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PII: S0308-8146(96)00189-6

Food Chemistry, Vol. 57, No. 4, pp. 545–547, 1996

0308-8146/96 $15.00+0.00

Thermal and freeze–thaw properties of starch of chickpea (*Cicer arietinum*)

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(Received 5 January 1996; revised version received and accepted 26 March 1996)

Hydroxypropylation of chickpea starch was carried out using starch slurry and propylene oxide under alkaline conditions at 44°C for 24 h. Hydroxypropylated starch was studied for pasting behaviour using Brabender amylograph. Freeze–thaw stability of the modified starch was also compared with native starch. Clarity of the starch was found to markedly increase whereas hot paste viscosity was constant for modified starch even after 60 min. Whereas the native chickpea starch did not possess freeze–thaw stability, upon hydroxypropylation there was a marked decrease in the tendency for syneresis. Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION

Of the total production of over 6000 tonnes of chickpeas, India produces more than 75% (Chavan *et al.*, 1987). Considerable work has been done on chickpea production, composition, antinutritional factors, storage, processing and utilization. Chickpea starch has also been investigated, but few attempts have been made to find applications for it. A limiting factor may be the high amylose content which causes the cooked paste to be prone to extensive retrogradation. This leads to cloudiness and syneresis, especially when these gels are subjected to freeze–thaw cycles. These properties limit the use of the starch in foods. Derivatizing to phosphate, acetate or hydroxypropyl ester prevents retrogradation and causes increases in paste viscosity and paste clarity and a marked reduction in the extent of syneresis (Tuschoff, 1987).

The effect of hydroxypropyl groups on the functional properties of cereal and tuber starches has been studied. However, with the exception of fieldpea starch (Hoover *et al.*, 1988) no comparable studies have been conducted on legume starches. The present work was thus undertaken to study hydroxypropylation of chickpea starch and thermal properties and freeze–thaw stability.

MATERIALS AND METHODS

One part of chickpea flour was slurried in four parts of 0.1% NaOH. The slurry was stirred well to prepare a smooth suspension without any lumps. This was centrifuged at 3000 rpm discarding the supernatant. The cake consists of two layers, namely starch and fibre. After separating the fibre layer, the starch was redispersed in alkali and centrifuged several times to remove proteins tested by biuret. Fibre was also essentially separated in the process. The purified starch was then washed with distilled water and centrifuged several times to remove alkali. The final slurry pH was adjusted to 6 with 2 N HCl and the resultant cake was tray-dried at 50°C. The dried flakes were pulverized to a fine powder.

Standard AOAC methods were used for proximate analysis including: moisture, protein, fat and ash (Williams, 1984). Colorimetric methods were used for amylose and amylopectin determination (McCready & Hassid, 1943).

Hydroxypropylation was done by the method described by Kesler & Hjermstad (1964). Starch (400 g; 10% moisture) was slurried in 1 litre water to which 40 g Na_2SO_4 was added. This mixture was taken in a three necked flask immersed in a water bath at 20°C and stirred constantly. NaOH (2–4 g) and propylene oxide (20–45 ml) were added before sealing the reactor. The reaction was carried out at 44°C for 24 h. After the completion of reaction, the starch was washed and centrifuged to remove alkali and unreacted propylene oxide. The cake was dried as before and powdered.

Pasting behaviour of both native and hydroxypropylated starch at 5 and 8% concentrations was studied using a Brabender amylograph (PT-100) equipped with 350 cmg sensitivity cartridge. The slurry was heated from 35°C to 95°C, held for 10 min and cooled to 40°C. Bowl rotation speed was maintained at 75 rpm. The holding period was extended to 60 min to observe

Table 1. Analysis of chickpea starch (as is basis)

Protein	0.5%
Moisture	10%
Carbohydrate	87%
Fat	1.5%
Ash	0.95%
Crude fibre	0.5%
Amylose	33%

the viscosity changes due to extended cooking conditions. The stability of starch to acid during cooking was studied by adjusting the slurry pH in the amylograph to 5.5, 4, 3, 2.75 and 2 with 2 N HCl.

Freeze–thaw stability was studied by subjecting 8% starch paste to alternate freezing and thawing by holding at −10°C for 18 h and at 30°C for 6 h followed by centrifuging at 3000 rpm for 10 min. The water separated was measured and the stability was expressed as the percentage of water separated after each cycle of alternate freezing and thawing.

RESULTS AND DISCUSSION

The starch yield, by the isolation method described above, was between 48 and 50% on the flour basis. This is much more than the alkali steeping method which gives a yield of about 38–42%. The proximate analysis of the starch is given in Table 1. The amylose content was also determined and was found to be 33%.

Pasting characteristics of the starch were studied using the Brabender amylograph. The salient features are given in Table 2. As the amount of propylene oxide increased, there was a considerable increase in the viscosity. Simultaneously, the gelatinization temperature decreased. The cooked pastes exhibited a marked increase in the clarity. Researchers have found higher clarity when they hydroxypropylated field pea starch (Hoover *et al.*, 1988) and buffalo gourd starch (Butler *et al.*, 1986) and acetylated legume starch (Hoover & Sosulski, 1986). This effect was seen because the strength of associative bonding forces within the micellar network decreased and there was an increase in the amount of water bound with the starch molecules. The increase in the water content also improved the stability against retrogradation.

Table 3. Viscosity of 8% native starch at different holding times

Holding time (min) at 95° C	Viscosity (Brabender units)
10	320
20	360
30	420
60	540

Table 4. Viscosity of 5% hydroxypropylated starches at different holding times

Hydroxypropylated starch	Viscosity (Brabender units) Initial	After 60 min
S1	300	280
S2	320	280
S3	360	320
S4	380	330
S5	460	400

The native chick pea starch exhibited single stage swelling. Amylograph studies on 8% native starch and 5% hydroxypropylated starch slurries showed that, whereas there was a continuous increase in viscosity even after holding the pastes of native starch for up to 60 min at 95°C (Table 3), the hydroxypropylated starch paste did not show much change during similar exposure (Table 4). This lack of change in paste characteristics even after extended holding periods at high temperatures is advantageous over the native starch which underwent almost 100% increase in the viscosity. The constant viscosity will maintain the properties of formulated foods during thermal processing as well as during warming.

Effects of acidity were also investigated by adjusting pH of the slurries to lower values and observing the paste characteristics. Table 5 shows the acid tolerance of various starches. Native starch was quite stable to acid and did not show any effect on viscosity even at pH 3.0, whereas hydroxypropylation decreased the stability. Higher amounts of propylene oxide increased the minimum pH to which there was no change in viscosity. Native starch granules are highly associated with an extensive and strongly bonded micellar structure which endows it high stability towards acid and heat (Schoch & Maywald, 1968). Hydroxypropylation reduced the strength of the bonds and the penetration of acid and breakdown of starch molecules became easier and as a result, the viscosity dropped during cooking.

Table 2. Pasting properties of different hydroxypropylated starches

Starch sample	Propylene oxide (ml)	Gelatinization temperature (°C)	Viscosity in Brabender units 95°C	10 min at 95°C	Cold paste viscosity (cP)
Native	—	78	40	60	60
S1	20	75	300	300	460
S2	30	70	320	280	560
S3	35	66.5	360	320	600
S4	40	62.5	380	340	640
S5	45	54	460	420	680

Table 5. Lowest pH values at which starches showed stability

Starches	pH
Native	3.00
S1	3.25
S2	3.50
S3	3.80
S4	4.10
S5	5.00

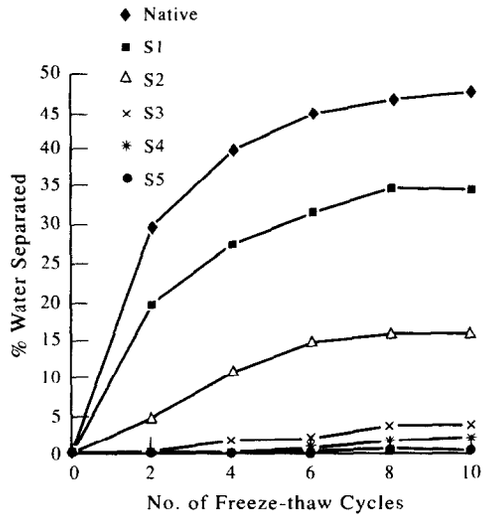

Fig. 1. Effect of freeze–thaw cycles on substitued starches.

Native chick pea starch did not tolerate even one freeze–thaw cycle, showing extensive syneresis Fig. 1. shows that there was 15% water separation after the first cycle, 30% after the second and 48% after 10 cycles. This poor freeze–thaw stability makes it unsuitable for use in custards, puddings and pie-fillings which are frozen stored. Hydroxypropylation, however, markedly decreased the tendency for syneresis. This stability improved with higher amounts of incorporated propylene oxide. This may be because of the steric hindrance exhibited by the bulky hydroxypropyl groups which obstructed the proper alignment of starch chains for maximum retrogradation.

The hydroxypropylation showed some useful changes in the properties of the chick pea starch although there was some loss of acid stability, the cooked paste viscosity remained fairly constant and the freeze–thaw stability increased substantially.

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