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Carbohydrate Research 329 (2000) 399–407

CARBOHYDRATE RESEARCH

Viscoelastic properties of pectin–co-solute mixtures at iso-free-volume states

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Received 10 April 2000; received in revised form 16 June 2000; accepted 20 June 2000

Abstract

Small-deformation oscillatory measurements were performed on pectin–sucrose–glucose syrup systems at a total level of solids of 81%, with the polysaccharide content being fixed at levels of industrial use (1%). The experimental temperature range was between 50 and − 50 °C. Analysis of the temperature dependence of viscoelastic processes by the equation of Williams, Landel, and Ferry provides values of fractional free volume for the temperatures covering the glass transition region. The shift factors used in the conversion of mechanical spectra into master curves were normalised at suitably different temperatures so that their temperature dependence becomes coincident. The treatment implies an iso-free-volume state and relates to changes in the monomeric friction coefficient with increasing levels of intermolecular interactions in the mixture. A free-volume related glass transition temperature was defined and manipulated markedly by introducing pectin of variable degrees of esterification to the sucrose–glucose syrup system. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Pectin; High solids; Iso-free-volume state; Rheological glass transition temperature

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1. Introduction

In synthetic polymer research, the theory of linear viscoelasticity has been used to obtain data on the time-dependent mechanical properties of amorphous systems [1]. Experimental techniques include creep testing under constant stress, the relaxation of stress at constant strain, and the real and imaginary parts of the complex dynamic modulus [2–4]. Commonly, mechanical spectra are obtained over a wide temperature range 50–150 °C and then combined by the use of Tobolsky's time–temperature superposition principle, which is equivalent to Ferry's reduced variables method, to obtain a master curve for the sample [5,6]. This demonstrates that all relaxation mechanisms have the same temperature dependence, so that when the temperature is changed from T_o to T_1 each relaxation time is multiplied by the same shift factor a_T. The value of a_T can be obtained simply from the ratio of the mechanical responses at the two temperatures [7]. The equation of Williams, Landel, and Ferry (WLF) in partnership with

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PII: S0008-6215(00)00193-2

the concept of free volume is then used to follow the temperature dependence of shift factors and, through the years, has provided a mainstay in utility and the theory of vitrification of amorphous systems [8,9].

Recently, we employed the technique of small deformation dynamic oscillation to monitor the viscoelasticity of four gelatin fractions in the presence of sucrose and glucose syrup [10]. The protein concentration was fixed at 25% but the molecular weight varied from 29.2 to 68 kD. Thermal profiles between 40 and −60 °C unveiled the rubbery, glass transition, and glassy states thus covering a shear modulus range of 10^3–10^{10} Pa. Then, we attempted to apply the three steps of the WLF analysis to the gelatin–co-solute mixtures as follows [11]: (i) the method of reduced variables was used to construct master curves of the experimental data as a function of frequency of oscillation and shift factors as a function of temperature; (ii) the readings of storage and loss modulus were correlated with each other, although they are independent at a single frequency, through the rigorous mathematical relations involving a function called the ‘distribution of relaxation times’ [12]; (iii) the concept of effective friction coefficient per monomer unit was employed to follow the acceleration in vitrification properties of the mixtures with increasing molecular weight of the proteinaceous constituent [13]. Results were rationalized on the basis of an inverse relationship between fractional free volume and the molecular weight of gelatin owing to additional free volume associated with molecular ends.

The purpose of the present investigation is to examine the role of network formation in the vitrification properties of polysaccharide–co-solute systems. In doing so, citrus pectin with two degrees of esterification (DE) is introduced to a mixture of sucrose–glucose syrup at low pH. Under these pH values and co-solute conditions, the high DE pectin would be expected to form a more cohesive network than the low DE counterpart. A quantitative relationship between monomeric friction coefficient and fractional free volume is advocated to rationalise the recorded mechanical properties. For each preparation, data is normalised at a reference temperature T_{isofv} of a constant free volume, thus demonstrating, for the first time, that at the state of iso-free-volume, the temperature dependence of vitrification properties can be described by a single process.

2. Experimental

Materials.—The citrus peel pectin was purchased from Sigma Chemical Co. It came in two grades: a rapid set sample (P-9561) with a galacturonate content (esterified and non-esterified) of 82% and a high degree of esterification on a dry weight basis (92%), and a sample (P-9311) with a galacturonate content of 62% and a low degree of esterification (22%). Chromatographic analysis using an Ultrahydrogel Linear Column and eight pullulan standards produced number average molecular weights of 154 and 111 kD for the high and low degree-of-esterification samples, respectively. Sucrose was AnalaR grade from Sigma. The glucose syrup used was a product of Cerestar, Vilvoorde, Belgium. The dextrose equivalent of the samples was about 42. The total level of solids was 83% and glucose syrup compositions in this work refer to dry solids. Gel permeation chromatography data showed an extensive degree of polydispersity, which prevents crystallisation of the material at subzero temperatures [14].

Samples were made at a total level of solids of 81%. The rheological profiles of the mixtures were contrasted with those of single co-solute preparations at 40.5% sucrose plus 40.5% glucose syrup. In mixtures, part of the co-solute was replaced with 1% high DE pectin and 1.32% low DE pectin to yield systems with a galacturonate content of 0.82%. Pectin was dissolved in deionised water at 90 °C using gentle stirring for 20 min. The temperature was dropped to 80 °C for addition of sucrose, followed by glucose syrup. Excess moisture was removed in a water bath held at 70 °C typically for 30 min. Finally, the pH was adjusted to 3.5 using 0.2 M HCl, a value which is optimum for pectin gelation in the presence of high levels of co-solute [15].

Methods

Chromatographic analysis. The chromatographic conditions employed were as reported previously with some modifications [16,17]. High-performance size exclusion chromatography (HPSEC) was performed using Hewlett–Packard 1090 HPLC with isocratic pump. Waters Ultrahydrogel linear column (300 × 7.8 mm) and Ultrahydrogel guard column were connected in series and mounted to the system. The mobile phase was 0.1 M NaCl (reagent grade) prepared with deionised water and filtered through 0.45 μm cellulose nitrate membrane filter. The solvent was degassed in the reservoir using helium gas. Twenty five μL of a 0.3 mg/mL standard sample were injected. The flow rate was set at 0.8 mL/min and column temperature was maintained throughout the run at 45 °C.

A differential refractive index (RI) detector from Hewlett–Packard model HP1047A with set temperature (45 °C) and sensitivity at 1×10^{-5} RIU/FS was used for molecular weight estimations. Pullulan standards were from Polymer Laboratories, Inc., Amherst, MA, USA. The number average molecular weight of the pullulans was 788, 404, 212, 112, 47, 23, 12, and 6 kD. For calibration of the molecular weight of citrus pectin, a standard curve was plotted using the log molecular weight of the pullulans versus their retention time.

Rheological testing. Small deformation measurements of storage (G') and loss (G'') modulus were made with the Advanced Rheometrics Expansion System (ARES), which is a controlled strain rheometer (Rheometric Scientific, Piscataway, NJ, USA). ARES has an air-lubricated and essentially non-compliant force rebalance transducer with a torque range between 0.02 and 2000 g cm. Nevertheless, particular care was taken to establish that any inherent machine compliance was insufficient to significantly offset measured values from the high modulus glass systems. This was achieved by progressive adjustment of geometry settings whilst measuring samples of known intermediate and high modulus (PDMS at 30 °C and ice at −20 °C). Thus the maximum plate diameter (5 mm) and minimum measuring gap (6 mm) between the two parallel plates consistent with accurate results could be established. In doing so, rubber-to-glass transitions were readily reproducible within a 2% error margin as a function of temperature or timescale of measurement.

For precise control of sample temperature, an air convection oven was used, which has a dual element heater/cooler with counter-rotating air flow covering a wide temperature range (between 130 and −60 °C). This allowed monitoring of the viscoelastic properties of our preparations from the rubbery and the glass transition to the glassy state. Samples were loaded onto the preheated platen of the rheometer (typically at 60 °C) and cooled at a scan rate of 1 °C/min. A silicone fluid (Dow Corning 100 cs) was used to cover the exposed edges between the parallel plates, thus preventing formation of skin on the surface of the sample. The fluid was of sufficient low molecular weight to remain liquid-like at subzero temperatures. Heating runs at the same scan rate were interrupted at constant temperature intervals of 3 °C to implement frequency sweeps.

3. Results and discussion

Experimental studies of viscoelastic behaviour of pectin–co-solute mixtures.—Following the synthetic polymer approach [18], a treatise of the linear viscoelastic behaviour of pectin–co-solute mixtures falls conveniently into three parts, namely: experimental observations of oscillatory testing, time or frequency dependence of mechanical properties and iso-free-volume states at separate reference temperatures. Fig. 1 shows the changes in storage and loss modulus observed during cooling or heating (1 °C/min) of the high solids preparations with and without pectin. For all samples, the dependence of mechanical processes on temperature is spectacular with changes in viscoelastic functions covering almost seven orders of magnitude. In the case of sucrose–glucose syrup, the sharp increase in storage modulus is noted at low temperatures, thus indicating a molecular mechanism in the sample with a substantial ‘sol fraction’.

Incorporation of the low DE pectin gives a closely similar trace of loss modulus with that of the co-solute at low temperatures, although at high temperatures the storage modulus is substantially higher than for the co-solute alone. The maximum value of tan δ (i.e., the ratio of G'' to G') of the low DE polysaccharide network is equal to 5.1 at −18 °C (frequency of 1 rad/s). However, then there is a substantial increase in modulus, which moves to progressively higher temperatures with increasing concentration of methyl esterified carboxyl groups on the pectin molecule. Thus, a degree of esterification of 92 yields a reduced maximum in tan δ of about 2.3, which is obtained at the higher temperature of 5 °C, as compared with the mechanical response of the pectin sample with DE of 22.

This behaviour can be understood qualitatively on the basis of the relaxation times, which govern the mechanical properties of amorphous synthetic materials with changing temperature [19]. Results from many laboratories who had measured the complex shear modulus of a specimen of polyisobutylene of relatively high molecular mass clearly showed three regions, namely: the rubbery, glass transition, and glassy state [20]. The pectin–co-solute mixtures reproduce this type of mechanical response. In the case of sucrose–glucose syrup, there is a direct passage in Fig. 1 from the glass transition to the terminal zone, where the viscoelastic properties are governed by the longest relaxation times [21,22], thus allowing the low molecular weight material to flow readily. Although the experimental evidence in Fig. 1 is indicative of vitrification phenomena in the pectin–co-solute system, we attempted to check in the following the validity of this assumption using a well-established quantitative framework from the investigations of linear viscoelasticity of synthetic polymers and diluted systems.

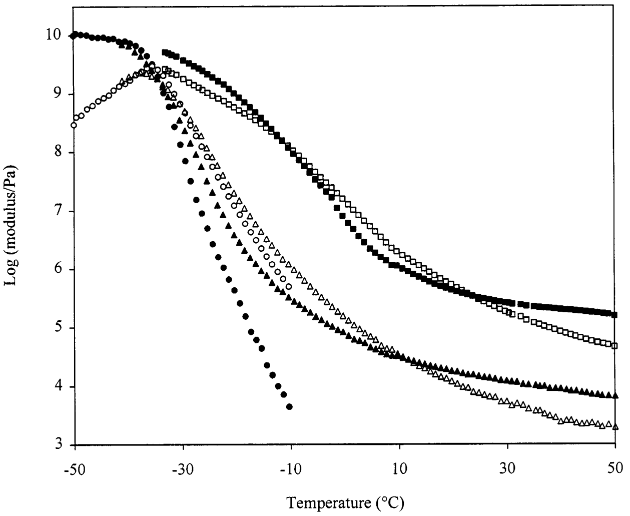

Fig. 1. Temperature variation of mechanical properties for 40.5% sucrose + 40.5% glucose syrup [G' (●); G'' (○)], 1.32% pectin (DE 22) + 39.84% sucrose + 39.84% glucose syrup [G' (▲); G'' (△)], and 1% pectin (DE 92) + 40% sucrose + 40% glucose syrup [G' (■); G'' (□)]. Samples were run at 1 °C/min and the frequency of oscillation was 1 rad/s.

Dependence of viscoelastic behaviour on oscillatory frequency or timescale of observation.—In the preceding section, a set of experimental curves of the storage and loss modulus as a function of temperature were recorded and discussed, with the effect of frequency or time on mechanical behaviour being only indirectly referred to [frequency (Hz) = 1/time (s)]. From a practical and theoretical viewpoint, however, the latter is of paramount importance owing to the large changes in structural/textural properties occurring in relation to the time function, which is perhaps more amenable to modelling than the changing temperature. The approach affords a device for enlarging the effective time scale available for experimental measurements, and it is realized by obtaining a sequence of frequency sweeps throughout the accessible temperature range.

Fig. 2 illustrates typical mechanical spectra of G' and G'' for 1.32% pectin (DE 22) in the presence of 39.84% sucrose and 40% glucose syrup. They were obtained for the most part at constant temperature intervals of 4°C thus spanning the temperature range −33 to 40 °C. The scheme for constructing a master curve involves empirical shifts of data along the logarithmic frequency axis. Thus, in the absence of a first-order thermodynamic transition (e.g., development of crystallinity), shear moduli measured at frequency ω and temperature T_1 are equivalent to those measured at frequency ωa_T and temperature T_o [23].

Implementation of the time–temperature superposition principle (TTS) in the pectin–co-solute mixture produces the master curves in Fig. 3. Good matching of the shapes of adjacent curves was observed, which allowed use of the same value of the shift factor a_T in

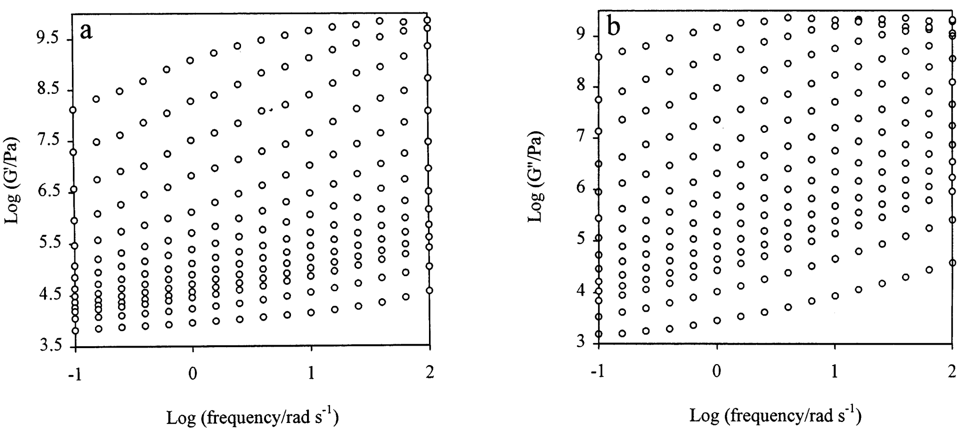

Fig. 2. Frequency variation of (a) storage modulus and (b) loss modulus for 1.32% pectin (DE 22) + 39.84% sucrose + 39.84% glucose syrup at successive temperatures spanning the glassy, glass transition and rubbery states illustrated from top to bottom of the frame: −33, −29, −25, −21, −17, −13, −9, −5, −1, 3, 7, 11, 20, 40 °C.

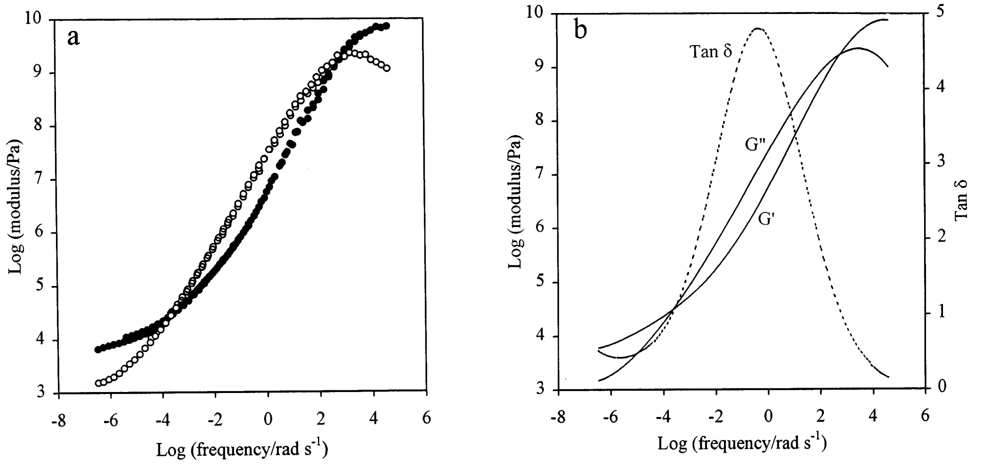

Fig. 3. (a) Application of the method of reduced variables to experimental storage modulus (●) and loss modulus (○) for the samples of Fig. 2. Best fits and tan δ of experimental data are given in (b). The reference temperature is −21 °C.

Table 1
Reference, glass transition, normalised and iso-free-volume temperatures, and their fractional free volumes for the pectin–co-solute system

Samples	T_o (°C)	f_o	T_g (°C)	f_g	T_{norm} (°C)	F_{norm}	T_{isofv} (°C)	f_{isofv}
co-solute [a]	−23	0.0378	−36	0.0301	−9	0.0462	−25.97	0.0360
pde22+sl [b]	−21	0.0391	−34	0.0310	−9	0.0465	−25.92	0.0360
pde92+sl [c]	0	0.0422	−12	0.0340	−9	0.0360	−9	0.0360

[a] Co-solute: 40.5% sucrose+40.5% glucose syrup.

[b] pde22+sl: 1.32% pectin (degree of esterification 22)+39.84% sucrose+39.84% glucose syrup.

[c] pde92+sl: 1% pectin (degree of esterification 92)+40% sucrose+40% glucose syrup.

the superposition of both G' and G'' data. Furthermore, the frequency dependence of viscoelastic functions has a form consistent with experience in synthetic polymer research [24]. Here the individual points for the different temperatures, far too numerous to display them all, were mostly within 2% of the master curve in Fig. 3(a). Best fits of the experimental results alongside the loss tangent are reproduced in Fig. 3(b). Reduction of data was implemented at the reference temperature of −21 °C (T_o in Table 1), which was chosen arbitrarily within the temperature range of the glass transition region and led to a frequency window of twelve orders of magnitude.

At high timescales of measurement (i.e., $< 10^{-4}$ rad/s), part of the plateau zone is captured where the storage modulus dominates the loss modulus and the values of tan δ remain below 1. Here the configurational rearrangements of the molecule, which are either shorter or longer than the distance between cross-links, are not expected to make a substantial contribution to the relaxation spectrum and the shear moduli flatten out. At higher frequencies, the glass transition zone makes its appearance and extends from about 10^4 to 10^9 Pa. Viscoelastic behaviour is governed by configurational changes of regions of the pectin molecule, which are shorter than the distance between cross-links. These contribute mainly to an energy dissipating process with the trace of G'' overtaking that of G'. The loss tangent achieves a maximum value of 4.8, which is close to the observation for the temperature-induced master curve of the same sample in Fig. 1. At the upper range of frequency (i.e., $> 10^3$ rad/s), no configurational rearrangements are possible and the sample develops predominantly a solid-like character. In the glassy state, the values of storage modulus approach 10^{10} Pa and those of tan δ drop below 1. As in the case of the temperature-dependent viscoelasticity in Fig. 1, the time function of data in Fig. 3 shows no signs of thermal hysteresis, thus remaining unaltered during cooling or heating, a result which further emphasizes the development of vitrification phenomena in the pectin–co-solute mixture.

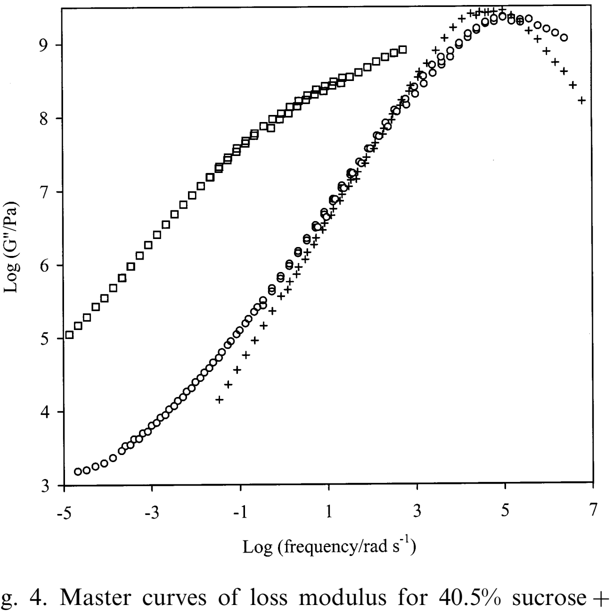

Fig. 4. Master curves of loss modulus for 40.5% sucrose + 40.5% glucose syrup (+), 1.32% pectin (DE 22) + 39.84% sucrose + 39.84% glucose syrup (○), and 1% pectin (DE 92) + 40% sucrose + 40% glucose syrup (□). The reference temperature is −9 °C.

Analysis of iso-free-volume states at different reference temperatures.—For comparing the time function in the high solids pectin system, master curves were also constructed for the co-solute and the high DE pectin mixture at the reference temperatures of −23 and 0 °C, respectively (graphs not shown). Results for the three samples were then reduced to a common temperature of −9 °C (T_{norm} in Table 1) and double logarithmic plots, for example, of the normalised loss modulus as a function of oscillatory frequency are depicted in Fig. 4.

As in the case of polymer melts [25], we were unable to achieve a satisfactory representation of the observed frequency-dependence of the loss modulus for our systems using the empirical expression of Andrade, which proffers an exponential relationship between mechanical properties and the reciprocal absolute temperature [26]. Instead, the WLF equation and its derivation on the basis of free volume considerations appears to satisfactorily explain the recorded progress in viscoelasticity. The central concept behind the approach is that the rate controlling step in molecular flow in the linear viscoelastic region is the formation of a void ('free volume') into which a chain segment can jump and hence produce flow [27]. The WLF equation is given as follows:

$$\log a_T = -\frac{C_1^0(T - T_0)}{C_2^0 + T - T_0} \quad (1)$$

where C_1^0 and C_2^0 are known as the WLF constants. In terms of the theory of free volume, C_1^0 and C_2^0 correspond to $B/2.303f_o$ and f_o/α_f, respectively. The ratio of free to total volume per unit mass of a material is known as the fractional free volume, f_o, the degree of thermal expansion is given by the coefficient α_f, and, for simplicity, B is taken equal to unity [28].

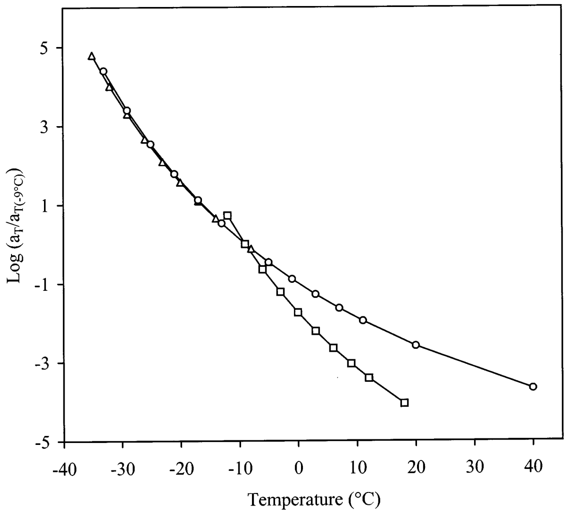

Fig. 5. Temperature variation of shift factors normalised at − 9 °C for 40.5% sucrose + 40.5% glucose syrup (△), 1.32% pectin (DE 22) + 39.84% sucrose + 39.84% glucose syrup (○), and 1% pectin (DE 92) + 40% sucrose + 40% glucose syrup (□).

The shift factors used to derive the master curves in Fig. 4 are plotted logarithmically against temperature in Fig. 5. Log a_T is zero at − 9 °C because this is arbitrarily chosen as the reference temperature. Experimental points determine how much the frequency scale shifts with temperature and this pattern is followed satisfactorily using the WLF scheme. Fitting of the shift factors can be achieved, for example, by plotting $1/\log a_T$ against $1/(T - T_0)$ and obtaining the two constants C_1^0 and C_2^0 from the slope and intercept of the linear fit, respectively. Details of the derivation of parameters pertinent to the theory of free volume are well documented and there is no need to dwell on them in the present communication [24,29].

Table 1 reproduces the predictions of the rheological glass transition temperature (T_g) for our preparations. It can be seen that introduction of high-molecular-weight material and, furthermore, increase in the degree of esterification of pectin accelerates the vitrification properties of the mixture as a whole. The values of the rheological T_g are congruent with the passage from the glass transition region to the glassy state, i.e., the cross over of G' and G'' traces, in the thermal profiles of Fig. 1. Mechanistically, this transformation coincides with diminishing free-volume phenomena at the end of the glass-transition region at which point the free volume falls to about 3% of the total volume of the material. As judged by the values of f_g in Table 1, glasses of reduced density are produced with increasing T_g from − 36 to − 12 °C. Relevant data can be obtained for any temperature within the glass transition region by recalculating the shift factors on the basis of the WLF algorithm and this is illustrated for the fractional free volume, f_o, at the reference temperature, T_o, in Table 1.

The reduced master curves in Fig. 4 are all based on the same reference temperature of − 9 °C, which represents different states of free volume for each preparation. Thus the shift factors used in the reduction of data for the co-solute and the low DE pectin mixture are somewhat different, as shown in the log a_T against T curves in Fig. 5. Such discrepancies are more pronounced in the case of the high DE pectin mixture, with its shift factors crossing the traces of the remaining samples with a different slope at − 9 °C ($\log a_T = 0$). The temperature dependence of shift factors can be analysed more simply by making the assumption that the horizontal separation in the glass transition of the master curves in Fig. 4 is attributable to the dependence of free volume on network formation. Quantitatively, this is represented by the relationship [30]:

$$\Delta \log \zeta_o = (1/2.303)(1/f - 1/f_o) \qquad (2)$$

where f_o is the fractional free volume of the most efficient vitrifier, i.e., the pectin sample with DE of 92.

Decrease in molecular mobility due to network formation is monitored by the local friction coefficient, ζ_o, which is 'a measure of the frictional resistance per monomer unit encountered by a chain segment in translatory motions' [31]. To evaluate the differences in ζ_o, which are responsible for the horizontal displacement in Fig. 4, the high DE pectin mixture was chosen as the reference with $T_{isofv} = -9$ °C, and the f_{isofv} was calculated to be 0.036. For each of the other two samples, a temperature was identified to correspond to the same value of fractional free volume. The resulting reference temperatures represent iso-free-volume states and are given in Table 1. Shift factors based on T_{isofv} were readily calculated for our samples and when $\log a_T$ was plotted against $T - T_{isofv}$, where T is the experimental temperature of the frequency sweeps, values for all samples coincided, as shown in Fig. 6.

It is gratifying to find that in these systems with a very wide range of molecular weight and distinct abilities of network formation, the temperature dependence of viscoelastic rate processes can be described by a single parameter T_{isofv}, which in turn is related to free volume. The solid curve in Fig. 6 corresponds to the WLF equation in the form:

$$\log a_T = -12.05(T - T_{isofv})/(53.0 + T - T_{isofv}) \qquad (3)$$

in which the basic reference temperature for the high DE pectin mixture is −9 °C. For each of the samples, $f_{isofv} = 0.036$ at its own T_{isofv}. The fractional free volumes of the samples can all be compared at −9 °C by calculating as follows:

$$f_{-9\,°C} = f_{isofv} + a_f(264 - T_{isofv}) \qquad (4)$$

where a_f is the relevant thermal expansion coefficient, and these are given as f_{norm} in Table 1. Significantly different fractional free volumes were predicted at −9 °C between the high DE pectin mixture and the remaining samples. Using Eq. (2), the contrast in the pattern of flow at the glass-transition region is reflected in the values of the monomeric friction coefficient ($\Delta \log \zeta_o$), which were found to differ by about −2.68 for the two types of systems.

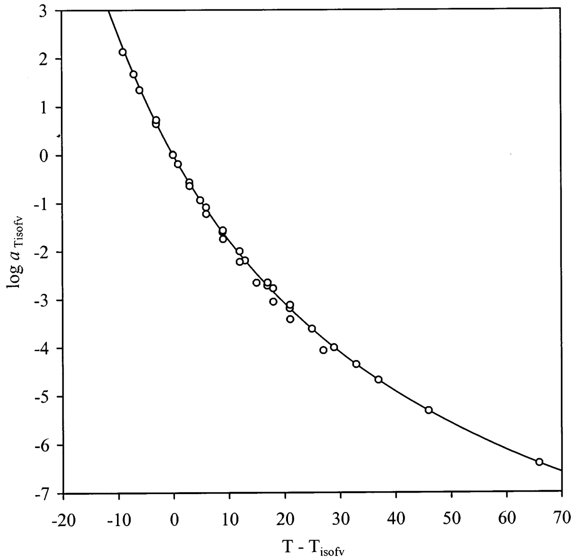

Fig. 6. Log a_T for reduction of dynamic oscillatory mechanical spectra of the pectin–co-solute system, with each sample reduced to its own T_{isofv} as given in Table 1 (the solid line is the WLF fit).

4. Conclusions

The present investigation defines the rheological glass transition temperature in terms of a kinetic process involving contraction of free volume from a relatively high value in the rubbery state or melt to only a few percent of the total volume of the pectin–co-solute system. The collapse of free volume at that temperature ushers in the glassy state where the only residual contraction is of a solid-like character, with the storage modulus overtaking the loss modulus and approaching values of 10^{10} Pa. The temperature dependence of the storage modulus was described by the method of reduced variables. The shift factors were identical for all preparations provided that each referred to a separate reference temperature corresponding to iso-free-volume states. Thus, the concept of dependence of mobility on free volume holds here where the free volume varies with the extent of intermolecular associations and network formation at a constant temperature. Intermolecular interactions are preserved in the high DE pectin sample leading to a reduction in polymeric mobility, which is seen as acceleration in the vitrification properties of the mixture. This, of course, is very different from the calorimetric glass transition temperature, which is dominated by the spectrum of the sugar-water alone [32,33] and invites a debate as to the true molecular nature of the glass-transition temperature measured by the two techniques.

Acknowledgements

The authors are pleased to acknowledge the staff working on the High Sugar Polysaccharide MAFF LINK project for support and stimulating discussions.

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