Extrusion of cassava starch with either variations in ascorbic acid concentration or pH

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Summary Thermal mechanical extrusion is used to make cassava products that are later expanded by frying. During extrusion the native starch granules are broken down and starch polymers degraded. This continuum of change to the starch has been termed starch conversion. Inclusion of ascorbic acid promoted starch conversion as measured by a range of techniques including measurement of water solubility, water absorption, hot paste and alkaline viscosities. It was found that the Rapid Visco Analyser (RVA, Newport Scientific, NSW, Australia) was particularly sensitive in the monitoring of the changes owing to extrusion. Expansion of the extruded product was increased at the higher starch conversions caused by ascorbic acid addition. Changes in starch conversion were greater in the presence of ascorbic acid compared with general acid treatment at equivalent pHs. Although the general acidification did encourage more starch conversion there was no measured change in the expansion properties.

Keywords Expansion, pH, RVA, water absorption index, water solubility index.

Introduction

Cassava is one of the most important metabolic sources of energy for millions of people in the tropics and is also an important raw material for other industrial uses (Rickard et al., 1991; Blanshard, 1994). There are many expanded snack foods commonly eaten in ASEAN countries that are based on cassava starch (Yu & Low, 1992). These products are often formed as pellets and are then expanded into a porous lowdensity product in an oven or fried in oil before consumption. The pellets can also be formed by extrusion cooking (Matz, 1993). Cassava starch has been reported to have a particularly high degree of expansion (Yu, 1991) and this is very important to the eating quality of snack foods. For example, crispness is said to be the most important sensory attribute in fish crackers (Yu,

*Correspondent: Fax: +44 115 9516142; e-mail: sandra.hill@nottingham.ac.uk vaporization inside the amorphous starch matrix at the initial stages of frying, but reaches a plateau before maximum moisture loss. During expansion the starch matrix must accommodate the water vapour within the bubble. Hence starch structure and molecular weight must be of importance as it will govern the viscosity of the matrix. Cooking alters native starch. The granular structure is disrupted and the amylose and amylopectin chains can be broken. The term starch

lopectin chains can be broken. The term starch conversion has been used to describe the continuum of changes that occur from the native starch granule to depolymerized starch molecules (Mitchell *et al.*, 1997). Important parameters that govern starch conversion are water levels, temperature, shear and the chemical environment. Starch conversion during extrusion has been well

1993) and the linear expansion often correlates

with a measure of crispness. Vasanti Nair *et al.* (1996) have proposed that the expansion of tapi-

oca chips takes place as a result of rapid water

documented but is typically considered only in terms of thermal and mechanical changes (Colonna & Mercier, 1983; Colonna *et al.*, 1984; Colonna *et al.*, 1989; Kokini *et al.*, 1992; Myllymäki *et al.*, 1997). It is sometimes considered that most of the depolymerisation of the starch that occurs is owing to mechanical action (Diosady *et al.*, 1985).

Work at the University of Nottingham has indicated that starches can be also be depolymerised by the action of redox agents and cassava starch is particularly liable to undergo oxidative reductive depolymerisation compared with other tuber and cereal starches (Paterson *et al.*, 1996). The agents sulfite and ascorbic acid have been shown to cause changes in viscosity of a range of starches when heated in excess water (Vallès-Pàmies *et al.*, 1997). We have now shown that the inclusion of ascorbic acid with cassava, when it is cooked with limited water at temperatures above of 100 °C, changes the amount of starch conversion which occurs (Sriburi *et al.*, 1999a).

Ascorbic acid is often used in wheat products, especially bread, as it is said to have a role in increasing loaf volume (Tsen, 1965; Thewlis, 1974; Elkassabany & Hoseney, 1980; Chamberlain, 1981; Lillard et al., 1982; Pachla & Reynolds, 1985; Grosch, 1986; Halliwall & Gutteridge, 1995). The action of the ascorbic and its oxidised form of dehydroascorbic acid (DHAA) is thought to be on the gluten in the flour promoting changes in the disulfide bonds (Fitchett & Frazier, 1986; Grosch & Wieser, 1999). However, the initial work of cassava starch could indicate that the starches may also be altered in some circumstances by the presence of ascorbic acid.

The objectives of the work reported in this paper are to demonstrate if ascorbic acid promotes depolymerisation of cassava starch when extruded and if additional depolymerisation occurs, does it affect changes in the expansion of the product.

Materials and methods

Materials

Commercial cassava starch (Target Brand, product of Thailand) with a moisture content of 13% (dry

basis) was supplied by National Starch and Chemical Company (Manchester, UK). The specifications from the supplier listed that the starch contained 0.5% protein, 0.2% fat and 97% carbohydrate on a dry basis.

L-Ascorbic acid, sodium hydroxide, metaphosphoric acid and 2,6-dichlorophenolindophenol (sodium salt) were purchased from Sigma Chemical Co. (Poole, UK). Potassium hydroxide, hydrochloric acid and lithium chloride were obtained from BDH Laboratory Supplies (Poole, UK). Glacial acetic acid and sodium bicarbonate were purchased from Fisher Scientific UK (Loughborough, UK). Ethyl alcohol, potassium hydrogen phthalate and the buffer salts (di-sodium phosphate:sodium-di-orthohydrogen hydrogen purchased phosphate) were from Fisons Equipment (Loughborough, UK). All reagents were of analytical grade. All measurements were carried out in a pH 6.5 phosphate buffer unless otherwise stated. Pure vegetable oil (Asda, UK) was used for frying of cassava extrudates.

Extrusion

We manufactured the samples using a Clextral BC-21 intermeshing twin screw extruder (Clextral, Firminy, France). Cassava starch was extruded under the following conditions of temperatures in the different barrel zones (40, 90, 110 and 75 °C). A screw speed of 200 r.p.m. and screw torque between 10 and 11 N.m was used. Cassava starch was fed into the extruder at 5 kg.h⁻¹. The extruder feed solution was normally 0.1 M phosphate buffer (pH 6.5) and was added at 3 kg.h⁻¹, in order to obtain a moisture content inside the extruder of around 37.5% (wet basis). Ascorbic acid was dissolved in the buffer immediately before extrusion. A range of extrudates was obtained with ascorbic acid level of 0, 0.1, 0.3, 0.5, 0.7 and 1.0% (starch basis). The specific mechanical energy (SME) of all experiments was around 55.5 w.h.kg⁻¹, as calculated below (Fan et al., 1996):

 $SME(w.h.kg^{-1}) =$ screw torque (N.m)×screw speed (s⁻¹)×no. of screws

mass flow rate (kg.h -1)

A ribbon type die with a 1 mm \times 30 mm dis-

charge slit was used to produce nonexpanded strips. We did two sets of experiments with ascorbic acid with a one month gap between runs. Extrusion for the pH control experiment was carried out on a third occasion using the same method.

Extruder feed solutions to regulate pH were as follows (Shugar *et al.*, 1981):

- pH 1 = 0.1 M HCl;
- pH 2 = 0.01 M HCl;
- pH 3 = 0.1 M potassium hydrogen phthalate (KHP) (750 ml) + 0.1 M HCl (334.5 mL);
- pH 4 = 0.1 M KHP (1000 mL) + 0.1 M HCl (20 mL);
- pH 5 = 0.1 M KHP (750 mL) + 0.1 M NaOH (339 mL);
- pH 6.5 (control) = 0.1 M sodium phosphate buffer.

Moisture content equilibration

On extrusion the strips of cassava product were cut into pieces approximately 2.5 cm square, cooled at room temperature for 12 h and dried in a 70 °C oven (Carbolite, Sheffield, UK) for 10 h. They were then equilibrated over saturated LiCl salt solution in air-tight plastic boxes for one week at room temperature to attain a final moisture content of 10-11% (dry basis). Apart from the examination of degree of expansion, samples for all other methods were ground using a coffee grinder (Moulinex, Ireland). The powder produced was sieved and fractions collected between the 106 and 422 µm sized sieves were used. Samples were stored in small plastic containers at ambient temperature. The moisture content was determined in two replicates by drying 1-2 g of samples using Infrared dryer (Sartorius Thermo Control YTC O1L, Germany) at 160 °C until constant weight.

Water absorption and water solubility indices

The water absorption index (WAI) measures the volume occupied by the granule or starch polymer after swelling in excess water. While water solubility index (WSI) determines the amount of free polysaccharide or polysaccharide released from the granule on addition of excess water. The WAI and WSI can be used to characterize extruded products

and are often important in predicting how the materials may behave if further processed. These methods are simple, easy to apply and the results are consistent when precise methodology is applied. It must be noted that the WAI and WSI measurements give results which depend specifically on the amount of sample being used in the assay as well as the particle size of the milled extrudates. The milling procedure might also alter the starch. It is therefore important to consider these features in order to provide reproducible data and when comparing these values. An increase in WSI denotes increasing starch conversion while WAI shows a maximum level at a certain amount of starch conversion. This maximum is when the starch granules are sufficiently damaged for these to imbibe water without disintegration (Mitchell et al., 1997).

Typically the method used was to mix 0.3 g of dried powdered sample with 10 mL of distilled water and allow to hydrate and sediment overnight. The suspensions were then subjected to centrifugation (Multex, MSE Centrifuge, UK) at 3000 r.p.m. (2045g) for 10 min and WAI expressed as the weight of pellet per gram of sample. The supernatant was evaporated to dryness at 105 °C until constant weight. WSI was the weight of dry solids in the supernatant expressed as a percentage of the original weight of sample (Sriburi *et al.*, 1999a).

Viscosity measurement of alkaline solutions

Viscosity of extruded samples gives information on the state of starch conversion as a result of the extrusion process. This estimate used in this study was based on that of Sriburi et al., (1999a). We mixed powdered extruded samples (0.2 g) with ethyl alcohol (0.5 mL). To this suspension was added 4 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 (0.5% starch) and the viscosities of aliquots (30 mL) of the resulting solutions were measured using a Bohlin CS10 Rheometer (Bohlin, Lund, Sweden) 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 suitable for measuring low viscosity fluids. The samples were equilibrated at 25.0 ± 0.1 °C for 10 min in the rheometer before the first measurement was taken. The results are reported at a shear rate of 10 s⁻¹.

Viscosity measurement using the Rapid Visco Analyser (RVA)

The RVA is an instrument for determining the viscous properties of starch under controlled heating conditions. When starch granules are heated in water beyond a certain temperature, the granules absorb a large amount of water and swell to many times their original size. When the majority of granules become swollen, a rapid increase in viscosity occurs as the fragile swollen granules break down. The peak viscosity occurs at the equilibrium point between swelling causing an increase in viscosity, and rupture of the swollen granules causing viscosity decrease. As the mixture is subsequently cooled, re-association between starch molecules can occur. In sufficient concentration this causes the formation of gel, and viscosity will normally increase to a final viscosity. An example of the RVA profile for native cassava starch is shown in Fig. 1.

Samples for RVA analysis were based on 3 g (dry weight basis) of samples plus buffer of 25 g. The paddle was placed into the canister containing the sample and buffer. The paddle blade was vigorously jogged up and down 10 times through

the sample. The sample was then inserted into the RVA Series 4 (Newport Scientific, NSW, Australia) which was used along with the accompanying software (Thermocline). The analysis used the standard 1 profile and the temperature of the system is shown in Fig. 1.

X-ray diffractometry

X-ray measurement detects the semicrystalline character, which reflects the presence of both the ordered and amorphous regions within the starch granule. These will be lost in starch gelatinization or high levels of starch conversion.

The pattern of crystallinity of the extruded product was assessed by X-ray diffraction. The powered samples were put into an aluminium holder, and were analyzed using Siemens D5005 X-ray diffractometer (Bruker Analytical, Germany). The sample was subjected to the following conditions: target, CuK α ; a graphite crystal monochromator; angular range, 4–32° (20); angular interval, 0.05° (20); copper tube; 40 kV; 50 mA; wavelength, 0.154 nm. Data were collected by a microcomputer and duplicate scans were made for each sample.

Measurement of linear expansion

Each extrudate piece with a weight between 1.5 and 2.0 g was marked using a marker pen (Edding



Figure 2 Sample preparation for measurement of linear expansion. The length of each line was measured before and after frying.



780, Ahrensburg, Germany) as shown in Fig. 2.

Linear expansion was calculated by measuring the 4 lines shown in Fig. 2 before and after frying in hot vegetable oil at 185 °C for 15 sec. Measurements were made on 10 replicates from each run for each treatment. The percentage linear expansion was calculated as follows (Yu *et al.*, 1981):

% Linear expansion = $\frac{(\text{length after frying} - \text{length before drying}) \times 100}{\text{length before frying}}$

Determination of ascorbic acid

Ascorbic acid levels were determined to find out how much ascorbic acid was used during extrusion cooking. The amount of ascorbic acid in the milled samples after extrusion was estimated by the method of titration with indophenol. There are advantages in using indophenol as it reacts almost instantaneously in a fixed stoichiometry with ascorbic acid at all concentration levels; it acts as a self-indicator; and because of the deep blue colour of its solutions, a very dilute titrant can be used without hampering visual detection of the end point. The last advantage accounts for the sensitivity of indophenol titration, which is much greater than those of other titrations (Verma *et al.*, 1996).

The ascorbic acid powder used in the preparation of the extrudates was the same as that used as the standards in the titrations. Care had been taken to use a new batch material at the start of the work. This batch was then subdivided and stored at 4 $^{\circ}$ C before use.

Determination of the amount of ascorbic acid

was based on the AOAC standard method (Helrich, 1990) and that of Kirk & Sawyer (1991), but a further two-fold dilution of the indophenol standard solution was made. The ascorbic acid content of samples was estimated by mixing 0.5 g of sample with 10 mL of extraction solution (metaphosphoric acid-acetic acid solution) for 1 h and titrating 5 mL of extract supernatant with 2,6-dichlorophenolindophenol and correcting for the blank using an equivalent amount of extraction solution. The percentage of ascorbic acid was calculated as follows:

% ascorbic acid (g/100 g sample) = $\frac{2.46 \times 10^{-2}}{(A - B)}$

where A and B are average volume (mL) of indophenol used for sample titration and blank titration, respectively.

Two samples were taken from each extruder run and titrated in duplicate. Results are averaged from the eight values thus obtained.

pН

The pH values were measured on 10% (w/v) suspensions of the powdered samples using a pH meter (Jenway 3320, Jenway, Essex, UK).

Statistical analysis

We have used either Analysis of Variance (ANOVA) or paired *t*-test where appropriate to analysis the data. Statistical differences are indicated in the text within the results' section. Most assays were replicated three times and mean values are given. Typically for the ascorbic acid studies, where two separate extruder trials had been

Table 1 The variations in the measures for the control cassava extrudates obtained for two runs using ascorbic acid and the control for the pH adjusted extruder run

Run no.	Cassava starch batch	pH of extrudate suspensions	WAI (g/g)	WSI (%)	RVA peak viscosity (mPa.s)	RVA final viscosity (mPa.s)	Alkaline viscosity (mPa.s)	Overall linear expansion (%)
Ascorbic	No.1	6.50	5.78	60.7	1384	393	1.69	77.3
Acid			(0.05)	(0.81)	(43)	(30)	(0.01)	(5.7)
RUN 1								
Ascorbic	No.2	6.75	8.94	32.6	2072	495	1.94	75.2
Acid			(0.09)	(0.77)	(7)	(10)	(0.01)	(5.8)
RUN 2								
pH adjusted	No.2	6.56	7.55	54.5	909	329	1.90	73.2
			(0.05)	(0.45)	(38)	(10)	(0.00)	(4.3)
RUN 3								

All extrudates were formed at pH 6.5. Values are mean with standard deviation, brackets, of three values for all assessment except linear expansion where 10 replicates were used.

done, the means from both runs were averaged. Numbers of replicates are shown on the tables and graphs.

Results and discussion

Cassava samples in ascorbic acid-buffer systems were produced by a twin-screw extrusion through a slit die to form nonpuffed samples. The extruder conditions used were as identical as possible. However, the results for the control samples, as shown in Table 1, indicate that there are significant differences (ANOVA, P < 0.001) between all the measures of starch conversion. This is not untypical of work using extrusion as it is very difficult to replicate exactly the performance of the equipment (El-Dash, 1981; Sheard *et al.*, 1986; Guha *et al.*, 1998). Another factor is that a different batch of cassava starch from another year was used for the second run for the ascorbic acid study compared to the first run. The second batch of starch was used for the pH study. This may have a significant effect on the levels of starch conversion detected as cassava starch is known to be very variable



Figure 3 Indicators of starch conversion in cassava extrudates formed by inclusion of ascorbic acid. Cassava starch was extruded under conditions of barrel temperatures (40, 90, 110 and 75 °C), screw speed (200 r.p.m.), starch feed rate (5 kg.h⁻¹), buffer feed rate (3 kg.h⁻¹) and moisture content (37.5% wet basis). Water absorption index (WAI) is shown in (a) and water solubility index (WSI) in (b). Two extruder runs were carried out; run 1 (\bigcirc) and run 2 (\triangle). Bars indicate \pm one standard deviation of three replicates.

Water absorption and solubility indices

A high WSI and low WAI would indicate that the starch has undergone extensive conversion. The results obtained for these two parameters after the addition of ascorbic acid are illustrated in Fig. 3(a), (b). WAI and WSI results show significant changes (ANOVA, P < 0.001) owing to ascorbic acid addition and therefore it could be supposed that ascorbic acid encourages gelatinization and molecular breakdown of the starch. The higher the level of ascorbic acid the greater the amount of starch conversion, but our results show that even very low additions of ascorbic acid cause a difference in the behaviour of the starch. Extrudate at 0.1% ascorbic acid concentration, the lowest level used, showed a significantly (paired ttest) higher WSI (P < 0.001) and lower WAI (P <0.002) than the milled controls.

Viscosities measured by the Rapid Visco Analyser in alkaline solutions

The RVA viscosity profiles of all samples were examined using the Standard 1 temperature profile at the minimum and maximum temperatures of 50 and 95 °C. The viscosity profiles are shown in Fig. 4. This figure gives the average of the results from both extruder runs. The results suggest that the milled extrudate appear to swell when added to water at a temperature below that necessary for cassava starch gelatinization. Also, no peak appears at the higher temperature which one would expect if native starch was present (Fig. 1). This indicates that the starch granules must be extensively broken down within the extruder.

Clearly, all addition levels of ascorbic acid have a significant effect on cassava starch during extrusion as shown by the RVA viscosities (Fig. 4). The swelling and the breakdown of the starch granules seems to be different, as demonstrated by the peak viscosity. The materials at the end of the temperature cycle should reflect the size of the macro-



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Figure 4 RVA profiles for cassava extrudates formed in the presence of ascorbic acid (extruder conditions given in Fig. 3). Milled extrudates (3g) were mixed with 25g buffer. Lines represent the average of the two extruder runs, with each extruder run representing three replicated assays. The temperature (°C) profile during the RVA measurement is shown.

molecular starch polymers. This final viscosity also decreases with ascorbic acid addition (Fig. 5).

Starches can be solubilized in potassium hydroxide and therefore viscosity estimates of these solutions can be assumed to be related to the actual average molecular size of the starch polysaccharides (Hoseney *et al.*, 1992). This should be a better measure of molecular size compared to the RVA final viscosities where starch aggregation could occur. The measurements on the extrudate material for alkaline viscosity were made on a



Figure 5 The effects of different levels of ascorbic acid on cassava extrudates (see legend to Fig. 3 for details of extrusion condition) on: (▲) RVA final viscosity and (*) alkaline viscosity. Each value is the mean of the two extruder runs with data for each run being replicated three times.

0.5% starch (dry weight basis). Under these conditions a low viscosity Newtonian solution was obtained.

The results for the RVA final viscosities and alkaline viscosities with the range of ascorbic acid concentration used are displayed in Fig. 5. The viscosities for both estimates are lower on addition of ascorbic acid. Even the addition of 0.1% ascorbic acid causes a significant change (paired *t*-test, P < 0.003) for both these estimates. These results could be explained by the concept that during the extrusion ascorbic acid has affected the starch polymer so that depolymerization of the starch macromolecules has occurred.

X-ray diffractometry

Using the X-ray diffraction technique, the data obtained in Fig. 6 suggests that native cassava



Figure 6 (X)-ray diffraction patterns of cassava extrudates formed by inclusion of ascorbic acid at various levels (extruder conditions given in Fig. 3). The pattern for native cassava starch is also shown.

starch can be designated as possessing an 'A' type pattern (Banks & Greenwood, 1975; Rickard *et al.*, 1991; Fernandez, 1996). Native cassava starch shows peaks at approximately 15 and 23° (2 θ) which are characteristics of the initial starch A-pattern. These features are not apparent in the extruded samples. It would appear that the native cassava granule order is completely lost when extrusion is carried out in both the absence and presence of ascorbic acid. The level of ascorbic acid does not seem to affect the X-ray pattern observed of these extruded samples which had been stored more than 18 h before assessment.

Determination of ascorbic acid

Figure 7 shows that the greater the level of ascorbic acid addition to form the extrudate the more it is consumed. However, it was found that at the higher rates of ascorbic acid inclusion of 0.7 and 1.0%, only 25% of the ascorbic acid was used while at the addition of 0.1%, 50% was utilized. There has been no attempt to find the products of the reaction and it is not known if the compound that initiates the changes in the starch is the ascorbic acid or the dehydro materials.

Linear expansion

Figure 8 shows the percentages of the linear expansion of cassava extrudates, which had been



Figure 7 Estimates of ascorbic acid content of extruded samples (see legend to Fig. 3 for preparation). Values are given as the weight of ascorbic acid used per 100 g of starch (\bullet) and as the percentage (\diamond) of the starting level. Each value represents duplicate readings from two samples taken from the two extruder runs.

prepared with a varying levels of ascorbic acid. Under frying conditions of 185 °C for 15 s and an initial moisture content between 10 and 11% (dry basis), four measures of expansion were observed. As can be seen from Fig. 8 all linear expansion measures increased with increasing ascorbic acid content. As the level of ascorbic acid increases, the degree of expansion during frying significantly increases (ANOVA, P < 0.0001).

According to Siaw et al. (1985), a linear expansion greater than 77% is required for an acceptable level of crispness. From this work, it can be said that all samples were satisfactory expanded, although the expansion in the direction in which extrusion took place (line 4) appeared to be relatively less than for the other directions. From the overall percentages of linear expansion, it seems possible that the linear expansion could be affected by the chemical action from ascorbic acid.

Influence of pH during extrusion

A factor that must be considered is the pH of the samples. Milled extrudates formed by the addition of ascorbic acid were suspended in the distilled water and the pH measured. Figure 9 represents data from the second extruder run and shows that the greater the addition of ascorbic acid, the lower the pH value. The lowest pH was



Figure 8 Variations in linear expansion of cassava extrudates (see legend to Fig. 3 for extruder details), after frying in vegetable oil at 185 °C for 15 sec. The orientations measured are described by Fig. 2; (\Diamond) diagonal lines, (\Box) line 3, (\triangle) line 4 and (\bigcirc) overall. Values are mean ± standard deviation of 20 samples (10 from each run).

1.00E-01

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1.0

Figure 9 The pH of milled cassava extrudates (10% suspension; w/v taken from extruder run 2 and 3). The extrudates had been formed in the presence of ascorbic acid (\Box) or by changing the hydrogen ion concentration of the extruder feed solution (\blacksquare) . See legend to Fig. 3 for further details of the extrusion condition.

4.3 and it could be expected that at this level acid hydrolysis of the starch could play an important role in altering the behaviour of the starch during and subsequent to extrusion. We therefore considered it necessary to carry out a series of experiments where the samples would experience a range of pHs similar to those shown by the ascorbic acid samples. Solutions were used in the liquid stream during extrusion that had pHs ranging between pH 1 to pH 6.5 and the resultant extrudates had pHs from 2.15 to 6.63 (see Fig. 9). Similar assessments to those carried out on the ascorbic acid treated samples were done on the extrudates formed by altering their pH.

The sample using 0.1 M HCl (starting pH of 1.0, extrudate pH of 2.25) did not form a ribbon of material, but a powderlike product was collected. Samples representing starting pH values 2 to 6.5 all formed ribbons of materials, which were similar in appearance to those formed by the inclusion of ascorbic acid. However, the ascorbic acid samples were lighter in colour compared to the pH adjusted samples.

Comparison of extrusion runs

All the pH changes were achieved in one extrusion run. As demonstrated for the two runs for the ascorbic acid addition, it is difficult to repli**Figure 10** Indicators of starch conversion; (\diamond) WAI and (\Box) WSI, in cassava extrudates formed using extruder feed solutions of differing pH. Values are the mean of three replicates.



cate results between runs. The control samples used for the pH adjusted extrudates should have the same values as the zero ascorbic acid level samples. Table 1 shows the extent of the variation that occurred despite the care in getting the condition the same. This variation between runs needs to be considered when comparing the data between the pH adjusted samples and the ascorbic acid samples.

WAI and WSI for pH adjustment

The WAI and WSI values show no great dependence on the pH of the sample except the samples at pH 1.0 (nominal). At this very low pH value there is a marked increase in the amount of soluble material and the ability of the particles to swell, as indicated by WAI, is much decreased when compared to the other samples (Fig. 10).

RVA and alkaline viscosity

The RVA curves representing the extrudates formed at a range of pH values are shown in Fig. 11. Clearly decreasing the pH of the extruder feed solution decreases the RVA viscosities (Fig. 12). The alkaline viscosity is also decreased when the pH values are decreased (Fig. 12).

Linear expansion

All the extruded ribbon products were fried and their expansion measured. The results are shown

in Fig. 13. There seems to be no clear relationship between the pH and the expansion values.

pH and product quality

Adjustment of the starch buffer system to achieve a range of pH values does seem to cause a variation in the rheological properties of the product, lower pHs causing a decreased viscosity. However, we found that the other measures such as WAI and expansion are not affected by moderate changes in pH.

Comparisons of pH values and ascorbic acid samples

To help negate the effects of the variations between runs, thereby elucidating if there were



Figure 11 RVA profiles for cassava extrudates formed using extruder feed solutions of differing pH (see legend to Fig. 3 for details of extruder condition).

Figure 12 The effects of using extruder feed solutions of differing pH (see legend to Fig. 3 for details of extruder condition) on cassava starch on: (■) RVA peak viscosity, (▲) RVA final viscosity and (*) alkaline viscosity.



specific ascorbic acid effects above the changes caused by lowering the pH, we directly compared six samples. These were the three control samples from the three runs as shown in Table 1 and a test sample from each run. The test samples from run 1 and 2 were the ascorbic acid additions of 1.0% (starch bases) which produced extrudates of pH 4.3. The pH adjusted sample made in run 3 from buffer of pH 3 was the third test sample. This material had a pH of 3.74, i.e. lower than for the ascorbic acid samples. Each of the assessments on these three samples was calculated as a percentage of the result obtained for their corresponding control, with positive values representing greater starch conversion. These results are shown in Fig. 14 and demonstrates that over the

range of assessments undertaken the inclusion of 1% ascorbic acid or the lowering of pH to 3.74 does promote starch conversion. It is also apparent that the magnitude of the affects is greater by the inclusion of ascorbic acid than by addition of phthalate and hydrogen chloride to produce an extrudate of lower pH than that of the ascorbic acid test samples.

Conclusions

The work described in this paper shows that the inclusion of ascorbic acid or a reduction in pH during extrusion alters cassava starch. Higher levels of conversion are observed, as measured by solubility, water absorption and changes in vis-



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Figure 14 Comparison of test samples for three extruder runs. Test values have been calculated as a % of the control for the corresponding extruder run. A positive value has been used to indicate promotion of starch conversion. The runs are labelled (1), (2) and (3). Runs (1) and (2) used 1% ascorbic acid (starch basis) as the test sample and run (3) used a sample produced using an extruder feed solution of pH 3. The pH of all the control samples were between pH 6.50 and 6.75. The pH of the test samples for runs (1), (2) and (3) were respectively 4.44, 4.27 and 3.80. Estimates of starch conversion were WAI, WSI, RVA peak and final viscosities, alkaline viscosity and linear expansion.

cosity. Although needing careful interpretation the RVA viscosity profiles was shown to be an easy and sensitive way of monitoring changes that had occurred during extrusion.

Alkaline viscosity results show a decrease as the ascorbic acid levels increase and therefore it is suggested that the ascorbic acid is causing a depolymerization of the starch macromolecules. Earlier work (Paterson *et al.*, 1996; Vallès-Pàmies *et al.*, 1997) has indicated that the reaction is a free radical attack and that the amylose and amylopectin are depolymerized.

A critical quality parameter for cassava starch products is its ability to puff. Expansion of the products was increased by the addition of ascorbic acid and therefore addition of this reducing agent could be directly related to the quality of final product.

Although the case for ascorbic acid addition changing the starch during extrusion seems well proven, two other factors needed to be considered when interpreting the results from the practical work. Firstly, there is a marked difference between the three sets of extrusion runs performed on different occasions. There was a time lapse of approximately one month between the sets of runs. It must be emphasized that each set of extrusion experiments was carried out with the outmost care with same experienced operators, yet there were differences between the control values obtained. The first set of work was done with one batch of cassava starch, but the second ascorbic acid and the pH extrusion runs were carried out using another batch of material. It is well known (El-Dash, 1981; Guha *et al.*, 1998) that reproducibility between extrusion runs is often poor and that often comparisons should only be made within one set of extruder runs.

The other and major consideration necessary for the interpretation of the ascorbic acid data is the lowering of the pH that the inclusion of the ascorbic acid causes. It could be considered that acid hydrolysis could account for the starch's behaviour in the presence of the vitamin C. By matching the results at similar pH values caused by the inclusion of ascorbic acid or by altering the solution using acids or buffers it is clear that much greater effects are seen with the ascorbic acid. However, acidic conditions do encourage starch conversion and this is marked at very low pH values, for example at pH values less than 2 it was not possible to obtain a ribbon of extrudate. What was surprising was that there was no suggestion that the expansion of the acid products was altered, even though the viscosity of the materials had been affected by the acid environment. Cabrera (1978 as quoted by Matz, 1993) found that wheat extrudates formed at pH values between 4.4 and 9.0 did not vary in their expansion ratio. In these experiments cassava products formed at pH values in the range 6.5 to 4.5 achieved by the inclusion of ascorbic acid, indicate a marked change in the expansion ratio. It is therefore possible that the mechanisms for the depolymerization brought about by acid hydrolysis and free radical attack are different and this affects the ability to expand. This is something that will be explored in later experiments.

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