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Study of plasticizer–oligomer and plasticizer–polymer interactions by dielectric analysis: maltose–glycerol and amylose–glycerol–water systems

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Abstract

Dielectric analysis was performed on amorphous maltose–glycerol and amylose–glycerol–water systems. A primary relaxation, appearing in the range of the calorimetric glass transition temperature, was observed in the maltose-glycerol system. From 0% (w/w) to approximately 30% (w/w) glycerol, a secondary relaxation was observed at lower temperature in both systems. In this concentration range, the addition of glycerol shifted the primary relaxation to lower temperature and the secondary relaxation to higher temperature. For mixtures containing around 30% (w/w) glycerol, the relaxation map revealed a merging of the primary and secondary relaxations or a disappearance of the secondary relaxation. Above 30% (w/w) glycerol in the amylose–glycerol–water system, indication of a phase separation was obtained. This behaviour is compared with the relaxation behaviour of some plasticized synthetic polymers (polyvinylchloride and polyisoprene).

Keywords: Plasticization; Amylose; Maltose; Glycerol; Relaxation

1. Introduction

The marked depressive effect of water on the glass transition temperature (*T*g) of α-glucans (mainly amylopectin) or oligosaccharides, which is related to changes in the mechanical properties of the resulting materials, has been the subject of many recent studies [1]. Water is often qualified as the "best plasticizer" of carbohydrates, which show a high susceptibility to atmospheric moisture. In the characterization of starch-based thermoplastic materials, many studies reviewed by Shogren [2] have reported the use of an additional plasticizer which is required to control the processing and properties of these materials. Systems with glycerol are widely studied and the variations in *T*g of starch–glycerol water system relative to water and glycerol content were described previously [3]. At any glycerol concentration lower than ≈20% (w/w) in a 66:20:14 starch–glycerol–water system,

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glycerol reduces Tg in relative conformity to the Couchman–Karasz relationship for a single phase system. However, for higher glycerol concentrations above this threshold, significant differences between experimental and predicted behaviour were observed which could be due to a phase separation [4,5]. This proposal awaits experimental confirmation.

The calorimetric Tg is associated with a primary mechanical relaxation, α. One or two other secondary relaxations (β or β, γ), which also have an impact on mechanical behaviour [6], have been reported in maltose, amylose and their water mixtures [7–10]. Although the molecular mechanisms for these low temperature relaxations have not been completely explained, their molecular origin could involve local motions of a few monomer residues [10], or the motion of the pendant hydroxymethyl group at C-6 [11,12] and is still a matter of debate.

The effects of water on the secondary relaxations of maltose and amylose have been examined. For example, Bradley et al. [8] have shown a clear dependence of the β relaxation of amylose on water content, decreasing from 248 to 213 K on increasing the water content from 2% (w/w) to 10.5% (w/w). More recent studies [7] on glucose–water and maltose–water systems have shown a strong effect of water on α and β relaxations. Concerning glycerol, previous studies gave a Tg at 190 K [13] and a primary dielectric relaxation at 222 K at 10 kHz [14]. Although secondary relaxations should be considered as a characteristic property of the liquid in or near the glassy state [15], as yet no data are available for glycerol.

The purpose of the present dielectric study was to build a relaxation map for a mixture of maltose or amylose and glycerol, in order to investigate the interactions between an α-glucan and a plasticizer other than water. A modification of molecular relaxations was expected due to the proximity between the β relaxation of the oligomer or polymer and the glycerol α relaxation.

2. Results

Amylose–glycerol–water.

Samples water content. Variations of water content with glycerol concentration in glycerol-plasticized starch films have been determined in a previous work [3]. The water content of amorphous starch films, conditioned at a constant relative humidity of 57%, was found to be 12.9% (w/w), expressed on a total weight basis. In the presence of glycerol, the water content in the samples stored in the same conditions increased slightly to reach 14% (w/w) for starch films containing approximately 22% (w/w) glycerol. In order to simplify the drawing of the relaxation map, the water content of comparable amylose films was approximated to 14% (w/w) in spite of its small dependence on glycerol content. Only variations of Tg dependent to glycerol content have been taken into account in this study.

Temperature dependence of dielectric behaviour. The temperature dependence of the dielectric permittivity E', and the dielectric loss E'', of the amylose–glycerol–water system for various glycerol contents is shown in Fig. 1 for glycerol contents of 0, 11.6, 14.2 and 19.1% (w/w). The data were obtained at 10 kHz, and the temperature range was centered about a loss maximum observed at 210–230 K. Above 300 K, a very high signal was observed for the loss factor E'' corresponding to conductive behavior. These data, reflecting properties not examined in the study, are not shown. The intensity and temperature of the loss maximum increased with increasing glycerol content. Dielectric permittivity E' increased in a continuous manner with temperature in the range studied. It also increased with increasing the glycerol content.

Temperature relaxation map for glycerol contents below 20% (w/w). Dielectric behaviour was examined as a function of glycerol composition for the

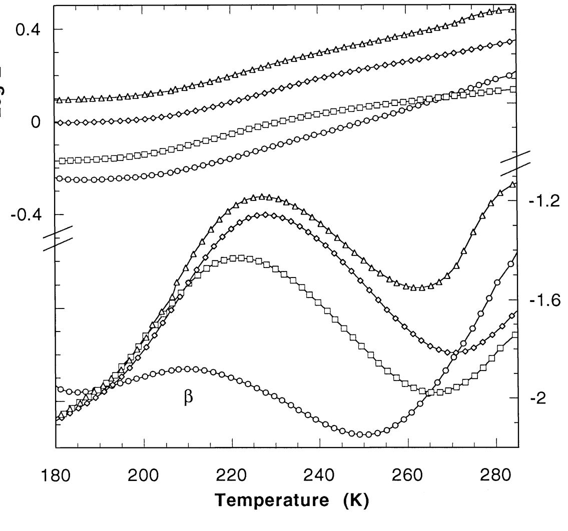

Fig. 1. Dielectric permittivity (E') and dielectric loss factor (E'') against temperature at 10 kHz for various glycerol contents (○, 0%; □, 11.6%; ◇, 14.2%; △, 19.1%) in a mix with amylose and approximately 14% water (by total weight).

ternary system, amylose–glycerol–water with water at 14% (w/w). These dynamic results were compared with the calorimetric transition temperature, using the method of Donth [16]. A relaxation temperature at 1 Hz was determined by a linear extrapolation of the loss maximum temperature in the range 100 Hz–1 MHz. These extrapolated temperatures and calorimetric *T*g of starch–glycerol–water system, measured in a previous study [3], are reported in Fig. 2 where the abscissa represents the glycerol level in the mix. For the secondary dielectric relaxation, the temperature of the loss maximum increased with increasing glycerol content, from 164 K for pure amylose with 14% (w/w) water to 199 K for a 68.8:17.2:14 amylose–glycerol–water content. At higher glycerol contents a small depression in the temperature of the relaxation in the range studied was observed. In the same range of plasticizer concentration (below 20% w/w), the *T*g of starch decreased rapidly with increasing glycerol content. When the glycerol content was above ≈20% (w/w) in the ternary system, the calorimetric signal corresponding to the glass transition became broad and *T*g was difficult to determine. No data at glycerol levels higher than 25% (w/w) were obtained. From previous studies [8,9], it is possible to assign the secondary relaxation observed for pure amylose containing 14% (w/w) water to a β process. For the binary 43:7 glycerol–water mix, the relaxation observed at 177 K is attributable to the glycerol α process with a depression of temperature due to the presence of water. For the ternary system containing amylose–glycerol–water, the relaxation appearing in the temperature range 150–200 K could be assigned to an α or β process. For the moment, pending further discussion, the relaxation of the ternary system will be referred to as a "low temperature relaxation".

In order to estimate the influence of water, dielectric experiments were carried out on samples dehydrated over phosphorus pentoxide. The low temperature relaxation of anhydrous films, shown in Fig. 2, was detected 10 to 30 K higher than for films containing water. This difference is particularly apparent for low glycerol contents. The general behaviour of dry samples remained similar to that of the ternary mixture: the low temperature relaxation increased with increasing glycerol content.

Arrhenius plots. The Arrhenius plots shown in Fig. 3 correspond to the frequencies of the maxima in the dielectric loss spectra, plotted against reciprocal temperature for the low temperature relaxation of some dry samples: amylose, glycerol, and a mixture 83.3:16.7 amylose–glycerol. Within the large frequency range shown in the Fig. 3, the non-Arrhenius behaviour of the glycerol α relaxation is revealed by the non linearity of the curve as previously described [17,18]. In fact, a primary relaxation activation energy generally decreases

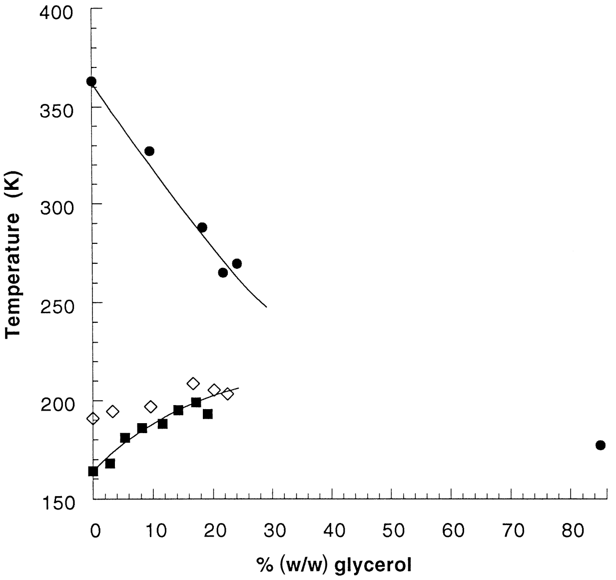

Fig. 2. Temperature relaxation map of the amylose–glycerol–14% water system reconstituted from calorimetric *T*g (●) and from the low relaxation temperature extrapolated at 1 Hz (■, dry samples; ◇, wet samples). In case of wet samples, the graduation indicates the glycerol amount in the mix amylose–glycerol–14% water.

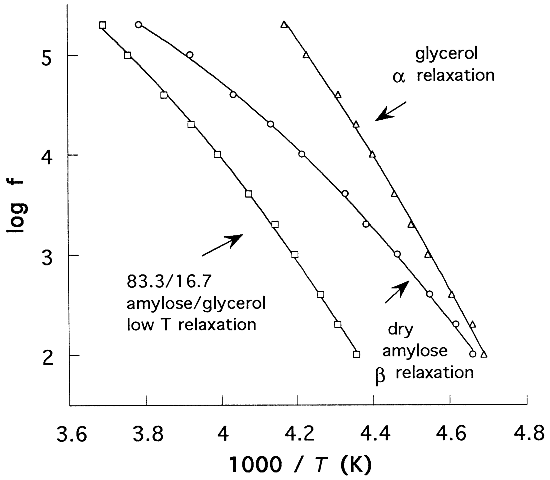

Fig. 3. A plot of the frequency of maxima in loss peaks of the different relaxations of dry samples against reciprocal temperature (○, amylose β-relaxation; △, glycerol α-relaxation; □, low relaxation of the 83.3:16.7 amylose–glycerol mix).

Table 1
Activation energies calculated for α, β and the low temperature relaxation within a frequency range from 100 to 10,000 Hz for the dry amylose–glycerol system

amylose–glycerol	$E_a\beta$ (kJ mol^{-1})	$E_a\alpha$ (kJ mol^{-1})	E_a mix (low T) (kJ mol^{-1})
100:0	84.8	—	—
96.7:3.3	—	—	102.2
90.4:9.6	—	—	107.0
83.3:16.7	—	—	105.3
79.8:20.2	—	—	105.0
77.5:22.5	—	—	127.0
0:100	—	128.5	—

with increasing temperature. In the case of glycerol, the dependence of the frequency of the loss maximum on temperature is known to be well-fitted by the Vogel–Tamman equation:

$$\log f_m = A - B/(T - To)$$

where A, B and To are adjustable parameters, f_m denotes the frequency at the loss maximum and T is absolute temperature.

Concerning the secondary relaxation of amylose (β relaxation), the origin of the non linearity of the curve was not explained. In order to compare activation energies of different relaxation processes, calculations have been performed with Arrhenius relationship in the frequency range from 100 to 10,000 Hz:

$$\log f_m = \log f_o - E_a/RT_m$$

where f_m is the frequency of the measurements, f_o the extrapolated frequency at high temperature, E_a the activation energy, R the gas constant and T_m the temperature of the loss maximum.

Activation energies calculated for all anhydrous compositions studied are shown in Table 1. These values have to be related to the frequency or the temperature range investigated. In dry amylose, an activation energy of 84.8 kJ mol^{-1} was higher than 56.8 kJ mol^{-1}, calculated from dynamic mechanical analysis (0.01–100 Hz) by Bradley et al. [8], and than 39.7 kJ mol^{-1} from dielectric properties (100–2000 Hz) reported by Nishinari [9]. These important differences could be due to the presence of residual water in the samples. The activation energy of 128.5 kJ mol^{-1} calculated for glycerol was also higher than the 91.9 kJ mol^{-1} calculated within a frequency range 100–10,000 Hz from data published by Shablakh et al. [18]. In this study, when 3.3% (w/w) glycerol was added to amylose, the activation energy increased rapidly from 84.8 to 102.2 kJ mol^{-1}. The activation energy remained relatively constant near a value of 105 kJ mol^{-1} in the 3.3–20.2% (w/w) glycerol domain. A slight increase from 20.2 to 22.5% (w/w) in glycerol content induced an important increase in activation energy from 105 kJ mol^{-1} to 127 kJ mol^{-1}. This previous value, obtained for a relatively low glycerol content, is near the activation energy of pure glycerol (128.5 kJ mol^{-1}).

Maltose-glycerol.

Temperature dependence of dielectric behaviour. The temperature-dependence of the dielectric permittivity E' and the dielectric loss factor E'' for various anhydrous maltose–glycerol mixtures is shown in Fig. 4. As noted for the previous system, dielectric behaviour at higher temperatures was affected by sample conductivity. E' and E'' values are given in arbitrary units. The signal detected

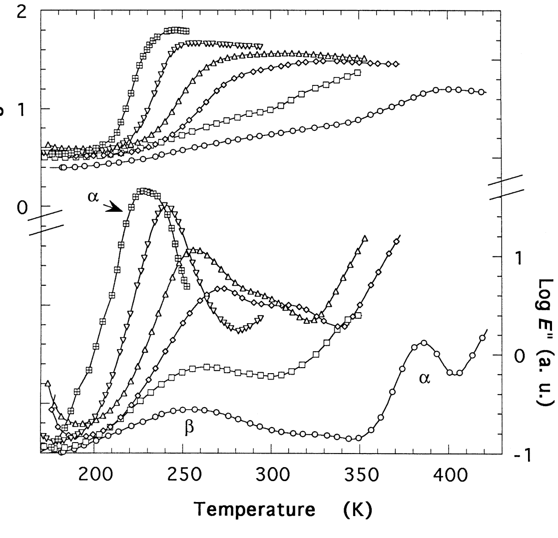

Fig. 4. Dielectric permittivity (E') and dielectric loss factor (E'') against temperature at 10 kHz for various glycerol contents (○, 0%; □, 9.0% ; ◇, 28.6%; △, 38.6%; ▽, 70.6%; ⊞, 100%) in a mix with maltose. The signal detected below 190 K was an artefact due to scanning equilibration.

below 190 K was an artefact due to scanning equilibration. Two maxima were observed in mixtures containing less than 28% (w/w) glycerol, but only one maximum, appearing at low temperature, was present for higher glycerol contents. When two distinct relaxations were observed, the high temperature process was designated a primary α relaxation, as in previous studies on maltose–water mixtures [7]. For the pure compounds, the β process of maltose (255 K at 10 kHz) and the α process of glycerol (227 K at 10 kHz) were observed at temperatures consistent with those of previous studies [14]. As in the case of the amylose–glycerol–water mixture discussed above, the relaxation in the maltose–glycerol mixture occurring between 227 and 277 K will be temporarily referred to as a “low temperature relaxation”.

Temperature relaxation map. The temperatures of the loss maximum, T_{max}, at 10 kHz for the different processes are reported in Fig. 5. The data, smoothed by a third order polynomial, are not reported in the 28 to 38% (w/w) domain of glycerol content because the continuity, disappearance or merger of different relaxation processes, is not clearly apparent. From 0 to 28% (w/w) glycerol content, the temperature of the α relaxation process decreased from $\approx$385 K (at 10 kHz) for pure maltose to $\approx$309 K (at 10 kHz) for the 71.4:28.6 maltose–glycerol mixture. In this domain, the change appeared to be continuous with glycerol content. This steady change in the temperature of the α process reflected the variation in calorimetric Tg of the mixture with composition. In the same composition range, the low temperature relaxation increased with increasing glycerol concentration, reaching about 277 K for the 71.4:28.6 maltose–glycerol mixture. Above this glycerol content, only one relaxation was observed. The temperature of this relaxation, measured at 10 kHz, decreased continuously from about 256 K for a 61.4:38.6 maltose–glycerol mix to 227 K for pure glycerol.

Arrhenius plots.—Arrhenius plots for pure maltose, pure glycerol and the mixture containing 38.6% (w/w) glycerol are shown in Fig. 6. Only relaxations appearing in the low temperature range are reported in the figure. Activation energies, calculated from the Arrhenius relation within the 100–10,000 Hz frequency range and corresponding to α, β and the mixture relaxations, are shown in Table 2. Concerning the low temperature relaxation, the activation energy of 47.5 kJ mol^{-1} in pure maltose was greatly modified at a relatively low glycerol content of 4.7% (w/w). However, it remained relatively constant at about 90–100 kJ mol^{-1} until 28.6% (w/w) of glycerol added. Over the same range, the activation energy calculated for the well identified α relaxation decreased from 387.0 kJ mol^{-1} to 267.1 kJ mol^{-1}. Above 28.6% (w/w) glycerol content, the activation energy of the low temperature relaxation increased rapidly from 98.5% (w/w) to reach a maximum of 160 kJ mol^{-1} at 52.5% (w/w), before decreasing at higher glycerol content, falling to the value of 128.5 kJ mol^{-1} calculated for pure

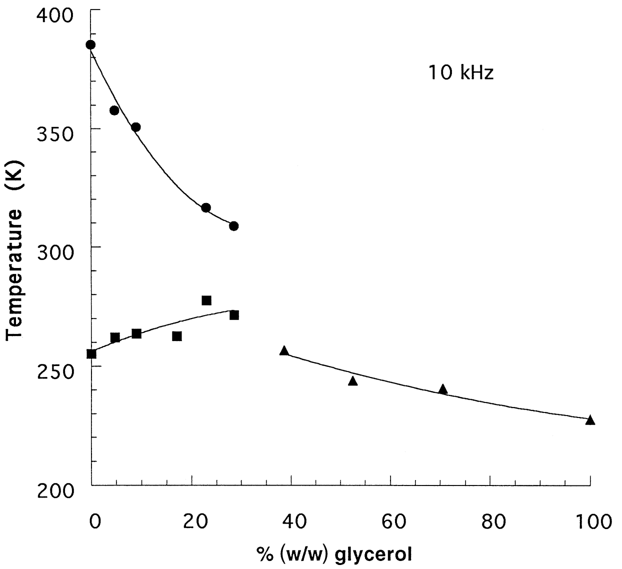

Fig. 5. Temperature relaxation map of the maltose-glycerol system from the loss maximum temperature at 10 kHz (●, maltose α-relaxation; ▲, glycerol α-relaxation; ■, maltose β-relaxation).

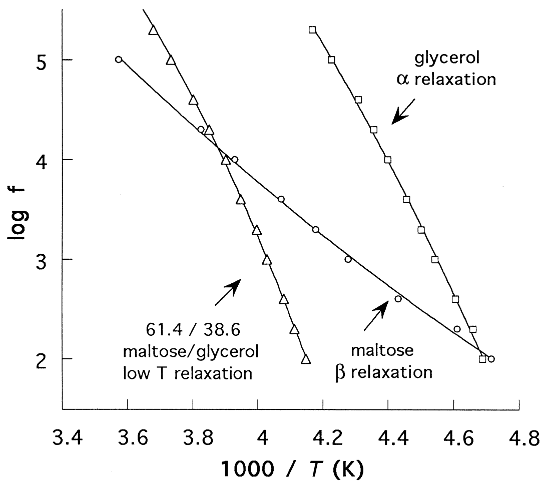

Fig. 6. A plot of the frequency of the maxima in the loss peaks of the different relaxations against reciprocal temperature (○, maltose β-relaxation; △, glycerol α-relaxation; □, low relaxation of the 61.4:38.6 maltose–glycerol mix).

Table 2
Activation energies calculated for α, β and the low temperature relaxation within a frequency range from 100 to 10,000 Hz for the maltose–glycerol system

maltose–glycerol	$E_a\beta$ (kJ mol^{-1})	$E_a\alpha$ (kJ/mol^{-1})	E_a mix (low T) (kJ mol^{-1})
100:0	47.5	387.0	—
95.3:4.7	—	328.8	90.9
91.0:9.0	—	—	100.7
82.9:17.1	—	—	96.2
77.0:23.0	—	284.2	100.2
71.4:28.6	—	267.1	98.5
61.4:38.6	—	—	151.0
47.5:52.5	—	—	160.2
29.4:70.6	—	—	136.3
0:100	—	128.5	—

glycerol. The possibility of the coexistence of two relaxations in a limited temperature domain cannot be ruled out. This is why the corresponding activation energy of this not well identified relaxation is noted in the column "*E*a mix".

3. Discussion

Variations in the temperature of the α relaxation in the maltose–glycerol system show many similarities with that of the amylose–glycerol–water system. For quantities below 28% (w/w), glycerol exerted a considerable depressive effect on the maltose α relaxation. However, in the maltose–glycerol system, at glycerol contents in the range 28 to 38% (w/w), a complex behaviour was observed for the primary relaxation. Results of calorimetric analysis obtained by Orford et al. [19] for malto-oligosaccharide–water systems indicated that *T*g variations in maltose–water systems cannot be predicted by a simple thermodynamic approach based on a regular mixture. The observed glass transition behaviour was quite different to that predicted by the Couchman–Karasz model [20], and might result from specific interactions (i.e., hydrogen bonds) between components. Similarly, for the amylose–glycerol–water system, addition of glycerol quantities from 0 to 25% (w/w) had a depressive effect on *T*g. At higher glycerol contents, discontinuous behavior was observed. An extrapolation of experimental data from the relaxation maps of both systems suggested a disappearance of the low temperature relaxation, or a merger with the primary α process, at a glycerol content of around 30% (w/w). This complex behaviour, never discussed in carbohydrate system, can be compared to that of other polymer-solvent systems. In the polyvinylchloride–tetrahydrofuran system [21], an α process assigned to segmental motions, and a β process observed in bulk PVC, merged at THF concentrations above 20% (w/w). According to Donth [16], this composition indicates the minimal polymer concentration required to generate conditions for a local mode β relaxation typical of polymers. The discontinuity in the α relaxation marked a structural change, related to the occurrence of the β process at this composition.

Several aspects of the behaviour to the aforementioned example are similar to that observed for the relaxation behaviour of maltose–glycerol and amylose–glycerol–water systems. At glycerol contents less than 20–35% (w/w), the behaviour was rather close to that expected for an oligomer (or polymer) modified by a low molecular weight diluent: both relaxations characteristic of maltose, or amylose, were detected in the mixture with glycerol. It appears reasonable to call both processes α and β as in the pure main component. For the system containing amylose, the polymer could form the continuous phase and the solvent occupy interstitial sites, which would account for the film-forming property in this plasticizer concentration range. The 20–35% (w/w) glycerol domain showed a discontinuity in relaxation temperatures and activation energies. Above this glycerol concentration, the motions relative to "low relaxation" seemed closer to those of the intrinsic glycerol α relaxation. The existence of glycerol-rich microdomains is consistent with the simultaneous presence of two mechanical relaxations at a high glycerol content (25% w/w) reported in a previous study of the starch–glycerol–water system [6]. The existence of a phase separation in plasticized systems containing amylose or starch is still debatable [3–5] and will be solved by a better definition of the size frontier of microdomains between nanoheterogeneity and phase separation. Unfortunately, the evaluation of size domain is limited actually by the lack of appropriate experimental methods.

We shall now focus on the particular behaviour of the low temperature relaxation at glycerol contents below 25% (w/w), In the two systems studied, amylose–glycerol (with or without water) and maltose–glycerol, the β relaxation did not decrease when glycerol was added, but showed an increase. It is noteworthy that the relaxation temperature of the mixture was higher than that of the pure components. This effect indicates that the low temperature relaxation is probably the result of a coupling of the β motions of maltose or amylose and the α relaxation of pure glycerol. Such additional relaxations, due to interactions between the polymer and solvent molecules, have been previously observed in the toluene–polyisoprene system [22]. The proximity of both relaxations in temperature and energy lends support to this proposal. In an advanced model developed by Ngai et al. [23,24], a coupling parameter n between the intramolecular motions of different adjacent molecules was found proportional to the strength of the mutual dynamical constraints. This coupling parameter model provides a logical link with mechanical properties.

No precise stoichiometry can be inferred for the systems studied in the present work, although a discontinuity was found for a glycerol concentration equivalent to 3 glycerol molecules per 2 maltose molecules and 2 glycerol molecules per 5 anhydroglucose units. This last value is not far from the stoichiometry estimated as 1 glycerol per 3 anhydroglucose units needed to get an helical complex formation between glycerol and amylose observed by Hulleman et al. [25].

4. Experimental

All concentrations are expressed as % (w/w, total weight).

Maltose-glycerol system.—Maltose monohydrate (Sigma, St Louis, MO) and anhydrous glycerol (E. Merck, Darmstadt, Germany) were used without further purification. Dry amorphous maltose was prepared by drying a melt of the monohydrate in a vacuum oven over P_2O_5 at 333 K. To obtain anhyd maltose–glycerol mixtures, samples with the appropriate glycerol content were melted in sealed tubes at 403 K.

Amylose–glycerol–water system.—Amylose from potato starch was purchased from Avebe (Foxhol, The Netherlands) and purified by solubilization in 95% Me_2SO, precipitation by EtOH and drying by solvent exchange. After this pretreatment, amylose was easily solubilized in water at 100 °C yielding a clear soln. The amylose–glycerol–water films were cast according to the following procedure: amylose was dissolved at a concn $\sim$1 mg/mL in boiling water under N_2 atmosphere. When dissolved, a known quantity of glycerol was added. The soln was then poured onto a Teflon-coated plate kept at 343 K and dried to a water content of about 10% (w/w). Samples with glycerol concns above 20% (w/w) were not examined due to an apparent phase separation during the drying step. This was not observed for plasticized starch films. Films were stored for 48 h in an atmosphere controlled by a saturated NaBr soln (R.H. 57% at 25 °C). For "anhydrous" films, samples were dried at 25 °C in a chamber containing P_2O_5 which maintained a relative humidity below 2%.

Dielectric analysis.—For the maltose–glycerol system, hot liquid was poured onto the lower electrode of the dielectric cell and the upper electrode mounted in place within the cell holder. For amylose–glycerol–water films, samples were directly cut and placed between the lower and upper electrodes. A dielectric thermal analyzer (Polymer Laboratories, Loughborough, UK), equipped with a Hewlett–Packard 4284A bridge and a stainless steel parallel plate cell (diameter 33 mm; gap 0.5 mm for sugar mix and 0.05 mm for films), was used for the measurements. Temperature was controlled between 160 and 410 K using a liquid N_2 cryostat and electric heating elements surrounding the sample cell which was placed within an enclosure. Measurements of the dielectric constant, $E'(T)$, and dielectric loss, $E''(T)$, were carried out in the 100 Hz to 1 Mhz frequency range under a linear scanning temperature of 1 K/mn.

Acknowledgements

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References

[1] J.M.V. Blanshard and P.J. Lillford, *The Glassy State in Foods*, University Press, Nottingham, 1993.

[2] R.L. Shogren, *Biodegradable Polymers and Packaging*, Technomic Publishing, Lancaster, 1993.

[3] D. Lourdin, L. Coignard, H. Bizot and P. Colonna, *Polymer*, 38 (1997) 5401–5406.

[4] M.T. Kalichevsky, E.M. Jaroszkiewicz and J.M.V. Blanshard, *Polymer*, 34 (1993) 346–358.

[5] P. Forssell, J. Mikkilä, T. Suortti, J. Seppälä and K. Poutanen, *J. Macromol. Sc. Pure Appl. Chem.*, A33 (1996) 703–715.

[6] D. Lourdin, H. Bizot and P. Colonna, *J. Appl. Polym. Sci.*, 63 (1997) 1047–1053.

[7] T.R. Noel, R. Parker and S.G. Ring, *Carbohydr. Res.*, 282 (1996) 193–206.

[8] S.A. Bradley and S.H. Carr, *J. Polym. Sc. Polym. Phys. Ed.*, 14 (1976) 111–124.

[9] K. Nishinari, *J. Polym. Sc. Polym. Phys. Ed.*, 18 (1980) 1609–1619.

[10] M. Scandola, G. Ceccorulli and M. Pizzoli, *Int. J. Biol. Macromol.*, 13 (1991) 254–258.

[11] T.R. Noel, S.G. Ring and M.A. Whittam, *J. Phys. Chem.*, 96 (1992) 5662–5667.

[12] J. Perez, *Physique et Mécanique des Polymères Amorphes*, Lavoisier, Paris, 1992.

[13] D.C. Champeney and F. Ould Kaddour, *Molecular Physics*, 52 (1984) 509–523.

[14] D.W. Davidson and R.H. Cole, *J. Chem. Phys.*, 19 (1951) 1484–1490.

[15] G.P. Johari and M. Goldstein, *J. Chem. Phys.*, 55 (1971) 4245–4252.

[16] E.-J. Donth, *Relaxation and Thermodynamics in Polymers*, Akademie Verlag, Berlin, 1992.

[17] C.A. Angell and D.L. Smith, *J. Chem. Phys.*, 86 (1982) 3845–3852.

[18] M. Shablack, R.M. Hill and L.A. Dissado, *J. Chem. Soc., Faraday Trans.*, 78 (1982) 625–638.

[19] P.D. Orford, R. Parker, S.G. Ring and A.C. Smith, *Int. J. Biol. Macromol.*, 11 (1989) 91–96.

[20] P.R. Couchman and F.E. Karasz, *Macromolecules*, 11 (1978) 117.

[21] K. Adachi and Y. Ishida, *J. Polym. Sci. Polym. Phys. Ed.*, 14 (1976) 2219–2230.

[22] K. Adachi, Y. Imanishi and T. Kotaka, *J. Chem. Soc. Faraday Trans.*, 85 (1989) 1075–1082.

[23] K.L. Ngai, R.W. Rendell, A.F. Yee and D.J. Plazek, *Macromolecules*, 24 (1991) 61–67.

[24] K.L. Ngai, R.W. Rendell and A.F. Yee, *Macromolecules*, 21 (1988) 3396–3401.

[25] S.H.D. Hulleman, W. Helbert and H. Chanzy, *Int. J. Biol. Macromol.*, 18 (1996) 115–122.