Carbohydrate Polymers **13** (1990) 69–84

Microstructural Changes during the Twin-Screw Extrusion Cooking of Maize Grits

A.-L. Ollett, R. Parker, A. C. Smith, M. J. Miles & V. J. Morris

AFRC Institute of Food Research, Norwich Laboratory, Colney Lane, Norwich NR4 7UA, UK

(Revised version received 10 July 1989; accepted 30 July 1989)

ABSTRACT

Microstructural changes which occur during the extrusion cooking of maize grits were studied using optical microscopy and X-ray diffraction. The complete disruption of the maize grit particles and their constituent starch granules was found to be related to changes in extruder die pressure, screw torque and product solubility and water absorption. The disruption was found to depend upon extrusion moisture, barrel temperature and screw configuration. It occurred over a narrow range of specific mechanical energy input, 115–145 W h kg^{-1}.

The E-type form of the crystalline amylose–lipid complex was found to occur throughout the temperature range 90–150°C when the maize grit was extruded with low conveying efficiency screws.

INTRODUCTION

The modern twin-screw extrusion cooker is a versatile piece of food processing machinery which can be used to produce a variety of microstructural transformations in starchy food materials. The microstructure is an important factor in determining the functional and textural properties of extruded products. It affects properties such as water solubility, dispersion viscosity (Doublier *et al.*, 1986), gelling behaviour (Mestres *et al.*, 1988), and digestibility (Bjorck *et al.*, 1984). Mechanical measurements of texture have been shown to be sensitive to the porous structure of foamed extrudates (Hayter *et al.*, 1986).

Microstructural changes occur at all length scales during extrusion from the molecular scale to the macroscopic. At the shortest length scale, the molecular scale, it has been shown that macromolecular degradation

Carbohydrate Polymers 0144-8617/90/\$03.50

of starch occurs (Colonna & Mercier, 1983) and amylose–lipid complexes form (Mercier *et al.*, 1979, 1980).

At the supramolecular scale the partially ordered semi-crystalline structure of the starch granule can be modified (Colonna *et al.*, 1987). Melting of the native crystallites can occur in the extruder which results in the water being redistributed throughout the granule. The birefringence of the granules disappears as the orientation of the crystalline regions is lost during melting and subsequent granule swelling (Blanshard, 1987). On leaving the extruder the material cools and there is potential for recrystallisation of amylose, amylopectin and their lipid complexes. The existing X-ray diffraction studies of extruded products have only revealed recrystallised amylose–lipid complexes (Mercier *et al.*, 1979) which indicates that the bulk of the amylose and amylopectin remains in an amorphous state.

At the microscopic length scale the granules can lose their integrity and be disrupted into a homogeneous plasticised melt. If a flour or grit is being extruded then a significant fraction of non-starch components is present and the starch granules are only part of a more complex composite structure. Just as at the granule scale, the particles of flour or grit can be disrupted with little retention of the native structure (Faubion & Hoseney, 1982). At the macroscopic scale extrudates foam resulting in an expanded porous structure of low bulk density.

This study is part of a larger investigation of screw configuration effects in the extrusion cooking of maize grits (Kirby *et al.*, 1988). The aim is to investigate the effects of screw configuration and its interaction with extrusion moisture and barrel temperature in controlling the microstructure of extruded maize grits. An instrumented twin-screw extruder was used which allowed die pressure and torque on the screws to be logged. The water absorption and solubility of the ground product were measured. Optical microscopy was used to give direct information on changes of microstructure at the grit particle and starch granule level. X-ray diffraction allowed a qualitative identification of the crystalline forms present in the product.

EXPERIMENTAL

Materials

The feed material was a single batch of maize grit ('extra fine snack grit', Pauls Agriculture Ltd, Hull) with a moisture content of 0·117 (wet weight basis (w.w.b.)).

Extrusion

A Baker-Perkins MPF50D co-rotating twin screw extruder (APV Baker, Peterborough, Cambridgeshire UK), fed by a KTRON loss-in-weight feeder (K-TRON-SODER AG, Niederlenz, Switzerland) was used in this study. The extruder barrel was heated by cartridge heaters in five zones along the length of the extruder. Each zone temperature was controlled by a Eurotherm controller (Eurotherm Ltd, Worthing, West Sussex, UK). The temperature profiles are shown in Table 1. They were chosen to give stable extrusion over the whole range of conditions studied. This limited experimentation to relatively low temperatures as compared with some earlier studies of the extrusion cooking of maize grits (Anderson *et al.*, 1969, Mercier & Feillet, 1975).

TABLE 1
Temperature Profiles on the Extruder Barrel

Zone	*Zone 6 temperature (°C)*			
	90	*110*	*130*	*150*
2	27	27	27	27
3	48	55	61	68
4	69	83	96	109
5	90	110	130	150
6	90	110	130	150

The overall moisture of the material in the barrel was controlled by pumping water into the extruder at a point close to the solids feed port. Screw speed and solids feed-rate were held constant at 200 rpm and 25·0 kg h^{-1}, respectively. Two 3·0 mm dies were fitted in the die-plate. Four screw configurations were built up from closely intermeshing conveying elements, self-wiping conveying elements and mixing paddles in order to produce a series of screws with different conveying efficiencies. The full details are described elsewhere (Kirby *et al.*, 1988). Fig. 1 shows the two screw configurations which correspond to the samples studied in detail. The elements making up these configurations are listed in Table 2. The die pressure and temperature were measured using a Gentran pressure/temperature probe (Gentran Inc., Sunnyvale, California, USA) positioned over the intermeshing zone at a point 21 mm beyond the end of the screws. The torque on the screws was measured electrically. No correction was made for losses in the motor which should not exceed

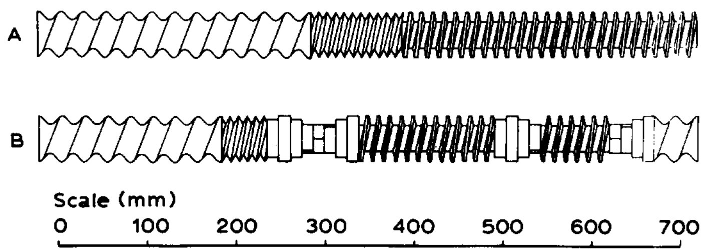

Fig. 1. Screw configurations A and B. Their elements are listed in Table 2.

TABLE 2
Screw Configurations

Configuration A
12 in. twin-start 1 in. pitch self-wiping screws.
4 in. twin-start ½ in. pitch self-wiping screws.
13 in. single start ½ in. pitch screws.

Configuration B
8 in. twin-start 1 in. pitch self-wiping screws.
2 in. twin-start ½ in. pitch self-wiping screws.
4 in. 8 × 30° forwarding mixing paddles.
6 in. single start ½ in. pitch screws.
2 in. 4 × 30° forwarding mixing paddles.
3 in. single start ½ in. pitch screws.
2 in. 4 × 30° forwarding mixing paddles.
2 in. twin-start 1 in. pitch self-wiping screws.

10% at maximum torque. The signals monitoring the extruder were all logged onto floppy disc by a Vector Graphics 2 microcomputer (Vector Graphic, Windsor, Berkshire, UK).

Product characterisation

The water solubility index (WSI) and water absorption index (WAI) were measured using the method of Anderson *et al.* (1969). The samples were first milled using a centrifuge mill to a mean particle size of approximately 180–250 μm. A series of 2·5 g samples were dispersed in 25·0 g of distilled water and stirred on a Camlab multipoint stirrer (Camlab, Cambridge, UK). After 30 min these were rinsed into tared centrifuge tubes, made up to 32·5 g and then centrifuged at 3000 × g for 10 min. The supernatant was decanted for determination of dissolved solids and the sediment weighed for the WAI. The WSI is expressed as a percentage.

Photomicrographs of aqueous pastes of the extruded grit were taken using a Vickers polarising light microscope (model M17) (Vickers Instruments, York, UK) and an Olympus camera (model OM-2N) (Olympus Optical Ltd, London, UK). This enabled loss of starch granule birefringence and the disruption of gelatinised granules and grit particles to be assessed. Intact grit particles which were too thick for the light to penetrate were gently squashed and carefully dissected with a scalpel to reveal their interiors.

Wide angle X-ray patterns were recorded photographically using a flat plate camera. The X-ray wavelength was the Cu-K_α line at 0·154 nm. The camera was flushed with helium to reduce air scatter. The reflection angles were calibrated by photographing the specimens both with and without a calcite standard. Sample moisture content was 0·08–0·11 (w.w.b.). The exposure times were two and a half hours using a fine focus tube (Philips Scientific, Cambridge, UK).

RESULTS

Die pressure and torque

The existence of one major microstructural transition is clearly revealed by the die pressure and torque measurements. Figure 2 shows these variables for the extrusion run employing an all-screw configuration (A), the highest conveying efficiency configuration studied. As the barrel

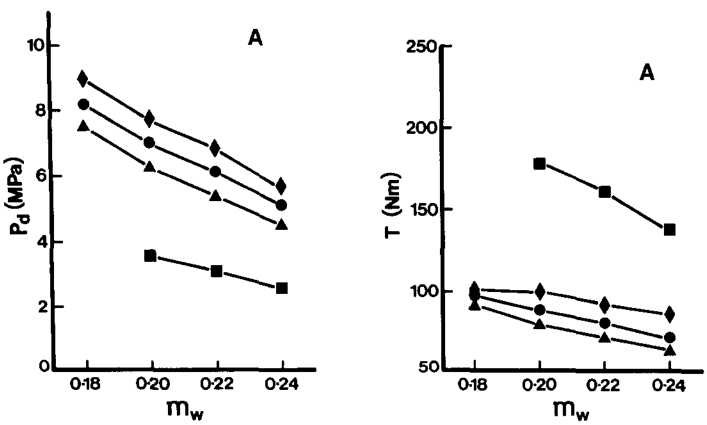

Fig. 2. The variation of die pressure and torque with barrel temperature and extrusion moisture for a high conveying efficiency screw configuration (A). Barrel temperature: ◆, 90°C; ●, 110°C; ▲, 130°C; ■, 150°C.

temperature is raised the die pressure initially drops slowly then, between 130°C and 150°C, there is a relatively large drop in pressure.

The temperature registered by the thermocouple in the die probe varied in the range 136–145°C for the experimental points above the transition at a barrel temperature of 150°C. Figure 2 also shows a near discontinuous change in the torque as the temperature rises. The torque on the screws initially falls with increasing temperature and then between barrel temperatures at 130°C and 150°C it more than doubles in magnitude. The changes in both die pressure and torque at barrel temperatures between 130°C and 150°C indicates a change in the material properties of the grit and an underlying microstructural transition.

The barrel temperature at which the transition occurs is not independent of screw configuration. Figure 3 shows the die pressure and

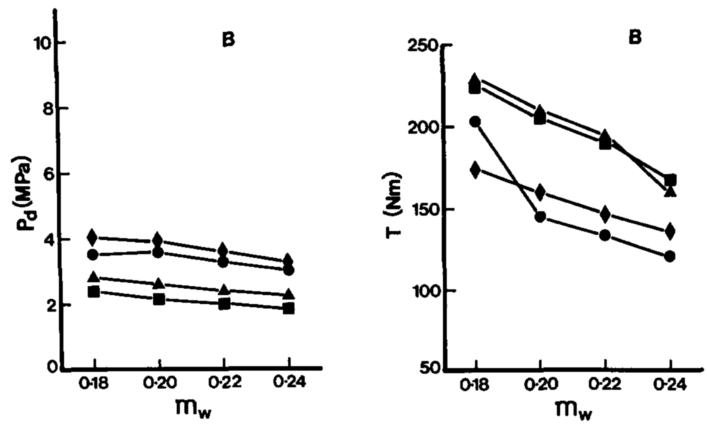

Fig. 3. The variation of die pressure and torque with barrel temperature and extrusion moisture for a low conveying efficiency screw configuration (B). Barrel temperature: ◆, 90°C; ●, 110°C; ▲, 130°C; ■, 150°C.

torque on the screws for configuration B which has three banks of mixing paddles and a self-wiping element at the discharge end of the screws. This configuration has a lower conveying efficiency than the all-screw configuration (A). The die pressures for configuration B are lower than those for configuration A and the torque on the screws is higher. The transition in die pressure now occurs at the lower barrel temperature of 110°C and as the moisture is reduced from 0·20 to 0·18. The die thermocouple registered a temperature increase from 126°C to 129°C between these points.

Water absorption and solubility

The microstructural transition which was inferred from the die pressure and torque also produced features in the product property results. The water absorption and solubility of all the samples which were measured in this study are summarised in Fig. 4. The filled symbols are those

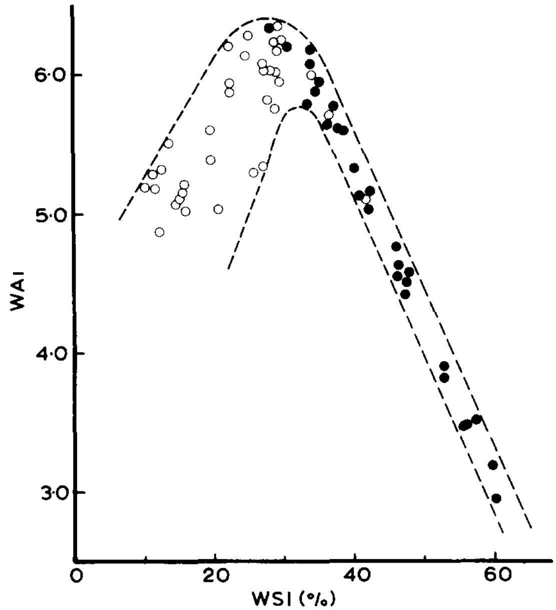

Fig. 4. Water absorption index plotted against water solubility index. Filled symbols correspond to those above transition.

samples for which the die pressure and torque indicate the transition has occurred. Clearly the transition coincides with a maximum in the WAI at about 32% WSI. The detailed dependence of water solubility and absorption on the extrusion variables of moisture content, barrel temperature and screw configuration is described elsewhere (Kirby *et al.*, 1988).

Meuser *et al.* (1984) have shown by using a 'lumped' approach and response surface methodology that the variation of water solubility is well described by a second-order polynomial in mechanical energy input and product temperature. Figure 5 shows the WSI plotted against the specific mechanical energy (SME) input for the maize grit samples. This

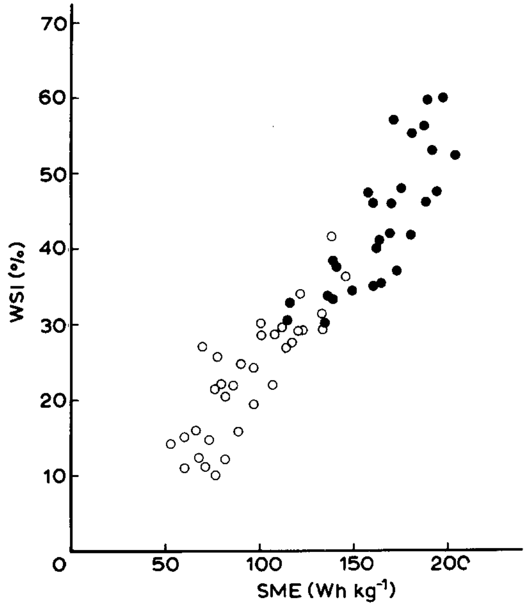

Fig. 5. Variation of water solubility (WSI) with specific mechanical energy input (SME). Filled symbols correspond to those above transition.

latter quantity is calculated from the torque, T, using the relationship

$$\mathrm{SME} = \frac{\omega T}{F},$$

where ω is the screw speed (rad s^{-1}) and F is the solids feed-rate (kg h^{-1}). The linear dependence of water solubility upon SME conforms with Meuser's model for the modification of wheat starch at low mechanical energy input (Meuser *et al.*, 1984). As before, the filled symbols correspond to samples above the transition. The linear relationship between WSI and SME shows no discontinuity at the transition which occurs over a narrow range of mechanical energy inputs at 130 ± 15 Wh kg^{-1}.

Optical microscopy

The nature of the microstructural transition was characterised by viewing samples of the extruded material taken from either side of the transition using a polarising light microscope. The samples selected for microscopy were those extruded at a moisture of 0·22 (w.w.b.) using the

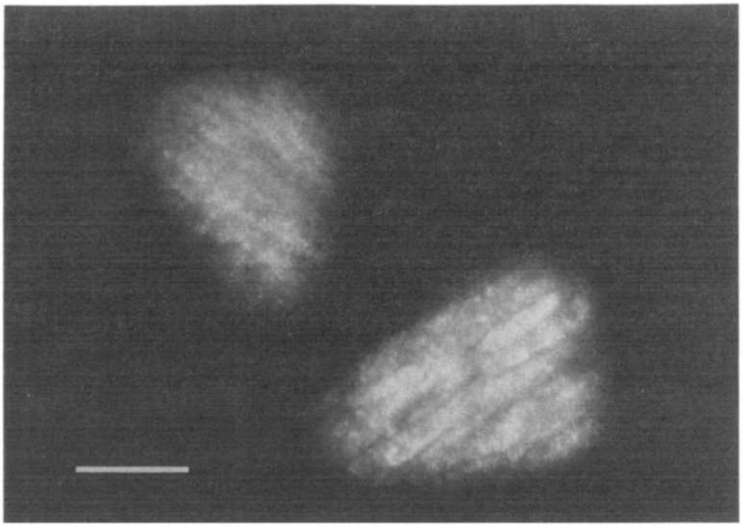

Fig. 6. Undisrupted grit particles in pasted extrudate at low magnification under crossed polarisers. Length bar = 200 μm.

all-screw configuration (A). Figure 6 shows a sample extruded at 130°C viewed at low magnification under crossed polarisers. Two virtually intact pieces of grit appear as bright triangle-shaped particles. No Maltese crosses, characteristic of ungelatinised maize starch, were apparent at this or higher magnifications. In order to discover the origin of the bright interiors of the extruded grit particles, one of them was dissected. Figure 7 shows the cut surface at higher magnification. Intact starch granules were apparent which showed Maltese cross patterns under crossed polarisers. The interior of the grit particles contain ungelatinised starch granules. The outer surface of the extruded grit particle is in view in the right-hand half of Fig. 7. There was a surface layer of gelatinised starch granules on the exterior of the grit particles. In an attempt to quantify the fraction of grit particles which survived the extrusion process a small sample (~ 12 mg) of extrudate was pasted and the number of intact grit particles counted. Over 80% of the grit particles had remained intact. A sample extruded at 150°C was viewed under identical conditions to those used above. At low magnification no bright particles were present and at higher magnification no ungelatinised or gelatinised starch granules were evident. The only recognisable structures were sheets of aleurone cells which are shown in Fig. 8. These are about the size of the original grit particles. The transition is clearly due to the collapse of the starchy portion of the grit particles and the

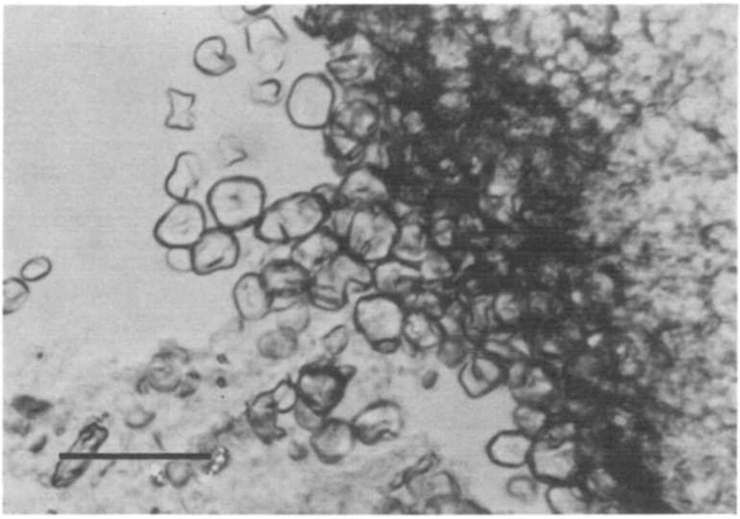

Fig. 7. Ungelatinised maize starch granules from the interior of an undisrupted grit particle under partially crossed (60°) polarisers. Length bar = 50 μm.

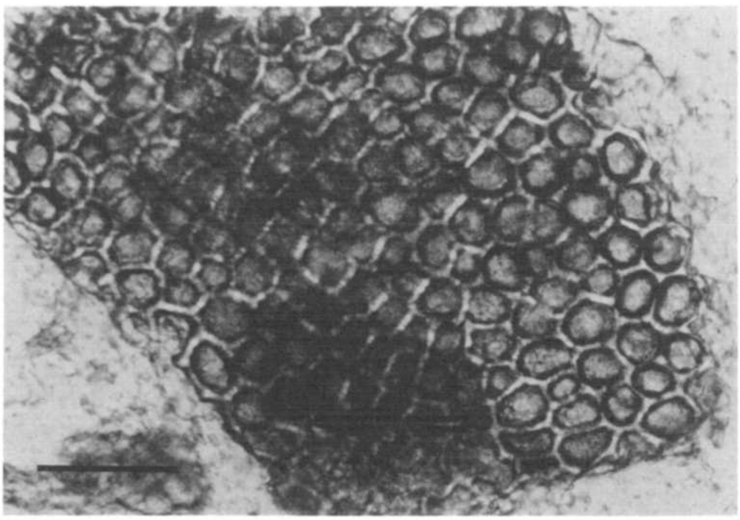

Fig. 8. Aleurone cells from a maize grit extrudate. Length bar = 100 μm.

gelatinisation and disruption of the constituent maize starch granules. The aleurone cells apparently survive the extrusion process intact.

X-ray diffraction

The results of X-ray diffraction studies of samples extruded using the all-screw configuration are shown in Fig. 9. The intensities of the reflections were estimated by visual inspection and the interplanar spacing, *d*, calculated from the reflection angle using Bragg's equation, assuming a first order reflection. The spacings for the raw sample in the region of 0·38, 0·49, 0·52 and 0·58 nm correspond to the strong reflections which characterise A-type starch (Zobel, 1964). Once the material has been extruded the X-ray pattern changes. Under mild extrusion conditions with an extrusion moisture 0·22 and barrel temperature of 90°C reflections not present in pure A-type starch appear. With interplanar spacings of 0·45 nm, 0·67 nm and 1·20 nm these characterise the V-type structure of crystalline amylose–lipid complexes.

The X-ray pattern of a sample extruded under more intense extrusion conditions (extrusion moisture, 0·20, barrel temperature, 150°C) is also shown in Fig. 9. This pattern does not correspond with either the A-type or the V-type patterns. The appearance of new patterns for extruded products has been reported by Mercier *et al.* (1979) and named 'E-type' patterns. The present pattern has a strong reflection corresponding to an interplanar spacing of 0·48 nm and a medium strength reflection corresponding to a 0·74 nm spacing as observed by Mercier *et al.* (1979). The 1·28 nm spacing differs from the 1·33 nm spacing observed by Mercier *et*

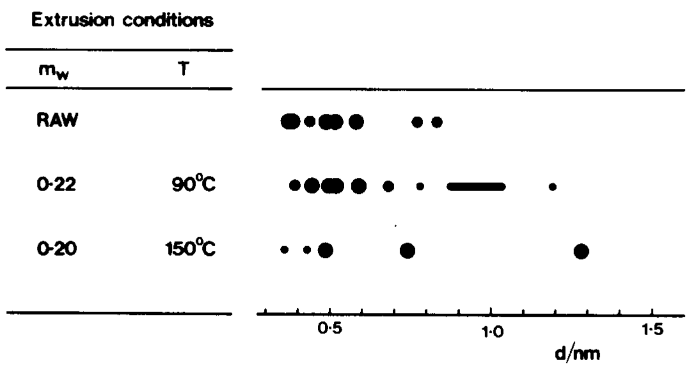

Fig. 9. Interplanar spacings from X-ray diffraction study of samples extruded with high conveying efficiency screws (A). Spot size indicates the relative intensity of the reflection. Extrusion moisture (w.w.b.), m_w; final zone temperature, T.

al. (1979) and a reflection corresponding to their 0·59 nm spacing was absent. However, overall, the pattern shows sufficient similarities with the results of Mercier *et al.* (1979) to be designated an E-type pattern.

The interplanar spacings of samples extruded with a lower conveying efficiency screw configuration (B) are shown in Fig. 10. The patterns are very similar to one another with the slight exception of the sample extruded at a barrel temperature of 110°C. The spacings of 0·48 nm and 0·75 nm are characteristic of the E-type and those at 0·43 nm and 0·67 nm of the V-type pattern. The samples are all mixtures of the E- and V-type forms of amylose complex. The sample extruded at 110°C apparently containing more V-type than the others.

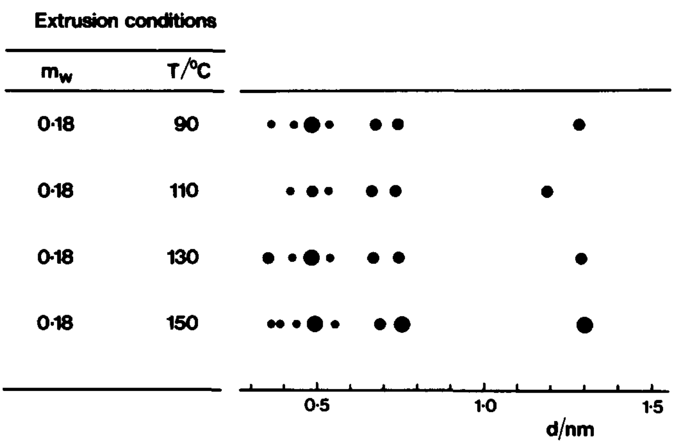

Fig. 10. Interplanar spacings from X-ray diffraction study of samples extruded with low conveying efficiency screws (B). Spot size indicates the relative intensity of the reflection. Extrusion moisture (w.w.b.), m_w; final zone temperature, T.

DISCUSSION

The variations of die pressure shown in Figs 2 and 3 can be understood in terms of the changing melt (see note) viscosity. Since the extruder is operated under conditions of constant solids feed-rate the volumetric throughput, which controls the shear-rates in the dies, is virtually constant. It will only be subject to small variations due to moisture addition and thermal expansion. The magnitude of the pressure drop over the dies is expected to be predominantly due to viscous forces with the elasticity of the melt making a relatively minor secondary contribution. The drop in viscosity as the grit is fully disrupted corresponds to the conversion of a dispersion of the rigid grit particles to a homogeneous melt. The melt viscosity decreases with increasing temperature and moisture content as has been shown using rigorous rheological techniques (Vergnes & Villemaire, 1987).

In comparison with die pressure the underlying factors which control the torque on the screws are relatively poorly understood. This is because the overall torque has contributions from along the length of the screws. A prerequisite for calculating the torque is a knowledge of the filling of the barrel and the power dissipated in conveying and deforming the 'cooking' material as it is transformed from grit through to melt. Figures 2 and 3 show that the torque on the screws for configuration B is higher than for configuration A. This is because the lower conveying efficiency of configuration B results in a higher barrel fill and more power dissipation. However, it is difficult to understand why the torque should increase at the microstructural transition when the viscosity at the dies is decreasing. The authors speculate that this may be due to the change in the extent to which the grits can leak over the flights of the extruder screws. Prior to the transition the intact grit particles are comparable in size to the leakage gaps between the screws and the extruder barrel. Once the particles are disrupted the molten material leaks more freely over the flights resulting in decreased pumping efficiency of the screws, an increased barrel fill and higher torque dissipation.

The lower die pressure and melt viscosity above the transition for screw configuration B is due to increased macromolecular degradation which occurs with higher torque and mechanical energy input (Vergnes & Villemaire, 1987; Vergnes *et al.*, 1987).

It is interesting to examine how closely the melting temperature of the maize starch in the extruder agrees with that measured in the laboratory using differential scanning calorimetry. Recent calorimetric results on waxy-maize starch (Russel, 1987), a representative A-type starch, show that the melting temperature rises from 147°C at a moisture content of 0·24 to 162°C at 0·18. For screw configuration A the die temperature was between 10°C and 18°C below these melting temperatures and for screw configuration B it was between 19°C and 33°C below. Unfortunately the thermocouple in the die probe is not ideally positioned to obtain a faithful measure of melt temperature. Under conditions of high internal heat generation the melt can be over 20°C above the extruder barrel temperature. However, despite the uncertainty, it appears that the starch is melting at lower temperatures than in the differential scanning calorimeter. It is not possible to identify the reasons for this as several factors are involved. In the extruder the melting is occurring under conditions of high shear stress with a non-uniform distribution of water, a more rapid rate of temperature rise than in the calorimeter and a relatively short residence time. The fact that the maize grit disrupted as the moisture content was reduced from 0·20 to 0·18 for screw configuration B suggests that mechanical forces may be important in the transformation.

The water solubility has been found to be correlated with intrinsic viscosity for extruded starches (Fitton, 1986, Vergnes *et al.*, 1987). From this we conclude that the water solubility gives an index of the extent of macromolecular degradation. The increase in water solubility index shown in Fig. 5 shows that macromolecular degradation increases with the intensity of the extrusion conditions throughout the range of specific mechanical energy input.

The identification of the transition as complete granule disruption allows the maximum in water absorption index in Fig. 4 to be interpreted. The WAI gives a measure of the volume of swollen gelled particles which maintain their integrity in aqueous dispersion (Mason & Hoseney, 1986). The initial increase in WAI with WSI is due to the increased proportion of the granules which are gelatinised. In aqueous dispersion the gelatinised starch absorbs water and forms swollen gelled particles. The maximum in WAI coincides with complete gelatinisation. The subsequent decrease in WAI is due to further macromolecular degradation which increases the solubility of the starch. The swollen gelled particles disperse into smaller aggregates which are not sedimented during the centrifugation stage of the water absorption test.

The occurrence of the different crystalline forms determined using X-ray diffraction are consistent with the microstructural changes found using optical microscopy. At low barrel temperatures the samples extruded using configuration A only had a small proportion (20%) of their grit particles disrupted. The major proportion of the particles have only had their surface layer of starch granules gelatinised. This results in a diffraction pattern corresponding to a mixture of the unmodified A-type with the recrystallised V-type (Fig. 9, extrusion moisture, 0·22, barrel temperature, 90°C). At higher temperatures the complete gelatinisation of the starch granules results in the liberation of amylose which can complex with the 0·8% of lipid material present in the maize grits. The amylose–lipid complexes start to crystallise during the expansion process after the material leaves the dies of the extruder and the melt temperature decreases. Crystallization is effectively arrested as the material passes through its glass transition (Zeleznak & Hoseney, 1987) whether this is during the final stages of the expansion process or during subsequent drying. E-type patterns (Fig. 9, extrusion moisture 0·20, barrel temperature 150°C) result from this process which apparently occur whenever the amylose–lipid complex is crystallised from low moisture content extruded melts.

The molecular origins of the E-type patterns are unclear and there may, in fact, be a range of E-type patterns which are sensitive to the preparation conditions. Figure 10 shows that the E-type form is occurring throughout the temperature range 90–150°C which is at lower temperatures than the range of 170–225°C previously reported by Mercier *et al.* (1979) for samples extruded at similar moisture contents. The same factors which created the low die pressure (Fig. 3) and high solubility for low conveying efficiency screws are extending the range of occurrence of the E-type form to lower extrusion temperatures. Longer residence time and greater deformation as the material passes through the extruder favour formation of the E-type form.

In Fig. 10 the absence of A-type structure at 90°C is in some ways anomalous in that the die pressure and torque in Fig. 3 (extrusion temperature 90°C, barrel moisture 0·18) indicate the sample is below the grit particle disruption transition. However, its water solubility index and water absorption index at 36% and 5·7, respectively (see Fig. 4) indicate that it is above the transition. Microscopic examination revealed no intact grit particles indicating that it is the torque and die pressure which are anomalous rather than the water solubility and absorption. Extruding maize grits at low moistures and temperatures with low conveying efficiency screws results in extensively modified products whilst maintaining relatively high melt viscosities.

CONCLUSIONS

Polarising light microscopy with the simplest of sample preparation techniques revealed the nature of a microstructural transition in the extrusion cooking of a maize grit. The transition resulted in changes in both the extruder die pressure and torque and the products' functional properties.

X-ray diffraction studies showed that the A-type starch could be melted and E-type amylose–lipid complexes crystallised at extrusion temperatures between 90°C and 150°C. The longer residence times in the extruder and higher deformation due to lower conveying efficiency screw configurations results in the E-type crystalline form occurring at lower extrusion temperatures than previously reported.

It has been shown that screw configuration is a useful process variable for controlling microstructure. This study has concentrated on structural changes in the starch components of the feed material. A full appreciation of the usefulness of the screw configuration variable will only be obtained once other processes as diverse as flavour producing reactions and mixing have been studied.

NOTE

In the absence of a better terminology 'melt' is used as a generic term for the fluid issuing from the dies of the extruder. It should not be taken to imply the absence of crystalline material in the fluid.

REFERENCES

Anderson, R. A., Conway, H. F., Pfeifer, V. F. & Griffin, E. L. (1969). *Cer. Sci. Today*, **14**, 4.
Bjorck, I., Asp, N.-G., Birkhed, D. & Lundquist, I. (1984). *J. Cer. Sci.*, **2**, 91.
Blanshard, J. M. V. (1987). In *Starch: Properties and Potential*, ed. T. Galliard, Wiley, Chichester, pp. 16–54.
Colonna, P. & Mercier, C. (1983). *Carbohydr. Polym.*, **3**, 87.
Colonna, P., Buleon, A. & Mercier, C. (1987). In *Starch: Properties and Potential*, ed. T. Galliard. Wiley, Chichester, pp. 79–114.
Doublier, J. L., Colonna, P. & Mercier, C. (1986). *Cer. Chem.*, **63**, 240.
Faubion, J. M. & Hoseney, R. C. (1982). *Cer. Chem.*, **59**, 529.
Fitton, M. G. (1986). In *Gums and Stabilizers for the Food Industry*, Vol. 3, ed. G. O. Philips, D. J. Wedlock & P. A. Williams, Elsevier, Applied Science Publishers, London, pp. 213–20.
Hayter, A.-L., Smith, A. C. & Richmond, P. (1986). *J. Mater. Sci.*, **21**, 3729.
Kirby, A. R., Ollett, A.-L., Parker, R. & Smith, A. C. (1988). *J. Food Eng.*, **8**, 247.
Mason, W. R. & Hoseney, R. C. (1986). *Cer. Chem.*, **63**, 436.
Mercier, C. & Feillet, P. (1975). *Cer. Chem.*, **52**, 283.
Mercier, C., Charbonniere, R., Gallant, D. & Guilbot, A. (1979). In *Polysaccharides in Food*, ed. J. M. V. Blanshard J. R. Mitchell. Butterworths, London, pp. 153–70.
Mercier, C., Charbonniere, R., Grebaut, J. & de la Gueriviere, J. F. (1980). *Cer. Chem.*, **57**, 4.
Mestres, C., Colonna, P. & Buleon, A. (1988). *J. Cer. Sci.*, **7**, 123.
Meuser, F., van Lengerich, B. & Reimers, H. (1984). *Stärke*, **36**, 194.
Russel, P. L. (1987). *J. Cer. Sci.*, **6**, 133.
Vergnes, B. & Villemaire, J. P. (1987). *Rheologica Acta*, **26**, 750.
Vergnes, B., Villemaire, J. P., Colonna, P. & Tayeb, J. (1987). *J. Cer. Sci.*, **5**, 189.
Zeleznak, K. J. & Hoseney, R. C. (1987). *Cer. Chem.*, **64**, 121.
Zobel, H. F. (1964). In *Methods in Carbohydrate Chemistry, Vol. 4, Starch*, ed. R. L. Whistler. Academic Press, New York, pp. 109–13.