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Phase and glass transition behaviour of concentrated barley starch–glycerol–water mixtures, a model for thermoplastic starch

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The effects of glycerol and water content on the thermal transitions of plasticized barley starch were examined using differential scanning calorimetry. The glycerol contents studied were 14, 20, 29 and 39% and the water content, obtained by conditioning in different relative humidities, varied in the range 1–28%. On the basis of the observed calorimetric glass transition temperatures and corresponding heat capacity increments it was inferred that a single phase system occurred at low water and glycerol contents, while in other cases phase separation occurred and the system was composed of starch-rich and starch-poor phases. Dynamic mechanical thermal analysis on a phase-separated sample showed mechanical loss peaks corresponding to the glass transitions of both phases. Amylopectin crystallization did not occur within 1 week of storage in mixtures having less than 20% water, indicating that glycerol interacted with starch, inhibiting crystallization of amylopectin. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The biodegradability and material properties of starch make it a promising raw material for the compounding of a thermoplastic polymer from a renewable source. Under the action of high temperature and shear, starch can be processed into a mouldable thermoplastic, a material which has come to be known as thermoplastic starch (TPS) (Shogren *et al.*, 1992; Shogren, 1992; Sala & Tomka, 1993). During processing, the semi-crystalline structure of starch and its granular form are lost and the starch polymers are partially depolymerized. If water is the only plasticizer used the resulting product is brittle when equilibrated with ambient humidity, similar to an extruded ready-to-eat breakfast cereal, whereas in the presence of other plasticizers, e.g. glycerol, a rubbery material can be prepared.

The glass transition temperature (T_g) is the most important parameter in determining the mechanical properties of amorphous polymers. It can also control the rates of kinetic processes such as recrystallization (Zeleznak & Hoseney, 1986) and physical aging (Hutchinson, 1995). The T_g of dry starch is experimentally inaccessible due to thermal degradation of starch polymers at elevated temperatures (Noel *et al.*, 1990). Based upon extrapolation of the glass transition temperatures of malto-oligosaccharides with different degrees of polymerization the T_g of dry amylopectin and amylose was estimated to be approx. 230°C (Orford *et al.*, 1989).

The plasticization of starch by water has been demonstrated through the decrease in the T_g of native and amorphous wheat starch (Zeleznak & Hoseney, 1987) and amorphous and partially recrystallized waxy maize starch (Kalichevsky *et al.*, 1992). The plasticization of starch by low molar mass carbohydrates has also been studied. Sucrose, glucose, xylose and fructose were found to plasticize waxy maize starch in the presence of water and the degree of plasticization increased with the decrease of the T_g of the pure amorphous sugar (Kalichevsky *et al.*, 1993). At low sugar contents the components were miscible but at higher sugar contents (e.g. starch–sugar ratio of 2:1) the occurrence of mechanical transitions at two different temperatures suggested immiscibility and

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phase separation. The effects of fructose and water content on the dynamic mechanical properties of waxy maize starch–fructose–water mixtures was investigated in more detail (Kalichevsky & Blanshard, 1993). In most cases two transitions were detected and it was concluded that the plasticizing effect of fructose was greatest at low water contents and that at high fructose content the mechanical properties were dominated by the lower temperature transition.

The plasticizing effect of other plasticizers, for example, glycerol, on starch polymers has not been thoroughly investigated. It has been reported that glycerol can drastically reduce the T_g of starch (Sala & Tomka, 1992, 1993). In addition to glycerol, glycols and urea have been shown to plasticize corn starch (Shogren *et al.*, 1992). In this study the effects of glycerol and water content on the thermal transitions of plasticized barley starch were studied in order to elucidate starch–glycerol interactions and to examine the relationship between the glass transition and the mechanical properties of a model thermoplastic starch. This builds on an earlier preliminary publication which reported a study of the effects of aging on the large strain tensile properties of these mixtures and a relatively limited calorimetric characterisation of the thermal transitions of these materials (Forssell *et al.*, 1996).

MATERIALS AND METHODS

Materials

Normal barley starch (28% amylose, according to iodine binding) was kindly donated by Raisio Company (Raisio, Finland) and glycerol was from Akzo Chemicals (85%).

Plasticization

Plasticization of barley starch with water and glycerol was performed in a melt mixer (Brabender Plasti-Corder). Barley starch and plasticizers were mixed and stored overnight before melt mixing. Four mixtures were prepared with glycerol contents 14, 20, 29 and 39% (dry basis) and with water contents 30, 25, 12 and 11.5%, respectively. Plasticization was performed at 170°C with 80 rpm for 15 min. Plasticized mixtures were ground under liquid nitrogen (Fritsch mill, Manufacturers of Laboratory Instruments, Idar-Oberstein, Germany). All percentages used in this report are based on dry weight except the water contents.

Controlled water content

Powdered samples (about 200 mg) were equilibrated in closed chambers over saturated salt solutions at 20°C for 1 week. Salts used were LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl and $(NH_4)_2SO_4$, providing relative humidities of 11, 33, 54, 76 and 81%, respectively (Greenspan, 1977). The dry powder (having a water content of about 1%) was prepared by drying the TPS samples in a vacuum desiccator over P_2O_5 at 60°C overnight. Moisture contents were obtained gravimetrically by drying in an oven (1 h at 130°C). The accuracy of the gravimetric determination of water content was established by Karl Fischer titration on selected samples.

Scanning calorimetry

Differential scanning calorimetry (DSC) (Mettler DSC30) was used to characterize the endothermic transitions and glass transitions in the TPS powders. The sample size was about 10 mg. The TPS powder was weighed into aluminium pans, which were sealed and scanned together with an empty reference pan. Plasticized and powdered samples with controlled moisture contents were heated, cooled immediately and reheated again with a scanning rate of 10°C/min. Glass transition temperatures were determined from the reheating thermograms as the mid-point of the transition.

Dynamic mechanical thermal analysis

Dynamic mechanical measurements were performed in the temperature range −100 to 60°C using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) MkII (Rheometric Scientific, Epsom, UK). Solvent cast films were prepared from the melt-mixed powders by heating 3.0% w/w aqueous dispersions of the powders to 96°C for 20 min, pouring the solutions into moulds and then drying at 20°C and 50% relative humidity for 2 days. Samples, typically 15 mm long, 10 mm wide and 0.2 mm thick, were cut from the films and then conditioned over saturated salt solutions to obtain the required water content. The DMTA was used in tensile mode at a frequency of 10 Hz and a nominal peak-to-peak displacement of 16 μm. The heating rate was 1°C min^{-1} and all samples were coated with petroleum jelly (Vaseline®) to limit changes in water content during the scan. The 'reducing force' option was used on all samples in which the constant tensile force, applied to maintain the sample in tension throughout the temperature scan, is reduced in step with the decreasing modulus of the sample.

Molar mass

Gel permeation chromatography (GPC) was used to analyze molar mass distributions and mass average molar masses of the starch polymers in the processed mixtures. μHydrogel columns 2000, 500 and 250 were used for fractionation. A dual angle laser light scattering detector (Precision detectors, Amherst, MA, USA) was used to determine the absolute molar masses. Samples were dissolved in 1 M NaOH (200 mg of starch in 10 ml of NaOH) and diluted 1:10 with 1 M NaOH. 50 mM NaOH was used as the eluent at a flow rate of 5 ml/min.

RESULTS AND DISCUSSION

Depolymerization

The weight average molar mass of native barley starch was greater than 10^8 g/mol which is above the detection limit of RI/DALLS (refractive index/dual angle laser light scattering detector) (Fig. 1 and Table 1). Despite relatively high total plasticizer levels (water plus glycerol greater than 40%) depolymerization, presumably thermomechanical, of starch polymers was observed to have occurred in the melt mixer. At lower glycerol contents more water was added in order to melt the starch granules. In spite of the higher water contents the degree of depolymerization increased with the decrease of glycerol content. The molar mass was greater than 10^7 g/mol at 39% glycerol and less than 10^6 g/mol at 20 or 14% glycerol.

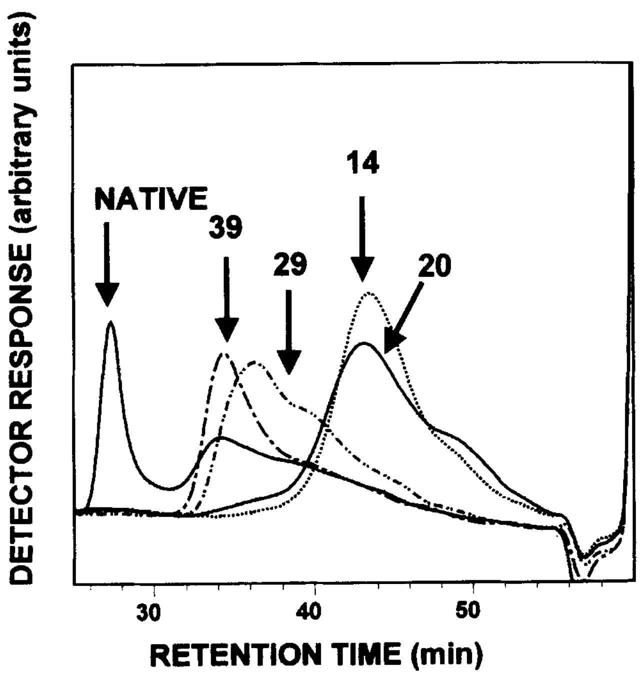

Fig. 1. GPC chromatograms of native and plasticized barley starch with different glycerol contents (14, 20, 29 and 39%).

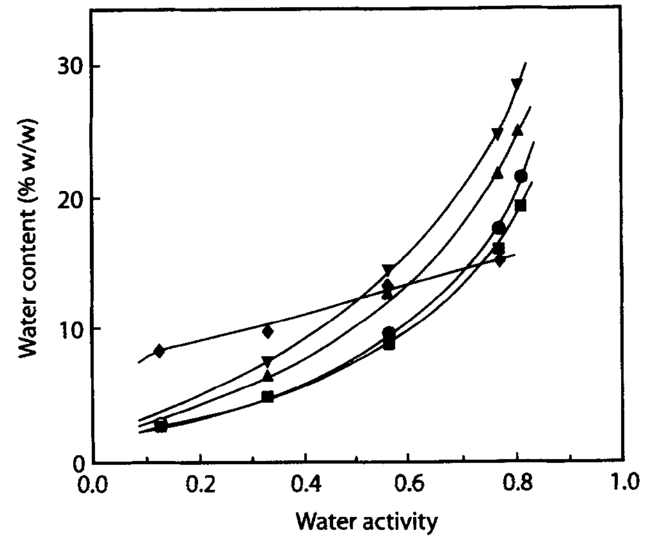

Fig. 2. Water sorption of native granular starch and melt-mixed starch–glycerol mixtures at 20°C. Native granular starch, ◆; 14% glycerol, ■; 20% glycerol, •; 29% glycerol, ▲; 39% glycerol, ▼.

Water sorption behaviour of starch–glycerol mixtures

The effect of glycerol content on the water sorption behaviour of melt-mixed starch–glycerol powders is shown in Fig. 2. This illustrates the water binding or 'humectant' action of the glycerol: as the glycerol content increases, increasing amounts of water are sorbed into the mixture. For comparison, the sorption of native granular barley starch is also shown in Fig. 2. At low water activities the glycerol–starch mixtures sorb considerably less water than the native granules, whereas at the higher water activities ($a_w > 0.8$) water sorption is greater.

Thermal transitions

The initial heating scans of the starch–glycerol–water mixtures showed some endothermic peaks which, depending upon the composition, were thought to arise from either enthalpy relaxation associated with a glass transition (Shogren, 1992; Hutchinson, 1995) or the melting of recrystallized material (Zeleznak & Hoseney, 1986). These interpretations can be better appreciated once the position of the glass transitions in these systems are known and so these latter measurements will be described first. Figure 3 shows the DSC rescans of duplicate samples containing 20% glycerol and

Table 1. Weight and number average molar masses of barley starch after processing in the melt mixer at 170°C for 15 min

Glycerol (%)	$M_w \times 10^6$ (g/mol)	$M_n \times 10^6$ (g/mol)	Polydispersity
14	0.5	0.25	1.7
20	0.7	0.20	3.3
29	5.2	2.0	2.6
39	15.0	11.0	1.4

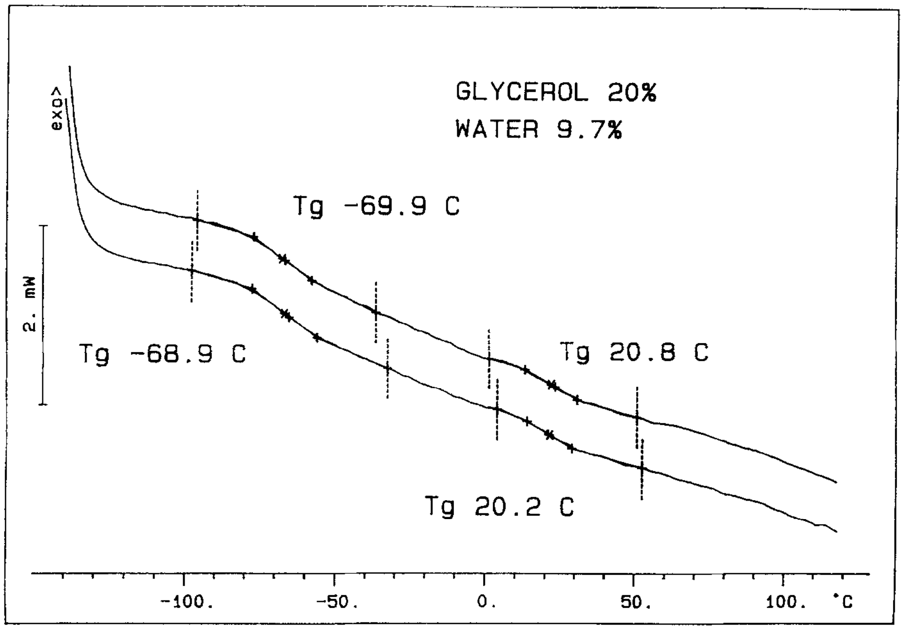

Fig. 3. Duplicate DSC rescans for starch–glycerol–water mixtures containing 20% glycerol and 9.7% water.

9.7% water, a composition with intermediate glycerol and water contents. The heat flow shows two broad steps centered around −69°C and 21°C which suggests two glass transitions of a phase-separated system. Depending upon the composition, the thermograms showed either one or two transitions. The transitions were always observed in particular temperature ranges, one in the range −14 to 145°C, which will be termed the 'upper transition' and the second in the range −98°C to −38°C, the 'lower transition'. Figure 4 and Table 2 show the variation of these glass transition temperatures with water and glycerol content. For comparison, the glass transition temperature of starch–water (Zeleznak & Hoseney, 1987) and glycerol–water mixtures (this study) are also plotted on Fig. 4. The upper glass transition is clearly related to the glass transition in starch–water mixtures. In both cases the glass transition temperature is depressed by the addition of water and the transition temperature of the mixtures containing glycerol are shifted to lower temperatures on the addition of glycerol. At the lowest water content (approx. 1% water) the upper transition of the starch–glycerol mixture decreases from 145 to 70°C as the glycerol content is increased from 14 to 29%. A water content of approx. 12% is required to depress the glass transition of a starch–water mixture to 70°C and so we can conclude that glycerol is a less effective plasticizer than water. Only the upper transition is observed at water contents less than 6% for the 14% glycerol content mixtures and water contents less than 3% for the 20% glycerol content mixtures. The heat capacity increment at the upper glass transition was relatively small and difficult to determine with precision, a maximum value of 0.12 J K^{-1} g^{-1} was observed at the lowest water and glycerol content and the value decreased with increasing water and glycerol content. The maximum value is considerably smaller than the value estimated for dry starch of 0.47 J K^{-1} g^{-1} (Orford *et al.*, 1989),

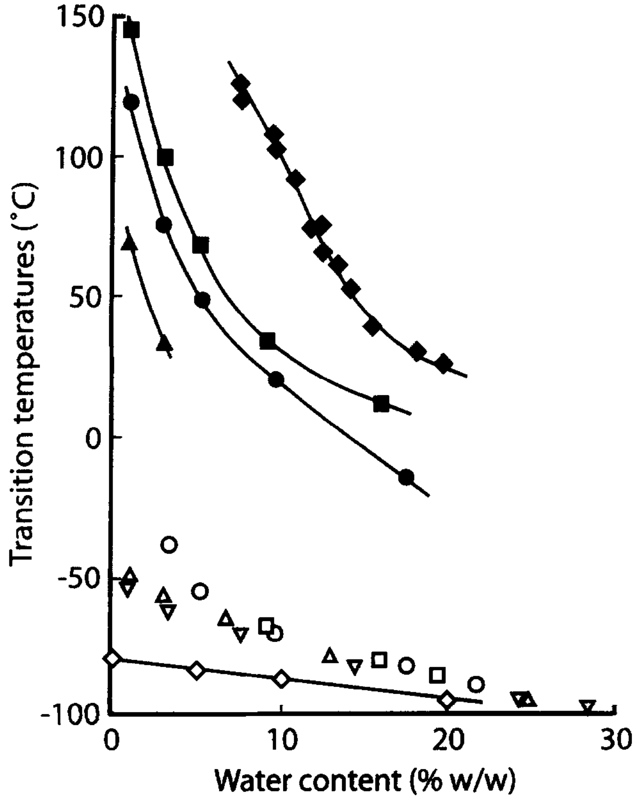

Fig. 4. Glass transition temperatures of starch–glycerol–water mixtures determined using DSC. Glycerol contents: 14%, □, ■; 20%, ○, ●; 29%, △, ▲; 39%, ▽. Starch–water results of Zeleznak and Hoseney, ◆. Glycerol–water results, this study, ◇.

Table 2. Glass transition temperatures of starch–glycerol–water mixtures of varying composition

RH (%)	Glycerol 14%w/w			Glycerol 20%w/w			Glycerol 29%w/w			Glycerol 39%w/w		
	W	T_g^{l}	T_g^{u}	W	T_g^{l}	T_g^{u}	W	T_g^{l}	T_g^{u}	W	T_g^{l}	T_g^{u}
P_2O_5	1.0	nd	145.0	1.0	nd	120.0	1.0	−49.0	70.0	1.0	−53.0	nd
11	2.9	nd	100.0	3.2	−38.0	76.0	3.0	−56.0	34.0	3.4	−61.0	nd
33	5.1	nd	68.0	5.2	−54.0	48.0	6.8	−64.0	nd	7.7	−70.0	nd
54	9.2	−67.0	34.0	9.7	−69.0	21.0	12.9	−77.0	nd	14.5	−82.0	nd
76	16.0	−80.0	12.0	17.6	−82.0	−14.0	21.6	−90.0	nd	24.5	−94.0	nd
81	19.3	−85.0	nd	21.6	−89.0	nd	24.8	−94.0	nd	28.3	−98.0	nd

RH, relative humidity at which the powders were conditioned; W, water content (%w/w), T_g^{l}, lower glass transition temperature (°C); T_g^{u}, upper glass transition temperature (°C); nd, not detected.

indicating a correspondingly smaller change in molecular mobility at the glass transition for the glycerol-plasticized starch.

As can be seen in Table 2 at intermediate plasticizer levels, between approx. 20 and 35% glycerol and water combined, the lower transition is observed in addition to the upper transition whereas at the highest plasticizer levels, greater than 35%, only the lower transition is observed. In mechanical and dielectric relaxation studies of amorphous polymers, the observation of two thermal transitions in a single phase material is usually assigned to a primary α-relaxation process associated with the glass transition and a lower temperature secondary sub-T_g β-relaxation process associated with relatively localised molecular motions (see, for example, McCrum *et al.*, 1967). In the present system the magnitude of the heat capacity increment for the lower transition (Fig. 5) indicates that it is related to the mobilization of a significant proportion of the mixture and so we favour an explanation in terms of the transitions corresponding to the glass transitions of two separate phases. In Fig. 4, the upper transition is clearly due to a starch-rich phase, whereas the lower transition is due to a starch-poor phase. The observation that the lower transition is only slightly elevated above the glycerol–water curve suggests that while this phase is rich in these two components it also contains a certain amount of polymeric material. The lower glass transition temperature decreases with increasing water content but is largely independent of glycerol content. Figure 5 shows the variation of the heat capacity increment for the lower transition with water and glycerol content. Having identified that phase separation is occurring in some of our mixtures logically the next question to ask is ‘what is the form of the phase diagram?’ or, in other words, ‘over what composition range is the system single phase and over what range is it biphasic?’ Firstly, we can unambiguously say that compositions showing two transitions are phase-separated. The filled symbols in Fig. 5 identify those compositions for which both upper and lower transitions are observable. The variation of heat capacity increment with water content for the lowest two glycerol contents (14 and 20%) are linear and, at low water contents, extrapolate to zero heat capacity increment. This is an indication that at the lower glycerol contents and low water contents the system contains only a single phase. In contrast, at 29% glycerol content the heat capacity increment extrapolates to a finite value at zero water content indicating that at this starch–glycerol ratio there is partial immiscibility and two separate phases. At higher glycerol contents only a single transition is observed and so it is not possible to distinguish whether the system is phase separated on the basis of the calorimetric measurements. At high plasticizer contents there is a correspondingly low amount of polymer and relatively less material to form a polymer-rich phase in a phase-separated system, which will make any thermal transitions of these phases difficult to detect calorimetrically. Other techniques such as microscopy and scattering are required to characterize whether phase separation is occurring in this composition range.

In order to link the calorimetric behaviour to small strain mechanical behaviour dynamic mechanical

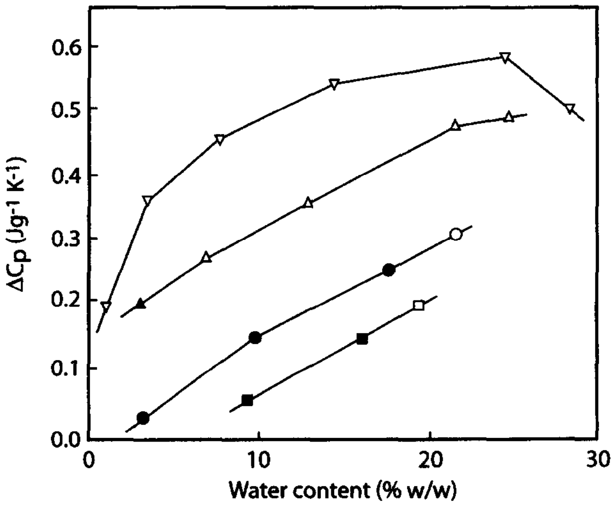

Fig. 5. The composition dependence of the heat capacity increment of the lower glass transition in starch–glycerol–water mixtures. Glycerol contents: 14% □; 20%, ○; 29%, △; 39%, ▽. The filled symbols correspond to those compositions for which an upper glass transition was also observed.

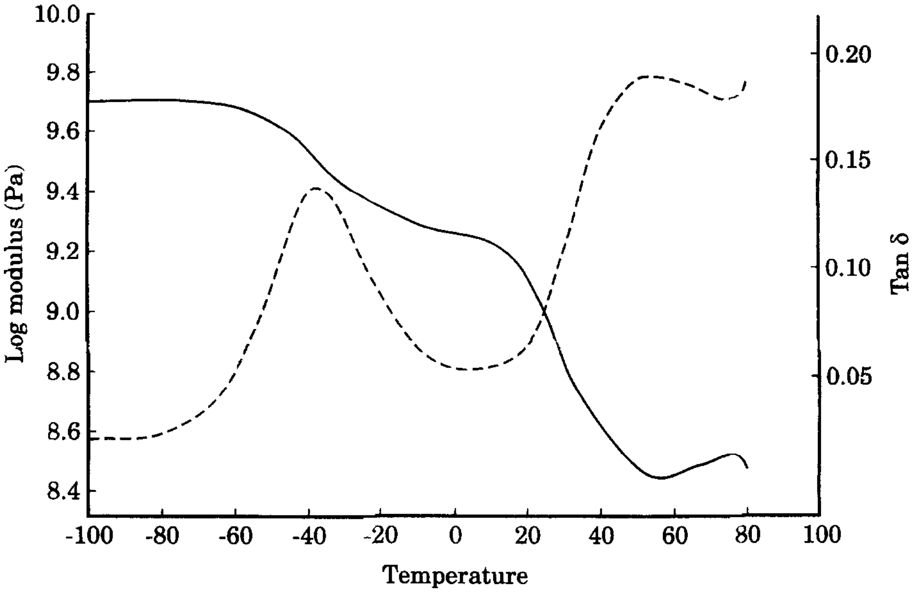

Fig. 6. Temperature dependence of the dynamic tensile modulus (solid line) and tan δ (dashed line) measured at 10 Hz for a starch–glycerol–water film containing 29% glycerol and 3% water.

thermal analysis was applied to solvent cast films prepared from the melt-mixed powders. Figure 6 shows the variation in the dynamic elastic modulus and tan δ measured over the temperature range −100°C to 80°C for a starch–glycerol–water mixture containing 29% glycerol and 3% water. The elastic modulus falls in two steps, the first between −60 and 0°C and the second between 0 and 55°C with corresponding peaks in tan δ at −36.5 and 54.0°C. In the DSC, calorimetric glass transitions were measured at −56 and 34°C which is consistent with probing the same relaxation processes as the DMTA. The temperature of tan δ_{max} measured at 10 Hz characterizes the relaxations associated with the glass transition at higher frequency than the calorimeter ($\upsilon \sim 1$ mHz) and so leads to a 20°C difference in the temperature at which they are observed.

The phase structure and total extent of phase separation in the phase-separated systems will depend on the thermal history of the samples (see, for example, Hikmet *et al.*, 1988; Callister *et al.*, 1990). Given the small amount of information we have concerning the phase diagram and its temperature dependence, only general comments can be made. The commonest type of behaviour of polymeric systems is to have a temperature, T_{mis}, above which the system is entirely miscible. If T_{mis} is below the temperature of the melt mixing of our samples then during the processing the plasticized melt will have been in a single phase portion of the phase diagram. Even if the T_{mis} had not been exceeded, the phase boundaries will be temperature dependent and so the cooling after the melt mixing will result in a change in the composition of the coexisting phases. If the glass transition of the starch-rich phase is crossed, its state will be transformed from a rubber to a glass, this will arrest structural change and 'freeze in' the microstructure. In our experiments this will have occurred in the lower glycerol content samples during the slow drying of the powders over the saturated salts to condition them to different water contents.

Our results on glycerol and water plasticized barley starch show several similarities with the behaviour of fructose and water plasticized waxy-maize starch (Kalichevsky *et al.*, 1993; Kalichevsky & Blanshard, 1993). The differences in behaviour largely appear to originate from the different glass transition temperatures of the fructose (7°C, Orford *et al.*, 1990) and the glycerol (−85.4°C, Champeney & Ould Kaddour, 1984). The lower glass transition temperature of glycerol means that it is potentially a better plasticizer than fructose. The observation of the thermal transitions at two distinct temperatures is common to both systems. The proximity of the transitions and their breadth in the case of the fructose meant that they could only clearly be observed using DMTA and were indistinct in the DSC. However, the DMTA proves to be a sensitive tool for resolving overlapping relaxations and the results show that peaks in tan δ separated by approx. 40°C can be distinguished in single frequency temperature scans (Kalichevsky *et al.*, 1993). The lower glass transition temperature of the glycerol has enabled both the upper and lower transitions to be observed calorimetrically (Fig. 4). The variation of the transition temperatures with composition is qualitatively similar. In each case the lower transition is above that of the plasticizer–water mixture and closes upon it as the water content is increased. At high glycerol and fructose contents this component dominates the transitions in the heat capacity and mechanical properties though the

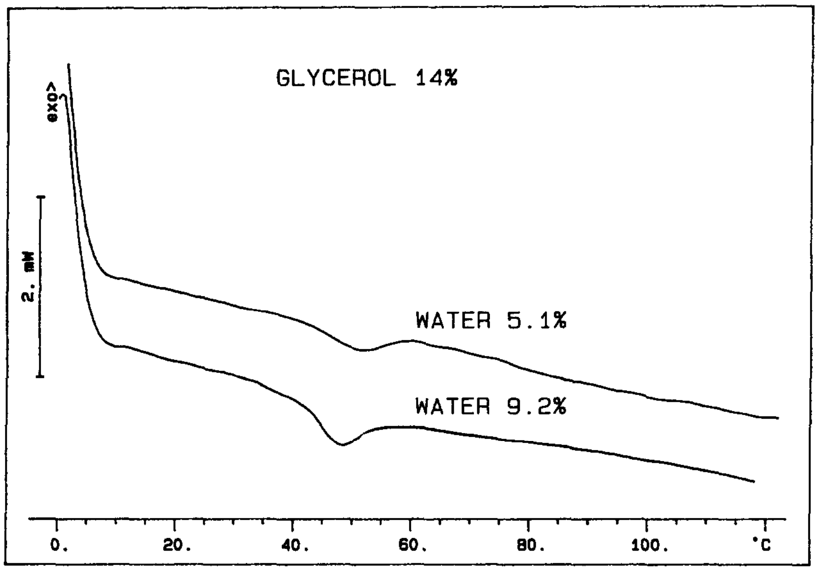

Fig. 7. Initial DSC scans on starch–glycerol–water mixtures showing enthalpy relaxation peaks. Glycerol content was 14% and water contents 5.1 and 9.2%.

polymeric component still dictates the overall mechanical properties i.e., these materials are stiff (rubbery) gels.

Figure 7 shows the initial DSC scans for starch–glycerol–water mixtures which have upper glass transitions at 68°C (5.1% water) and 34°C (9.2% water). Both show endothermic peaks between 40 and 60°C, which are thought to be a result of enthalpy relaxation, a result of the recovery of enthalpy trapped in the material during aging in the glassy state (Shogren, 1992; Hutchinson, 1995). The dry powders which had higher upper glass transitions did not show any endothermic peaks, probably because the relatively high glass transition temperatures of these samples resulted in negligible aging rates in these experiments.

Broad endotherms were observed between 50 and 90°C in the initial DSC scans of samples having water contents of at least 20%, and were most likely due to melting of amylopectin crystallites (Fig. 8). The melting temperature was higher than in normal starch gels because of the presence of glycerol, which has been demonstrated to increase the gelatinization temperature of starches (Evans & Haisman, 1982). The melting enthalpy at 29 and 39% glycerol was 7–9 J per gram of dry starch, which is similar to the melting enthalpy of amylopectin crystallites in normal starch gels (Orford *et al.*, 1993). In other starch–glycerol mixtures, even

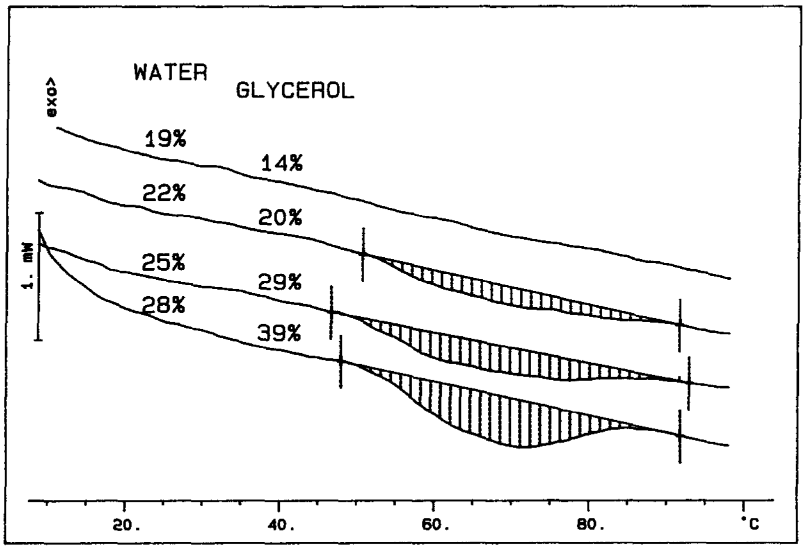

Fig. 8. Initial DSC scans on starch–glycerol–water mixtures showing broad enothermic peaks at approx. 70°C. Water and glycerol contents 19, 22, 25, 28% and 14, 20, 29, 39%, respectively.

those studied in the rubbery state, crystal formation did not occur. This indicated that glycerol interacted with starch polymers and inhibited or retarded amylopectin crystallization.

CONCLUSIONS

Two glass transitions were detected in barley starch–glycerol–water mixtures analyzed by DSC and the corresponding mechanical relaxations were observed by DMTA. The position of the upper glass transition depended on glycerol and water content, while the lower glass transition was mainly dependent on the water content and located at a somewhat higher temperature than the glass transition of the corresponding glycerol–water mixture. The upper glass transition is related to a starch-rich phase and the lower one to a starch-poor glycerol-rich phase and with increasing water content the starch content of the starch-poor phase decreased. Results demonstrated that at least at intermediate glycerol and water contents phase separation occurred. The composition dependence of the heat capacity increment of the lower glass transition indicated that at the two lowest glycerol contents and low water contents the system comprised one single phase. Crystallization of amylopectin was detected only at high water contents in the range 20–28%, indicating that at intermediate and low water contents glycerol inhibited or retarded amylopectin crystallization.

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