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Influence of temperature on the dynamic and steady-shear rheology of pectin dispersions

J.A. Lopes da Silva

Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr António Bernardino de Almeida, 4200 Porto, Portugal

M.P. Gonçalves*

Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua dos Bragas, 4099, Porto Codex, Portugal

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M.A. Rao

Department of Food Science and Technology, Cornell University, Geneva, New York 14456, USA

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The influence of temperature on the dynamic and steady-shear rheology of ionic polysaccharides, high-methoxyl and low-methoxyl pectins, has been studied and compared with the behaviour of locust bean gum, a virtually neutral biopolymer. Using the time-temperature superposition principle, the rheological parameters were reduced to an arbitrary reference temperature. Activation energies were calculated and their dependence on temperature and shear rate analysed. Concerning the viscosity dependence on temperature, two approaches have been considered: one associated with the theory of absolute reaction rates leading to an Arrhenius type equation, and the other associated with the free volume theory, expressed by the Williams–Landel–Ferry equation. The difficulties encountered in the superposition of the dynamic properties of the pectin dispersions, the high activation energies, yield values and elastic plateau at low oscillatory frequency, are consistent with a macromolecular organization of these polymers dominated by important aggregation phenomena, which could be attributed to important intermolecular interactions like hydrogen bonding and hydrophobic interactions, especially in conditions of low degree of ionization of the carboxylic groups.

INTRODUCTION

Pectins are polysaccharides that can be regarded as copolymers of α-D-galacturonic acid (linked 1 → 4) and L-rhamnose (linked 1 → 2 to the 'backbone'), in which the galacturonic acid units are partially esterified with methanol and are in considerable excess relative to the rhamnose units and other neutral sugars present as side chains. They are widely used in food formulations, mainly as gelling agents. However, as a major structural component of the primary cell walls of plants, they can be found in several liquid food formulations, where they have an important role in the rheological behaviour. The rheological properties of pectin dispersions are related to their polyelectrolytic nature. In conditions of high degree of ionization of the carboxylic groups (about neutral pH) pectins were shown to display in solution a random coil conformation (Axelos *et al.*, 1989; da Silva *et al.*, 1992), while in conditions of low degree of ionization the rheological behaviour changed markedly, with aggregation phenomena appearing as the main feature of its properties (da Silva *et al.*, 1993).

Locust bean gum is a virtually neutral galactomannan polymer extracted from the seeds of the carob tree (*Ceratonia siliqua*). It is accepted that its structure consists of a linear chain of (1 → 4) linked β-D-mannose units, with single α-D-galactose units occurring as side groups, not uniformly distributed, linked (1 → 6) with

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*To whom correspondence should be addressed.

the main chain, with the average mannose: galactose ratio generally considered equal to about 4. Its rheological behaviour is essentially governed by physical entanglements, characteristic of random coil polymers (Doublier & Launay, 1981; Morris *et al.*, 1981).

Little work has been done on the properties of pectin dispersions at low degrees of dissociation of their carboxylic groups (low pH). In these conditions, some difficulties could arise from the uncertainty in the determination of the degree of dissociation and of the polymeric contribution to the ionic strength of the systems, and also from precipitation that could occur at low pH. However these conditions are frequently found in the processing of fruit and vegetable juices; for example, the pectins have great importance in the consistency of homogenized fruits and vegetables and in the often undesirable cloudy appearance (Rombouts & Pilnik, 1978).

In the present work, the effect of temperature on the viscoelastic properties of high-methoxyl and low-methoxyl pectin dispersions was studied and compared with the behaviour of a virtually neutral biopolymer, locust bean gum, over a range of about 60°C and for moderately concentrated dispersions. As different temperatures are often encountered during the processing, storage, transportation and consumption of liquid and semi-solid foods, the knowledge of the temperature dependence of the rheological properties of these systems could be useful in the practical applications of these polysaccharides in processing operations, as well as in understanding the mechanism of deformation and flow of these macromolecules. Special attention was devoted to explore time–temperature superposition, considering the different chemical and structural characteristics of these biopolymers, by measuring their rheological properties in steady and dynamic shear.

EXPERIMENTAL

Materials

Commercial high-methoxyl pectin (HMP) and low-methoxyl pectin (LMP) were supplied by HP Bulmer Pectin (Hereford, UK). The pectins were prepared from a mixture of lime and lemon peels, extracted using nitric acid and the extract concentrated and precipitated with isopropanol. The LMP was obtained by de-esterification by homogeneous acid hydrolysis of the concentrated extracted. Both samples were purified by complexation with cupric ions (da Silva *et al.*, 1992). Commercial locust bean gum (LBG) was obtained from INDAL (Faro, Portugal) and purified by precipitation with isopropanol as described previously (da Silva & Gonçalves, 1990). Some physico-chemical parameters of these biopolymers are presented in Table 1. Details of the analytical procedures are given elsewhere (da Silva *et al.*, 1992).

Table 1. Physico-chemical parameters of high-methoxyl pectin (HMP), low-methoxyl pectin (LMP), and locust bean gum (LBG) samples

	Purified LBG	Purified HMP	Purified LMP
Intrinsic viscosity (dl/g)[a]	13·7	4·73	3·04
Viscosity-average molecular weight ($\times 10^{-5}$)	19·6	1·15	0·628
Mannose/galactose ratio	4·08	—	—
Anhydrogalacturonic acid (%)	—	85·2	91·6
Degree of methylation (%)	—	65·8	35·1

[a]The values shown are the means of Huggins and Kraemer extrapolations, obtained in triplicate measurements. The pectin samples were analysed in NaCl 0·1 M, pH 7·0.

Preparation of solutions

The required amount of gum was gradually added under strong agitation to an appropriate amount of solvent (water or 0·1 M NaCl) containing 0·02% of sodium azide as a preservative. The LBG dispersion was moderately stirred for 1 h, at room temperature, and then heated to 85°C in a water bath for 30 min. The HMP and LMP dispersions were moderately stirred for 12 h at room temperature. Both dispersions were then centrifuged for 1 h at 28 000*g* and allowed to stand for 12 h before measurements. The pectin solutions were prepared in conditions of low ionic strength, without addition of external salt, or in 0·1 M NaCl, and the pH adjusted to 3·0. Final concentrations were 3·5% (w/w) for the pectins dispersions and 1% (w/w) for the LBG dispersion.

Rheological determinations

All rheological measurements were performed with a controlled stress rheometer (Carri-Med CS-50, Carri-Med Ltd, Dorking, UK), with cone and plate geometry (cone angle of 0·069 radians and a diameter of 50 mm). A strain amplitude ranging from 3 to 10% was selected in order to obtain well resolved displacement readings and to work in a region of linearity of the measured dynamic properties. Oscillatory measurements were conducted over a frequency range 0·01–10 Hz. Tests in steady shear at intermediate shear rates ($\dot{\gamma} \approx 0{\cdot}1$–$100\,\mathrm{s}^{-1}$) were performed first in increasing order of applied torque followed by decreasing order in a continuous manner. The time for the up an down curves was standardized. The torque amplitude was imposed using a logarithmic ramp, in order to decrease the initial acceleration and the effects due to instrument inertia. Good temperature control was achieved with a Peltier system in the bottom plate. Solvent evaporation was minimized by applying a thin layer of low viscosity paraffin oil to the exposed surface of the sample.

Nonlinear regression

The parameters of the nonlinear models were obtained by an iterative search algorithm that determined the values that minimized the residual sum of squares. The algorithm used was a compromise between using a straight linearization method (Gauss–Newton) and the method of steepest descent (Statgraphics software v.5, STSC Inc., 1991). The possibility of convergence to a local minimum was avoided by performing the analysis several times with widely differing initial estimates for the parameters.

Temperature superposition

The rheological parameters obtained in the temperature range of 5–65°C were tentatively reduced to an arbitrary reference temperature ($T_o = 25°C$), using the time–temperature superposition principle (Ferry, 1980). The storage (G') and loss moduli (G'') data as a function of frequency were first plotted using modulus shift factors calculated from the temperature–density correction factor ($T_o\rho_o/T\rho$), where ρ and ρ_o are the densities at the absolute temperature of measurement, T, and at the reference temperature, T_o. Then, the appropriate frequency shift factor, a_T, was obtained empirically by graphical shift of the data obtained at different temperatures, using logarithmic ordinates.

The shift factors were first obtained for the dynamic viscoelastic functions $G'(\omega)$ and $G''(\omega)$, by simultaneous superposition of both curves, and later for the steady-shear flow data, $\eta(\dot{\gamma})$. Then, assuming that the temperature dependence of all relaxation times can be described by the single factor a_T, the shift factors obtained were used to reduce other viscoelastic functions. When the simultaneous superimposition of the functions $G'(\omega)$ and $G''(\omega)$ was difficult, the superposition was tested for each function separately. Also, we tested the superposition by applying a vertical shift in excess of that introduced by the temperature–density factor.

RESULTS AND DISCUSSION

Modeling the rheological behaviour under continuous shear flow

From the flow data obtained for the pectin dispersions under continuous shear conditions, there was an evidence for yield stress, especially for the higher temperature range studied.

The Carreau (1972) and the Cross (1979) models can be modified to include a term due to yield stress, as shown in eqns (1) and (2), respectively, and are useful to describe the shear-thinning behaviour and the relatively low yield values of pectin dispersions (da Silva *et al.*, 1990):

$$\eta = \sigma_o\dot{\gamma}^{-1} + \eta_\infty + \frac{(\eta_p - \eta_\infty)}{[1 + (\alpha\dot{\gamma})^2]^{(1-n)/2}} \tag{1}$$

$$\eta = \sigma_o\dot{\gamma}^{-1} + \eta_\infty + \frac{(\eta_p - \eta_\infty)}{[1 + (\lambda\dot{\gamma})^m]} \tag{2}$$

where η is the apparent viscosity, $\dot{\gamma}$ is the shear rate, σ_o the yield stress, η_p the plateau viscosity, η_∞ the limiting viscosity at infinite shear rate, α and λ are characteristic time constants, and n and m are dimensionless exponents of the Carreau and Cross equations, respectively. The Carreau model with the yield term was previously employed for the study of the rheological behaviour of glass-filled polymers (Poslinski *et al.*, 1988). Both models have been used successfully to describe the behaviour of aqueous scleroglucan solutions (Lapasin *et al.*, 1990).

These models have been used to fit our experimental data on pectin dispersions, and the fit obtained by both models was generally good. For the galactomannan sample, the unmodified models, without the yield term, have been applied. The degree of fit that each model provided was estimated by the residual sum of squares (RSS) and the mean relative deviation (MRD):

$$\mathrm{MRD} = \frac{\sqrt{\sum_{i=1}^{n}\left[\left(\frac{\eta_i - \eta_i'}{\eta_i'}\right)^2\right]}}{n} \tag{3}$$

where η_i is the ith experimental value, η_i' the correspondent fitted value and n is the total number of points. Slightly better fits were generally obtained with the modified Cross model. However, from an analysis of the ratios of the estimates to their standard errors, it emerged that with the Carreau model generally better precision was obtained, especially for the 3·5% HMP dispersion. Some of the results obtained are given in Tables 2 and 3.

As for most polymer systems, the estimated values of η_∞ were much smaller than η_p or η_o, and they usually could not be observed over the experimental shear rate range. Also, the fit of the models with the η_∞ term often gave negative values for this parameter, without any physical meaning. Therefore, in these cases, the modeling was done taking $\eta_\infty = 0$.

The parameters α and λ have the dimensions of time and can be identified as relaxation times, characterizing the viscoelastic behaviour of the system, and are related to the onset of shear thinning. High standard errors in the estimates of these parameters were obtained for the HMP dispersions. These difficulties could be related to the flow behaviour of these dispersions, without a well defined Newtonian plateau. Therefore, they required additional care in the interpretation of the values obtained. For the LMP dispersions, we obtained much more precise values for the relaxation times, with large ratios of the estimates to their standard errors.

Table 2. Parameters of the Carreau model with a yield term, as a function of the temperature, for aqueous 3·5% pectin dispersions at pH 3·0. Flow data obtained by increasing the applied stress. The parameters shown are defined in the text

Systems		σ_o (Pa)	η_p (Pa s)	α (s)	n	MRD ($\times 10^3$)[a]	RSS[b]
3·5% HMP	15°C	0·270	13·3	4·48	0·732	3·49	7·42
	25°C	0·262	6·99	4·95	0·786	4·05	2·37
	35°C	0·229	5·11	10·9	0·810	3·52	0·768
	45°C	0·234	2·65	3·12	0·815	3·12	0·543
	55°C	0·248	1·77	2·47	0·832	2·94	0·436
	65°C	0·236	1·06	2·51	0·857	2·58	0·0956
3·5% LMP	5°C[c]	—	119·4	5·75	0·349	5·95	74·3
	15°C	0·556	23·8	2·90	0·556	8·30	9·66
	25°C	0·433	4·50	0·596	0·651	5·71	2·09
	30°C	0·425	1·96	0·181	0·682	2·98	0·272
	35°C	0·309	0·840	0·134	0·800	4·07	0·263
	40°C	0·354	0·323	0·0223	0·853	1·81	0·0226

[a] MRD, mean relative deviation.
[b] RSS, residual sum of squares.
[c] Fitted with the Carreau model without the yield term.

Table 3. Parameters of the Cross model with a yield term, as a function of the temperature, for aqueous 3·5% pectin dispersions at pH 3·0. Flow data obtained by increasing the applied stress. The parameters shown are defined in the text

Systems		σ_o (Pa)	η_p (Pa s)	λ (s)	m	MRD ($\times 10^3$)[a]	RSS[b]
3·5% HMP	15°C	0·206	19·9	1·54	0·419	1·73	7·77
	25°C	0·235	10·7	1·43	0·344	1·55	1·30
	35°C	0·217	9·90	13·0	0·268	1·78	0·533
	45°C	0·232	5·14	0·845	0·287	1·65	0·512
	55°C	0·243	2·35	0·181	0·318	1·47	0·441
	65°C	0·231	1·58	0·276	0·256	1·11	0·0730
3·5% LMP	5°C[c]	—	141·6	2·83	0·901	44·2	325·6
	15°C	0·212	37·7	1·97	0·604	1·42	5·68
	25°C	0·399	5·33	0·119	0·607	1·29	0·620
	30°C	0·410	2·14	$2{\cdot}34 \times 10^{-2}$	0·667	1·38	0·138
	35°C	0·300	0·973	$8{\cdot}15 \times 10^{-3}$	0·445	3·04	0·150
	40°C	0·352	0·335	$6{\cdot}26 \times 10^{-4}$	0·605	1·90	0·0209

[a] MRD, mean relative deviation.
[b] RSS, residual sum of squares.
[c] Fitted with the Cross model without the yield term.

The general trend observed for the pectin and LBG dispersions was an increase in the relaxation time with decrease in temperature and increase in ionic strength for the pectin samples. Similar behaviour was found for the plateau viscosity corresponding to the Newtonian plateau.

The values of yield stress could be attributed to the high levels of structure enhanced by the suppression of electrostatic repulsions at the low pH studied. They were almost independent of temperature. Despite some scatter in the low yield values obtained at different temperatures, the LMP dispersions presented higher values of yield stress than the HMP dispersions.

Viscoelastic behaviour under oscillatory shear flow

To ensure the good interpretation of the time-dependent behaviour shown by pectin dispersions (Fig. 1), extreme care in handling these samples is required. The oscillatory measurements were conducted after the sample remained on the rheometer plate for about 60–90 min depending on the temperature so that all the structure broken during the loading operation could be rebuilt. Also due to this time dependent behaviour, and to the development of very weak interactions between the pectin macromolecules, the region of linearity is even smaller than previously found (da Silva *et al.*, 1993), and very close to the limit of the measuring system. The onset of non-linearity could not be avoided, especially at low frequencies. Because disperse systems under oscillatory shear flow conditions generally exhibit a non-linear response at high concentrations of the disperse phase, even at small strain amplitudes (Onogi & Matsumoto, 1981; Amari & Watanabe, 1983; Lapasin & Pricl, 1992), the results with pectin dispersions suggest the colloidal behaviour of our systems, where

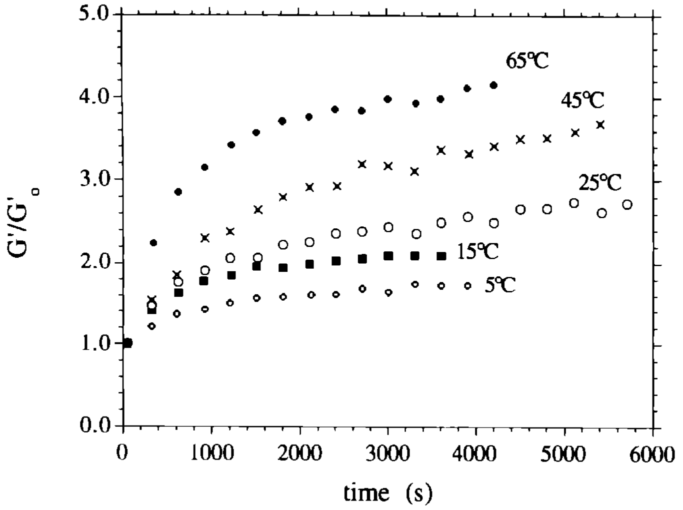

Fig. 1. Time dependent behaviour of the normalized storage modulus (G'/G'_0) for a 3·5% HMP aqueous dispersion (pH 3·0) at several temperatures. G'_0 denotes the storage modulus measured at each temperature, 5 min after the sample was loaded on the rheometer plate.

weak interactions could occur at low amplitude strain, with the formation of microaggregates and some structure.

Figures 2(a) and 2(b) show magnitudes of $G'(\omega)$ and $\eta'(\omega)$ from dynamic viscoelastic measurements on 3·5% aqueous HMP and LMP dispersions (pH 3), respectively. From the mechanical spectra at different temperatures, the liquid-like behaviour with $G'' > G'$ was observed only for an intermediate frequency range, although with a lower dependence on frequency than the expected values for a liquid system. The characteristic interception point ($G' = G''$) at high frequency, corresponding to the beginning of the elastic plateau zone, could be observed only for the LMP dispersions at low temperatures. It moved to lower frequencies when the temperature decreased, or when the ionic strength increased.

The different density of charged groups in these polymers, even in the conditions of low degree of ionization (low pH) that have been employed, seems to play a determinant role in the rheology of these systems. The general viscoelastic behaviour of the LMP is much more sensitive to changes in temperature or in ionic strength than that of the HMP dispersions. Solid-like behaviour over a wide range of frequencies could be observed for the LMP dispersions especially at low temperatures and high ionic strength (Fig. 3). The screening of charges promoted by the increase in ionic strength, associated with the lower esterification of the carboxyl groups, leads to important intermolecular interactions probably regulated by hydrogen bonding.

For both pectin samples, an elastic plateau was found at low frequencies, which was also reported for highly structured systems like concentrated suspensions (Onogi & Matsumoto, 1981; Amari & Watanabe, 1983). This elastic behaviour could also be attributed to organized intermolecular interactions, taking place in conditions of low degree of dissociation of the pectin chains and at low frequency and strain amplitude.

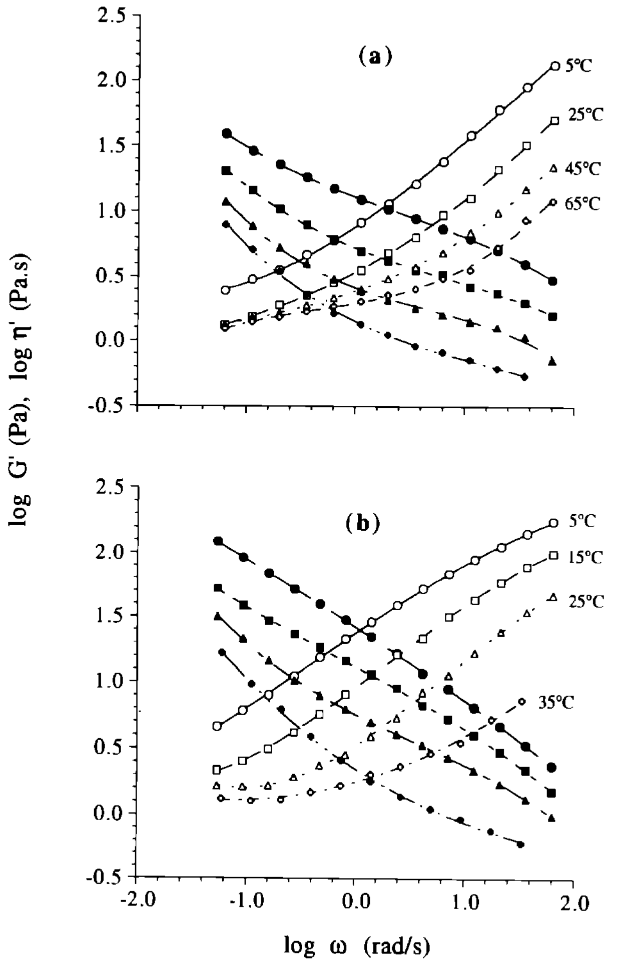

Fig. 2. Dynamic viscosity η' (filled symbols) and storage modulus G' (open symbols) for (a) 3·5% aqueous HMP dispersion (pH 3·0), and (b) 3·5% aqueous LMP dispersion (pH 3·0), as a function of angular frequency at several temperatures.

Time–temperature superposition

The time–temperature superposition principle (Ferry, 1980), or method of reduced variables, suggests that all contributions to the dynamic moduli should be proportional to ρT, and is based on the assumption of equal temperature dependence of all relaxation times. Thus, the effect of a change in temperature from T to an arbitrary reference temperature T_0 should cause a change in the moduli G' and G'' equivalent to multiplying them by the temperature–density correction factor ($T_0\rho_0/T\rho$), due to the effect of thermal expansion and to the entropy-spring nature of the stored elastic energy, and to multiplying the frequency scale by a_T. Although the shift factor a_T is determined empirically, it has a physical significance—it is the ratio of maximum

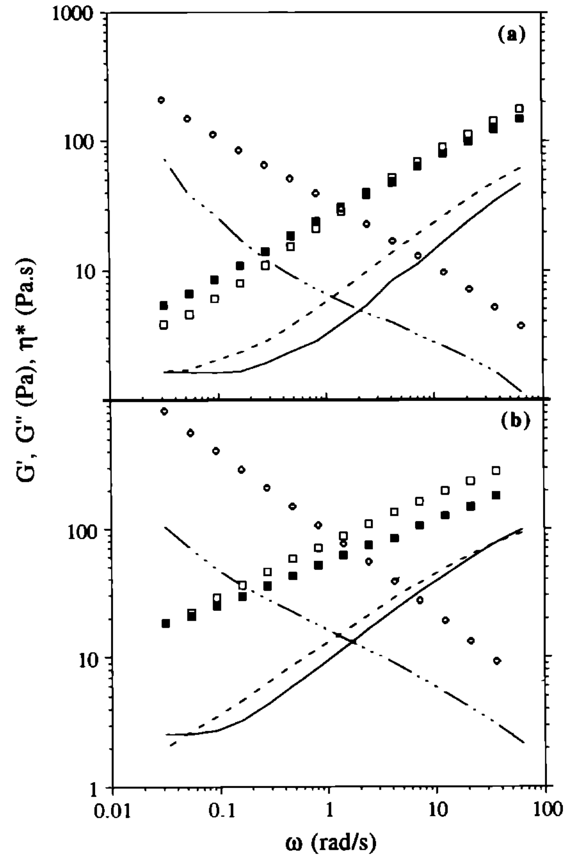

Fig. 3. Mechanical spectra for a 3·5% LMP dispersion (pH 3·0) (a) in water, and (b) in 0.1 M NaCl. Comparison between the behaviour at 5°C (symbols) and 25°C (lines). (□, ——) storage modulus ($G'(\omega)$); (■, – – –) loss modulus ($G''(\omega)$); (◇, ··· —) complex viscosity ($\eta^*(\omega)$).

relaxation times at different temperatures to the maximum relaxation time at the reference temperature T_0 (Vinogradov & Malkin, 1980). For simple temperature reduction to be applied, all the viscoelastic mechanisms that contribute to the overall rheological behaviour should have the same temperature dependence.

The frequency–temperature superposition (analogous to time–temperature superposition in transient experiments) was tested for the HMP dispersions in water and in 0·1 M NaCl for the temperature range 5–65°C, but a smooth master curve could not be obtained, for both moduli simultaneously (Fig. 4) or for each one individually.

Slightly higher discrepancies were found for the LMP dispersions. Over the temperature and frequency range studied, the time–temperature superposition principle could not be applied to simultaneous superposition of $G'(\omega)$ and $G''(\omega)$ data. Also, satisfactory reduction of the data to a single curve was not obtained, irrespective of the frequency shift factor used, for each modulus individually (Fig. 5) or with vertical shift factors higher than those calculated by the temperature–density factor.

The same difficulties were found for the steady shear flow data obtained by increasing the applied stress, especially in the low region of shear rate. For the steady shear data obtained by decreasing applied stress, after shearing the sample, satisfactory superposition could be obtained only by applying vertical shift factors higher than those obtained by the temperature–density factors (Table 4). Figure 6 shows the master curves obtained for a 3·5% LMP dispersion (pH 3·0) in water and in 0·1 M NaCl. It was found for several other systems that a shift along the log-modulus axis is required in order to have a satisfactory reduction of the dynamic functions, as, for example, in the case of semicrystalline polymers (Ward & Tobolsky, 1967) or for cross-linked gels (Schultz & Myers, 1969), in which the vertical shifts have been directly related to the enthalpy of the cross-linking reaction. The validity of the application of this procedure to our pectin dispersions could be questioned. However, the need for the vertical shifts higher than

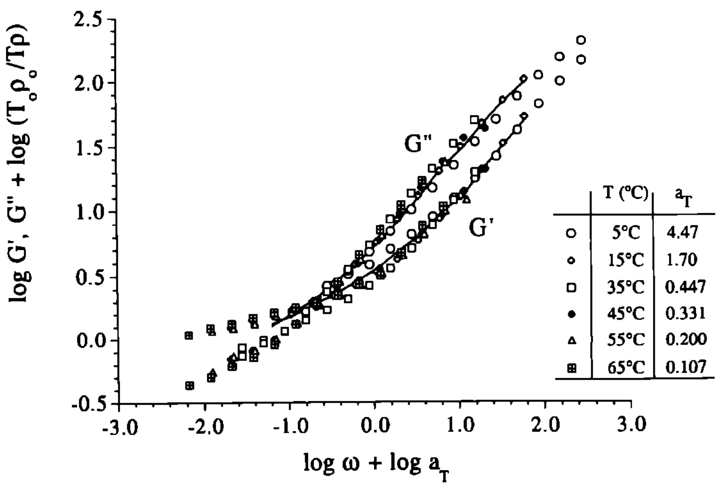

Fig. 4. Attempt at simultaneous frequency/temperature superposition of the dynamic moduli (G' and G'') for 3·5% HMP (water, pH 3·0) taking into account the temperature density factor for vertical shift. Data for the reference temperature (T_0 = 25°C) are represented by the solid line, and various symbols indicate results for the other temperatures.

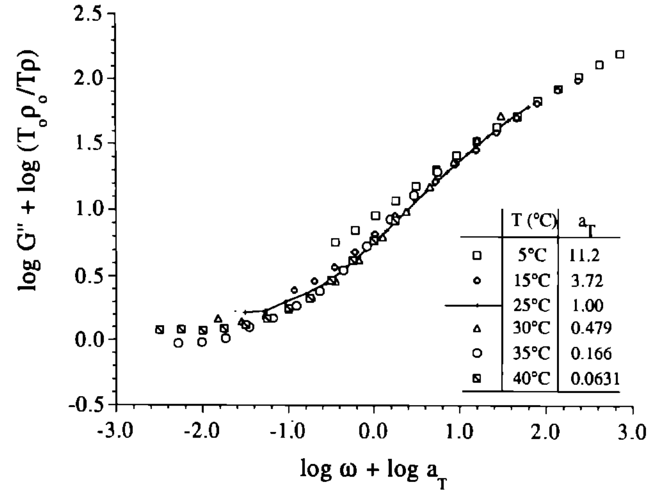

Fig. 5. Attempt at frequency/temperature superposition of the loss modulus (G'') for 3·5% LMP (water, pH 3·0), taking into account for the vertical shift only the temperature density factor. Data for the reference temperature ($T_o = 25°C$) are represented by the solid line, and various symbols indicate results for the other temperatures.

those obtained by the temperature–density factors may be related to enthalpic changes of the aggregation process.

The change in temperature affects the complex set of hydrogen, electrostatic and hydrophobic bonds that could play an important role in the interchain interactions among the pectin macromolecules at a low degree of dissociation of the charged groups. So, there must be structural changes in the pectin aggregates when the temperature changes, and, therefore, it is not surprising that the time–temperature superposition principle fails to apply to these materials, since the relaxation processes are probably not confined to one mechanism and do not have the same dependence on temperature.

In contrast to the pectin systems, the time–temperature superposition principle could be applied successfully to LBG dispersions. The dynamic functions, $G'(\omega)$ and $G''(\omega)$, for a 1% LBG dispersion were simultaneously superimposed as a master curve at the reference temperature of 25°C (Fig. 7), which means that at different temperatures essentially the same molecular processes were taking place, only at different speeds. The same shift factors (a_T) could be used satisfactorily to reduce other viscoelastic functions $\eta'(\omega)$ and $\eta''(\omega)/\omega$, and the steady shear flow data. We assume that this system is thermorheologically simple within the temperature range studied (Schwarzl & Staverman, 1952).

The master curves at the reference temperature of 25°C represent the dynamic functions as they would have been measured at 25°C over a wider range of oscillatory frequency. One of the advantages of the method is it allows the extension of the effective frequency or shear rate beyond the range accessible experimentally. In our case, the displacement sensitivity experimentally available did not enable a large extension of the temperature range.

The factor $T_o\rho_o/T\rho$ for the vertical shift of the moduli of our samples for the relatively small ranges of temperature and density, had a low magnitude and a small effect on the master curves.

Temperature dependence on the viscoelastic parameters

The temperature dependence of the shear viscosity $\eta(\dot{\gamma})$ can usually be described, in a narrow range of temperature, by an Arrhenius relationship,

$$\eta_a = A\exp\left(\frac{E_a}{RT}\right) \tag{4}$$

where A is the pre-exponential factor, E_a is the activation energy for viscous flow, R is the gas constant ($8{\cdot}314\,\mathrm{J\,mol^{-1}\,K^{-1}}$), and T is the absolute temperature.

The dependence on temperature of the plateau viscosity (η_p, corresponding to the Newtonian plateau) of the pectin samples, and of the zero-shear rate viscosity (η_o) of the LBG solutions, has been compared with the

Table 4. Shift factors used to apply the time–temperature superposition principle to the flow data obtained for pectin dispersions, by decreasing the applied stress (T_o = 25°C)

T (°C)	3·5% HMP (water, pH 3·0)		3·5% HMP (NaCl 0·1 M, pH 3·0)		3·5% LMP (water, pH 3·0)		3·5% LMP (NaCl 0·1 M, pH 3·0)	
	a_T	b_T	a_T	b_T	a_T	b_T	a_T	b_T
5	66·1	8·81	28·1	6·78	60·3	24·5	197·2	103·0
15	5·33	2·43	3·63	2·17	8·32	4·90	16·2	8·81
25	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00
30	—	—	—	—	0·269	0·447	0·194	0·313
35	0·394	0·570	0·367	0·501	0·0468	0·168	0·0360	0·106
45	—	—	0·167	0·327	—	—	—	—
55	0·0769	0·209	0·0424	0·164	—	—	—	—
65	0·0176	0·111	0·0089	0·0861	—	—	—	—

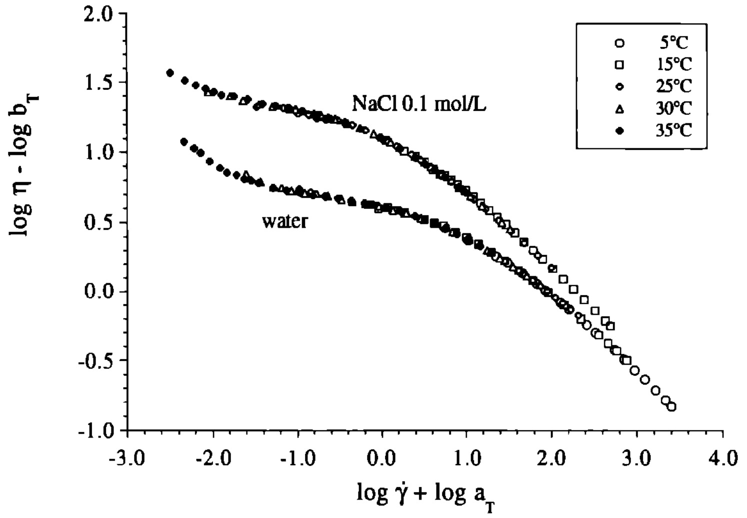

Fig. 6. Shear rate/temperature superposition of the apparent viscosity for a 3·5% LMP dispersion (pH 3·0) in water and 0·1 M NaCl. Flow data obtained by decreasing applied stress after shearing the sample. Master curves at the reference temperature (T_o) of 25°C. The shift factors are as shown in Table 4.

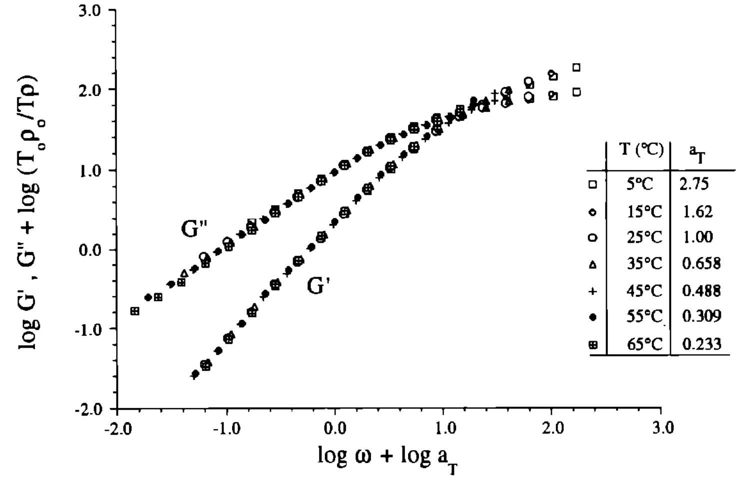

Fig. 7. Frequency/temperature superposition of the dynamic moduli (*G'* and *G"*) for a 1% LBG solution. Master curve at the reference temperature (T_o) of 25°C.

temperature dependence of the time constant (λ) of the Cross model (Fig. 8), fitted to the flow data obtained by decreasing applied stress. This parameter can be identified with a relaxation time characteristic of the viscoelastic behaviour of the system, and has been shown to be in good agreement with the relaxation times obtained from stress relaxation measurements or from direct measurement of the recoverable shear strain (Cross, 1979). The relaxation times from the Cross and Carreau models could be evaluated with satisfactory precision for the LBG and LMP dispersions, but for the HMP, the scattered results obtained for the fitted relaxation times prevented a similar analysis.

Linear Arrhenius relationships were obtained for the plateau viscosity, with an activation energy for the viscous flow clearly higher for LMP. The activation energy for LBG was in close agreement with those obtained for the relaxation time and for the dependence on temperature of the shift factor a_T, and other previously published results (Sabater de Sabates, 1979). For the LMP, a linear Arrhenius relationship for the temperature dependence of the Cross relaxation time could not be obtained for the entire temperature range; however, in the range 5–25°C, the value of the activation energy also agrees with that from the plateau viscosity. There is a major change in the relaxation mechanism of this system around 25°C, with a higher dependence on temperature of the relaxation time in the temperature range of 30–40°C. It appears that the temperature dependence of viscosity and mechanical relaxation is not the same when important macromolecular aggregation phenomena are present.

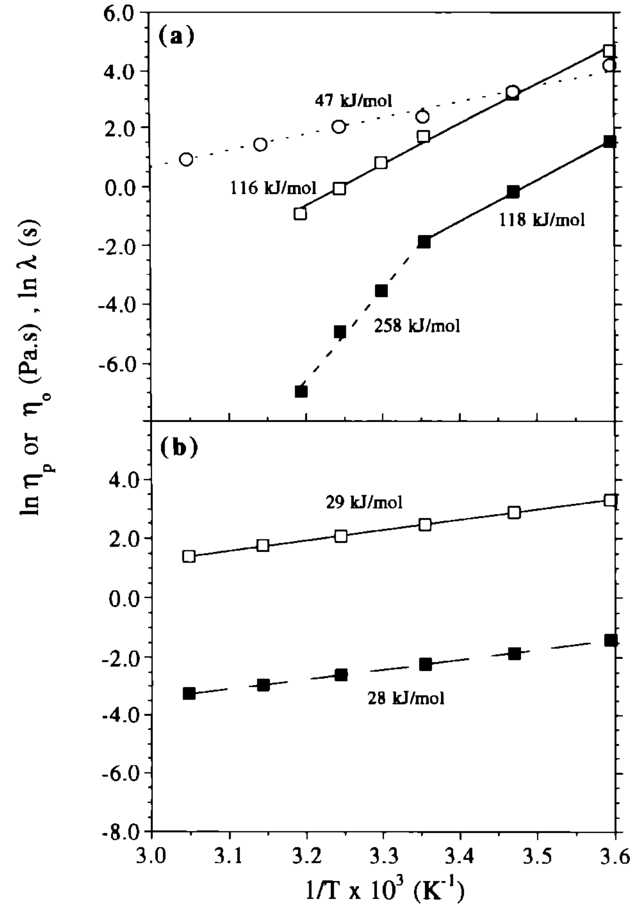

Fig. 8. Arrhenius plots comparing the temperature dependence of the plateau viscosity and of the time constant obtained from the fit with the Cross model, for: (a) aqueous 3·5% LMP (η_p,□; λ,■) and 3.5% HMP (η_p,○) at pH 3·0; (b) 1% LBG (η_o,□; λ,■).

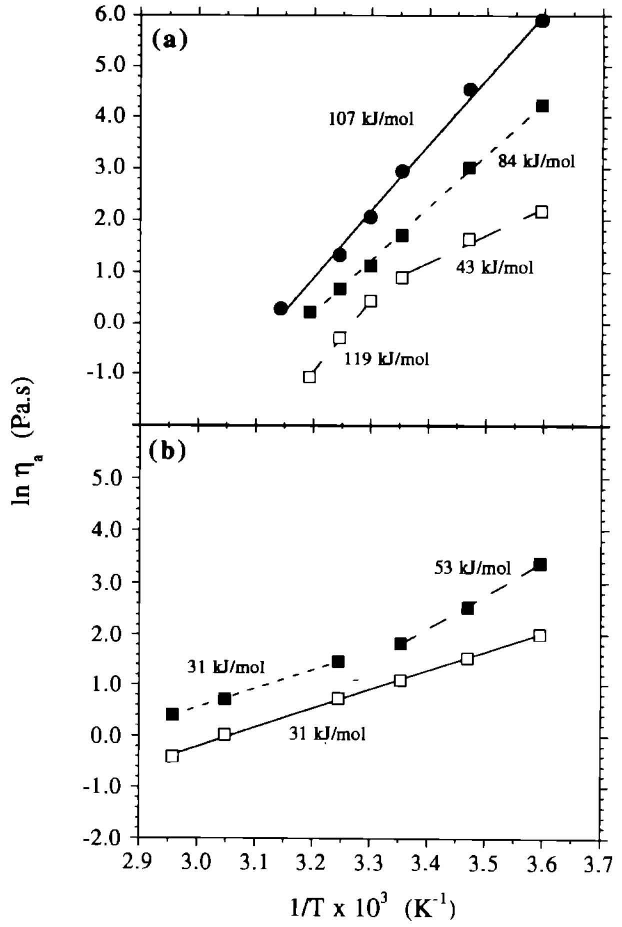

Fig. 9. Shear rate influence on the temperature dependence of the apparent viscosity for pectin dispersions. Arrhenius plots at $\dot{\gamma} = 0{\cdot}1\,\mathrm{s}^{-1}$ (filled symbols) and $\dot{\gamma} = 10\,\mathrm{s}^{-1}$ (open symbols), for: (a) 3·5% LMP (pH 3·0) in water (■,□) and in 0·1 M NaCl (●); (b) aqueous 3·5% HMP.

The activation energies for the LBG and pectin dispersions were determined at several values of shear rate. As expected, the activation energy for viscous flow was a function of the applied shear rate. For LBG, by increasing shear rate, the E_a decreased from 29 kJ mol^{-1} (Newtonian plateau) to 12 kJ mol^{-1} at $\dot{\gamma} = 30\,\mathrm{s}^{-1}$. The increasing shear rate leads to shorter lifetimes of the chain entanglements, and consequently low energy is needed to promote the viscous flow. Shear rate has a more complex effect on the temperature dependence of pectin steady viscosity. Figure 9 shows the value of activation energy obtained at two shear rates, 0·1 and 10 s^{-1}, for 3·5% LMP (Fig. 9(a)) and 3·5% HMP (Fig. 9(b)) aqueous dispersions, and the considerable effect of increasing the ionic strength for LMP. Higher dependence on temperature is observed at higher ionic strength, resulting from increasing aggregation effects. Two different temperature ranges could be seen for both pectin samples, with a discontinuity point around 25–30°C, in which, depending on shear rate, there was a different temperature dependence of the viscosity, with corresponding different values of activation energy for the viscous flow. At the same shear rate and in the low temperature range, the higher activation energy for LMP could be ascribed to the higher level of hydrogen bonding due to the lower number of esterified carboxylic groups. For LMP, the higher sensitivity to temperature in the high temperature range, especially with increasing shear rate, could be attributed to the build up (decreasing temperature) or breakdown (increasing temperature) of molecular aggregation by temperature-dependent hydrogen bonding. In the HMP dispersion, this effect is probably lower, and the opposing effect of additional intermolecular interactions by hydrophobic bonds, which increase when temperature increases (Oakenfull & Fenwick, 1977), could also be present. In addition, changes in the strength and kind of intermolecular interactions between chains, as a result of changing the degree of esterification, could lead to changes in the size of the pectin molecule, which could also have an important influence on the rheological behaviour.

Without satisfactory shift factors for applying the time–temperature superposition principle, we tested the temperature dependence of the arbitrary shift factors (a_T) obtained from the superposition of the flow data for the pectin samples (Table 4). The results obtained for aqueous dispersions of HMP and LMP are shown in Fig. 10. However, they should be regarded with caution, especially the magnitudes of the activation energy, due to the procedure used in the construction of the master curves. However, they support the different thermal behaviours of HMP and LMP, above the discontinuity temperature of 25–30°C, previously detected with basis on the shear flow data.

Discontinuities in the temperature dependence of the viscosity of pectin dispersions were previously found for HMP and LMP, taking into consideration the apparent viscosity at high shear rate (Kawabata, 1977), and the temperature dependence of specific viscosity (Davis *et al.*, 1980). In our case, a different behaviour was found for LMP, with a higher activation energy in the high temperature range than in the low temperature range. However, the concentration studied was higher, and the temperature range was not extended to such high values as those used by Kawabata (1977) and Davis *et al.* (1980).

The temperature dependence of viscosity associated with the free volume theory is usually expressed by the Williams–Landel–Ferry (WLF) equation (Williams *et al.*, 1955),

$$\log a_T = \frac{-c_1^{\mathrm{o}}(T - T_{\mathrm{o}})}{c_2^{\mathrm{o}} + (T - T_{\mathrm{o}})} \tag{5}$$

where the constants c_1^{o} and c_2^{o} are related to thermal expansion coefficients. This equation could be satisfactorily applied to the LBG and HMP dispersions, considering the master curves obtained using the vertical shifts higher than the temperature–density factors, but not to LMP. Using the values of c_1^{o} and c_2^{o} calculated from the plots of $(T\text{-}T_{\mathrm{o}})/\log a_T$ *versus* $(T\text{-}T_{\mathrm{o}})$, the dependence on temperature of the apparent activation energy (ΔH_{a}) for HMP and LBG was expressed with a modified WLF equation (eqn (6)) (Williams *et al.*, 1955; Ferry, 1980) (Fig. 11).

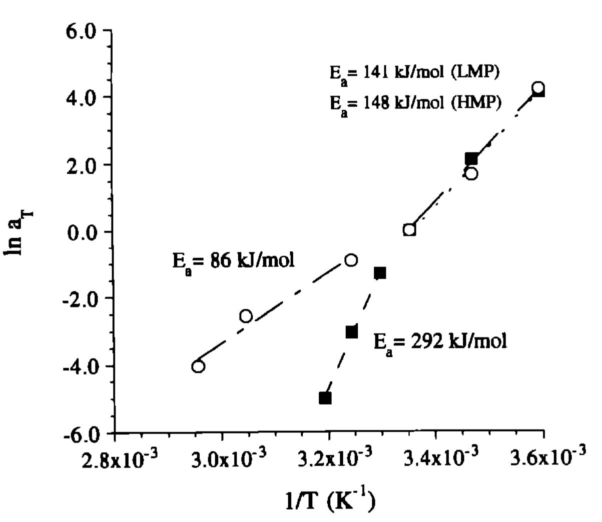

Fig. 10. Arrhenius plot for the flow shift factor a_T. Aqueous 3·5% LMP (pH 3·0) (■), and aqueous 3·5% HMP (pH 3·0) (○).

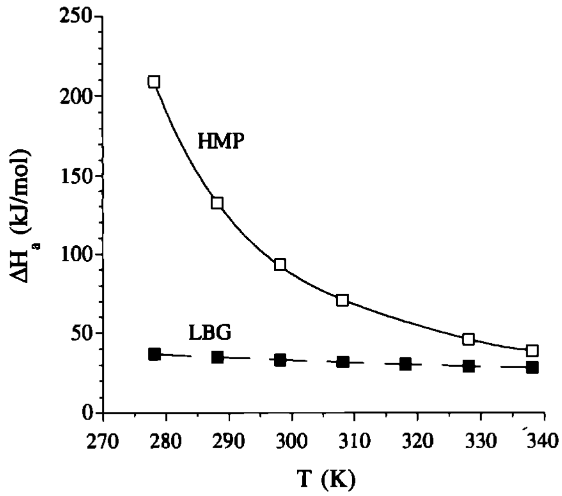

Fig. 11. Dependence on temperature of the apparent activation energy, obtained from the modified WLF equation (eqn (6)). Aqueous 3·5% HMP (□) and 1% LBG (■).

$$\Delta H_{\mathrm{a}} = R\,\frac{\mathrm{d}\ln a_T}{\mathrm{d}\,T^{-1}} = \frac{2{\cdot}303\,R\,c_1^{\mathrm{o}} c_2^{\mathrm{o}}\,T^2}{(c_2^{\mathrm{o}} + T - T_{\mathrm{o}})^2} \tag{6}$$

As expected, this dependence is much lower for LBG, for which the values of apparent activation energy obtained ranged from 37 kJ mol^{-1} (5°C) to 28 kJ mol^{-1} (65°C), compared with the values of 209 kJ mol^{-1} at 5°C and 39 kJ mol^{-1} at 65°C, obtained for the HMP dispersion.

CONCLUSIONS

The general effect of increasing temperature on the steady shear viscosity and dynamic functions was the expected decrease in these functions, as a result of increased chain mobility. However, in pectin dispersions at low pH, there were important deviations from the random coil behaviour shown by the LBG dispersions, as a consequence of more specific intermolecular interactions that induced a higher degree of chain stiffening and higher levels of structure. The latter phenomena, as could be seen clearly in LMP dispersions, in turn were enhanced by suppression of electrostatic repulsions due to increased ionic strength. Therefore, it was not surprising that deviation from the linear Arrhenius behaviour typical of random coil polymer solutions was observed. The failure of the time–temperature superposition principle to apply to pectin dispersions, in the range of temperature studied, could be attributed to structural changes in the pectin aggregates resulting from temperature changes that in turn affected the chain mobility on which the rates of all configurational rearrangements depend. The higher values of the shift factors and activation energies of pectin samples, in comparison with those of LBG, are the result of greater temperature sensitivity of the intermolecular interactions taking place in these systems.

The complex behaviour of pectin dispersions due to changes in temperature is the result of the effects of intermolecular forces whose relative importance is difficult to quantify. Intermolecular hydrogen bonds, electrostatic bonds, and hydrophobic interactions could have developed between the different functional groups of the pectin chains. Structural differences (e.g. degree of methylation), solvent properties (e.g. ionic strength), degree of ionization of the carboxylic groups of the pectins (e.g. changes in pH), will have a great influence on these intermolecular interactions. In addition, these interactions are influenced by temperature, each to a different extent and manner.

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