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Extrusion of waxy maize starch: melt rheology and molecular weight degradation of amylopectin

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Waxy maize starch was extruded initially using a co-rotating twin-screw extruder. This extrudate was then equilibrated to either 18 or 23% moisture content, and subsequently re-extruded in a single-screw extruder at either 110 or 130°C to characterize the melt viscosity. The melts exhibited shear thinning behaviour under all conditions; the power law index m increased with temperature, but did not significantly change with moisture content. Molecular weights of selected samples were measured by multi-angle laser light scattering (MALLS) in dimethyl sulfoxide/water (90/10 v/v). The initial extrusion pass reduced the molecular weight from 336×10^6 to 40×10^6. Molecular weight reductions during the second pass increased with increasing specific mechanical energy, and were less drastic than the initial drop. The observed M_w values display a semi-logarithmic dependence on the specific mechanical energy, with $r^2 = 0.925$. Specific mechanical energy can therefore be used to estimate molecular weight degradation, regardless of variations in extruder type or conditions during multiple passes. Molecular weight distributions determined using gel permeation chromatography correlated well with the single-point molecular weight determinations. © 1997 Published by Elsevier Science Ltd.

(Keywords: extrusion; starch; molecular weight degradation)

INTRODUCTION

Extrusion of starch has received considerable attention in recent years for both food and plastics applications. Food processing typically involves high temperature, short time (HTST) extrusion cooking to produce expanded products[1]. Plastics processing, on the other hand, often involves less severe extrusion conditions in which melting and mixing are of primary importance, and degradation is preferably minimized[2,3]. One exception to this approach is the production of expanded starch foam materials which compete with expanded polystyrene, in which the extrusion conditions are similar to the HTST conditions used in food processing. In contrast to food extrusion, plastics materials often experience more than one processing history, which may involve extrusion compounding, followed by injection moulding or film extrusion. Therefore, the effects of multiple extrusion passes on the molecular weight of starch are of interest, because of the role molecular weight plays in the rheological and mechanical properties of polymers.

The degradation of starch during extrusion, and its role in the rheological properties, have been characterized under a variety of extrusion cooking conditions. Extrusion generally produces little if any detectable low molecular weight saccharides, which is consistent with shear induced fragmentation, to which the largest molecules are the most susceptible. Molecular weight degradation has been shown to increase with increasing specific mechanical energy (SME) during twin-screw extrusion[4–12]. It has been suggested that degradation can lead to negative power law exponents during extrusion through slits dies[13]. While extrusion parameters such as moisture content, screw configuration and temperature interact to influence the degree of degradation, strong correlations between SME and degradation have been observed. It has been suggested that the degradation during extrusion is due to preferential scission of either alpha (1–4) bonds in amylose[14] or by debranching[15].

A model for the mechanical degradation of starch during single-screw extrusion was developed by Davidson *et al.*[16]. A first-order relationship between the extent of degradation and the product of the residence time and the nominal shear stress was given. The degradation measurement was limited to the amylopectin content, and determined by the amount of material eluted in the void volume in column chromatography. Few data have been published relating degradation during single-screw extrusion with SME.

Prior studies of extrusion-induced starch degradation have generally considered only single-pass extrusion of starch. This processing step is unique in that the starch is converted from its native granular state into a thermoplastic melt. Quantitative evaluation of starch

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Table 1 Screw design for initial extrusion pass (twin-screw extruder)

Type of element	Number of elements	Configuration[a]	Total length (mm)
Conveying	7	42/42	294
Conveying	6	28/28	462
Kneading block	1	45/5/28	490
Kneading block	1	45/5/28 LH	518
Conveying	1	28/28	546
Kneading block	1	45/5/28	574
Kneading block	1	45/5/28 LH	602
Conveying	1	28/28	630
Kneading block	1	45/5/28	658
Kneading block	1	90/5/28	686
Conveying	1	28/28	714
Kneading block	2	45/5/42	798
Conveying	1	20/10 LH	808
Conveying	3	42/42	934
Conveying	9	28/28	1186
Conveying	7	20/20	1326
Conveying	1	20/10	1336

[a] LH = left-handed element; numbers denote length of screw flight/length of element (conveying) or stagger angle/number of blocks/length of element (kneading blocks)

Table 2 Process parameters for twin-screw extrusion

Feed rate (lb min^{-1})	0.33 (~0.15 kg min^{-1})
Screw speed (rev min^{-1})	90
Moisture content (%)	35
Maximum barrel temperature (°F)	245 (~118°C)
Dies	2 (4 mm diameter)

degradation during subsequent extrusion passes has not been reported. Kollengode *et al.*[17] have shown that a second extrusion pass increases the degradation of starch during single-screw extrusion, as indicated by shifts to longer retention times in gel permeation chromatography (g.p.c.), but no molecular weight data were reported. Bastioli *et al.*[18] have shown that the rheological behaviour of starch/ethylene–vinyl alcohol copolymer blends is not affected after three extrusion passes at 170°C[18]. Since many plastics applications involve multiple extrusion histories, it is of interest to characterize the effects of multiple extrusion passes on starch degradation.

The objectives of this paper are to characterize the melt rheology and degree of degradation experienced by waxy maize starch during a second extrusion pass after the initial conversion from native granules into a thermoplastic melt.

EXPERIMENTAL

The starch used was a waxy maize starch (Waxy 7350, A.E. Staley, Decatur, IL), with less than 2% amylose. The initial extrusion step was performed using a Werner & Pfleiderer ZSK-30 co-rotating twin-screw extruder, with the screw configuration shown in *Table 1*. Starch with ambient moisture was fed into the extruder, and deionized water was injected via a port in the extruder barrel. The moisture content (MC) during this step was calculated using the ambient moisture in the starch and the pump rate. The extrusion parameters are given in *Table 2*; under these conditions, the SME was 620 J g^{-1}.

The extrudate from the first extrusion pass was chopped into pellets and equilibrated to either 18 or 23% MC. Attempts to equilibrate to MC greater than 23% resulted in mould growth on the pellets; torque and pressure values at high screw speeds were excessive when MC was less than 18%. Second pass extrusion for rheological characterization was performed using a 19 mm diameter single-screw extruder with a 3/1 compression screw (Brabender, South Hackensack, NJ) at either 110 or 130°C with a 2 mm diameter capillary die ($L/D = 10$, 15 or 20). Output was varied by changing the screw speed. Torque and pressure data were electronically logged and stored, and output was measured under steady state conditions. Output and pressure data were converted into shear rate ($\dot{\gamma}$) and shear stress (τ), respectively, and the apparent melt viscosity was calculated as the ratio $\tau/\dot{\gamma}$. Shear rate data were corrected for non-Newtonian effects using the Rabinowitsch correction. The SME was calculated using the relation:

$$\mathrm{SME} = \frac{2\pi\omega T}{\dot{m}} \qquad (1)$$

where ω is the screw speed (rev s^{-1}), T is the torque (Nm) and $\dot{m}$ is the output (g s^{-1}). The units of SME are J g^{-1}.

Extrudates for light scattering (LS) and g.p.c. analysis were prepared by cryogenically grinding the extrudates in a high speed mill (Fritsch). Samples for g.p.c. were dissolved in water. The g.p.c. analysis was performed with a Spectraphysics SP 8810 isocratic pump at a flow rate of 0.5 ml min^{-1}, with Shodex OH Pak columns in series (KB-804 and KB-806) and a Waters 410 differential refractometer detector.

Samples for LS were prepared by dissolving 1–2 mg ml^{-1} ground starch in dimethyl sulfoxide/water (90/10 w/w) with gentle agitation. Solutions were sequentially filtered through a 5 μm filter, followed by a 1 μm filter. Solvent was filtered through 0.2 μm polyester membrane filters (Poretics Corp., Livermore, CA). Concentrations were measured before and after filtration by optical rotation using a specific rotation of 190 at 589 nm[19]; filtration did not reduce the concentration.

Cylindrical scattering cells were cleaned immediately prior to use by exposure to a low temperature oxygen plasma (Plasmod, March Instruments, Concord, MA). This technique has been shown to produce glass surfaces with superior optical clarity[20]. Scattering measurements were taken using a multi-angle laser LS unit (Wyatt Technology Corp.) at a wavelength of 632.8 nm. Toluene was used for calibration. The specific refractive index was 1.4570, and a value of 0.074 ml g^{-1} was used for dn/dc. Weight average molecular weights M_w were calculated with the instrument's software package, using Berry plots. A representative Berry plot is shown in *Figure 1*. The M_w values reported are the average of at least two duplicate runs.

X-ray diffraction analysis was performed with a Phillips Automated Powder Diffractometer, over a scattering angle (2θ) range of 4–40°, with a step size of 0.05°. Samples for scanning electron microscopy (SEM) were dried by immersion in absolute ethanol and sputter coated with Au.

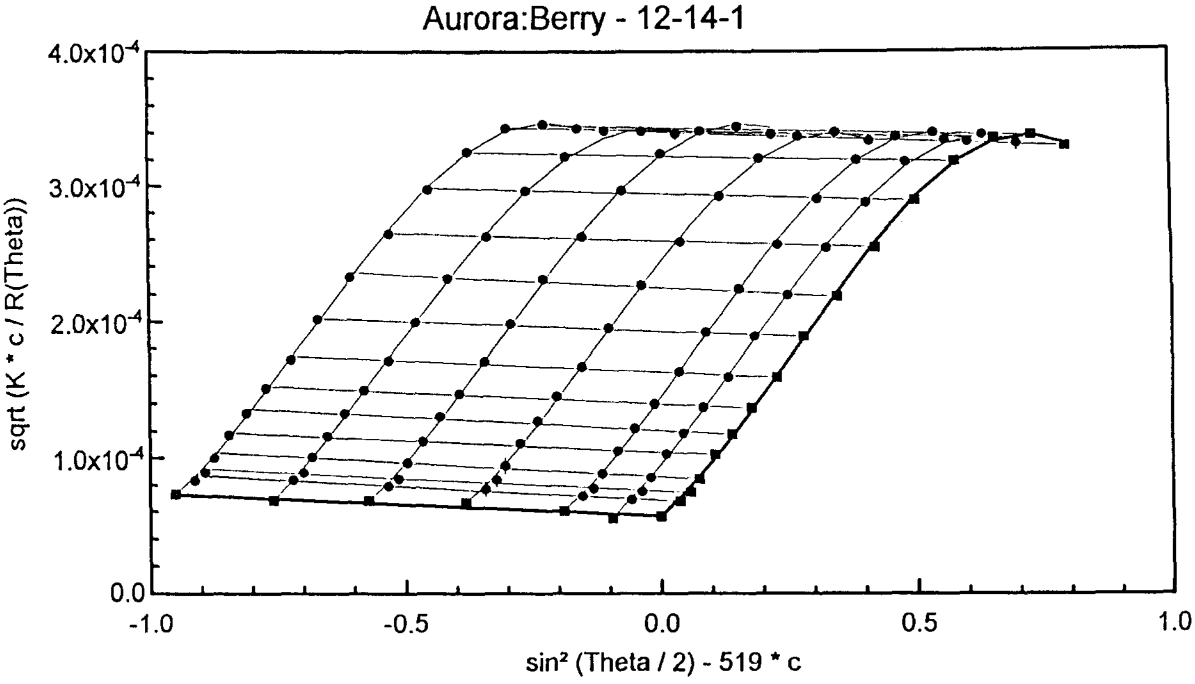
RESULTS AND DISCUSSION

Residual granule structure and crystallinity may be present in starch extrudates, depending on extrusion conditions[21]. The X-ray diffraction and SEM results of *Figure 2* indicate that the first extrusion pass was sufficiently aggressive to eliminate residual crystallinity or granule structure, converting the waxy maize starch into a homogeneous thermoplastic melt.

Apparent viscosity data from the second extrusion pass are shown in *Figure 3*. The waxy maize starch melts display power law (shear thinning) behaviour, as observed in previous first pass extrusion studies[12,22,23]. Increasing either the MC or the temperature reduces the viscosity. Note that the rheological behaviour at 110°C/23% MC is essentially identical to that at 130°C/18% MC. *Table 3* lists the power law parameters consistency K and index m obtained by least squares analysis of the data in *Figure 3*. Values for the reduced activation energy E/R (10 100 K) and MC coefficient (12.6) are comparable to those found in other studies of starch extrusion[12,24].

The increase in the power law index m with temperature is consistent with the other studies of normal corn starch (23% amylose) processed under similar conditions, while the values of m are greater[25,26]. Increases in m with temperature have also been observed with waxy maize starch during first-pass twin-screw extrusion[12,22]. Values from this work are lower than those for waxy maize found by Della Valle *et al.*[12], who used higher temperatures at comparable MC (24.5 *versus* 23%). The effect of MC is not as clear, but the data of *Figure 3* suggest a slight increase in m with increasing MC, an effect also observed in pre-extruded normal corn starch[25,26]. Vergnes *et al.*[10] found a positive relationship between MC and m for maize starch[10]. However, Lai and Kokini[22] found that m for waxy maize starch decreased with increasing MC during the first pass in a twin-screw extruder, and similar behaviour has been observed with potato starch[11]. Villar *et al.*[27] found little change in m with MC for various starches (plasticized with glycerol and water) and their blends with an ethylene–vinyl alcohol copolymer, while Wang *et al.*[28] obtained similar results for starch–poly(vinyl alcohol) blends. Increasing extrusion temperature therefore appears to increase the power law index m, while the effect of MC on m appears to be related to prior processing and the presence of other plasticizers and/or other polymers.

Values of m for waxy maize are greater than those of normal corn starch processed under similar conditions[25,26]. Similar effects have been observed when



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RMS Radius       : 207.5 +/- 13.4 nm
Molecular Weight : (3.13 +/- 0.3)e8 g/mol
2nd Virial Coef. : (4.96 +/- 1.0)e-7 mol ml/g**2
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Figure 1 Berry plot of the MALLS data for native waxy maize starch in DMSO/H_2O

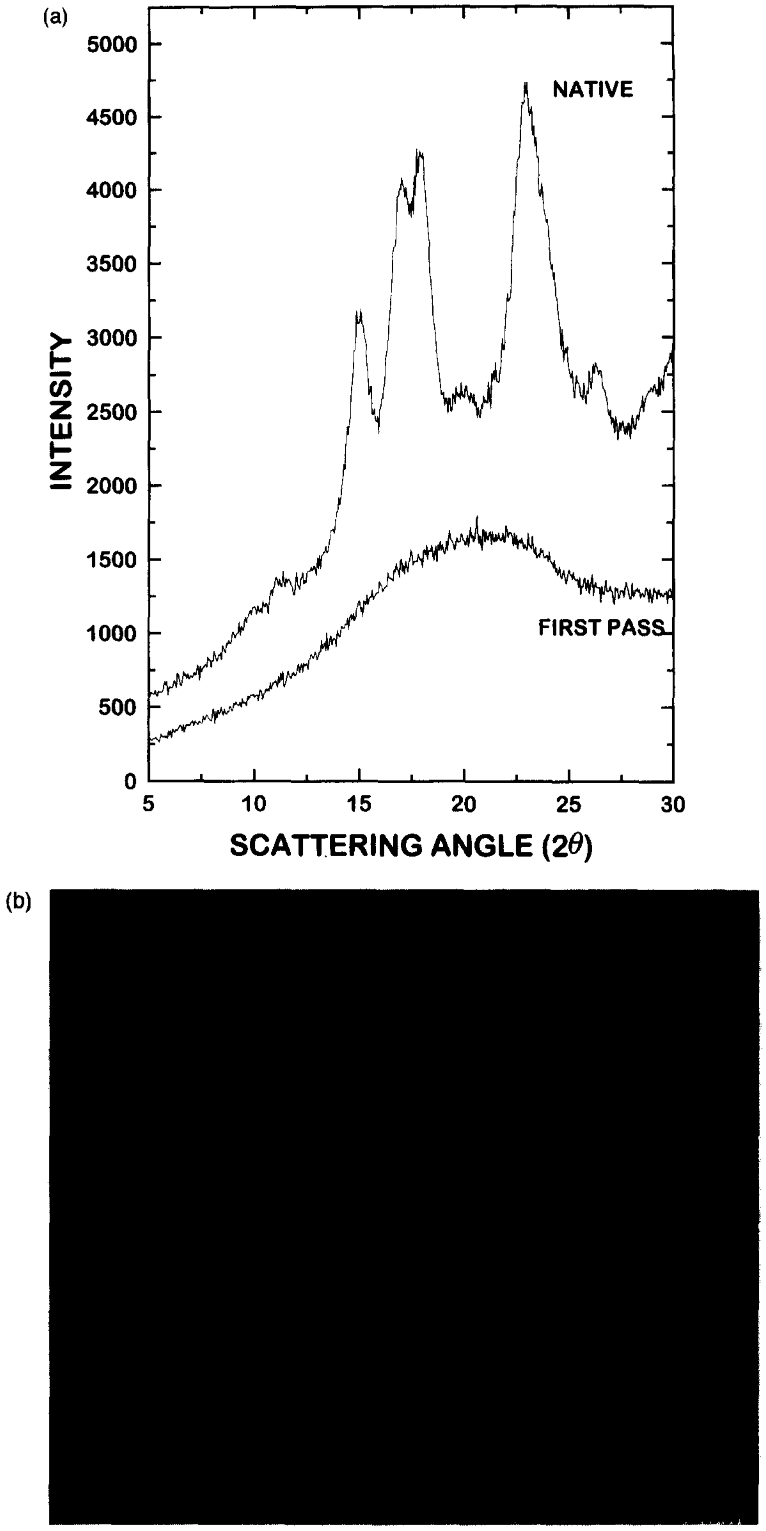

Figure 2 (a) X-ray diffraction patterns of native starch and extrudate from twin-screw extruder; (b) scanning electron micrograph of twin-screw extrudate (scale marker is 10 μm). No evidence of residual crystallinity or granular structure is observed in extrudate with either technique

comparing waxy maize starch to high amylose starch[12,22]. Della Valle *et al.*[12] showed that, as the amylose content increased from 0 to 70%, m decreased from approximately 0.75 to 0.4, although the exact values varied with processing conditions[12]. The decrease in the power law index with increasing amylose content is generally attributed to an increase in entanglements with amylose content; the highly branched amylopectin is not expected to form entanglements well.

The output during the second extrusion pass, during which the rheological measurements were made, was controlled by changing the screw speed. Because the single-screw extruder operates under flood feed conditions, extrudates at low speed experience a different shear/residence time/torque history than those at high speed. At constant temperature and MC, increasing screw speed increases both the torque and the die pressure, while decreasing the mean residence time. Therefore, the degradation of a shear and thermally sensitive polymer such as starch is expected to be a function of screw speed.

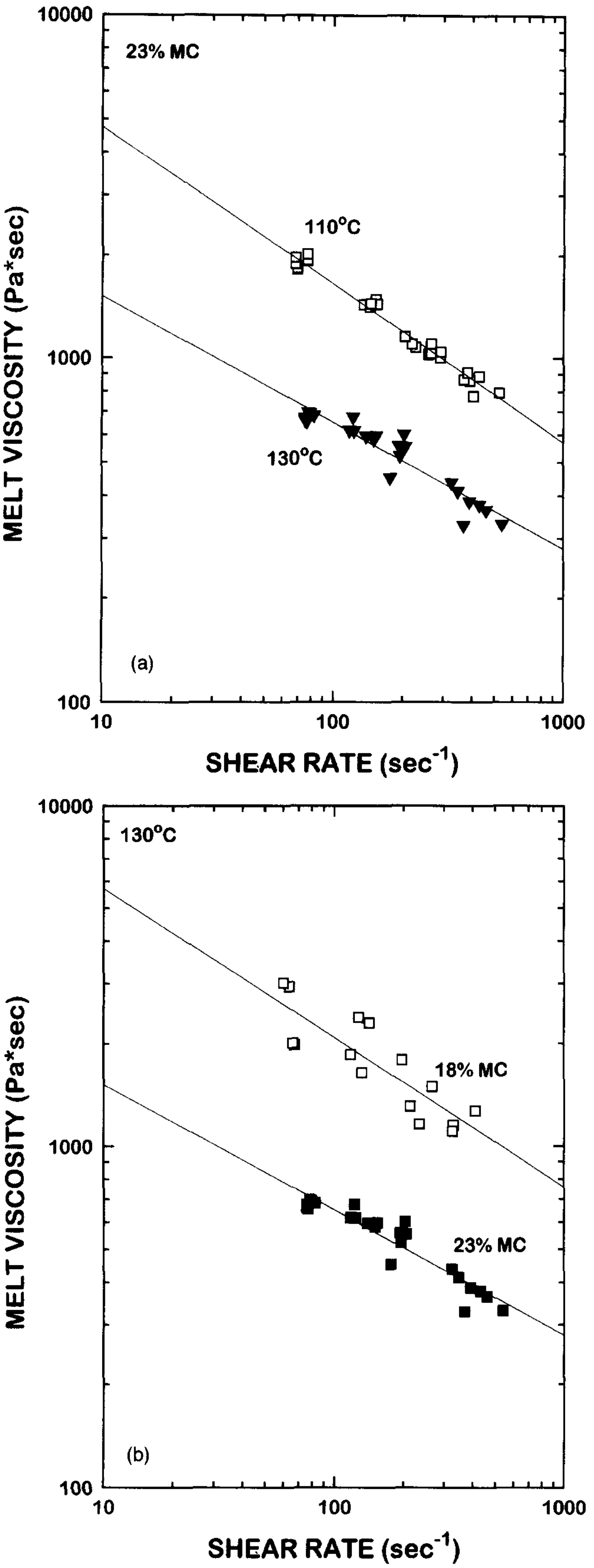

Figure 3 Melt viscosity as a function of shear rate for waxy maize starch during the second extrusion pass: (a) effect of temperature; (b) effect of MC

If so, the molecular weight at different extremes of the melt viscosity/shear rate curves will be different.

Molecular weight data for samples selected at the extremes of shear rate from the extrusion runs of *Figure 3* are plotted against SME in *Figure 4*. The first extrusion pass in the twin-screw extruder decreased the molecular weight of the native starch from 336 (±31) × 10^6 to 40 (±4) × 10^6. Further degradation occurred during the second extrusion pass, and increased with increasing SME. M_w values for the native starch (SME = 0) are somewhat dependent on the polynomial fits used by the Berry plot software, and range from 297 × 10^6 to 368 × 10^6. These high molecular weights for the native starch are consistent with other reported values for amylopectin[29–31].

Table 3 Power law parameters for waxy maize starch melts

Extrusion conditions (°C/% MC)	Log consistency (Pa s^m)	Power law index m	Correlation coefficient
110/23	4.10 (0.03)[a]	0.54 (0.01)	0.98
130/18	4.16 (0.15)	0.56 (0.07)	0.74
130/23	3.53 (0.06)	0.63 (0.03)	0.88

[a] Numbers in parentheses are standard errors

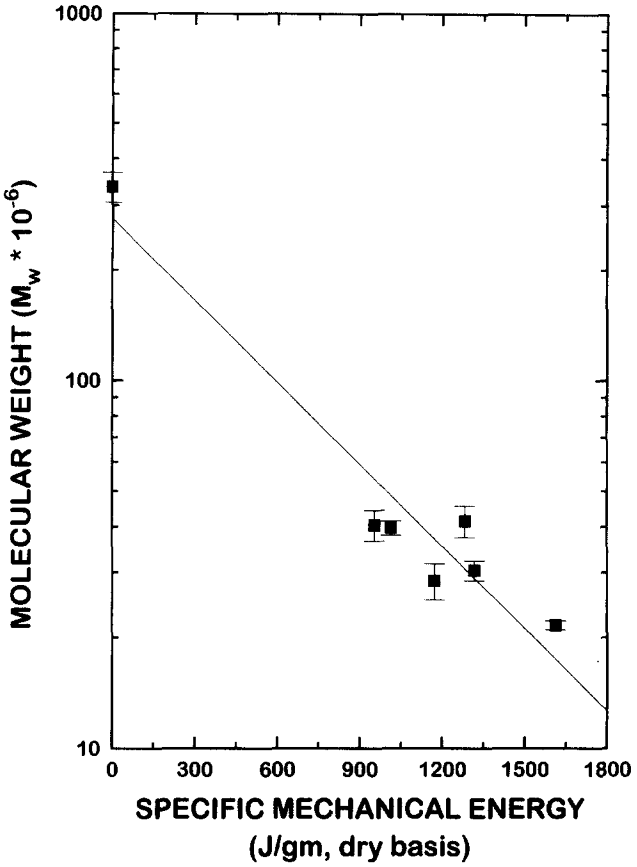

Figure 4 Relationship between weight average molecular weight (M_w) and SME. Native starch value is at 0 SME

The data of *Figure 4* can be described by a first-order relationship ($r^2 = 0.925$):

$$\ln M_w = 19.44 - (1.7 \times 10^{-3}) \times \text{SME} \qquad (2)$$

The standard errors are 0.27 for the intercept and 0.2 × 10^{-3} for the slope. This relationship indicates that the relative decrease in molecular weight is a cumulative function of SME for amylopectin melts. In addition, equation (2) suggests that the SME is a 'universal' parameter, incorporating temperature, residence time and shear effects—a concept discussed by others[32,33].

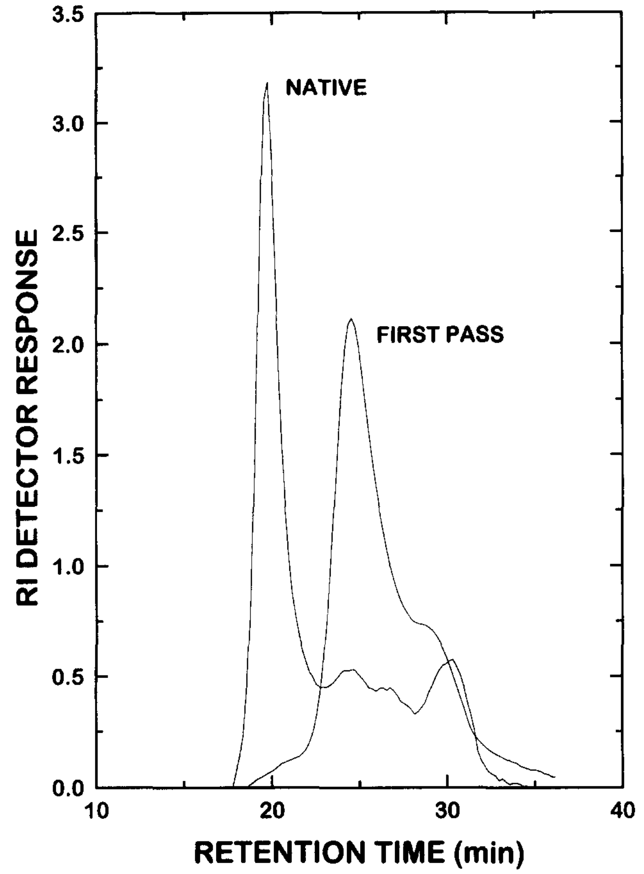

Figure 5 G.p.c. data for native starch and extrudate from twin-screw extruder (first pass)

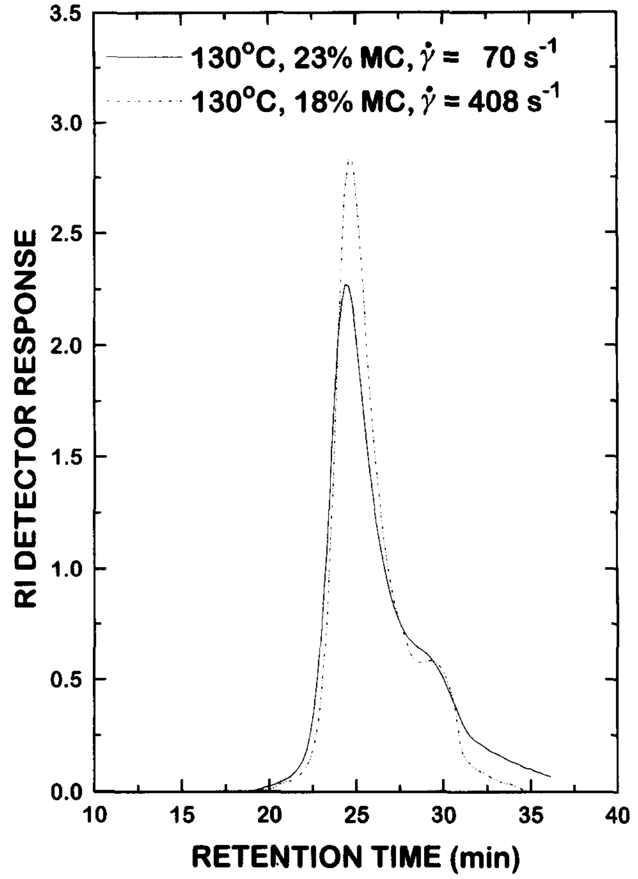

Figure 6 G.p.c. data for extrudates from single-screw extruder (second pass, 130°C) at specified MC and shear rates

Therefore, estimation of molecular weight degradation of amylopectin during multiple extrusion passes requires only the relationship between SME and extrusion parameters such as temperature, screw speed and moisture content.

The data of *Figures 3* and *4* indicate that the extrusion-induced changes in molecular weight of extruded waxy maize starch do not significantly alter the power law behaviour of the melts, within experimental error. This result is consistent with the behaviour of synthetic polymer melts at high shear rates, such as linear[34,35] and branched[34] polystyrenes. The zero-shear viscosities of linear polymer melts are strongly dependent on molecular weight, due to entanglements, and scale as approximately the cube of the molecular weight[36]. At high shear rates, however, the melt viscosity is independent of molecular weight, since the time scale of deformation is such that rearrangements occur only on length scales shorter than the spacing between entanglements. It has been proposed that, inasmuch as shear thinning represents changes in entanglement density, the power law index m is a relative measure of the ability of a given polymer to disentangle under shear[35]. Polymers with low m values, such as polystyrene[35], disentangle less easily, and therefore exhibit a higher degree of non-Newtonian behaviour compared to polymers with large m values, such as polybutadiene[37]. The relatively high values of m for amylopectin melts suggest that amylopectin has either a relatively low entanglement density, or that it disentangles easily under shear, or both.

Rauwendaal[2] has discussed differences in power law index values for amorphous and semi-crystalline polymers. Semi-crystalline polymers often have m values greater than those of amorphous polymers. The processing temperatures (T_p) for the semi-crystalline polymers are often much greater than their glass transition temperatures, because of the requirement to process above the melting point. On the other hand, the processing temperatures of amorphous polymers are closer to T_g. Since non-Newtonian behaviour decreases with increasing temperature difference $T_p - T_g$, semi-crystalline polymers are more Newtonian in their melt behaviour. $T_p - T_g$ is approximately 50 to 100°C in this work, closer to conditions used in processing amorphous polymers. The relatively high m values compared to linear amorphous polymers processed under similar $T_p - T_g$ conditions also suggest a low degree of entanglement in amylopectin melts.

The g.p.c. analysis of selected extrudates and native starch are consistent with the measured molecular weights, as shown in *Figures 5* and *6*. The native starch shows a large peak at the exclusion limit of the columns, followed by lesser amounts of lower molecular weight material. After the initial extrusion pass in the twin-screw extruder, the peak has shifted to a considerably longer elution time, corresponding to a significant reduction in molecular weight. There is still a small amount of the original high molecular weight material in this sample eluting near the peak time of approximately 20 min, while traces of the largest material, if present, are in amounts below the detection limit.

Figure 6 illustrates the g.p.c. spectra of the two second pass extrudates with the lowest and highest molecular weights. There are only minor differences between the two molecular weight distributions, although the M_w values differ by a factor of 2 (21×10^6 *versus* 40×10^6).

At retention times of less than about 25 min, the sample extrudes at 23% MC and low shear rate has a slightly greater fraction than the one extruded at 18% MC and high shear rate. Near the peak region, the lower molecular weight sample has a greater intensity, and the peak is slightly shifted to longer elution time. While in qualitative agreement with the LS data, these differences are relatively minor compared to the changes observed during the first extrusion pass. In the absence of another detection method which directly measures the molecular weight, such as LS or intrinsic viscosity, the chromatograms shown in *Figures 5* and *6* should be interpreted in a qualitative manner. It is important to note, however, that the fraction with the largest hydrodynamic volume, in the elution range of approximately 18–22 min, has been reduced during the second extrusion pass. Since this higher molecular weight material will produce a stronger LS signal, the reduction of this fraction during the second pass is consistent with the observed molecular weight reductions. The molecular weight distribution data in *Figures 5* and *6* emphasize the point that the most extensive degradation occurs in the first extrusion pass, and are consistent with a shear-induced degradation mechanism.

CONCLUSIONS

Waxy maize starch which has been previously extruded to eliminate granule structure exhibits shear thinning behaviour, becoming more Newtonian as either temperature or MC is increased, as measured by the power law index m. The weight average molecular weight M_w smoothly decreases with increasing SME input over two extrusion passes, at different combinations of temperature, MC, screw speed and extruder type. The reduction in M_w could be described by a first-order equation in SME, with a correlation coefficient of 0.925. The g.p.c. results were consistent with the LS data, indicating the degradation of fractions with large hydrodynamic volumes (short elution times). These results indicate that the SME is a powerful tool for predicting the molecular weight degradation of amylopectin during extrusion, if the relationships between extrusion parameters and SME are known.

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