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Effect of glucose and storage time on the viscosity of wheat starch dispersions

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Abstract

The effect of glucose addition, time of constant temperature heating (t_{CTH}) and storage time on the rheological properties of starch dispersion systems was examined. A fixed starch mixture of 5% (w/v), and glucose concentrations of 0–6% (w/v) were used. The starch dispersion was heated up to 80°C, then kept for 0, 10, 20, or 30 min, then cooled and kept at 8°C for 1, 2, 3, or 4 days. The apparent viscosity was then measured at 25°C as a function of shear rate. The apparent viscosity was also measured, at constant shear rate, as a function of shearing time. The Herschel–Bulkley model was used to fit the flow behavior of the above starch dispersions. It was found that the flow behavior index approached unity for 0 and 1% dextrose concentrations at low t_{CTH} values. It was also found that as t_{CTH} was increased, for a given glucose concentration, both yield stress, τ_o, and consistency coefficient, m, increased. The presence of glucose also resulted in an increase of both τ_o and m. Regarding the time-dependent rheological behavior, it was found that the examined starch dispersions were adequately described by the Weltman model and found to be thixotropic. In addition, as storage time increased, in the absence of dextrose, starch dispersions changed their flow behavior from Bingham to shear-thinning fluids. On the other hand, the presence of glucose almost kept the flow behavior constant. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Wheat starch; Glucose; Shear thinning; Thixotropy; Rheology

1. Introduction

Starch is a natural polymer, the monomeric unit of which is glucose. It exists in two forms: straight and branched. Amylose is a predominantly straight-chain, water-insoluble polymer of glucose, and amylopectin is a branched-chain, water-imbibing polymer of glucose (Bailey & Ollis, 1986).

Rheological properties are important in the design of flow processes, quality control, storage and shelf-life assessment, and in processing stability. Rheological properties of starch dispersions are important in applications, where starch is utilized as a thickening agent, such as in milk-based sweets and jellies, sauces, custards, and desserts. Moreover, it is used as a dispersed phase in electro-rheological fluids (Lopes Vieira & Fonseca de Arruda, 1998) and in starch-based coating colors (Groen & Eklund, 1998a).

In the preceding applications, the technique used to prepare the product, which takes into account, for example, water content (Conde-Petit & Escher, 1995), amylose/amylopectin ratio, pH, temperature (Groen & Eklund, 1998b), and the presence of other organic/inorganic materials (Matser & Steeneken, 1997), is an important factor that determines the flow behavior of starch dispersion systems. Furthermore, processing-induced effects, like work intensity (shear rate), is another important factor affecting the flow behavior (Dintzis & Bagley, 1995; Fasina & Tyler, 1997).

Nguyen, Jenfen, and Kristensen (1998) defined a dimensionless ratio (η_0/η_∞) as a measure of the relative extent of thixotropic breakdown, where the apparent viscosity drops from the initial value, η_0, to the final equilibrium (steady-state) value, η_∞, and they found that such a measure decreases with increasing shear rate. Ahmad and Williams (1999) studied the effect of sugars on thermal and rheological properties of sago starch. They found that sugars increased the gelatinization temperature, T_{gel}, and gelatinization enthalpy. Moreover, the swelling factors in the presence of sugar were found to be higher compared to the control (water alone) for sugar concentrations below 25%, but were lower at sugar concentrations greater than 25%. They discussed the effects in terms of the anti-plasticizing effect of sugars compared with water, the influence of sugar–starch interactions.

The effect of glucose concentration on the apparent viscosity, as a function of shear rate, of starch dispersions

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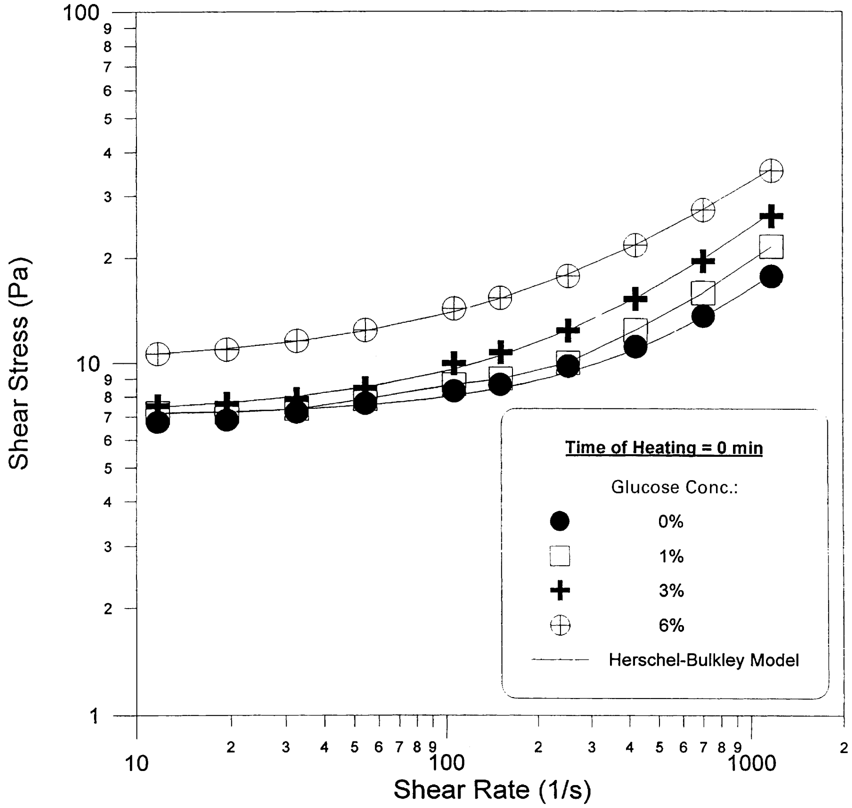

Fig. 1. Effect of glucose concentration on flow curves of starch dispersions at $t_{CTH} = 0$ min.

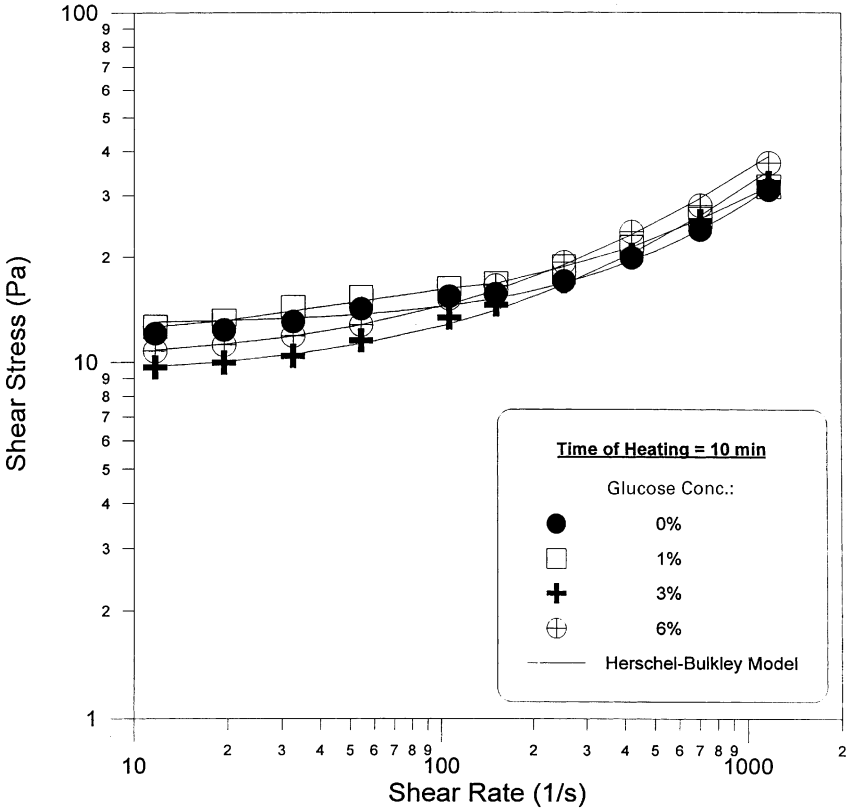

Fig. 2. Effect of glucose concentration on flow curves of starch dispersions at $t_{CTH} = 10$ min.

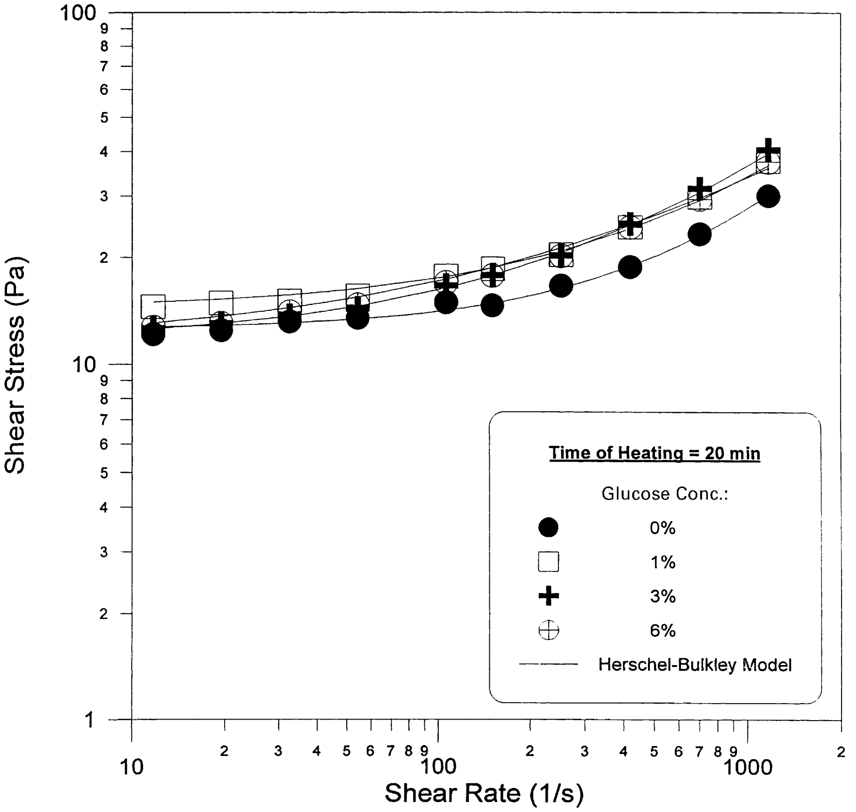

Fig. 3. Effect of glucose concentration on flow curves of starch dispersions at t_{CTH} = 20 min.

at the thermal processing temperature of 80°C was investigated by Al-Malah, Azzam and Abu-Jdayil (2000). They reported that the presence of glucose resulted in an increase in the apparent viscosity and an increase in both the yield stress and the consistency coefficient compared to that of glucose-free starch dispersions.

Table 1
Fitted parameters for the Herschel–Bulkley model, for different concentrations of glucose and time of constant temperature heating (t_{CTH})

Glucose concentration (w/v%)	t_{CTH} (min)	τ_o (Pa)	n	m (mPa s^n)
0	0	7.1	1.0	9.2
	10	12.8	1.0	15.8
	20	12.6	1.0	15.1
	30	12.1	1.0	12.9
1	0	7.1	1.0	12.4
	10	13.9	1.0	16.0
	20	14.0	0.85	61.6
	30	14.4	0.81	74.9
3	0	7.1	0.86	45.3
	10	9.1	0.81	84.7
	20	11.6	0.74	149.5
	30	19.1	0.68	300.0
6	0	9.9	0.77	114.2
	10	10.0	0.76	135.5
	20	11.7	0.70	181.1
	30	14.8	0.47	1207.0

In the present investigation, the effect of storage time on the rheological properties of wheat starch–glucose dispersion systems was examined. Samples, prepared at 80°C, were stored at 8°C for 1, 2, 3 or 4 days, after which, the apparent viscosity was measured at 25°C as a function of shear rate and shearing time. Herschel–Bulkley and Weltman models were used to model the rheological data.

2. Materials and methods

Glucose anhydrous powder (MW = 180.16; 99% extra pure) was obtained from S.D. Fine Chemicals, Ltd. Wheat starch was obtained from Chemlab Company, Burley, West Yorks, England.

All measurements were made in phosphate buffer (0.01 M, pH 7) prepared using de-ionized water. Rheological flow properties of starch dispersions were measured using a rotational, concentric cylinder viscometer (Searle-type; Haake VT500/MV1) with a fixed outer cylinder and a rotating measuring bob. The gap width between the two cylinders was 0.96 mm. The radius and length of the rotating cylinder were 20.04 and 60 mm, respectively.

3. Methodology

An aqueous starch solution, made of phosphate-buffer

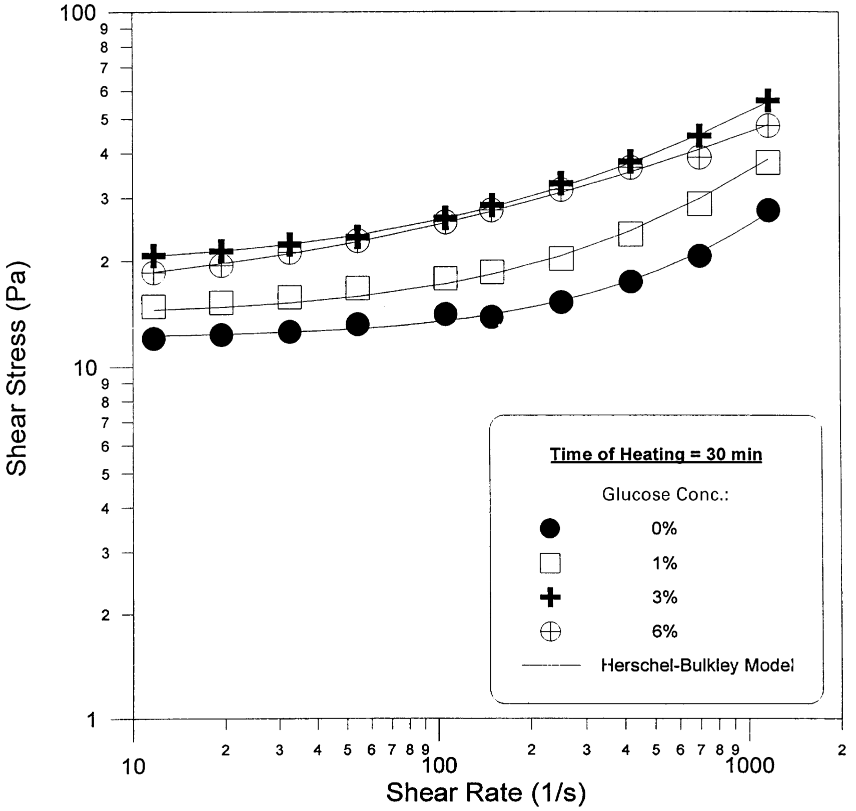

Fig. 4. Effect of glucose concentration on flow curves of starch dispersions at $t_{\mathrm{CTH}} = 30$ min.

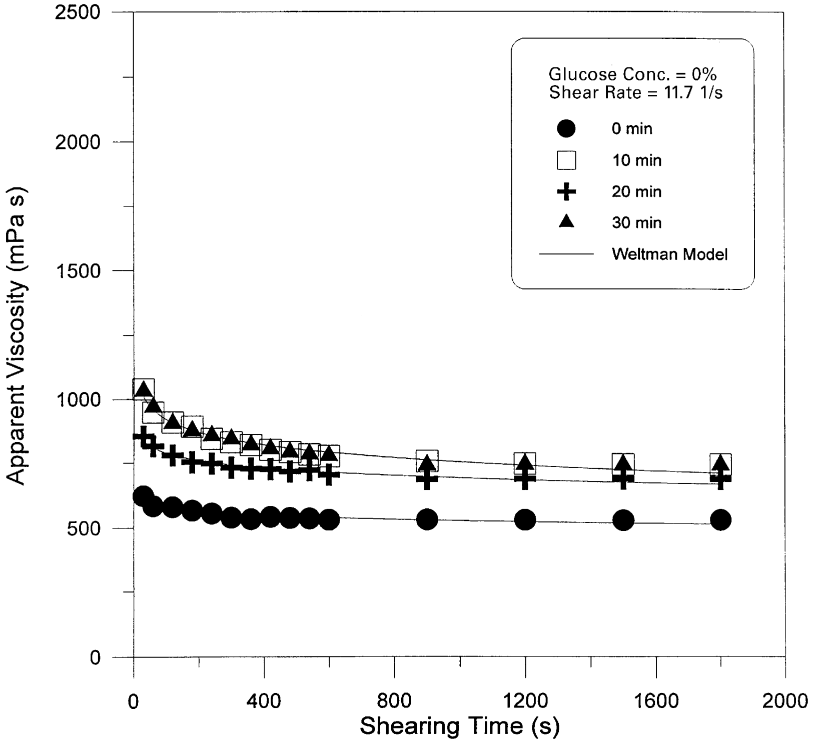

Fig. 5. Apparent viscosity of starch dispersions as a function of shearing time at glucose concentration = 0%, and shear rate = 11.7 l/s.

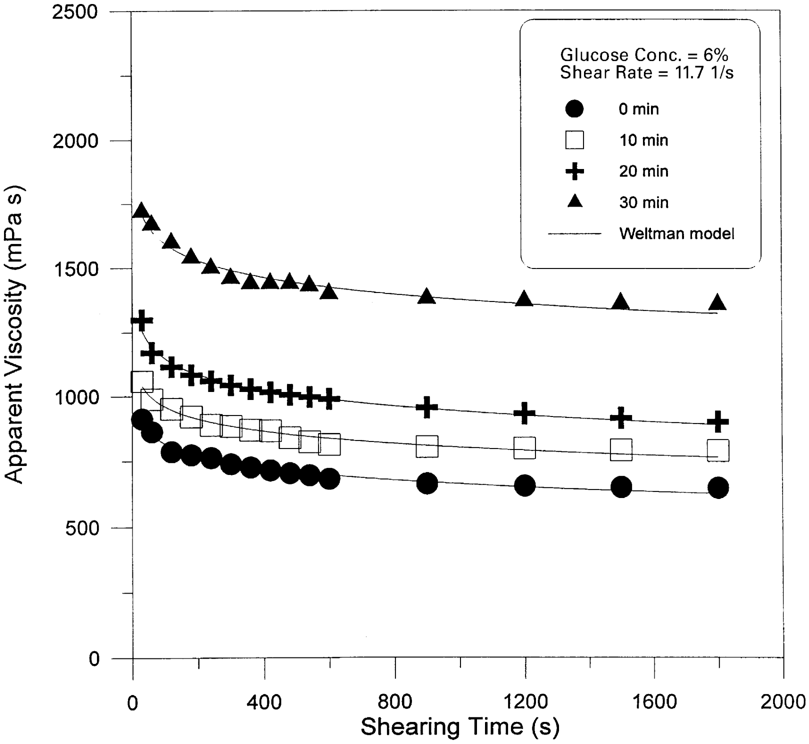

Fig. 6. Apparent viscosity of starch dispersions as a function of shearing time at glucose concentration = 6%, and shear rate = 11.7 l/s.

concentration (5% w/v) and a glucose concentration of 0, 1, 3, or 6% w/v, was prepared. The aqueous starch solution was poured into a beaker. The beaker was then immersed in a water bath and heated. During heating, continuous stirring at 200 rpm was maintained until 80°C was reached. The samples were kept at 80°C for a specified period of time (0, 10, 20, or 30 min), after which the starch dispersion samples were placed in a refrigerator in order to cool the starch dispersion samples down to about 8°C. They were then kept for 1, 2, 3, or 4 days. It should be mentioned that each time a test was carried out a fresh sample lot was used.

When it was time to carry out the test, the sample was placed within the annulus of the concentric cylinders of the viscometer, where the temperature was kept at 25°C. The test was carried out after thermal equilibrium was achieved. The apparent viscosity, η, was measured as a function of shear rate, $\dot{\gamma}$, which was varied between 11.7 and 1169 s^{-1}. Measurements of viscosity were carried out and recorded after 30 s (time needed for initial apparatus noise to disappear).

Moreover, the apparent viscosity was measured as a function of shearing time, for values of shear rate of 11.7, 54.3, 106, and 252.3 s^{-1}. The shear stress, τ, was calculated using:

$$\tau = \eta\dot{\gamma} \tag{1}$$

4. Results and discussion

Figs. 1–4 show the flow curves, i.e. shear stress versus shear rate, for 0, 10, 20, and 30 min t_{CTH} at 80°C, after 1 day of storage, respectively. Each figure also shows data points for 0, 1, 3, and 6% (w/v) glucose concentration. This pasting temperature of 80°C yields undercooked starch dispersions, i.e. with limited swelling and slight amylose solubilization.

As observed from Figs. 1–4, it is clear that these starch dispersion systems are non-Newtonian fluids. The Herschel–Bulkley (H–B) model (Eq. (2)) was found to best describe the shear stress versus shear rate data with R^2 values greater than 0.99.

$$\tau = \tau_o + m\dot{\gamma}^n \tag{2}$$

Figs. 1–4 also show that the H–B model fits the shear stress versus shear rate data. Table 1 shows the parameters in the H–B model obtained from regression analysis on data after one day's storage.

The Bingham model is a special case of the Herschel–Bulkley model when the flow behavior index, n, is equal to 1. The data in Table 1 shows that this model fits the results for zero glucose concentration, regardless of t_{CTH}, and for 1% glucose concentration for 0- and 10-min t_{CTH}. In contrast to the above results where measurements were made out at 25°C after 1 day of storage time, Al-Malah et al. (2000) reported that at the thermal processing temperature

Table 2
Weltman model parameters used to describe the change in apparent viscosity with time for different glucose starch dispersions under different shear rates and t_{CTH}

%Glucose (w/v)	Shear rate (l/s)	t_{CTH} (min)	A (mPa s)	B (mPa s)
0	11.7	0	679	−22.0
		10	1255	−72.6
		20	980	−41.7
		30	1266	−74.3
	54.3	0	196	−9.9
		10	380	−22.9
		20	302	−19.0
		30	323	−20.4
	106.0	0	126	−7.0
		10	266	−15.0
		20	211	−14.7
		30	227	−14.2
	252.3	0	120	−9.0
		10	155	−10.3
		20	137	−9.6
		30	132	−7.6
1	11.7	0	846	−37.2
		10	1430	−78.7
		20	1736	−88.5
		30	1854	−111.8
	54.3	0	203	−10.7
		10	413	−29.3
		20	512	−37.6
		30	554	−40.7
	106.0	0	135	−7.8
		10	285	−15.3
		20	409	−25.0
		30	413	−25.9
	252.3	0	93	−6.5
		10	145	−8.6
		20	238	−13.4
		30	251	−16.3
3	11.7	0	762	−28.3
		10	905	−44.7
		20	1129	−57.9
		30	1725	−97.8
	54.3	0	225	−13.0
		10	322	−22.3
		20	429	−29.1
		30	760	−63.4
	106.0	0	161	−10.5
		10	249	−19.7
		20	321	−22.3
		30	414	−26.4
	252.3	0	105	−7.8
		10	135	−11.7
		20	167	−14.5
		30	235	−17.0
6	11.7	0	1123	−66.6
		10	1269	−68.0
		20	1560	−89.7
		30	2034	−95.7
	54.3	0	314	−18.8
		10	365	−24.2
		20	384	−25.0
		30	576	−40.0
	106.0	0	240	−16.7
		10	286	−17.3
		20	311	−19.0
		30	387	−27.4
	252.3	0	128	−8.9
		10	160	−9.6
		20	167	−10.4
		30	247	−19.3

(80°C), starch–glucose dispersions behaved like Bingham fluid, regardless of the glucose concentration and t_{CTH}.

A value of n less than unity means that the substance exhibits shear-thinning behavior. This behavior was evident with the rest of the samples, i.e. 1% (but with longer t_{CTH} than 0 and 10 min), 3 and 6% glucose concentrations. It is also noticed from Table 1 that values of n decrease as both t_{CTH} and glucose concentration increase.

In general, it can be seen from Table 1 that as t_{CTH} increases, for a given glucose concentration, both the yield stress, τ_o, and the consistency coefficient, m, increase. An increase in m with increase in t_{CTH}, at a given temperature, was also found by Chamberlain, Rao and Cohen (1999) for waxy maize starch dispersions. Moreover, the presence of glucose results in an increase in both τ_o and m, compared with the control sample (0% glucose). In particular, the presence of glucose has a synergistic effect as far as the effect of t_{CTH} on the consistency index, m, is concerned.

The latter findings are in agreement with what was reported by Ahmad and Williams (1999) that the swelling factors in the presence of sugar were higher compared to the control (0% sugar) sample for sugar concentrations below 25%. Moreover, Rao, Okechukwu, Da Silva and Oliveira (1997) found that the consistency coefficient of the dispersions increased with the granule mean diameter. Based on this, one may conclude that the consistency coefficient increases with the presence of sugar as a result of the increase in swelling factor (granule mean diameter).

In the absence of glucose, the apparent viscosity was found to increase slightly with t_{CTH}, as observed from Fig. 5, which could be due to an increase in the mean diameter of the heated starch granules as t_{CTH} is increased (Chamberlain et al., 1999). On the other hand, the presence of glucose resulted in a further increase in the apparent viscosity, as t_{CTH} was increased (Fig. 6), compared with that of glucose-free starch dispersion. Ahmad and Williams (1999) suggested that the presence of glucose results in an increase in the swelling factor (i.e. an increase in granule mean diameter), which in turn results in an increase in the apparent viscosity. Bagley and Christianson (1982) also observed this for wheat starch.

Time-dependent flow properties of starch dispersions were assessed by examining η versus shearing time. The associated behavior is denoted as either thixotropic (a decrease in viscosity with time) or anti-thixotropic (an increase in viscosity with time). Figs. 5 and 6 show that starch dispersions and starch–glucose dispersions are thixotropic. For low starch concentration systems, it is thought that thixotropic/anti-thixotropic behavior is attributed to the destruction/formation of some forms of "aggregate" that depend on the balance between intra- and intermolecular interactions (Dentzis, Bagley, & Felker, 1995). In addition, Chamberlain et al. (1999) attributed the anti-thixotropic behavior of 2.6 wt.% starch dispersions to the formation of shear-induced structure, in the form of clusters.

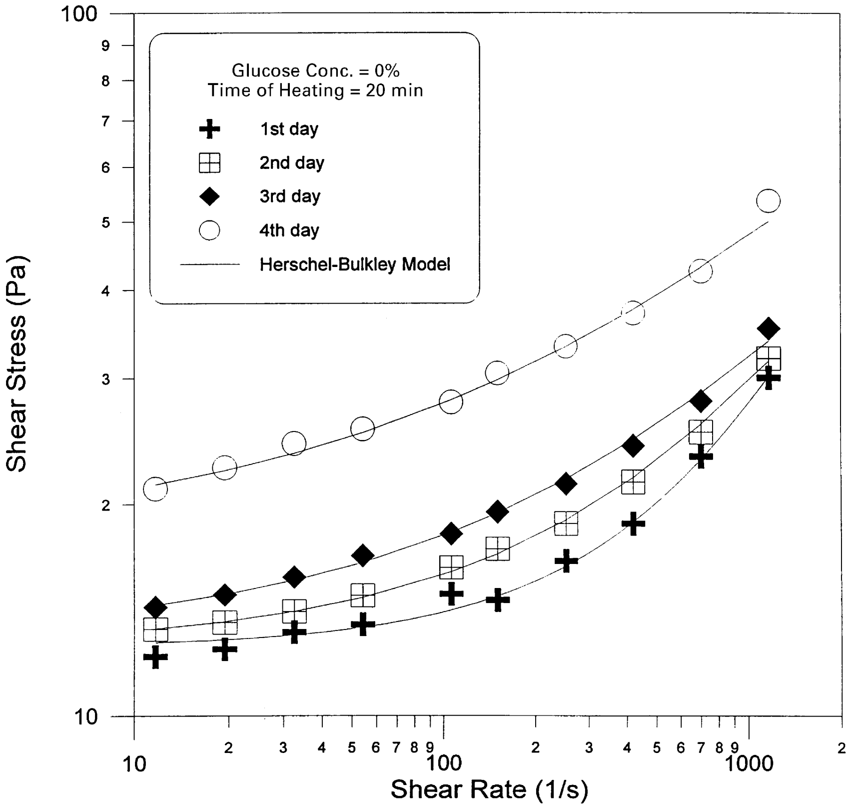

Fig. 7. Effect of storage time on flow curves of starch dispersions at glucose concentration = 0%, and t_{CTH} = 20 min.

The time-dependent flow properties of starch dispersions were also tested using the Weltman model (Weltman, 1943):

$$\eta = A + B\ln(t) \tag{3}$$

Table 2 shows the parameters A and B in the Weltman model obtained by regression for 0, 1, 3, and 6% (w/v) glucose concentrations, different t_{CTH}, and different shear rates. A zero value of B (the coefficient of thixotropic breakdown) indicates that the apparent viscosity of the fluid is independent of time (i.e. the fluid is neither thixotropic nor anti-thixotropic). The magnitude of B, in general, decreases with increasing shear rate. A negative B value measures the degree of destruction of aggregates or clusters arising from shear rate. In other words, it measures how fast the apparent viscosity drops from the initial value, to the final equilibrium (steady-state) value. Our finding that B decreases with increasing shear rate is in agreement with that of Nguyen et al. (1998).

The effect of storage time on the flow curves in the absence and presence of dextrose was also investigated. The results of this investigation are presented in Figs. 7 and 8, respectively.

In the absence of glucose, Fig. 7 shows that increasing the time of storage increases the shear stress, and therefore increases the apparent viscosity. This difference almost disappeared in the presence of glucose, as seen in Fig. 8.

Table 3 shows the parameters in the Herschel–Bulkley model, obtained at 0 and 6% glucose concentrations both having t_{CTH} values of 20 min. In the absence of glucose, as the storage time proceeds, starch dispersions change their flow behavior from Bingham to shear-thinning fluids with an apparent increase in both τ_0 and m (an indication of retrogradation effect) toward the end of the storage period. On the other hand, the presence of glucose almost kept the flow behavior of starch dispersions constant over the examined storage period (see Fig. 8). It is thought here that sugars decrease retrogradation probably because of the increase in glass-transition temperature caused by increasing the average molecular weight of the dispersions (Slade & Levine, 1991).

Finally, Table 4 shows the regressed parameters of the Weltman model, applied to 0 and 6% glucose concentrations both having t_{CTH} value of 20 min and were sheared at 106 s^{-1}. In the absence of glucose, the magnitude of B increased with increasing storage time, whereas in the presence of glucose, it remained almost independent of storage time. This supports the above conclusion that the presence of glucose decreases retrogradation by keeping constant moisture content over the examined period of time and renders the composition invariant.

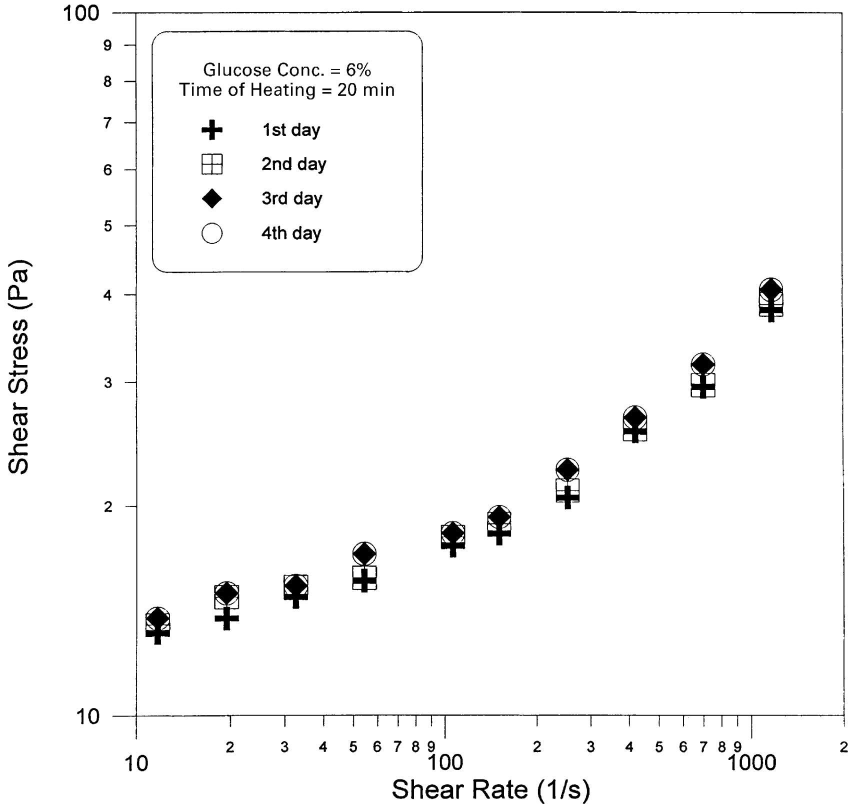

Fig. 8. Effect of storage time on flow curves of starch dispersions at glucose concentration = 6%, and t_{CTH} = 20 min.

5. Conclusions

Starch dispersion systems are non-Newtonian fluids with a yield stress that can be modeled by the Herschel–Bulkley equation. In the absence of glucose, regardless of the time of constant temperature heating, t_{CTH}, or at low glucose concentration, but with low t_{CTH}, the data were characterized by a flow behavior index, n, very close to unity, indicating that the systems behave as Bingham fluids. As both the concentration of dextrose and t_{CTH} increase, n decreases, hence, a pronounced shear-thinning behavior. Moreover, as t_{CTH} increases for a given glucose concentration, both τ_o and m increase. The presence of glucose results in an increase of both τ_o and m, compared with the control sample (0% glucose).

Regarding the time-dependent rheological behavior of starch dispersions, it was found that the examined starch dispersions were adequately described by the Weltman model and found to be thixotropic in behavior. The magnitude of the coefficient of thixotropic breakdown (B), in general, was found to decrease with increasing shear rate. In addition, for a given glucose level, the magnitude of B generally increases with increasing t_{CTH}.

As far as the magnitude of the apparent viscosity is concerned, starch dispersions with t_{CTH} of 0 min show the lowest values at all levels of glucose concentration

Table 3
Herschel–Bulkley parameters for to 0 and 6% (w/v) glucose starch dispersions, with t_{CTH} = 20 min, for different storage periods

Glucose concentration (w/v%)	Storage time (day)	τ_o (Pa)	n	m (mPa s^n)
0	1	12.6	1.0	15.1
	2	12.6	0.71	126.0
	3	12.8	0.56	403.0
	4	17.8	0.48	1087.0
6	1	11.5	0.67	227.4
	2	12.0	0.65	267.0
	3	12.3	0.61	319.0
	4	12.4	0.61	359.0

Table 4
Weltman model, parameters for 0 and 6% (w/v) glucose starch dispersions, evaluated at $\dot{\gamma} = 106\ \mathrm{s}^{-1}$ and $t_{\mathrm{CTH}} = 20$ min, for different storage periods

Glucose concentration (w/v%)	Storage time (day)	*A* (mPa s)	*B* (mPa s)
0	1	211	−14.7
	2	226	−18.4
	3	241	−21.4
	4	323	−32.3
6	1	311	−19.0
	2	294	−19.2
	3	261	−19.9
	4	253	−20.5

investigated and in general, as both t_{CTH} and glucose concentration increase, the apparent viscosity increases.

Finally, it was found that in the absence of glucose, as storage time proceeds, starch dispersions change their flow behavior from Bingham to shear-thinning fluids with an apparent increase in both τ_0 and m (an indication of retrogradation effect) toward the end of the storage period. On the other hand, the presence of glucose almost kept the flow behavior of starch dispersions constant over the examined storage period.

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