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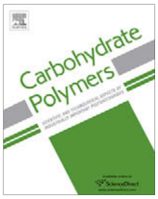

Viscous fragility of concentrated maltopolymer/sucrose mixtures

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The rheological properties of low moisture content glass-forming solutions of a maltopolymer and sucrose were measured over a range of temperatures. The results showed near-Newtonian behaviour throughout the measureable regime. Shear and dynamic viscosity data were combined and modelled as a function of temperature by a restricted Vogel–Fulcher–Tammann (VFT) equation. The fragility parameter ($F_{1/2}$) ranged from 0.6 to 0.7, which represents moderate to fragile behaviour. Fragility decreased with increased moisture content for some carbohydrate compositions, but experienced little change for others. Carbohydrate compositions with lower weight-average molecular weight and/or lower degrees of polydispersity were more fragile. Some basis for expecting a polydispersity dependence can be found in empirical relations used to model the glass transition temperature and melt viscosity of carbohydrate polymers, which employ number-average and weight-average dependencies, respectively.

1. Introduction

The rate at which the viscosity (or relaxation time) increases on cooling can be used to classify liquids according to a "strong"/"fragile" scheme (Angell et al., 1994). The thermal fragility of a carbohydrate glass-forming composition is particularly relevant to industrial practices such as melt extrusion because it provides a link between melt viscosity (an important processing parameter) and the glass transition temperature (T_g). The latter is often used to predict product properties during storage (Kasapis, 2008). A more fragile composition will increase in viscosity more steeply on cooling within the glass transition region compared to a strong composition.

The melt extrusion of glassy carbohydrate products is becoming increasingly important industrially. Traditional products such as hard candies, food wafers and oral lozenges are examples of materials that employ a temperature induced vitrification during their manufacture. More recently, glasses have been chosen for food and nutraceutical applications to limit molecular mobility during storage and thereby preserve labile biochemicals (Gouin, 2004). For example, omega-3 fatty acids can be physically encapsulated in carbohydrate compositions that after melt extrusion form glassy particles at room temperature (Valentinotti, Armanet, & Porret, 2006).

In addition to providing guidance towards thermal processing, fragility data also finds practical application for characterizing relaxations near and within the glassy state (Pikal, Chang, & Tang, 2004; Shamblin, Tang, Chang, Hancock, & Pikal, 1999). Understanding and controlling mobility within glassy products is a widely shared ambition in both the food (Le Meste, Champion, Roudaut, Blond, & Simatos, 2002) and pharmaceutical industries (Shamblin, Hancock, & Pikal, 2006). Studies on amorphous pharmaceutical solids, which can offer improved availability of an active compared to the crystalline state, in particular have brought much attention to measures of fragility. For such work, it is common to assess fragility through thermal methods (Crowley & Zografi, 2001), which are often simple and rapid to perform, or by mechanical and dielectric spectroscopies (Angell, Ngai, McKenna, McMillan, & Martin, 2000), which can be used to probe relaxations over broad time and temperature ranges spanning from liquid to glass range behaviours. Reasonable correlation is often found between a number of calorimetric and spectroscopic measurements (Ito, Moynihan, & Angell, 1999; Matyushov & Angell, 2007).

Results presented here are from viscosity measurements on liquids and reach a maximum of only ~10^7 Pa s, which is well below the glass transition range (~10^{12} Pa s). The temperature dependence of a number of relaxation modes is known to decouple from shear viscosity near and below the glass transition temperature (Debenedetti & Stillinger, 2001). Therefore, extending fragility results derived from viscosity measurements to the glassy state may require some consideration of the specific relaxation mode of interest and how its behaviour may differ from bulk viscosity.

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While fragility for a broad range of pure materials has been reported elsewhere, there is less information available on the specific influences of composition for molecular mixtures. The goal of the current work is to systematically study the effect of changes in carbohydrate composition on viscous fragility. Mixtures of sucrose and maltopolymers were selected because such compositions are typical of a number of commercially available extruded glassy products. Formulation ratios were chosen in such a way as to provide a range of number-average (M_n) and weight-average (M_w) molecular weight values. Each composition was also plasticized with various amounts of water. Both shear and dynamic viscosity measures were employed and results were then modelled as a function of temperature to yield fragility parameters.

Eq. (1) gives the Vogel–Fulcher–Tammann (VFT) equation, which relates viscosity (η) to temperature (T), through model constants η_o, D, and T_0. The pre-exponential parameter (η_o) represents the viscosity of the liquid at infinite temperature. The T_0 parameter, which has been called the Vogel temperature or ideal glass transition temperature, is a point below T_g (the kinetic glass transition temperature) and above 0 K, where viscosity (and relaxation time) approaches infinity. "D" represents a dimensionless fragility parameter which takes a low value (e.g. less than 5) for "fragile" liquids and high values (up to 100) for "strong" liquids. The modeling can be facilitated by combining the ($D*T_0$) expression into a single parameter, which is called "B" or the curvature parameter.

$$\eta = \eta_0 \exp\left(\frac{DT_0}{(T - T_0)}\right) \tag{1}$$

One factor that challenges readers who wish to compare fragility parameters reported in the literature is that the VFT model is often applied in very different ways. With three unrestricted parameters, it is a flexible equation. Particularly for data sets that span small ranges of η and T, the model parameters are sufficiently interdependent that often a number of solutions exist, each fitting the experimental data reasonably well. In the case of the current data set, the results are limited by boiling or decomposition at high temperatures and high viscosity at low temperatures. One approach is to restrict one of the model parameters to a fixed value. Within this work, η_o is restricted to 10^{-5} Pa s. This route has broad precedent (Angell, 1997) and some have argued that it is justified (Nascimento & Aparicio, 2007). However, it is not a universally followed practice. The fragility parameters reported here will differ from those reported, for example, by modeling with η_o restricted to slightly different values (Giordano, Russell, & Dingwell, 2008; Rampp, Buttersack, & Ludemann, 2000), or through restrictions on either the B (Elias & Elias, 1999) or T_0 (Recondo, Elizalde, & Buera, 2006) parameters.

A second challenge for readers is that there are also several other parameters reported as fragility (in addition to D) that are not necessarily equivalent expressions. Within this text we also present "$F_{1/2}$", which describes the degree of departure from an Arrhenius process, i.e. one that follows $\eta = \eta_o \exp(E/k_bT)$. $F_{1/2}$ varies between 0, for very strong liquids with Arrhenius-based relaxation dynamics, to 1 for a very fragile hypothetical liquid that undergoes an instantaneous drop in viscosity on heating (Wang, Angell, & Richert, 2006). $F_{1/2}$ can be calculated by Eq. (2), where $T_{1/2}$ is the temperature at which the viscosity reaches a point halfway between its value at T_g (10^{12} Pa s) and η_o (10^{-5} Pa s) on a logarithmic scale. Within this text, $T_{1/2}$ therefore occurs at the temperature at which viscosity equals $10^{3.5}$ Pa s.

$$F_{1/2} = \frac{2T_g}{T_{1/2}} - 1 \tag{2}$$

2. Materials and methods

Mixtures of maltodextrin (Star Dri 18DE or Star Dri 5DE, Tate & Lyle, Decatur, IL, USA) and sucrose (pure cane extra fine granular sucrose, Domino Foods, Inc., Yonkers, NY, USA) were prepared on an anhydrous mass basis. The DE or dextrose equivalence value is a term used for maltopolymer products to describe the degree of starch hydrolysis. The DE value describes the number of reducing end groups per unit mass compared to that of pure glucose and is therefore inversely related to number-average molecular weight.

The powder mixtures were dissolved in approximately 30 wt.% deionised water and heated to yield a clear solution. A small amount (0.46 g/kg of the dry carbohydrate mixture) of potassium hydroxide (VWR, Westchester, PA, USA) was added with the aim of neutralizing the maltodextrin and thereby preventing the hydrolysis of sucrose into glucose and fructose. The moisture content was then reduced by boiling within a stirred glass reaction vessel (LR2, Ika Works, Inc. Wilmington, NC, USA). Aliquots were collected periodically to provide a series of samples with a range of moisture contents for each carbohydrate composition. These were centrifuged whilst still hot in 50 mL tubes (VWR) using an Eppendorf model 5804 centrifuge (Westbury, NY, USA) at 8000 rpm for 5 min to remove bubbles.

The M_n of the melt aliquots was measured by freezing point osmometry using the method described by Rong, Sillick, and Gregson (2009). This was done using a μ-Osmette 5400 freezing point osmometer (Precision Systems, Inc., Natick, MA, USA) at concentrations of approximately 20 wt.% in water. By Rong's method, the osmolality readings were corrected to account for salt impurities, the concentrations of which were estimated based on conductivity measurements.

The M_w of the 5DE and 18DE maltodextrins was calculated based on size exclusion chromatography (SEC) data. The separation system was comprised of a 1000 series tower with G1322A degasser, G1311A quaternary pump, G1311A ALS (autosampler), G1316 Colcom column compartment and Chemstation software (all from Agilent Technologies, Santa Clara, CA, USA). Detection was made with a miniDawn light scattering detector at 690 nm and scattering angles of 41.5°, 90° and 138.5° as well as with an Optilab RI detector ($dn/dc = 0.135$) (both from Wyatt Technology Corporation, Santa Barbara, CA, USA). Data treatments were made with Astra software (Wyatt Technology Corporation).

The M_w values of the 5DE maltodextrin/18 DE maltodextrin/sucrose compositions were in turn calculated from the SEC determined M_w values and the dry weight fractions (w) of each component by Eq. (3). A value of 342 g/mol was used for the molecular weight of sucrose (M_{wS}).

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = (w_S * M_{wS}) + (w_{18DE} * M_{w18DE}) + (w_{5DE} * M_{w5DE}) \tag{3}$$

Calorimetric measurements were made using a TA Instruments (New Castle, DE, USA) Q200 DSC calibrated for temperature based on the melting point of indium. Sub-samples from each aliquot were prepared and measured in triplicate. The glass transition temperature was taken as the midpoint from the inflection of heat capacity on rescan at +10 °C/min after quenching. This protocol will produce slightly higher T_g values compared to those based on onset T_g.

Rheology was assessed using a TA Instruments AR2000 rheometer and the concentric cylinder geometry. Dynamic and steady state measurements were used in order to broaden the experimental regime. Though often supersaturated, all aliquots reported here were homogeneous and free of crystals when observed using a polarized light microscope (BX51, Olympus America, Center Valley, PA, USA) both before and after the rheological tests. The data set for the very sucrose-rich compositions is sparse because in several cases crystals were detected after the rheological tests. The results were discarded in such cases.

The natural log of viscosity was modelled as a function of temperature using a log version of Eq. (1) with the software Curve Expert 1.3 (Daniel Hyams, Hixon, TN, USA). The infinite temperature viscosity parameter (η_o) was restricted to 10^{-5} Pa s ($\ln \eta_o = -11.513$) leaving two remaining parameters, B and T_0, to be fit by non-linear regression. The fragility parameter (D) was subsequently calculated by dividing B by T_0. $F_{1/2}$ was calculated here using a T_g value predicted from modelled viscosity (i.e. the temperature at which viscosity extrapolated to 10^{12} Pa s). Thus, calorimetry data was not used for the fragility parameter calculations.

Moisture content was measured by Karl Fisher titration using a DL31 titrator (Mettler-Toledo Inc., Columbus, OH, USA). A one-component titrant (Comp5, EMD AquaStar, VWR) was used with a fresh solvent mixture of 15 mL methanol (Hydranal®, Sigma Aldrich, St. Louis, MO, USA) and 15 mL formamide (Hydranal®, Sigma Aldrich). Sub-samples were dissolved in measured amounts of formamide prior to analysis. The small amount of moisture in the formamide (<0.01 wt.%) was measured and accounted for.

3. Results and discussion

3.1. Molecular weight characterization

The compositions studied for this report can be considered as two separate series. These are illustrated in Fig. 1. One set of experiments explored binary blends of sucrose and an intermediate molecular weight (18DE) maltopolymer (Series 1). A second orthogonal set of experiments was conducted on compositions which contained 50% sucrose and 50% maltopolymer on a dry basis (Series 2). Within the second series, the maltopolymer fraction was composed of blends of 18DE and 5DE maltodextrins.

Fig. 2 plots M_w and M_n for each composition and the data remain arranged into two near orthogonal trends, just as in Fig. 1. This treatment, in which sucrose is considered a low molecular weight polymer led to rather polydisperse compositions; M_w/M_n values were all greater than 8. Both M_n and M_w were strong functions of the maltopolymer to sucrose ratio. Within Series 1, the M_n and M_w values both increase by approximately a factor of 2 as the mass fraction of sucrose changed from 0.5 to 0.

The second series of experiments explored the effect of exchanging 5DE for 18DE maltodextrin for compositions which include 50% sucrose. The data show an interesting phenomenon. Substituting 5DE for 18DE maltodextrin led to very large changes in M_w (up to a 500% increase), but only very small increases in M_n (a maximum of only 10%). The Series 2 data set became increasingly polydisperse with the inclusion of 5DE maltodextrin, up to a maximum M_w/M_n value of ~55.

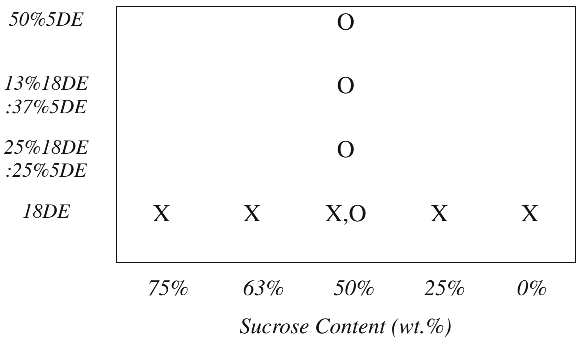

Fig. 1. Illustration of the Series 1 (X) and Series 2 (O) compositions.

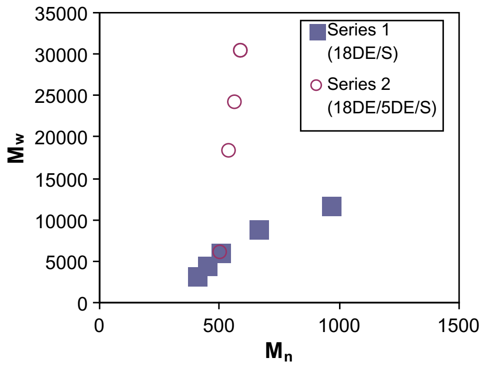

Fig. 2. Molecular weight information of the Series 1 and Series 2 compositions. The specific composition for any point on the chart can be determined by comparing Figs. 1 and 2. The 5DE and 18DE maltodextrins had M_n:M_W values of 2120:60480 and 970: 11740, respectively.

One shortcoming of the molecular weight treatments performed here is that sucrose and maltodextrin are not from the same homologous polymer series. In fact, sucrose and the maltopolymer of equivalent molecular weight (maltose) differ significantly in T_g and perhaps also in fragility. Our treatment of the Series 1 compositions makes the assumption that the influence of molecular weight is large compared to the influence of sugar type.

3.2. Rheology measurements and effect of shear rate

Dynamic viscosity (η^*) was transformed by the Cox–Merz rule (Eq. (4)). By this empirical relation, dynamic viscosity (η^*) as a function of frequency (ω) is transformed into the equivalent shear viscosity (η) as a function of shear rate ($\dot{\gamma}$). Example data in Fig. 3 shows close agreement between the values derived from the oscillation measurements and separate and independent flow measurements at each temperature step. Based on this close agreement, dynamic measurements were used to gain information at high viscosities and shear rate ranges where flow measurements were not possible.

$$\eta^*(\omega) = \eta(\dot{\gamma}); \text{ and } \omega = \dot{\gamma} \tag{4}$$

The Cox–Merz rule (Cox & Merz, 1958) applies to many polymeric solutions and melts, but often fails for colloidal systems such as emulsions and dispersions, as well as Boger fluids and certain polymer solutions (Al-Hadithi, Barnes, & Walters, 1992). This is related to a combination of viscoelasticity and the loss of structure at larger deformations in colloidal systems. However, the rule is thought to hold for all liquids irrespective of their microstructure at the lower limiting values of frequency and shear rate.

Chamberlain and Rao (1999) showed that the Cox–Merz rule did not apply to starch solutions, whereas it did apply to acid hydrolyzed starch. The former also exhibited an apparent yield stress. This work showed that the weak gel network that forms in high molecular weight starch solutions results in the breakdown of the Cox–Merz rule, however, it does apply to solutions when structure formation is not possible. A similar break-down of the Cox–Merz rule due to weak structure formation was found by Park, Chung, and Yoo (2004) for pastes of octenylsuccinylated and native starch, as well as Zimeri and Kokini (2003) for inulin-waxy maize starch systems.

In the work described in this paper, the melts measured were non-colloidal and unentangled due to the high concentration of small molecular weight molecules. Furthermore, no evidence was seen for the existence of a network structure that could be broken

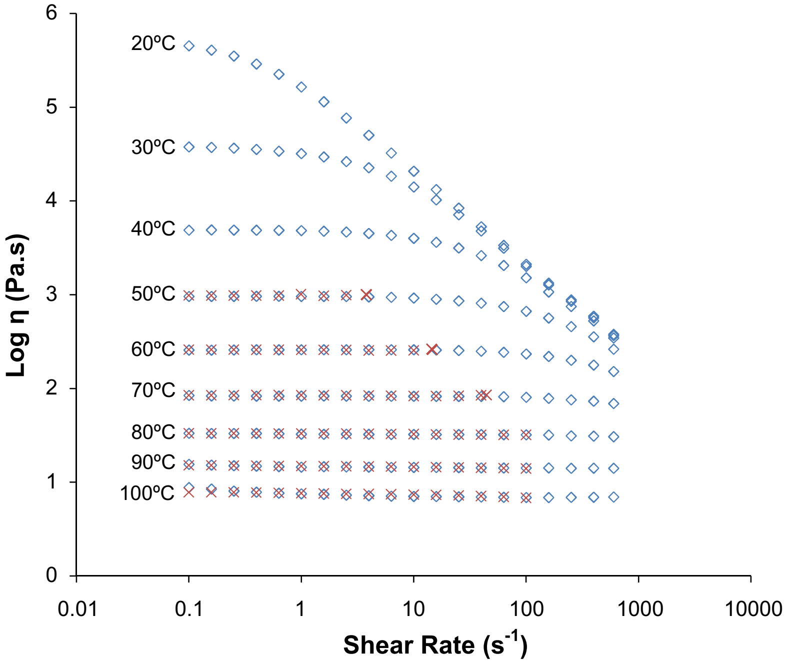

Fig. 3. Example viscosity data from flow (X) and dynamic (◇) measurements for a 100%18DE composition containing 16.2% water.

down under large deformation. In fact, the melts were found to be practically Newtonian in all cases. Example data in Fig. 3 shows Newtonian behaviour at high temperatures and an apparent decay in viscosity at high shear rate and low temperature, which may have been caused by instrument compliance. The true shear dependence of viscosity in these regimes remains unknown. For such cases, viscosity was extrapolated to zero-shear rate, where the Cox–Merz rule should apply to all materials.

Some samples which contained high levels of 5DE maltodextrin showed slight shear thinning even at high temperatures during flow experiments. Even for the most shear thinning cases, power law indices (i.e. b values when fit by $\sigma = \dot{\gamma}\eta^b$) were >0.98, which indicates that the degree of shear thinning was small. To simplify subsequent modelling of temperature dependence, these samples too were fit using the Newtonian model and a single viscosity value independent of shear rate was acquired from each experiment. The data were further reduced by excluding dynamic viscosity data in the temperature regions for which flow measurements were also made.

3.3. VFT modelling of the effect of temperature

Example viscosity data for the 50%18DE:50%S composition is plotted in Fig. 4 as a function of temperature. At each moisture content level, viscosity decreased dramatically with increasing temperature. Isothermal viscosity also decreased significantly with increasing moisture content. In other words, water is a strong plasticizer of these carbohydrate compositions.

3.3.1. η_o parameter

In polymeric systems, η_o has been reported to shift upward by an amount that has a strong dependence on molecular weight and as a result, viscometry was discouraged as a route for characterizing fragility for polymers (Angell et al., 1994). The compositions studied here are combinations of water, oligomers, and moderate molecular weight polymers. Modelling with both restricted and unrestricted versions of the VFT equation yielded results that fit the experimental data very well ($r^2 > 0.99$ in each case). By unrestricted modelling, results for the η_o parameter range from $10^{-3.5}$ to 10^{-6} Pa s and showed no clear dependence on either molecular weight or moisture content. In this facet of their behaviour and also in the low degree of shear-thinning character, the compositions appeared to be more similar to small molecule liquids than polymers. Thus, the choice of restricting of η_o to 10^{-5} Pa s seems reasonable.

3.3.2. Fragility parameters

The fragility parameters (D and $F_{1/2}$) are given in Figs. 5 and 6 as functions of the moisture content. The two charts appear to report the same information: fragility increases with increasing $F_{1/2}$ and decreasing D values. The compositions ranged in $F_{1/2}$ values from 0.606 for 50%5DE:50%S with 7.4% moisture to 0.685 for 25%18DE:75%S with 13.4% water. These values represent moderate to fragile behaviour.

While literature values for these specific compositions are unavailable, Angell (2002) reported that the $F_{1/2}$ of pure sucrose may be as high as 0.82, which is significantly higher than any of the compositions in Fig. 6. Supersaturated solutions of pure sucrose are not sufficiently stable enough to measure by the current approach. Maltodextrin melts may also be relatively fragile materials. Descamps, Palzer, and Zuercher (2009) reported a high steepness index (m of 117) based on calorimetric measurements. This can be translated to an $F_{1/2}$ value of 0.74 through $F_{1/2} = (m - 17)/(m + 17)$. The validity of this relation depends on the assumption that there are 17 orders of magnitude separating the η at T_g and η_o (Angell, 2002). This value ($F_{1/2} = 0.74$) also is higher than all of those shown in Fig. 6.

Moisture did not have the same effect on fragility for each composition. Instead, while the Series 1 compositions each appeared to become less fragile with increasing moisture content, several of the Series 2 compositions had consistently low fragility throughout the moisture content range. These were the compositions that contain high levels of 5DE maltodextrin.

There is some basis, but not full consensus, in the literature for expecting decreasing fragility with inclusion of water in carbohydrate melts. Sucrose, for example, showed a modest yet definite

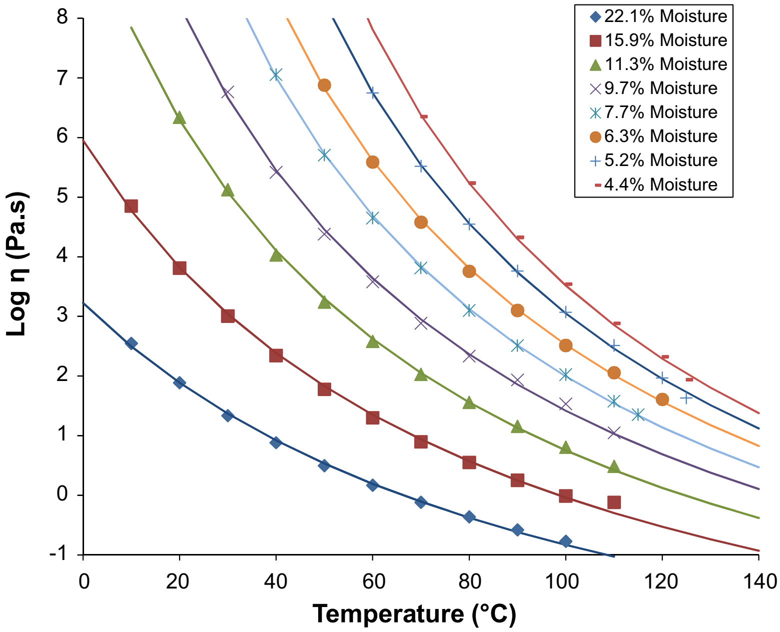

Fig. 4. Example viscosity data of the 50%18DE/50%S composition with various moisture contents plotted as a function of temperature. Behaviour predicted by the restricted VFT model (lines) fit the experimental data (points) very well ($r^2 > 0.99$ in each case).

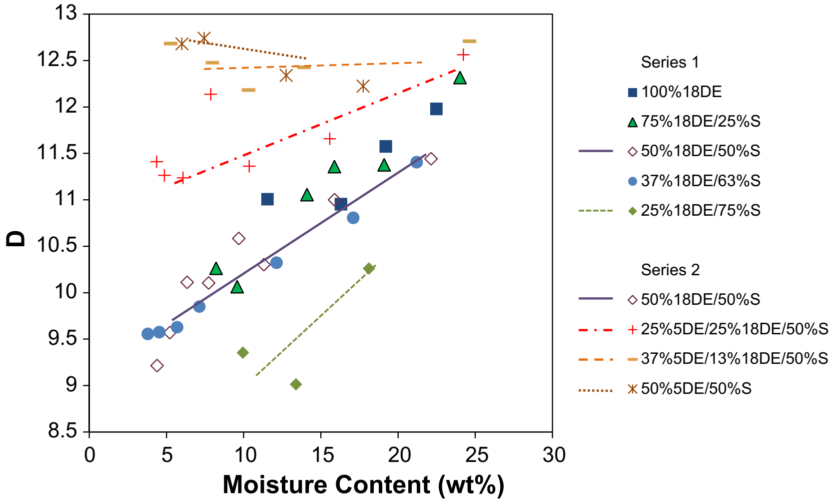

Fig. 5. Fragility parameter D plotted as a function of moisture content for the Series 1 and Series 2 compositions. Several compositional trend lines are drawn to guide the eye.

decrease in fragility with increasing moisture content (Angell et al., 1994; Quintas, Brandao, Silva, & Cunha, 2006). Another study on sucrose though predicted weak or no dependence on moisture content (Mathlouthi & Reiser, 1994). (Viscosity data from Quintas et al. and Mathlouthi & Reiser were fit using a restricted VFT equation by the current authors to assess fragility; results are not shown.) Modest decreases in fragility with increasing moisture content have also been reported for low moisture content solutions of amylopectin (Borde, Bizot, Vigier, & Buleon, 2002) and also pullulan (Lazaridou, Biliaderis, & Kontogiorgos, 2003). This suggests that the decreasing relation may continue for high molecular weight polysaccharides.

Figs. 5 and 6 also show that compositions with higher molecular weight 5DE maltodextrin were distinctly less fragile than the Series 1 compositions when compared at lower moisture content levels. The compositions containing 5DE maltodextrin are highly polydisperse and have M_w values that lie well above those for Series 1, yet have M_n values within the same range. Within both Series 1 and Series 2, while any two adjacent trends in Figs. 5 and 6 may overlap, there still persists a general trend of decreasing fragility with increasing molecular weight. The $F_{1/2}$ values were fit by linear models to predict fragility of each composition with 10% moisture, a value that lies near the middle of the range of data. The results show decreasing fragility with increasing M_w in Fig. 7.

These results contrast with molecular weight dependences reported elsewhere. Fragility is expected to increase dramatically with molecular weight for a broad range of rigid chain polymers reviewed by Sokolov, Novikov, and Ding (2007). Work by Park, Saruta, and Kojima (1998) also showed an increasing relation for a series of dihydroxyl alcohols. Park et al. attributed the increase in fragility to the decrease in the concentration of end hydroxyl groups that accompanies the increase in molecular weight. While maltopolymers will also experience a reduction in hydroxyl group concentration on increasing molecular weight, the proportional decrease is much smaller because maltopolymers contain both non-terminal and end-group hydroxyl moieties.

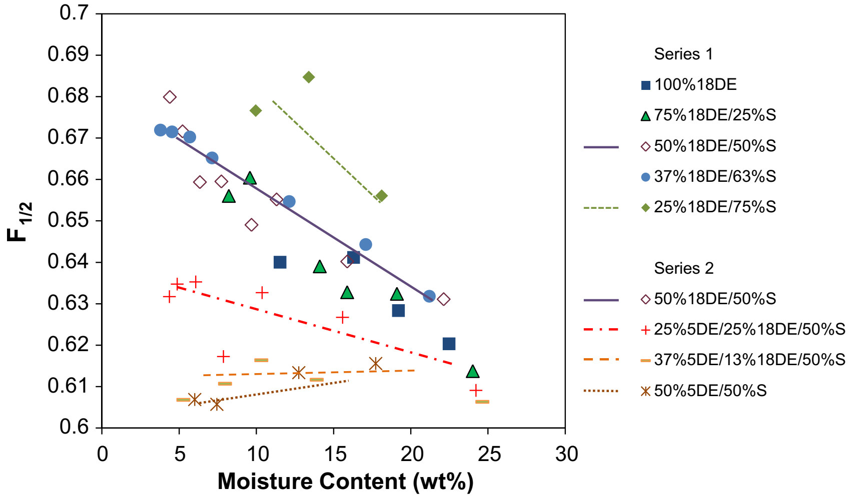

Fig. 6. Fragility parameter $F_{1/2}$ plotted as a function of moisture content for the Series 1 and Series 2 compositions. Several compositional trend lines are drawn to guide the eye.

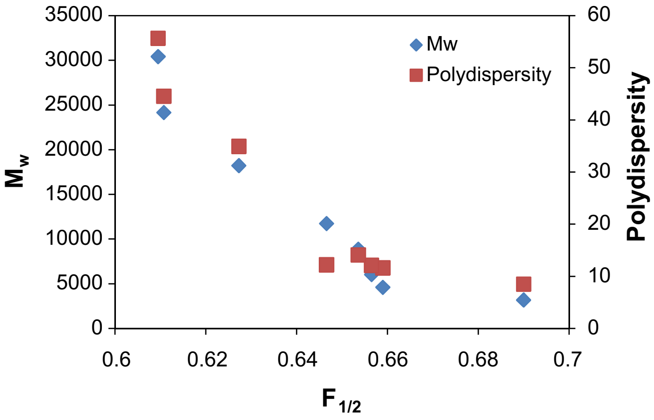

Fig. 7. Relations between the fragility parameter $F_{1/2}$ of compositions with 10% moisture and both the M_w and polydispersity values for the carbohydrate fraction.

The compositions chosen for this work, unfortunately, are more complex than most of those reported elsewhere which tend to be studies on pure materials. In particular, the mixtures reported here contain significant amounts of oligomer and very polydisperse molecular weight distributions. As polydispersity too appears to lead to a decrease in fragility (Fig. 7), the specific influence of M_w *vs.* polydispersity cannot be resolved from the current data set.

One study that is similar to the work reported here, mixed sorbitol with hydrated solutions of pullulan. Lazaridou et al. (2003) found little dependence of fragility on the M_w of the pullulan, but a marked decrease with the inclusion of 10% sorbitol. Fig. 6 contradicts this in that there was an increase in fragility with addition of a low molecular weight additive (sucrose) to maltodextrin. However, the results find agreement if compared on the basis of polydispersity. Sorbitol is a polyol with a molecular weight about half of that of sucrose. Adding 10% sorbitol to pullulan, a very high molecular weight polysaccharide, significantly increased polydispersity and decreased fragility. Fig. 7 also shows a decrease in fragility with increasing polydispersity.

3.3.3. T_0 parameter

The T_0 parameter was found to decrease steadily for all compositions with increasing moisture content (Fig. 8). Additionally, the trends appear to lie roughly in order of M_n, though there may be several exceptions. Unlike fragility, which was shown to vary with M_w in Fig. 7, T_0 appears to also be heavily influenced by M_n.

The T_0 parameter can alternatively be described by Eq. (5) (Angell, Richards, & Velikov, 1999) as a function of both the glass transition temperature and a fragility parameter (D). One advantage of doing so is that both the plasticizer dependence and the molecular weight dependence of T_g are reasonably well understood.

$$\frac{T_g}{T_0} = 1 + D\ln(\eta_g/\eta_0) \tag{5}$$

The T_g of carbohydrate compositions has been widely demonstrated to increase with molecular weight and decrease with increasing moisture content and at a rate that can be approximated by the Gordon–Taylor expression (Franks, 2000; Gordon & Taylor, 1952; Roos & Karel, 1991b). This expression (Eq. (6)) models the T_g of a mixture of two components with weight fractions w_1 and w_2 and glass transition temperatures T_{g1} and T_{g2} using the model constant k.

$$T_g = \frac{w_1 T_{g1} + k w_1 T_{g1}}{w_1 + k w_2} \tag{6}$$

Calorimetric T_g data of the Series 1 and Series 2 compositions is plotted as a function of moisture content in Fig. 9. The experimental data were fitted by binary Gordon–Taylor models with the dry carbohydrate mixture and water considered as the two respective components. While originally used to predict the T_g of simple two-component polymer blends, the Gordon–Taylor model has proven useful when extended to mixtures similar to those modelled here on numerous occasions (Omar & Roos, 2007; Roos & Karel, 1991a; Ubbink, Giardiello, & Limbach, 2007). Maltodextrin tends to be a very polydisperse material and might itself be considered a mixture of homopolymers when compared to the synthetic polymers studied by Gordon and Taylor. A broad range of maltodextrin/water systems have been demonstrated to follow the Gordon–Taylor equation (Roos & Karel, 1991b).

Fig. 9A show that each parallel Gordon–Taylor trend lies in order of M_n. Series 2, which differed in M_n by only small amounts, were sufficiently similar that they could each be fit successfully by a single trend ($r^2 > 0.999$) as shown in Fig. 9B. Hence, the M_n appears to be the primary influence on the T_g *vs.* moisture content trends despite very dramatic increase in M_w and polydispersity for the Series 2 compositions.

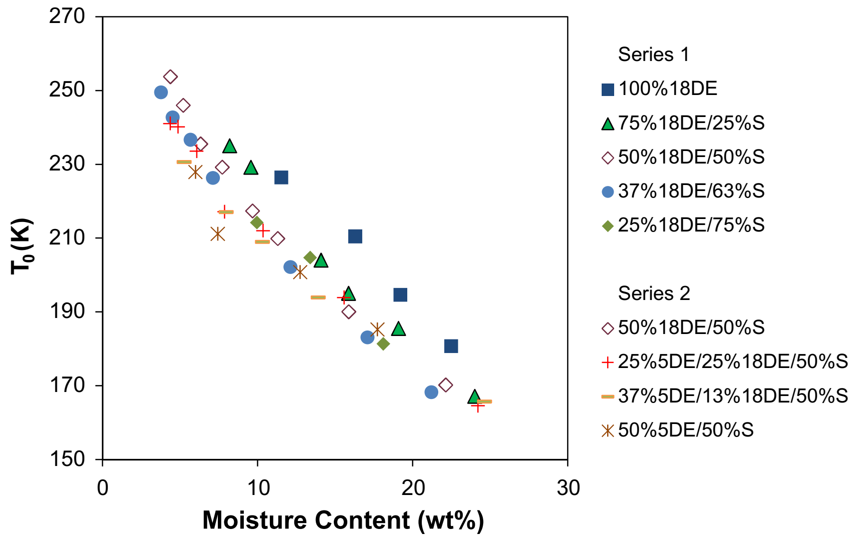

Fig. 8. T_0 parameter plotted as a function of moisture content for the Series 1 and Series 2 compositions.

The correlation between T_g and T_0 can be assessed by comparing Figs. 8 and 9, which indeed show clear similarities. T_0 also decreases with increasing moisture content and roughly follows an M_n dependence, because of the strong influence of both parameters on T_g. However, the compositions are each slightly closer together in T_0 values than in T_g values at any given moisture content because of the influence of fragility. Fragile compositions have smaller T_g/T_0 ratios compared to strong compositions in Eq. (5).

3.4. Viscosity–temperature relationship versus T_g

The viscosity–temperature relationship has often been assumed to follow the WLF equation with universal constants. Ollett and Parker (1990), for example, explored the use of this equation for the prediction of T_g from viscosity data. With this assumption, the viscosity–temperature behaviour can be predicted based only on the glass transition temperature. However, it is now widely acknowledged that universal constants are a dramatic over simplification, and that the viscosity–temperature behaviour is highly dependent on composition. The results in this paper provide further evidence against a single universal behaviour.

The fragility concept is a convenient method to describe and compare viscosity–temperature behaviour. Within the context of melt extrusion, fragility has relevance because it serves to link the T_g of a glass-forming liquid with its melt viscosity at higher temperatures. If two compositions share the same T_g value and one assumes T_g occurs at a viscosity of 10^{12} Pa s, a lower melt viscosity can be expected for the more fragile composition. Conversely, if formulated to have similar melt viscosity, one would expect higher T_g values for fragile compositions.

DSC is frequently used as a rapid and convenient method of measuring T_g. As a result, it is worth considering the link between calorimetric and rheological based results. Ollett and Parker (1990) used the VFT and other models to predict the T_g of pure fructose and glucose based on viscosity measurements similar to those detailed in this paper. The rheologically based T_g was compared to the values obtained by DSC. Despite the difficulty of conducting rheological and calorimetric measurements on ‘pure’ sugars and the dramatic influence of even small amounts of water on T_g and viscosity close to the anhydrous condition, the measurements by the two techniques agreed well.

Kasapis, Mitchell, Abeysekera, and MacNaughtan (2004) showed that in some cases there can be a major discrepancy between calorimetric and rheological T_g for high sugar systems which include small concentrations of biopolymer (0.5–1.3%). Whereas the calorimetric T_g was found to be determined mainly by the distribution of sugars and the moisture content, the rheological T_g was also influenced by the presence of biopolymer networks. Polymers that had a propensity to gel, such as κ-carrageenan with added potassium, had a higher rheological than calorimetric T_g below 90% solids. At very high solids levels (>90%) and for polymers which do not tend to gel, such as guar and locust bean gum, no significant difference was found between rheological and calorimetric T_g. It was proposed that high levels of sugars reduce the tendency for chain–chain association.

These findings support the results for maltodextrin–sucrose systems described in this paper in that no evidence was found for network structure in any of the samples despite the ability of maltodextrins to gel at lower concentrations (Reuther et al., 1983). Also, and perhaps for this very reason, a strong link was found between glass transition values obtained from the two techniques (data not shown).

3.5. Rationale for a polydispersity dependence for fragility

The influences of molecular weight distribution on T_g and melt viscosity are often considered independently, but rarely in concert. T_g has been shown to vary with molecular weight via the Fox–Flory relation (Eq. (7)) which relates the T_g of a polymer to molecular weight (M) by $T_{g\infty}$, the glass transition temperature extrapolated to infinite molecular weight, and a polymer specific constant ‘K’ (Roos & Karel, 1991b). For polydisperse compositions, M_n can be used successfully within the Fox–Flory equation (Bicerano, 2002). Indeed M_n seems to be an appropriate parameter for describing the trends in Fig. 9, at least more so than M_w. Alternatively, other authors have developed an empirical relationship for the T_g of maltopolymers based on another molecular weight averaging scheme that takes interchain plasticization into consideration (Avaltroni, Bouquerand, & Normand, 2004). Here, the “M_E” that was used for predicting T_g had an even lower value than M_n.

$$T_g = T_{g\infty} - \frac{K}{M} \tag{7}$$

Melt viscosity on the other hand, was found very early on to depend on the *weight-average* degree of polymerization for synthetic polymers (Sperling, 2001). An empirical relation for the zero-shear

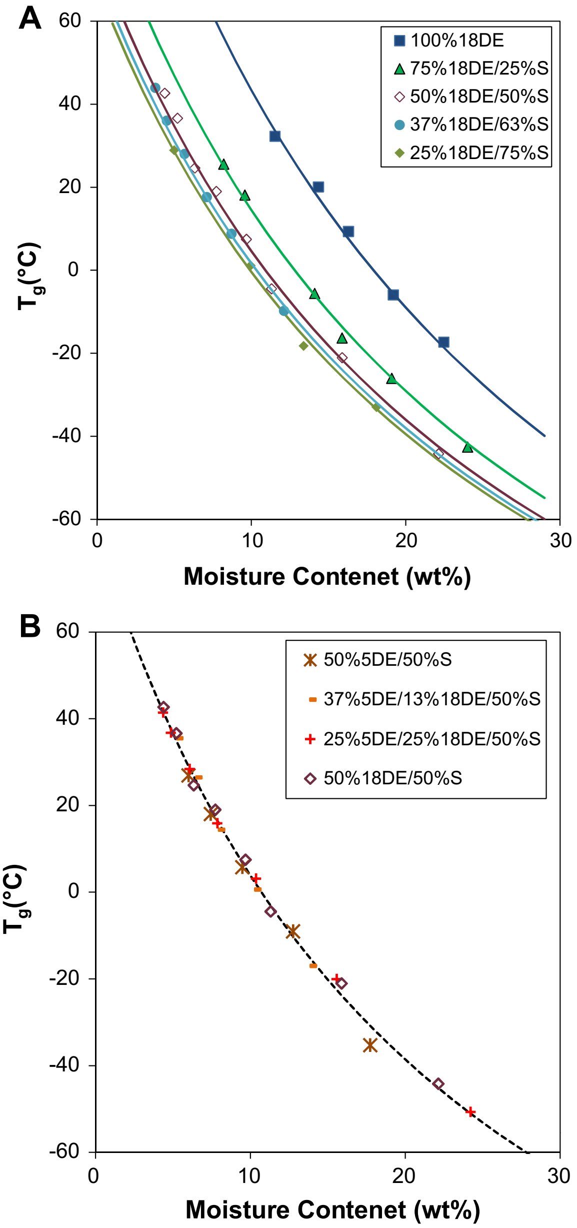

Fig. 9. Calorimetric glass transition temperature data *vs.* moisture content. Trend lines represent fits via Gordon–Taylor models.

viscosity is often used (Eq. (8)), where b can be 1 or 3.5 depending on whether the material has exceeded the overlap concentration (Dealy & Wissburn, 1999). This suggests a very strong influence of M_w on viscosity.

$$\eta_{\text{zero}} = a * M_w^b \tag{8}$$

Hence, T_g and melt viscosity, are widely viewed as increasing with M_n, or some other average value from the lower end of the distribution, and M_w, which lies in a higher portion of the distribution, respectively. As fragile compositions are those that have high T_g and low melt viscosity, these empirical relations in Eqs. (7) and (8) imply an influence of the molecular weight distribution. If compared in isolation, polydispersity could decrease fragility as it will lead to a higher M_w (melt viscosity) value for any given M_n (T_g) value.

4. Concluding remarks

The text provides modelled viscosity data for a broad range of maltopolymer/sucrose compositions at various moisture levels that are relevant to an assortment of industrial applications. The results were examined to determine viscous fragility (i.e. the degree to which the temperature dependence of viscosity exceeds that predicted by Arrhenius kinetics). Understanding the compositional dependence of fragility, including the roles of molecular type, molecular weight, and plasticizer content is a challenge that is still very much in progress. The data reported suggests an additional role of the molecular weight distribution. Low moisture content molecular mixtures of a maltopolymer and sucrose with broad molecular weight distributions were less fragile than compositions with lower degrees of polydispersity.

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