (dielectric thermal analyser) at Polymer Laboratories, which allowed measurements at the frequencies of 1, 5 and 10 kHz.

NMR relaxation measurements

Relaxation measurements were carried out on a 60 MHz NMR spectrometer constructed in these laboratories with a Varian 1·4 Tesla magnet. Samples (generally amorphous or partially crystalline powders) were placed in a 7 mm o.d. tube. A 90° pulse of 8 μs length was applied to the system; the repetition rate was 1 s; 16 transients were co-added. The decay time was measured directly from the free induction decay (FID), which consists of 1024 points. The data were analysed by a BBC microcomputer, interfaced with the NMR spectrometer.

The temperature range in T_2 experiments was from −80 °C to +100 °C. The temperature of the sample was measured with a thermocouple with an accuracy of ±1 °C. The sample was allowed to equilibrate at a given temperature for 5 min, after which the measurement was made.

CP-MAS experiment

Spectra were obtained on a Bruker CXP 300 NMR spectrometer equipped with a wide bore Oxford Instruments superconducting magnet and a Bruker double bearing MAS probe.

The spectrometer was operated at a frequency of 75·44 MHz. The sample spinning speed was 4 kHz. Spectra were acquired using the standard Bruker pulse program CPCYCLE, using a ^{13}C pulse width of 4·4 μs and a ^{1}H pulse width of 9 μs; the contact time was 1 ms and spectra were typically produced from an average of 2000 transients.

Determination of the static elastic modulus (E) by the Instron texturometer

The static elastic (Young's) modulus was determined by a three-point bend test (Faubion & Hoseney, 1982) using an Instron texturometer. The samples were prepared from hydrated (15–30% (w/w) H_2O), pregelatinized waxy maize starch pressed at 90 °C at 20 tons psi ($1{\cdot}4 \times 10^3$ Pa) to form a 'glassy', transparent sheet approximately 2 mm thick. Strips were prepared of width 8 mm and at least 30 mm long. A cross-head speed of 50 mm per minute was employed.

RESULTS

Amorphous amylopectin

DSC and DMTA

DSC scans of amorphous amylopectin are shown in Fig. 2. Figure 2a shows that the temperature of the higher temperature transition is very dependent on water content while that of the lower temperature transition is much less so. Figure 2b shows that the glass transition can be observed immediately after rescanning, whereas the 'low temperature transition' is observed on the first run and thereafter only after storage. The origin of the peak at ~50 °C (low temperature transition) is uncertain. It was first thought to be a lipid melting transition, but waxy maize starch contains relatively little lipid (0·14%; Tan &

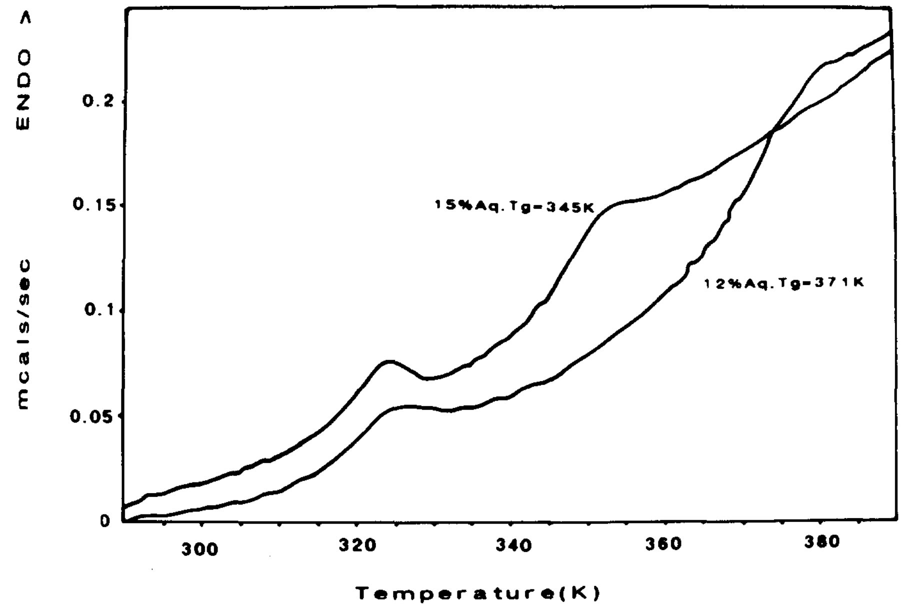

Fig. 2a. Two DSC runs, each showing a low temperature transition and T_g at two different water contents (15% and 12% Aq.).

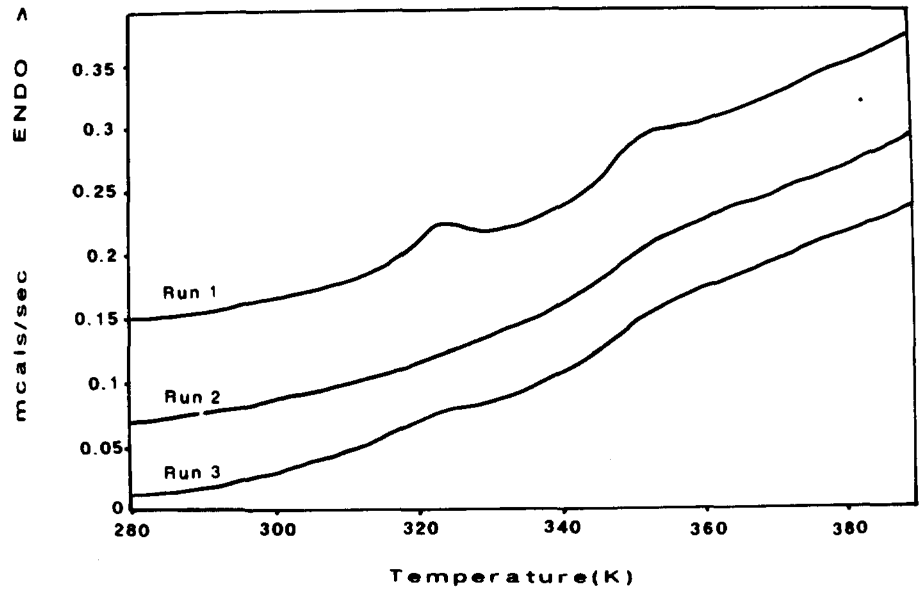

Fig. 2b. Three DSC scans of one sample of amorphous amylopectin containing 15% water. Run 2 is an immediate rescan after cooling at 10°C/min and run 3 is a rescan after the same sample has been left at room temperature overnight.

Morrison, 1979). Additionally the peak size appears to be proportional to the water content, which is the opposite to what would be expected if it were due to lipid. The origin of this peak is under further investigation. The amylopectin T_g by DSC, as a function of water content, is plotted in Fig. 3.

Figure 4 contains the DMTA results for amorphous amylopectin (the variation of the positions of the tan δ peak, the change in slope of the modulus (E') and the low temperature tan δ peak). The DSC results from Fig. 3 are also included for comparison.

There is approximately a difference of 20° between the onset of a drop in the modulus ($\Delta E'$ slope) and the tan δ peak. The T_g values determined by DSC, shown in Fig. 3 and as a dashed line in Fig. 4, fall between these two values, perhaps being slightly closer to the values obtained from the change in slope of E' by DMTA. The DSC T_g would be expected to be at a lower temperature than the tan δ peak as it is effectively a static technique, whereas the tan δ peak is obtained at a frequency of 1 Hz.

Low temperature transitions were also recorded. A low temperature transition frequently observed by DMTA was found to be plasticized by water in the same way as the main transition. An endothermic transition was consistently observed by DSC in the drier samples at 50°C but its temperature was not

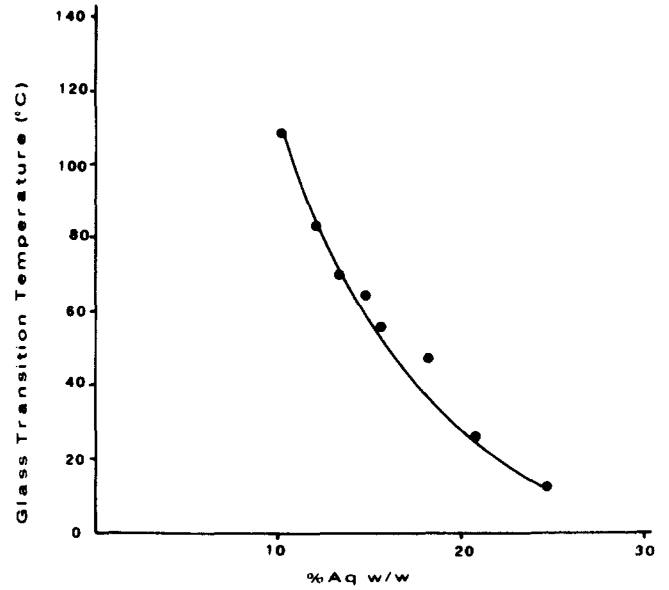

Fig. 3. Graph of DSC T_g for amorphous amylopectin as a function of water content.

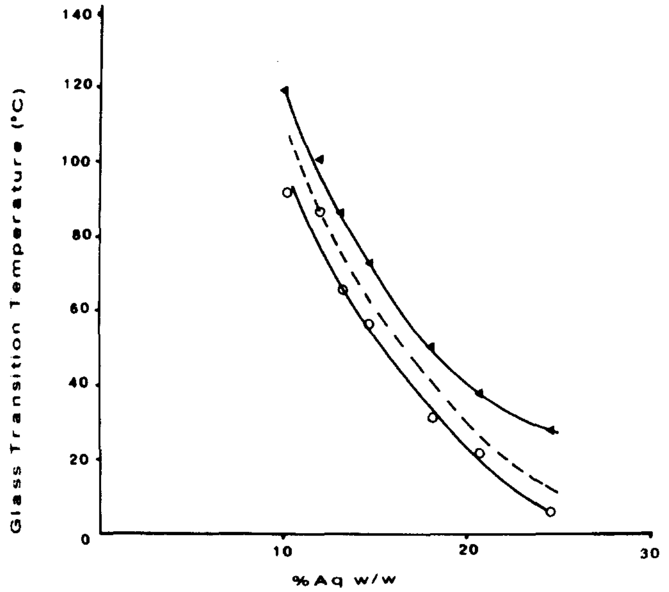

Fig. 4. DMTA tan δ peak (▲) and change in E' slope (○) as a function of water content. The DSC curve is drawn for comparison (- - -).

influenced by water content, therefore it is assumed that the origin of these transitions is different.

The effect of frequency on the tan δ peak temperature was studied by DMTA using a range of frequencies from 1 to 30 Hz. A sample at RH 85% was also studied using DETA (dielectric thermal analysis, kindly made available by Polymer Laboratories), at frequencies of 1-10 kHz. The tan δ peak temperature was found to increase with increasing frequency as was expected. When log frequency was plotted against $1/T$ (an Arrhenius plot) there appeared to be a good agreement

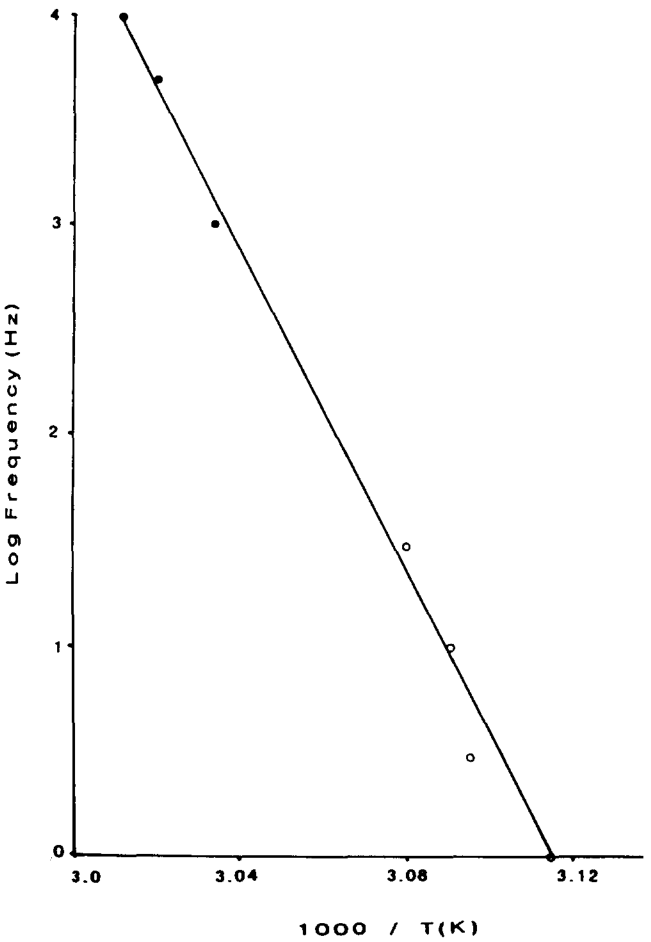

Fig. 5. Arrhenius plot of DMTA (○) and DETA (●) log measurement frequency against inverse tan δ peak temperature.

iin the frequency dependence of tan δ between DETA and DMTA measurements (Fig. 5).

Values of the Arrhenius activation energy by DMTA varied between 300 and 740 kJ/mol with no definite dependence on water content. Glass transition processes generally have high activation energies indicating a large degree of segmental mobility (Rials & Glasser, 1988) and a high degree of co-operativity (Starkweather, 1988).

Nuclear magnetic resonance

Pulsed NMR. The typical decay obtained from samples after the application of a 90° pulse is of the form shown in Fig. 6. The decay obviously had two components which could be fitted reasonably well by the superposition of Gaussian and Lorentzian curves of the form:

$$h = h_R \exp(-t^2/2T_{2R}) + h_M \exp(-t/T_{2M})$$

where h is the signal intensity at time t and h_R and h_M are proportional to the number of protons in the 'rigid' and 'mobile' states, respectively. T_{2M} is the spin-spin relaxation time for the mobile component while T_{2R} is

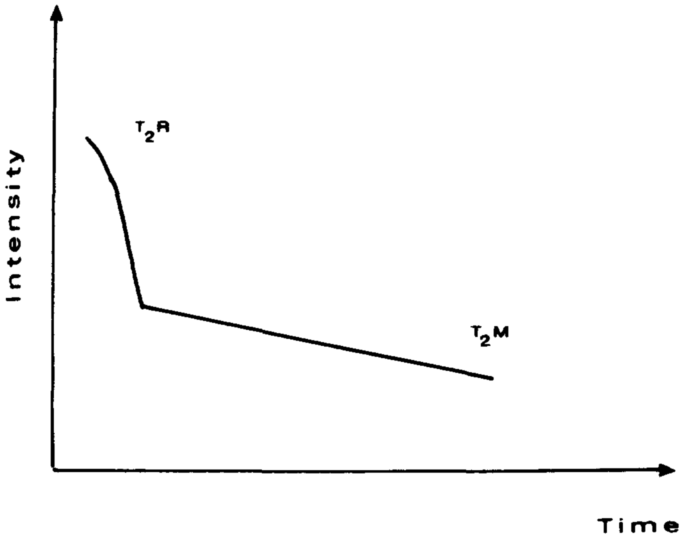

Fig. 6. Typical two-component decay after application of a 90° pulse to an amylopectin/water sample in the glassy state.

the relaxation time related to 'rigid' Gaussian component.

The first part of the decay is ascribed to solid polysaccharide protons in the glassy or partially crystalline states. These protons provide information on the changes in the mobility of the main chain. Below T_g the two phases (i.e. amorphous glass and crystalline) are indistinguishable in this type of NMR experiment.

The second part of the decay is ascribed to protons of reduced mobility water plus exchangeable protons of the polysaccharide. Due to inhomogeneities of the magnet, this simple experiment will not provide any information on the degree of the mobility of the water.

The general temperature dependence of the decay times is shown in Fig. 7. At low temperatures below T_g, T_{2R} spin–spin relaxation is independent of temperature and has a value of approximately tens of μs, typical of rigid lattice behaviour. After passing through the rigid lattice limit (RLL), T_{2R} begins to increase with temperature. This increase in the T_{2R} with temperature is attributed to the onset or increase in frequency of the motion of groups containing hydrogen.

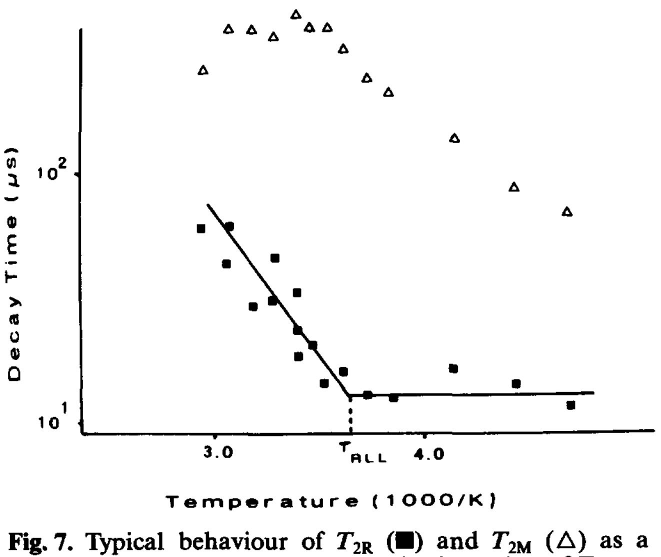

Fig. 7. Typical behaviour of T_{2R} (■) and T_{2M} (△) as a function of inverse temperature in the region of T_g.

The variation of the RLL, determined by NMR for several samples of amylopectin of different moisture contents over a wide temperature range, is shown in Fig. 8 and is compared with the results by DSC.

CP-MAS NMR. CP-MAS NMR spectra of amylopectin with different water contents run at 20 °C show clear signs of changes with water contents of >17·5% (Fig. 9), for example, the disappearance of the signal at 82 ppm characteristic of amorphous amylopectin. At 23·3% H_2O, the C-1 signal at 100 ppm shows evidence of a triplet multiplicity, characteristic of the A-amylose structure as shown by Gidley and Bociek (1988). Such structure is what ought to be expected when reorganization occurs at that water content.

Comparison with the plots of T_g versus water content as determined by NMR (RLL), DSC and DMTA suggest that the CP-MAS results coincide most closely with those of the NMR (RLL). Although the CP-MAS NMR technique is primarily concerned with the determination of order, whereas the NMR (RLL) method explores molecular dynamics, it is important to remember that the CP-MAS NMR technique records ordering on an atomic scale, i.e. the organized disposition of valency bonds, and does not require the development of domains of organized molecules as is necessary where X-ray diffraction is employed.

Instron

The results of the three-point bend tests which were carried out at room temperature on a series of amorphous amylopectin samples containing 5–30% water are plotted in Fig. 10. The Young's modulus was calculated from the initial slope of the force versus deformation trace after taking note of the sample dimensions. Each point on the graph corresponds to the average of at least three samples equilibrated at a particular RH.

The values of Young's modulus obtained by an Instron three-point bend test are thought to be more accurate than those obtained by DMTA as the DMTA result is very dependent on the accurate measurement of the sample dimensions and sample presentation. Also, end corrections were not taken into account. The values of Young's modulus at 20 °C by DMTA were compared with the Instron DMTA results. The same qualitative changes with changing water content were observed by both techniques, but the modulus values from the Instron were higher by a maximum of 3·6 Pa (~6% of the log value). This difference may be partially due to the higher strain rate used in the three-point bend test.

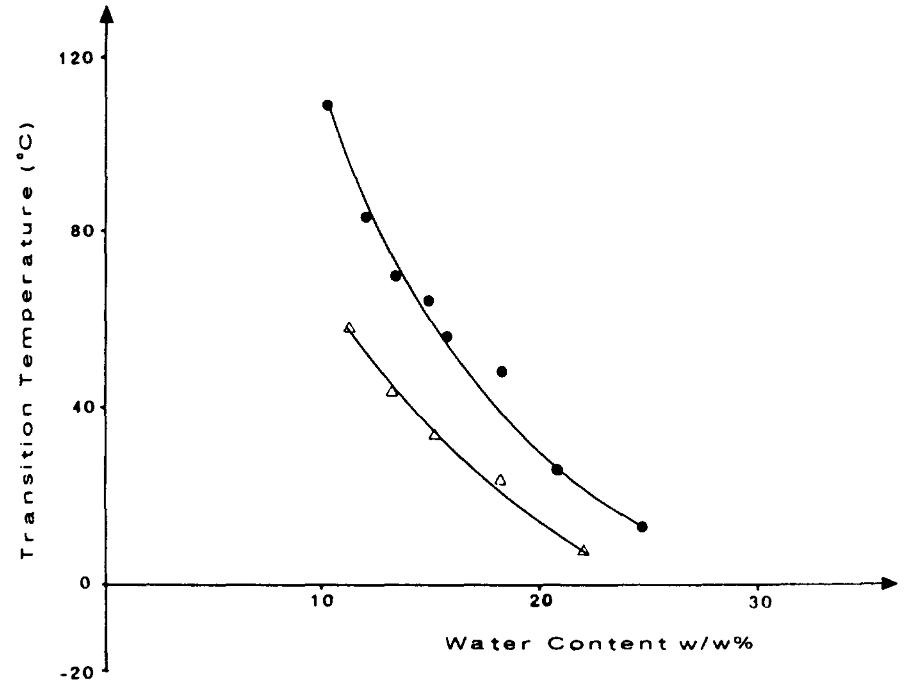

Fig. 8. NMR RLL (△) and DSC (●) transition temperatures for amorphous amylopectin as a function of water content.

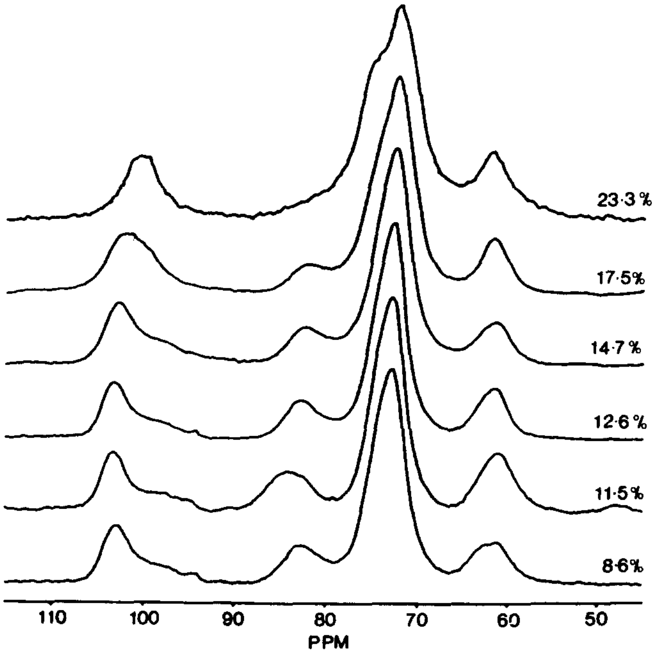

Fig. 9. CP/MAS spectra of amylopectin at various moisture contents.

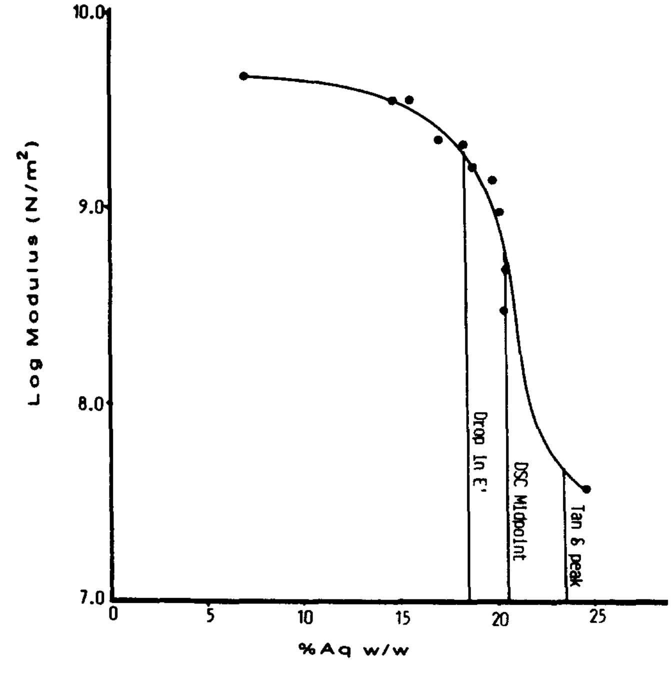

Fig. 10. Young's modulus as a function of water content at room temperature as measured by an Instron three-point bend test.

Partially crystallized amylopectin

DSC and DMTA

Initially, samples were prepared from native waxy maize starch gelatinized at 90–100°C and allowed to retrograde. By this method, samples of 2, 4 and 5·5% crystallinity were obtained (as determined by X-ray). Both DSC and DMTA became more difficult with increasing crystallinity, as the samples became increasingly brittle and the glass transition became broader and less easy to observe by DSC.

The results obtained for the 5·5% crystalline sample were too scattered and uncertain for any conclusions to be drawn. The 2% crystalline sample gave similar DMTA results to those obtained for amorphous

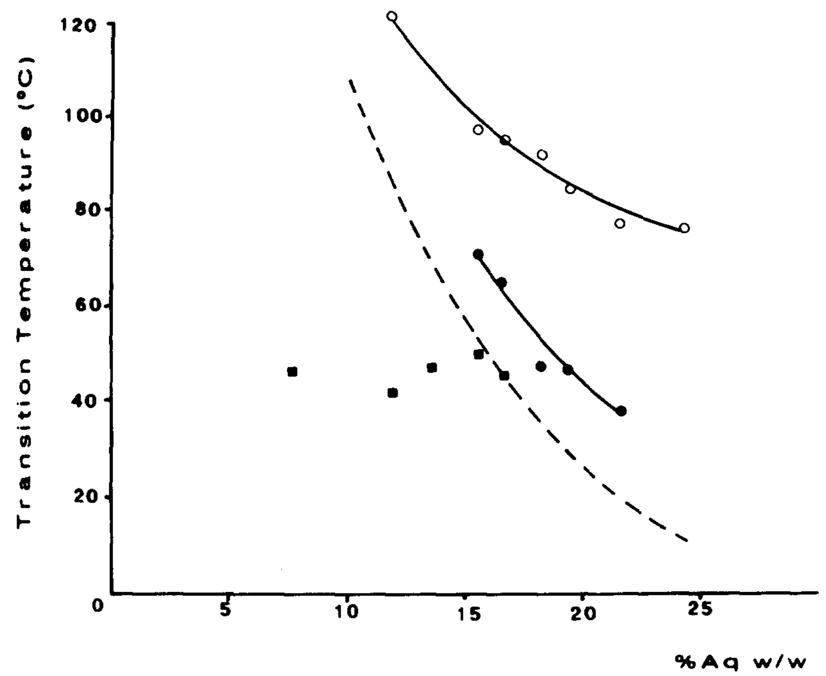

Fig. 11. Summary of DSC results for 4% crystalline amylopectin as a function of water content. Melting point (○), T_g midpoint (●), low temperature transition (■).

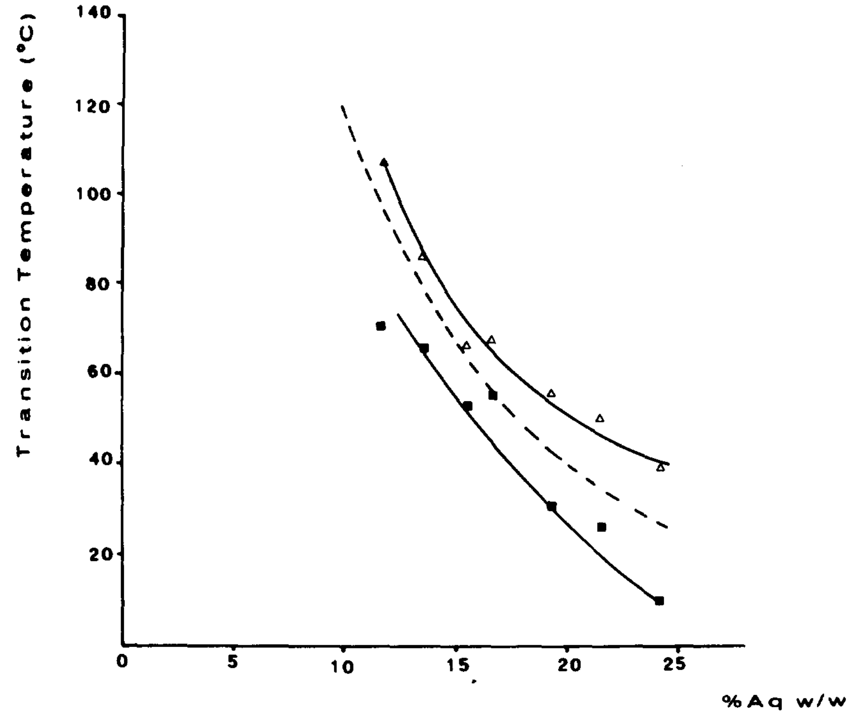

Fig. 12. Summary of DMTA results for 4% crystalline amylopectin as a function of water content. Tan δ peak (△), drop in elastic modulus (■).

amylopectin. There was a possible slight increase in the DSC T_g of 4°C.

The 4% crystalline samples gave more interesting results. The DSC results are plotted in Fig. 11 and show an apparent increase of 13°C in T_g. The DMTA tan δ peak temperatures for the main and low temperature transition also appeared to be shifted to higher temperatures, by about 10°C (Fig. 12).

After these experiments were carried out, an improved sample preparation method was developed using pregelatinized waxy maize starch. (This allowed samples to be prepared at lower moisture content.) The

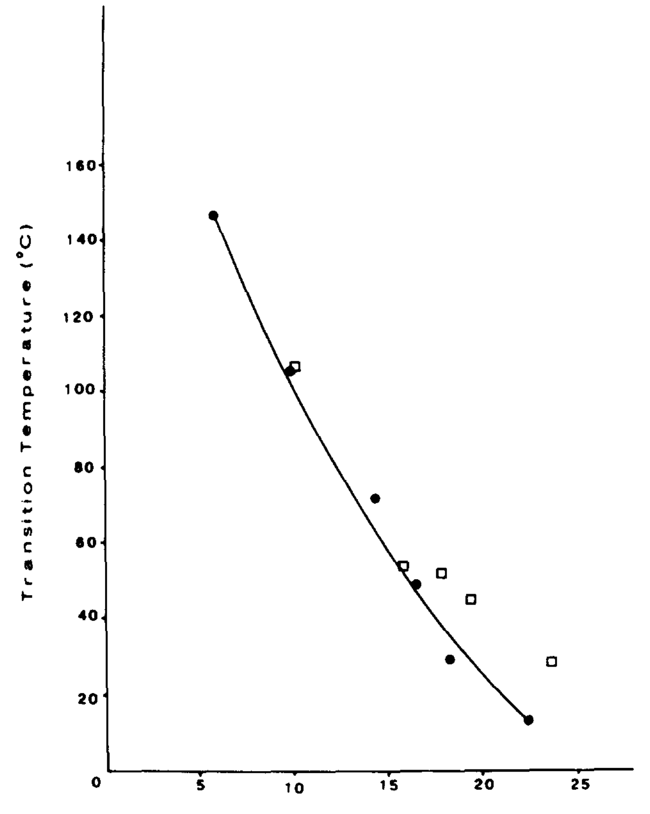

Fig. 13. DSC T_g for amorphous (●) and 11% crystalline (□) amylopectin as a function of water content.

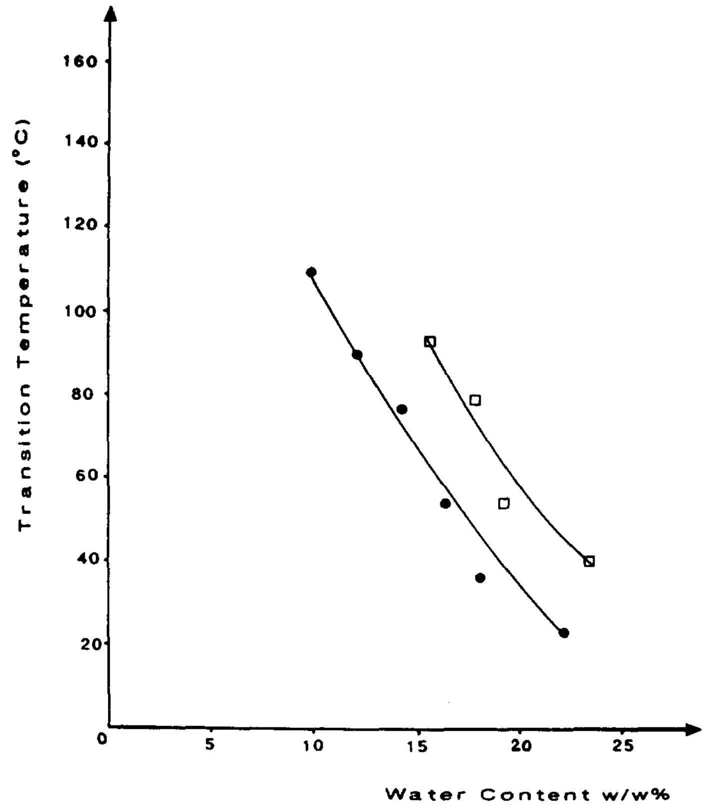

Fig. 14. Variation of temperature of maximum in DMTA tan δ peak for amorphous (●) and 11% crystalline (□) amylopectin as a function of water content.

glass transition of an amorphous sample as measured by DMTA and DSC was similar to the results obtained by the other method, but was 4–10 °C lower. The difference may be due to the presence of some residual granular structure in samples prepared from native starch. These results were compared with those for 11% crystalline amylopectin. The DSC results (Fig. 13) show an increase in T_g of 3–18 °C, the difference being greatest at high water contents. The DMTA $\Delta E'$ values are scattered and very difficult to determine and therefore no conclusions are drawn from these. The tan δ peak temperature shows a 14–35 °C increase for the 11% crystalline sample and varies with water content in similar fashion to the DSC results. The DMTA results are plotted in Fig. 14.

NMR

Spin–spin relaxation times were measured as a function of temperature (−60 °C to 100 °C) as before. The RLL was found to depend, as expected, on water content and also on the degree of crystallinity. The presence of crystallinity, which introduces extra stiffness in the chain, caused the RLL to move to higher temperatures by 25–30 °C (Fig. 15). There was no difference between the NMR response of 2%, and 4% crystallinity in amylopectin, but a significant difference between 0 and 2% crystallinity.

DISCUSSION

Comparison of values for T_g determined by different techniques

The rigid lattice limit (RLL) determined by pulsed NMR usually occurs at a temperature of approximately 20–30 °C lower than the T_g measured at the median point of the specific heat change monitored by DSC. In practice, the RLL usually occurs some 10–20 °C below the change in slope of the modulus. The maximum in tan δ, on the other hand, is found at some 10 °C above the DSC T_g midpoint. Overall, therefore, various techniques indicate significant changes in molecular mobility and state, all of which might reasonably be referred to as a glass/rubber transition. By that we are not inferring that there is a multiplicity of transitions but that the techniques are sensitive to different degrees of molecular mobility. These results reflect the fact that the glass transition is not observed at a unique temperature, but is related to the frequency and nature of the measurement technique.

The dependence of the tan δ peak temperature on frequency for DMTA and DETA results has been shown in Fig. 5. Thus, for these techniques, increasing the measurement frequency increases the tan δ peak temperature as predicted. The DSC midpoint temperature

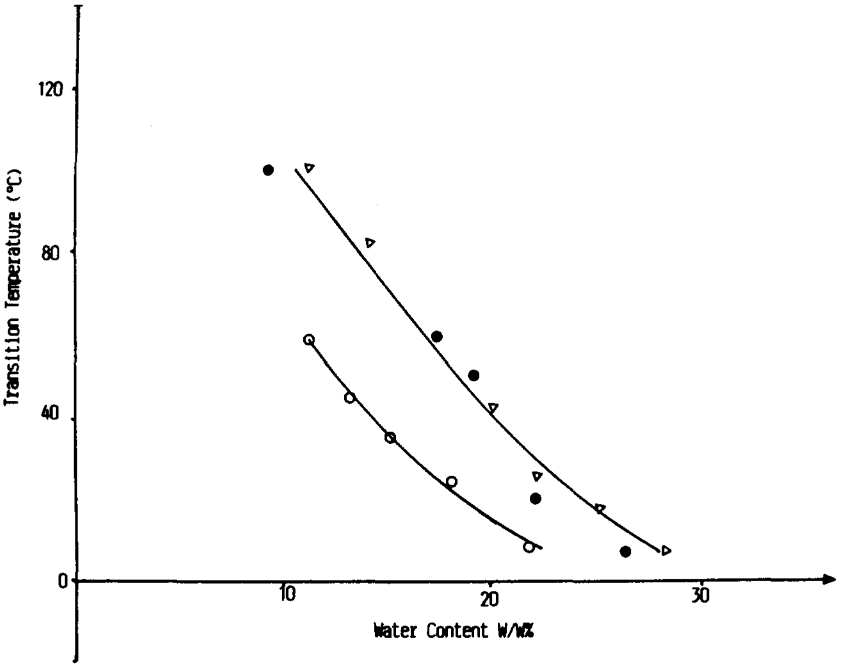

Fig. 15. NMR RLL for 2% (●) and 4% (△) crystalline amylopectin as a function of water content as compared with 0% crystalline amylopectin (○).

depends on the heating rate used, as it is a kinetically determined transition. At a heating rate of 10 K/min the DSC midpoint corresponds to a longer relaxation time or lower frequency measurement than by DMTA and as such is expected to give a lower transition temperature than the tan δ peak, as observed.

The pulsed NMR RLL measurement may occur at a lower temperature than T_g measurements by other techniques, as it is probing a much lower mobility distance scale. DSC and DMTA observe a transition when the main chain or substantial proportion of the sample has an increased mobility, whereas NMR is looking at the mobility of protons.

It is obviously important to establish what is the relation of such results to the commonly perceived change from the rigid, highly brittle glassy state to the more elastic rubbery state. The results obtained from a direct measurement of the Young's modulus (*E*) for varying water contents are an excellent indication of such a phenomenon. Figure 10 shows how *E* varies with water content at 20 °C. In addition, the values of water content which give rise to the transition at 20 °C determined by, DSC and DMTA (change in slope of *E'* and tan δ peak) are indicated.

Undoubtedly, the oral and manual perception of the T_g for such a sample is at a water content of 21% (w/w). It is therefore interesting that events which contribute to the glass transition and are monitored by different techniques occur over some 40–50 °C in the biopolymer system under consideration. This may be of importance to a fuller understanding of the stability of food materials in the region of the glassy/rubbery transition.

The effect of partial recrystallization

From the DMTA results it appears that the presence of crystallinity broadens the glass transition region and particularly increases the tan δ peak temperature. The increasing breadth of the transition and the greater difficulty in determining T_g by DSC may be explained by the more heterogeneous nature of the sample, namely a mixture of crystalline and amorphous regions. The rapid reduction in DSC ΔC_p at T_g with increasing crystallinity has been observed and explained by many workers in starch and synthetic polymers (e.g. Biliaderis *et al.*, 1986; Cheng *et al.*, 1990) by the presence of a rigid amorphous fraction which does not contribute to ΔC_p. The contrast between the NMR and DSC/DMTA results for this system is interesting. The DSC/DMTA results seem to suggest a continuously increasing T_g with increasing crystallinity, whereas NMR shows an initial difference between the amorphous and 2% crystalline samples, but no significant difference between 2 and 4% crystalline samples. The explanation for this may be that NMR looks at short range mobility whereas DMTA and DSC look at larger scale effects. This suggests that short range changes occur which cannot be detected by X-ray. It is also possible that the increase in X-ray crystallinity may be due to crystal growth rather than an increase in the number of crystallites. This may be investigated further by X-ray scattering (low angle studies and/or Debye Scherrer measurements).

The study of partially crystalline systems may give some understanding as to why it is difficult to measure

T_g in native starch. In the low water starch systems that have been examined in this work, the system becomes progressively heterogeneous with increasing crystallinity and the determination of the T_g by any of the above physical methods becomes more problematical. It is somewhat surprising, therefore, that Zeleznak and Hoseney (1987) were able to measure T_g for native wheat starch when this is approximately 20% crystalline. Their success may be due to the more ordered nature of granular starch in comparison to retrograded (recrystallized) starch.

Comparison with theoretical predictions

Although the most commonly used theory to account for the effect of plasticizer upon the glass transition temperature is the free volume approach, the more recent application of classical thermodynamics by Couchman and Karasz (1978) to explain the glass transition of polymer mixtures is more appropriate to the calorimetric techniques used in this paper. Ten Brinke *et al.* (1983) adopted the Couchman and Karasz model to describe the effect on T_g of polymer/diluent mixtures. The equation predicted is of the form:

$$T_g = \frac{W_1 \Delta C_{p_1} T_{g_1} + W_2 \Delta C_{p_2} T_{g_2}}{W_1 \Delta C_{p_1} + W_2 \Delta C_{p_2}}$$

where

T_{g_1} is the glass transition temperature of diluent
T_{g_2} is the glass transition temperature of the polymer
ΔC_{p_1} is the change in heat capacity at T_{g_1}, equal to 1·94 J/g per K for water
ΔC_{p_2} is the change in heat capacity at T_{g_2}, equal to 0·47 J/g per K for starch (Orford *et al.*, 1989)
W_1 is the weight fraction of diluent
W_2 is the weight fraction of polymer

Figure 16 shows how the NMR and DSC results for amorphous waxy maize amylopectin correlate with the calculated curves for starch, using van den Berg's (1981) theoretical value for dry starch (424 K) and an extrapolated value of 500 K (Orford *et al.*, 1989). The curve calculated using $T_g = 424$ K falls well below the experimental results for both NMR and DSC, the deviation being much larger for DSC results. However, if a value for the T_g of amylose of 500 K which was derived by Orford *et al.* (1989) by a process of extrapolation is used instead, the experimental curve for DSC/DMTA fits the theoretical curve very well but the NMR results lie on average about 30 °C below.

Comparison with previous measurements of T_g of starch

The glass transition temperature (T_g) obtained by DSC for waxy maize amylopectin is higher at a given water content than the values obtained by Zeleznak and Hoseney (1987) for pregelatinized wheat starch. Preliminary work on extruded wheat starch in this laboratory has also indicated that wheat starch has a lower T_g than waxy maize amylopectin. The presence of 25% linear amylose in wheat starch might be expected to increase the T_g of that system. In practice the opposite was found. It is more likely that the structure of the amylopectin which varies between starch sources is responsible, wheat amylopectin

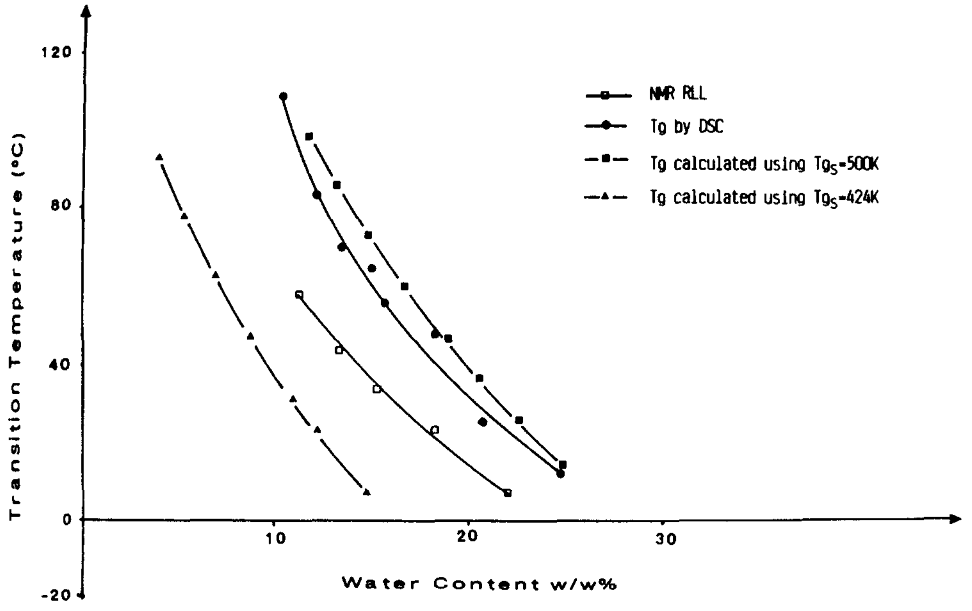

Fig. 16. NMR RLL and DSC T_g of amorphous amylopectin compared with two theoretical T_g curves as a function of water content.

having shorter and more numerous side chains than the amylopectin of waxy maize. Such chains will have a plasticizing effect (i.e. reduce the T_g of the system).

CONCLUSION

The wide temperature range over which glass transition related phenomena may be observed in amylopectin/water systems suggests that the temperatures controlling diffusion of volatiles, reorientation of polymer chains, or mechanical perception of glassiness may not be the same. Increasing crystallinity appears to enhance the heterogeneity and brittleness of amylopectin, so that the glass transition is less well defined; this may also have an effect on product quality.

ACKNOWLEDGEMENTS

MTK and EMJ warmly acknowledge the financial support of the industrial members of the ACTIF (Amorphous Crystalline Transitions in Food) Research Club and the MAFF (Ministry of Agriculture, Fisheries and Food). The authors have greatly appreciated stimulating discussions with Drs Louise Slade and Harry Levine.

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