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Food Research International, Vol. 28, No. 5, pp. 473–480, 1995
Elsevier Science Ltd

0963–9969/95 $9.50 + .00

Rheological properties of starch solutions under aseptic processing temperatures

K. A. Abdelrahim, H. S. Ramaswamy* & F. R. van de Voort

Department of Food Science and Agricultural Chemistry, Macdonald Campus of McGill University,
Ste. Anne de Bellevue, PQ, Canada H9X 3V9

Rheological properties of cross-linked waxy maize starch in the concentration range of 3–6% w/w were evaluated using a computer controlled rotational viscometer equipped with a high temperature/high pressure attachment and a magnetic coupling. The influence of temperature on the rheological parameters was evaluated in the temperature range 60–140°C. The flow curves essentially followed the power law model and both the consistency coefficient and flow behaviour index were sensitive to changes in temperature and concentration. Temperature dependency followed the Turian model.

Keywords: Starch, rheology, processing, rheological models, high temperature.

INTRODUCTION

Lack of rheological data at the elevated temperatures is one of the major problems facing modelling of aseptic processing of low acid liquid foods containing particulates. Most liquid foods are viscous and non-Newtonian in nature. Thermal process design for liquid foods with or without particulates requires accurate information on the flow behaviour of the fluid as well as particle/fluid relative velocities in the holding tube to arrive at processing conditions which ensure safety and improve quality factor retention (Subramaniam & Zuritz, 1990; Alcairo & Zuritz, 1990). The relative velocity between the liquid medium and the food particle may also influence the fluid to particle convective heat treader coefficients in the holding tube (McCoy *et al.*, 1987; Hallström *et al.*, 1988; Dail & Steffe, 1990).

Starches are widely used in foods as thickening agents in foods which result from the swelling of the starch granules occurring at the gelatinization temperatures (Self *et al.*, 1990). Recently, a modified cross-linked starch was used to simulate carrier fluids in liquid foods containing particulates (Chandarana *et al.*, 1989, 1990). It has been recognized that the rheological properties of fluids depend on concentration of the active compound, temperature and shear rate (Harrod, 1989*a*). Consequently the rheological properties have to based on: (1) a representative model product, (2) an appropriate measuring technique, (3) measurement of flow properties over wide ranges of shear rate, temperature and concentration; and (4) investigation of the time-dependency of the flow properties. In a useful contribution, Harrod (1989*a,b,c*) reported some effects of concentration, preparation method and time-dependency on the rheological properties of modified (cross-linked and esterified) potato starch.

Available data on cross-linked waxy starches at elevated temperatures are limited. Dail and Steffe (1990*a,b*) studied starch rheology under aseptic processing conditions using relatively low concentrations (1·82, 2·72 and 3·15% g dry starch/100 g water) over a small range of shear rate (35–175 s^{-1}). Harrod (1989*a*) and Self *et al.* (1990), on the other hand, employed high concentrations, but at relatively low temperatures (10–90°C). Most experimental data on Residence Time Distribution (RTD) and heat transfer studies pertaining to liquid foods containing particulates have been reported at near room temperatures (Chandarana *et al.*, 1989, 1990), probably due to the lack of rheological data specifically obtained on starch especially at high temperatures.

The objectives of this work were: (1) to study the flow behaviour of modified cross-linked starch solutions (3–6% w/w) by evaluating the relationship of the

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*To whom all correspondence should be addressed.

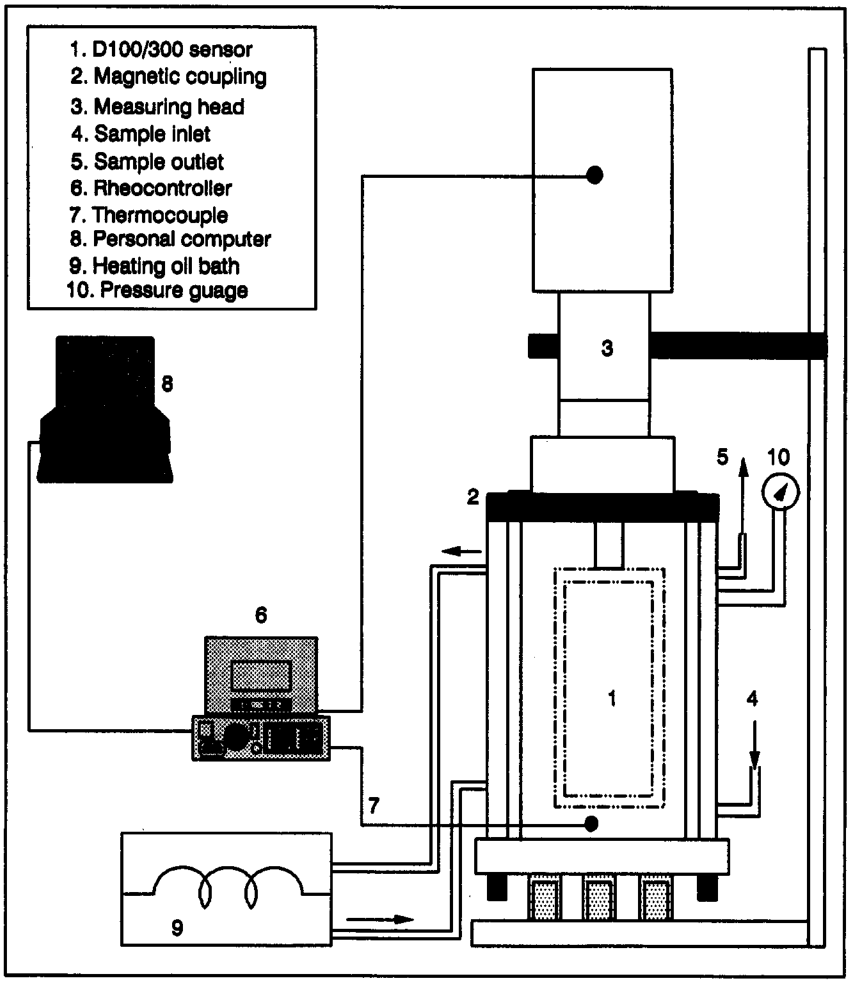

Fig. 1. Schematic diagram showing the experimental set-up for the high temperature sensor system (D100/300).

shear stress/shear rate data; and (2) to study the effects of temperature, concentration, preparation and gelatinization on starch rheology.

MATERIALS AND METHODS

Test samples of starch were freshly prepared using commercially available Therm-flo starch Lot # HK 4254 (National Starch and Chemical Corp., Bridgewater, NJ). This starch is a cross-linked waxy maize recommended for low acid foods that are thermally processed. Four concentrations (3, 4, 5 and 6% w/w) were used. Prior to measurements starch samples were gelatinized at 140°C employing the aseptic processing system previously described by Abdelrahim *et al.* (1993).

Rheological measurements were carried out using a Haake rotational viscometer Model RV20 (Haake Mess-Technik GmbH u. Co., Karlsruhe, Germany), equipped with an M5 OSC measuring head used in the rotational mode and programmed via a computer controlled Rheocontroller RC20 module. A D100/300 rotor assembly sensor system capable of operation under high temperature/high pressure conditions of aseptic processing was used for measurements. The rotor inside the sample compartment is operated by a magnetic clutch assembled to the measuring head. The system was calibrated to cancel the effect of this magnetic coupling before performing the measurements by using silicone oil standards and a conventional sensor (MV1). The lay-out of the sensor system as well as the experimental set-up is outlined in Figure 1. The sample is kept inside a jacketed chamber heated by circulating silicone oil using an immersion circulator, PolyScience Model 800 (Cole Parmer, Chicago, IL). Temperature of the sample was monitored by a platinum resistance thermometer installed at the bottom of the chamber and connected to the rheocontroller.

Test samples of starch solutions were loaded into the test chamber and allowed to equilibrate to the required temperature (~10 min). Samples were sheared at a programmed rate increasing from 0 to 500 s^{-1} in 10 min, held steady at 500 s^{-1} for 20 min, followed by a linearly decreasing shear from 500 to 0 s^{-1} in 10 min. A full factorial experimental design with five levels of starch (3, 4, 5 and 6% w/w) and five levels of temperature (60, 80, 100, 120 and 140°C) was employed with three replicates. Experimental data were corrected for magnetic coupling effect using the calibration factor obtained with silicone oil standards and MV1 sensor.

Flow curve evaluation

The flow curves (rheograms) were evaluated by using the power law, the Herschel-Bulkley, Casson and the Bingham linear rheological models (equations (1)–(4), respectively):

Power law $\sigma = m\dot{\gamma}^{n}$ (1)
Herschel–Bulkley $\sigma - \sigma_0 = m\dot{\gamma}^{n1}$ (2)
Casson $\sigma^{1/2} = (m_{oc})^{1/2} + (m_c\dot{\gamma})^{1/2}$ (3)
Bingham $\sigma = \sigma_0 + \eta\,\dot{\gamma}$. (4)

The combined effect of temperature and concentration on the consistency coefficient (*m*) and the flow behaviour index was evaluated through a multiple regression analysis by using a modified Turian approach (1964) as reported by Ramaswamy and Basak (1991):

$$\log_{10}(m) = \log_{10}(m_o) - AT \quad (5)$$

$$n = n_o + BT. \quad (6)$$

A modified Weltmann (1943) logarithmic was used to evaluate time dependency of starch solutions as proposed by Ramaswamy and Basak (1991):

$$\sigma = A_w - B_w \log(t/t_m) \quad (7)$$

RESULTS AND DISCUSSION

Sensor calibration

The D100/300 sensor system and the measuring head (M-5 OSC) of the viscometer are connected by magnetic coupling as explained earlier. Therefore the sensor has to be calibrated to cancel the effect of the magnetic clutch on the rheological data. Shear stress–shear data for D100/300 and MV1 sensors with silicone oil standards at 60°C are shown in Figure 2. Higher shear stress values were observed with the D100/300 sensor. This was corrected by correlating the shear stress data of the two senors and a correction factor of 10·33 was obtained for the three viscosity standards used. The corrected D100/300 data showed good agreement with the MV1 data (Fig. 3).

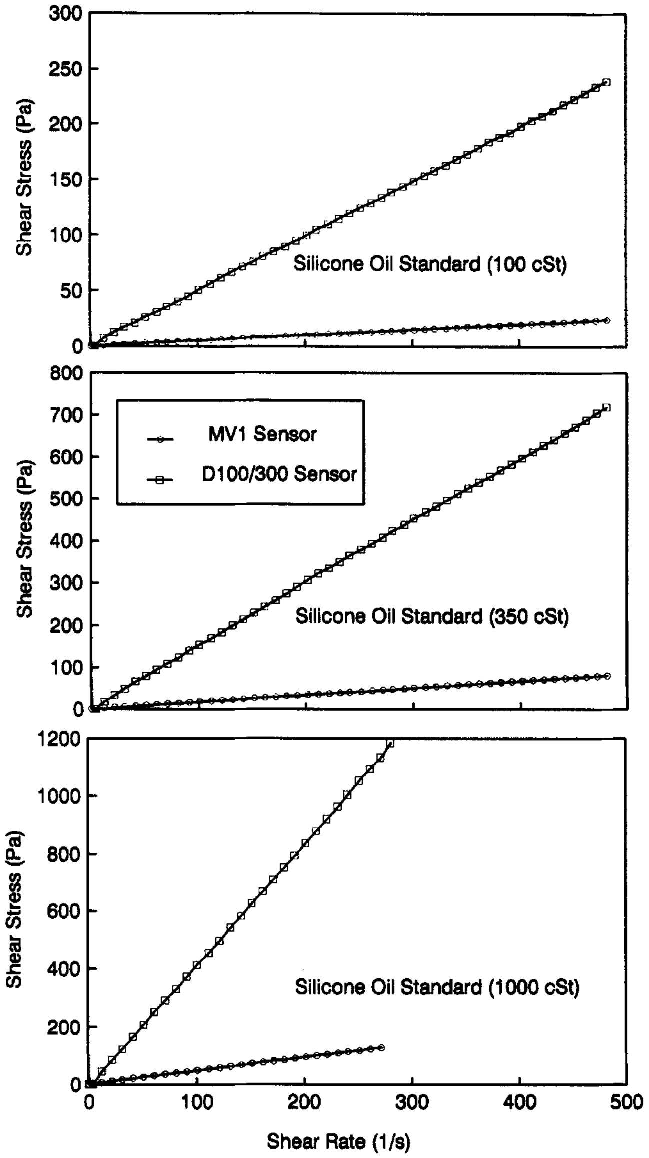

Fig. 2. Shear stress–shear rate data for silicone oil standards using D100/300 and MV1 sensor systems at 60°C under a dynamic shearing cycle.

Characterization of the flow curves

Typical flow curves for different concentrations (3, 4, 5 and 6% w/w) of Therm-flo starch at 120 and 140°C under dynamic and steady shearing are presented in Figure 4. Higher concentrations of starch were associated with higher viscosities as indicated by the higher shear stress values under a given shear rate, while increased temperature resulted in decreased viscosities. Starch solutions showed only a negligible structural breakdown under a steady shear rate of 500 s^{-1} for 20 min (i.e. solutions were not strongly time-dependent). With 3% starch, there were some fluctuations with the shear stress–shear rate data, perhaps due to prevailing low viscosities resulting in turbulence, as well as the low sensitivity of the instrument.

Rheological models of starch

The suitability of different rheological models was tested for fitting the shear stress/shear rate data of

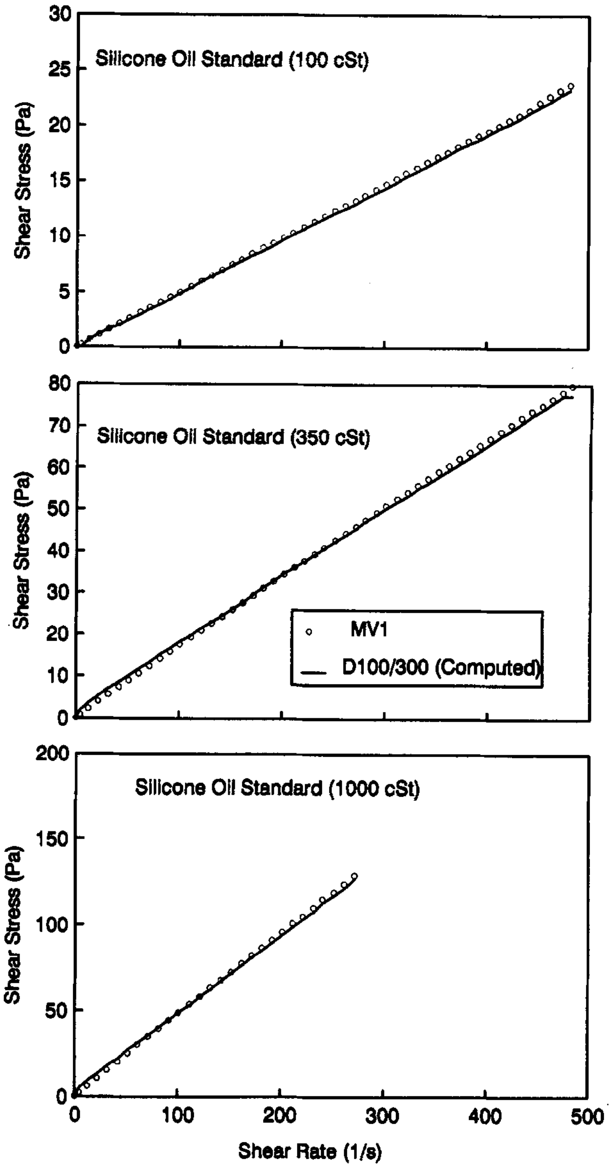

Fig. 3. Corrected shear stress–shear rate data for the D100/300 system with silicone oil standards at 60°C under a dynamic shearing cycle.

Therm-flo starch solutions as detailed in Table 1. The Bingham linear model was suitable among others for the lower concentration of starch (3%) with determination coefficients (r^2) of 0·91 and 0·95 for the upward and downward flow curves, respectively. At high concentrations (4–6%), power law model was dominant (r^2 = 0·99). Models such as Herschel–Bulkley and Casson also showed good fit over the shear stress/shear rate data (r^2 = 1·00 for Herschel–Bulkley model) at the concentration of 6% (Table 1). However, throughout this study the power law model was used for the analysis because of its overall good fit (based on the determination coefficients, r^2 as in Table 1) of the data and its inherent compatibility as far as engineering calculations are concerned (Lalonde *et al.*, 1991).

Table 1. Different rheological models parameters of the different Therm-flo starch concentrations (3–6% w/w) at 120°C

Conc. (%)	Model	Upward curve Intercept	Slope	r^2	Downward curve Intercept	Slope	r^2
3	Linear	0·1018	0·066	0·91	0·1576	0·041	0·95
	Power law	0·2037	0·530	0·76	0·1812	0·527	0·75
	H. Bulkley	0·0349	1·185	0·77	0·0243	0·759	0·87
	Casson	0·0241	0·053	0·86	0·1041	0·015	0·89
4	Linear	3·6510	0·126	0·98	3·3793	0·120	0·99
	Power law	0·2110	0·686	0·98	0·1467	0·664	0·97
	H. Bulkley	0·1176	0·722	0·96	0·1290	0·682	0·96
	Casson	2·1620	0·055	0·96	2·0500	0·051	0·97
5	Linear	4·9260	0·257	0·98	4·2690	0·257	0·98
	Power law	0·2165	0·689	0·99	0·1429	0·728	0·99
	H. Bulkley	0·1970	0·826	0·88	0·1455	0·822	1·00
	Casson	2·6063	0·130	0·99	2·0810	0·140	1·00
6	Linear	9·0000	0·506	0·97	9·6700	0·443	0·99
	Power law	0·7315	0·565	0·99	0·5390	0·650	0·99
	H. Bulkley	0·2398	0·784	0·95	0·4982	0·731	1·00
	Casson	4·4180	0·274	0·99	5·4340	0·209	1·00

Table 2. The rheological parameters of Therm-flo starch as affected by concentration and temperature using the power law model[a]

Con. (%)	Temperature (°C)	Upward curve m^b	n^b	Downward curve m	n
3	60	0·511±0·033	0·411±0·003	0·475±0·010	0·384±0·020
3	80	0·421±0·011	0·420±0·010	0·311±0·043	0·451±0·024
3	100	0·293±0·037	0·467±0·007	0·224±0·017	0·497±0·045
3	120	0·204±0·011	0·530±0·023	0·181±0·005	0·527±0·021
3	140	0·151±0·033	0·550±0·029	0·150±0·022	0·601±0·010
4	60	0·464±0·030	0·480±0·015	0·411±0·030	0·498±0·010
4	80	0·398±0·032	0·495±0·015	0·287±0·016	0·573±0·028
4	100	0·279±0·052	0·609±0·063	0·201±0·022	0·593±0·011
4	120	0·211±0·027	0·686±0·029	0·147±0·025	0·664±0·108
4	140	0·182±0·005	0·692±0·068	0·093±0·014	0·836±0·018
5	60	0·694±0·028	0·647±0·018	0·498±0·048	0·695±0·017
5	80	0·489±0·025	0·648±0·006	0·327±0·028	0·707±0·011
5	100	0·356±0·028	0·672±0·021	0·221±0·017	0·719±0·014
5	120	0·217±0·032	0·689±0·011	0·143±0·021	0·728±0·043
5	140	0·193±0·029	0·697±0·027	0·116±0·020	0·750±0·026
6	60	1·154±0·081	0·527±0·004	0·898±0·054	0·639±0·018
6	80	0·897±0·025	0·608±0·004	0·721±0·033	0·647±0·010
6	100	0·790±0·013	0·594±0·008	0·646±0·020	0·648±0·010
6	120	0·732±0·010	0·565±0·011	0·539±0·038	0·650±0·015
6	140	0·678±0·019	0·614±0·006	0·432±0·023	0·662±0·007

[a] $\sigma = m\,\gamma^n$.
[b] Results are means of triplicates.

Table 3. Analysis of variance on the rheological parameters of Therm-flo® starch as influenced by concentration temperature using the power law

Factor	Treatment	D.F.	Upward curve MS[1]	%SS[2]	Downward curve MS	%SS
m	Main effects	7	0·6175[a]	96·83	0·9325[a]	97·25
	Concentration	4	1·0046[a]	67·51	0·4423[a]	61·50
	Temperature	3	0·3272[a]	29·32	0·2571[a]	35·75
	Interactions	12	0·0065[a]	1·76	0·0027[c]	1·13
	Residual	40	0·0016	1·41	0·0012	1·63
n	Main effects	7	0·0589[a]	79·11	0·0825[a]	76·65
	Concentration	4	0·0963[a]	55·44	0·1365[a]	54·37
	Temperature	3	0·0309[a]	23·67	0·0420[a]	22·28
	Interactions	12	0·0058[a]	13·26	0·0095[a]	1·13
	Residual	40	0·006	1·41	0·0012	1·63

[1] Means sum of squares.
[2] Percentage contribution to the total sum of squares.
[a,b,c] Significant at $P \leq 0·001$, $P \leq 0·01$ and $P \leq 0·05$; respectively.
[n] Not significant, $P > 0·05$.

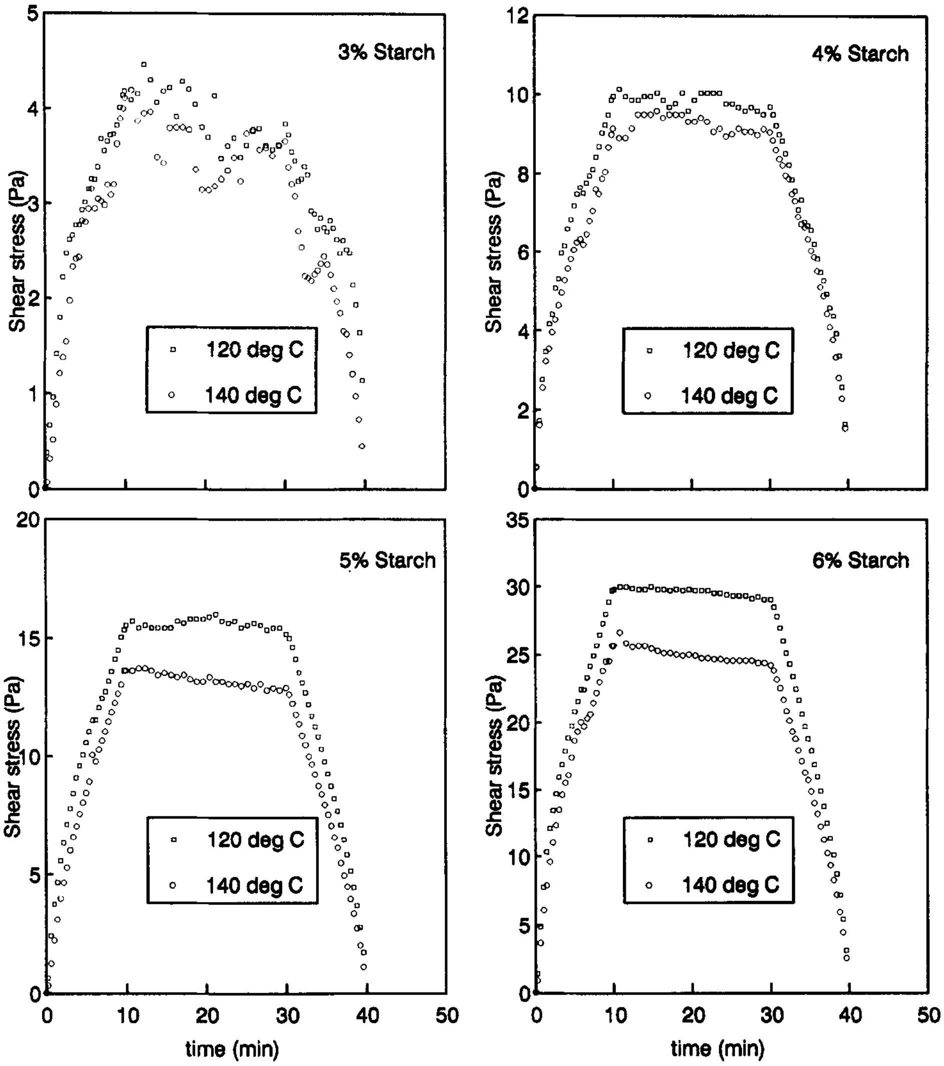

Fig. 4. Influence of concentration on shear stress–shear rate data of starch solutions at 120 and 140°C using the high temperature/high pressure (D100/300) sensor system.

Effects of temperature and concentration

The mean and standard deviations of the power law parameters (*m* and *n*) of starch are presented in Table 2. Analysis of variance showed that both *m* and *n* (Table 3) were significantly ($P \leq 0{\cdot}05$) influenced by concentration, temperature and their interactions. The effect of concentration was more dominant on *m* for both upward and downward flow curves (67·5 and 61·5% of total variability, respectively). The trend was almost the same, with the flow behaviour index (~55·4 and 54·4% of total variability for the upward and downward flow curves; respectively). The general trend was that: consistency coefficient (*m*) increased with concentration and decreased with temperature, while the effects were reversed with the flow behaviour index as indicated by the means plots (Fig. 5).

Time-dependent flow behaviour

Time-dependent or thixotropic behaviour of Therm-flo starch was investigated using the Weltmann (1943) model. Structural breakdown was minor (Fig. 4). Melting and swelling of starch was probably complete at 140°C, and obvious structural build-up or loss was not observed. Both temperature and starch concentration were not significant ($P > 0{\cdot}05$) as the maximum structural accounted only for <5% in all cases (Fig. 4). Time-dependent flow behaviour is usually associated with partially gelatinized starches, due to the on-going melting and swelling of the starch granules as a result of the exposure to higher temperatures (Donovan *et al.*, 1983; Biliaderis, 1991).

A combined model for starch rheology

From a practical stand-point, it will be very useful to describe the effect of temperature and concentration by only one equation. In literature, the Arrhenius model was frequently used to model effects of temperature, while the effect of concentration was described by

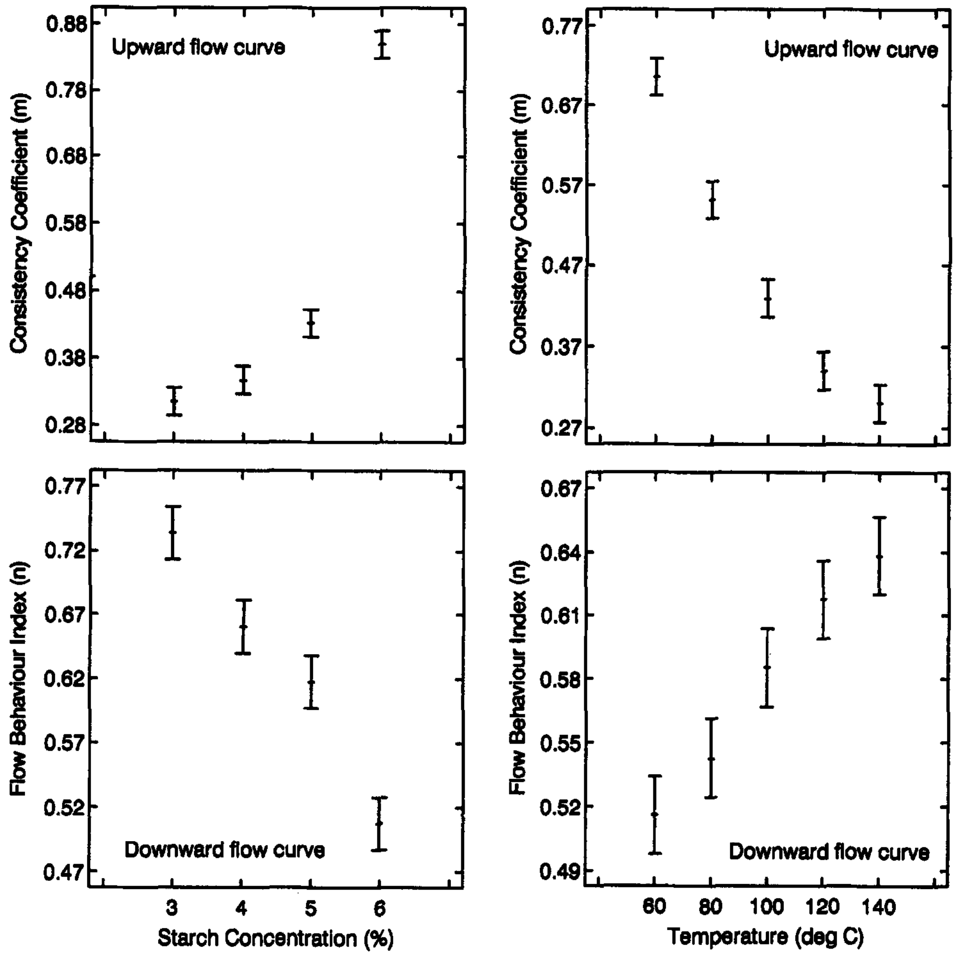

Fig. 5. Means plots for consistency coefficient (*m*) and flow behaviour index (*n*) of the starch solutions for upward and downward flow curves as influenced by starch concentration and temperature.

either an exponential or a power relationship (Fichtali *et al.*, 1993). However, Arrhenius was not suitable for Therm-flo® starch especially at lower starch concentrations as the coefficients of determination were relatively low ($r^2 < 0{\cdot}7$). The alternative was a modified Turian approach taking into account the effects of both temperature and concentration on consistency coefficient and flow behaviour index. Both *m* and *n* were related to temperature and concentration by multiple regression analysis. The following predictive equations involving various temperature and concentration functions were introduced for the upward flow curve (R^2 = 0·91 and 0·76 for $\log_{10}(m)$ and *n*, respectively):

$$\log_{10}(m) = -3{\cdot}50 + C \{0{\cdot}39 + 0{\cdot}0013\,T + (2{\cdot}01/T)\} + 7{\cdot}16/C - 0{\cdot}011\,T \quad (8)$$

$$n = 1{\cdot}83 - C \{0{\cdot}091 + 0{\cdot}001\,T + (0{\cdot}86/T)\} - 3{\cdot}86/C + 0{\cdot}004\,T. \quad (9)$$

Similar predictive equations were developed for the downward flow curve (R^2 were 0·91 and 0·79 for $\log_{10}(m)$ and *n*, respectively):

$$\log_{10}(m) = -5{\cdot}06 + C \{0{\cdot}57 + 0{\cdot}001\,T + (1{\cdot}91/T)\} + 10{\cdot}13/C - 0{\cdot}010\,T \quad (10)$$

$$n = 1{\cdot}67 - C \{0{\cdot}063 + 0{\cdot}001\,T\} - 4{\cdot}00/C + 0{\cdot}006\,T. \quad (11)$$

Plots for the observed vs predicted *m* and *n* are presented in Figure 6. The model will be useful as rheological data at aseptic processing conditions is very limited. The equations can readily applied for heat transfer studies (Ramaswamy *et al.*, 1995) and dimensional analysis for flow processes (Grabowski & Ramaswamy, 1994; Abdelrahim *et al.*, 1994).

CONCLUSIONS

The use of magnetic coupling with D100/300 sensor system allowed adequate evaluation of starch rheology at high temperatures. The power law model showed an

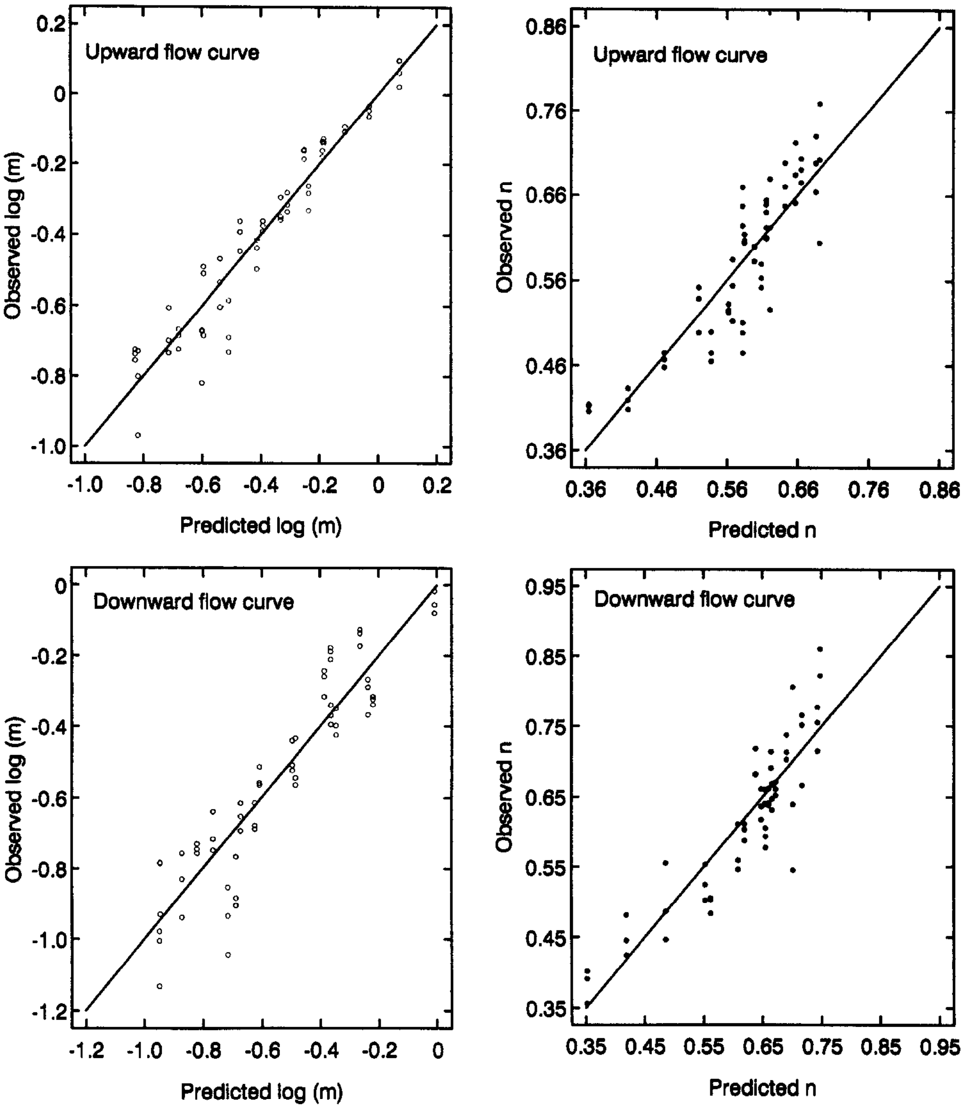

Fig. 6. Plots for experimental vs calculated *m* and *n* of the starch solutions for the upward and downward flow curves.

overall good fit over starch flow curves. The rheological properties were temperature and concentration sensitive. These effects need to be taken into consideration using Therm-flo starch as a carrier fluid for particulate foods while designing continuous aseptic processing.

ACKNOWLEDGEMENTS

This research was supported by the Strategic Research Program of the Natural Science and Engineering Research Council (NSERC) of Canada and McGill University Major Scholarships Program (Hydro Quebec Scholarship).

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(Received 25 April 1994; accepted 30 August 1994)