

Digestibility of legume starches as influenced by their physical and structural properties

Kawaljit Singh Sandhu, Seung-Taik Lim *

School of Life Sciences and Biotechnology, Korea University, 5-1 Anam-dong, Sungbuk-ku, Seoul 136-701, South Korea

Received 16 March 2007; received in revised form 21 May 2007; accepted 24 May 2007

Available online 9 June 2007

Abstract

Digestibility of common legumes in India (black gram, chickpea, mung bean, lentil, field pea and pigeon pea) was studied and related to their physical (thermal and pasting) and structural (amylose content and crystallinity) properties. All legume starches exhibited a characteristic C-type diffraction pattern with relative crystallinity ranging between 27.2% and 33.5%. Pigeon pea starch showed the highest values for molecular weight (M_w) of amylopectin (389×10^6 g/mol) and amylose (3.64×10^6 g/mol) whereas, field pea starch showed the lowest values for M_w of amylopectin (239×10^6 g/mol). The enthalpy for melting (ΔH) was the highest for field pea starch whereas, mung bean showed the lowest. Peak viscosity (PV) ranged from 3942 mPa s (chickpea) to 6107 mPa s (mung bean). Slowly digestible starch (SDS) content followed the order: mung bean > chickpea > field pea > lentil > black gram > pigeon pea, whereas, the resistant starch (RS) content followed the following order: pigeon pea > lentil > black gram > field pea > chickpea > mung bean. The hydrolysis indices (HI) of the legume starches ranged from 8.2 to 20.0, and the estimated glycemic indices (GI) based on the HI were between 44.2% and 50.7%. Several significant correlations were observed among different starch properties as revealed both by Pearson correlation (PC) and principal component analysis (PCA). Together, the first two PCs represent 86.6% of total variability. Digestibility of starch was negatively correlated with starch granule diameter ($r = -.791$, $p < .05$) and M_w of amylopectin and amylose ($r = -.845$ and $-.837$, respectively, $p < .05$). A negative correlation between relative crystallinity and amylose content was observed ($r = -.775$, $p < .5$). M_w of amylopectin was positively correlated to relative crystallinity ($r = .914$, $p < .01$) and negatively correlated to amylose content ($r = -.874$, $p < .05$).

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Legume starch; Physical; Thermal; Molecular; Digestibility

1. Introduction

Legumes occupy an important place in the diets of the population in third world countries. They are a rich source of “lente” carbohydrates, which provide several beneficial physiological effects (Tharanathan, 2002). In recent years, glycemic index (GI) has become a useful tool for planning diets for the patients of diabetes, dyslipidemia, cardiovascular disease, and even certain cancers in the general population (Jenkins et al., 1981). Due to poor digestibility compared to that of other cereals, legume starches promote

slow and moderate postprandial glucose and insulin responses, and have low GI values (Jenkins, Wolever, Taylor, Barker, & Fielden, 1980). Several properties of legumes affect starch digestibility, including high content of viscous soluble dietary fiber constituents, the presence of various antinutrients, including polyphenols and phytic acid, and relatively high amylose/amylopectin ratios (Deshpande & Cheryan, 1984; Thomson & Yoon, 1984). The digestibility of starch in foods varies widely (Björck, Granfeldt, Liljeberg, Tovar, & Asp, 1994), therefore a nutritional classification of dietary starch has been proposed. This proposed classification system takes into account both the kinetic component and the completeness of the starch's digestibility and is comprised of rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch

* Corresponding author. Tel.: +82 2 3290 3435; fax: +82 2 927 5201.
E-mail address: limst@korea.ac.kr (S.-T. Lim).

(RS) (Englyst, Kingman, & Cummings, 1992). SDS is generally the most desirable form of dietary starch and completely, but more slowly, digested in the small intestine, and it attenuates postprandial plasma glucose and insulin levels (Jenkins et al., 1981). RS has been defined as the fraction of starch that escapes digestion in the small intestine and has functional and nutritional properties in common with dietary fibre (Themeier, Hollmann, Neese, & Lindhauer, 2005). Legumes have been shown to contain significant amounts of RS when compared to cereals and tubers (Tovar & Melito, 1996; Velasco, Rascon, & Tovar, 1997).

There have been many reports on starch digestibility from different Legumes (Chavan, Shahidi, Hoover, & Pereira, 1999; Hoover & Zhou, 2003; Ratnayake, Hoover, Shahidi, Perera, & Jane, 2001); however, very little information exists regarding the relationship between starch digestibility, and its structural and physical characteristics. In this study, the relationship between the above-mentioned properties and the digestibility of legume starches was investigated.

2. Materials and methods

2.1. Materials

Different legumes (black gram, chickpea, mung bean, lentil, field pea and pigeon pea) were procured from Punjab Agricultural University, Ludhiana, India. Starches were isolated from the legumes following the method described by Singh, Sandhu, and Kaur (2004).

2.2. Size distribution

Size distribution of the isolated starches was measured using a Laser light scattering particle size analyzer (1064 LD, CILAS, France) following the method described by Kaur, Singh, Sandhu, and Guraya (2004).

2.3. X-ray diffraction analysis

X-ray diffraction analysis was conducted using an X-ray diffractometer (Philips, X'pert MPD high resolution XRD, Almelo, The Netherlands) operated at 40 kV and 40 mA. Diffractograms were obtained from 4° (2θ) to 30° (2θ) at a scanning speed of $4^\circ/\text{min}$. The degree of relative crystallinity was determined quantitatively following the method described by Nara and Komiya (1983) using peak-fitting software (Origin-Version 6.0, Microcal Inc., Northampton, MA, USA).

2.4. Amylose content

Amylose content of the legume starches was determined by following the method of Williams, Kuzina, and Hlynka (1970). A starch sample (20 mg) was taken and 10 ml of 0.5 N KOH was added to it. The suspension was thoroughly mixed. The dispersed sample was

transferred to a 100 ml volumetric flask and diluted to the mark with distilled water. An aliquot of test starch solution (10 ml) was pipetted into a 50 ml volumetric flask and 5 ml of 0.1 N HCl was added followed by the 0.5 ml of iodine reagent. The volume was diluted to 50 ml and the absorbance was measured at 625 nm. The measurement of the amylose was determined from a standard curve developed using amylose and amylopectin blends.

2.5. Thermal properties

Thermal properties of isolated starches were analyzed using a Differential Scanning Calorimeter (Seiko Instrument, DSC 6100, Chiba, Japan) following the method described by Singh, Kaur, Sandhu, and Guraya (2004). After conducting thermal analysis, samples were stored in the refrigerator at 4°C for 7 days for retrogradation studies. Retrogradation was measured by reheating the sample pans containing the starches at the rate of $10^\circ\text{C}/\text{min}$ from 25 to 100°C .

2.6. Pasting properties

The pasting properties of starches were evaluated using a Rapid Visco Analyzer (RVA-3D, Newport Scientific, Warriewood, Australia) following the method described by Sandhu and Singh (2007). Viscosity profiles of starches from different legume types were recorded using starch suspensions (8%, w/w; 28 g total weight).

2.7. Molecular weight analysis

To measure the structural properties of the starch sample, starch was purified following the method described by Han and Lim (2004). The molecular structure of the starch was then analyzed using high performance size exclusion column chromatography (HPSEC), connected to a multi-angle laser light scattering detector (MALLS). The mobile phase used for HPSEC was aqueous NaNO_3 solution (0.15 M) that had been filtered through $0.1\ \mu\text{m}$ cellulose acetate filters (Whatman, UK) and degassed with a vacuum pump for 4 h before use. The SEC column ($2.6 \times 70\ \text{cm}$) contained Toyopearl HW 65 F resin (Tosoh Corp. Tokyo, Japan) with particle and pore sizes of $30\text{--}60\ \mu\text{m}$ and $1000\ \text{\AA}$, respectively. The system consisted of a pump (P2000, Spectra System, San Jose, CA), an injector valve with a 1 ml loop (model 7072, Rheodyne, Cotati, CA), a SEC column, a multi-angle laser light scattering detector (MALLS, 632.8 nm, DAWN DSP-F, Wyatt Technology, Santa Barbara, CA), and a refractive index detector (RI, Optilab DSP, Wyatt Technology, Santa Barbara, CA). The flow rate and pump pressure were 0.8 ml/min and 40 psi, respectively. The starch solution was filtered through $0.8\ \mu\text{m}$ cellulose acetate filters while hot ($\approx 70^\circ\text{C}$) before injection into the HPSEC system.

2.8. In vitro digestibility

In vitro starch digestibility was analyzed following the method described by Englyst et al. (1992) as modified by Chung, Lim, and Lim (2006). Porcine pancreatic α -amylase (No. 7545, Sigma–Aldrich, St. Louis, MO), and amyloglucosidase (No. 9913, Sigma–Aldrich) (3.89 g) was dispersed in water (25.7 ml) and centrifuged for 10 min at 2500g, and 18.7 ml of supernatant was collected. Amyloglucosidase (No. 9913, Sigma–Aldrich) (1 ml) and deionized water (2 ml) were added to enzyme solution. The solution was freshly prepared for the digestion analysis.

Aliquots of guar gum (10 ml, 5 g/l) and sodium acetate (5 ml, 0.5 M) were added to the starch samples (0.5 g, db) in a test tube. Seven glass balls (10 mm diameter) and 5 ml of enzyme solution were then added to each tube, following the incubation in a water bath (37 °C) with agitation (170 rpm). Aliquots (0.5 ml) were taken at intervals and mixed with 4 ml of 80% ethanol, and the glucose contents in the mixture were measured using glucose oxidase and peroxidase assay kits (No. GAGO-20, Sigma–Aldrich). The total starch content in the starch samples was measured according to Englyst et al. (1992). The starch classification based on its digestibility was: RDS as the starch that was hydrolyzed within 20 min of incubation, RS as the starch not hydrolyzed with 120 min, and SDS as the starch digested during the period between 20 and 120 min.

2.8.1. Estimated glycemic index (GI)

Using the hydrolysis curve (0–180 min), the hydrolysis index (HI) was calculated as the percentage of total glucose released from the sample compared to that released from white bread (Goñi, Garcia-Alonso, & Saura-Calixto, 1997; Granfeldt, Björck, Drews, & Towar, 1992). The glycemic indices of the samples were estimated according to the equation described by Goñi et al. (1997): $GI = 39.71 + 0.549HI$.

2.9. Statistical analysis

Statistical analysis of the results was conducted using Minitab Statistical Software version 15 (Minitab Inc, State College, PA, USA). Pearson correlation coefficients (r) for relationships between various starch properties were calculated. A principle component analysis (PCA) of measured starch properties was carried out to provide a ready means of visualizing the differences and similarities among starches from different types of legumes.

3. Results and discussions

3.1. Size distribution

Mean granule diameter of the starch granules followed the following order: pigeon pea > field pea > lentil > mung bean > chickpea > black gram (Table 1 and Fig. 1). Granule size and shape are related to the biological source from

Table 1

Mean granule diameter, amylose content and crystallinity of starches from different legume types^{A,B}

Legume types	Mean granule diameter (μ m)	Amylose content (%)	Relative crystallinity (%)
Black gram	14.6 ^a	32.8 \pm 0.5 ^c	28.1 \pm 0.3 ^b
Chickpea	15.3 ^{ab}	30.4 \pm 0.4 ^b	27.6 \pm 0.4 ^{ab}
Field pea	19.6 ^d	33.1 \pm 0.5 ^c	27.2 \pm 0.2 ^a
Lentil	17.5 ^c	31.6 \pm 0.6 ^{bc}	30.6 \pm 0.3 ^d
Mung bean	16.3 ^b	31.6 \pm 0.7 ^{bc}	29.1 \pm 0.3 ^c
Pigeon pea	20.3 ^e	28.4 \pm 0.5 ^a	33.4 \pm 0.4 ^e

^A Means followed by same superscript within a column do not differ significantly ($p < .05$).

^B Mean (\pm standard deviation) of triplicate analysis.

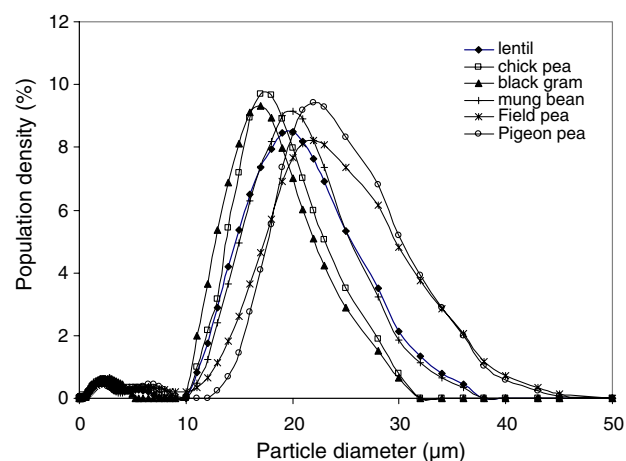


Fig. 1. Particle size distributions of starches from different legume types.

which the starch is isolated (Lindeboom, Chang, & Tyler, 2004). Black gram starch was relatively small compared to other legume starches (mean diameter of 14.6 μ m). Pigeon pea starch granules were larger than those of other legume starches with mean granule diameter of 20.3 μ m, followed by field pea starch (19.6 μ m). Starch granule size may affect its physicochemical properties, such as gelatinization and pasting, enzyme susceptibility, crystallinity, and solubility (Lindeboom et al., 2004).

3.2. Amylose content

Amylose content of the legume starches ranged from 28.4% to 33.1%, the lowest being found in pigeon pea and the highest in field pea starch (Table 1). Legume starches have previously been found to have a relatively high amylose content (30–40%) (Madhusudhan & Tharanathan, 1995).

3.3. Crystallinity by X-ray diffraction

The crystalline patterns of different legume starches as determined by X-ray diffraction are shown in Fig. 2. All legume starches showed a characteristic C-type diffraction

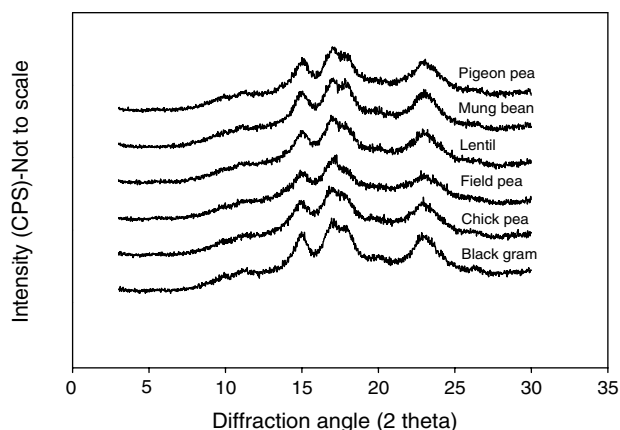


Fig. 2. X-ray diffractograms of starches from different legume types.

pattern, which actually consisted of a mixture of A and B-type crystalline structures (Donald, 2004). All starches showed diffraction peaks at 15° , 17.2° and 23.2° (2θ). Black-gram, mung bean and pigeon pea starches, however, had an extra peak at 18.0° (2θ), which indicate a difference in the crystalline structure of these starches from that of chickpea, field pea and lentil starches. A C-type X-ray pattern for different legume starches has been previously reported (Hoover & Ratnayake, 2002; Ratnayake et al., 2001). X-ray diffraction pattern may depend on starch origin as well as environmental growth conditions (Huang et al., 2007). The relative crystallinity measured based on diffraction intensity was the highest for pigeon pea starch (33.4%), whereas, field pea starch had the lowest value (27.2%) (Table 1). Similar values of relative crystallinity ranging between 27.1% and 33.5% for C-type legume starches have been reported (Zhou, Hoover, & Liu, 2004). A negative correlation between crystallinity and amylose content was observed ($r = -0.775$, $p < .05$). The low relative crystallinity of field pea starch may be due to its high amylose content compared to that of other starches.

3.4. Thermal properties

Transition temperatures and enthalpy of crystal melting (ΔH) of the starches, from different legumes are pre-

sented in Table 2. Significant differences ($p < .05$) were observed in transition temperatures among the starches. Peak (T_p) and conclusion temperatures (T_c) of the melting endotherm of the starches were in the following order: pigeon pea > black gram > mung bean > lentil > chickpea > field pea. The enthalpy for melting (ΔH) followed the order: field pea > lentil > pigeon pea > chickpea > black gram > mung bean. Gelatinization involves melting and uncoiling of the external chains of amylopectin that are packed together as double helices in clusters. The enthalpy in DSC (ΔH) is mainly due to the disruption of the double helices rather than long-range disruption of crystallinity (Cooke & Gidley, 1992). The lower transition temperatures and higher ΔH of field pea and lentil starches suggests that disruption of double helices (in amorphous and crystalline regions) during gelatinization is more pronounced in these two starches than in other starches. The molecular interactions (hydrogen bonding between starch chains) that occur after cooling of the gelatinized starch paste are known as retrogradation (Hoover, 2000). The magnitude of enthalpy of retrogradation (ΔH_{ret}) followed the order: pigeon pea > lentil > field pea > mung bean > chickpea > black gram whereas, % retrogradation (%R) followed the order: pigeon pea > mung bean > lentil > chickpea > black gram > field pea.

3.5. Pasting properties

Pasting viscosity profiles from different legume starches are summarized in Table 3. Significant differences ($p < .05$) in pasting properties among different legume starches were observed. Mung bean starch had the highest values for peak (PV), trough (TV) viscosities and breakdown (BD), whereas, chickpea starch showed the lowest values for these parameters. Final viscosity (FV) was found to be the lowest for mung bean (4779 mPa s) and the highest for field pea (5991 mPa s) starch. Setback (SV) ranged between 1195 and 2930 mPa s: the lowest being observed in starch from mung bean and the highest for lentil starch. FV and SV were positively correlated to ΔH_{gel} ($r = .930$ and $.861$, respectively, $p < .01$).

Table 2
Thermal properties of starches from different legume types^{A,B}

Legume types	T_o ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	ΔH (J/g)	R	ΔH_{ret} (J/g)	%R
Black gram	70.5 ± 0.4^d	74.5 ± 0.5^{cd}	78.7 ± 0.3^d	8.6 ± 0.3^b	8.2 ± 0.4^a	4.2 ± 0.2^a	48.8 ± 0.5^b
Chickpea	59.3 ± 0.6^b	65.3 ± 0.3^b	69.8 ± 0.4^b	9.2 ± 0.2^{bc}	10.5 ± 0.5^c	4.6 ± 0.3^{ab}	50.0 ± 0.4^{bc}
Field pea	55.9 ± 0.5^a	61.4 ± 0.4^a	66.5 ± 0.6^a	12.3 ± 0.3^d	10.6 ± 0.3^c	5.5 ± 0.4^b	44.7 ± 0.3^a
Lentil	57.8 ± 0.5^{ab}	66.8 ± 0.6^{bc}	71.0 ± 0.4^b	11.2 ± 0.4^{cd}	13.2 ± 0.4^c	6.0 ± 0.3^c	53.5 ± 0.3^c
Mung bean	62.2 ± 0.7^c	67.4 ± 0.5^c	72.1 ± 0.5^c	7.9 ± 0.3^a	9.9 ± 0.3^b	5.0 ± 0.4^{ab}	63.2 ± 0.4^d
Pigeon pea	69.3 ± 0.3^d	75.5 ± 0.4^d	80.6 ± 0.6^c	10.7 ± 0.4^c	11.3 ± 0.4^d	7.2 ± 0.4^d	67.2 ± 0.6^c

T_o , onset gelatinization temperature; T_p , peak gelatinization temperature; T_c , conclusion gelatinization temperature.

R , gelatinization range ($T_c - T_o$); ΔH , enthalpy of gelatinization (dw, based on starch weight).

ΔH_{ret} , enthalpy of retrogradation; %R, ratio of enthalpy of retrogradation to enthalpy of gelatinization.

^A Means followed by same superscript within a column do not differ significantly ($p < .05$).

^B Mean (\pm standard deviation) of triplicate analysis.

Table 3
Pasting properties of starches from different legumes^{A,B}

Legume types	Pasting temperature (°C)	Peak viscosity (mPa s)	Trough viscosity (mPa s)	Breakdown (mPa s)	Final viscosity (mPa s)	Setback (mPa s)
Black gram	50.3 ± 0.2 ^a	5147 ± 20 ^c	3538 ± 11 ^c	1609 ± 13 ^c	4968 ± 8 ^b	1430 ± 7 ^b
Chickpea	51.4 ± 0.3 ^b	3942 ± 17 ^a	3045 ± 8 ^a	897 ± 11 ^a	5541 ± 12 ^c	2496 ± 11 ^c
Field pea	52.5 ± 0.1 ^c	4398 ± 13 ^c	3239 ± 13 ^b	1159 ± 8 ^b	5991 ± 11 ^d	2752 ± 13 ^{cd}
Lentil	50.3 ± 0.2 ^a	4637 ± 12 ^d	3035 ± 12 ^a	1602 ± 9 ^c	5965 ± 7 ^d	2930 ± 12 ^d
Mung bean	50.2 ± 0.3 ^a	6107 ± 21 ^f	3584 ± 9 ^c	2523 ± 10 ^d	4779 ± 13 ^a	1195 ± 13 ^a
Pigeon pea	50.9 ± 0.2 ^{ab}	4025 ± 9 ^b	3058 ± 10 ^a	967 ± 9 ^{ab}	5940 ± 11 ^{cd}	2882 ± 9 ^d

^A Means followed by same superscript within a column do not differ significantly ($p < .05$).

^B Mean (±standard deviation) of triplicate analysis.

3.6. Molecular characteristics

The structural data measured using the HPSEC-MALLS-RI system for different legume starches are shown in Table 4. Significant differences of molecular weight (M_w) of amylopectin and amylose were observed between different legume starches. Pigeon pea starch had the highest M_w of amylopectin (389×10^6 g/mol) and amylose (3.64×10^6 g/mol), whereas, field pea starch had the lowest values for M_w of amylopectin (239×10^6 g/mol). Pigeon pea with the highest values of M_w s of amylopectin showed the highest radius of gyration (R_g) for amylopectin (460 nm) and amylose (186 nm). The M_w of amylopectin decreased as the amylose content increased ($r = -.874$, $p < .05$). Similar inverse relationship between M_w of amylopectin and amylose content has been reported earlier for mango and banana starches (Millan-Testa, Mendez-Montealvo, Ottenhof, Farhat, & Bello-Pérez, 2005) and wheat starch (Yoo & Jane, 2002). M_w of amylopectin was positively correlated to crystallinity ($r = .914$, $p < .01$).

3.7. Digestibility studies

The readily digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) contents of different legume starches are shown in Table 5 and their hydrolysis curves are shown in Fig. 3. RDS is rapidly and completely digested in the small intestine and is associated with more rapid elevation of postprandial plasma glucose. The RDS content of legume starches ranged between 4.2% and

10.9%, the lowest being found in pigeon pea starch and the highest in chickpea starch. SDS and RS contents of legume starches ranged between 16.9–40% and 50.3–78.9%, respectively. SDS content, which is generally the most desirable form of dietary starch, followed the order: mung bean > chickpea > field pea > lentil > black gram > pigeon pea. RS content of different legume starches measured as the residue resistant to 120 min of enzymatic hydrolysis followed the order: pigeon pea > lentil > black gram > field pea > chickpea > mung bean. However, hydrolysis continued after 120 min, and RS content measured based on the hydrolysis at 120 min may not show the actual amount of resistant starch. Total digestibility of starches (RDS + SDS) varied from 21.1% to 49.7%, the lowest for pigeon pea and the highest for mung bean was observed. Differences in the digestibility of native starches among species have been attributed to the interplay of many factors, such as starch source (Ring, Gee, Whittam, Orford, & Johnson, 1988), granule size (Snow & O'Dea, 1981), amylose/amylopectin ratio (Hoover & Sosulski, 1985), degree of crystallinity (Chung et al., 2006; Hoover & Sosulski, 1985) and type of crystalline polymorphic forms (Jane, Wong, & McPherson, 1997). Raw starch digestibility is greatly influenced by plant type and depends on physicochemical characteristics of the starch and plant microstructure and composition, and is influenced by processing and storage conditions (Ring et al., 1988). Digestibility was negatively correlated to starch granule diameter ($r = -.791$, $p < .05$). Size of starch granules may affect digestibility, as the relationship between surface area and starch volume, and thus contact between substrate and enzyme, decreases as the size of granule increases (Svihus, Uhlen, & Harstad, 2005). Digestibility of starches was negatively correlated to M_w of amylopectin and amylose ($r = -.845$ and $-.837$, respectively, $p < .05$). A similar inverse relationship between M_w s of amylose and amylopectin and digestibility has been previously reported in chickpea and finger millet starches (Madhusudan & Tharanathan, 1996).

3.7.1. Hydrolysis index (HI) and estimated glycemic index (GI)

The hydrolysis and glycemic indices of different legume starches are shown in Table 5. The hydrolysis indices (HI) of the legume starches ranged from 8.2 to 20.0, and the esti-

Table 4
Molecular characteristics of starches from different legumes^{A,B}

Legume type	M_w ($\times 10^6$ g/mol)		R_g (nm)	
	Amylopectin	Amylose	Amylopectin	Amylose
Black gram	270 ± 1.8 ^b	1.62 ± 0.9 ^{ab}	411 ± 2.5 ^c	138 ± 1.9 ^a
Chickpea	298 ± 2.1 ^c	1.45 ± 0.7 ^a	354 ± 1.8 ^a	133 ± 0.8 ^a
Field pea	239 ± 2.5 ^a	2.44 ± 0.6 ^c	358 ± 2.8 ^{ab}	180 ± 1.7 ^b
Lentil	333 ± 0.9 ^d	3.28 ± 0.5 ^{cd}	398 ± 3.2 ^b	140 ± 2.2 ^a
Mung bean	264 ± 1.4 ^b	1.83 ± 0.7 ^b	344 ± 1.9 ^a	139 ± 1.3 ^a
Pigeon pea	389 ± 2.7 ^c	3.64 ± 0.5 ^d	460 ± 2.7 ^d	186 ± 1.8 ^b

M_w , molecular weight; R_g , radius of gyration.

^A Means followed by same superscript within a column do not differ significantly ($p < .05$).

^B Mean (±standard deviation) of triplicate analysis.

Table 5
Digestibilities of legume starches and starch fractions from different legumes^{A,B}

Legume type	RS (%)	Digested starch (%)		HI	GI ^C
		RDS (%)	SDS (%)		
Black gram	60.9 ± 1.1 ^d	9.5 ± 0.6 ^d	29.6 ± 0.8 ^b	16.5 ± 0.8 ^c	48.7 ± 0.3 ^c
Chickpea	54.3 ± 0.9 ^b	10.9 ± 0.4 ^e	34.8 ± 0.6 ^{cd}	18.4 ± 0.4 ^d	49.8 ± 0.2 ^d
Field pea	58.0 ± 1.4 ^c	8.1 ± 0.5 ^c	33.9 ± 0.4 ^c	16.8 ± 0.5 ^c	48.9 ± 0.4 ^c
Lentil	65.2 ± 0.9 ^e	5.2 ± 0.6 ^b	29.7 ± 0.5 ^b	13.0 ± 0.7 ^b	46.8 ± 0.5 ^b
Mung bean	50.3 ± 1.3 ^a	9.7 ± 0.6 ^d	40.0 ± 0.8 ^d	20.0 ± 0.7 ^e	50.7 ± 0.3 ^d
Pigeon pea	78.9 ± 0.8 ^f	4.2 ± 0.3 ^a	16.9 ± 0.7 ^a	8.2 ± 0.3 ^a	44.2 ± 0.6 ^a

RDS, readily digestible starch; SDS, slowly digestible starch; RS, resistant starch; HI, hydrolysis index; GI, glycemic index.

^A Means followed by same superscript within a column do not differ significantly ($p < .05$).

^B Mean (±standard deviation) of triplicate analysis.

^C GI was calculated using the equation proposed by Goni et al. (1997): $GI = 39.71 + 0.549 HI$.

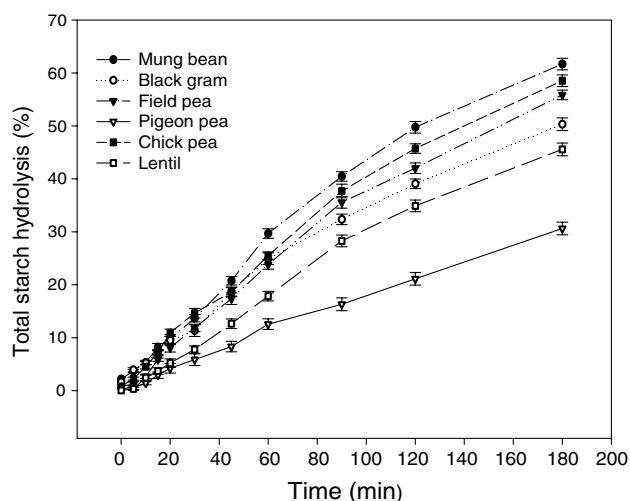


Fig. 3. Enzymatic digestion of starches from different legume types.

mated glycemic indices based on HI were between 44.2% and 50.7%. In general, legume starches have lower HI and GI than cereal starches (Madhusudhan & Tharanathan, 1995). Percent hydrolysis among different legume starches varied significantly with mung bean having the highest (61.6%) and that of pigeon pea having the lowest value (30.6%). After 20 min of hydrolysis, all starches showed hydrolysis percent of less than 11%. After 120 min of hydrolysis, the percent hydrolysis of mung bean starch was 49.7%, followed by chickpea (45.7%), while the lowest was observed for pigeon pea (21.1%). ΔH_{ret} was negatively correlated to HI and GI ($r = -0.858$, $p < .05$). HI and GI was positively correlated to RDS and SDS ($p < .01$) content of the starch.

3.8. Principal component analysis studies

The variables subjected to principal component analysis (PCA) are listed in Table 6 and the results of analysis are shown in Figs. 4 and 5. The PCA plots provide an overview of the similarities and differences between different legume starches as well as the interrelationships between the measured properties. The distance between the locations of any

Table 6
Variables examined by PCA

Description	Variable
Amy	Amylose
Cry	Crystallinity
Hgel	Enthalpy of gelatinization
Hret	Enthalpy of retrogradation
PV	Peak viscosity
FV	Final viscosity
SB	Set back
Map	Molecular weight of amylopectin
Ma	Molecular weight of amylose
RDS	Readily digestible starch
SDS	Slowly digestible starch
RS	Resistant starch
HI	Hydrolysis index
GI	Glycemic index
Dig	Digestibility

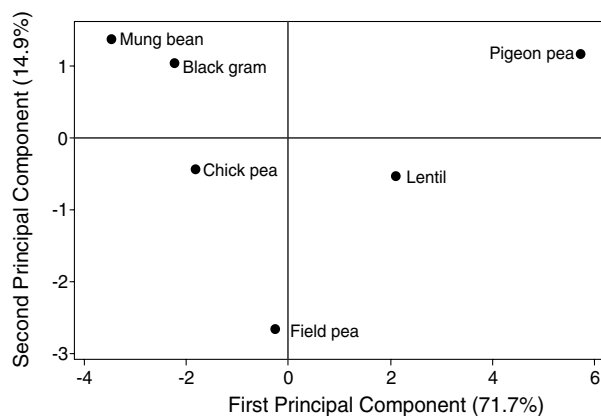


Fig. 4. Principal component analysis: score plot of first principal component (PC1) and second principal component (PC2) describing the overall variation among starches from different legume types.

two starches on the score plot is directly proportional to the degree of difference or similarity between them (Fig. 4). Overall, the pigeon pea and field pea starches were different from the other starches with a highly positive and negative scores on the plot. The first and the second principal components (PCs) described 71.7% and 14.9% of the variance, respectively. Together, the first two PCs rep-

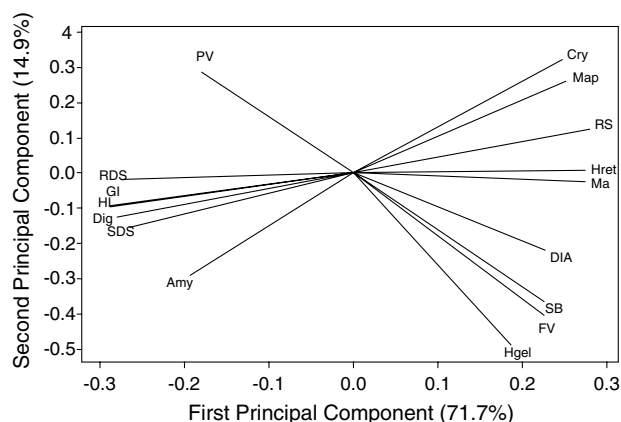


Fig. 5. Principal component analysis: loading plot of PC1 and PC2 describing the variation among properties of starches from different legume types. A heavy solid line and nearby second line indicate two highly correlated properties.

resent 86.6% of the total variability. The loading plot of the two PCs provided information regarding the correlations between measured physicochemical, structural and digestibility properties (Fig. 5). The properties with curves that lie close to each other on the plot are positively correlated, whereas, those with curves going in opposite directions are negatively correlated.

4. Conclusions

All legume starches showed a characteristic C-type X-ray diffraction patterns. Pigeon pea starch had the highest values for M_w of amylopectin and amylose whereas, field pea starch had the lowest values for M_w of amylopectin. Legume starches have been reported to have lower digestibility as compared to cereal starches. Legume starches and their fractions varied significantly in their digestibility. Lowest digestibility and GI of pigeon pea starch make it more suitable for the diabetic patients. Mung bean starch, on the other hand had the highest digestibility and GI, and is therefore more suitable for malnourished patients. Correlation analysis indicated a valuable relationship between the physical, molecular and digestibility properties of legume starches. The digestibility of starch was negatively correlated to starch granule diameter and M_w of amylopectin and amylose. M_w of amylopectin was positively correlated to relative crystallinity and negatively correlated to amylose content.

References

- Björck, I. M., Granfeldt, Y., Liljeberg, H., Tovar, J., & Asp, N.-G. (1994). Food properties affecting the digestion and absorption of carbohydrates. *American Journal of Clinical Nutrition*, 59, 699S–705S.
- Chavan, U. D., Shahidi, F., Hoover, R., & Perera, C. (1999). Characterization of beach pea (*Lathyrus maritimus* L.) starch. *Food Chemistry*, 65, 61–70.
- Chung, H.-J., Lim, H. S., & Lim, S.-T. (2006). Effect of partial gelatinization and retrogradation on the enzymatic digestion of waxy rice starch. *Journal of Cereal Science*, 43, 353–359.
- Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinization: Origin of enthalpic transition. *Carbohydrate Research*, 227, 103–112.
- Deshpande, S. S., & Cheryan, M. (1984). Effects of phytic acid, divalent cations and their interactions on α -amylase activity. *Journal of Food Science*, 49, 516–519.
- Donald, A. M. (2004). Understanding starch structure and functionality. In A. C. Eliasson (Ed.), *Starch in food: Structure, function and applications* (pp. 156–184). Cambridge/New York: Woodhead Publishing Limited/CRC Press LLC.
- Englyst, H. N., Kingman, S. M., & Cummings, J. H. (1992). Classification and measurement of nutritionally important starch fractions. *European Journal of Clinical Nutrition*, 46, S33–S50.
- Goñi, I., Garcia-Alonso, A., & Saura-Calixto, F. (1997). A starch hydrolysis procedure to estimate glycemic index. *Nutrition Research*, 17, 427–437.
- Granfeldt, Y., Björck, I., Drews, A., & Towar, J. (1992). An in vitro procedure based on chewing to predict metabolic responses to starch in cereal and legume products. *European Journal of Clinical Nutrition*, 46, 649–660.
- Han, J.-A., & Lim, S.-T. (2004). Structural changes of corn starches by heating and stirring in DMSO measured by SEC-MALLS-RI system. *Carbohydrate Polymers*, 55, 265–272.
- Hoover, R. (2000). Composition, molecular structure and physicochemical properties of tuber and root starches: A review. *Carbohydrate Polymers*, 45, 253–267.
- Hoover, R., & Ratnayake, W. S. (2002). Starch characteristics of black bean, chickpea, lentil, navy bean and pinto bean cultivars grown in Canada. *Food Chemistry*, 78, 489–498.
- Hoover, R., & Sosulski, F. (1985). Studies on the functional characteristics and digestibility of starches from *Phaseolus vulgaris* biotypes. *Starch*, 37, 181–191.
- Hoover, R., & Zhou, Y. (2003). In vitro and in vivo hydrolysis of legume starches by α -amylase and resistant starch formation in legumes – A review. *Carbohydrate Polymers*, 54, 401–417.
- Huang, J., Schols, H.-A., Soest, J.-J.-G., Jin, Z., Sulmann, E., & Voragen, A.-G.-J. (2007). Physicochemical properties and amylopectin chain profiles of cowpea, chickpea and yellow pea starches. *Food Chemistry*, 101, 1338–1345.
- Jane, J. L., Wong, K. S., & McPherson, A. E. (1997). Branch structure differences in starches of A and B types X-ray patterns revealed by their Naegeli dextrins. *Carbohydrate Research*, 300, 219–227.
- Jenkins, D. J. A., Wolever, T. M. S., Taylor, R. H., Barker, H., & Fielden, H. (1980). Exceptionally low blood glucose responses to dried beans, comparison with other carbohydrate foods. *British Medical Journal*, 281, 578–580.
- Jenkins, D. J. A., Wolever, T. M. S., Taylor, R. H., Barker, H., Fielder, H., Baldwin, J. M., et al. (1981). Glycemic index of foods: A physiological basis for carbohydrate exchange. *American Journal of Clinical Nutrition*, 34, 362–366.
- Kaur, M., Singh, N., Sandhu, K. S., & Guraya, H. S. (2004). Physicochemical, morphological, thermal, and rheological properties of starches separated from kernels of some Indian mango cultivars (*Mangifera indica* L.). *Food Chemistry*, 85, 131–140.
- Lindeboom, N., Chang, P. R., & Tyler, R. T. (2004). Analytical, biochemical and physicochemical aspects of starch granule size, with emphasis on small granule starches: A review. *Starch/Stärke*, 56, 89–99.
- Madhusudan, B., & Tharanathan, R.-N. (1996). Structural studies of linear and branched fractions of chickpea and finger millet starches. *Carbohydrate Research*, 284, 101–109.
- Madhusudhan, B., & Tharanathan, R.-N. (1995). Legume and cereal starch – Why difference in digestibility? Part I. Isolation and composition of legume (green gram and bengal gram) starches. *Stärke*, 47, 165–171.
- Millan-Testa, C. E., Mendez-Montealvo, M. G., Ottenhof, M.-A., Farhat, I. A., & Bello-Pérez, L. A. (2005). Determination of the molecular and structural characteristics of okania, mango, and banana starches. *Journal of Agricultural and Food Chemistry*, 53, 495–501.

- Nara, S., & Komiya, T. (1983). Studies on the relationship between water-saturated state and crystallinity by the diffraction method for moistened potato starch. *Starch/Stärke*, 35, 407–410.
- Ratnayake, W. S., Hoover, R., Shahidi, F., Perera, C., & Jane, J. (2001). Composition, molecular structure and physicochemical properties of starches from four field pea (*Pisum sativum* L.) cultivars. *Food Chemistry*, 74, 189–202.
- Ring, S. G., Gee, J. M., Whittam, M. A., Orford, P. D., & Johnson, I. T. (1988). Resistant starch: Its chemical form in food stuffs and effects of digestibility in vitro. *Food Chemistry*, 28, 97–109.
- Sandhu, K. S., & Singh, N. (2007). Some properties of corn starches II: Physicochemical, gelatinization, retrogradation, pasting and gel textural properties. *Food Chemistry*, 101, 1516–1524.
- Singh, N., Kaur, M., Sandhu, K. S., & Guraya, H. S. (2004). Physicochemical, thermal, morphological, and pasting properties of starches from some Indian black gram (*Phaseolus mungo* L.) cultivars. *Starch/Stärke*, 56, 535–544.
- Singh, N., Sandhu, K. S., & Kaur, M. (2004). Characterization of starches separated from Indian chickpea (*Cicer arietinum* L.) cultivars. *Journal of Food Engineering*, 63, 441–449.
- Snow, P., & O'Dea, K. (1981). Factors affecting the rate of hydrolysis of starch in foods. *American Journal of Clinical Nutrition*, 34, 2721–2727.
- Svihus, B., Uhlen, A. K., & Harstad, O. M. (2005). Effect of starch granule structure, associated components and processing on nutritive value of cereal starch: A review. *Animal Feed Science and Technology*, 122, 303–320.
- Tharanathan, R. N. (2002). Food derived carbohydrates – Structural complexity and functional diversity. *Critical Reviews in Biotechnology*, 22, 65–84.
- Themeier, H., Hollmann, J., Neese, U., & Lindhauer, M. G. (2005). Structural and morphological factors influencing the quantification of resistant starch II in starches of different botanical origin. *Carbohydrate Polymers*, 61, 72–79.
- Thomson, L. U., & Yoon, J. H. (1984). Starch digestibility as affected by polyphenols and phytic acid. *Journal of Food Science*, 49, 1228–1229.
- Tovar, J., & Melito, C. (1996). Steam-cooking and dry heating produce resistant starch in legumes. *Journal of Agricultural and Food Chemistry*, 44, 2642–2645.
- Velasco, Z. I., Rascon, A., & Tovar, J. (1997). Enzymic availability of starch in cooked black beans (*Phaseolus vulgaris* L.) and cowpeas (*Vigna* sp.). *Journal of Agricultural and Food Chemistry*, 45, 1548–1551.
- Williams, P. C., Kuzina, F. D., & Hlynka, I. (1970). A rapid calorimetric procedure for estimating the amylose content of starches and flours. *Cereal Chemistry*, 47, 411–420.
- Yoo, S. H., & Jane, J. (2002). Structural and physical characteristics of waxy and other wheat starches. *Carbohydrate Polymers*, 49, 297–305.
- Zhou, Y., Hoover, R., & Liu, Q. (2004). Relationship between α -amylase degradation and the structure and physicochemical properties of legume starches. *Carbohydrate Polymers*, 57, 299–317.