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Volumetric behaviour of maltose–water, maltose–glycerol and starch–sorbitol–water systems mixtures in relation to structural relaxation

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Abstract

The densities of amorphous maltose–water, maltose–glycerol and starch–sorbitol–water mixtures were measured using a vibrating-tube density meter and pycnometry. The volumetric change on mixing was investigated through the calculation of the quantity $\Delta V/V$, the difference between (experimental) volume of the mixture and the linear composition weighted pure constituent volumes (ideal mixing). For all of the systems studied the quantity $\Delta V/V$ was negative and approached a minimum of -0.03 and -0.015 at mass fractions of maltose in the region of 0.75 and 0.85 for the maltose–water and maltose–glycerol mixtures, respectively. Results are discussed in the context of volume change due to structural relaxation of vitreous materials and related to the phenomenon of antiplasticisation.

Keywords: Starch; Maltose; Excess volume; Plasticization

1. Introduction

Starch and its hydrolysis products are often used in the nearly dry state in food and non-food applications. In view of the quantity of residual water present in these products, typically between 5 and 12%, the processed starch products are usually glasses at room temperature. The structural relaxation time of a glass is typically >100 s, and the materials behave in this sense as solids. Low-molecular-weight species are generally added to modify the physical and/or organoleptique properties of these materials. State diagrams for representative systems and their associated methodologies are well-described in the literature.[1–4] Some of them demonstrate the plasticising effect of water and other diluents in depressing the glass transition temperature, T_g.

Below T_g, the molecular basis for macroscopic behaviour such as mechanical characteristics or gas permeability is not well understood.[5,6] While there are relationships describing the effect of local polymer mobility on physical properties,[7] the effect of the volumetric behaviour of the mixtures on polymer mobility and material properties is less clear.[8] A previous study of these systems examined the time-dependent change in material properties in the glassy state (physical ageing) arising as a result of a slow structural relaxation. This study demonstrated that a densification of the glass on ageing was accompanied by changes in the physical properties of the material, including its mechanical properties and permeability to small molecules.[9] For example, during the physical ageing of maltose containing 5% water over a 20-h period, a negative relative volume change, $\Delta V/V$ of the order of 1.5×10^{-3} was observed. This volume change was accompanied by an increase of 50% in Young's modulus from 2.08×10^{10} to 3.13×10^{10} N/m^2. For a starch-based glass the change in volume, $\Delta V/V$, was 0.5×10^{-3} over an 80-h period and was accompanied by an increase of 30% in Young's modulus from 3.17×10^9 to 4.09×10^9 N/m^2. These results showed that starchy

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materials became stiffer and more brittle during physical ageing. Another origin of density change in polymeric systems is that obtained on mixing a polymer and diluent. For synthetic polymer systems these effects can be small; in homologues of polymers the volume is additive.[10] In biopolymer systems these effects may be much larger because of the strength of hydrogen-bonded interactions.

Densitometry has been used for a long time to study liquids and liquid mixtures at equilibrium. The density of liquid mixtures can be used to infer information on molecular packing and the strength of molecular interactions through the determination of the excess volume of mixing. In this study we determine volume changes on mixing maltose and starch with plasticisers, including water, for compositions which are glassy or near-glassy at room temperature.

2. Materials and methods

2.1. Materials

Maltose monohydrate was purchased from Sigma (St Louis, MO), and anhydrous glycerol from E. Merck (Darmstadt, Germany). Both 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. Maltose–water and maltose–glycerol mixtures were melted and stirred in sealed tubes at 403 K. Amorphous starch–sorbitol mixtures were prepared by extrusion of native potato starch, containing 25% water, with various sorbitol contents. The extruded starch mixture was granulated ($\sim$1 mm^3) and conditioned at a relative humidity of 57%. Sorbitol content of the product was determined using an enzymatic kit (Boehringer). Water content was determined by the Karl Fischer method. All analyses were carried out in triplicate.

2.2. Calorimetry

Samples ($\sim$10 mg) were sealed in pre-weighed aluminium pans in an argon atmosphere. DSC experiments were performed using a Perkin–Elmer DSC 7 fitted with a robotic autosampler. The DSC was calibrated for temperature, at each heating rate used, from the melting points of indium (429.7 K) and dodecane (263.5 K). The heat flow was calibrated from the heat of melting of indium (28.45 J/g), and the calibration for heat capacity used a sapphire standard. The calorimetric measurement procedure was similar for all samples that were glassy at room temperature. A first scan was performed from ambient to 383 K to ‘erase’ the effects of structural relaxation during the conditioning and storage of the samples. This was followed by rapid cooling at 25 K/min to 243 K to freezes in the amorphous sample well below T_g. The actual measurement was performed during a second scan at 10 K/min. T_g was determined as the midpoint of the sharp heat capacity change at the transition.

2.3. Density measurements

Densities of solutions were measured with a high precision vibrating tube digital Anton Paar DMA 60 density meter in combination with the Anton Paar DMA 602 density measuring cell. The temperature was regulated at ± 0.001 K by a thermostat controlled by a Hewlett–Packard 2804A quartz thermometer. The temperature of the oscillating tube was controlled at 298.15 ± 0.05 K. The solutions were injected into the U-tube from a 1 cm^3 disposable syringe. The instrument was calibrated using water and aqueous KCl solutions of known density.[11] The density of solid materials was determined at 298.15 ± 0.05 K using a pycnometer, calibrated for volume from measurement of the mass of degassed water required to fill it. A known mass of solid sample (about 1 g) was introduced into the pycnometer which was further filled with degassed decane (Aldrich, HPLC grade). The decane was immiscible with the carbohydrate sample. The system was immersed in a water bath regulated to ± 0.001 K, made up to volume after thermal equilibration, cooled to ambient temperature, the outside dried and then weighed. The density of the decane (measured using the density meter) was 0.72614 g/cm^3 at 298.15 K, and the density of the solid carbohydrate calculated. Repeated measurements were found to be within ± 0.0001 g/cm^3 using this approach.

3. Results and discussion

3.1. Calorimetric behaviour

The dependence of the glass transition temperature on the mass fraction plasticiser, for the systems maltose–water and maltose–glycerol is shown in Fig. 1 and reported in Tables 1 and 2. For the maltose–water system the results obtained are in agreement with those obtained by Orford et al.[12] (shown as the full line). The value of glass transition of water reported in Table 1 is from Sugisaki et al.[13] The T_g of the maltose–glycerol mixture shows a continuous dependence on composition falling to 190 K for pure glycerol[14]. These state diagrams show that both water and glycerol plasticise maltose, with water being the more effective plasticiser. Previous work[12,15] showed the dependency of glass transition with composition which can be predicted using the thermodynamic approach of Couchman Karasz.[16] This theory models the glass transition as a

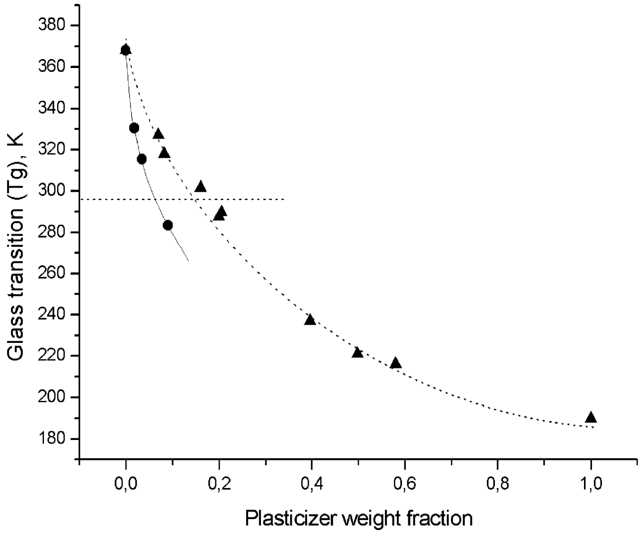

Fig. 1. Composition dependence of T_g (in K) for maltose–water (●); and maltose–glycerol (▲) mixtures.

second-order transition whose position is determined by the equality of the entropy in the liquid and glassy state.

3.2. Density measurements

At 298 K mixtures containing <0.07 and 0.19 mass fraction of water and glycerol, respectively, are vitreous. At higher concentrations of plasticiser, the T_g of the mixture is less than 298 K. For these compositions, structural relaxation is relatively rapid, and as a consequence volumetric equilibrium is easily achieved on mixing. For compositions which are vitreous at 298 K (see Fig. 1, mass fraction of water and glycerol <0.07 and 0.19, respectively), it has been shown that volumetric equilibrium cannot be achieved on practical timescales, as a consequence of the slow structural relaxation. To obtain reproducible results for the vitreous materials, densities were measured immediately after a standard thermal treatment to erase history effects—heating during 10 min to 10 K above T_g, followed by a quench to the temperature of measurement. These materials we term as minimally aged.

In Tables 1–3 we report the measured densities (ρ_{meas}) for the systems maltose–water, maltose–glycerol, and starch–sorbitol–water, respectively. The reported densities marked with (a) in the table refer to materials where the volume could further change as a result of structural relaxation. The other values refer to materials that are completely relaxed. These values are compared with those calculated (ρ_{calc}) from the known densities of the pure and non-aged components and the composition of the mixture, assuming an ideality of mixing. This permitted calculation of the quantity $\Delta V/V$ from the relationship

$$\Delta V/V = (1/\rho_{meas} - 1/\rho_{calc})/1/\rho_{meas} \quad (1)$$

Figs. 2 and 3 show the dependence of $\Delta V/V$ on composition for the maltose–water and the maltose–glycerol mixtures, respectively. For all of the systems studied, the quantity $\Delta V/V$ is negative. The values of $\Delta V/V$ approach a minimum of -0.03 and -0.015 at mass fractions of maltose in the region of 0.75 and 0.85 for the maltose–water and maltose–glycerol mixtures, respectively. These compositions correspond to an approximate stoichiometry of six molecules of water to one of maltose, and one molecule of glycerol to one of maltose. For the maltose molecule it should be noted that eight hydroxyl groups are available for interaction with water, and the presence of an intramolecular hydrogen bond would reduce this number to six. In a recent study, Matsuoka et al.[17] found the maltose hydration number n_h, to be 5.9 water molecules per maltose molecule. The observed density of starch–water mixtures was comparable to that observed previously.[18] For the more complex system, the starch–sorbitol–

Table 1
Composition dependence of T_g and density of maltose–water mixtures and associated volume change on mixing

Mass fraction of maltose	Mass fraction of water	T_g (K)	Density (g/cm^3) measured	Density (g/cm^3) calculated	$\Delta V/V$
0	1	134 [b]	0.9970	0.9970	
0.335	0.665		1.1439	1.1268	−0.0151
0.372	0.628		1.1625	1.1432	−0.0168
0.473	0.527		1.2160	1.1906	−0.0213
0.700	0.300		1.3504	1.3131	−0.0284
0.795	0.205		1.4127	1.3721	−0.0293
0.796	0.204		1.4127	1.3727	−0.0291
0.910	0.090	283	1.4807	1.4511	−0.0204
0.966	0.034	315	1.5140 [a]	1.4929	−0.0142
0.982	0.018	330	1.5141 [a]	1.5053	−0.0058
1	0	368	1.5195 [a]	1.5195	

[a] The volumetric equilibrium for composition was not achieved.
[b] From Ref. 13.

Table 2
Composition dependence of T_g and density of maltose–glycerol mixtures and associated volume change on mixing

Mass fraction of maltose	Mass fraction of glycerol	T_g (K)	Density (g/cm^3) measured	Density (g/cm^3) calculated	$\Delta V/V$
0	1	190	1.2577	1.2577	
0.042	0.958		1.2666	1.2669	0.0002
0.137	0.863		1.2890	1.2882	−0.0007
0.240	0.760		1.3141	1.3112	−0.0016
0.420	0.580	216	1.3639	1.3557	−0.0060
0.502	0.498	221	1.3911	1.3768	−0.0103
0.520	0.480		1.3956	1.3814	−0.0102
0.604	0.396	237	1.4160	1.4037	−0.0087
0.795	0.205	290	1.4766	1.4573	−0.0132
0.800	0.200	288	1.4789	1.4588	−0.0138
0.840	0.160	301			
0.918	0.082	318	1.5086 [a]	1.4939	−0.0098
0.931	0.069	327	1.5137 [a]	1.4979	−0.0105
1	0	368	1.5195 [a]	1.5195	

[a] The volumetric equilibrium for composition was not achieved.

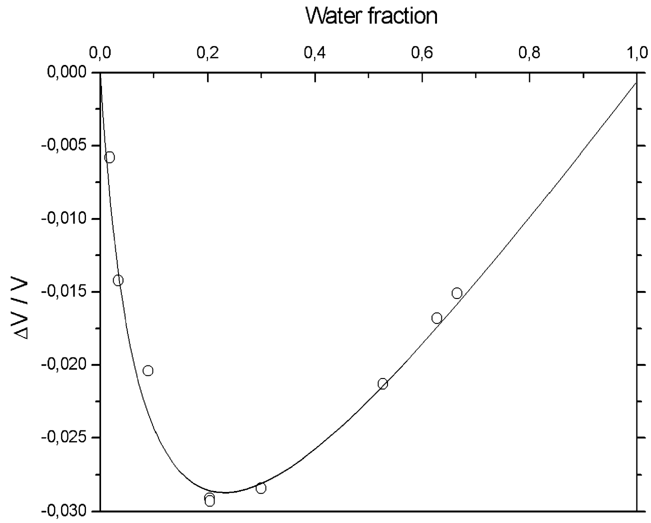

Fig. 2. Composition dependence of volume change ($\Delta V/V$) for a maltose–water mixture at 298 K.

water system, the minimum in $\Delta V/V$ of -0.06 occurs at a composition of 0.83:0.05:0.12. The evolution of $\Delta V/V$ with time during the course of the structural relaxation is difficult to predict.

The (negative) excess volume of mixing is dependent on molecular packing and the strength of the interaction between the different species. When the interaction between the components of the mixture is stronger than the interaction between molecules of the same species, a negative excess volume of mixing may be expected. It is well known[19] that simple carbohydrate monomer–water mixtures have negative excess volumes of mixing, arising as a result of the strength of the hydrogen-bonded interactions between water and the carbohydrate. The results obtained in the present study indicate that this effect is relevant to an oligomeric and polymeric starch-based systems. The observed relative volume changes arising as a result of mixing (of the order of 10^{-2}) are an order of magnitude greater than those observed during physical ageing (of the order of

Table 3
Composition dependence of the density of starch–sorbitol–water mixtures and associated volume change on mixing

Mass fraction of starch	Mass fraction of sorbitol	Mass fraction of water	Density measured (g/cm^3)	Density calculated (g/cm^3)	$\Delta V/V$
0	1	0	1.4455		
1	0	0	1.4985		
0	0	1	0.9970 [a]		
0.870	0	0.130	1.4706	1.4066	−0.0455
0.828	0.050	0.122	1.4866	1.4003	−0.0616
0.819	0.096	0.085	1.4872	1.4323	−0.0383
0.796	0.131	0.073	1.4921	1.4388	−0.0370
0.750	0.169	0.081	1.5030	1.4314	−0.0500
0.632	0.287	0.081	1.4808	1.4255	−0.0388

[a] Ref. 20.

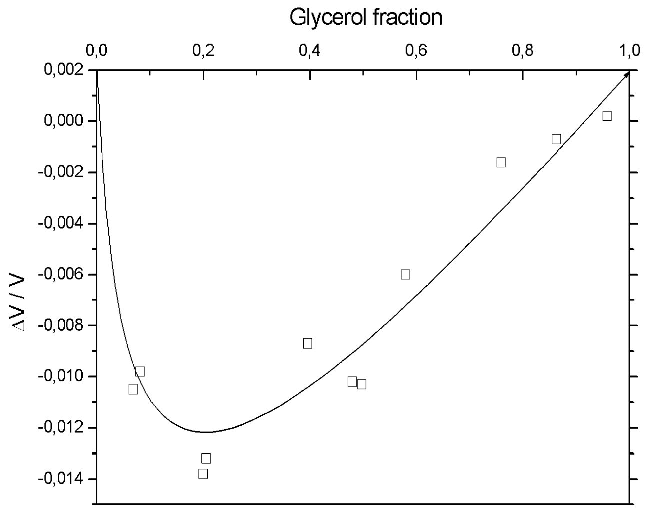

Fig. 3. Composition dependence of volume change ($\Delta V/V$) for a maltose–glycerol mixture at 298 K.

10^{-3}). Consequently it can be expected that the negative volume change on mixing starch oligosaccharides and polysaccharides with water will have important consequences for materials properties in glassy and near-glassy systems. It has been observed that starch–water mixtures exhibit antiplasticisation,[5,6] that is although water can depress T_g, the addition of water can actually lead to an increase in stiffness of the material. In the same way that the negative volume change that occurs on the physical ageing of starch materials is associated with an increase in material stiffness and an embrittlement, the negative volume change which occurs on mixing components has a larger effect. This volume change will also affect other characteristics of these materials such as their permeability to low-molecular-weight species.

4. Conclusions

This research on the density of starch–water systems has shown that the volume changes obtained on mixing components is comparable to that observed on physical ageing. The strong affinity of maltose and starch for low-molecular-weight polar molecules such as water and glycerol induces a negative volume change. It is proposed that this volume change has a one-to-one correspondence with the previously observed antiplasticisation phenomenon in starch systems.

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