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Starch characteristics of black bean, chick pea, lentil, navy bean and pinto bean cultivars grown in Canada

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Abstract

The physicochemical properties of starches from different cultivars of black bean, chick pea, lentil, navy bean, smooth pea and pinto bean were examined. Starch granule size ranged from 8 to 35 μm. The starch granules were round to elliptical with smooth surfaces. The total amylose content ranged from 23.0 to 29.5%, of which 6.0–14.9% was complexed by native lipid. All starches showed a 'C' type X-ray pattern. The peak at $2\theta = 5.54$ (characteristic of B type starches) was most pronounced in pinto bean and black bean starches. Relative crystallinity followed the order: pinto bean > lentil ~ smooth pea ~ chick pea ~ black bean ~ navy bean. The swelling factor (at 80 °C) followed the order: black bean > smooth pea ~ chick pea > lentil > navy bean > pinto bean, whereas, amylose leaching (at 80 °C) followed the order: lentil > smooth pea > chick pea > black bean > navy bean > pinto bean. Pinto bean starches showed the highest gelatinization transition temperatures and enthalpies of gelatinization, whereas, the highest gelatinization temperature range was exhibited by black bean starches. All legume starches exhibited high thermal stability during the holding cycle (at 95 °C) in the Brabender viscoamylogram. However, they differed significantly with respect to the viscosity at 95 °C and the degree of set-back. These differences were more pronounced in pinto bean starches. The extent of syneresis followed the order: black bean > chick pea ~ lentil > smooth pea > navy bean > pinto bean. Differences in physicochemical properties were more marked among cultivars of black bean, and between cultivars of chick pea and smooth pea starches. This study showed that black bean and pinto bean starches differed significantly from each other, and from the other starches, with respect to the magnitude of interaction between starch chains within the amorphous and crystalline domains. © 2002 Published by Elsevier Science Ltd.

Keywords: Legume starches; Physicochemical properties

1. Introduction

Starch is the most abundant carbohydrate in the legume seed (22–45%; Hoover & Sosulski, 1991). Canada is the second largest legume producer (41, 439, 300 Mt; FAO, 1999), the total world production being 54, 691, 059 Mt (FAO, 1999). The Canadian legume industry has grown rapidly in recent years and is now valued at over one billion dollars per year. There are now approximately 1000 legume-processing companies in Canada. Unlike many commodity crops, legume grains are commonly shipped after a primary process. There is a great deal of opportunity to expand value added activities in Canadian legumes (black bean, *Phaseolus vulgaris*, pinto bean, *Phaseolus vulgaris*, navy bean, *Phaseolus vulgaris*, chick pea, *Cicer arietinum* L., smooth pea, *Pisum sativum* L., and lentil, *Lens culinaris* to secondary and tertiary levels of processing.

Extensive research has been conducted on cereal, potato, sweet potato and cassava starches due to their ready availability and wide usage in food and non-food applications. However, there is a dearth of information on structure–property relationship among legume starches due to lack of availability in many countries. Starches from cultivars of oat (Hoover & Senanayake, 1996; Wang & White; 1994; Zhou, Robards, Gilennie-Holmes, & Helliwell, 1998), wheat (Wootton & Mahder, 1993), maize (Yun & Matheson, 1993), barley (Bhatty & Rossnagel, 1998), sweet potato (Collado, 1997) and Cassava (Asaoka, Blanshard, & Rickard, 1991) have been shown to vary in starch composition and properties. The greatest variation in starch properties is among oat cultivars. However, variations in starches composition and properties have been reported only for field pea cultivars (Ratnayake, Hoover, Shahidi, Perera, & Jane, 2001). Therefore, it is difficult to ascertain whether the

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physicochemical properties of legume starches reported in the literature are truly representative of the particular legume starches. Therefore, the purpose of this study was to evaluate the composition and physicochemical properties of starches extracted from some newly introduced cultivars of black bean, pinto bean, navy bean, chick pea, smooth pea and lentil. Recognition of variation in starch properties among cultivars could be useful for plant breeders, who may wish to develop or select potentially useful cultivars with certain functional properties of their starches. The results of this study would form the basis for further investigations on physical and chemical modification to improve the functional properties of the above starches.

2. Materials and methods

2.1. Materials

Black bean (*Phaseolus vulgaris*) cultivars (*UI 906, Midnight, Nighthawk*), pinto bean (*Phaseolus vulgaris*) cultivars (*AC.Ole, Pin ray*), navy bean (*Phaseolus vulgaris*) cultivars (*HR 67–1675, Hansall*) were obtained from the Harrow Research Center, Agriculture and Agri-Food, Canada. Lentil (*Lens culinaris*) cultivars (*Milestone, glamis*), chick pea (*Cicer arietinum* L.) cultivars (*Desiray, Yuma*) and smooth pea (*Pisum sativum* L.) cultivars (*Verdi, Handel*) were obtained from the Crop Development Center, University of Saskatchewan, Canada. Crystalline porcine pancreatic α-amylase (EC 3·2·1·1, type 1 A) was purchased from Sigma Chemical Co., (St. Louis, MO, USA). Chemicals and solvents were of ACS-certified grade. Solvents were distilled from glass before use.

2.2. Starch isolation

Three lots of legume seeds were taken, representing whole samples from the experimental plots of each cultivar. Starch was extracted from each lot using the procedure of Hoover and Sosulski (1985). Sub-sub samples from each sub sample of starch from each cultivar were taken for the experiments.

2.3. Granule morphology

The size and shape of native starches were examined by a Carl Zeiss microscope. The range of granule size was determined by measuring the length and width of 100 granules from a 1.0% starch suspension at 50×, measured with an eye piece micrometer. Granule surface was studied by scanning electron microscopy. Starch samples were mounted on circular aluminium stubs with double sticky tape and then coated with 20 nm of gold and examined and photographed in a Hitachi (S 570) scanning electron microscope (Nissei Sang yo Inc, Rexdale, ON, Canada) at an accelerating potential of 20 kV.

2.4. Chemical composition of starch

Quantitative estimations of moisture, ash, nitrogen, and starch damage were performed by the standard AACC methods (1984). Starch lipids were determined by procedures outlined in an earlier publication (Vasanthan & Hoover, 1992).

2.5. Amylose content

Apparent and total amylose content was determined by a modification (Hoover & Ratnayake, 2001) of the method of McGrance, Cornell, and Rix (1998).

2.5.1. Apparent amylose content

Starch (20 mg, db) was dissolved in 90% dimethylsulfoxide (8 ml) in 10 ml screw-cap reaction vials. The contents of the vials were vigorously mixed for 20 min and then heated in a water bath (with intermittent shaking) at 85 °C for 15 min. The vials were then cooled to ambient temperature, and the contents diluted with water to 25 ml in a volumetric flask. The diluted solution (1.0 ml) was mixed with water (40 ml) and 5ml I_2/KI solution (0.0025 M I_2 and 0.0065 M KI) and then adjusted to a final volume of 50 ml. The contents were allowed to stand for 15 min at ambient temperature, before absorbance measurements at 600 nm.

2.5.2. Total amylose content

The total amylose contents of starch samples were determined by the above procedure, but with prior defatting with hot *n*-propanol–water (3:1 v/v) for 7 h. In order to correct for over estimation of apparent and total amylose content (due to complex formation between I_2 and the outer branches of amylopectin), amylose content was calculated from a standard curve prepared using mixtures of pure potato amylose and amylopectin (over the range 0–100% amylose).

2.6. X-ray pattern and relative crystallinity

X-ray diffractograms were obtained with a Rigaku RU 200R X-ray diffractometer (Rigaku-Denki Co., Tokyo, Japan) with operating conditions as: target voltage 40 kV, target current—100 mA, aging time—5 min, scanning range—3–35°, scan speed—2.000°/min, step time—4.5 s, divergence slit width—1.00, scatter slit width—1.00 and receiving slit width—0.60. Relative crystallinity of the starches was calculated using the method of Nara, Mori, and Komiya (1978) using a peak-fitting software (Origin—Version 6.0, Microcal Inc., Northampton, MA, USA). Amorphous starch was

prepared by heating a 10% starch solution at 95 °C for 30 min with continuous agitation and then drying it at 100 °C for 24 h. The dried sample was ground into a free-flowing powder, using a RP 202 Pulaerit comminutator (Geoscience Instruments Corp., New York, NY, USA) with denatured alcohol as the solvent. The ground sample was air-dried for 24 h and passed through a 250 μm sieve. The moisture content of all starches used in X-ray analysis was ~16%. Powdered quartz was used as the 100% crystalline reference.

2.7. Swelling factor (SF)

The SF of the starches when heated at 60 °C in excess water was measured according to the method of Tester and Morrison (1990). This method measures only intragranular water, and hence, the true SF at a given temperature. The SF is reported as a ratio of the volume of swollen starch granules to the volume of the dry starch.

2.8. Amylose leaching (AML)

Starches (20 mg, db) in water were heated at 60 °C in volume-calibrated sealed tubes for 30 min. The tubes were then cooled at ambient temperature (25–27 °C) and centrifuged at 2000 ***g*** for 10 min. The supernatant liquid (1 ml) was withdrawn and its amylose content was determined as described by Hoover and Ratnayake (2001). Percentage amylose leaching was expressed as mg of amylose leached per 100 g of dry starch.

2.9. Differential scanning calorimetry (DSC)

Gelatinization parameters of native starches were measured using a Seiko DSC 210 (Seiko Instruments Inc., Chiba, Japan) differential scanning calorimeter equipped with a thermal analysis data station and data recording software. Water (11 μl) was added with a microsyringe to starch (3.0 mg) in the DSC pans, which were then sealed, reweighed and allowed to stand for 2 h at room temperature before DSC analysis to attain an even distribution of water. The scanning temperature range and the heating rates were 20–120 °C and 10 °C/min, respectively. In all measurements, the thermogram was recorded with an empty aluminium pan as the reference. The transition temperatures reported are the onset (T_o), peak (T_p) and conclusion (T_c). The enthalpy of gelatinization (ΔH) was estimated by integrating the area between the thermogram and a base line under the peak and was expressed in terms of Joules per gram of dry starch.

2.10. Pasting properties

A Brabender viscoamylograph (Model VA-V) equipped with a 700 cm cartridge (C.W. Brabender Instruments Inc., South Hackensack, NJ, USA) was used to study pasting properties at a concentration of 9% (w/v) and pH 5.5.

2.11. Freeze-thaw stability

The gels (6% db) were subjected to cold storage at 4 °C for 16 h (to increase nucleation) and then frozen at −16 °C. To measure freeze-thaw stability, the gels frozen at −16 °C for 24 h, were thawed at 25 °C for 6 h and then refrozen at −16 °C. Five cycles of freeze-thaw were performed. The excluded water was determined by centrifuging the tubes (30 diam.×100 mm) at 1000 ***g*** for 20 min after thawing.

2.12. Statistical analysis

All determinations were replicated three times and mean values and standard deviations reported. Analyses of variance (ANOVA) were performed and the mean separations were performed by Tukey's HSD test ($P<0.05$) using SigmaStat® Version 2.0 (Jandel Scientific/SPSS Science, Chicago, IL, USA).

3. Results and discussion

3.1. Chemical composition of the starches

The data on yield and composition are presented in Table 1. The purity of the starches was judged on the basis of composition and microscopic examination. The yields of starch from the legume seeds ranged from 20.1 to 37.4%. The values for black bean and navy bean were much lower than for the other legumes, but were within the range (18–45%) reported for most legume starches (El Faki, Desikachar, Paramahans, & Thavanathan, 1983; Grelda, Farlas, Moreno-Valencia, Falcon-Villa Ma del Refugio, & Barron-Hoyos, 1997; Gujska, Reinhard, & Khan, 1994; Hoover & Sosulski, 1985, 1991; Lai & Varriano-Marston, 1979; Srisuma, Rueng-sakulrach, & Ubersax, 1994).

Isolation of starches from legumes is generally difficult owing to the presence of a highly hydrated fine fibre fraction which is derived from the cell wall enclosing the starch granules (Hoover & Sosulski, 1985; Schoch & Maywald, 1968). The ash content (black bean ~ navy bean > chick pea ~ lentil ~ navy bean ~ smooth pea; Table 1) which reflects contamination by fine fibre, suggests that the low yield of starch from black beans and navy beans is due to their higher fine fibre content. The nitrogen content (0.04–0.09%; Table 1) was low in all starches. These low values indicated the absence of non-starch lipids (lipids associated with endosperm, proteins). Therefore, total lipids (obtained by acid hydrolysis) in the legume starches (0.2–0.5%; Table 1) mainly

Table 1
Chemical composition (%) of legume starches[a]

Starch source and cultivar	Composition%							
	Yield	Starch damage	Ash	Lipid[b]	Nitrogen	Amylose		Amylose complexed by native starch lipids[e]
						Apparent[c]	Total[d]	
Black bean								
Night hawk	22.2±0.5b	1.5±0.1a	0.65±0.01a	0.40±0.05c	0.05±0.01a	25.1±0.4e,f	29.5±0.3f	14.9±0.5a
Midnight	20.6±0.4a	2.0±0.2a	0.64±0.01a	0.30±0.02b	0.07±0.03a	24.1±0.3d,e	28.2±0.4d,e	14.5±0.5a
UI 906	20.1±0.4a	1.7±0.3a	0.63±0.03a	0.20±0.03a	0.04±0.01a	23.2±0.5c,d	27.2±0.5c,d	14.7±0.6a
Chick pea								
Desiray	30.4±0.5d	1.6±0.3a	0.06±0.01b	0.20±0.02a	0.09±0.01a	20.7±0.5a	23.0±0.3a	10.0±0.4b
Yuma	31.3±0.5d	2.1±0.4a	0.05±0.02b	0.50±0.03d	0.10±0.03a	21.2±0.6a,b	23.3±0.4a	9.0±0.4b,c
Lentil								
Milestone	37.4±0.4g	1.5±0.4a	0.03±0.02b	0.40±0.02c	0.06±0.02a	22.1±0.5b,c,d	23.5±0.5a,b	6.0±0.5d
Glamis	34.1±0.4e	1.6±0.4a	0.04±0.01b	0.30±0.02b	0.05±0.01a	23.1±0.5c,d	24.7±0.4b	6.5±0.4d
Navy beans								
HR 67–1675	23.8±0.5c	1.5±0.4a	0.65±0.02a	0.30±0.01b	0.07±0.02a	26.1±0.4f	28.6±0.4e,f	8.7±0.5c
Hansall	24.9±0.4c	1.8±0.3a	0.60±0.01a	0.30±0.03b	0.08±0.01a	26.0±0.5f	28.2±0.5d,e	7.8±0.4c
Smooth pea								
Verdi	35.8±0.5f	1.9±0.5a	0.04±0.02b	0.40±0.01c	0.05±0.01a	22.0±0.5a,b,c	23.9±0.4a,b	7.9±0.4c
Handel	30.0±0.4d	2.0±0.5a	0.04±0.01b	0.30±0.05b	0.05±0.01	22.1±0.4b,c,d	24.1±0.5a,b	8.3±0.5c
Pinto bean								
AC ole	30.1±0.5d	1.5±0.2a	0.26±0.02b	0.55±0.05b	0.07±0.02a	29.6±0.1e	35.0±0.4g	15.7±0.1h
Pin ray	29.5±0.7d	1.6±0.3a	0.27±0.03b	0.50±0.01b	0.06±0.01a	30.1±0.2e	35.5±0.1g	15.5±0.1h

[a] All data reported on a dry basis. Values followed by the same letter in each column are not significantly different ($P<0.05$) by Tukey's HSD test.

[b] Lipids obtained by acid hydrolysis (25% HCl) of native starch.

[c] Apparent amylose determined by iodine binding without removal of free and bound lipids.

[d] Total amylose determined by iodine binding after removal of free and bound lipids with hot-*n*-propanol–water 3:1 (v/v).

[e] $\frac{\text{Total amylose} - \text{apparent amylose}}{\text{Total amylose}} \times 100.$

represent the free and bound lipids. The total amylose content of pinto bean (35.0–35.5%) was much higher than those of the other starches (23.0–29.5%; Table 1). A comparison of the apparent and total amylose contents (Table 1) showed that higher percentages of amylose chains were complexed by native starch lipids in pinto bean (15.5–15.7%) than in the other legume starches (6.0–10.0%). The extent of starch damage was low (1.5–2.0%) in all starches (Table 1). The results showed that differences in composition between and among (black bean) cultivars were significant ($P<0.05$) for lipid content (smooth pea, lentil, chick pea and black bean) and total amylose content (black bean).

3.2. Morphological granular characteristics of the starches

Microscopic examination showed that the shapes (round, irregular, elliptical, oval) of the legume starches were similar. The surfaces of all starches appeared to be smooth and showed no evidence of fissures when viewed under the scanning electron microscope. Pinto bean starches showed the highest variation (length and width) in size distribution (Table 2).

3.3. X-ray diffraction

All legume starches showed the characteristic "C" pattern of legume starches (Colonna, Buleon, & Mercier, 1981; Gernat, Radosta, Damaschun, & Schierbaum, 1990; Hoover, Li, Hynes, & Senanayake, 1997; Hoover & Sosulski, 1985). Gernat et al. (1990) have shown that the legume starch "C" crystalline polymorph is a mixture of 'A' and 'B' unit cells, and that these starches contain pure 'A' and 'B' polymorphs in varying proportions. The intensity of the peak (at 5.2 Å), characteristic of 'B' type starches, followed the order: pinto bean (AC Ole ~ Pin ray) > black bean (UI 906 > Midnight) > lentil (Glamis) > pea (Handel) > pea (Verdi). This suggests a higher proportion of 'B' unit cells in pinto bean starches. Chick pea (Desiray and Yuma), lentil (Milestone), black bean (Night hawk) and

Table 2
Size of legume starch granules

Starch source	Mean granule length (μm)	Length range (μm)	Mean granule width (μm)	Width range (μm)
Black bean				
Night hawk	21.5	12–28	19.0	7–30
Midnight	21.0	12–25	19.4	8–28
UI 906	22.0	14–26	18.8	8–29
Chick pea				
Desiray	22.4	14–31	18.8	9–30
Yuma	22.0	15–30	18.5	10–28
Lentil				
Milestone	19.5	9–24	17.8	8–28
Glamis	19.0	8–25	18.1	7–26
Navy bean				
HR67–1675	22.8	15–28	19.1	9–30
Hansall	22.5	14–26	19.2	8–32
Smooth pea				
Verdi	22.6	17–35	20.5	15–32
Handel	23.0	15–37	21.0	14–30
Pinto bean				
AC Ole	22.0	14–39	19.0	6–30
Pin ray	22.5	16–42	19.2	7–32

Table 3
Relative crystallinity[a] of legume starches

Starch source	Relative crystallinity (%)[b]
Black bean	
Nighthawk	21.7±0.5f
Midnight	18.3±0.6a,b,c
UI 906	17.0±0.5a
Chick pea	
Desiray	17.6±0.7a
Yuma	18.0±0.6a,b
Lentil	
Milestone	18.7±0.7a,b,c,d
Glamis	18.7±0.6a,b,c,d
Navy bean	
HR 67–1675	19.5±0.6b,c,d,e
Hansall	20.5±0.6e,f
Smooth pea	
Verdi	19.9±0.6c,d,e
Handel	20.3±0.7d,e,f
Pinto bean	
AC Ole	25.5±0.5g
Pin ray	25.0±0.2g

[a] Crystallinity $= \Sigma\,[I_s - I_a]/\Sigma[I_c - I_a] \times 100$, where I_s–I_a = difference between the sample and amorphous intensities and I_c–I_a = difference between the 100% crystalline (quartz) and amorphous intensities.

[b] Values followed by the same letter are not significantly different ($P < 0.05$) from each other by Tukey's HSD test.

navy bean (HR 67–1675) showed no evidence of a peak at 5.2 Å.

The relative crystallinity of the starches followed the order: pinto bean > black bean ~ chick pea ~ lentil ~ navy bean ~ pea. Generally differences in relative crystallinity between starches could be attributed to the following: (1) crystal size, (2) amount of crystalline regions (influenced by amylopectin content and amylopectin chain length, (3) orientation of the double helices within the crystalline domains, and (4) extent of interaction between double helices. The differences in relative crystallinity (Table 3) between pinto bean and the other starches cannot be attributed to differences in crystallite size (since the sharpness in X-ray pattern in identical in all starches) or to amylopectin content (since pinto bean with a lower amylopectin content (Table 3) exhibits the highest relative crystallinity). Therefore, the higher relative crystallinity of pinto bean starches could be due to an interplay of the following factors: (1) higher extent of interaction between double helices, (2) better orientation of the crystallites, and (3) a longer amylopectin chain length (unpublished results).

3.4. Swelling factor (SF) and amylose leaching (AML)

The swelling factor (SF) and amylose leaching (AML) at 60 °C are presented in Table 4. There was a significant difference ($P < 0.05$) in SF among the starches (black bean > chick pea ~ smooth pea ~ lentil > navy bean > pinto bean). The SF has been shown to be influenced by: (1) amylose–lipid complexes (decreases SF) (Hoover & Manuel, 1995; Maningat & Juliano, 1980; Tester & Morrison, 1990; Tester, Morrison, & Schuiman, 1993), (2) a strongly bonded micellar network (Gujska et al., 1994), and (3) amylopectin molecular structure (Tester et al., 1993). In this study (Table 4), differences in SF are probably influenced by differences in amylopectin chain length (unpublished results) rather than by amylose–lipid complexes, since black bean starch, having a higher proportion of lipid complexed amylose chains (Table 1) exhibits the highest SF (Table 4). The low SF are pinto bean starches, indicates the presence of a larger number of crystallites (formed by association between long amylopectin chains). Crystallite formation would increase granular stability, thereby reducing the extent of granular swelling. The extent of amylose leaching followed the order: black bean > lentil > smooth pea > chick pea > navy bean > pinto bean. This suggests that interactions (within the granule interior) between amylose–amylose and/or amylose–amylopectin chains are more pronounced in pinto beans than in the other starches. Significant differences ($P < 0.05$) in SF and AML were observed only among

Table 4
Swelling factor (SF) and amylose leaching (AML) of legume starches at 60 °C[a]

Starch source	SF[b]	AML[c]
Black bean		
Nighthawk	29.6±0.5a	29.1±0.6a
Midnight	24.5±0.5b	24.2±0.5b
UI 906	24.8±0.8b	24.0±0.4b
Chick pea		
Desiray	18.2±0.5c	21.7±0.3c
Yuma	15.0±0.4d	18.5±0.4d
Lentil		
Milestone	21.0±0.2e	24.5±0.5e
Glamis	21.5±0.4e	24.8±0.4e
Navy bean		
HR-67–1675	12.0±0.6f	11.8±0.6f
Hansall	12.5±0.5f	12.1±0.5f
Smooth pea		
Verdi	18.5±0.5c	22.7±0.7g
Handel	16.0±0.5d	20.0±0.5h
Pinto bean		
AC Ole	10.0±0.3g	11.8±0.2i
Pin ray	10.5±0.3g	12.2±0.4i

[a] Values followed by the same letter in the same column are not significantly different ($P<0.05$) by Tukey's HSD test.
[b] The SF is reported as the ratio of the volume of swollen starch granules to the volume of the dry starch.
[c] AML is expressed as the amount (mg) of amylose leached for 100 mg (dry basis) starch.

cultivars of black bean and between cultivars of chick pea and smooth pea (Table 4).

3.5. Gelatinization characteristics

The gelatinization transition temperatures [T_o (onset), T_p (mid point) and T_c (conclusion)] and the enthalpy of gelatinization (ΔH) are presented in Table 5. The gelatinization temperatures of the legume starches ranged from 59.4 to 85 °C. There were significant differences ($P<0.05$) in T_o, T_p and T_c among cultivars of black bean and between cultivars of lentil and smooth pea (Table 5). The T_o of pinto bean starches, were much higher than that of other legume starches (Table 5). The gelatinization temperature range (T_c–T_o) varied significantly ($P<0.05$) among cultivars of black bean, and between cultivars of chick pea starches (Table 5). In the legume starches, T_c–T_o ranged from 8.0 (pinto bean cv AC Ole) to 20.8 (black bean, cv Midnight).

The ΔH, calculated on the basis of amylopectin content, ranged from 12.6 J/g (chick pea, cv. Desiray) to 24.9 J/g (pinto bean cv AC Ole). ΔH varied significantly ($P<0.05$) among cultivars of black bean and between cultivars of chick pea and smooth pea (Table 5). The ΔH of both cultivars of pinto bean (23.8–24.9 J/g) were much higher than cultivars of the other legume starches (12.6–18.8 J/g). Noda et al. (1998) have postulated that T_o, T_p, T_c are influenced by the molecular architecture of the crystalline region, which corresponds to the distribution of amylopectin short chains (DP 6–11), and not by the proportions of crystalline region which correspond to the amylose/amylopectin ratio. The above authors showed that low T_o, T_p and T_c reflect the presence of abundant short amylopectin chains.

Tester (1997) postulated that the gelatinization and swelling properties are controlled in part by the molecular structure of amylopectin (perfection and ordering of amylopectin crystallites, length of the external 'A' chains of amylopectin, extent of branching, molecular weight and polydispersity), starch composition (amylose/amylopectin ratio, lipid complexed amylose chains) and granule architecture (crystalline to amorphous ratio). Cooke and Gidley (1992) showed that ΔH reflects loss of double helical order rather than the loss of crystallinity. However, Tester and Morrison (1990) postulated that ΔH reflects the overall crystallinity (quality and amount of crystallites) of amylopectin.

The larger differences in T_o between pinto bean and the other legume starches (Table 5) reflect the interplay of the following factors: (1) higher content of lipid-complexed amylose chains (Table 1), (2) higher degree of crystallinity (Table 2), (3) longer and larger proportion of the outer 'A' branches of amylopectin (unpublished results). The difference in T_c–T_o between pinto bean and the other legume starches (Table 5), suggests a higher degree of homogeneity of crystallites within granules of pinto bean starches. The variations in the values of ΔH/AP (Table 5) among legume starches, reflect differences in the molecular architecture of amylopectin. The high ΔH/AP of pinto bean starches (Table 5), suggests that the long outer 'A' branches of amylopectin chains form longer double helices that require a higher level of thermal energy for disruption and melting.

3.6. Pasting characteristics

The pasting characteristics of the starches at a concentration of 9.5% (w/v) and pH 5.5 are presented in Table 6. At this pH and concentration, most legume starches (Hoover, Swamidas, & Vasanthan, 1993; Schoch & Maywald, 1968) exhibit pasting temperatures in the region 65–87 °C, viscosities (at 95 °C) greater than 80 Brabender units (BU) and a gradual increase in viscosity (40–140 BU) during the holding period at 95 °C. The pasting characteristics of the starches (Table 6) were typical of legume starches (Chavan, Shahidi, Hoover, & Perera, 1999; Grelda et al., 1997;

Table 5
Gelatinization[a] characteristics of legume starches[b]

Starch source	Transition temperature[c] (°C)			T_c–T_o (°C)[d]	ΔH[e] J/g	ΔH/(AP)[f] J/g
	T_o	T_p	T_c			
Black bean						
Nighthawk	64.1±0.5a	76.1±0.7b	84.2±0.8d	20.1±0.4a	12.9±0.4a	18.3±0.4a
Midnight	62.0±0.5b	69.9±0.8c	82.8±0.7d	20.8±0.3a	12.1±0.3a	16.5±0.3b
UI 906	66.9±0.5c	76.5±0.5b	83.0±0.9d	16.1±0.4b	12.4±0.4a	17.0±0.4b
Chick pea						
Desiray	59.4±0.6d	64.7±0.6e	71.1±0.9g	11.7±0.4d	9.7±0.5b	12.6±0.5c
Yuma	59.7±0.6d	67.7±0.5f	78.2±0.8h	18.5±0.5e	12.4±0.4a	16.2±0.4b
Lentil						
Milestone	63.0±0.5e	69.6±0.7c	78.7±0.8h	15.7±0.4f	13.3±0.4a	17.4±0.4b
Glamis	60.7±0.5f	66.1±0.9g	76.1±0.8i	15.4±0.5f	12.6±0.4a	16.7±0.4b
Navy bean						
HR 67–1675	66.0±0.6g	75.1±0.8h	85.0±0.8d	19.0±0.3e	13.2±0.5a	18.5±0.5a
Hansall	65.6±0.6g	74.4±0.9h	84.8±1.0d	19.2±0.3e	13.5±0.3a	18.8±0.3a
Smooth pea						
Verdi	60.8±0.4d	66.9±0.5f	73.4±0.9g	12.6±0.5f	13.8±0.5a	18.1±0.5a
Handel	61.6±0.5f	67.4±0.5f	74.5±0.8k	12.9±0.5f	10.8±0.5c	14.2±0.5d
Pinto bean						
AC Ole	72.5±0.5h	75.5±0.4h	80.5±0.5l	8.0±0.5g	16.2±0.4d	24.9±0.4e
Pin ray	72.0±0.5h	75.0±0.5h	81.0±0.5l,d	9.0±0.5g	15.4±0.4e	23.8±0.4e

[a] Starch: water ratio = 1:3 (w/w dry basis).
[b] Values followed by the same letter, in the same column are not significantly different ($P < 0.05$) by Tukey's HSD test.
[c] T_o, T_p and T_c indicate the temperatures of the onset, midpoint and end of gelatinisation, respectively.
[d] T_c–T_o indicates the gelatinization temperature range.
[e] Enthalpy of gelatinization.
[f] Enthalpy of gelatinization (ΔH) expressed on the basis of amylopectin content (AP).

Gujska et al., 1994; Hoover & Manuel, 1995; Hoover & Sosulski, 1985; Lai & Varriano-Marston, 1979; Lineback & Ki, 1975; Srisuma et al., 1994; Tolmasquim, Correa, & Tolmasquim, 1972). Pinto bean starches exhibited higher pasting temperatures, lower viscosities (at 95 and 50 °C) and a lower degree of set-back than the other starches. The low 95 °C viscosity exhibited by pinto bean starches, reflects their higher crystallinity (Table 3), lower SF and lower extent of AML (Table 4). The large difference in set-back (Table 6) between pinto bean and the other starches reflects decreased amylose leaching (Table 4) and/or a lower extent of starch chain aggregation in pinto bean starches.

Black bean starches also behaved differently from the other starches (Table 6) with respect to a higher 95 °C viscosity [reflects lower crystallinity (Table 3), higher SF (Table 4) and higher extent of AML (Table 4)], and a higher degree of set-back (reflects higher extent of AML and/or stronger aggregation of starch chains; Table 6). Differences in pasting characteristics were seen only among cultivars of black bean and between cultivars of chick pea and smooth pea (Table 6).

3.7. Freeze-thaw stability

The freeze-thaw stability of starch gels is an important characteristic of food starches. This stability is determined by gravimetric measurement of the water exuded (syneresis) from a gel after it has been frozen and thawed. This exudation occurs owing to the reassociation of linear starch molecules (retrogradation). The extent of syneresis (14–72%; Table 7) of legume starch gels stored at −16 °C (after five freeze-thaw cycles) followed the order: black bean > chick pea ~ lentil > smooth pea > navy bean > pinto bean. With the exception of navy bean starches, there were no significant differences ($P < 0.05$) in syneresis between or among (black bean) cultivars (Table 7). Pinto bean starches showed a much lower extent of syneresis (16–22%) than the other starches (28–72%). This suggests that interactions between starch chains during frozen storage occur either slowly or are of a very low order of magnitude in pinto bean starches. Structural differences (degree of polymerization of amylose, amylopectin chain length, proportion of short chains) between

Table 6
Pasting characteristics of legume starches[a]

Starch source	Pasting temperature[b] (°C)	Viscosity at 95 °C (BU)[c]	Viscosity after 30 min at 95° (BU)[c]	Viscosity at 50 °C (BU)[c]	Set-back[d] (BU)[c]
Black bean					
Nighthawk	70a	780a ± 10	920a ± 10	1360a ± 20	440a
Midnight	75b	810b ± 10	910a ± 10	1200b ± 20	375b
UI-906	75b	800b ± 5	920a ± 5	1210b ± 15	390b
Chick pea					
Desiray	75b	460c ± 15	620c ± 10	880c ± 20	260c
Yuma	75b	410d ± 10	560d ± 15	800d ± 10	240d
Lentil					
Milestone	72a	560e ± 10	615c ± 15	920e ± 10	305e
Glamis	72a	540e ± 10	630c ± 10	900e ± 10	270e
Navy beans					
HR 67–1675	70a	400d ± 15	620c ± 10	810d ± 10	190f
Hansall	72a	410d ± 10	610c ± 10	800d ± 10	190f
Smooth pea					
Verdi	75b	300f ± 10	420b ± 15	720f ± 15	300g
Handel	74b	330f ± 10	440b ± 20	770g ± 20	330h
Pinto bean					
AC Ole	82c	170g ± 15	320e ± 15	500h ± 10	180i
Pin ray	80c	190g ± 10	350e ± 10	510h ± 10	160i

[a] Values followed by the same letter in the same column are not significantly different ($P < 0.05$) from each other (Tukey's HSD test).
[b] Starch concentration 9.5% w/v and pH 5.5.
[c] Brabender Units.
[d] Viscosity at 50 °C−viscosity at 95 °C after 30 min.

Table 7
Freeze-thaw stability of legume starches

Starch source	Syneresis (%)[a]
Black bean	
Nighthawk	72 ± 6a
Midnight	64 ± 8a
UI-906	66 ± 7a
Chick pea	
Desiray	48 ± 6c
Yuma	50 ± 4c
Lentil	
Milestone	54 ± 3c
Glamis	50 ± 4c
Navy bean	
HR 67–1675	38 ± 7d
Hansall	28 ± 2e
Smooth pea	
Verdi	52 ± 4c
Handel	48 ± 6c
Pinto bean	
AC Ole	18 ± 5f
Pin ray	14 ± 7f

[a] The results are for five freeze-thaw cycles. Values followed by the same letter are not significantly different ($P < 0.05$) from each other.

starches may have been the causative factors responsible for the observed differences in syneresis.

4. Conclusions

The effect of cultivar on the physicochemical properties of black bean, chick pea, lentil, navy bean, smooth pea and pinto bean starches was studied. Significant differences in physicochemical properties were observed among cultivars of black bean and between cultivars of chick pea and smooth pea. This was indicative of differences in starch structure. This seems plausible, since the above cultivars of each legume source were grown in the same location and under identical experimental conditions. Pinto bean starches differed significantly from the other starches in exhibiting a wider granule size distribution, higher relative crystallinity, higher gelatinization transition temperatures and enthalpy of gelatinization, a narrower gelatinization temperature range, and lower granular swelling, amylose leaching, Brabender viscosities and syneresis. This suggests that pinto bean starch crystallites are of a higher order of stability and more homogeneous than crystallites in other starches, and that interactions involving amylose chains within the amorphous domains of pinto bean

starches are also of a higher order of magnitude. Black bean starches also differed significantly from the other starches with respect to higher granular swelling, amylose leaching, Brabender viscosities and syneresis, and a broader gelatinization temperature range. This suggests a more heterogeneous crystalline structure, and weaker interactions between amylose–amylose and/or amylose–amylopectin chains within the amorphous domains of black bean starches.

Work is now in progress on the structure and properties of amylose and amylopectin fractionated from the above starches. The information obtained may provide an insight into the relationships between these properties and the physicochemical properties of the starches.

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