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Depolymerisation of cassava starch

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Abstract

A factor in the use of native cassava starch for commercial food production is its variability. Agronomic factors and processing protocols alter the performance of starch in food products. Work carried out at the University of Nottingham has indicated that cassava is particularly susceptible to starch conversion when being extruded. Also, cassava seems particularly liable to undergo oxidative reductive depolymerisation compared with other tuber and cereal starches. Low addition rates of substances that interact with oxygen to produce free radicals cause changes in the behaviour of starches. Agents that seem to have an effect on cassava include: sulfite, ascorbic acid and glutathione. The actual level of these compounds is important as maximum degradation is caused at a specific addition rate. Changes caused by the inclusion of the redox agents can be stopped or at least reduced by the use of the free radical terminator, propyl gallate. The inclusion of sulfite with cassava starch has been shown to alter the gelatinisation properties of the granules, the viscosity of pastes and the average molecular weight of amylose or amylopectin or of both polysaccharides. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cassava starch; Starch conversion; Depolymerisation; Sulphite; Extrusion

1. Introduction

Cassava (*Manihot esculenta* Crantz) is grown chiefly as a food—it is one of the most important sources of metabolic energy for 500 million people in the tropics and it also has several significant industrial uses (Cock, 1985; Rickard et al., 1991; Blanshard, 1994). Starch is the major carbohydrate in the roots, ranging from 73.7 to 84.9% of the root dry weight. Essentially this starch is one of the most important raw materials in the food industry because of its properties, i.e. a low gelatinisation temperature (160°F or 71°C), a low tendency to retrograde, no residual proteinaceous material or soil residues, noncereal flavour, high viscosity, high water binding capacity, bland taste, translucent paste and relatively good stability (Glicksman, 1969). However, cassava starch does show certain characteristics that introduce an unacceptable level of variability or process limitations in foods manufactured from this starch. Within this paper three factors that seem to alter the behaviour of cassava starch are highlighted. The first demonstrates the high variability in native starch samples. The other examples demonstrate that both chemical and physical environmental factors are important to the subsequent behaviour of cassava starch.

The changes in cassava starch are demonstrated by its physical behaviour in water and alkaline solutions. In cold water undamaged starch does not swell or solubilise to any notable extent. However, on treatment these properties alter and their estimation indicates the degree of gelatinisation and molecular weight reduction of the amylose and amylopectin. The molecular weight changes can also be followed by measuring the viscosity of starch suspensions in water or of starch solutions in potassium hydroxide.

The gelatinisation and molecular weight changes for the cassava starches have been brought about during the preparation of the starches, by heating in excess water (with and without the presence of additives) and by the thermomechanical process of extrusion.

2. Materials and methods

2.1. Starch samples

Cassava starch samples were obtained from three sources. The M4 variety, the Malaysian and Target Brand (native tapioca) cassava starches were supplied by Central Tuber Crop Research Institute (Trivandrum, India), Sarawak State (Malaysia) and National Starch and Chemical Company (Manchester, UK), respectively.

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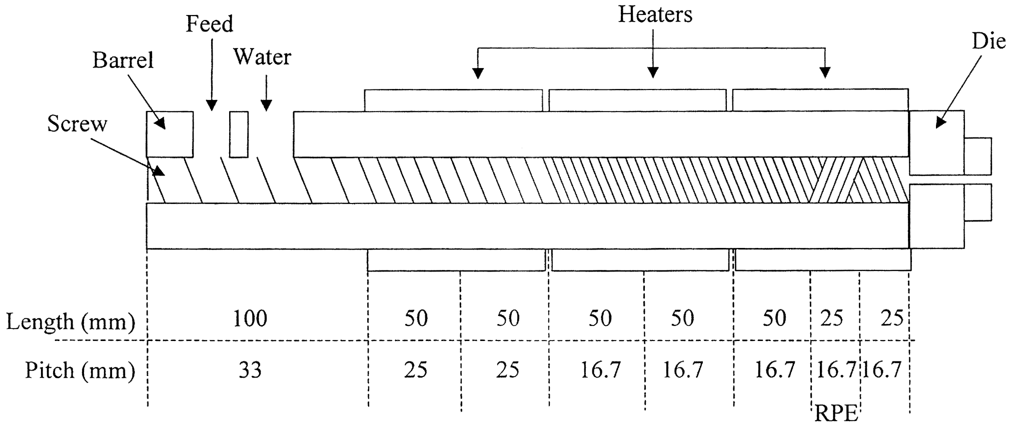

Fig. 1. Schematic diagram of screw profile for Clextral BC-21 intermeshing twin-screw extruder showing components and zones.

2.2. Analytical reagents

All laboratory reagents were obtained from Sigma (Poole, UK), and were of analytical grade unless otherwise stated.

2.3. Comparisons of native starches using estimates of swelling volume (Mat Hashim et al., 1992; Griffiths, 1997)

The swelling volume was determined by heating starch pastes (1% w/v) at 95°C in a water bath for 30 min. During the first 5 min of pasting the starch suspensions were agitated to ensure that they were dispersed. After pasting the starch pastes were cooled to room temperature, and then transferred to 15-ml conical centrifuge tubes. The starch pastes were centrifuged ($1000 \times g$) for 20 min. The swelling volume was obtained directly by reading the volume of sediment in the tube. The swelling volume was expressed as volume of sediment per 100 ml of starch solution.

2.4. Effect of additives on starch pastes using steady shear viscosity measurement (Vallès Pàmies et al., 1997)

The starch used was the M4 from India. Initially starches were prepared as pastes by adding 5% (w/v) starch to 0.1 M sodium phosphate buffer at pH 7.0. These samples were heated for 30 min at 90°C with gentle stirring. These gelatinised samples were then sheared using a Silverson mixer for 2 min and the samples were aliquoted into 50-ml portions with a suitable amount of additive. The additives used were 0.1% sodium sulfite, 0.01% ascorbate, 0.001% ascorbate without and with 0.05% propyl gallate, and 0.1% glutathione. All samples were stored for known times at 60°C in a water bath. Just prior to analysis aliquots of 5 ml were rapidly cooled and the shear viscosity of pasted starch was measured using a Bohlin CS10 rheometer (Bohlin Rheology, Lund, Sweden) at 25°C. Viscosities were assessed over 12 h after the addition of the additive. The viscosity was measured at 14 shear rates varying between 1 and 70 s^{-1}. The data reported are at a shear rate of 27 s^{-1}.

2.5. Production and estimation of extruded cassava starch samples

2.5.1. Extrusion

The cassava used was Target Brand. Cassava extrudates were prepared using a Clextral BC-21 intermeshing twin screw extruder. Heating within the barrel was composed of four heating zones. Screw configurations were relatively simple with only forward conveying elements. Heating conditions and screw configurations are shown in Fig. 1. The specific mechanical energy (SME) was calculated as (Fan et al., 1996):

$$\text{SME (W.h/kg)} = \text{screw torque (N.m)} \times \text{screw speed } (s^{-1}) \times \text{no. of screws/mass flow rate (kg/h)} \qquad (1)$$

Cassava starch was extruded under conditions of increasing temperatures in the different barrels zones (40, 90, 110 and 130°C). A range of extrudates was obtained by factorially varying the screw speeds (200 and 300 rpm) and feed rates (5 and 8 kg/h). These conditions were denoted as 200/5, 200/8, 300/5 and 300/8 and the respective SME for each condition was 75.7, 70.0, 109.8 and 112.7 W.h/kg. On manufacture, the extrudates were cooled to room temperature and sealed in polyethylene bags for further testing.

2.5.2. Estimates on extruded products

Extruded samples were dried at 60°C for 24 h and ground using a centrifugal mill, then the samples were passed through fine sieves. The fractions used were those collected between the 106 and 422 μm sized sieves. Samples were stored in small plastic containers at ambient temperature.

2.5.3. Water absorption and water solubility indices (Anderson et al., 1969)

Typically the method was to mix 0.3 g of dried sample with 10 ml of distilled water and allow to hydrate and sediment overnight. The suspensions were then subjected to

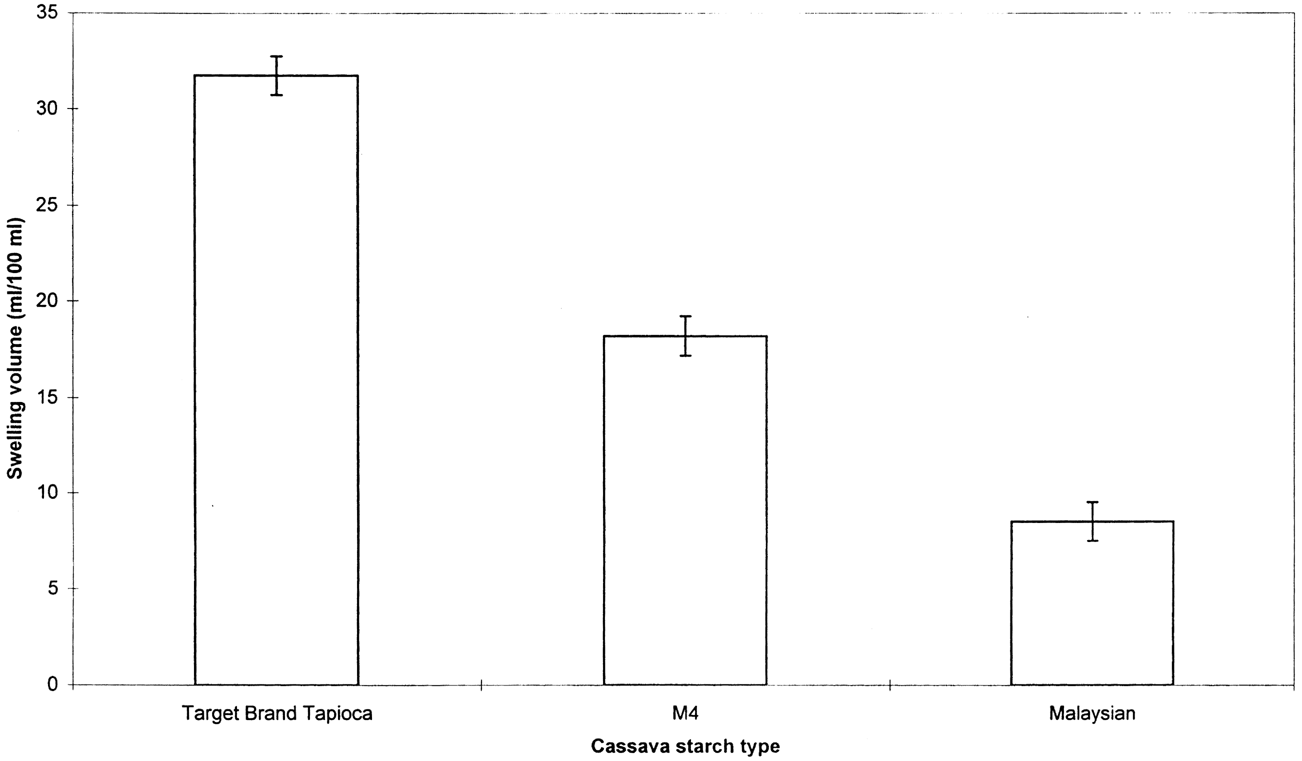

Fig. 2. Variations in the swelling volume of cassava starches pasted at 95°C for 30 min (results represent the mean and standard error of at least three replicates).

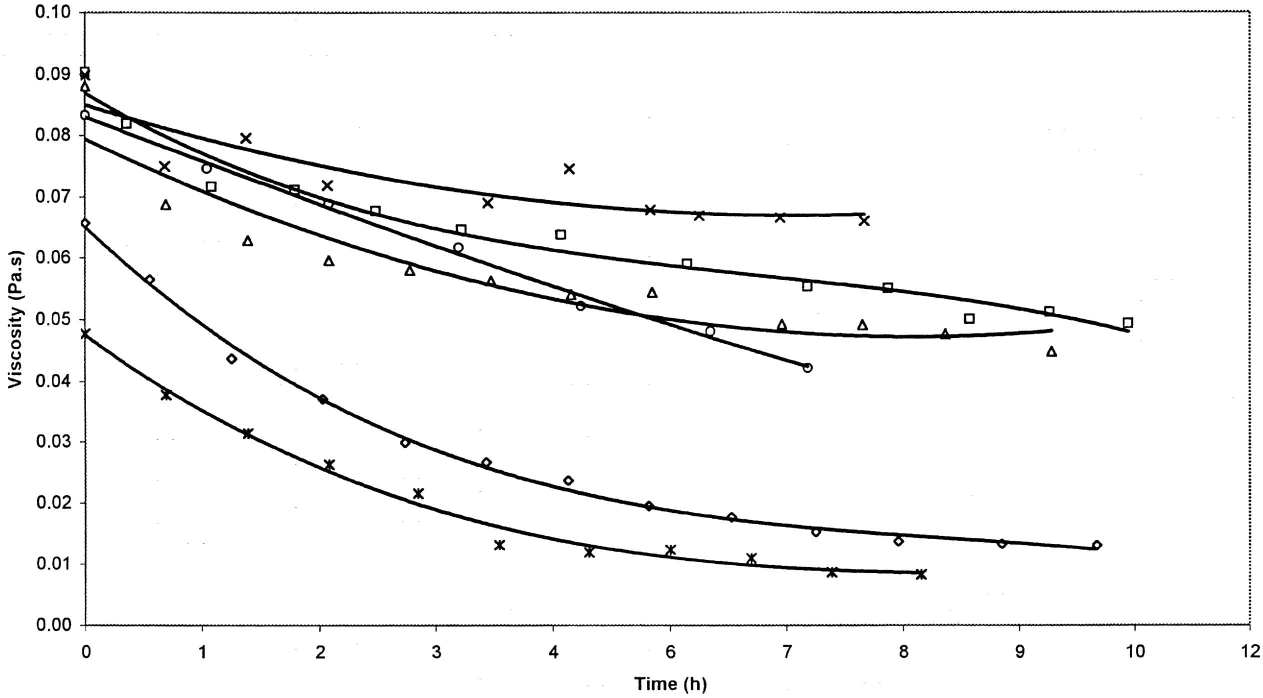

Fig. 3. The effect of additives on the viscosity of sheared cassava starch samples held at 60°C and measured at a shear rate of 27 s^{-1}: □, no additive; ◇, 0.1% sulfite; ∗, 0.01% ascorbate; △, 0.001% ascorbate; ×, 0.001% ascorbate + 0.05% propyl gallate; ○, 0.1% glutathione.

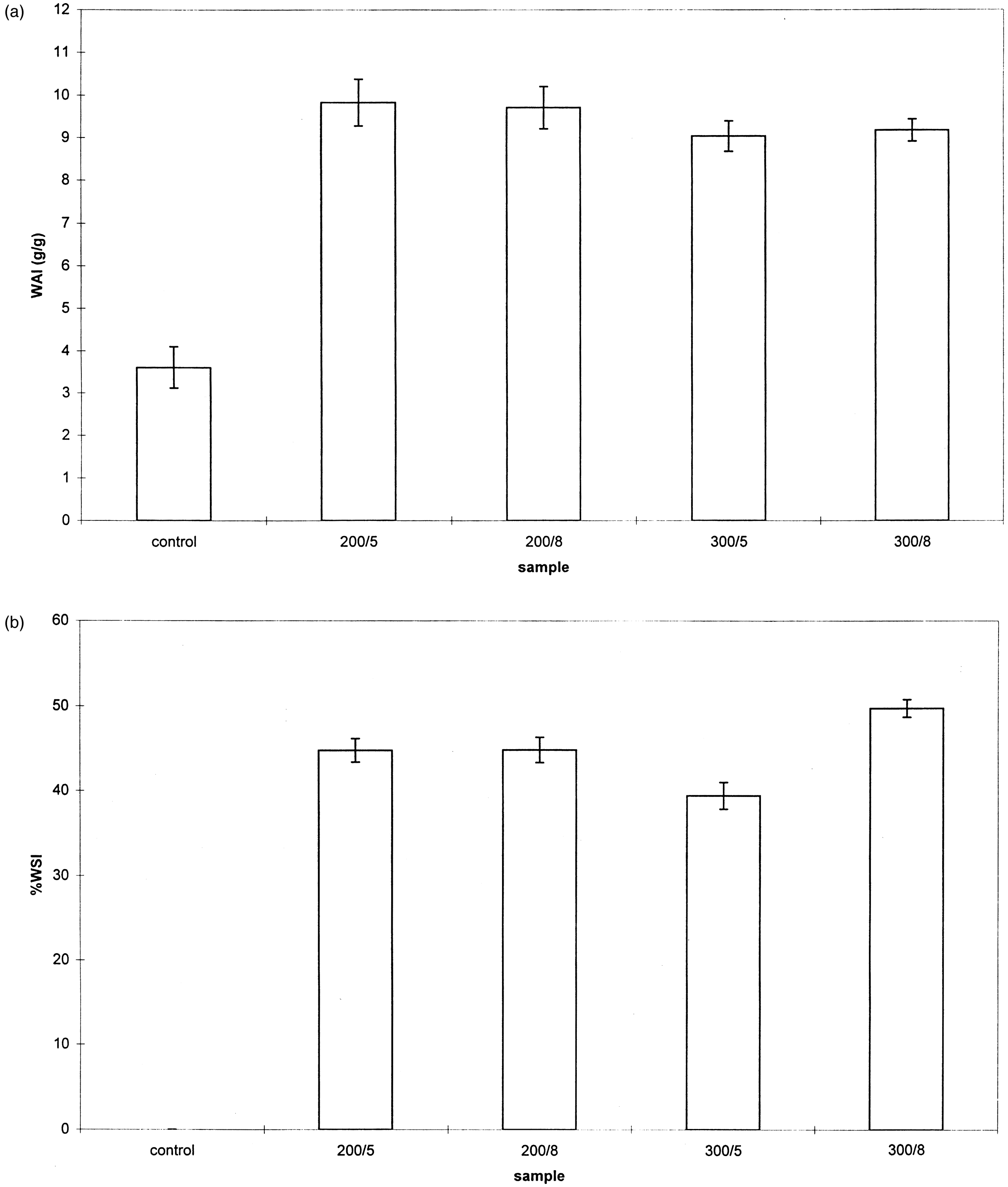

Fig. 4. Estimates on cassava samples (mean and standard error of at least three replicates) prepared using a twin screw extruder under conditions of increasing temperatures in four different barrel zones. Extrudates were obtained by factorially varying the screw speeds (200 and 300 rpm) and feed rates (5 and 8 kg/h), and were denoted as 200/5, 200/8, 300/5 and 300/8. (a) Water absorption index of cassava extrudates; (b) Water solubility index of cassava extrudates; (c) Viscosity of alkaline solutions (1% starch) prepared from cassava extrudates.

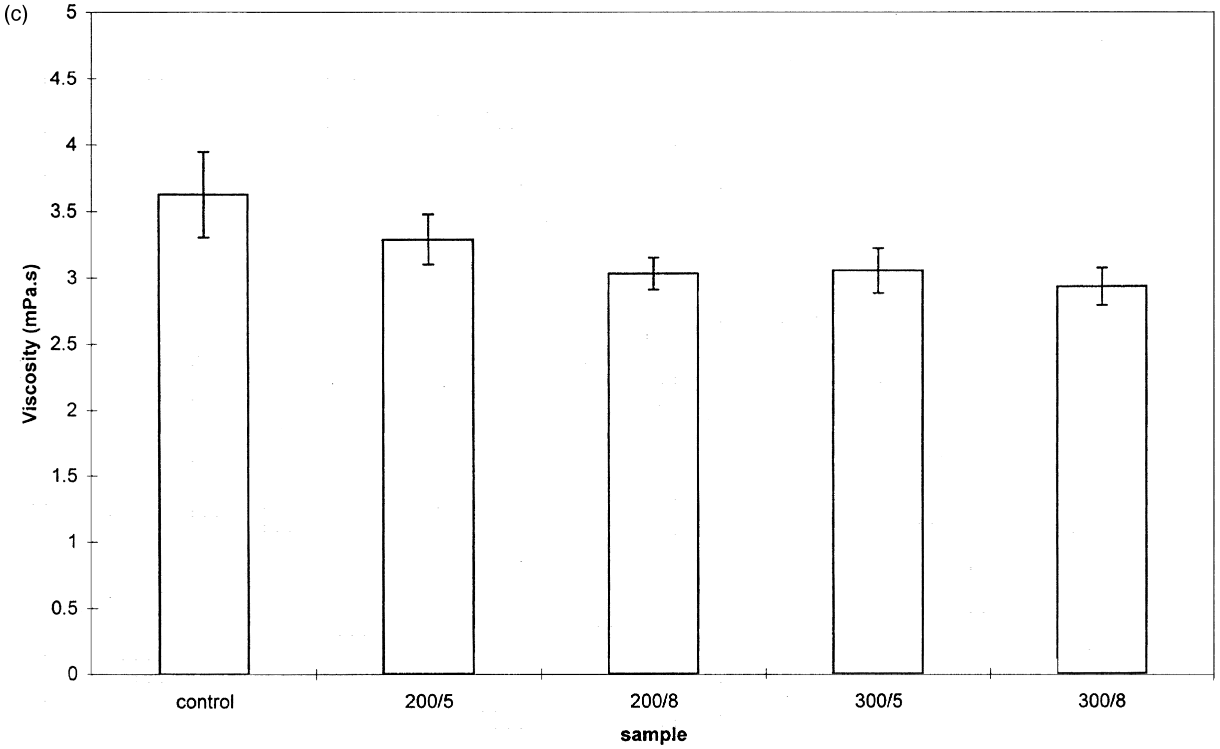

Fig. 4. (*continued*)

centrifugation (Multex, MSE Centrifuge, UK) at 3000 rpm (2045 × *g*) for 10 min and the water absorption index (WAI) expressed as the weight of pellet per gram of sample. The supernatant was evaporated to dryness at 105°C until constant weight. The water solubility index (WSI) was the weight of dry solids in the supernatant expressed as a percentage of the original weight of sample.

2.5.4. Alkaline viscosity measurements of solubilised starch macromolecules (based on Paterson et al., 1996)

Starch samples (0.4 g) were mixed with ethyl alcohol (1 ml). To this suspension was added 8 ml of 5 M KOH. The samples were stirred overnight and a clear solution was then visible. These solutions were diluted to 40 ml with water (1% starch) and aliquots (30 ml) of the resulting solutions were measured using a Bohlin CS10 Rheometer using a double gap concentric cylinder measuring geometry (DG 40/50) over the increasing shear rate range 1–100 s^{-1}. Owing to its large surface area, this particular measuring geometry is most suitable for measuring low viscosity fluids. The samples were equilibrated at 25.0 ± 0.1°C for 10 min on the rheometer before the first measurement was taken. The results are reported at a constant shear rate of 10 s^{-1}.

2.6. Statistical analysis

Statistical analysis was by Analysis of Variance (ANOVA).

3. Results and discussion

3.1. Comparison of native starches

Starches from three main sources were used. The swelling volume estimates for all the three samples differed. Target Brand, the commercially available cassava starch, exhibited the highest swelling volume (Fig. 2). These results clearly indicate the wide variation in performance of cassava starches.

3.2. Effect of additives on starch pastes

Fig. 3 demonstrates the decrease in viscosity that occurs when holding pregelatinised and sheared cassava samples (M4) at 60°C. Three different additives demonstrate that their inclusion promotes the loss of viscosity. Each of the assay points represents a separate assay and other work from the Nottingham group (Vallès Pàmies et al., 1997) confirms that there is a significant loss in viscosity occurring due to the presence of 0.1% sulfite, 0.01% ascorbate, 0.001% ascorbate, or 0.1% glutathione in a 5% sheared cassava starch paste.

As additives are added to the pregelatinised and homogenised starch pastes, it suggests that degradation of the polymer is important rather than the degradation mechanism being based solely on the granule swelling phenomenon. Addition of propyl gallate reduces the viscosity loss, even when compared to the control.

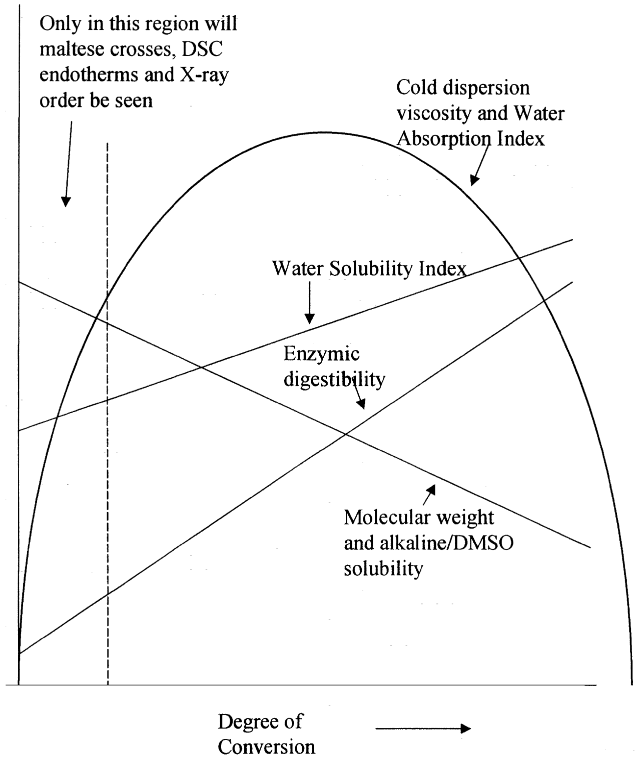

Fig. 5. Typical relationships between parameters used to estimate the amount of starch conversion.

3.3. Thermomechanical treatment: extrusion

Extrusion was carried out on Target Brand as this was a native cassava starch that gave high swelling volume (Fig. 2) when compared to research samples (Griffiths, 1997). Extrusion cooking can be regarded as a combination of thermal and mechanical action, and is becoming increasingly important in the food industry for transforming materials into intermediate or finished products (Camire et al., 1990; Chinnaswamy, 1993).

Samples were produced by extrusion in the twin-screw extruder through a slit die to form non puffed samples. All the samples produced using the four experimental sets of conditions appeared similar but had differing moisture contents. After drying and milling, all four samples had moisture contents between 9.88 and 10.63% (dry basis).

The degree of conversion of starch from the granule form during processing was assessed by the techniques of WAI, WSI and viscosity measurements. The results are shown in Fig. 4a–c. The WAI and WSI characterise the extrudate products and are often important in predicting how the extruded materials may behave if further processed. A high WSI and low WAI would indicate that the starch has undergone extensive conversion. The estimates of starch granule behaviour are clearly different for the extruded samples compared with the non extruded control. In the high shear environment within the extruder the granules are being damaged and thus water can easily penetrate into the granule when the extrudates are mixed with water. The granules become highly expanded and starch molecules become soluble and can then leave the granule.

The viscosity of the system solubilised in potassium hydroxide allows starch solutions to be estimated rather than suspensions. It can be assumed that these viscosities are related to the molecular size of the starch polysaccharides (Hoseney et al., 1992). The measurements were made on 1.0% starch (dry weight basis). Under these conditions a low viscosity Newtonian solution was obtained. The results displayed in Fig. 4c show that raw cassava starch provided the highest viscosity; however no statistical difference was detected between the extruded samples. The significant decreases of viscosity values for the extruded samples compared to the native control sample show that as well as starch granule damage the actual molecular structure of the amylose and/or amylopectin is disrupted during the extrusion process.

The screw and feed rates were varied in the experiments and this caused a variation in the specific mechanical energy (SME) between 70 and 112.7 W.h/kg. Despite the use of the wide range of SMEs little differences between the samples can be detected using WAI, WSI or alkaline viscosity. Increasing the feed rate or the screw speed tends to increase the SME. Increased SME normally subjects the starch granule to more damage and this is measured as increased starch conversion. The typically reported (Wang et al., 1992) relationships between the parameters estimated and degree of starch conversion are shown in Fig. 5.

4. Conclusions

Cassava starch can be a variable starting material for food product manufacture. The variability would appear to be due to intrinsic and extrinsic factors. It has been observed that cassava cultivars from different environments provide starches that are markedly different (Mat Hashim et al., 1992; Fernandez, 1996; Griffiths, 1997). The results from Fernandez (1996) suggested that the functional behaviour of native cassava starches of different origin appeared to be associated with molecular structure and the architecture of the starch granule. There has been considerable rhetorical evidence and some rheological findings (Mestres et al., 1996; Mestres and Rouau, 1997) that the method of drying cassava starch may alter its properties; sun dried cassava starch behaving differently from oven dried samples. Certainly the three starch samples reported in this work have very different behaviour on gelatinisation. It is possible that sun drying and the effect of the additives—sulfite, ascorbate and glutathione—are due to the same phenomenon. It has been proposed that addition of additives can promote an oxidative reductive depolymerisation reaction. The effects of the additive sodium sulfite on the viscosity of cassava starches were investigated by Mat Hashim et al. (1992), Paterson et al. (1996) and Vallès Pàmies et al. (1997) and

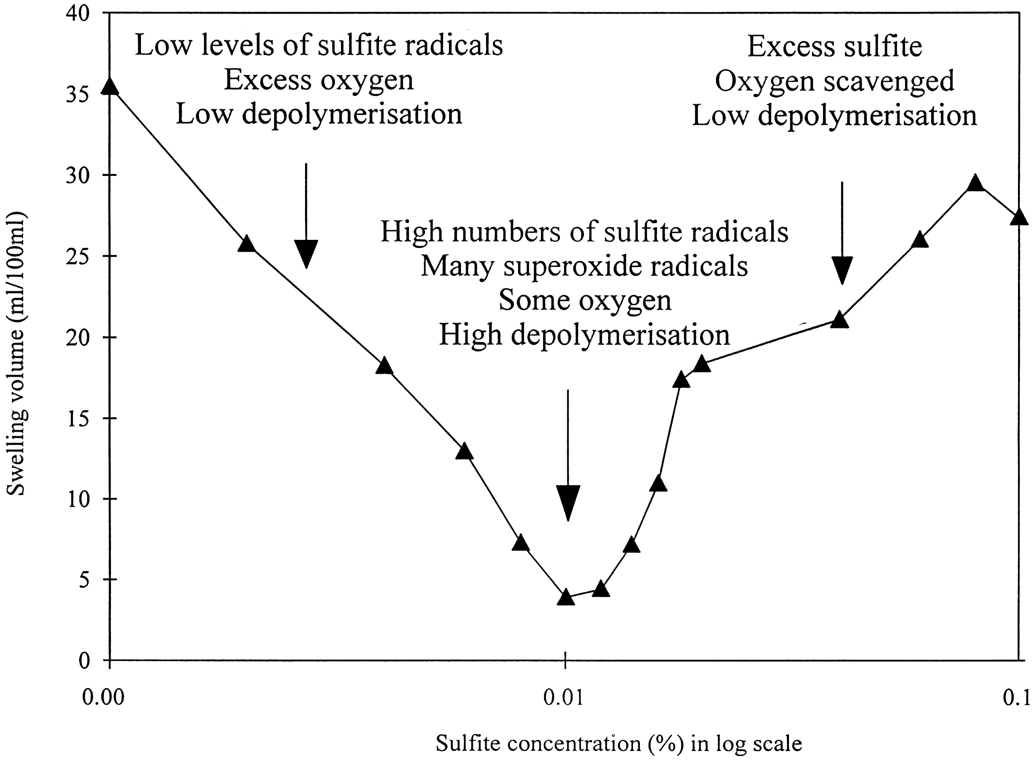

Fig. 6. Swelling volume changes due to pasting cassava starch in the presence of differing levels of sulfite. Possible reasons for the finding are annoted.

the suggested mechanism of the sulfite was thought to be due to free radical mechanisms causing oxidative reductive depolymerisation. Suggested reasons for the pattern of starch behaviour in the presence of differing levels of sulfite are shown in Fig. 6.

Interestingly, Griffiths (1997) reported that a native cassava starch (Target Brand) irradiated by UV light for 48 h could show a marked decrease in paste viscosity. It is suggested that the UV light may well be generating radicals that behave in a manner equivalent to those generated by additives such as sulfite and ascorbic acid.

The major changes to the starch during extrusion would be expected to come from the mechanical damage to the starch granules. Breakage of the granule structure in a limited water environment could be expected as the molten mass passes between the flight of the screw and the barrel wall. The parameters that affect the change are expected to relate to the SME that reflects the viscosity of the mix and hence the shear forces experienced by the starch. However, on occasions (as shown in this study) poor correlation exists between the mechanical energy in the system and the measured amount of starch conversion.

The work of Vallès Pàmies et al. (1997) has demonstrated that additives can affect the properties of starch pastes on addition at temperatures as low as 30°C, while studies by Paterson et al. (1996) showed marked differences to wheat starch depending on the level of sulfite addition at 120°C. Any free radical action that is generated in an extruder could therefore be expected to influence the properties of the extruded product. These extruded samples can be defined as half-products (Matz, 1993) which can be expanded by frying or baking without using complex high-pressure extrusion apparatus. It would be expected that this expansion would be greatly influenced by the molecular weight of the starch polysaccharides and hence by the amount of oxidative reductive depolymerisation.

To conclude, cassava starch is affected by chemical, thermal and mechanical degradation. In the future, more information on the interaction between these causes of the changes to starch will be elucidated. It is hoped that these results might aid in explaining why native starches show so much variation.

Acknowledgements

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References

Anderson, R.A., Conway, V.F., & Griffin, E.L. (1969). Gelatinization of corn grits by roll- and extrusion-cooking. *Cereal Sci. Today, 14 (1)*, 4–11.

Blanshard, J.M.V. (1994). Cassava starch, structure, properties and implications for contemporary processing. In *Proceedings of the 2nd International Scientific Meeting: The Cassava Biotechnology Network* (pp. 625–638), Bogor, Indonesia.

Camire, M.E., Camire, A., & Krumhar, K. (1990). Chemical and nutritional changes in foods during extrusion. *CRC Crit. Rev. Food Sci. Nutr.*, *29 (1)*, 35–57.

Chinnaswamy, R. (1993). Basis of cereal starch expansion. *Carbohydr. Polym.*, *21*, 157–167.

Cock, J.H. (1985). *Cassava: new potential for a neglected crop* (p. 12). Boulder, CO: Westview Press.

Fan, J., Mitchell, J.R., & Blanshard, J.M.V. (1996). The effect of sugars on the extrusion of maize grits: I. The role of the glass transition in determining product density and shape. *Int. J. Food Sci. Technol.*, *31*, 55–65.

Fernandez, A.Q. (1996). Effects of processing, procedures and cultivar on the properties of cassava flour and starch. Ph.D. Thesis. University of Nottingham, UK.

Glicksman, M. (1969). Starches. In M. Glicksman (Ed.), *Gum technology in the food industry* (p. 278). New York: Academic Press.

Griffiths, W.V. (1997). Variations in the physico-chemical properties of cassava starches: How and why do they differ? Student Project Dissertation. University of Nottingham, UK.

Hoseney, R.C., Mason, W.R., Lai, C.-S., & Guetzlaff, J. (1992). Factor affecting the viscosity and structure of extrusion-cooked wheat starch. In J.L. Kokini, C.T. Ho & M.V. Karwe (Eds.), *Extrusion science and technology* (pp. 277–305). New York: Marcel Dekker.

Mat Hashim, D.B., Moorthy, S.N., Mitchell, J.R., Hill, S.E., Linfoot, K.J., & Blanshard, J.M.V. (1992). The effect of low levels of antioxidants on the swelling and solubility of cassava starch. *Stärke*, *44 (12)*, 471–475.

Matz, S.A. (1993). *Snack food technology* (3rd ed., p. 159). New York: AVI.

Mestres, C., & Rouau, X. (1997). Influence of natural fermentation and drying conditions on the physicochemical characteristics of cassava starch. *J. Sci. Food Agric.*, *74*, 147–155.

Mestres, C., Boungou, O., Zakhia, N., Rouau, X., & Faure, J. (1996). Comparison of the ability of fermented maize flour and cassava starch for making bread-like products. Posters #80 AACC Annual Meeting. September, Baltimore, MD.

Paterson, L., Mitchell, J.R., Hill, S.E., & Blanshard, J.M.V. (1996). Evidence for sulfite induced oxidative reductive depolymerisation of starch polysaccharides. *Carbohydr. Res.*, *292*, 143–151.

Rickard, J.E., Asaoka, M., & Blanshard, J.M.V. (1991). Review: The physico-chemical properties of cassava starch. *Trop. Sci.*, *31*, 189–201.

Vallès Pàmies, B., Barclay, F., Hill, S.E., Mitchell, J.R., Paterson, L.A., & Blanshard, J.M.V. (1997). The effects of low molecular weight additives on the viscosities of cassava starch. *Carbohydr. Polym.*, *34*, 34–38.

Wang, S.S., Chiang, W.C., Zheng, X., Zhao, B., Cho, M.H., & Yeh, A.-I. (1992). Application of an energy equivalent concept to the study of the kinetics of starch conversion during extrusion. In J.L. Kokini, C.T. Ho & M.V. Karwe (Eds.), *Extrusion science and technology* (pp. 165–176). New York: Marcel Dekker.