ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 329 (2000) 179–187

CARBOHYDRATE RESEARCH

Dynamic oscillation measurements of starch networks at temperatures above 100 °C

Stefan Kasapis [a,*], Shyam S. Sablani [a], Costas G. Biliaderis [b]

[a] *Department of Food Science & Nutrition, College of Agriculture, Sultan Qaboos University, PO Box 34, Al-Khod 123, Oman*

[b] *Department of Food Science & Technology, Aristotle University, PO Box 256, Thessaloniki 54006, Greece*

Received 26 October 1999; received in revised form 8 May 2000; accepted 15 May 2000

Abstract

Small deformation oscillatory studies were performed on wheat flour paste with a starch content of 75.4%. Work focused on temperatures above 100 °C in an effort to seek molecular understanding of such high-temperature processes as bakery operations which are characterised by evaporation of water. The moisture content of the sample decreased from about 32% at 100 °C to 6.5% at 130 °C. Viscoelastic spectra produced a sigmoidal profile with a disproportionate viscous element also seen in the glass transition of semiamorphous synthetic polymers and high sugar/polysaccharide mixtures during cooling. It is argued that the loss of water upon heating reduces the available free volume between neighbouring chain segments, thus generating a high-density thermoplastic melt suspending granule fragments. The configurational rearrangements of the disordered chains contribute mainly to an energy-dissipating process, as observed in the vitrification of cooled high-solids systems. The equation of Williams, Landel, and Ferry was modified with a 'moisture term' in order to describe the temperature function of viscoelasticity.

Keywords: Starch gels; High solids systems; Free volume; Williams–Landel–Ferry kinetics; 'Moisture term'

1. Introduction

Starch granules are insoluble in cold water at ambient temperatures because of the strong hydrogen bonding [1,2]. When wetted or exposed to high humidities, the granules absorb water and swell slightly. The abundance of hydroxyl groups in the starch granule is a primary factor in their tendency to absorb water. The swelling is reversible and the granules shrink on drying [3,4].

When a slurry of starch in water is heated beyond a critical temperature (which ranges from 56 °C upwards depending on the starch), the hydrogen bonds holding the granules together begin to weaken, permitting the granule to swell uniformly to many times its original size. This process is known as gelatinisation [5–7]. As this swelling occurs, the granules first lose their birefringence and then, as they begin to take up water, the clarity of the slurry and viscosity increases. At the so-called gelatinisation temperature, amylose starts to leach out into the solution. Finally, if enough heat is supplied, the granule reaches its maximum hydration and then begin to rupture and collapse, yielding a dispersion of granule fragments, starch aggregates, and disordered molecules [8,9]. The viscosity then decreases before reaching a stable value.

---

* Corresponding author. Tel.: +968-515256; fax: +968-513418.

E-mail address: stefan@squ.edu.om (S. Kasapis).

PII: S0008-6215(00)00161-0

The aforementioned changes in the structural properties of starch have been the subject of numerous rheological investigations [10–13]. Levine and Slade argued that melting and/or disintegration of the starch spherulite during gelatinisation results in systems akin to a semi-crystalline synthetic polymer [14]. These then should exhibit a viscoelastic transformation from the melt and the rubbery plateau to the leathery region in the way recorded for the synthetic counterparts as a function of temperature or time-scale of measurement [15,16]. Nelson and Labuza monitored the structural properties and the change in phase behaviour of starch systems as a function of temperature with the Arrhenius equation [17]. The approach yields a constant energy of activation, which is related to the energetic requirement for crystallite melting during the gelatinisation of starch [18,19].

In cases where breaks are observed in Arrhenius plots, the equation of Williams, Landel, and Ferry (WLF) has been suggested as an alternative for modelling the temperature dependence of food systems [20,21]. However, applications of the WLF approach have been confined to the rubbery state of biomaterials or the crystallisation of small molecules (such as lactose), which are at variance with the original demonstration of the principle in amorphous synthetic polymers and diluted systems [17,22]. There, the WLF expression was used to fit a steep transition in viscoelastic properties, known as the glass-transition region, which was ascribed to large-scale vibrational motions of the polymeric backbone. An array of materials was examined using mainly the technique of small deformation dynamic oscillation, which pinpointed the glass-transition temperature and delineated the plateau and terminal zones of the relaxation and retardation spectra [23–25].

Oscillatory studies have also been employed to probe the thermal effect on the phase behaviour of starch, but measurements have been confined to temperatures below 100 °C [26–30]. However, most food-related applications of starch (such as ultra high temperature, bakery fillings, extrusion, and others) are performed at higher temperatures and may lead to additional physicochemical transformations. The present work focuses on changes in viscoelastic properties of starch above 100 °C with a view to discussing them in terms of underlying fundamentals.

2. Materials and methods

Work was carried out mainly on plain wheat flour provided by the Oman Flour Mills Company. It contained 75% starch, 9.5% protein, 1.2% fat and about 0.6% ash. Wheat flour was mixed with distilled water to the desired moisture content (35% at 30 °C) and stored in moisture-tight plastic containers at room temperature for approximately 3 h allowing hydration of the starch molecules. Experiments were repeated with wheat starch purchased from Sigma (product number: S 5127). The amylose content of wheat starch in the literature is 21% [31]. Results were reproduced in terms of temperature range and overall signal, thus arguing that the viscoelastic transformations observed in wheat flour are also due to starch. However, the granular nature of starch pastes at high levels of solids exhibits a degree of slippage and syneresis which can deteriorate the adhesion between the sample and the flat surface of the measuring geometry, thus increasing the noise-to-signal ratio of the recorded spectrum.

Aggregation processes between agarose, κ-carrageenan or deacylated gellan chains result in brittle networks with similar problems of slippage. To circumvent the difficulty, Richardson and Goycoolea constructed a three-piece device of a smooth outer cup, a perforated middle cylinder, and a perforated inner cylindrical bob, with gelation locking the polysaccharide chains and the measuring geometry together, thus preventing breakdown of adhesion [32,33]. This, of course, would not help in the case of starch at temperatures below the gelatinisation point, since the weak interfacial forces between the starch spherulites would allow dislocation and slippage to occur in the system. However, the elastic nature of gluten maintains adhesion between the wheat flour paste and the smooth surface of the measuring geometry thus allowing accurate recording of the thermal transformations of the starch network.

Small-deformation measurements of storage and loss modulus (G' and G'', respectively) were made using a parallel-plate geometry of 7.9 mm diameter, with the measuring gap being 3 mm. A controlled strain rheometer was used which employs an actuator to apply a deforming strain to the sample and a separate transducer to measure the resultant stress developed within the sample (Advanced Rheometric Expansion System of Rheometric Scientific, Piscataway, NJ, USA). The high resolution actuator has a low end dynamic strain of 5 microradians. The transducer is essentially non-compliant and covers a torque range from 0.02 to 2000 g cm. During experimentation the torque varied accordingly to maintain a constant strain which allowed recording of modulus values in excess of 10^8 Pa.

Control of sample temperature was achieved by an air convection oven with counter-rotating air flow capable of reaching temperatures of 135 °C. Samples were loaded onto the rheometer at 30 °C and were then heated to 135 °C at 2 °C min^{-1}. In a separate experiment, mechanical spectra were recorded at temperature intervals of 3 °C between 100 and 130 °C. Profiles of shear moduli were superimposed as a function of time-scale of measurement for subsequent quantitative analysis. Results are the average of three replicates, with the rubber-to-glass transition being readily reproducible within a 3% error margin as a function of temperature or time-scale of measurement.

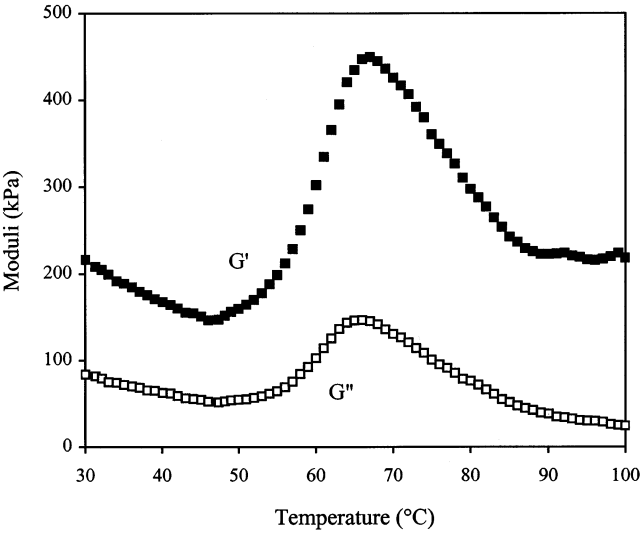

Fig. 1. Changes in G' and G'' as a function of heating of the wheat flour paste (frequency: 1 rad s^{-1}; scan rate: 2 °C min^{-1}).

3. Results and discussion

Dependence of viscoelastic behaviour on temperature.—As a preliminary to this investigation, the effect of temperature on the viscoelastic functions of the starch network was followed during gelatinisation. Fig. 1 shows the changes in G' and G'' observed during heating from 30 to 100 °C at a rate of 2 °C min^{-1}. There is a progressive reduction in the values of G' within the temperature range 30–50 °C which was found to be thermally reversible. Thus, it should be attributable to the increasing thermal motion of the system without changing the characteristics of the granule. Further increase in temperature sees a dramatic development in the elastic component of the sample, which achieves a maximum of 450 kPa at about 67 °C. This observation is the result of water absorption and swelling of the granule to many times its original size which characterises the phenomenon of gelatinisation [5–7]. The subsequent decrease in storage modulus is associated with the loss of granule integrity, with the system transforming into a mixture of leached amylose molecules, melted amylopectin sites, and granule fragments [8,9]. At the upper range of temperature, the values of G' approach an equilibrium at a similar level to that observed at 30 °C prior to gelatinisation (230 kPa).

In the main series of experiments we heated the sample at temperatures in excess of 100 °C, looking for molecular processes of potential interest. Fig. 2 illustrates the changes in both moduli throughout the experimental temperature range, which extends to 135 °C. The ratio of the viscous to the elastic response, $\tan \delta = G''/G'$, of the network is also reproduced. Clearly, there is a disproportionate drop in the values of loss modulus following gelatinisation maxima, with the trace of $\tan \delta$ steepening as the temperature is raised from 67 to 100 °C (G''/G' ratios of 0.33 and 0.11, respectively). Within this temperature

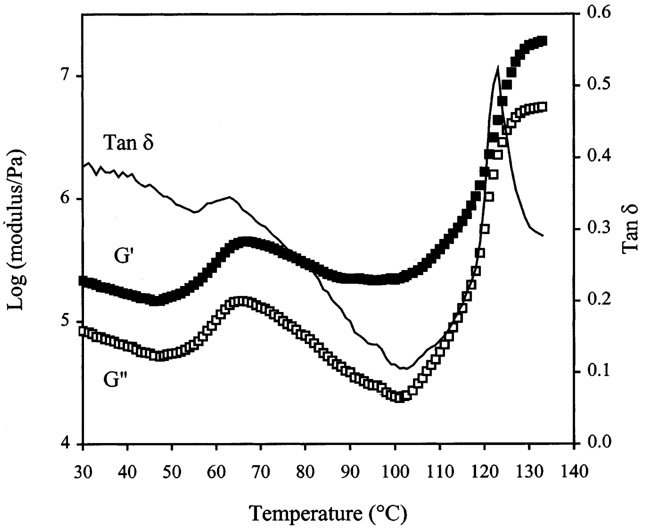

Fig. 2. Changes in G', G'' and their viscoelastic ratio, tan δ, as a function of heating of the wheat flour paste (experimental as in Fig. 1).

range, the presence and distribution of entanglements of disordered chains should be noticeable following leaching of such soluble components as amylose and increased melting of the crystalline frame of the granule. It appears, therefore, that those entanglements are seen increasingly as contributors to the cohesion of the network which, within the experimental time-scale of measurement, exhibits a depleted viscous component.

Modulus traces show a sharp up-turn on further heating with the values of G' approaching $10^{7.5}$ Pa at 135 °C. Furthermore, the viscous transition becomes sharper than the increase in G' leading to convergent traces with a tan δ value of 0.53 at 125 °C. Finally, the temperature course of viscoelasticity becomes broad with a dominant elastic component which reduces the tan δ ratio to 0.29 at 135 °C.

Pictorially, this type of response has been seen in the transition zone between rubberlike and glasslike consistency of synthetic polymers and diluted systems. For example, the rubbery region of poly(n-octyl methacrylate) shows a flat temperature dependence of viscoelastic functions at around $10^{5.5}$ Pa [23,25]. Cooling of the polymer results in a sharp increase in modulus and tan δ values which signify the glass-transition zone. Eventually, the modulus traces level off showing a dominant elastic component and a drop in the tan δ ratio, as observed at the top of the temperature range in Fig. 2, which is known as the glassy state. This behaviour can be understood qualitatively on the basis of free volume, which is present as voids between molecules due to their thermal motion or packing irregularities [34,35]. Cooling slows down the string-like rearrangements of the polymeric backbone and the configurational vibrations of repeat units and small molecules thus reducing the free volume in the sample. The process mainly dissipates energy and is weighted towards the viscous component of the network. These ideas are pursued further in the following section in an effort to rationalise the data in Fig. 2 recorded at temperatures above 100 °C.

Dependence of viscoelastic behaviour on time.—Application of the free volume approach to a high solids system implies that the variation in temperature generates a set of viscoelastic corresponding states. Thus, the reinforcement of modulus reflects a change in state which sometimes is called the 'second order thermodynamic transition' [36]. By contrast, a first order thermodynamic transition follows the path between two unrelated physicochemical states and is known as a change in phase (as in crystalline melting). The turn around in viscoelasticity recorded as a function of temperature at a constant frequency can be reproduced as a function of time provided that all relaxation processes in the system have the same temperature dependence. In this context, the frequency of oscillation is the reverse of the time-scale of measurement, namely freq(Hz) = 1/time(s).

Experimentally, this type of data-fitting can be carried out using the method of reduced variables also known as the time–temperature superposition principle [35,37]. It postulates that the shear moduli obtained as a function of frequency, ω, at a fixed temperature are equivalent to the viscoelastic response of the system at a reference temperature, T_o, provided that ω is multiplied by a shift factor, a_T. In its simplest form, the method also advocates uniform treatment of long and short retardation processes which creates a single set of shift factors for both traces of storage and loss modulus.

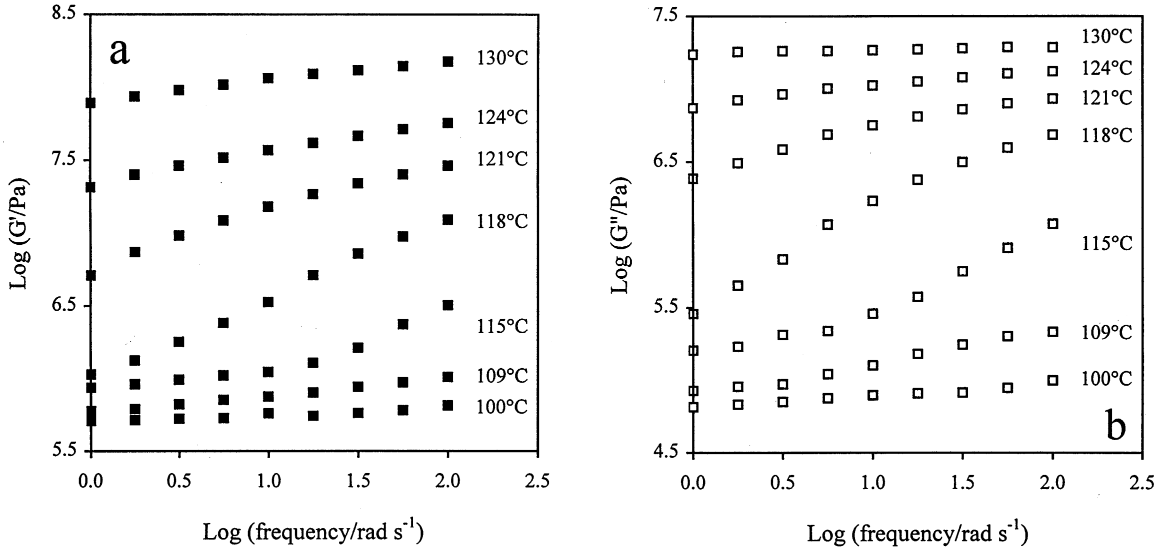

Fig. 3. Mechanical spectra showing the frequency-dependence of G' (■) and G'' (□) for the wheat flour paste within the temperature range 100–130 °C.

To examine how this method can produce parameters that relate the time dependence of viscoelasticity to molecular constitution of the wheat flour paste, we recorded a series of frequency sweeps from 1 to 100 rad s^{-1} at constant temperature intervals of 3 °C, thus covering the temperature range 100–130 °C. Fig. 3 depicts selected traces of G' and G'' plotted logarithmically against the frequency of oscillation. Below 110 °C and above 125 °C values of modulus do not change much with frequency. At intermediate temperatures, a sigmoidal transition appears which reinforces the viscoelastic response by two orders of magnitude. Next, we chose arbitrarily 100 °C as the reference temperature and shifted the mechanical spectra of the remaining temperatures horizontally along the frequency axis until a single curve without gross fluctuations or irregularities was obtained (Fig. 4). In doing so, the horizontal distance between each pair of adjacent curves of frequency sweeps was measured with a pair of dividers and recorded as the difference in the shift factor ($\Delta \log a_T$). Where the values of $\Delta \log a_T$ from G' and G'' were the same with reasonable error, the average was taken. The selected values of $\Delta \log a_T$ were then added progressively from T_o to obtain $\log a_T$ at each temperature. The reduced plot is known as the composite curve or master curve [37] that allows prediction of the viscoelastic properties of a system over a much wider frequency range than experimentally available at a single temperature (12 orders of magnitude in our case).

Vitrification of amorphous synthetic polymers and diluted systems unveils a point of cross over in the time–temperature course of storage and loss modulus with the latter becoming dominant ($\tan \delta > 1$). This is followed by a spectacular rise in viscoelasticity that can be up to four orders of magnitude; see for

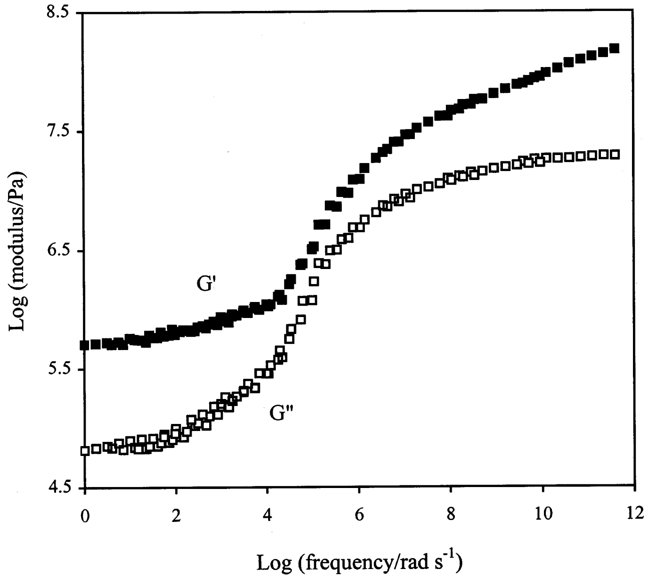

Fig. 4. Composite curve of G' and G'' obtained by superimposing horizontally along the frequency axis the mechanical spectra of Fig. 3 (reference temperature: 100 °C).

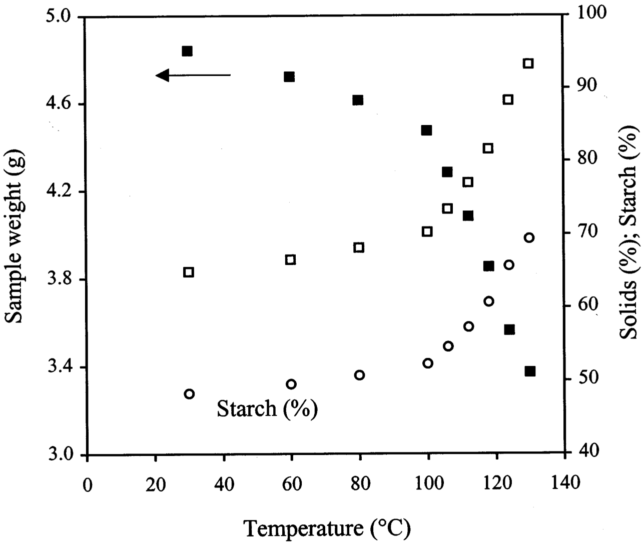

Fig. 5. Moisture loss estimated by weight differences during heating of the wheat flour paste following the experimental routine of the rheological investigation.

example the glass transition of 'standard' polyisobutylene in Ref. [38]. Similarly, mixtures containing lightly cross-linked polysaccharides at levels of normal industrial use ($< 1\%$) and high levels of sugar (up to 85%) undergo vitrification with a predominant viscous component (the value of tan δ can be as high as 3 in [39,40]). In both types of systems, increase in macromolecular order or small molecule crystallinity results in a fall in modulus of the glass transition, which is between one and two orders of magnitude, and a drop in the values of tan δ below the 'critical point' of one. This is evident in the case of copolymerised styrene and butyl acrylate nanocomposites reinforced by cellulose whiskers, and κ-carrageenan–sugar mixtures in the presence of 20 mM KCl that support aggregation of the polysaccharide chains [41,42]. The time–temperature course of viscoelasticity in Figs. 2 and 4 exhibits a sigmoidal transition of two orders of magnitude with a dominant elastic element (that is, tan $\delta < 1$). Granule fragments and molecular aggregates are ordered entities which contribute towards the elastic component of the network, whereas disordered molecules enhance the viscous element of the system. Therefore, results argue that the wheat flour paste behaves as a semiamorphous dispersion containing substantial amounts of granule fragments and molecular aggregates embedded in a matrix of disordered molecules.

Modelling of molecular rate processes in relation to changing moisture content.—Traditionally, the rates of chemical reactions are followed by an empirical equation developed first by Arrhenius for the hydrolysis of sucrose [43]:

$$\eta = A \exp(B/RT) \tag{1}$$

where the pre-exponential factor A is independent of temperature, R is the ideal gas constant and B is considered to be the energy of activation, E_a, required for the reaction to ensue. Doolittle, on the other hand, found that over a wide range of temperatures the following equation describes better the viscosity of monomeric liquids [44]:

$$\eta = A \exp(B/f) \tag{2}$$

where the fractional free volume, f, is the ratio of free volume to the total volume per gram of material.

Of particular interest in the present investigation is the application of the foregoing equations to a system with variable moisture content as a function of increasing temperature. Fig. 5 reproduces the moisture loss of the wheat flour paste subjected to the experimental routine of the rheological investigation. Clearly, the moisture content of the sample remains virtually constant at about 32% within the temperature range 30–100 °C. At higher temperatures, however, there is a substantial loss in sample weight with the moisture content at 130 °C being reduced to 6.5%. This approaches the levels of water expected to be tightly bound on the material in the form of an adsorbed monomolecular layer [45].

In adapting Doolittle's equation for systems with changing levels of solids, we considered an exponential dependence of viscoelasticity on moisture content:

$$G = A \exp(\lambda E_a/f) \tag{3}$$

where λ is the 'moisture term'. Free volume is a rather ill-defined concept, but it is assumed that f increases linearly with temperature as follows [35]:

$$f = f_o + \alpha_f(T - T_o) \tag{4}$$

where f_o is the fractional free volume at the reference temperature T_o and α_f is the thermal expansion coefficient. Substitution of Eq. (4) in Eq. (3) and for changing the temperature from T_o to T we obtain:

$$\log a_T = -\frac{C_1(T-T_o)}{C_2+T-T_o}\frac{M-M_o}{M_o} \tag{5}$$

where the shift factor, a_T, is the ratio of $G(T)/G(T_o)$. The parameters C_1 and C_2 can be identified as being equal to $E_a/2.303f_o$ and f_o/α_f, respectively. Expression (5) is the WLF equation incorporating the additional 'moisture term', λ. Alternatively, if the temperature dependence of the relaxation processes had followed Eq. (1) with a 'moisture term':

$$G = A\exp(\lambda E_a/RT) \tag{6}$$

one should have derived the corresponding Arrhenius expression with a constant energy of activation:

$$\log a_T = \frac{E_a}{2.303R}\frac{1}{T}\frac{M-M_o}{M_o} \tag{7}$$

Fig. 6 illustrates the temperature dependence of the shift factor a_T derived from the horizontal superposition on a logarithmic time-scale of the mechanical spectra in Fig. 3. Log a_T is zero at 100 °C because this is arbitrarily chosen as the reference temperature. The factor a_T is an exponential function of the reciprocal absolute temperature between 100 and 115 °C, which corresponds to the flat portion of the composite curve at frequencies below 10^3 rad s^{-1} (Fig. 4). Thus using Eq. (7) we obtain a constant energy of activation as a function of temperature with a numerical value of 56 kJ mol^{-1}. This is of the same order of magnitude with predictions in preparations of high sugar–κ-carrageenan and high methoxy pectin [46,47], and is attributed to the energy required to overcome a barrier to rotation of the polymeric backbone or of a side chain. It appears, therefore, that crystalline melting of the amylopectin skeleton is the most significant molecular mechanism occurring in the wheat flour paste within the temperature range 100–115 °C.

The Arrhenius expression fails to follow the temperature function of viscoelastic properties above 115 °C in Fig. 6, which is better described with Eq. (5). For the purpose of the quantitative analysis, the shift factor of the mechanical spectrum at 115 °C was set to 1 (reference temperature T'_o), and the remaining a_T values were adjusted accordingly. Experimental data in this temperature range correspond to the sigmoidal transition of G' and G'' traces at frequencies above 10^3 rad s^{-1} in Fig. 4. In contrast to Eq. (7), the factor a_T is

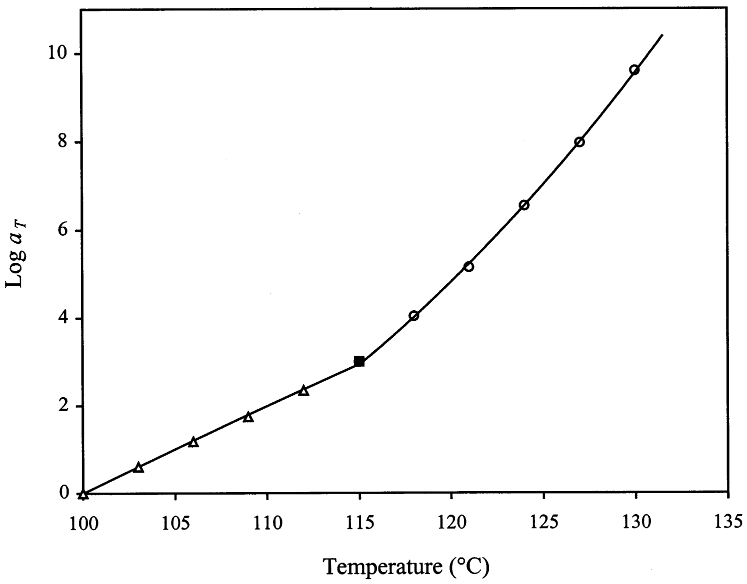

Fig. 6. Dependence of two distinct rates of relaxation processes (△; ○) on temperature plotted in terms of the factor a_T. The solid lines spanning the bottom and top range of temperature reflect fits of the Arrhenius and WLF equations, respectively, modified with a 'moisture term'.

not an exponential function of the reciprocal absolute temperature and the predicted energy of activation increases rapidly with increasing temperature. Therefore, at the upper range of temperature, the modified WLF equation argues for an increasing energy of activation, which reflects the difficulty for the occurrence in the glass transition of configurational rearrangements of the densely packed disordered chains.

A least-squares fit (STATISTICA, Version 5.0) to Eq. (5) was used to minimise the difference between the observed and predicted values of a_T thus yielding a loss function of less than 10^{-7}. Regardless of the input values of C_1 and C_2, the output for the two parameters at the reference temperature of 115 °C was 11.6 and 2.1°, respectively. Based on the observation that $T'_o - C_2 = T_g - 50$ [21,35], the free-volume theory predicts a glass-transition temperature of 163 °C. However, completion of the process of vitrification is not feasible since pyrolytic reactions at those temperatures cause decomposition of the sample.

4. Conclusions

In thermoplastic melts the concept of free volume has proved useful in discussing large scale vibrational motions and transport characteristics such as viscoelasticity and diffusion. Cooling of amorphous synthetic polymers and diluted systems or mixtures of polysaccharide, water, and high levels of sugar is accompanied by collapse of the free volume which controls the aforementioned molecular processes. Small molecules in these systems act as solvent and plasticiser, thus determining the glass-transition temperature of the isotropic mixture.

Along these lines, in water, the starch granules gelatinise and at high enough temperatures lose substantially their order and crystallinity. Water uptake takes place mainly in the amorphous regions and assists in keeping the conformational mobility of the disordered chains which interact in the form of a topological entanglement. Increasingly, however, the evaporation of water reduces the size of interstices between neighbouring chain segments, thus restricting their mobility. This process is equivalent to the reduction of available free volume in high solids systems due to ongoing cooling. The contraction in free volume of the wheat flour paste is seen as a sigmoidal profile of storage and loss modulus with increasing temperature in Figs. 2 and 4. Thus the resonance of the closely packed chains mainly propagates an energy-dissipating mechanism also seen in the glass transition of cooled materials. This is, then, followed by the WLF equation normalised in terms of the moisture content of the mixture.

References

[1] Y.G. Moharram, O.R. Abou-Samaha, M.H. Bekheet, in D. Wetzel, G. Charalambous (Eds.), *Instrumental Methods in Food and Beverage Analysis*, Elsevier, Amsterdam, 1998, p. 49.

[2] J.M.V. Blanshard, in T. Galliard (Ed.), *Starch: Properties and Potential*, Wiley, New York, 1987, p. 16.

[3] P. De Cock, *European Food and Drink Directory*, 1995–6, p 31.

[4] W.R. Morrison, J. Karkalas, in P.M. Dey (Ed.), *Methods in Plant Biochemistry*, *Vol. 2: Carbohydrates*, Academic, London, 1990, p. 323.

[5] V.J. Morris, *Trends Food Sci. Technol.*, July issue (1990) 2–6.

[6] C.G. Biliaderis, *Food Technol.*, June issue (1992) 98–109.

[7] R.D. Waniska, M.H. Gomez, *Food Technol.*, June issue (1992) 110–123.

[8] N.W. Cervone, J.M. Harper, *J. Food Process. Eng.*, 2 (1978) 83–95.

[9] H.F. Zobel, in R.L. Whistler, J.N. BeMiller, E.F. Paschall (Eds.), *Starch: Chemistry and Technology*, Academic, London, 1984, p. 285.

[10] J.-L. Doublier, *Stärke*, 33 (1981) 415–420.

[11] J.-L. Doublier, *J. Cereal Sci.*, 5 (1987) 247–262.

[12] H.S. Ellis, S.G. Ring, M.A. Whittam, *J. Cereal Sci.*, 10 (1989) 33–44.

[13] J.P. Mua, D.S. Jackson, *J. Cereal Sci.*, 27 (1998) 157–166.

[14] H. Levine, L. Slade, in H. Faridi, J.M. Faubion (Eds.), *Dough Reology and Baked Product Texture*, AVI Publishing, New York, 1990, p. 157.

[15] G.W. White, S.H. Cakebread, *J Food Technol.*, 1 (1966) 73–82.

[16] R.S. Marvin, H. Oser, *J. Res. Nat. Bur. Stand.*, 66B (1962) 171–180.

[17] K.A. Nelson, T.P. Labuza, *J. Food Eng.*, 22 (1994) 271–289.

[18] M.-Y. Baik, K.-J. Kim, K.-C. Cheon, Y.-C. Ha, W.-S. Kim, *J. Agric. Food Chem.*, 45 (1997) 4242–4248.

[19] W.H. Yang, M.A. Rao, *J. Food Process. Eng.*, 21 (1998) 191–207.

[20] R. Karmas, M.P. Buera, M. Karel, *J. Agric. Food Chem.*, 40 (1992) 873–879.

[21] M.L. Williams, R.F. Landel, J.D. Ferry, *J. Am. Chem. Soc.*, 77 (1955) 3701–3707.

[22] Y. Roos, M. Karel, *J. Food Sci.*, 57 (1992) 775–777.

[23] W. Dannhauser, W.C. Child, J.D. Ferry, *J. Colloid Sci.*, 13 (1958) 103–113.

[24] K. Ninomiya, J.D. Ferry, *J. Colloid Sci.*, 14 (1959) 36–48.

[25] J.W. Berge, P.R. Saunders, J.D. Ferry, *J. Colloid Sci.*, 14 (1959) 135–146.

[26] C.J.A.M. Keetels, T. van Vliet, in G.O. Phillips, P.A. Williams, D.J. Wedlock (Eds.), *Gums and Stabilisers for the Food Industry 7*, IRL Press, Oxford, 1994, p. 271.

[27] K.E. Petrofsky, R.C. Hoseney, *Cereal Chem.*, 72 (1995) 53–58.

[28] A. Rolee, M. Le Meste, *Cereal Chem.*, 74 (1997) 581–588.

[29] R.C. Yuan, D.B. Thompson, *Cereal Chem.*, 75 (1998) 117–123.

[30] M.A. Rao, J. Tattiyakul, *Carbohydr. Polym.*, 38 (1999) 123–132.

[31] P.D. Orford, S.G. Ring, V. Carroll, M.V. Miles, V.J. Morris, *J. Sci. Food Agric.*, 39 (1987) 169–177.

[32] R.K. Richardson, F.M. Goycoolea, *Carbohydr. Polym.*, 24 (1994) 223–225.

[33] L.E. Whittaker, I.M. Al-Ruqaie, S. Kasapis, R.K. Richardson, *Carbohydr. Polym.*, 33 (1997) 39–46.

[34] M.C. Shen, A. Eisenberg, in H. Reiss (Ed.), *Progress in Solid State Chemistry*, Vol. 3, Pergamon, Oxford, 1967, p. 407.

[35] J.D. Ferry, *in Viscoelastic Properties of Polymers*, Wiley, New York, 1980, p. 264.

[36] G. Allen, in J.M.V. Blanshard, P.J. Lillford (Eds.), *The Glassy State in Foods*, Nottingham University Press, Nottingham, 1993, p. 1.

[37] A.V. Tobolsky, *J. Appl. Phys.*, 27 (1956) 673–685.

[38] I.M. Ward, D.W. Hadley, *Mechanical Properties of Solid Polymers*, Wiley, Chichester, 1993, p. 84.

[39] V. Evageliou, S. Kasapis, M.W.N. Hember, *Polymer*, 39 (1998) 3909–3917.

[40] G. Sworn, S. Kasapis, *Carbohydr. Res.*, 309 (1998) 353–361.

[41] V. Favier, H. Chanzy, J.Y. Cavaillé, *Macromolecules*, 28 (1995) 6365–6367.

[42] S. Kasapis, I.M.A. Al-Marhoobi, in G.O. Phillips, P.A. Williams (Eds.), *Gums and Stablisers for the Food Industry 10*, Royal Society of Chemistry, Cambridge, UK (in press).

[43] P.W. Atkins, *Physical Chemistry*, second ed., Oxford University Press, Oxford, 1984, p. 922.

[44] A.K. Doolittle, *J. Appl. Phys.*, 22 (1951) 1031–1035.

[45] N.N. Potter, *Food Science*, fourth ed., Chapman and Hall, New York, 1986, p. 294.

[46] V. Evageliou, S. Kasapis, *MFLRBER*, 62 (1997) 1313–1320.

[47] S. Kasapis, *Agric. Sci.*, 4 (1999) 63–71.