Carbohydrate Polymers 28 (1995) 255–264

0144-8617/95/$09.50+.00
0144-8617(95)00111-5

The extrusion behaviour of potato starch

G. Della Valle[a] *, Y. Boché[a], P. Colonna[a] & B. Vergnes[b]

[a]INRA, Centre de Recherches Agro-Alimentaires, BP 1627, 44316 Nantes Cedex 03, France
[b]CEMEF, Ecole des Mines de Paris, BP 207, 06904 Sophia-Antipolis Cedex, France

(Received 23 May 1995; revised version received 2 August 1995; accepted 9 August 1995)

Potato starch was extruded under various thermomechanical conditions in order to elucidate its behaviour in twin screw extruders. Extensive macromolecular degradation was found to be linked to thermomechanical treatment as evaluated through the measurement of specific mechanical energy SME ($100 < \mathrm{SME} < 320$ kWh/t). Melt viscosity was measured using a specific slit die rheometer for shear rates ranging from 10 to 600/s. Compared with other starches processed under the same extrusion conditions, higher values of viscosity were found which were attributed to higher molecular weights of amylose and amylopectin. Furthermore, beyond a certain level of SME (120–150 kWh/t), potato starch was observed in the molten state in screw sections located 10 C-chambers before a restrictive element, in which starch is usually conveyed under a solid form. These main findings explain the high energy requirements for potato starch extrusion.

INTRODUCTION

The extrusion behaviour of cereal starches has been thoroughly studied compared to potato starch (Colonna *et al.*, 1989). In the few studies referring to potato starch extrusion, processing difficulties are often reported and solved by running the process at higher moisture contents. Mercier (1977) first reported the tremendous increase in solubility and expansion of extruded potato starch, with increasing extrusion temperature. Extrusion conditions were not reported in detail, since the process was quite new at that time. Subsequently, interest mainly focused on the modified properties of the products rather than on the processing behaviour. Senouci and Smith (1986) studied the effect of extrusion on potato starches, native and pregelatinized, and stated that native starch 'could not be extruded alone at low moistures and with small dies'. Therefore, a high moisture content was used ($> 30\%$ on a total wet basis) and, as expected, low levels of specific mechanical energy (SME) were obtained (< 120 kWh/t), for potato granules. Later, the study of the viscosity of molten dehydrated potato granules using a single slit die rheometer showed the need for high inputs of specific mechanical energy, up to 600 kWh/t (Senouci & Smith, 1988). Yamada *et al.* (1990) studied the chromatographic patterns of extruded potato starch, confirming the extent of macromolecular chain splitting. However, only barrel temperature was investigated and no results for SME were reported. Due to the specifications of the extruder employed (power 30 kW) and low moisture content, this parameter could have reached high values (~300 kWh/t). In a study on the use of the extruder as a chemical reactor, Meuser *et al.* (1990) found that maximum reaction efficiency for the carboxymethylation of potato starch should require higher SME values (> 280 kWh/t), which are not experimentally realisable. Thus, to achieve the high potential of potato starch as an ingredient, whether for food or non-food applications, requires a better understanding and thus control of the processing by extrusion (De Vries, 1991).

The aim of this work is to provide some explanations for the difficulties encountered during extrusion of potato starch in order to improve its processability. Specific attention has been devoted to the chain splitting phenomenon during thermomechanical treatment. Another important point is starch viscosity, since it governs the transport phenomena in the screw channels, once starch is in the homogeneous molten phase. Therefore, this variable was measured using a purpose built slit die rheometer. The attainment of the homogeneous molten phase during extrusion was also studied specifically, by equipping the extruder with a longitudinally split barrel module.

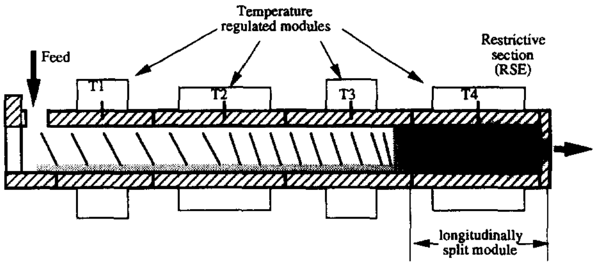
MATERIALS AND METHODS

Materials

Potato starch was supplied by Roquette (F. 62 Lestrem). Its moisture content was 0.18. (In this paper all moisture contents are quoted g H_2O/g total wet weight.)

---

*Author to whom correspondence should be addressed.



Pitch (mm) :	50	35	25	15	15	2 x ø4 die
Length (mm):	400	200	150	200	50	30

Fig. 1. Axial section of the twin screw extruder showing different zones, and of screw configuration.

Extrusion

Starch was processed on a twin screw extruder Clextral BC 45 (length:1.00 m) provided with four electrically heated and water cooled modules. Screw configuration included positive displacement trapezoidal screw elements with decreasing pitches and a reverse screw element at the end, just before the die (Fig. 1).

Standard extrusion experiments

The die was composed of two cylindrical tubes of length 30 mm and diameter 4 mm. The solid feed rate was kept constant (25 kg/h) and the following parameters were modified in the range indicated:

- temperature of the last heating zone T_b: 120/210 °C
- screw rotation speed N: 140/200 rpm
- rate of added water (in % of solid feed rate) $w+$: 5/25%.

The control of the extrusion was performed through the measurement of product pressure (P_d) and temperature (T_p) at the die and the measurement of specific mechanical energy (SME), according to the procedure described previously (Della Valle *et al.*, 1989). Total feed rate was measured by weighing the product exiting the die for a given interval of time. The checked total throughput was compared with the sum of input feed rates, water and starch, and was up to 3% higher than the latter, due to loss of water as steam. Sampling at the die was carried out when the three process variables (P_d, T_p, SME) reached a steady value, each time one of the three parameters (T_b, N, $w+$) was modified. Samples were then dried for 20 min in an air convection oven at 100°C and ground in order to pass through a 500 mm mesh sieve.

Sampling along screws

In order to study the transformation along the screw, a longitudinally split barrel module (length:0.25 m) was used just before the die. The upper part could be removed within 2 min after a deadstop of the machine and rapidly cooled down to a temperature lower than 100°C. Thereby, samples were taken in the channels of the screws and then vacuum-dried at 40°C. They were finally ground in a grinder cooled with liquid nitrogen. These specific drying and grinding procedures were chosen to minimize the modification of the starch in the samples. Three trials were conducted with this arrangement.

Melt viscosity measurements

A slit die rheometer with balanced feed rate, called Rheopac, was attached to the die head, replacing the simple one. The basic principle of this device is to vary the shear rate in the die whilst maintaining extrusion conditions steady, so that the product receives the same thermomechanical treatment. This is done by adjusting the piston valves at the entrance of the channels, to keep the upstream pressure constant. Its precise design and working conditions are described in detail by Vergnes *et al.* (1993). Data were analysed according to the classical slit die rheometry procedures (see for instance, Dealy & Wissbrun, 1989) in order to derive the apparent shear rate:

$$\dot{\gamma}_a = \frac{6Q}{\rho W h^2} \tag{1}$$

and the wall shear stress:

$$\tau_w = \frac{h}{2}\frac{1}{1+\frac{h}{W}}\frac{\Delta P}{\Delta L} \tag{2}$$

where Q is the mass flow rate in the channel, ρ the density of the melt, linearly computed from ρ_s, the density of starch granule ($\rho_s = 1450\,\mathrm{kg/m^3}$; Colonna *et al.*, 1989) and water density, h and W the height and width of the rectangular channel and $\Delta P/\Delta L$ the pressure gradient along the channel. The Rabinowitsch correction is then performed to derive the real shear rate:

$$\dot{\gamma}_r = \frac{2m+1}{3m}\dot{\gamma}_a \tag{3}$$

where

$$m = \frac{d(\log \dot{\gamma}_a)}{d(\log \tau_w)}$$

Finally, the viscosity is given by:

$$\eta = \frac{\tau_w}{\dot{\gamma}_r} \tag{4}$$

For each condition of flow, one sample was taken, dried and ground for further analysis.

Starch characterization

Granular structure disruption

Differential scanning calorimetry (DSC) was used in order to determine the residual crystalline structure of starch after processing, mainly in the trials with the opening barrel. Twenty milligrams of vacuum-dried samples were weighed in the DSC pan and the pan was filled with approximately 100 mg of water. A Setaram DSC 111 was used with a heating rate of 3°C/min, up to 90°C. Temperatures of peak, onset and end were recorded and the specific enthalpy of the gelatinization endotherm measured.

Suspensions of extruded samples were observed on an Olympus light microscope (×300) equipped with polarizing filters: the presence of residual birefringence revealed the remaining granular structure.

Macromolecular degradation

The intrinsic viscosity of a solution of 250 mg of starch diluted into 50 ml KOH (0.2 N) was measured on an automated Ubbelhode viscometer (25°C, solvent flow time: 166 s) by repeated dilutions up to six times, in the range 5–0.8 mg/ml.

Low pressure size exclusion chromatography was performed by injecting 2 ml of 0.1 N KOH solution of starch on a Fractogel HW 75 column (flow rate: 18 ml/h). Total recovery was about 95%.

When conducted on samples taken from Rheopac series, intrinsic viscosity measurements were performed at least on three points of the series, corresponding to the first, last and average shear rate values. Iodine was added to collected fractions and tested on a spectrophotometer to determine the wavelengths of maximum absorption (λ_{max}). These values were 540 and 620–640 nm for amylopectin and amylose, respectively (John *et al.*, 1983).

RESULTS AND DISCUSSION

Thermomechanical treatment and macromolecular degradation

A preliminary set of trials was conducted in order to select the best extrusion conditions for the viscosity measurements. These conditions and results are reported in Table 1, which shows the wide range of thermomechanical treatments carried out, at different values of P_d, T_p and SME.

The values encountered here ($100 < \text{SME} < 350$ kWh/t) were much larger than the ones reported by Senouci and Smith (1986) for potato granules in the same range of moisture content, but extrusion parameters (screw speed, temperature, screw geometry) were not detailed in this work. The same authors later reported much

Table 1. Extrusion conditions and global results obtained for potato starch

	Extrusion conditions							Main results		
Set no.	Screw speed N (rpm)	Total feed rate Q (kg/h)	Barrel or die temperature T_d (°C)[a]	Moisture content (MC)	Product temperature T_p (°C)	Specific mechanical energy (SME) (kWh/t)	Pressure at diehead P_d (MPa)	Intrinsic viscosity $[\eta]$ (ml/g)	Power law index (m)	Consistency K (Pa.s**m)
A[b]	140	25	120	0.22	122	232	5.8	140		
B	200	25	120	0.26	122	310	3	127		
C	140	25	210	0.32	168	143	1.4	170		
D	140	25	120	0.35	121	107	5.1	210		
E	200	25	120	0.35	123	190	2.75	140		
1	145	25	155	0.22	165	275	6.2	70	0.45	2352
2	130	25	155	0.26	160	215	7.4	108	0.48	3242
3	145	25	155	0.26	162	220	7	112	0.49	2707
4	180	24	155	0.26	162	320	5.7	98	0.65	974
5	145	35	135	0.32	139	125	9.5	185	0.34	7630
6	170	31	139	0.32	140	165	8.5	150	0.42	4200
7	145	28	155	0.32	160	130	7.4	180	0.46	3440
8	220	27	155	0.32	162	200	4.6	150	0.4	2762
9	145	26	172	0.32	176	127	4.8	170	0.49	1700
10	150	24	180	0.32	190	255	4.1	80		
11	125	30	180	0.34	190	125	2.9	135		
C1[c]	160	36	150	0.26	160	120	5.3	103	0.54	1664
C2	160	35	155	0.32	160	130	5	93	0.72	486

[a] For trials A–E, the temperature indicated is for the barrel section before the die, whereas for 1–11, it is the temperature of the Rheopac die.

[b] Trials noted by letters were performed on standard extrusion configurations, whereas those noted by figures were made with the Rheopac die. Trials B, D and E were repeated with the longitudinally split barrel module.

[c] C1 and C2 refer to maize starch with the same ratio AMY/AMP as potato starch.

higher values of SME ($300 < \mathrm{SME} < 600\,\mathrm{kWh/t}$), for potato granules, using various screw speeds (100–250 rpm) and a slit die, which is more restrictive, and is supposed to increase the degree of filling of the extruder (Senouci & Smith, 1988). The determination of the specific mechanical energy is important since it is known to affect directly the macromolecular state of starch, as shown in Fig. 2 (reported values of intrinsic viscosity are the average of three measurements and vary within a 5% error interval). An increase in mechanical energy leads to a decrease of intrinsic viscosity, interpreted as a drop in the degree of polymerization. This depolymerization for starch extrusion has already been demonstrated before, for cereal starches (Meuser & Van Lengerich, 1984; Vergnes *et al.*, 1987; Della Valle *et al.*, 1989; Parker *et al.*, 1990), but the extent of degradation is all the more important in the case of potato, as the value for native starch is high ($[\eta] = 450\,\mathrm{ml/g}$) compared to the values given for maize starch in the previously mentioned work ($\sim 220\,\mathrm{ml/g}$). The vertical line represents a limit observed experimentally ($\mathrm{SME} > 150\,\mathrm{kWh/t}$), beyond which extrudates begin to have a brown colour, whatever the extrusion conditions.

Chromatograms (SEC profiles) provide another insight into this phenomenon. Elution volume, expressed as K_{av}, is inversely related to the hydrodynamic volume, i.e. molecular weight. In the case of native starch, a first peak is obtained after the void volume, for $K_{av} < 0.3$, which corresponds to the amylopectin macromolecules (75–80% of total recovered material), and a second one around $K_{av} = 0.5$, which corresponds to the amylose macromolecules as shown by the values of λ_{max} (Fig. 3). Chromatograms of extruded samples exhibit several features making them distinct from native: firstly, there is a sharp decrease of the amylopectin peak eluted at $K_{av} < 0.35$; secondly, this peak is shifted towards higher K_{av}; thirdly, the amylose peak is much higher and as for amylopectin, it is shifted towards higher K_{av}, in most cases (Fig. 3b and c). Iodine spectra have not been shown here, because they were very similar to native starch. The interactions of iodine with either amylose or amylopectin were not modified after extrusion cooking. Colonna and Mercier (1983) demonstrated that the chemical structures of amylose and amylopectin are not modified significantly by random degradation occurring during extrusion cooking. Furthermore, amylose depolymerization gives macromolecules, the degree of polymerization (DP) of which is higher than 100, a limit beyond which interactions with iodine are constant whatever the DP. These results are also in agreement with those of Yamada *et al.* (1990). This degradation is all the more remarkable as SME is increased for a constant temperature (160°C) (Fig. 3b). In contrast, this trend is not straightforward in the case of temperature variations (160/190°C), for constant SME (130 kWh/t) (Fig. 3c). In the latter case, the influence of temperature is not so obvious, because different values of intrinsic viscosities were obtained for the same SME, reflecting

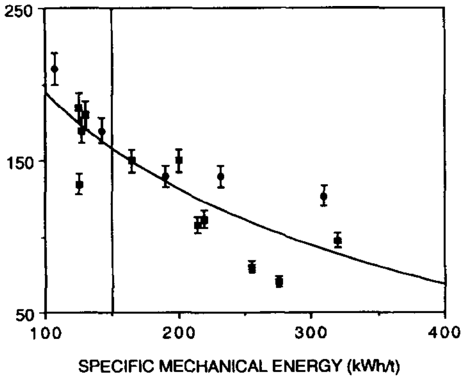


Fig. 2. Intrinsic viscosity of extruded potato starch as a function of SME for all experiments. Cylindrical die (●); and slit die rheometer Rheopac (■).

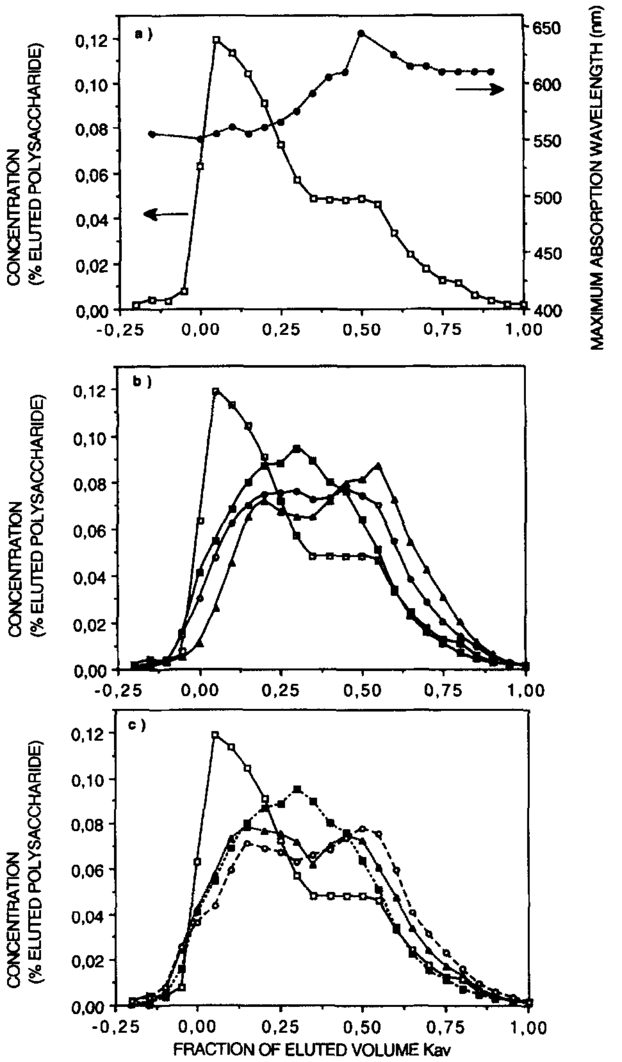


Fig. 3. SEC profiles of (a) native (□); and processed starches; (b) for various SME at 160°C: (■) 130 kWh/t; (○) 215 kWh/t; (▲) 320 kWh/t; (c) for various temperatures at 130 kWh/t: (■) 160°C; (●) 176°C; (▲) 190°C.

different average macromolecular weights. This finding may seem contradictory to those of Yamada *et al.* (1990) who found an increase in the macromolecular degradation of potato starch with increasing extrusion temperature; but, as SME was not measured in this study, it cannot be concluded that this observation was either a consequence of an increase of severity of the mechanical treatment or the influence of temperature.

Viscous behaviour

Except for the last conditions, achieved at high temperature (Table 1, Nos 10 and 11), all pressure profiles in the slit die were linear (Fig. 4a). At 190°C, the pressure drop became steeper near the outlet (Fig. 4b), which can be explained by the apparition of vapour bubbles in this part of the channel, since the melt pressure is lower than the pressure of water vapour (p_{vs} ~1.2 MPa). Except in these trials (Nos 10–11), potato starch exhibited pseudoplastic behaviour and its viscosity could be described by a power law:

$$\eta = K\dot{\gamma}_r^{m-1} \qquad (5)$$

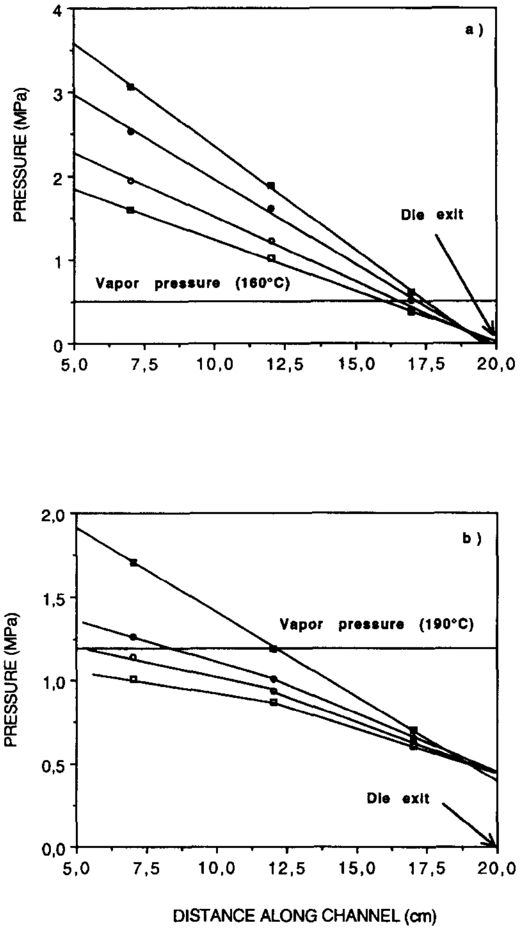


Fig. 4. Example of pressure profiles for various shear rates: (■) 100/s; (●) 65/s; (○) 33/s; (□) 20/s. (a) representative of classical extrusion condition (trial 7); (b) at high temperature (190°C; trial 10).

As for other starches, the consistency K and the power-law index m depend on moisture, temperature and thermomechanical history of the melt. This last factor is controlled mainly by the SME and assessed by the measurement of intrinsic viscosity, as shown previously. The thermomechanical history inside the barrel along the screws was of interest, rather than the effect of shear in the die rheometer. It was checked that, during the rheological measurements, the macromolecular state of starch was not modified. Firstly, the motion of the piston valves did not induce any change in the extruder's operating conditions and the value of SME remained constant. Secondly, it was shown that the intrinsic viscosity, measured on the samples produced under extreme and average shear condition in the die channel, for the same extrusion conditions, did not vary beyond a 5% error interval. Lastly, chromatograms performed on two samples produced under the same extrusion conditions (No. 7), but under extreme average shear rates in die channel, did not exhibit significant differences (Fig. 5). All three observations show that there is no significant modification of the macromolecular state due to the variation of shear rate in the die channel, over the experimental range encountered in this device (10–100/s). In fact, depolymerization is obtained for much higher shear rates ($>10^4$/s) and stresses (>0.1 MPa) than in our case, when processing sweet potato starch on a capillary rheometer (Fujio *et al.*, 1993). Thus, in our work, macromolecular degradation is only due to the thermomechanical treatment in the screw channels and not in the die.

The influence of this factor on melt viscosity can be shown at 160°C for two levels of moisture content, comparing sets 3 and 4 (moisture content (MC) = 0.26) and sets 7 and 8 (MC = 0.32). At low moisture content, the increase of SME from 220 to 320 kWh/t induced a decrease of average macromolecular weight, as shown by the decrease of intrinsic viscosity (from 112 to 98 ml/g). The corresponding drop in melt viscosity may be

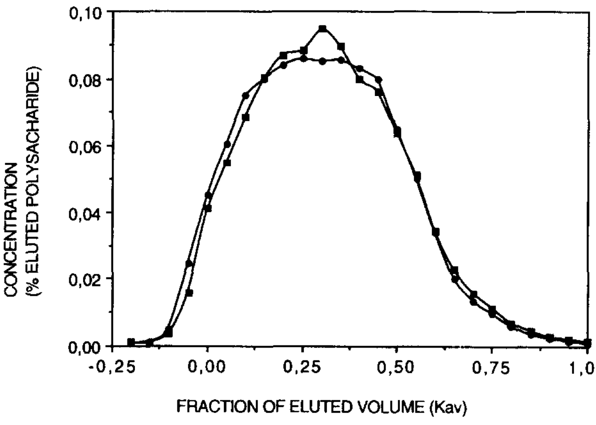


Fig. 5. SEC profiles of extruded starch (trial 7) for two different shear rates in the die channel: (■) 120/s; (●), 20/s.

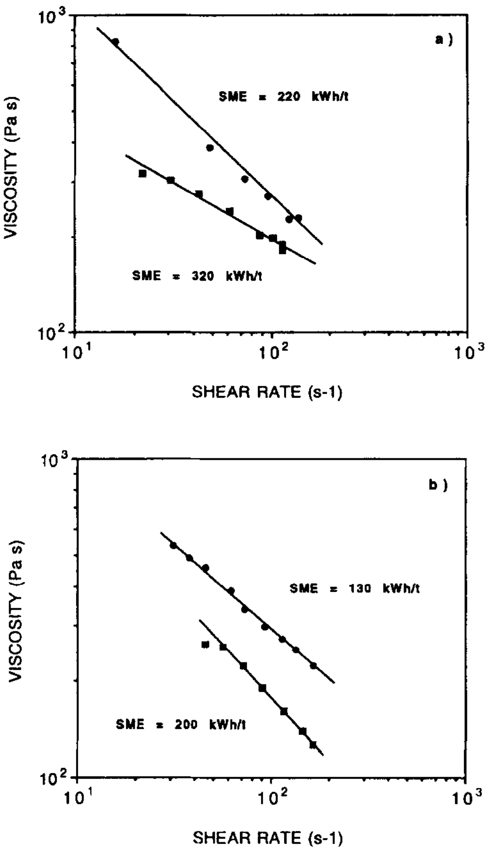


Fig. 6. Melt potato starch flow curves for two levels of moisture content (a: MC = 0.26; b: MC = 0.32) and two levels of thermomechanical treatments at 160°C.

seen in Fig. 6. For higher moisture content, an increase in SME also leads to a decrease of melt viscosity. These observations are essentially confirmatory, as Vergnes and Villemaire (1987) and Parker *et al.* (1990) already noticed a decrease of maize starch melt viscosity with intrinsic viscosity, as a consequence of an increase of SME; it underlines the necessity of taking macromolecular degradation into account when measuring starch melt viscosity.

The influence of temperature was tested for MC = 0.32 and SME~130 kWh/t, between 140 (No. 5), 160 (No. 7) and 176°C (No. 9). As expected, a decrease in melt viscosity was observed (Fig. 7). However, this decrease seemed larger between 160 and 176°C, and this may be due to the lower intrinsic viscosity $[\eta]$ obtained for experiment 9 (170 ml/g), in agreement with the preceding results.

For similar reasons, the influence of MC could not be observed directly, because reducing MC led to an increase of SME, for instance when comparing trials 7 and 3. However, when comparing sets 8 and 3 ($[\eta] = 150$ and 112 ml/g respectively), it was observed that the increase in MC led to the expected decrease in melt viscosity.

Senouci and Smith (1988) proposed a model of the viscosity of molten potato granules, but this model contains a term depending on screw speed, which may affect viscosity differently according to the kind of extruder and screw geometry employed. So, taking into account the impact of macromolecular degradation on melt viscosity and its link with the specific mechanical energy, we would rather consider the model suggested by Vergnes and Villemaire (1987) and Parker *et al.* (1990), for maize starch:

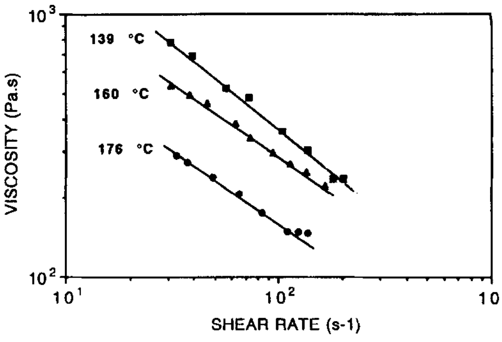


Fig. 7. Melt potato starch flow curves as a function of temperature for MC = 0.32, SME~130 kWh/t.

$$\eta = K\dot{\gamma}_r^{m-1} \tag{6}$$

with

$$K = K_0 \exp\left[E/R\left(\frac{1}{T_a}\right) - \alpha\mathrm{MC} - \beta W\right] \tag{7}$$

and

$$\begin{aligned} m = m_0 + \alpha_1 T + \alpha_2\mathrm{MC} + \alpha_3\mathrm{SME} + \alpha_{12}\mathrm{TMC} \\ + \alpha_{13}\mathrm{TSME} + \alpha_{23}\mathrm{MCSME} \end{aligned} \tag{8}$$

where T_a is the temperature in K. Values of coefficient (K_0, E/R, α, β, m_0, α_1.... α_{23}) were calculated by multilinear regressions on the values of K and m reported in Table 1. The results are given in Table 2, which also contains the corresponding values for starch obtained by Vergnes and Villemaire (1987). Regression coefficients (r^2) for K and m were 0.88 and 0.92, respectively. In the case of potato starch, the dependency of K on temperature (coefficient E/R) and on macromolecular degradation (coefficient β) was higher than for maize starch. According to the value of intrinsic viscosity of native potato starch, this difference may have been due to the larger size of potato starch macromolecules, mainly amylose (Klinger & Zimbalski, 1992), which enhanced the thermomechanical sensitivity of this substrate.

Vergnes *et al.* (1993) have shown the procedure for assessing the adequacy of such model by extending the time–temperature superposition principle to the other variables, MC and SME in order to compute a master curve by plotting $\eta/a = f(\dot{\gamma}_r a)$, where a is a generalized shift factor. When we choose curve 3 as the reference curve (MC = 0.26, T = 162 °C, SME = 220 kWh/t) for

Table 2. Values of coefficients of the rheological models of molten starch

Model	m_0	α_1 $(°C)^{-1}$	α_2	α_3 $(kWh/t)^{-1}$	α_{12} $(°C)^{-1}$	α_{13}	α_{23} $(kWh/t)^{-1}$	K_0 $(Pa.s^m)$	E/R (K)	α	β $(J/m^3)^{-1}$
Maize (Vergnes & Villemaire, 1987)	0	$6.54x10^{-4}$	0.112	—	$7.28x10^{-3}$	—	—	7.36	4250	10.6	$0.89x10^{-9}$
Potato (present work)	14.33	−0.997	−60.6	0.044	0.418	$-2.1x10^{-4}$	−0.0341	0.34	5710	9.45	$1.56x10^{-9}$

our results, the shift factor for every other flow curve i, is computed by:

$$a(T, \mathrm{MC}, \mathrm{SME})_i = \exp\left[\frac{E}{R}\left(\frac{1}{T_i} - \frac{1}{T_3}\right) - \alpha(\mathrm{MC}_i - \mathrm{MC}_3) - \beta(\mathrm{SME}_i - \mathrm{SME}_3)\right] \quad (9)$$

where T_i, MC_i and SME_i are the values of the variables for the flow curve i. The resulting master curve obtained from nine experimental flow curves is shown in Fig. 8; every flow curve superimposes satisfactorily onto flow curve 3. It also enables the definition of the viscous behaviour of molten potato starch over the range 10–600/s, which corresponds to the range of conditions usually encountered in the twin screw extrusion process.

Comparison with maize starch has already shown that, under the same conditions of extrusion (T_p, MC, SME), potato starch is more viscous. However, if the comparison is made for same macromolecular state, i.e. for same value of intrinsic viscosity, the difference in melt viscosity between the two starches is considerably reduced (Della Valle *et al.*, 1992). Meanwhile, the difference in amylose/amylopectin ratio may also have some influence on molten starch viscous behaviour (Lai & Kokini, 1990; Della Valle *et al.*, 1994). Thus, a comparison should be made for same value of amylose content, i.e. 0.23 for potato starch. In a previous work, such blends have been made starting from starches with high amylose content (amylomaize, 70% amylose) and without amylose (waxy maize) (Della Valle *et al.*, 1994).

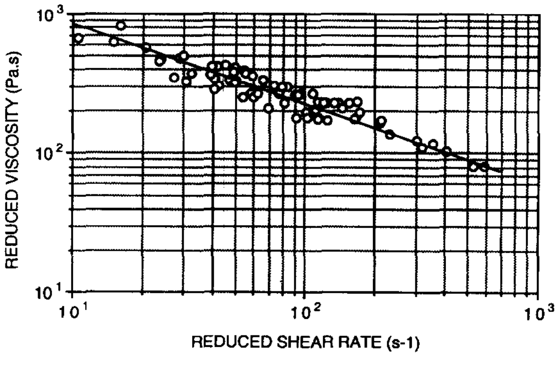


Fig. 8. Master curve of potato starch at $T_p = 160°C$, MC = 0.26, SME = 220 kWh/t.

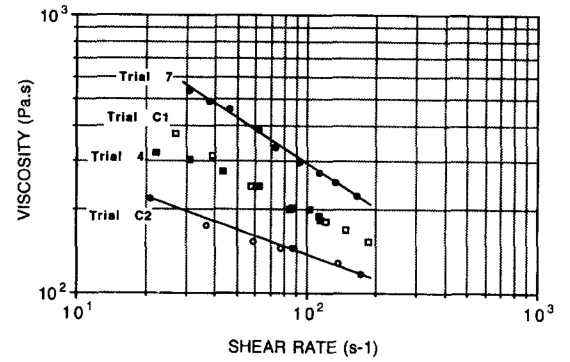


Fig. 9. Comparisons between potato starch (filled symbols) and blend of maize starch (open symbols) having the same amylose content, for the same thermomechanical treatment (SME = 125 kWh/t) ((○): $[\eta] = 94$ ml/g; (●): $[\eta] = 180$ ml/g) and same macromolecular degradation ($[\eta] = 100$ ml/g) ((□): SME = 120 kWh/t; (■): SME = 320 kWh/t).

Two sets of experiments, namely C_1 and C_2, have been selected and main results also reported in Table 1. C_2 can be compared to trial 7, having the same values of MC (0.32), T_p (160 °C) and SME (130 kWh/t); however, the flow curve of potato remains much higher as its intrinsic viscosity is very high: 180 ml/g, instead of 95 ml/g for the maize blend of same amylose content (Fig. 9). If a comparison is made between the trials having closer values of intrinsic viscosity (C_1 and C_4, 103 and 98 ml/g, respectively) and for similar conditions of moisture content (MC = 0.26) and temperature (160°C), the flow curves are very close to each other; this comparison is possible because SME was considerably greater in the case of potato starch (320 kWh/t for trial 4, instead of 120 kWh/t for trial C_1) in order to reach a similar level of macromolecular degradation.

To summarize, for the same extrusion conditions (T_p, MC, SME), molten potato starch exhibits much higher viscosity, mainly because of its higher initial molecular weights of amylose and amylopectin. This feature leads to higher power requirements and a more difficult processing behaviour.

Obtaining a homogeneous molten phase

The transition between the solid conveying zone and homogeneous molten phase has been observed after deadstops and barrel opening, for three thermomechanical treatments (B, D, E). Firstly, in experiment B, the highest amount of SME (310 kWh/t) was reached for a high screw speed (200 rpm) and a low moisture content (MC = 0.26). Then, in experiment E, by increasing moisture content (MC = 0.35), SME was reduced (200 kWh/t). In experiment D, SME reached its lower level (107 kWh/t) by decreasing the screw speed. Once the final part of the barrel was opened, the contents of 12–13 C-chambers on both screws could be observed.

In all three experiments, the whole reverse screw element and two to three C-chambers before were completely filled with a continuous phase, which became glassy during cooling before opening. The preceding chambers were incompletely filled with a similar product, except in the case of experiment D (lowest SME), where the starch had a solid powder form, five or six chambers before the filled section. These observations are reported in Fig. 10, which also shows optical micrographs of samples taken at various locations. In their native form, starch granules are easily recognizable. For trial D (screw (a)), in the zone where samples were taken in a powdery form (No. 12), large solid entities were found, with partly lost birefringence, which may result from minor deformation of the granule under shear. For higher SME (trials B and E, screw (b)), for a similar location, only smaller particles could be seen, with faded birefringence, lost in a molten mass of starch. For other locations (C-chambers 7 and 2), nearer to the die, samples were under the same form whatever the SME, with more or less numerous and small amorphous particles, and complete loss of birefringence, probably resulting from glassy sample grinding. Samples taken in the reverse screw element (RSE) were darker and browner, with the local increase of SME.

Differential scanning calorimetry (DSC) was performed on the samples taken in C-chamber 12, i.e. about 20 cm from the die end. An endotherm could be detected only in the case of trial D, for the lowest SME conditions, but this endotherm was much smaller compared with the one obtained for native starch (Fig. 11). This is consistent with the preceding observations, since no endotherm was seen for samples taken from trials performed at higher SME.

Thus, a homogeneous molten phase could be obtained before the material was compressed in the

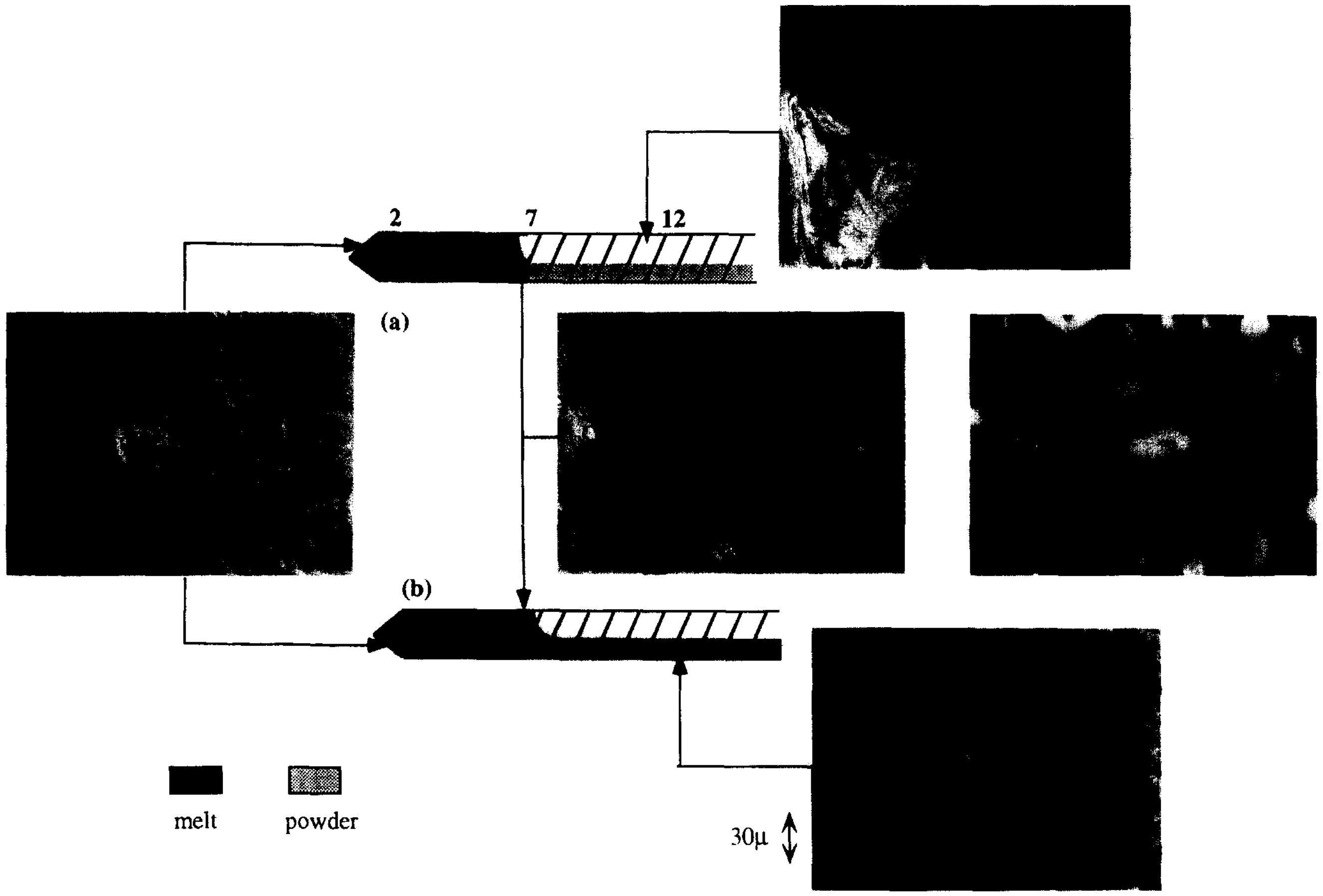


Fig. 10. Influence of SME on degree of filling, macroscopic and microscopic state of potato starch along the screw (a) for trial D (SME = 107 kWh/t); and (b) for trials B and E (SME = 190 and 310 kWh/t). Reverse screw element (RSE) is located just before the die and occupies three C-chambers.

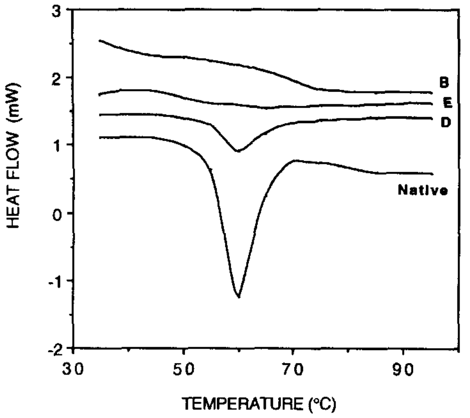


Fig. 11. Thermograms, in an excess of water, of extruded samples of potato starch, taken 20 cm from the die.

screw channels, in the unfilled section usually called 'conveying section', provided the SME was sufficiently high (SME > 110 kWh/t). These results can be connected to the previous ones, showing an increased degradation (appearance of brown colour) as soon as the SME became greater than 150 kWh/t. However, they are in contradiction with the mechanism currently suggested, according to which solid/melt transition occurs very rapidly (one or two C-chambers), just after compaction (or sintering) in the last direct screw elements preceding a restrictive element, the active part of the screw being a low fraction of total length. This mechanism relies on numerous observations made on maize starch (Colonna *et al.*, 1983), wheat starch (Diosady *et al.*, 1985; Cai & Diosady, 1993), maize grits (Kirby *et al.*, 1988), wheat flour (Barrès *et al.*, 1990). Such observations have not been made for potato starch, except by Senouci and Smith (1986), who reported the presence of a continuous glassy phase located before the kneading paddles, but only for a higher MC (50%). This difference in behaviour, compared to cereal starchy materials, is characterized, in the case of potato starch, by an early appearance of the homogeneous molten phase.

It may be caused by a greater sensitivity to interparticulate friction or heat. The first phenomenon is difficult to study in the kinetic conditions of extrusion. However, results obtained on a Jenike shear cell can offer an initial basis of comparison. The dependence of the friction coefficient, determined from Coulomb's plots, on moisture content, did not show any significant difference between potato starch and other starchy materials (Della Valle & Vergnes, 1994). In contrast, DSC results obtained on starch thermal transition show that the melting temperature of potato starch is 30–15°C lower than those of wheat starch for moisture contents between 15 and 30%, which corresponds to the moisture levels used in this study (Donovan *et al.*, 1983). Although these results concern melting in a shear-free environment, it is possible to suggest that starch melting occurs earlier in the extruder because of lower transition temperatures.

Whatever the cause of 'early melting', the usual solid conveying mechanism turns to a viscous melt conveying one. Resistance to flow is more significant for viscous fluids than for powders, since the shear stress is different from zero in the first case, when the relative pressure is zero. Thus it is likely that melt viscous conveying is more energy-consuming. The energy requirement is particularly high as the melt viscosity of potato starch is higher than other starches. As a consequence, macromolecular degradation is increased because of the more intense thermomechanical treatment. An improvement of processability may result from shortening the conveying section, in order to obtain the melting transition just before the restrictive elements, as found for other starches. Increased cooling of barrel and screws may also help to keep the product temperature lower than its melting temperature, by balancing the heating effect of interparticle friction. The theoretical study of Barrès *et al.* (1991) also suggests that screw speed should be kept as low as possible, and feed rate as high as possible, to limit this phenomenon. This is consistent with the necessity of maintaining a low level of SME, provided that power requirements of the motor drive allow it. Adding water may not improve the processability, since melting temperature is lower for higher moisture contents, and it also leads to reduced die expansion.

CONCLUSION

Potato starch extrusion exhibits two main differences when compared to other starches: high melt viscosity and early melting in the extruder. Both explain the difficulties usually encountered when processing this material, characterized by high energy requirements. Early melting may be due to transition temperatures lower than the values encountered for cereal starches. High melt viscosity is linked to the higher molecular weight of potato starch. Once macromolecular chains are split and the molecular weight reduced to the same level as other starches, under the effect of thermomechanical treatment, identical melt viscosity is found for the same moisture content and temperature, whatever the botanical origin of starch.

These difficulties may be solved by shortening the screw length in which starch is in a homogeneous molten phase. This requires a better knowledge of the melting transition of low water starchy products under high shear stresses. A better control of these phenomena would also help in reducing macromolecular degradation at this stage, which, whatever the origin of starch, results in a loss of functional properties.

REFERENCES

Barrès, C., Vergnes, B. & Tayeb, J. (1991). *J. Food Eng.*, **15**, 167–185.

Barrès, C., Vergnes, B., Tayeb, J. & Della Valle, G. (1990). *Cereal Chem.*, **67**, 427–433.

Cai, W. & Diosady, L.L. (1993). *J. Food Sci.*, **58**, 872–875, 887.

Colonna, P., Melcion, J.P., Vergnes, B. & Mercier, C. (1983). *J. Cereal Sci.*, **1**, 115–125.

Colonna, P. & Mercier, C. (1983). *Carbohydr. Polym.*, **3**, 87–108.

Colonna, P., Tayeb, J. & Mercier, C. (1989). In *Extrusion Cooking*, eds C. Mercier, P. Linko & J.M. Harper. AACC, St. Paul, pp. 247–320.

Dealy, J.M & Wissbrun, K.F. (1989). In *Melt Rheology and its Role in Plastics Processing*. Van Nostrand Reinhold, New York, 665 pp.

Della Valle, G., Kozlowski, A., Colonna, P. & Tayeb, J. (1989). *Lebensm. Wiss. u.- Technol.*, **22**, 279–286.

Della Valle, G., Patria, A., Colonna P. & Vergnes, B. (1994). In *Progress and Trends in Rheology, IV*, eds C. Gallegos *et al.* Steinkopf, Darmstadt, pp. 224–227.

Della Valle, G. & Vergnes, B. (1994). In *La Cuisson-Extrusion*, eds Colonna P., Della Valle G. Lavoisier Tec and Doc, Paris, pp. 439–468.

Della Valle, G., Vergnes, B., Tayeb, J. & Boché, Y. (1992). In *Theoretical and Applied Rheology*, eds P. Moldenaers & R. Keunings. Elsevier, London, pp. 702–704.

De Vries, J.A. (1991). *Int. Food Ing.*, **1**, 51–54.

Diosady, L.L., Paton, D., Rosen, N., Rubin, L.J. & Athanasoulias, C. (1985). *J. Food Sci.*, **50**, 1697–1699, 1706.

Donovan, J.W., Lorenz K. & Kulp, K. (1983). *Cereal Chem.*, **60**, 381–387.

Fujio, Y., Igura, N., Hayashi, N. & Hayakawa, I. (1993). *Starch*, **45**, 432–436.

John, M., Schmidt, J. & Kneifel, H. (1983). *Carbohydr. Res.*, **119**, 254–259.

Kirby, A.R., Ollett, A.L., Parker, R. & Smith, A.C. (1988). *J. Food Eng.*, **8**, 247–272.

Klinger, R.W. & Zimbalski, M. (1992). *Starch*, **44**, 414–419.

Lai, L.S. & Kokini, J.L. (1990). *J. Rheol.*, **34**, 1245–1266.

Mercier, C. (1977). *Starch*, **29**, 48–52.

Meuser, F., Gimmler, N. & Oeding, J. (1990). *Starch*, **42**, 330–336.

Meuser, F. & Van Lengerich, B. (1984). In *Thermal Processing and Quality of Foods*, eds P. Zeuthen *et al.* Elsevier, London, pp. 180–184.

Parker, R., Ollett, A.L. & Smith, A.C. (1990). In *Processing and Quality of Foods*, ed. P. Zeuthen. Elsevier, London, pp. 1290–1295.

Senouci, A. & Smith, A.C. (1986). *Starch*, **38**, 78–82.

Senouci, A. & Smith, A.C. (1988). *Rheol. Acta*, **27**, 546–554.

Vergnes, B., Della Valle, G. & Tayeb, J. (1993). *Rheol. Acta*, **32**, 465–476.

Vergnes, B. & Villemaire, J-P. (1987). *Rheol. Acta*, **26**, 570–576.

Vergnes, B., Villemaire, J-P., Colonna, P. & Tayeb, J. (1987). *J. Cereal Sci.*, **5**, 189–202.

Yamada, T., Suzuki, K., Katuzaki, H., Hisamatsu, M. & Komiya, T. (1990). *Die Stärke*, **42**, 217–223.