Effect of Altered Solvent Environment on the Pasting Characteristics of Pigeonpea (*Cajanus cajan*) and Cowpea (*Vigna unguiculata*) Starches

Mwanjala A. Mwasaru

Department of Food Science and Technology, Jomo Kenyatta University of Agriculture and Technology, P.O. Box 62000, Nairobi, Kenya.

ABSTRACT

The (Brabender) pasting characteristics of pigeonpea and cowpea starches as a function of pH, sucrose concentration, added corn oil and legume protein isolates were investigated. Adjusting pH to 2 resulted in complete loss in paste consistency at 97°C for both starches. For pigeonpea starch, incorporation of corn oil and 10% sucrose resulted in significant ($p<0.05$) increase in the initial pasting temperature. Separate additions of corn oil and protein isolates caused significant reductions ($p<0.05$) in the paste consistency of pigeonpea starch at 97° and 50°C, respectively. For cowpea starch, adjusting pH to 2, and the addition of protein and sucrose caused significant ($p<0.05$) increases in the initial pasting temperature. The paste consistency of cowpea starch at 97°C was decreased and increased significantly ($p<0.05$) by adjusting the pH to 2 and 4, respectively. Incorporation of corn oil caused a significant increase in the consistency of cowpea starch at 50°C whereas adjusting pH to 4 and addition of protein resulted in significant ($p<0.05$) reductions. It was concluded that the pasting properties of the legume starches were influenced by both the botanical sources of the starches and altered solvent environment.

1.0 INTRODUCTION

Although the major component of pulses such pigeonpea and cowpea is starch, great attention has been given to their proteins (Hoover *et al.*,1993; El Faki *et al.*, 1983; Sathe and Salunkhe, 1981). Legume starches are deemed to be of commercial interest by virtue of their unique quality that differs from those of classical starches (Zhu *et al.*, 1990). Mung bean starch, in particular, is already established in terms of technical processes in the production of glass noodles and carbonless copy paper (Zhu *et al.*, 1990; Sosulski *et al.*, 1989). It is a well-established fact that the gelatinization and viscosity of star[illegible]e affected not only by their origin but also by coexisting substances (Yamada *et al.*, 198[illegible]).

The presence of salts, sugars, surfactants, proteins and changes in pH are construed to affect the pasting and gelatinization characteristics of starch by altering the immediate solvent environment. The effects of salts on gelatinization have been shown to be in accordance with the Hofmeister lyotropic series, salt hydration capacity, and their effects on water structure (Jane, 1993; Takahashi and Wada, 1992; Biliaderis and Seneviratne, 1990). Starch hot paste viscosity is also significantly affected by the presence of protein (Hamaker and Griffin, 1993; Chedid and Kokini, 1992). Increasing sugar concentration delays viscosity development in the amylograph and inhibits paste breakdown of wheat starch (Kim and Walker, 1992; Johnson *et al.*, 1990; Bean and Yamazaki, 1978; Savage and Osman, 1978). The addition of sucrose has been reported to affect the clarity of starch pastes (Craig *et al.*, 1989). Polymeric fractions of cornmeal (starch and protein) contribute to glass transition temperature (T_g) based on the weight fraction of each polymer (Teoh *et al.*, 2001).

Although much work has been reported on the effects of altered solvent environment on the pasting properties of cereal, tuber and root starches, scant information is available pertaining to legume starches. The present study was aimed at investigating the effects of altered solvent environment in terms of pH, and additives such as sucrose, corn oil and legume protein isolates on the pasting characteristics of pigeonpea and cowpea starches. It is envisaged that the results obtained might be useful in predicting the behavior of these starches under similar solvent conditions in actual food systems.

2.0 MATERIALS AND METHODS

2.1 Starch extraction

Starch was extracted from pigeonpea and cowpea seeds, purchased from a commodity dealer in Nairobi, by a laboratory-scale wet milling process. The seeds were steeped in distilled water for 24h at 10°C. The steep water was drained, the seeds washed severally in distilled water and then macerated in a Braun Multiquick System blender (Braun AG, Kronberg, Germany) for 5 minutes. The macerated mass was passed through a set of screens (300, 180, and 106 μm aperture) on a Retsch vibratory shaker (Retsch GmbH & Co. KG, Haan, Germany) equipped with a nozzle for spraying water on the screen assembly. The underflow stream was collected and the starch allowed to sediment for 2h.

The supernatant was decanted and the starch-rich sediment was suspended in excess water and homogenized (Ultra Turrax T25, Janke and Kunkel GmbH & Co. KG, Stauffen, Germany) at 8000rpm for 5 min. The homogenate was allowed to sediment for 1h. The sedimented starch was repeatedly washed with a jet of water until the surface was deemed to be free of all contaminating colored material. The cleaned starch was then dried at 50°C for 48h under vacuum. The purity of the extracted starches (AOAC method 979.10, 1990) were 97.04% and 94.16% for pigeonpea and cowpea, respectively.

2.2 Materials

The pigeonpea and cowpea proteins used in this study were isoelectrically-precipitated isolates extracted using 0.1M NaOH solution adjusted to pH 8.5 with 0.1N HCl. Corn oil and sucrose were obtained from Sigma Chemical Co, St. Loius, MO, USA.

2.3 Effects of pH on pasting properties

The effects of pH on the pasting properties were determined by obtaining amylographs of 5% (w/v) of starch suspensions in distilled water adjusted to pH 2 and 4 using 0.1N HCl.

2.4 Effect of sucrose concentration on pasting properties

The effects of sucrose concentration were determined by adding 10%, 20%, and 40% levels (starch weight basis) to a 5% (w/v) starch suspension prior to analysis on the amylograph.

2.5 Effects of corn oil and legume proteins on pasting properties

The effects of corn oil and legume protein isolates were assessed by obtaining amylographs of 5% (w/v) starch suspensions to which 5% of corn oil or 10% protein (starch weight basis) had been incorporated. For tests involving incorporation of sucrose, protein isolates, and corn oil, the calculated quantities were added to the starch and well mixed prior to the addition of distilled water.

2.6 Brabender viscoamylography

The pasting properties of the starch suspensions were determined using the Brabender Viscoamylograph (Brabender GmbH, Duisburg, Germany) according to procedures described by Deffenbaugh and Walker (1989) with some modifications. Starch (dry weight basis) was weighed to give a 5% suspension (w/v) in 400ml distilled water adjusted to pH 6.5 using 2.5% $NaHCO_3$ (except for tests pertaining to the effect of pH). The suspension was heated at a uniform rate of 1.5°Cmin^{-1} from 30°C to 97°C, held at 97°C for 30min, cooled at the same rate to 50°C and held at this temperature for 30min. The following parameters were determined from the amylogram: the onset of pasting temperatures, consistency in Brabender units (BU) at 97°C, consistency after 30min at 97°C, consistency at 50°C, and consistency after 30min at 50°C.

2.7 Statistical Analysis

Analysis of variance and Duncans multiple range test were calculated using the Statistical Analysis System Package (SAS Institute, 1987).

3.0 RESULTS AND DISCUSSION

The effects of pH (2 and 4), incorporation of 5% corn oil, 10% legume protein isolates, and sucrose (10-40%) on the initial pasting temperatures of pigeonpea and cowpea starches are shown in Table 1. For both starches, adjusting pH to 2 resulted in a significant loss in paste consistency during the holding period at 97°C, due to hydrolysis by the acidic medium. The paste consistency of cowpea starch at 97°C increased significantly at pH 4. Incorporation of corn oil elicited no significant effects on the paste consistencies of pigeonpea and cowpea starches at 97°C and during the subsequent holding period. Addition of corn oil did not significantly affect the consistencies of pigeonpea and cowpea starch pastes at 97°C. For pigeonpea starch, adjusting pH to 4 and incorporation of corn oil significantly ($p<0.05$) decreased the paste consistency at 50°C and during the holding period at this temperature. Incorporation of pigeonpea protein isolate caused the highest reduction in the cold paste consistency of the pigeonpea starch. The effects of pH and incorporation of protein isolate on paste consistency of cowpea starch were similar to those observed for pigeonpea starch. Cowpea starch pastes incorporating corn oil exhibited consistency of 870 BU at 50° C, which was significantly higher than that of the control (710 BU).

Table 1. Effects of pH, and additives on the Brabender initial pasting temperature of 5% pigeonpea and cowpea starch pastes[1]

Treatment	Initial Pasting Temperature	
	Pigeonpea starch	Cowpea starch
Control	80.0^{c}	71.5^{d}
pH 2	80.0^{c}	75.3^{a}
PH 4	81.5^{abc}	71.8^{cd}
5% corn oil	83.8^{a}	70.0^{d}
10% protein	81.5^{abc}	74.0^{ab}
10% sucrose	83.0^{ab}	73.8^{ab}
20% sucrose	80.8^{bc}	72.5^{bc}
40% sucrose	80.0^{c}	74.0^{b}

[1] Values given are means of duplicate determinations. Means in a column followed by the same letter are not significantly different ($p<0.05$)

The initial pasting temperature of pigeonpea starch increased significantly ($p<0.05$) upon incorporation of corn oil and 10% sucrose compared to the untreated sample. Incorporation of protein, sucrose (10-40%), and adjustment of pH to 2, significantly increased the initial pasting temperature of cowpea starch from 71.5°C to 74.5°C; 72.5-74.0°C; and 75.7°C, respectively. As shown in Tables 2 and 3, incorporation of protein significantly decreased the paste consistency at 97°C of pigeonpea starch but had minimal effect on cowpea starch. The paste consistencies of both starches during the holding period at 97°C decreased significantly upon addition of protein isolates.

As shown in Table 2, increasing sucrose concentration from 10 to 40% had no significant effect ($p<0.05$) on the consistency of pigeonpea starch pastes at the characteristic reference points. However, pastes incorporated with 40% sucrose exhibited significantly higher consistencies during the holding period at 50°C than those containing 20% sucrose. Similar trends were observed for cowpea starch as shown in Table 3.

Table 2. Effects of pH, corn oil, protein and sucrose on the Brabender consistency of 5% pigeonpea starch pastes at characteristic reference points[1]

Treatment	Paste consistency (BU) at:			
	97°C	After 30 min at 97°C	50°C	After 30 min at 50°C
Control	125.0^{ab}	232.5^{ab}	325.0^{a}	377.5^{a}
pH 2	100.0^{b}	10.0^{d}	0.0^{c}	-
pH4	150.0^{a}	235.0^{ab}	290.0^{b}	330.0^{b}
5% corn oil	90.0^{bc}	210^{bc}	285.0^{b}	325.0^{b}
10% protein isolate	55.0^{c}	200.0^{c}	250.0^{b}	270.0^{c}
10% sucrose	100.0^{b}	225.0^{abc}	320.0^{abc}	380.0^{ab}
20% sucrose	105.0^{b}	250^{a}	335.0^{a}	360.0^{bc}
40% sucrose	120.0^{ab}	250.0^{a}	350.0^{a}	415.0^{a}

[1] Values given are means of duplicate determinations. Means in a column followed by the same letter are not significantly different ($p<0.05$)

Table 3. Effects of pH, corn oil, protein and sucrosse on the Brabender consistency of 5% cowpea starch pastes at characteristic reference points[1]

Treatment	Paste consistency (BU) at:			
	97°C	After 30 min at 97°C	50°C	After 30 min at 50°C
Control	330.0^{bc}	370.0^{a}	500.0^{bc}	710.0^{b}
pH 2	130.0^{d}	10.0^{c}	0.0^{f}	-
pH4	370.0^{a}	335.0^{ab}	400.0^{d}	610.0^{a}
5% corn oil	325.0^{bc}	360.0^{a}	585.0^{a}	870.0^{a}
10% protein isolate	305.0^{c}	320.0^{b}	360.0^{e}	460.0^{e}
10% sucrose	340.0^{ab}	375.0^{a}	490.0^{c}	685.0^{bc}
20% sucrose	340.0^{ab}	367.0^{a}	490.0^{c}	645.0^{cd}
40% sucrose	350.0^{ab}	375.0^{a}	510.0^{b}	720.0^{b}

[1] Values given are means of duplicate determinations. Means in a column followed by the same letter are not significantly different ($p<0.05$)

Comer and Fry (1978) reported that pea and faba bean starches exhibited excellent resistance to citric acid addition and reported final amylograph viscosities which were higher than those recorded for the same starch pastes in distilled water. The above observations are at variance with the results obtained in the present study using HCl that indicated complete hydrolysis of both pigeonpea and cowpea starches at 97°C. Hydrolysis of pigeonpea starch in 2.2M HCl at 35°C (Hoover *et al.*, 1993) revealed that pigeonpea starch was quite resistant to acid hydrolysis at temperatures below the gelatinization temperature. Yamada *et al.* (1986) reported that while treatment of potato starch with citric and acetic acids at pH 4 increased the pasting and peak temperatures, reduced the peak viscosity, retarded viscosity breakdown, these condition had only slight effects on corn starch. The effects reported for corn starch are similar to those observed in the present study for cowpea and pigeonpea starches except that viscosity breakdown was significant in the current study. Lin et al (1990) reported an increase in the pasting temperature of pea flour as the pH was increased from 4 to 7 and attributed this observation to the presence of protein and other constituents present in the pea flour.

The presence of disulfide bonds in proteins has been reported to restrict starch swelling and thus render swollen granules less susceptible to shear (Hamaker and Griffin, 1993). It has been suggested that proteins form complexes with wheat starch and prevent exudation of amylose from the swollen granule resulting in an elevation of pasting temperature (Olkku and Rha, 1978). The presence of protein and starch has been reported to affect the glass transition temperature of maize meal (Teoh *et al.*, 2001).

The observed elevation of the initial pasting temperature upon incorporation of protein into cowpea starch, and decreases in cold paste consistencies of cowpea and pigeonpea starches in the present study are in agreement to the observations by Chedid and Kokini (1992). The above investigators reported that viscosity changes of starch pastes were affected by the amylose/amylopectin ratio, the type of protein added, and temperature. The observation that addition of non polar lipids to starch results in higher maximum viscosity (Olkku and Rha, 1978) is consistent with the results obtained for cowpea starch in the present study in which the highest consistency at 50°C was observed in pastes supplemented with corn oil. Lipids are known to form complexes with amylose and consequently affect starch paste viscosity (Zhou *et al.*, 1998, Ghiasi *et al.*, 1982).

Addition of surfactants has also been reported to significantly increase the initial pasting temperatures of pigeonpea and cowpea starches (Mwasaru and Muhammad, 2001).

Incorporation of sucrose at different concentrations resulted in varied responses of pigeonpea and cowpea starch paste consistency. Addition of 10-40% sucrose significantly increased the initial pasting temperature of cowpea starch compared to the control whereas for pigeonpea starch only the 10% level elicited a significant effect. However, incorporation of sucrose at all levels had no significant effect on the paste consistencies at the characteristic reference points relative to the controls except the addition of 20% sucrose to cowpea starch which resulted in a significant decrease in cold paste consistency. The results on the effect of sucrose addition on paste consistencies in the present study are different from those reported for cereal and tuber studies. Savage and Osman (1978) reported extensive retardation of viscosity development of wheat starch with increasing concentrations of disaccharides. Chungcharoen and Lund (1978) observed that addition of 40% sucrose increased the onset temperature and decreased the enthalpy of rice starch whereas Bean and Yamazaki (1978) reported an increase in the temperature of birefrigence disappearance of wheat starch in the presence of sucrose. Spies and Hoseney (1982) suggested that addition of sugars to starch decreased the water activity of the system resulting in higher energy requirements for gelatinization.

Differential scanning calorimetry studies indicated delayed gelatinization in the presence of sugars that was attributed to limited available water, lowered water activity, anti-plasticizing effects, water mobility and formation of sugar bridges between starch chains (Kim and Walker, 1992; Johnson *et al.*, 1990). It has been postulated that ungelatinized starch can be considered to be a partially crystalline glassy polymer, and gelatinization a non-equilibrium melting process (Biliaderis *et al.*, 1986; Levine and Slade, 1992). The glass transition temperature in amorphous systems is influenced by materials that serve as a plasticizer; water is a ubiquitous plasticizer. When sucrose is added to water the solution becomes less effective as a plasticizer resulting directly in depression of the glass transition temperature and indirectly in the shift of gelatinization endotherm to a higher temperature (Fan *et al.*, 1996). The observed elavation of the initial pasting temperature of cowpea starch in the presence of sucrose in the present study was consistent with the above hypotheses proposed by Kim and Walker (1992) and Johnson *et al.* (1990).

4.0 CONCLUSIONS

The effects of altered solvent environment on the pasting properties of the legume starches was influenced by the botanical origin of the starch and this fact should be taken into account when different legume starches are used in food systems. The responses of the two legume starches to altered solvent environment in the present study were fundamentally different from those previously reported for cereal and tuber starches.

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