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Effect of Freezing Rate on the Rheological Behaviour of Systems Based on Starch and Lipid Phase

A. S. Navarro,[a] M. N. Martino[a,b] & N. E. Zaritzky[a,b]

[a]Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), CONICET, Facultad de Ciencias Exactas, [b]Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad Nacional de La Plata, 47 y 116, La Plata, Buenos Aires, Argentina

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ABSTRACT

Starch gelatinized pastes with a lipid phase are important components of precooked frozen foods. These non-equilibrium systems undergo rheological modifications on freezing. The effect of freezing rate was analysed on different formulations containing wheat flour and corn and wheat starches, shortening and xanthan gum. Gelation characteristics of the pastes were also studied. The viscoelastic behaviour of the formulations was analysed by their transient shear stress curves (τ versus time) obtained with a rotational viscometer. The Bird–Leider model fitted the experimental curves satisfactorily. Viscoelasticity and relaxation time parameters from the model quantified the rheological changes. High freezing rates maintained the textural characteristics of the unfrozen samples. Low freezing rates increased the viscoelasticity of the pastes and decreased their apparent viscosity. These changes would reduce consumer acceptibility of the product. Wheat proteins were responsible for the better performance of frozen wheat flour pastes. No effect of freezing rate was observed when xanthan gum was added to the pastes. Thus, the presence of the stabilizer (0·3%) reduces the negative effect of low freezing rates without losing product quality.

INTRODUCTION

One of the major applications of starch is to impart suitable rheological properties to a product. Precooked frozen foods containing sauces, gravies, pie fillings or desserts undergo freeze damage which may alter the desired

characteristics of the products and reduce consumer acceptability. Characterization of the thickening agents and their interaction with stabilizers and other components of the formulation such as lipids, would enable the manufacturer to develop a structure–property response profile.

Heat-induced gelatinization of starch suspensions involves a two-stage irreversible process: an initial swelling of the granules and its eventual dissolution (Kokini *et al.*, 1992). Depending on the concentration level, a turbid viscoelastic paste or an elastic gel is obtained upon cooling. This product is composed of swollen granules with an amylopectin skeleton which fill an interpenetrating amylose network (Morris, 1990).

Upon ageing, starch retrogradation takes place, starch molecules reassociate depending on the affinity of hydroxyl groups and the attractive forces or hydrogen bonding between hydroxyl groups on adjacent chains (Pomeranz, 1985). The process induces an increase in paste rigidity and phase separation. According to several authors, starch retrogradation kinetics consist of two distinct processes, a rapid gelation of amylose with the aggregation of long helical sequences and a slow recrystallization of short amylopectin chain segments (Miles *et al.*, 1985; Morris, 1990; Biliaderis, 1992).

Morris (1990) suggested that recrystallization of amylopectin stiffens the granules, resulting in the reinforcement of the amylose gel matrix. Amylose–amylopectin co-crystallization may also occur, improving the binding of granules within the amylose gel. Thus, rheological characteristics of the paste highly depend on the interrelation of swollen granules and the surrounding amylose network.

The lipid phase improves palatability and modifies the texture of the starch pastes. The natural fatty acids of the starches and added monoglycerides modify granule swelling capacity and retard retrogradation. Such effects have been attributed mainly to the formation of amylose–lipid complexes and more recently to amylopectin–lipid interactions (Evans, 1986; Gudmundsson & Eliasson, 1990; Biliaderis, 1992). Non-molecular bound lipids outside the granule tend to form a barrier to water absorption and reduce swelling properties of the granule (Howling, 1980).

Polysaccharides are used in processed foods as thickeners, stabilizers, gelling agents and, in some cases, emulsifiers. They are claimed not only to improve product stability during transport and storage but also to impart the qualities desired by the consumer. However, their method of action is not fully understood and vary from one hydrocolloid to another.

Rheology helps in understanding the responses of food structure to the applied forces or deformations and also provides information on the dependence of food structure on composition and interaction among the components (Shoemaker *et al.*, 1992). Rheological characterization of a product is important with regard to texture, stability and process design. During storage, the maintenance of product stability is also related to rheology, particularly when emulsions and dispersions are involved.

Pastes thickened by starches and proteins are complex viscoelastic materials that fall between the two extremes: elastic solids and viscous fluids. Their flow properties usually depend upon time as well as shear rate (Figoni & Shoemaker, 1981; Shoemaker & Figoni, 1984; Harrod, 1989).

The objectives of this paper are:

— to analyse the gelation of just gelatinized pastes of corn and waxy maize starches and wheat flour in order to establish uniform conditions before freezing;
— to analyse the effect of freezing rate on the viscoelastic behaviour of corn starch, wheat starch and flour pastes with and without triglycerides as lipid phase;
— to study the effect of xanthan gum addition to the pastes.

MATERIALS AND METHODS

Four different thickeners were used in the experiments: corn starch, wheat starch, wheat flour and waxy maize starch. The composition of commercial corn starch (Refinerías de Maíz, Argentina) was (% w/w wet basis): 11·3 water, 0·3 protein, 0·6 lipid, 0·3 ash, ratio amylose/amylopectin 25/75.

Wheat starch and wheat flour were used in order to compare the effect of protein content on the rheological behaviour of the pastes. Wheat starch (Droguerías Rettienne, Argentina) had the following composition (% w/w wet basis): 14 water, 0·4 protein, 0·8 lipid, 0·15 ash, ratio amylose/amylopectin 25/75 and the wheat flour (Molinos Río de La Plata S.A., Argentina) contained (% w/w wet basis): 12·5–13 water, 10 protein, 1·5 lipid, 0·6 ash, 0·6 fibre, ratio amylose/amylopectin 25/75.

Polar Gel 5 (Amaizo, USA) was used to differentiate the roles of amylose and amylopectin on the rheological behaviour of the pastes. This is a modified waxy maize starch which contains only trace amounts of amylose.

Xanthan Gum (Saporitti Hnos., SACIF, Argentina) with a water content of 11% (w/w), ash 9% (w/w), and maximum values of arsenic 3 ppm and lead with other heavy metals 10 ppm, was used to analyse the effects of a hydrocolloid. The viscosity of a 1% solution of the gum containing NaCl 1% was 1·4 Pa s.

A shortening of triglycerides (Molinos Río de La Plata S.A., Argentina) with a Mettler dropping point of 38°C was used as the lipid phase. The composition of the main fatty acids was: oleic 76·5%, stearic 14·2%, palmitic 6·2%, linoleic 1·8% and traces of myristic, pentadecanoic, arachidic and behenic acids.

Corn starch, wheat starch, waxy starch and wheat flour pastes (10% w/w wet basis) were prepared by mixing the powder in cold distilled water. Gelatinization was performed by heating 1000 ml batches (in a 11 cm diameter, 15 cm high vessel) in a thermostatic bath at $90 \pm 0{\cdot}2$°C. The suspensions were stirred to maintain uniform temperature with a mixer at 680 rev/min. At the final point, the swollen granules had lost their Maltese Crosses but still kept their identity.

Pastes containing 5% w/w melted shortening and 7% w/w corn starch were gelatinized as described formerly. The same percentage of lipid phase was added either to 10% w/w wheat flour or to 10% w/w wheat starch. All the percentages are expressed on a wet basis.

To analyse the effect of xanthan gum as a stabilizer, 0·3% w/w wet basis

was included in several samples. Xanthan gum was finely dispersed at 40°C in three quarters of the water volume used in the suspension with continuous agitation until total solubilization (15 min). This preparation was added to the corresponding suspensions, with or without lipid phase, brought to volume with distilled water and heated as described previously.

All suspensions were cooled in a constant temperature room at 20 ± 1°C over 6 h.

Freezing procedure

Samples of 50 g weight were placed in plastic cylinders of 4·5 cm in diameter. Then samples were frozen in a cold chamber at −20°C (slow freezing) and by immersion in a cryostat bath MGW Lauda UK50DW (Germany) at −40°C (ultra-rapid freezing) to a final temperature of −20°C. Thermal histories during freezing were recorded with copper–constantan thermocouples. Freezing rates were determined according to the International Institute of Refrigeration (IIR, 1982) as the minimum distance from the surface to the thermal centre divided by the time elapsed between the moment the surface reaches 0°C and the moment the thermal centre reaches a temperature of 10°C colder than the temperature of initial ice formation in the system. The measured initial freezing point of the starch paste was −0·6°C. Freezing rates were 0·3 cm/h, characteristic of a cold room freezing and 31 cm/h, corresponding to an ultra-rapid freezing. Frozen samples were thawed under controlled conditions in a constant temperature bath at $60°C \pm 0·2°C$.

Rheological measurements

A Haake Rotovisco RV2 (Germany) rotational viscometer with a thermostatic system, and a concentric cylinder sensor MVIP with profiled surfaces was used.

In order to analyse the viscoelastic behaviour of the pastes during the early stages after gelatinization (gel network formation) rheological measurements were done at 25°C. Runs were performed at different times during the 24 h after paste gelatinization.

The effect of freezing rate was analysed through rheological measurements of samples thawed at 60°C which is the consumer temperature.

The curves of transient shear stress (shear stress, τ, versus time, t) were obtained at different constant shear rates (γ) ranged from 16 to 1024 s^{-1}. Each run was performed in duplicate with a fresh sample in order to avoid effects of shear history.

Mathematical modelling

The Bird–Leider model (Kokini & Dickie, 1981) describes the rheological behaviour of systems which show changes in the shear stress during shear time and includes both viscous and elastic responses. This model has been applied successfully to several polymeric materials (Dickie & Kokini, 1982; Mason *et al.*, 1982) and has the following form:

$$\tau = k\gamma^n[1 + (b\gamma t - 1)\exp(-t/c)] \quad (1)$$

where b and c are adjustable parameters. The dimensionless parameter b is related to the viscoelasticity of the material and c to the relaxation time. As is shown, at long times the Bird–Leider model converges to the power law model:

$$\tau_\infty = k\gamma^n \quad (2)$$

where τ_∞ is the equilibrium shear stress, k is the consistency index and n the flow behaviour index. If $n<1$ the fluid is pseudoplastic and if $n>1$ is dilatant.

The equilibrium value of shear stress (τ_∞) was measured at times longer than 120 s from the transient curves. Pairs of τ_∞ and γ were used to calculate k and n values of the power law model (eqn (2)). Non-linear regression analysis was applied to experimental data to estimate the parameters of the Bird–Leider model (Systat version 5·0, Systat, Inc. USA). In order to compare flow properties of the pastes, apparent viscosities were calculated as the τ_∞/γ ratio at $\gamma = 512\ s^{-1}$.

RESULTS AND DISCUSSION

The characteristics of Bechamel sauce were targeted, thus, only formulations with an apparent viscosity between 4 and 6 Pa s at $\gamma = 16\ s^{-1}$ were selected for comparison. In order to obtain that viscosity, in the case of corn starch pastes with lipid phase a lower thickener content was used (7% w/w wet basis) instead of the 10% (w/w wet basis) used for the pastes without shortening. The same thickener content was used for wheat flour and wheat starch pastes with and without shortening.

Transient shear stress curves obtained at different constant shear rates for pastes of corn starch just gelatinized are shown in Fig. 1. All runs were performed with new samples. The curves showed two characteristic regions. The first part of the curves up to the overshoot is characterized by the b parameter of the Bird–Leider equation. The second part or structural breakdown is characterized by the exponential term $\exp(-t/c)$, and the limits are the overshoot and the constant shear stress reached at long times.

Gelation of gelatinized pastes

The gel network development leads to a viscoelastic material. This phenomenon was evaluated during the first 24 h after gelatinization. The viscoelastic changes were characterized by the b parameter of the Bird–Leider model corresponding to the transient curves obtained at different times.

The variations in viscoelasticity parameter (b) with time for gelatinized pastes of corn and waxy maize starches and wheat flour are shown in Fig. 2. During the first 300 min b values increased for corn starch pastes, reaching an asymptotic value shown at 24 h after gelatinization. However the b values corresponding to waxy maize starch remained constant during the entire period. This behaviour clearly shows that amylose is responsible for the

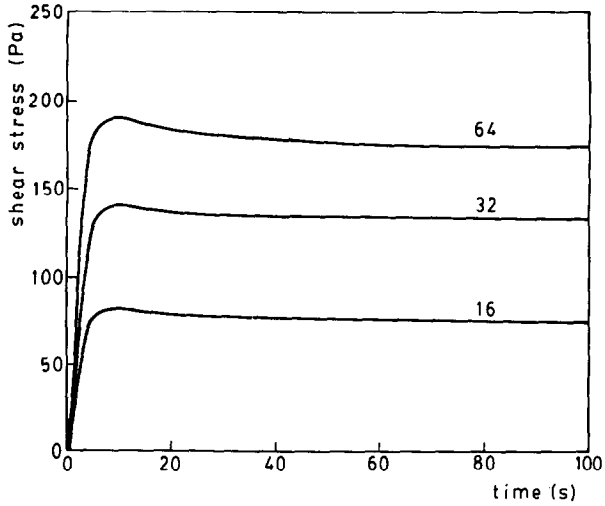

Fig. 1. Shear stress versus shear time for different constant shear rates in just gelatinized corn starch (10% w/w) paste. Figures on each curve represent shear rate γ in s^{-1}.

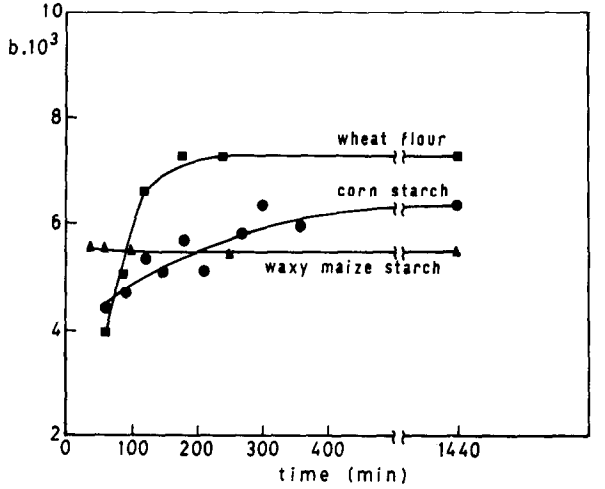

Fig. 2. Dimensionless parameter b of Bird–Leider model versus time after gelatinization for pastes formed from different thickeners (wheat flour, corn starch and waxy maize starch). Parameters b (viscoelasticity) were obtained from transient shear curves at $\gamma = 16\ s^{-1}$.

viscoelasticity increase in corn starch, since waxy maize starch is essentially composed of amylopectin.

Wheat flour pastes showed an increase in b values up to 150 min after gelatinization (Fig. 2). Wheat flour paste in addition to the swollen starch granules, may have an interconnecting network composed mainly of protein (Evans & Haisman, 1979) which can contribute to complete gelation in a

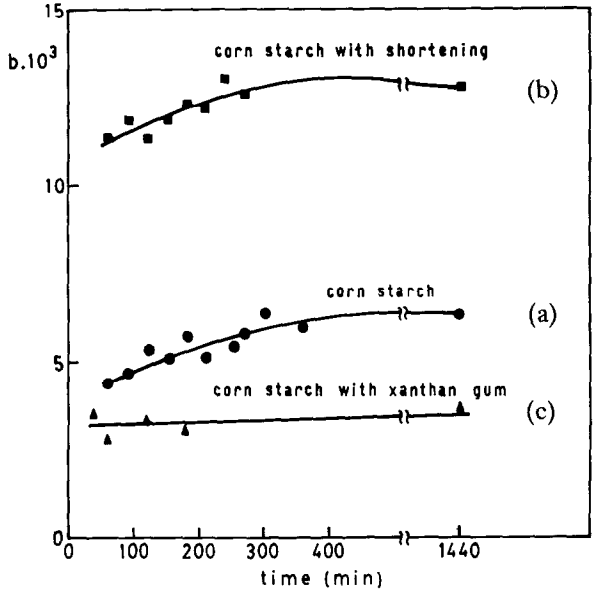

Fig. 3. Dimensionless parameter *b* of Bird–Leider model versus time for: (a) corn starch (10% w/w); (b) corn starch (7% w/w) with shortening (5% w/w); (c) corn starch (10% w/w) with xanthan gum (0·3% w/w) pastes. Parameters *b* (viscoelasticity) were obtained from transient shear curves at $\gamma = 16\ s^{-1}$.

shorter time compared to corn starch paste. All the thickeners reached a constant *b* value during the 24 h period.

Figure 3(a, b) shows the increase in the viscoelasticity parameters *b* during the early stages after gelatinization for corn starch pastes with and without shortening. Although the thickener concentration of the pastes with the lipid phase was lowered to attain the same apparent viscosity, the shortening contributed to an increase in the viscoelastic properties of the paste; characteristic *b* values were between 0·011 and 0·015. This behaviour was also evidenced macroscopically since pastes showed a more solid-like appearance.

Monoacyl lipids are well known for their ability to form complexes with amylose molecules, thus retarding the rate of retrogradation (Eliasson *et al.*, 1988; Eliasson & Ljunger, 1988; Biliaderis, 1992). In the present case, however, the lipid phase used did not contribute to a decrease in the changes after gelatinization. The shortening used as the lipid phase is mainly composed of triglycerides and, due to steric hindrance, has few possibilities to complex with amylose. Likewise, Germani *et al.* (1983) through texture measurements, showed that degree of unsaturation, high percentage of triglycerides and short fatty acid chains decrease the rate of retrogradation. However, since these measurements were quantified at 1 day after paste gelatinization the analysed phenomenon should correspond to amylopectin retrogradation.

The effect of xanthan gum addition on the gel formation of corn starch paste is shown in Fig. 3(c). The hydrocolloid contributed to maintaining the

viscoelastic characteristics of just gelatinized pastes, giving b values between 0·003 and 0·004.

The constant b values show a beneficial interaction between xanthan gum and amylose molecules which avoids amylose retrogradation. During gelatinization the amylose molecules are released from the starch granule and form a polymeric matrix in which the starch granules are embedded, therefore the amylose chains have more opportunities than the amylopectin chains to interact with other molecules like hydrocolloids. Amylose–hydrocolloid interaction might prevent the association between amylose molecules decreasing the rate of diffusion-controlled processes like retrogradation (Slade & Levine, 1986). Biliaderis and Zawitowski (1990) also observed a reduction in gel rigidity when adding starch hydrolysis products to wheat starch pastes. They attributed this fact to a competitive inhibition of amylose chain association; the hydrolysates of low dextrose equivalent seem to participate in the junction zones and inhibit the formation of a continuous network of amylose chains. Previous studies using differential scanning calorimetry (DSC) (Ferrero *et al.*, 1993) have shown that xanthan gum did not avoid amylopectin retrogradation, therefore the major contribution of xanthan gum should be focused on the amylose fraction.

These results show that amylose retrogradation had been completed 5 h after paste gelatinization. Therefore, to evaluate the effect of freezing and to have similar initial conditions, samples were frozen in all cases at times longer than 5 h. Likewise, 24 h were not exceeded to avoid amylopectin retrogradation (Miles *et al.*, 1985).

Effect of freezing rate

The effect of freezing rate was analysed on pastes of corn and wheat starches and wheat flour, with and without shortening and xanthan gum. With regard to the macroscopic appearance, once thawed, slowly frozen samples showed a more compact, less homogeneous texture. An undesirable spongy structure was observed for corn starch pastes. Rapidly frozen samples presented minor deteriorative changes and remained similar to unfrozen pastes.

Figures 4(b) and 4(a) show the transient shear stress curves for non-frozen, rapidly and slowly frozen pastes of corn starch with and without shortening, respectively. In both formulations, rapidly frozen samples maintained the behaviour of unfrozen samples. However, at long times the shear stress (τ) of rapidly frozen samples showed lower values which indicate a decrease in apparent viscosity due to freezing. At short times, slowly frozen samples showed an overshoot related to the viscoelastic characteristics of the pastes. Afterwards, a marked stress decay was observed with increasing shear time. The lipid phase increased the viscoelastic characteristics of corn starch paste evidenced through the structure breakdown of slowly frozen samples (Fig. 4(b)).

Slowly frozen pastes of wheat flour with lipid phase (Fig. 5, solid line) did not evidence a sharp overshoot like those observed for corn starch (dashed line) and wheat starch (centre-line). While wheat starch contains only 0·4% (w/w basis) proteins, wheat flour contains 10%, this being the main

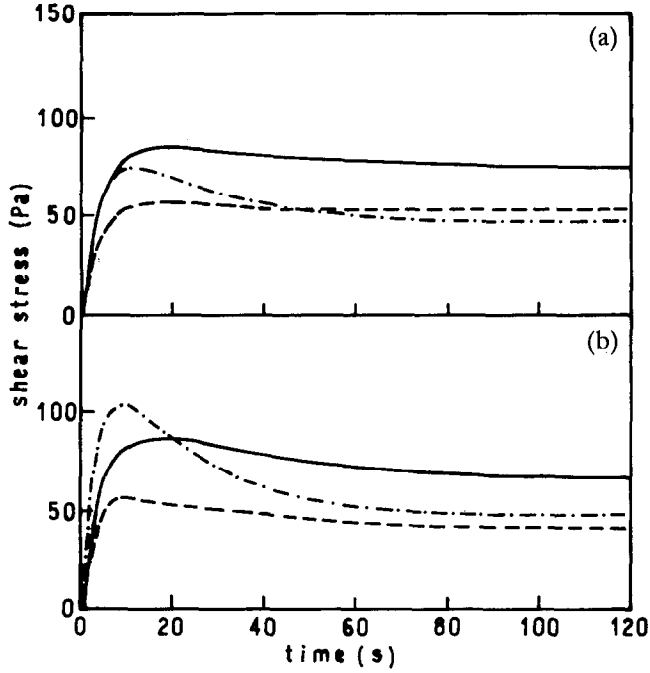

Fig. 4. Effect of freezing rate on shear stress versus shear time curves in: (a) corn starch (10% w/w); (b) corn starch (7% w/w) with shortening (5% w/w) pastes. Transient shear stress curves were obtained at $\gamma=16\ s^{-1}$ (————, unfrozen; ----, rapid freezing (31 cm/h); ·····, slow freezing (0·3 cm/h)).

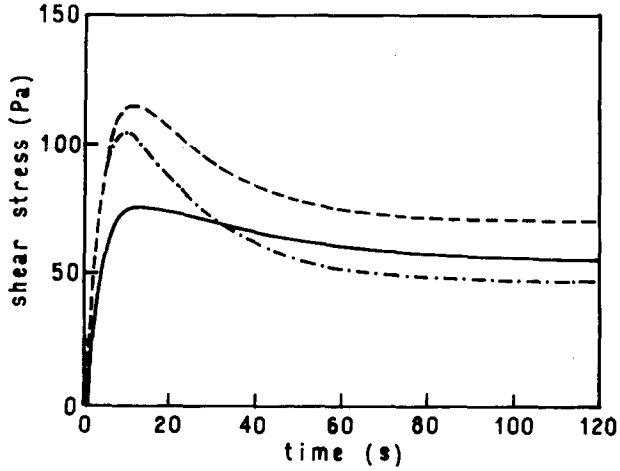

Fig. 5. Effect of different thickeners on shear stress versus shear time curves of slowly frozen pastes with shortening (5% w/w): (————, wheat flour (10% w/w); ----, corn starch (7% w/w); ·····, wheat starch (10% w/w). Transient shear stress curves were obtained at $\gamma=16\ s^{-1}$. Freezing rate: 0·3 cm/h.

difference in their composition. Thus, the higher protein concentration of the flour seems to be responsible for the higher stability shown by the frozen pastes with lipid phase. Moreover, the rheological behaviour of wheat starch pastes was similar to corn starch, which confirms that the structure preservation should be attributed to proteins rather than to starch of vegetable origins.

Figure 6 shows the rheological curves of pastes of wheat flour with shortening and xanthan gum after the freezing process at different rates. Both flour and starch pastes with xanthan gum showed a smooth texture, without the presence of curdles, which corresponded to an acceptable macroscopic appearance. The unfrozen texture was maintained regardless of the freezing rate used.

It was previously mentioned that the amylose–hydrocolloid interaction competes with the amylose–amylose one, minimizing the retrogradation process. Moreover, when a lipid phase is added, part of the stabilizing effect of the hydrocolloids, like xanthan gum, seems to be related to its adsorption at the oil/water interphase, forming a hydrated rigid film. Another relevant characteristic of hydrocolloids is their ability to form networks within the continuous phase due to their solubility in water (Dickinson & Stainsby, 1982). The mechanism behind the ability of certain hydrocolloids to modify ice recrystallization during frozen storage is still questioned. Keeney (1982) based on the important contribution of hydrocolloids to the system viscosity, suggested that hydrocolloids might restrict water mobility, decreasing its opportunity to freeze or increase the size of the ice crystals. However, Ferrero *et al.* (1993) working on a similar system found that xanthan gum does not modify ice recrystallization kinetics during frozen storage. Budiaman and Fennema (1987*a*,*b*) and Reid *et al.* (1987) studying other hydrocolloids behaviour, arrived at similar conclusions.

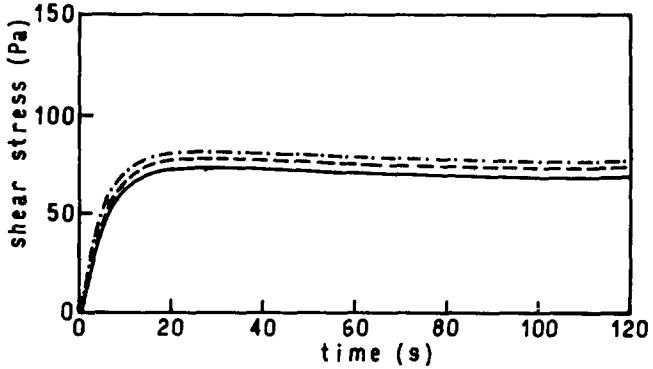

Fig. 6. Effect of freezing rate on shear stress versus shear time curves in wheat flour pastes (10% w/w) with shortening (5% w/w) and xanthan gum (0·3% w/w). Transient shear stress curves were obtained at $\gamma = 16\ s^{-1}$ (————, unfrozen; ----, rapid freezing (31 cm/h); - · - ·, slow freezing (0·3 cm/h)).

Mathematical modelling

The Bird–Leider model (eqn (1)) was used to fit the experimental data of τ versus shear time. A satisfactory goodness of fit was obtained with correlation coefficients (R^2) between 0·99 and 0·96.

A modified Bird–Leider model developed by Mason *et al.* (1982) was also used to fit the experimental data, with the following equation:

$$\tau = k\gamma^n [1 + (b\gamma t - 1) \sum_{1}^{i} b_j \exp(-t/c_j)] \quad (3)$$

where b_j and c_j are adjustable parameters. This model has a series of relaxation times which tend to improve the characterization of the transient shear stress curves compared to eqn (1). In this case the best fit was obtained with two relaxation terms. Even though the correlation coefficient varied between 0·99 and 0·98, the standard deviation of the computed parameters were not smaller, in all cases, than those corresponding to the simpler model of eqn (1). Thus, results were analysed with the Bird–Leider

TABLE 1
Dimensionless Parameter (b) for Different Unfrozen and Frozen Pastes

Paste composition	*Dimensionless parameter $b \times 10^3$ (viscoelasticity)*		
	Unfrozen	*Rapid freezing (31 cm/h)*	*Slow freezing (0·3 cm/h)*
CS	5·94	6·97	17·33
	(0·13)	(0·10)	(0·42)
CS + XG	3·64	3·59	4·64
	(0·27)	(0·34)	(0·27)
CS* + SH	10·77	12·48	29·29
	(0·35)	(0·35)	(0·94)
CS* + SH + XG	9·73	5·73	13·60
	(0·23)	(0·24)	(0·33)
WF	9·11	8·70	15·47
	(0·23)	(0·16)	(0·46)
WF + XG	7·08	6·84	7·08
	(0·24)	(0·27)	(0·24)
WF + SH	8·05	8·10	12·02
	(0·22)	(0·21)	(0·50)
WF + SH + XG	4·61	4·31	4·69
	(0·09)	(0·21)	(0·11)
WS	11·83	9·10	19·37
	(0·53)	(0·28)	(0·82)
WS + SH	8·88	7·53	14·87
	(0·27)	(0·38)	(0·52)
WS + SH + X	3·92	3·69	5·77
	(0·48)	(0·58)	(0·42)

Standard deviations in parentheses.
CS, corn starch (10%); CS*, corn starch (7%); WS, wheat starch (10%); XG, xanthan gum (0·3%); SH, shortening (5%); WF, wheat flour (10%).

TABLE 2
Time Relaxation Values *c* (s) for Different Unfrozen and Frozen Pastes

Paste composition	*Relaxation time, c (s)*		
	Unfrozen	*Rapid freezing (31 cm/h)*	*Slow freezing (0·3 cm/h)*
CS	10·41	7·87	9·21
	(0·42)	(0·20)	(0·21)
CS + XG	8·91	10·06	10·24
	(0·45)	(0·73)	(0·52)
CS* + SH	11·00	8·67	8·59
	(0·48)	(0·29)	(0·26)
CS* + SH + XG	8·09	9·57	10·33
	(0·38)	(0·45)	(0·36)
WF	11·44	10·32	9·32
	(0·36)	(0·32)	(0·31)
WF + XG	8·69	8·41	8·69
	(0·42)	(0·37)	(0·42)
WF + SH	11·96	10·38	9·64
	(0·43)	(0·38)	(0·48)
WF + SH + XG	10·18	12·02	8·99
	(0·35)	(0·95)	(0·34)
WS	12·83	12·15	11·67
	(0·63)	(0·45)	(0·48)
WS + SH	12·03	10·65	9·59
	(0·49)	(0·66)	(0·35)
WS + SH + XG	9·36	8·91	9·93
	(0·78)	(0·85)	(0·55)

Abbreviations as in Table 1.

model (eqn (1)) because of its simplicity and its satisfactory goodness of fit. Besides, the Bird–Leider model allowed a more direct physical interpretation of parameters *b* and *c*.

Tables 1 and 2 show the effect of freezing rate on the viscoelasticity (*b*) and time relaxation (*c*) parameters of the model. The values of *b* of rapidly frozen pastes are similar to unfrozen pastes. However, a marked increase in the viscoelastic parameter *b* was observed in most of the slowly frozen samples. The only exceptions were those formulations containing xanthan gum as stabilizer.

As temperature decreases slowly during low freezing rates, amylose molecules have the opportunity to align themselves and eliminate water bound to the amylose matrix. This freezing condition would favour amylose retrogradation.

On the other hand, when xanthan gum is present the mobility of amylose molecules is restricted due to space hindrances. Likewise, the high hydrophilic character of the gum helps to minimize the structure deterioration.

As previously mentioned, freezing increased the viscoelasticity of pastes with the lipid phase. However, the addition of shortening tempered the

TABLE 3
Apparent Viscosities μ (mPa s) Calculated at $\gamma=512\ s^{-1}$ for Unfrozen and Frozen Pastes

Paste composition	*Apparent Viscosities (mPa s)*		
	Unfrozen	*Rapid freezing (31 cm/h)*	*Slow freezing (0·3 cm/h)*
CS	362	242	214
CS+XG	205	195	204
CS*+SH	258	196	154
CS*+SH+XG	299	236	174
WF	296	277	280
WF+XG	239	211	217
WF+SH	358	357	296
WF+SH+XG	333	340	355
WS	399	283	355
WS+SH	371	409	302
WS+SH+X	280	239	207

Abbreviations as for Table 1.

deleterious effect of freezing rate. The ratio between the b values of slowly frozen samples to rapidly frozen ones was smaller for the formulations containing shortening than for those without the lipid phase (Table 1). In the case of wheat flour pastes these ratios were 1·78 and 1·48 for the pastes without and with the shortening; 2·48 and 2·34 for corn starch pastes without and with the shortening, respectively. The three thickeners showed the same effect.

Table 2 shows a general decreasing tendency of the relaxation time (c) values with decreasing freezing rates for the pastes without the gum, while the pastes with the gum remained constant, evidencing the protective effect of the hydrocolloid. A lower relaxation time indicates a shorter time needed to reach the fluid state when a certain deformation is applied. The results of Table 2 show c values of unfrozen samples that are higher than the rapidly and slowly frozen ones and agree with the decrease in apparent viscosity with freezing of Table 3.

Since at long times the Bird–Leider model converges to the power law this equation was applied to analyse the freezing rate effect on the rheological properties of the different pastes. Starch pastes with and without the lipid phase presented pseudoplastic behaviour at long shear times (eqn (2)). The apparent viscosity of the different pastes was calculated at $\gamma=512\ s^{-1}$ (Table 3); the shear rate chosen corresponded to that part of the entire rheological curve where the power law is valid. In most of the cases the apparent viscosities decreased after freezing when compared to the value of unfrozen pastes; the deteriorative changes produced by freezing depended on freezing rate.

However no significant ($p<0·05$) influence of freezing rate was found when xanthan gum was added to the pastes. These results correlate well with the transient curves of shear stress shown in Fig. 6.

CONCLUSIONS

The gel formation completed during 5 h after gelatinization has been attributed to the rearrangement of amylose molecules. The waxy maize characterized by its low content of amylose did not show the viscoelasticity increase associated with the rigid gel formation of the other pastes. These gelation studies allowed the conditions prior to freezing to be standardized.

Freezing rate is an important factor in paste quality preservation. Low freezing rates led to higher structural changes involving a large viscoelasticity increase of the paste rheology. However, high freezing rates maintained the characteristics of unfrozen pastes.

The transient curves treatment of the data helps in understanding the rheological behaviour of the pastes, distinguishing between the viscoelastic and structural breakdown characteristics.

The Bird–Leider model gave more information about the freezing rate effect than other methods previously used like the power law model. The presence of a higher content of proteins in wheat flour pastes had a beneficial role on the stability of pastes during freezing either with or without shortening. The addition of a lipid phase moderated the effect of freezing rate; a lower viscoelasticity increase, expressed by the *b* parameter, was observed in pastes with the lipid phase.

Xanthan gum addition to any of the formulations helped to maintain the rheological characteristics of unfrozen pastes even under the worst freezing conditions. Thus, the addition of low amounts of the stabilizer would allow the use of low freezing rates.

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