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Dynamic mechanical and dielectric characterisation of amylose–glycerol films

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Abstract

The dynamic mechanical, dielectric and calorimetric behaviour of amylose films, plasticised with glycerol, was examined as a function of temperature and glycerol content. Two separate relaxation processes were observed. Whereas the temperature of the lower temperature transition, in the vicinity of −50°C, showed a weak dependence on composition, the temperature of the upper transition, in the range 150–50°C, decreased with increasing glycerol content. The activation energy of the lower temperature transition, obtained from the dependence of the frequency of the relaxation peak upon temperature, was typical of a primary α-relaxation or glass transition process. This indicated that although glycerol was an effective plasticiser of amylose, amylose–glycerol mixtures are only partially miscible. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Amylose; Glycerol; Plasticisation

1. Introduction

Starch, the plant storage polysaccharide, has potential use as a component of biodegradable materials of industrial usefulness. Compared to synthetic polymers there is less extensive information on the relationship between molecular properties and material characteristics and it is only relatively recently that the melting (Moates, Noel, Parker & Ring, 1996) and glass transition behaviour of starch has been investigated (Zeleznak & Hoseney, 1987; Orford, Parker, Ring & Smith, 1989; Kalichevsky, Jaroszkiewicz, Ablett, Blanshard & Lillford, 1992).

Starch occurs as partially crystalline, water-insoluble granules which may be destructurised through heating in the presence of a diluent, usually water, to give an amorphous product which, when dry, is glassy at room temperature. The glass transition temperature, T_g, of the dry material is not accessible experimentally due to thermal degradation. Extrapolation of the observed T_g's of dry maltooligomers gives a value of 230°C for the high molecular limit of T_g (Orford et al., 1989). Water has a strong depressing effect on the T_g of starch, addition of ~20% w/w water depresses the T_g to room temperature (Zeleznak & Hoseney, 1987). Most starches contain two main polysaccharides, amylose and amylopectin, both of which are based on chains of $(1 \rightarrow 4)$ linked α-D-glucose. Whereas amylopectin is highly branched, the amylose component is essentially linear with typical molecular weights in the region of 10^5–10^6 g mol^{-1} (Banks & Greenwood, 1975). In concentrated aqueous solution the starch polysaccharides are immiscible, and amylose-rich and amylopectin-rich phases can be formed (Kalichevsky & Ring, 1987). Water is also a relatively poor solvent for these polysaccharides. In concentrated aqueous mixtures at room temperature there is a separate phase separation/crystallisation of the amylose and amylopectin chains which can lead to time-dependent changes in material properties (Miles, Morris & Ring, 1985; Ring et al., 1987). For both polymers the crystallisation from concentrated aqueous solution produces the B-type crystalline form of starch. At room temperature the phase separation and subsequent crystallisation of amylose is the more rapid process.

The sensitivity of starch materials to fluctuations in water content is one potential drawback to its more extensive usage as a thermoplastic. There is a need for more information on the choice and use of plasticisers for starch and a characterisation of their effect on material properties. Ideally the plasticiser should be non-volatile; reduce the sensitivity of the material properties of starch to fluctuations in water content; and reduce the sensitivity of the material to ageing through crystallisation.

In experimental studies a range of plasticisers have been

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used including dimethyl sulphoxide (Nakamura & Tobolsky, 1967), urea (Shogren, 1992; Lourdin, Coignard, Bizot & Colonna, 1997b), amino acids (Stein, Gordon & Green, 1999), sodium lactate (Lourdin et al., 1997b) and low molecular weight carbohydrates (Kalichevsky, Jaroszkiewicz & Blanshard, 1993; Kalichevsky & Blanshard, 1993; Lourdin, Bizot & Colonna, 1997; Gaudin, Lourdin, le Botlan, Ilari & Colonna, 1999). One commonly employed starch plasticiser is the hydroxy compound glycerol (Shogren, 1992; Forssell, Mikkila, Moates & Parker, 1997; Lourdin et al., 1997a; Lourdin, Ring & Colonna, 1998). Calorimetric studies (Forssell et al., 1997) of starch–glycerol–water mixtures revealed two distinct heat capacity increments, one at sub-zero temperatures, in the range −50 to −100°C, and one at a higher temperature (150°C for a low water content starch mixture containing 14% w/w glycerol). The temperature of the lower temperature transition did not show a strong dependence on glycerol content but decreased with increasing water content. Addition of water and glycerol depressed the temperature of the upper transition. It was proposed that the material had a phase separated structure, containing starch-rich and glycerol-rich phases and the heat capacity increments were associated with the glass transitions of the separate phases. The complexity of the system, however—two polymers and two diluents at temperatures and compositions which are metastable with respect to crystallisation—makes a more detailed interpretation difficult. A similar proposal of partial miscibility was made in a study of the ternary system amylose–glycerol–water (Lourdin et al., 1998). Dielectric studies on mixtures of glycerol with the $(1 \rightarrow 4)$ linked disaccharide maltose showed that, as glycerol content was increased, the primary relaxation split into two components, suggesting immiscibility, before merging again at higher glycerol contents (Lourdin et al., 1998). At high glycerol contents there is also the possibility of other interactions between glycerol and the amylose chain as indicated by the formation of the V-type crystalline form of amylose (Hulleman, Helbert & Chanzy, 1996). As a development of this research we now report on the mechanical and dielectric characterisation of the binary amylose–glycerol system.

2. Materials and methods

2.1. Sample preparation and composition

Chemicals (all >99% purity) were from Sigma (Poole, UK). Amylose was prepared from pea starch (Grinsted Products, Bury St. Edmunds, UK) as its 1-butanol complex as described (Miles et al., 1985). Its iodine binding behaviour, expressed as g I_2/100 g polysaccharide, was 19.5% w/w, as determined by a semi-micro potentiometric technique, which indicated that the preparation was >95% amylose (Banks & Greenwood, 1975). Amylose films were made from a 3% w/v amylose–butanol complex suspension (8 ml) by mixing with the appropriate volume of glycerol, heating to 100°C to ensure complete melting of the complex, pouring the solution into a circular mould and then drying in a forced-air oven at 40°C. This was followed by a vacuum-drying step in a vacuum oven at 40°C over P_2O_5 for 16 h. To determine the final film composition, samples of dry films (~30 mg) were, first, accurately weighed into screw-topped test tubes and dissolved in dimethyl sulphoxide (DMSO) (5 ml). Glycerol analysis was carried out by ion-exchange HPLC using an Aminex HPX-87H column (Bio-Rad Laboratories, Hemel Hempstead, UK) eluted with 12 mM H_2SO_4 at a flow rate of 0.7 ml min^{-1} (Pecina, Bonn, Burtscher & 1984). Glycerol eluted at 11.5 min and DMSO at 25 min. The amylose content of the films was determined using a colorimetric assay. 10 μl of amylose in DMSO solution (~5 mg ml^{-1}) was added to 0.99 ml of 0.5 mM iodine in 2% w/w KI, and the amylose quantified through the absorbance measured at 470 nm. Performing a mass balance using the glycerol and amylose analyses indicated that the water content of the dry films was less than 2% w/w.

2.2. Differential scanning calorimetry (DSC)

The glass transition temperatures (T_g) of the dry amylose films were determined by calorimetry using a Perkin–Elmer DSC2 to measure heat capacity as described previously (Orford et al., 1989). T_g was taken to be the mid-point between the onset and end temperatures.

2.3. Dynamic mechanical thermal analysis (DMTA)

The dynamic (elastic) tensile modulus, E', and tan δ were measured in the temperature range −100 to 160°C using a Polymer Laboratories DMTA Mk II instrument (Rheometric Scientific, Loughborough, UK). Typical sample dimensions were 11 mm × 9 mm × 0.15 mm. The measurement frequency and nominal peak-to-peak displacement were 10 Hz and 16 μm, respectively. 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. During initial sample cooling the sample enclosure was purged with nitrogen to remove moist air and then sealed for the duration of the experiment. The measurements were made while the sample was heated at a rate of 1°C min^{-1}.

2.4. Dielectric thermal analysis (DETA)

Dielectric thermal analysis was performed using a DETA Mk II instrument (Rheometric Scientific, Loughborough, UK) equipped with a General Radio 1689M Precision RLC Digibridge and a stainless steel parallel-plate cell (diameter, 33 mm; typical gap, 0.1 mm). 33 mm diameter discs were cut from amylose films before the films were fully dry while the material was not brittle and were then

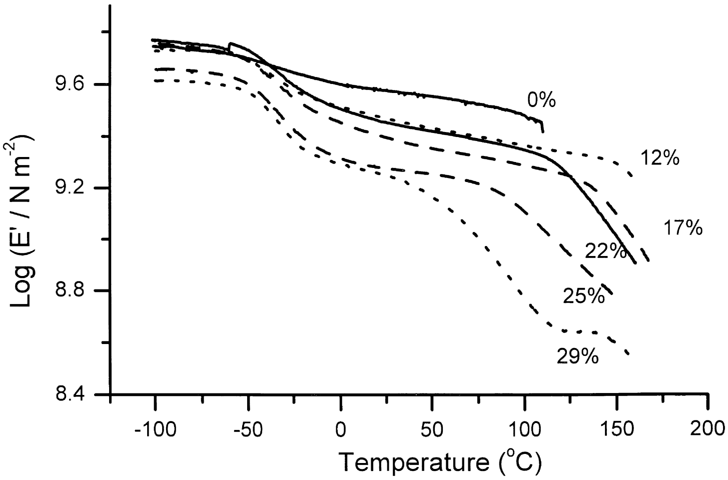

Fig. 1. Dynamic tensile modulus of glycerol-plasticised amylose films at 10 Hz as a function of temperature and glycerol content (% w/w, rounded).

dried in vacuo at 40°C over P_2O_5 for 16 h prior to analysis. Measurements of the dielectric constant, ϵ', and tan δ were made at 9 frequencies in the range 100–100 kHz, as the temperature was linearly ramped from −110 to 150°C at a rate of 1°C min^{-1}. A dry atmosphere was maintained within the measurement enclosure by adding a dish of P_2O_5 desiccant close to the sample and, to remove any moist air from the chamber before commencing cooling, by flushing the enclosure with dry argon. The argon atmosphere was maintained during the experiment.

3. Results and discussion

3.1. Calorimetric behaviour

Examination of the calorimetric behaviour of glycerol-plasticised amylose films (25–50% w/w glycerol) showed the presence of a weak, relatively broad, glass transition, as indicated by a change in heat capacity, in the region of −55°C. Measured under the same conditions, the calorimetric glass transition temperature of glycerol was −76°C. For glycerol contents examined (25–50% w/w) there was no evidence of a glass transition at higher temperatures within the experimental temperature range, i.e. temperatures up to 137°C.

3.2. Mechanical behaviour

Figs. 1 and 2 show the variation of the dynamic tensile modulus, E', and tan δ with temperature for amylose–glycerol films with a glycerol content ranging from 0% to 29.5% w/w. The moduli at −100°C are in excess of 10^9 N m^{-2}, which is typical of glassy amorphous solids. For all samples there is a weak mechanical relaxation process indicated by a drop in E' and a peak in tan δ in the temperature range −37 to −22°C. For the unplasticised amylose film the loss peak is very weak and centred at about −22°C. When glycerol (12.3% w/w) is added the tan δ peak increases in height and shifts to a lower temperature

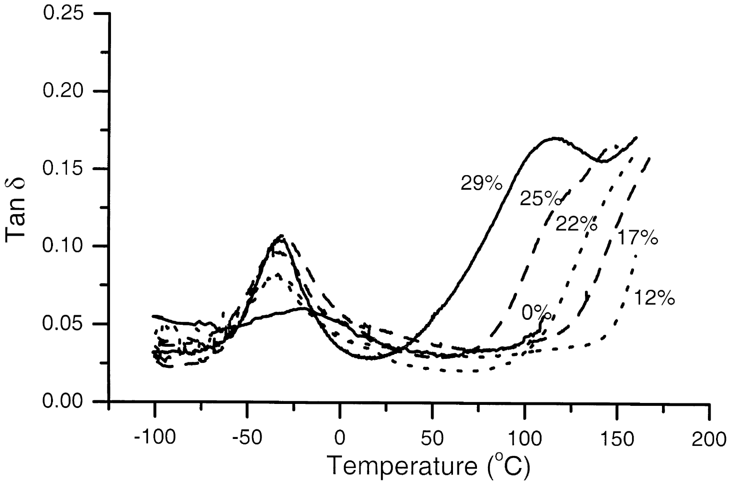

Fig. 2. Tensile tan δ of glycerol-plasticised amylose films at 10 Hz as a function of temperature and glycerol content (% w/w, rounded).

Table 1
Temperatures characterising the relaxations in amylose–glycerol films observed in dynamic mechanical measurements at 10 Hz (–, not observed)

Glycerol content (% w/w)	tan $\delta_{\max}$, lower (°C)	tan $\delta_{\max}$, upper (°C)	E' onset (°C)
0	−22	–	–
12.3	−37	–	147
16.6	−35	–	138
22.1	−33	–	118
24.8	−35	–	86
29.5	−32	116	50

(~ − 37°C). As further glycerol is added, up to 29.5% w/w, the height of the loss peak progressively increases with a small shift in temperature of the maximum to ~ − 32°C.

For the glycerol-plasticised films, a stronger mechanical relaxation is observed at higher temperatures. While a peak in tan δ is observed for the sample with 29.5% w/w glycerol, only the onset of this relaxation is observed at the lower glycerol contents. The onset of this relaxation, determined from the intercept of the extrapolated line of the initial E' and that of the steepest slope in E', decreases from ~147 to ~50°C as the glycerol content is increased from 12.3 to 29.5% w/w (Table 1). For glycerol contents in the range 12.3–24.8% w/w the relaxation is not complete within the experimental temperature range. The fall in E' which accompanies this relaxation is relatively small, dropping from 1.8×10^9 to $4.2 \times 10^8\ \mathrm{N\,m^{-2}}$. Typically, for amorphous high molecular weight synthetic polymers, the fall in modulus at the glass transition would be 3 or 4 orders of magnitude, though for crosslinked or partially crystalline materials the fall in E' can be much less (Ferry, 1980). As amylose is a carbohydrate there is also the possibility of relatively strong polar and hydrogen bond interactions between components of the mixture which would reduce chain flexibility and increase the modulus of the rubbery material. The amylose films prepared in this way also contain a small proportion of crystalline material, as assessed by X-ray diffraction, with weak reflections similar to those of the B-type crystalline polymorph of starch being observed (Cairns, 1999). Unambiguous assignment to particular crystalline polymorphs, as has been achieved for similar materials made with starch (Forssell, Hulleman, Myllärinen, Moates & Parker, 1999), was not possible.

3.3. Dielectric behaviour

Figs. 3 and 4 show the temperature variation of dielectric permittivity, ϵ', and tan δ at 1 kHz for glycerol-plasticised amylose films of varying glycerol content. A low temperature dielectric relaxation is clearly observed in the temperature range −100–0°C, which gives a peak in tan δ. For pure amylose this peak is weak. The temperature of the maximum in tan δ shifts somewhat with increasing glycerol content from −52°C for the pure amylose (at 1 kHz), increasing to −23°C for the sample containing 27% w/w glycerol before falling again to ~ − 49°C as the glycerol content is increased to 75% w/w (Table 2). For the glycerol-plasticised amylose films, there is a close correspondence between the low temperature dielectric and mechanical relaxations (Tables 1 and 2).

At higher temperatures, the dielectric permittivity (Fig. 3) shows somewhat more complex behaviour than the tensile modulus (Fig. 1) with the experimentally

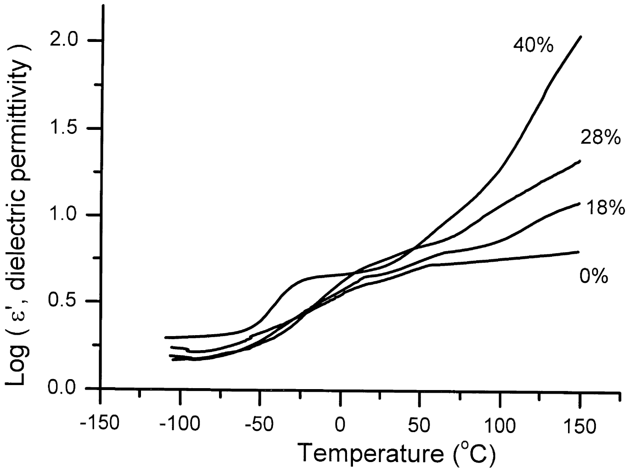

Fig. 3. Dielectric permittivity of amylose–glycerol films at 1 kHz as a function of temperature and glycerol content (% w/w).

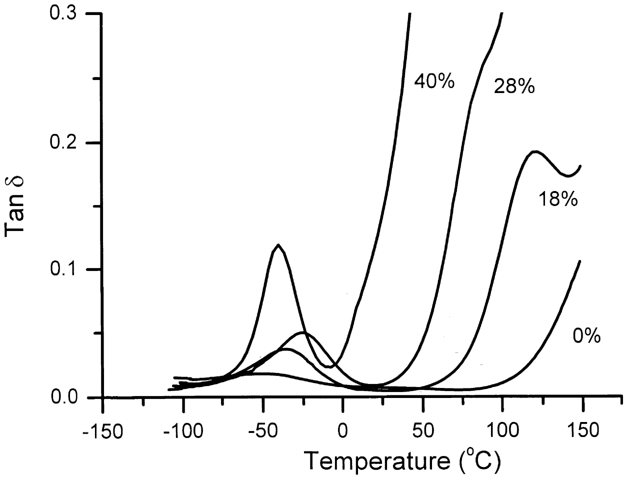

Fig. 4. Dielectric tan δ of amylose–glycerol films at 1 kHz as a function of temperature and glycerol content (% w/w).

Table 2
Temperatures and activation energies characterising the relaxations in amylose–glycerol films observed in dielectric measurements at 1 kHz (–, not observed)

Glycerol content (% w/w)	tan δ_{max} (°C)	Activation energy from tan δ_{max} (ΔH (kJ mol^{-1}))	M''_{max}, lower (°C)	M''_{max}, upper (°C)
			°C	°C
0	−52	53	−64	–
7.5	−43	102	−48	–
18	−36	112	−42	113
21.6	−34	–	−39	–
27	−23	–	−29	101
28	−26	119	−30	81
37	−31	–	−33	53
40	−40	148	−44	48
42	−54	–	−35	51
56	−46	–	–	–
75	−49	–	–	–

observed dielectric behaviour being influenced by conductivity and polarisation effects. For pure amylose, a further peak in dielectric tan δ is not observed at the maximum experimental temperature of 150°C. For the plasticised samples of intermediate glycerol content (18–28% w/w) an underlying dielectric relaxation process appears as a shoulder in tan δ which is increasing with increasing temperature. For the higher glycerol contents (>28% w/w), the observed behaviour, in the region of the observed high temperature mechanical relaxation, is dominated by conductivity which masks any underlying dielectric process.

An alternative data analysis of dielectric behaviour which has proved useful for extracting additional information on the relaxation processes in conducting materials is the "electric modulus formalism" (Pathmanathan & Johari, 1991;Astl, Chan & Johari, 1992). The complex electric modulus M^* is related to the (complex) dielectric permittivity ϵ^* through the relationships

$$M^* = (\epsilon^*)^{-1} = M' + iM''$$

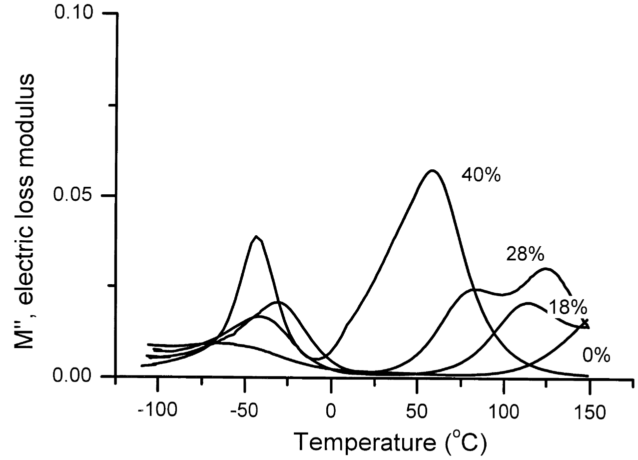

Fig. 5. Electric loss modulus, M'', of amylose–glycerol films at 1 kHz as a function of temperature and glycerol content (% w/w).

which can be expressed

$$M' = \epsilon'/(\epsilon'^2 + \epsilon''^2) \text{ and } M'' = \epsilon''/(\epsilon'^2 + \epsilon''^2).$$

Fig. 5 shows the data of Fig. 4 replotted using M'', the electric loss modulus. For the sample containing 18% w/w glycerol a peak in M'' is observed at 113°C, which is due to a high temperature dielectric relaxation. For the amylose film containing 28% w/w glycerol, two peaks are observed in the high temperature region with maxima in M'' at ~81 and 125°C, corresponding to a dielectric relaxation and a conductivity relaxation. The dielectric peak in M'' is associated with the high temperature mechanical relaxation as observed through a marked drop in tensile modulus in this temperature region. At higher glycerol contents (>28% w/w) the peaks in M'' attributed to dipolar and conductivity relaxation merge into a single peak.

Fig. 6 summarises the temperatures characterising the calorimetric, mechanical and dielectric relaxations of amylose films as a function of glycerol content in the range 7–42% w/w. The quantities used to characterise the relaxation differ somewhat depending on the experimental technique and differences will be observed in the temperature of the transition depending on the timescale (frequency) of the measurement technique employed. Bearing in mind these considerations, examination of Fig. 6 shows the presence of two separate transitions. The temperature of the upper transition falls from ~150 to ~50°C as the glycerol content is increased from ~10 to 40% w/w. Over the same concentration range, the temperature of the lower transition increases from ~ − 50°C to a maximum of −30– − 25°C at a glycerol content of ~27% w/w before falling at higher glycerol contents.

There are two possible explanations for the observed behaviour which need to be considered. Firstly, assuming the system is a single homogeneous phase, the upper transition would be ascribed to an α-relaxation of the main polymer backbone, and the lower transition to a β-relaxation involving a more localised motion. The observation that the addition of plasticiser (7.5–30% w/w glycerol)

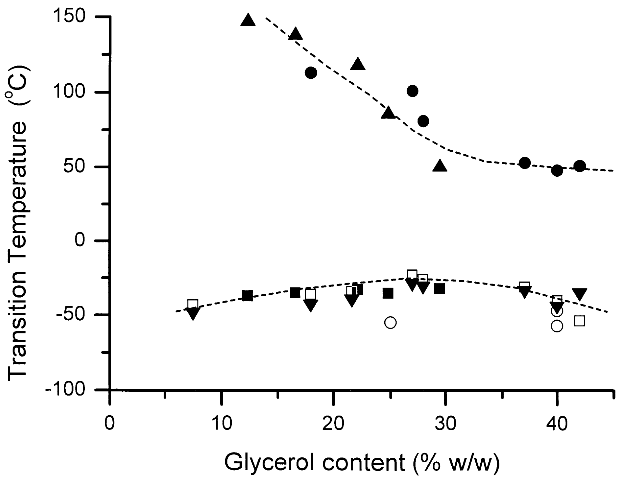

Fig. 6. Effect of glycerol content on the temperature of the observed transitions in relaxation behaviour of amylose–glycerol mixtures, where (○), calorimetric glass transition; (■), tensile tan δ_{max} at 10 Hz; (▲), onset of tensile E' transition at 10 Hz; (□), lower dielectric tan δ_{max} at 1 kHz; (▼), lower electric modulus M''_{max} at 1 kHz; and (●), upper electric loss modulus M''_{max} at 1 kHz. Dashed lines are only intended as an aid to the eye.

depresses the α-relaxation yet increases the temperature of the polymeric β-relaxation is known as “antiplasticisation” (Ngai, Rendell, Yee & Plazek, 1991). The increase in temperature of the polymeric β-relaxation at low glycerol contents suggests a coupling of the motion of glycerol to that of the polymer.

An alternative explanation is that amylose and glycerol are only partially miscible. A phase separated system results which contains amylose-rich and glycerol-rich domains. In this interpretation the observed transitions are identified as the α-relaxation processes of the separate phases. The observation that the lower relaxation is 25–40°C higher than the α-relaxation of pure glycerol (Champeney & Ould-Kaddour, 1987) suggests that the glass transition of the glycerol-rich domain is influenced by the presence of polymer. Support for the proposal that the lower transition is an α-process comes from an examination of the activation energy. Fig. 7 is an Arrhenius plot, log frequency versus 1/*T*, for the tan δ peak of the low temperature relaxation for amylose–glycerol mixtures in the range 7.5–40% w/w glycerol. Included for comparison is data on pure glycerol. Within the range 100 Hz–100 kHz the plots appear to be linear. The activation energies for the low temperature relaxation of all the plasticised films are in the range 102–148 kJ mol^{-1} (Table 2) and are comparable to that of pure glycerol at 128 kJ mol^{-1} and quite distinct from the activation energy of 53 kJ mol^{-1} which was found for pure amylose which can be ascribed to a β-relaxation process (Scandola, Ceccorulli & Pizzoli, 1991). The low temperature relaxation of the plasticised films was therefore assigned to an α-process. This interpretation suggests partial miscibility even at the smallest glycerol contents studied (7.5% w/w).

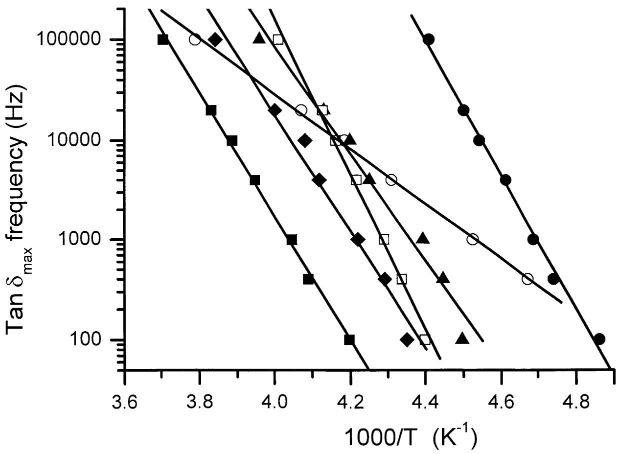

Fig. 7. Arrhenius plots for tan δ_{max} of the lower temperature dielectric relaxation in amylose–glycerol mixtures with composition: (▲), 7.5% w/w glycerol; (◆), 18%; (■), 28%; (□), 40%; (●), 100%, pure glycerol; (○), pure amylose.

The temperature of the upper electric loss peak and the onset of the tensile transition (Fig. 6) indicate that the glass transition of the amylose-rich phase is above room temperature. During film preparation the glass transition of the amylose-rich phase would arrest the structural evolution of the phase separating mixture. Similarly we predict that this would also stabilise the phase structure and composition during the thermal analysis experiments. Additional stabilisation of the structure would result from the small proportion of crystalline amylose present. Future experiments should characterise the structure of the phases and their dependence upon temperature-water content history.

4. Conclusions

At room temperature dry amylose is a brittle glassy solid. Addition of glycerol plasticises the amylose, reducing the onset temperature of the upper relaxation process. The observed dynamic mechanical and dielectric behaviour of amylose–glycerol mixtures can be interpreted on the basis that they are partially miscible. Amylose-rich and glycerol-rich phases are formed and the relaxation behaviour of both phases influences the observed calorimetric, mechanical and dielectric behaviour.

Acknowledgements

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