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Evaluation and modelling of rheological properties of high pressure treated waxy maize starch dispersions

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Abstract

Samples of 10% waxy maize starch dispersions were treated at pressures from 450 to 600 MPa for 0–120 min. The rheological properties of the dispersions were studied by viscosity and low deformation viscoelastic measurements. At 450 MPa, the consistency coefficient did not exceed 7 Pa s^n even after a treatment time of 110 min, whereas at 550 MPa a value of 20 Pa s^n was reached in about 5–10 min. G' measurements as a function of treatment times at different pressures gave almost identical results to viscosity measurement, except that at longer treatment times G' decreased, indicating that excessive pressurisation seemed to weaken the gel structure. A sigmoidal type model was found to adequately correlate the consistency coefficient values, obtained at different holding times and processing pressures, with the F value of the process, a value representing an equivalent processing time at specified reference pressure and temperature conditions, defined analogously to the traditional thermal processing terminology. © 1999 Published by Elsevier Science B.V. All rights reserved.

Nomenclature	
A, B, C	empirical constants defined in Eq. (4)
a, b, c, d	empirical parameters defined in Eq. (5)
E_a	activation energy, J/mol
F	equivalent time at some constant reference pressure and temperature conditions that produces the same effect (on a particular product attribute) as the actual processing under the particular pressure and temperature profile, s
G'	storage modulus, Pa
K	consistency coefficient, Pa s^n
n	flow behaviour index
P	pressure, MPa
R	universal gas constant, 8.314 J/(mol K)
T	temperature, K (unless otherwise explicitly stated)
t	time, min
V_a	activation volume, cm^3/mol
Greek symbols	
α, β	parameters defined in Eq. (3)
$\dot{\gamma}$	shear rate, s^{-1}
σ	shear stress, Pa
Subscripts	
0	initial condition
1, 2	particular processing stage: 1: end of first linear pressure increase, 2: end of second linear pressure increase
a	initial condition
b	final condition
f	end of holding time
o	beginning of holding time
ref	reference value

1. Introduction

It is well established that starches can be gelatinised by high pressure even at room temperature. Research results indicate that pressure induced gelatinisation is significantly different from heat gelatinisation (Stute, Klingler, Boguslawski, Eshtiaghi & Knorr,1996).

Waxy maize starch is a specialty starch characterised by its very high amylopectin content (>98%). The granule size of waxy maize is 2–30 μm, and the gelatinisation/pasting temperature is 63–72°C (Whistler & BeMiller, 1997).

It has been stated that amylopectin only gels at rather high concentrations and after long periods. Ring et al. (1987) studied the heat induced gelation of waxy maize amylopectin. The storage modulus of a 10% gel

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approached a limiting value of about 1000 Pa after six weeks storage at 1°C. The storage moduli of 25% solutions of various amylopectins studied by Kalichevsky, Orford and Ring (1990) reached values of the order of 10 000 Pa after 30 days storage at 1°C. Cameron, Durrani and Donald (1994), however, showed that amylopectin forms a weak gel directly following dissolution of waxy maize granules by heat. This visually clear and homogenous gel had a rather low storage modulus of the order of 10 Pa, but its rheological properties were definitely those of a gel. That earlier researchers have not detected gels formed under these conditions, may according to Cameron et al. (1994) reflect the improved sensitivity of the new generation of rheometers. Moduli as low as 10 Pa have previously been hard to detect.

This work focuses on the pressure induced gelation of waxy maize starch dispersions. Rather few studies on the effects of high pressure on waxy maize starch dispersions have been conducted. Hibi, Matsumoto and Hagiwara (1993) discovered many swollen granules without polarisation crosses in 50% waxy maize starch dispersions treated at 500 MPa (17–23°C) for 20 and 60 min. The X-ray diffraction pattern showed destruction of the A-type crystalline structure and the pattern tended to change into a faint B-type pattern. Rubens, Goossens & Heremans (1997) made in situ observations of the gelatinisation of waxy maize starch in a diamond anvil cell with Fourier transform infrared spectroscopy. The midpoint of transition occurred at 440 MPa. Stute et al. (1996) reported that a 5% waxy maize starch dispersion was completely gelatinised after a 15 min pressure treatment at 600 MPa and 20°C. The gelatinisation was not complete after a comparable treatment at 500 MPa. The starch granules swelled and showed an almost complete disintegration, which led to a considerable increase in viscosity.

The aim of this study was to investigate the structural changes of high pressure treated dispersions of waxy maize starch (10%) as function of treatment time at various pressures. The structure of the treated samples was studied by rheological methods. Modelling of the process was carried out allowing quantitative prediction of the time–pressure effect on the consistency coefficient for the starch dispersions.

2. Materials and methods

2.1. Starch

Waxy maize starch (AMIOCA) was obtained from National Starch & Chemical Limited (Great Britain). The dry matter content of the product was 90.13%. A 10% starch dispersion was used in the following studies.

2.2. Preparation of starch samples

The samples were prepared using a method where the bulk of native starch is suspended in a pregelatinised starch dispersion, in order to reduce the sedimentation of starch during pressure treatment (Krüsi & Neukom, 1984; Roulet, MacInnes, Würsch, Sanches & Raemy, 1988; Conde-Petit & Escher, 1994).

100 g of a starch-water dispersion containing 2 g starch (dry matter basis) and 24 mg sodium azide was gelatinised by heating on a boiling water bath for 15 min. During the first 5 min of heating the bottle containing the dispersion was shaken continuously in order to avoid lump formation. The pregelatinised starch was cooled to room temperature and 90.92 g of it and 9.08 g (dry matter basis) of native starch was mixed with a spatula until a homogenous mixture was obtained. Small plastic pouches (3 cm × 8 cm) were filled with the 10% waxy maize starch dispersion and heat sealed.

2.3. High pressure treatment

One pouch of sample was put into each of the six cylindrical vessels of the high pressure apparatus (Resato International B.V., The Netherlands). Each vessel has an internal diameter of 25 mm and 85 mm length for a capacity of 42 cm^3. The temperature was kept at 30°C by a water jacket surrounding the vessels. The pressure was manually raised to the desired value. The rate of pressure build-up was approximately 10 MPa min^{-1} up to 100 MPa and 20 MPa min^{-1} from 100 MPa upwards. The temperature slightly increased during pressurisation, due to the adiabatic heating. The increase in temperature was 10°C at maximum, and the set value of 30°C was again reached after a processing time of approximately 15 min (at constant pressure). The samples were kept at pressures from 450 to 600 MPa for 0–120 min (after the constant processing pressure had been reached) and examined rheologically directly after the pressure treatment.

2.4. Heat treatment

A plastic pouch containing the starch dispersion was immersed in a water bath at 90°C and kept in it for 30 min. The sample was allowed to cool at room temperature and examined rheologically the following day.

2.5. Rheological measurements

Rheological measurements were performed at 20°C with a controlled strain rheometer (Bohlin VOR, Bohlin Reologi AB, Lund, Sweden). For the measurements a couette type cup and bob measuring system (C-14) was used.

The pressurised sample was loaded into the cup and allowed to rest for 10 min. A strain sweep was performed using the oscillatory mode of the rheometer. The strain, with a frequency of 1 Hz, was gradually increased from 0.000206 to 0.206 in 40 logarithmic steps. The storage modulus G', the loss modulus G'', and phase angle δ in the linear viscoelastic range were recorded.

After the strain sweep measurement, the viscosity of the sample was measured at an increasing shear rate from 18.5 to 184 s^{-1}, followed by a decreasing shear from 184 to 18.5 s^{-1}. The total shearing time was 170 s. Due to the thixotropic nature of the samples, the shearing loop was repeated five times, with a 30 s interval between the measurements, until no or only slight thixotropy was observed. Measurements during the last loop were analysed based on the power law model. The power law model

$$\sigma = K\dot{\gamma}^n \tag{1}$$

where σ is the shear stress, $\dot{\gamma}$ the shear rate and K and n the consistency coefficient and the flow behaviour index, respectively, is the most frequently used model to describe the flow behaviour of shear-thinning materials. The parameters of the model, K and n, were determined using the software of the rheometer.

3. Results and discussion

During the pressurisation, the apparent viscosity of the sample increased and the colour turned from white to transparent. These changes were dependent on the applied pressure and duration of the pressure treatment.

3.1. Viscosity measurements

The power law model adequately described the shear stress versus shear rate data. The correlation coefficient, R^2, was, in all cases, greater than 0.99. The accuracy of the power law model is illustrated in Fig. 1 for starch samples processed at 450 MPa for selected holding times.

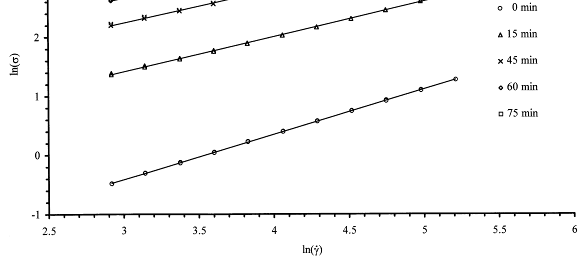

Fig. 1. Linearized power law model plots for starch samples processed at 450 MPa for selected holding times.

For the majority of the cases studied, the flow behaviour index was between 0.5 and 0.6 only slightly affected (decreased) with increasing processing pressure (Table 1). It decreased with increasing processing time (observe slopes of curves in Fig. 1) approaching within 15 min (for the low pressures and even faster for the higher pressures) a final value of about 0.5.

The consistency coefficient K increased faster the higher the applied pressure was and seemed to reach a plateau of about 20–25 Pa s^n after a certain treatment time. At 450 MPa, the consistency coefficient did not exceed 7 Pa s^n even after a treatment time of 110 min (Table 1), whereas at 550 MPa a value of 20 Pa s^n was reached in about 5–10 min. At 600 MPa, the final K value was reached as soon as the constant processing pressure was attained (i.e., at zero holding time, Table 1). An average (over all holding times) K value of 25.40 (±8.37) Pa s^n was obtained for the samples treated at 600 MPa. Scattering of the K values was generally observed for all samples, but it was more pronounced for the samples treated at 600 MPa. One reason for this could be the fast rate of structural changes at this specific pressure. Even small differences in the process parameters, like rate of pressure build-up, gave rise to relatively large differences in structure between the performed experiments. Another reason could be the difficulty and decreased reliability of the viscosity measurements, for the most viscous samples.

3.1.1. Modelling of the consistency coefficient

An attempt was made to model the time–pressure effect on the consistency coefficient for the starch dispersions. From graphs of K versus treatment time (e.g., Fig. 2), one can observe that the K value initially increased with increasing processing time, and thereafter, a plateau is reached where no further change on the K value is observed.

Our approach in modelling the experimental data was based on relating the K values not directly to the processing time, but to the F value of the process. This process F value is defined, analogously to the traditional thermal processing terminology, as the equivalent time at some constant reference pressure and temperature conditions that produces the same effect (on a particular product attribute) as the actual processing under the particular (probably variable) pressure and temperature profile. In analogy to thermal processing (e.g., Hendrickx et al., 1995), and assuming that the effect of temperature (under constant pressure) as well as the effect of pressure (under constant temperature) on the rate constant of the reaction under consideration (i.e., the reaction describing the effect of processing on a particular product attribute) is given by an Arrhenius

Table 1
Processing parameters, consistency coefficient (K) and flow behaviour index (n) at the beginning (K_o and n_o) and the end of the holding time (K_f and n_f)

Experiment ID	P_1 (MPa)	t_1 (min)	P_2 (MPa)	t_2 (min)	Holding time (min)	K_o (Pa s^n)	K_f (Pa s^n)	n_o	n_f
1	225	15.0	450	30.0	75	0.07	3.72	0.76	0.53
2	100	12.0	450	30.1	60	0.37	2.09	0.62	0.57
3	100	10.2	450	27.6	110		6.64		0.50
4	100	13.0	480	34.0	60	0.40	18.72	0.61	0.46
5	100	12.0	480	33.0	75	0.29	14.77	0.65	0.49
6	100	11.4	480	32.7	110		24.02		0.47
7	250	13.8	500	27.6	100	0.55	21.78	0.58	0.50
8	250	14.1	500	33.0	60	0.48	21.06	0.60	0.50
9	100	7.0	500	25.0	40	0.61	24.59	0.59	0.48
10	100	12.0	500	27.0	40	0.53	23.07	0.59	0.48
11	100	12.2	500	29.2	80		27.81		0.47
12	100	13.0	520	35.0	20	0.59	23.15	0.61	0.50
13	100	13.0	520	32.0	60		26.41		0.48
14	260	10.5	520	21.0	50		20.77		0.50
15	100	12.0	520	32.0	40	0.44	23.22	0.62	0.51
16	100	13.0	550	34.9	60	2.28	20.05	0.59	0.53
17	100	14.1	550	36.0	20	6.13	25.30	0.51	0.49
18	100	12.2	550	32.5	60		22.44		0.51
19	100	12.0	570	36.0	12		20.84		0.52
20	100	11.0	570	32.0	25	12.67	24.47	0.52	0.49
21	100	11.0	570	32.0	25	7.87	17.69	0.52	0.53
22	100	12.2	570	32.4	25	8.38	17.95	0.48	0.51
23	100	12.2	600	30.1	10	32.17	41.36	0.50	0.38
24	100	12.2	600	33.5	5		17.60		0.53
25	100	12.2	600	33.2	10	28.94	22.35	0.46	0.53

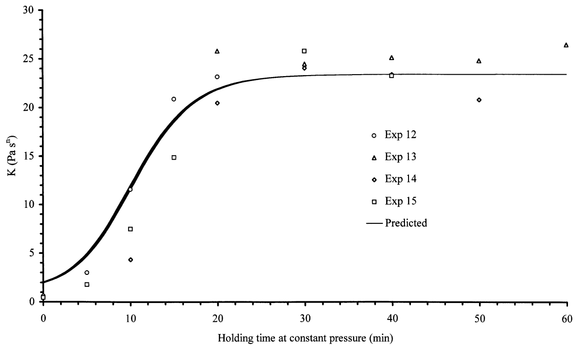

Fig. 2. Effect of holding time on the consistency coefficient (K) for starch samples processed at 520 MPa.

type relationship (Johnson & Eyring, 1970), the F value can be defined as

$$F_{\mathrm{ref}} = \int_{t_a}^{t_b} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{ref}}}\right)-\frac{V_a}{R}\frac{(P-P_{\mathrm{ref}})}{T}\right]\mathrm{d}t \tag{2}$$

For the particular experimental conditions used in the present study, one might consider constant processing temperature but a three step pressure profile. In particular, a pressure profile comprised of an initial linear pressure increase from P_0 (0.1 MPa) to P_1 of t_1 duration, a second linear pressure increase from P_1 to P_2 of t_2–t_1 duration, and a final constant pressure period at P_2 of t ($t > t_2$) duration must be considered (Table 1). Under these conditions, integration of Eq. (2), for $t \geqslant t_2$, gives

$$F = \alpha\left[\frac{t_1}{\beta(P_1-P_0)}(\mathrm{e}^{-\beta P_0}-\mathrm{e}^{-\beta P_1}) + \frac{t_2-t_1}{\beta(P_2-P_1)}(\mathrm{e}^{-\beta P_1}-\mathrm{e}^{-\beta P_2}) + (t-t_2)\mathrm{e}^{-\beta P_2}\right] \tag{3}$$

Note that all constant terms in Eq. (2) have been incorporated in parameters α and β of Eq. (3).

Among the various relationships tested to express K as a function of the F value, a sigmoidal type curve produced rather satisfactory results. Eq. (4) is an explicit presentation of the sigmoidal function used for the data description.

$$\ln(K) = \frac{A}{1+\exp(BF+C)} \tag{4}$$

Substituting Eq. (3), for the F value, into Eq. (4), and incorporating parameters α and β of Eq. (3) with A, B and C of Eq. (4) into new variables a, b, c and d, we obtain Eq. (5), the final expression used for the available data (K values for $t > t_2$) modelling.

Table 2
Parameters for the consistency coefficient (K) determination, as a function of processing time and pressure, for the starch system studied

Parameter	Estimate	Asymptotic 95% confidence interval	
		Lower	Upper
a	-0.1759×10^{-9}	-0.4514×10^{-9}	0.0997×10^{-9}
b	−0.0406	−0.0437	−0.0375
c	1.568	1.054	2.082
d	3.152	3.117	3.188

$$\ln(K) = d \Big/ \left\{ 1 + \exp\left(a \left[\frac{t_1}{b(P_1 - P_0)} \left(\mathrm{e}^{-bP_0} - \mathrm{e}^{-bP_1}\right) + \frac{t_2 - t_1}{b(P_2 - P_1)} \left(\mathrm{e}^{-bP_1} - \mathrm{e}^{-bP_2}\right) + (t - t_2)\mathrm{e}^{-bP_2} \right] + c \right) \right\} \tag{5}$$

With proper parameter estimation, Eq. (5) allows the prediction of the consistency coefficient, K, as a function of processing time and pressure. The experimental data (K, as a function of processing time and pressure) were fitted through Eq. (5), using the SAS/STAT (SAS Institute Inc., Cary, NC, USA) multiple nonlinear (NLIN) procedure, and the appropriate parameters (i.e., a, b, c, and d) were estimated simultaneously, treating all data as a single data set. In estimating the parametric values shown on Table 2, the data for 600 MPa were omitted, due to the large scattering of the K values for these samples.

Using the estimated kinetic parameters (Table 2), the model (Eq. 5) predicted the consistency coefficients satisfactorily, as is illustrated in Figs. 2 and 3. On these figures, one might distinguish several, practically overlapping, predicted lines for each processing pressure. These are the result of different pressure come up conditions (i.e., P_1, t_1, P_2 and t_2, Table 1) encountered in each experiment.

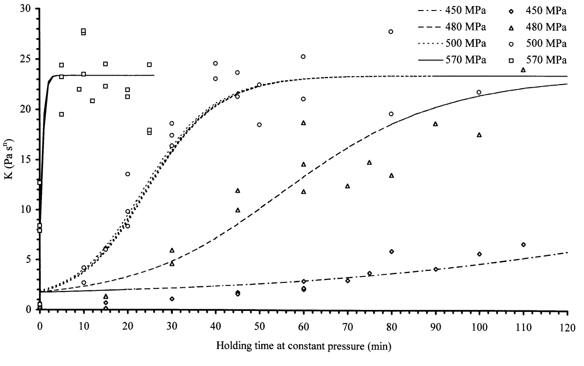

Fig. 3. Predicted and experimental K values as function of holding time and processing pressure. (Symbols refer to experimental data while lines to predicted values.)

Comparison between predicted and experimental K values is presented in Fig. 4. Discrepancies between predicted and experimental data (systematic overprediction) at low K values, which correspond to short holding times at low processing pressures could be possibly improved if the complete time–temperature history of the process was known and taken into account, or if a pressure dependence on the activation energy (and/or a temperature dependence on the activation volume) was considered. The aforementioned scattering of the K values for the most viscous samples (high processing pressures and/or long holding times) is also illustrated in Fig 4.

Overall, the developed model allows satisfactory prediction of the consistency coefficient value as a function of the F value of the process, as defined here in Eq. (3), or in its more general form (applicable to dynamic conditions) in Eq. (2).

3.2. Strain sweep measurements

The storage modulus G', is a measure of the energy stored in the sample during the measurement. For a gel, it is directly related to the cross-link density of the network (Ferry, 1980). G' behaved almost similarly as the consistency coefficient as function of pressure and treatment time (Fig. 5). At pressures from 520 MPa upwards, however, G' increased to a maximum and then started to decrease during further pressurisation. The highest values of G' were obtained at 600 MPa immediately after

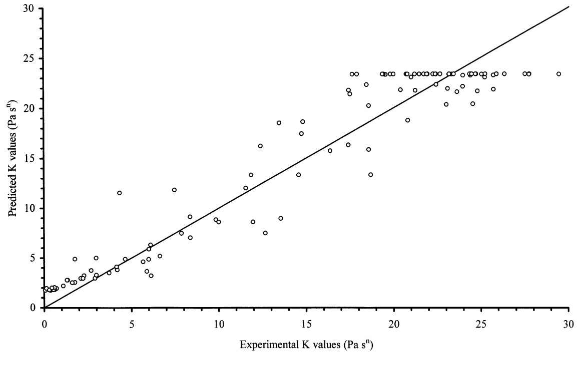

Fig. 4. Comparison between predicted and experimental K values.

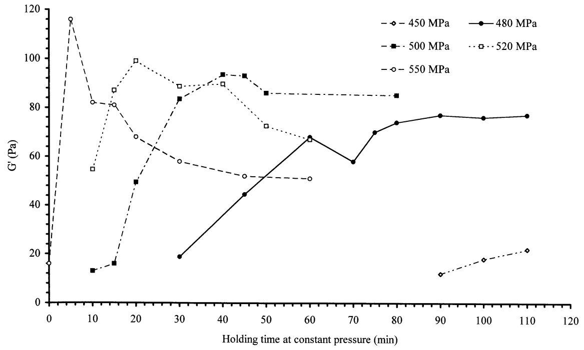

Fig. 5. Effect of holding time and processing pressure on the storage modulus of pressure induced gels, G'. (Each point represents the average of replicate G' values.)

the desired pressure was reached (holding time of 0 min). The phase angle at this point was 13°.

The measurements show that a 10% waxy maize starch dispersion formed a weak gel under pressure. Excessive pressurisation seemed to weaken the gel structure. The storage modulus of the pressure induced gel was approximately 100 Pa (phase angle of about 15°), whereas the storage modulus of the corresponding heat induced gel was approximately 10 Pa (phase angle of about 30°), which is in good agreement with the results of Cameron et al. (1994). No major differences in viscosity was observed between the samples. The results strongly indicate that pressure induced gelatinisation of waxy maize starch differs from heat induced gelatinisation, despite earlier report (Stute et al., 1996) that the swelling and disintegration of starch granules is almost identical in both cases.

Acknowledgements

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