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Review

Morphological, Hydrolytic and Thermal Properties of Legume Starches

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Abstract. Legumes are an excellent source of carbohydrate and provide an inexpensive source of protein. With the exception of beach pea (12.3%), the percentage yields of extracted legume starches fall within the range of 18.0-45.0% on a whole seed basis. The total lipid contents of legume starches range from 0.01-0.87%. Legume starches have variable granule diameters, generally between 4 and 80 µm. Granule shape may be oval, spherical, elliptical or irregular, depending on the source. Legume starches exhibit a two-stage solubilization pattern; the rates of hydrolysis for the first and second stages are identical in some legume starches but differ in others. Most legume starches exhibit C-type X-ray diffraction patterns. The degrees of crystallinity of most legume starches are similar to, or slightly lower than, those of cereal starches. Most legume starches exhibit nearly identical gelatinization transition temperatures and enthalpies. However, their gelatinization temperature ranges ($T_C - T_O$) differ. Legume starches easily retrograde due to their relatively high amylose contents, although long term retrogradation is attributed to short chains of amylopectin.

Keywords: legume, starch, granule morphology, hydrolysis, gelatinization, retrogradation, thermal properties, granule crystallinity

Introduction

The legume fruit is formed from a single carpel, which splits along the dorsal and the ventral sutures, and usually contains a row of seeds borne on the inner side of the ventral suture. Grain legumes are dicotyledonous seeds of plants that belong to the family Leguminosae having 16,000-19,000 species in approximately 750 genera (Allen and Allen, 1981). They rank fifth in terms of annual world grain production (171 million metric tons) after wheat, rice, corn and barley (FAO, 2003; Deshpande and Damodaran,1990). Approximately 12 species of the Leguminosae, which is the third largest family of flowering plants, are widely used as food (Chavan *et al*., 1999). Examples include lima bean, garbanzo bean, lentil bean, mung bean, pinto bean, adzuki bean, red kidney bean, smooth pea, wrinkled pea, and the two oilseed legumes, soybean and groundnut. The food legumes are rich in starch, protein, dietary fibre, minerals and water-soluble vitamins. Legumes constitute an important source of carbohydrates for a large part of human population, mainly in the developing world. India is the largest producer and consumer of legumes in the world (Singh et al.,2008). The total carbohydrate contents of food legumes vary from 24% (winged bean) to 68% (cowpea) (Ratnayake *et al*., 2001). Starch is the most abundant carbohydrate in the seed (22-45%; Hoover and Sosulski, 1991). Legumes are used as food and feed (Leon *et al*., 1991) as the seed is a good source of both starch and protein, 36.7-50% (Leon *et al*., 1989; Duke, 1981) and 29.7% (Clemente *et al*., 2000; Menkov, 2000; Kessler, 1985), respectively. But lentil seeds contain more protein than other legume seeds, the protein content ranges from 24.3% to 30.2% for different cultivars (Wang and Daun, 2006). Variations in the values for the starch and protein contents of legumes reported in the literature may be attributed, in part, to differences in the methods of analyses.

A major factor which has an adverse effect on the widespread utilization of legume starches in the food industry is their relatively high amylose contents (Hoover and Sosulski, 1985). The association between amylose molecules and the outer branches of amylopectin in

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cooked starch pastes leads to extensive retrogradation, which results in cloudiness and syneresis, especially when legume starch gels are subjected to repeated freeze-thaw cycles (Hoover *et al.*, 1988). The degree of syneresis seen in native legume starch gels would be unacceptable in most food products (Hoover *et al.*, 1988). The physico-chemical properties and functional characteristics that are imparted by starches to aqueous systems and their uniqueness in various food applications vary with the biological origin (Svegmark and Hermansson, 1993). Starches contribute greatly to the textural properties of many foods and have many industrial applications as thickeners, colloidal stabilizers, gelling agents, bulking agents, water retention agents and adhesives (Singh *et al.*, 2003). Methods used in the chemical analysis of legume starches are applicable to starches from other botanical sources.

Legume starches are usually extracted from the source using a procedure similar to that of Hoover and Sosulski (1985). Quantitative estimations of moisture, ash, nitrogen and damaged starch are performed by standard American Association of Cereal Chemists International (AACCI, 1984) or Association of Official Analytical Chemists International (AOACI, 1990) methods. Many methods of characterizing starch have been developed which could be used for screening large number of genotypes for unique properties (Kim *et al.*, 1995). A large number of techniques, such as differential scanning calorimetry (DSC) (Donovan, 1979), X-ray diffraction (Zobel *et al.*, 1988), small angle neutron scattering (Jenkins, 1994) and Kofler hot stage microscopy (Watson, 1964), have been used to study the gelatinization behavior of starches. Additionally, DSC is well suited to investigate the phase transitions of starch/water systems, for it allows the study of starch gelatinization over a wide range of starch/water ratios, determination of gelatinization temperatures above 100°C and estimation of transition enthalpies (Biliaderis *et al.*, 1980). DSC has been used to study starch phase transitions from a physico-chemical approach (Donovan, 1979; Marchant and Blanshard, 1978; Lelievre, 1973). Biliaderis *et al.* (1980) studied legume starches specifically using DSC. Polarizing light microscopy had been used to determine the size, shape, and position of the hilum of common starches (McCrone and Delly, 1973; Schoch and Maywald, 1967; Reichert, 1913). The scanning electron microscope (SEM) is superior to the polarizing light microscope for the study of starch granule morphology. Advantages of SEM include a greater depth of focus and much higher resolution and magnification (Jane *et al.*, 1994). SEM has been used to relate paste structures to paste properties (Fannon and BeMiller, 1992; Fannon *et al.*, 1992a) and also to relate granule morphology to starch genotype (Fannon *et al.*, 1992b). Many other studies involving scanning electron microscopy of starch granules have been reported in the literature (Fannon *et al.*, 1990; Fitt and Snyder, 1984; Banks and Greenwood, 1975; Schoch and Maywald, 1967).

Wide angle X-ray diffraction has been applied to the study of legume starches (Davydova *et al.*, 1995; Gernat *et al.*, 1990; Hoover and Sosulski, 1985; Colonna *et al.*, 1982). From DSC and X-ray studies, Bogracheva *et al.* (1998) were able to deduce a relationship between the ‘A’ and ‘B’ polymorphs of gelatinized legume starches. Identical methods were utilized for the calculation of the composition of ‘A’ and ‘B’ polymorphs of legume starches (Davydova *et al.*, 1995). Other X-ray diffraction studies of starches have shown the dependence of starch crystallinity on amylose content, average chain length (CL) of amylopectin and the mole percentage of short chain fractions of amylopectin (Cheetham and Tao, 1997). The pasting and viscometric properties of starches have been studied with the Brabender visco-amylograph, the rapid visco-analyzer (RVA) and rotational viscometers (Wiesenborn *et al.*, 1994).

Many researchers have used the dynamic rheometer for studying the viscoelastic or rheological properties of starches (Hsu *et al.*, 2000; Tsai *et al.*, 1997; Lii *et al.*, 1996). Laser light scattering has been used to characterize granule diameter based on the assumption that granules are spherical (Wiesenborn *et al.*, 1994). Unlike wide angle X-ray scattering (WAXS) which quantifies crystalline order throughout starch granules, small angle X-ray scattering (SAXS) quantifies differences (periodicity) at the level of amorphous-crystalline lamellae radiating from the hilum to the periphery of starch granules (Tester *et al.*, 2000). More detailed discussion regarding the application of this technique to the investigation of structural, gelatinization and hydrothermal mechanisms of starches can be found in the literature.

In this review, information is presented on the yield, composition, swelling, morphological and thermal characteristics of legume starches.

Yield, composition and crystallinity. Data on the yield and composition of legume starches is presented in Table 1. The purity of legume starches has been judged on the basis of composition and microscopic observation. The low nitrogen and ash contents and the absence of any adhering protein is related to the purity of the starches. With the exception of beach pea (12.3%; Chavan *et al.*, 1999), the yields fell within the range (18-45%) reported by Hoover and Sosulski (1991) for most legume starches. The yield of great northern bean starch has been reported to be 18.2% (Sathe and Salunkhe, 1981). Naivikul and D'Appolonia (1979) reported yields of 40.3, 38.3, 39.9, 42.5 and 34.5% for navy bean, pinto bean, faba bean, lentil, and mung bean starches, respectively. Lineback and Ke (1975) obtained a starch yield of 37% from horse bean flour. Schoch and Maywald (1968) reported starch yields of 27, 38, and 37% from navy bean, lentil and mung bean, respectively. Differences in legume starch yield can be attributed, in part, to differences in the method of isolation. Difficulties in the isolation of starches from legumes have been attributed to the presence of a highly hydrated fine fiber fraction (Vose, 1977) which is derived from the cell wall enclosing the starch granules (Schoch and Maywald, 1968).Recently,the importance of lentil starches were re-emphasised and this had led to studies been conducted on them (Chung *et al.*, 2009; Chung *et al.*, 2008a; Lee *et al.*,2007).

Starch is one of the most abundant organic chemicals in the world. It is synthesized in the form of granules within cellular organelles (amyloplasts) and also found in the leaves of green plants in the plastids. The major polysaccharide of legume plants is starch. Starch consists of two polymers within its granules: amylose and amylopectin. Debranching (Takeda *et al*., 1992) and chain length (CL) studies (Shibanuma *et al.*, 1994) on amylose have shown that the α-(1-4)-linked glucose polymer is actually a mixture of linear and randomly limited branched polymers.

In contrast, amylopectin is a branched polymer with one of the highest molecular weights known among naturally occurring polymers (Abd Karim *et al.*, 2000). Starch is semi-crystalline in nature with varying levels of crystallinity (Singh *et al*., 2003). The crystallinity is solely associated with the amylopectin component, while the amorphous regions mainly represent amylose (Zobel, 1988a, 1988b). Crystalline lamellae are made up of amylopectin double helices, which are packed in a parallel fashion, whereas the amylopectin branch points are in the amorphous zones (Jacobs and Delcour, 1998). Using SAXS and neutron scattering, a periodicity of 9 – 11 nm has been found for starches from various botanical sources (Jenkins *et al*., 1993; Cameron and Donald, 1992; Oostergetel and Van Bruggen, 1989; Blanshard *et al.*, 1984;Muhr *et al.*, 1984; Sterling, 1962). Kassenbeck (1978) and Yamaguchi *et al*. (1979) attributed the periodicity to the repeat distances of crystalline and amorphous lamellae.

The amylose content of starch varies with the botanical source (Table 1) and is affected by the climatic conditions and soil type during growth (Morrison and Azudin, 1987; Asaoka *et al.*, 1985; Morrison *et al.*, 1984; Inatsu *et al.*, 1974; Juliano *et al.*, 1964). Apart from Table 1, recent studies show that apparent amylose content of field pea,kidney bean,chickpea,blackgram,pigeon pea and mung bean starches to be 39.9%, 36.0%, 34.4-35.5%, 32.9-35.6%, 38.0-41.5% and 31.7-33.8% respectively (Chung *et al.*, 2008b; Nishinari,2008; Kim *et al.*,2007;Tan *et al.*,2006). In contrast,the apparent amylose concentration of chickpea starches varies from 28% to 40% (Hughes *et al.*, 2009; Singh *et al.*, 2004) and that of smooth pea and wrinkled pea starches vary from 30-40% and 60-76%, respectively (Ratnayake *et al.*, 2002). Limited co-crystallization between amylose and amylopectin has been suggested by Blanshard (1987) and Jenkins and Donald (1995). WAXS has revealed three forms of packing of amylopectin double helices, A, B, and C crystal types, and the features of starch ^{13}C CP/MAS (solid state ^{13}C cross polarization/magic angle spinning) spectra are consistent with starch being a combination of amorphous (single chain) and ordered (double-helix components) material (Gidley and Bociek, 1985). Legume starches exhibit the typical mixed-state pattern 'C'. Many studies tend to show that the 'C-type' pattern is characteristic of all legume starches. Beach pea, green pea and grass pea starches (Hoover *et al.*, 1997; Hoover and Manuel, 1996; Gernat *et al*., 1990; Hoover and Sosulski, 1985; Colonna *et al.*, 1981), field pea starches (Davydova *et al.*, 1995; Gernat *et al.*, 1990; Hoover and Sosulski, 1985; Colonna *et al*., 1982), mung bean starches (Tan *et al.*, 2009), lentil starches (Sodhi *et al.*, 2009), chickpea starches (Polesi *et al.*, 2011) and black gram starches (Singh *et al.*, 2004) all showed the characteristic 'C-type' pattern of legume starches. However, these X-ray patterns of legume starches were characterized by different intensities. In general, most legume starches exhibit C-type X-ray diffraction patterns characterized by two very distinct intensity lines at 17.2 and 18.1° (2□) angles (Table 2). The differences in X-ray intensities were attributed to the manner in which the double helices are arranged within the crystalline domains of the granule (Chavan *et al.*, 1999). According to Gernat *et al.* (1990), 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. Both 'A' and 'B' type starches are based on parallel stranded double helices, in which the helices are closely packed in the 'A' type starch but loosely packed in the 'B' type starch (Ratnayake *et al.*, 2001). Bogracheva *et al.* (1998) reported from studies of gelatinized pea starch that the 'A' and 'B' polymorphs are present in the same granule and that the 'B' polymorph is situated in the centre of all granules surrounded by the 'A' polymorph.

Table 2 shows some of the X-ray diffraction behaviours of some legume and other starches. Legume starches generally have higher amylose content than non-legume starches (Hoover and Manuel, 1995; Gernat *et al.,* 1990; Hoover and Sosulski, 1985; Colonna *et al.,* 1981). The degrees of crystallinity of most legume starches, such as broad bean (18.5%), smooth pea (18.9%) and wrinkled pea (15.4-16.0%) are similar to, or slightly lower than, those of cereal starches (Table 2). The degrees of crystallinity of wheat, maize, waxy maize and amylomaize starches are 19.5, 21.8, 31.0 and 17.0%, respectively (Gernat *et al.,*1993; Gernat *et al.,* 1990).

Navy bean, pinto bean, faba bean, lentil and mung bean starch granules exhibited similar birefringence characteristics in polarized-light photomicrographs (Naivikal and D' Appolonia, 1979).

Starch paste behavior in aqueous systems depends on the chemical and physical characteristics of the starch granules, such as mean granule size, granule size distribution, amylose/amylopectin ratio and mineral content (Madsen and Christensen, 1996). Morrison *et al.* (1993a,b) reported the presence in starches of two amorphous forms of amylose, namely lipid-free amylose and lipid-complexed amylose. Both forms of amylose are found in legume starches. The amylose content of native legume starches (Table 1) is generally higher than that of unmodified cereal and tuber starches. This association of legume starches with high amylose content explains their higher degree of retrogradation and syneresis compared to either cereal or tuber starches. Ratnayake *et al.* (2001) reported the amylose contents of four cultivars of field pea (*Pisum sativum* L.) to be in the range of 48.8 – 49.6% (Table 1). These values were much higher than those reported by Chavan *et al.* (1999) for beach pea (29.0%), green pea (36.7%), grass pea (36.0%) starches (Table 1), and lower than those of smooth pea (52.6-57.0%) and wrinkled pea (94.0%) (Czuchajowska *et al.*, 1998), but comparable to that of mung bean starch (45.3%; Hoover *et al.*, 1997) (a different sample than that described in Table 1).More contradicting is that amylose content of 40.69% was proposed for mung bean starch (MBS) by Thao and Noomhorm (2011) while Li and Gao (2010) indicated a different value of 27.73% for MBS. Biliaderis *et al.* (1980) reported the amylose content of MBS to be

Table1. Chemical composition of some legume starches.

Legume	Phosphorus	Amylose	Fat	Yield	Ash	Nitrogen
	(%)					
Adzuki bean	0.013[a]	34.9[a]	0.60[h]	21.5[i]	-	-
Smooth pea	0.006[a]	33.1[a]	-	-	-	-
Garbanzo bean	0.010[a]	34.1[a]	0.11-0.12[g]	38.0-40.0[j]	0.042-0.053[j]	0.044-0.047[j]
Red kidney bean	0.016[a]	35.0[a]	-	-	-	-
Lentil	0.008[a]	45.5[a]	0.27-0.38[f]	42.5[i]	0.054-0.060[j]	0.031[j]
Navy bean	0.011[a]	36.0[a]	0.11[g]	40.3[i]	0.051[j]	0.041-0.046
Mung bean	0.016[a]	34.9[a]	0.32[e]	34.5[i]	-	-
Faba bean	0.010[a]	32.5[a]	-	39.9[i]	-	-
Lima bean	-	32.6[b]	0.54[b]	23.0-30.0[j]	0.14[b]	0.036-0.070
Field pea	-	48.8-49.6[c]	0.28-0.34[c]	32.7-33.5[c]	0.03-0.14[c]	0.04-0.07[c]
Beach pea	-	29.02[d]	0.16[d]	12.3[d]	0.22[d]	0.08[d]
Green pea	-	36.70[d]	0.19[d]	30.0[d]	0.07[d]	0.09[d]
Grass pea	-	36.37[d]	0.12[d]	26.0[d]	0.05[d]	0.07[d]

[a] Biliaderis *et al.*, 1980; [b] Betancur-Ancona *et al.*, 2003; [c] Ratnayake *et al.*, 2001; [d] Chavan *et al.*, 1999; [e] Hoover *et al.*, 1997; [f] Hoover and Manuel, 1995; [g] Hoover *et al.*, 1988; [h] Tjahjadi and Breene, 1984; [i] Naivikul and D'Appolonia, 1979; [j] Schoch and May wald, 1968.

34.9% (Table 1). Tjahjadi and Breene (1984) reported a rather low value of 28.8% for the amylose content of adzuki bean. Other researchers (Biliaderis *et al*., 1980; 1979) reported a value of 34.9% for the amylose content of adzuki bean. The different values for the amylose content of the same starch (e.g. mung bean starch and adzuki bean starch) show that the literature is replete with conflicting information with respect to the amylose contents of legume starches. The reported variations in amylose content have been attributed to differences in variety and to the use of different starch isolation procedures and to different methods of analysis, i.e., colorimetry versus potentiometry (Kim *et al*., 1995; Naivikul and D'Appolonia, 1979). The activity of the enzymes involved in starch biosynthesis may also be responsible for the variations in amylose content among starches (Krossmann and Lloyd, 2000).

Minor constituents commonly found in starch include lipids, proteins, phosphorus and other minerals (Ca, K, Mg and Zn) (Ellis *et al*., 1998). Although the proportion of amylose and amylopectin and their properties are paramount in determining the characteristics of the starch, minor constituents of the starch granule seem to affect the properties relevant to its use in food and non-food applications. These minor constituents are materials that are associated with the surface of the granule or are true internal components.Protein has been classified as either surface protein or integral protein, and its association with starch granules varies in amount between and within species (Ellis *et al*., 1998). One of the granule surface proteins, friablin, has been linked with kernel hardness in wheat (Anjum and Walker, 1991). Lipids associated with legume starch granules have been found to occur on the surface, as well as inside the granule (Morrison, 1981). The surface lipids are principally triglycerides, but also include free fatty acids, glycolipids and phospholipids (Vasanthan and Hoover, 1992; Galliard and Bowler, 1987; Morrison, 1981). Vasanthan and Hoover (1992), Morrison (1981) and Hargin and Morrison (1980) each reported that the internal lipids were predominantly monoacyl lipids with the major components being lysophospholipids and free fatty acids. The total lipid contents of legume starches were found to be in the range of 0.01-0.87% (Hoover and Sosulski, 1991). All of the values shown in Table 1 for the total lipid contents of different legume starches fall within the stated range. Morrison (1981) and Mikus *et al*. (1946) postulated that starch lipids may be present in the free state or bound to starch components, either linked via ionic or hydrogen bonding to hydroxyl groups of the starch components or in the form of amylose inclusion complexes in which the ligand resides within the central hydrophobic core of the helix. Total lipid contents of 0.28-0.34% have been ascribed to field pea starches (Table 1; Ratnayake *et al*., 2001) and this is similar to the range reported for mung bean (0.32%; Hoover *et al*., 1997), and lentil (0.27-0.38%; Hoover and Manuel, 1995) starches, but higher than that reported for beach pea (0.16%), green pea (0.19%) grass pea (0.12%) starches (Chavan *et al*., 1999) and chickpea (0.01%) starches (Hoover and Ratnayake,2002). The discrepancies in the lipid contents of the legume starches described above may be due to various reasons. Many researchers (Kawano *et al*., 1989; Goshima *et al*., 1985; Maningat and Juliano, 1980; Melvin, 1979; Lorenz, 1976; Goering *et al*., 1975; Medcalf *et al*., 1968) have used different lipid extractants, which differ in their ability to extract firmly bound lipids (Vasanthan and Hoover, 1992; Morrison and Coventry, 1985; Morrison, 1981). Because of the utilization of different solvents for the extraction of total lipids (both surface and internal) from legume starches, it is difficult to compare results from different published data. Additionally, some solvent systems utilized have proved ineffective in the removal of internal starch lipids. The same is true for bound lipids, especially those complexed with amylose. Controversy still exists with regard to lipid binding ability to the short linear (15-20 glucose units) portions of the outer branches of amylopectin (Eliasson and Ljunger, 1988a; Gidley and Bociek, 1988; Biliaderis and Vaughan, 1987; Hahn and Hood, 1987; Evans, 1986; Destefanis *et al*., 1977; Goering *et al*., 1975; Krog, 1971; Lagendijk and Pennings, 1970). Internal lipid content increases with amylose content, and unless the granule integrity is disrupted, the lipids remain inaccessible to normal fat solvents, suggesting that they are present as an amylose inclusion complex. There is limited information in the literature on minor constituents of legume starches as compared to what is available regarding cereal and tuber starches.

Swelling, solubility and hydrolysis. Starch granule swelling is known to begin in the bulk, relatively mobile, amorphous fraction and in the more restrained amorphous regions immediately adjacent to the crystalline region (Donovan, 1979). Leach *et al*. (1959) postulated that the bonding forces within the starch granule influence the extent of swelling. Thus, highly associated starch granules should be relatively resistant to swelling and amylose leaching (Vasanthan and Hoover, 1992). Furthermore, the swelling factor (SF) has been shown to be influenced by amylose-lipid complexes (Hoover and Manuel, 1995, 1996; Tester *et al*., 1993). The swelling power and amylose leaching (AML) of pea starches increased with increasing temperature (Table 3). Chavan *et al.* (1999) and Ratnayake *et al.* (2001) investigated the SF and AML of pea starches over the temperature range of 50-95°C. Ratnayake *et al.* (2001) found no significant differences in the SF of starches from four cultivars (Curneval, Carrera, Grande and Keoma) of field pea (*Pisum sativum* L.) (Table 3).

These authors showed that the SFs (at 95°C) of field pea starches were lower than those reported for beach pea (30.72), green pea (34.1) (Chavan *et al*., 1999), mung bean (43.6) and gold lentil (31.0) starches, but was comparable to that of Laird lentil starch (26.0) (Hoover and Manuel, 1995). They also reported that the AML values of field pea cultivars at 95°C (Table 4) were much higher than those reported by (Chavan *et al*., 1999) for beach pea (12.94), green pea (17.08), grass pea (19.07), but lower than those reported for gold lentil (35.5) and Laird lentil (38.5) starches (Hoover and Manuel, 1995).

In all four starches studied by Ratnayake *et al.* (2001), SF and AML increased dramatically between 60 and 85°C (Table 4); thereafter, the increase were gradual. An identical trend has been observed for other legume starches (Chavan *et al*., 1999; Hoover and Manuel,

Table 2. X-ray diffraction patterns of some legume and other starches

Starch source	Moisture content (%)		Diffraction angle (□)				Source
Maize starch (Type A)	N.A.	23.0^{vs}	18.0^{m}	17.2^{m}	15.1^{s}		(Gernat *et al*., 1990)
Potato starch (Type B)	N.A.	24.0^{m}	22.0^{m}	17.2^{vs}	13.5^{m}	5.4^{vs}	(Gernat *et al*., 1990)
Kidney bean	10.3	23.0^{s}	21.4^{w}	17.8^{vs}	17.2^{vs}		(Hoover and Sosulski, 1985)
Northern bean	10.5	22.9^{s}	-	17.2^{vs}	15.3^{m}		(Hoover and Sosulski, 1985)
Pinto bean	10.4	23.0^{vs}	18.0^{vs}	17.2^{vs}	15.1^{m}		(Hoover and Sosulski, 1985)
Navy bean	10.7	22.9^{s}	17.8^{vs}	17.2^{vs}	15.3^{w}		(Hoover and Sosulski, 1985)
Black bean	10.4	23.1^{s}	17.8^{vs}	17.2^{vs}	15.3^{w}		(Hoover and Sosulski, 1985)
Broad bean	14.0	24.0^{s}	-	17.0^{vs}	15.1^{m}		(Colonna *et al*., 1981)
Smooth pea	15.9	23.0^{w}	-	17.0^{vs}	15.1^{m}	5.5^{m}	(Colonna *et al*., 1981)
Lentil	9.7	23.0^{m}	-	17.2^{m}	13.4^{w}		(Hoover and Sosulski, 1986; Hoover and Manuel, 1995)
Field pea	9.8	23.0^{s}	-	17.2^{s}	13.4^{w}		(Hoover and Sosulski, 1986)
Adzuki bean	N.A.	24.0^{s}	18.0^{vs}	17.0^{vs}	15.0^{s}		(Biliaderis *et al*., 1981)
Wrinkled pea	N.A.	24.0^{m}	20.0^{m}	17.0^{vs}	15.0^{m}	5.5^{m}	(Biliaderis *et al*., 1981)

^{vs} = very strong intensity; ^{s} = strong intensity; ^{m} = medium intensity; and ^{w} = weak intensity.

Table 3. Swelling factors (SF) and amylose leaching (AML) values for beach pea, green pea and grass pea starches at different temperatures[1,2] (Chavan *et al*., 1999)

Temp.		SF			AML	
(°C)	Beach pea	Green pea	Grass pea	Beach pea	Green pea	Grass pea
50	7.33 ± 0.17^{a}	7.52 ± 1.01^{a}	1.42 ± 0.14^{b}	*	*	*
60	8.55 ± 0.05^{a}	8.94 ± 1.08^{a}	1.56 ± 0.14^{b}	*	*	*
70	16.73 ± 0.18^{a}	17.9 ± 1.06^{a}	10.02 ± 0.08^{b}	3.43 ± 0.03^{b}	6.16 ± 1.09^{a}	6.25 ± 0.09^{a}
80	18.43 ± 0.10^{b}	21.11 ± 1.07^{a}	13.03 ± 0.07^{c}	7.54 ± 0.08^{b}	14.33 ± 1.03^{a}	15.07 ± 0.54^{a}
85	19.61 ± 0.13^{b}	22.41 ± 1.03^{a}	14.90 ± 0.07^{c}	9.84 ± 0.29^{b}	15.08 ± 1.10^{a}	15.66 ± 0.53^{a}
90	24.92 ± 0.21^{b}	28.01 ± 0.37^{a}	19.58 ± 0.13^{c}	11.55 ± 0.52^{b}	16.69 ± 1.02^{a}	17.68 ± 0.10^{a}
95	30.72 ± 0.82^{b}	34.13 ± 0.24^{a}	26.01 ± 0.07^{c}	12.94 ± 0.18^{b}	17.08 ± 1.59^{a}	19.07 ± 0.13^{a}

[1] = The data represent means of four determinations ± SD. Means in each row with different superscripts are significantly different ($p<0.05$); [2] = Swelling factor is ratio of volumes of wet to dry granules; * = Amylose leaching was not observed at these temperatures.

Table 4. Swelling factors (SF) and amylose leaching (AML) values for field pea starches at different temperatures (Ratnayake *et al.*, 2001)

Starch source	Temperature (°C)						
	50	60	70	80	85	90	95
Carneval SF	4.2 ± 0.21	8.5 ± 0.25	13.7 ± 0.16	19.4 ± 0.11	24.3 ± 0.04	26.5 ± 0.03	26.7 ± 0.21
AML	0.0 ± 0.00	10.5 ± 0.23^{q}	16.3 ± 0.17^{q,r}	19.6 ± 0.12^{q}	25.1 ± 0.03	26.3 ± 0.22^{q}	26.6 ± 0.16^{q,r}
Carrera SF	4.2 ± 0.22	8.6 ± 0.21	13.8 ± 0.22^{p}	19.4 ± 0.05	24.2 ± 0.05	26.4 ± 0.21	26.7 ± 0.24
AML	0.0 ± 0.00	10.1 ± 0.22^{p}	15.1 ± 0.12^{p}	18.1 ± 0.25^{p}	24.8 ± 0.24^{p}	25.1 ± 0.19^{p}	25.2 ± 0.10^{p}
Grande SF	4.1 ± 0.21	8.4 ± 0.22	13.8 ± 0.11	19.4 ± 0.10	24.2 ± 0.05	26.5 ± 0.16	26.7 ± 0.23
AML	0.0 ± 0.00	10.5 ± 0.23^{q}	16.0 ± 0.10^{q}	20.2 ± 0.08^{r}	25.7 ± 0.10^{r}	26.0 ± 0.12^{q}	26.2 ± 0.09^{q}
Keoma SF	4.1 ± 0.18	8.4 ± 0.22	13.3 ± 0.11	19.2 ± 0.20	24.1 ± 0.20	26.4 ± 0.20	26.5 ± 0.05
AML	0.0 ± 0.00	10.7 ± 0.15^{q}	16.6 ± 0.20^{r}	20.3 ± 0.06^{r}	25.5 ± 0.16^{r}	26.6 ± 0.20^{r}	26.8 ± 0.02^{r}

Values for AML followed by the same letter, in the same column, are not significantly different (P<0.05) by Tukey's HSD test. No significant differences (P<0.05) were observed among values for SF within the same column by Tukey's HSD test (Ratnayak*e et al.*, 2001).

1995; Hoover and Sosulski, 1985; Tolmasquim *et al*., 1971; Schoch and Maywald, 1968). Ratnayake *et al*., (2001) suggested that the rapid increases in SF and AML of four cultivars of field pea starches, between 60 and 85°C (Table 4), were probably due to an increase in molecular mobility of the amorphous region, which causes unraveling and melting of the double helices present within the amorphous and crystalline domains. Other authors (Chavan *et al*., 1999) suggested that SF was determined by interactions between amylose chains within the amorphous domains of the granule and suggested that AML in these legume starches (beach pea, green pea and grass pea) (Table 3) is influenced by the interplay between differences in amylose content and bound lipid content and by the magnitude of the interactions between amylose chains within the native granule. When starch molecules are heated in excess water, the crystalline structure is disrupted and water molecules become linked by hydrogen bonding to the exposed hydroxyl groups of amylose and amylopectin, which causes an increase in granule swelling and solubility (Singh *et al*., 2003). The presence of lipids in starch may have a reducing effect on the swelling of the individual granules (Galliard and Bowler, 1987). Swelling power and solubility provide evidence of the magnitude of the interactions between starch chains within the amorphous and crystalline domains. The extent of this interaction is influenced by the amylose to amylopectin ratio and by the characteristics of amylose and amylopectin in terms of molecular weight distribution, degree and length of branching, and conformation (Hoover, 2001). Differences in the swelling and solubility behaviour of starches from different botanical sources, and of starches from different cultivars of a botanical source, are caused by differences in amylose and lipid content, as well as in granule organization (Singh *et al*., 2003).

Many researchers (Chavan *et al*., 2010; Kevate *et al*., 2010; Chavan *et al.*, 2009; Ratnayake *et al*., 2001; Chavan *et al*., 1999; Biliaderis *et al*., 1980) hydrolysed legume starches (smooth pea, wrinkled pea, adzuki bean, mung bean, red kidney bean, green lentil, field pea, beach pea, green pea, grass pea,moth bean,rice bean and horse gram) with 2.2N HCl and found that they all exhibited a two-stage solubilization pattern. The same two-stage hydrolysis pattern has also been reported for corn, waxy corn, wheat, potato and rice starches (Robin *et al*., 1974, 1975). These authors reported a relatively fast rate of hydrolysis during the first eight or ten days, followed by a slower rate between ten and twenty days. The faster first stage corresponds to the hydrolysis or degradation of the more amorphous parts of the starch granule (Cairns *et al*., 1990; Biliaderis *et al*., 1981; Kainuma and French, 1971). The slow degradation during the second stage has been attributed to the erosion of the crystalline material (Robin *et al*., 1974; Kainuma and French, 1971). Despite the two-stage solubilization pattern, the rates of hydrolysis for the first and second stages were identical in some legume starches but differed in others. Ratnayake *et al.* (2001) investigated the acid hydrolysis of starch from four cultivars (Carneval, Carrera, Grande and Keoma) of field pea. They observed no significant differences in the extent of hydrolysis among the starches during the first eigt days and further showed that at the end of 20 days, the legume starches were hydrolyzed to the same extent. Identical rates of hydrolysis of starch in the first solubilization stage has been attributed to similar degrees of packing and orientation of the starch chains in the amorphous regions (Ratnayake *et al.*, 2001). Chavan *et al.* (1999) and Hoover and Manuel (1995) reported comparable extents of hydrolysis for other legume starches.

The identical kinetics of the second solubilization stage (from 10 to 20 days) has been attributed to similar amounts of double helices within the crystalline region, and similar crystallite size, in all four starches. In contrast, Chavan *et al.* (1999) hydrolyzed legume (beach pea, grass pea and green pea) starches with 2.2N HCl and reported differences in the two-stage solubilization pattern.

It seems the differences in the susceptibility towards acid hydrolysis during the first 10 days is influenced by the interplay of bound-lipid content and amylose chain associations within the amorphous domains of the starch granule (Chavan *et al.*, 1999). Morrison *et al.* (1993) have shown by studies on lintnerized barley starches that lipid-complexed amylose chains are resistant to acid hydrolysis. To account for the slower hydrolysis rate of the crystalline parts of the starch granule, several hypotheses have been proposed (Hoover and Manuel, 1996; Kainuma and French 1971; BeMiller, 1965). Firstly, it has been suggested that the dense packing of starch chains within the starch crystallites does not readily allow the penetration of H_3O^+ into these regions. Secondly, a change in conformation of D-glucopyranose units (from chair to half chair) is a pre-requisite for hydrolysis of glucosidic bonds by H_3O^+. Additionally, these transformations in conformation could be more difficult in amylose-complexed lipid chains, due to a decrease in chain flexibility. The crystalline regions (consisting basically of double helices of external A and B chains of amylopectin) are generally less accessible than the amorphous regions to attack by hydrated protons (Cairns *et al.*, 1990; Robin *et al.*, 1974; Kainuma and French, 1971) due to dense packing of starch chains within the starch crystallites and to the high energy of activation (Wu and Sarko, 1978) required to cause the conformational change of the glucose units (within the starch crystallites) from chair to half chair (a pre-requisite for acid hydrolysis).

Morphological properties. Amylose and amylopectin molecules are arranged together in a relatively water-insoluble granule of definitive size, shape and morphological characteristics peculiar to a particular plant source (Jane *et al.*, 1994). Variation in the size and shape of starch granules is attributed to differences in biological origin (Svegmark and Harmansson, 1993), genotype and cultural practices (Singh *et al.*, 2003), and maturity (Manners, 1974). The morphology of starch granules depends on the biochemistry of the chloroplast or amyloplast, as well as the physiology of the plant (Badenhuizen, 1969). The shape of the starch granule is also influenced by the growth environment (Hizukuri, 1969).

Many researchers (Fannon *et al.*, 1990; Fitt and Synder, 1984; Banks and Greenwood, 1975; Schoch and Maywald, 1967) have studied and identified starch granules with SEM, and other researchers (McCrone and Delly, 1973; Reichert, 1913) did the same with light microscopy. The size, shape, and position of the hilum of legume starch granules has been observed most often using polarized light microscopy or scanning electron microscopy (SEM). SEM showed field pea starch granules from four cultivars (Carneval, Carrea, Grande and Keoma) to have irregular shapes, which varied from round (5-7 µm) to elliptical (shorter diameter, 10 µm; longer diameter, 25 µm; Ratnayake *et al.*, 2001). These values were lower than those reported for other legume starches (Czuchajowska *et al.*, 1998; Hoover and Sosulski, 1991). Microscopic examination showed that beach pea, green pea and grass pea starch granules had irregular shapes, which varied from round (6-33 µm) to elliptical (shorter diameter, 11-22 µm; longer diameter, 17-35 µm; Chavan *et al.*,1999). The surfaces of pea starch granules appeared smooth and showed no evidence of fissures when viewed by SEM (Miao *et al.*,2009; Ratnayake *et al.*, 2001; Chavan *et al.*, 1999). Other researchers (Liu and Shen,2007 ; Tan *et al.*,2007) indicated that MBS granule ranged from 6.5 to 43.4µm in dimension and 14-15µm in width, 18-21µm in length with oblong or kidney-like shape (Liu and Shen, 2007). According to Tjahjadi and Breene (1984), the granules of adzuki bean starch were mostly oval to kidney shaped, although some were irregular in shape, when viewed under the light microscope. Scanning electron micrographs of these granules revealed that the fissures extended to the surfaces of the granules (Tjahjadi and Breene, 1984). These surface irregularities appeared to be characteristic of adzuki bean starch granules and presumably caused by the way the granules are packed within the protein matrix of the cotyledon (Lineback and Ke, 1975). The size of the adzuki starch granules ranged from 15-45 µm with an average size of 32 µm (Tjahjadi and Breene, 1984). These authors also reported that the granules possessed striae and centric positioned hila. Jane *et al*. (1994) extensively studied starch granule morphology using SEM. These authors used a magnification of x1500 and emphasized the importance of identical magnification with SEM for the purpose of comparing observations of starch granules from different studies. Bean and pea starches are characterized as thick disks with a 'cut' around the middle or at the end and an indentation at one end. The actual cause for the individual characteristics and morphologies are not known, but obvious factors are genetical control, types and amounts of synthetic enzymes in the biosynthesis of the starch molecules, membranous structure of the amyloplast organelle, and arrangement and association of starch molecules (Jane *et al*., 1994). Physicochemical properties, such as percent light transmittance, amylose content, swelling power and water-binding capacity, were significantly correlated with the average granule size of starches separated from different plant sources (Kaur *et al*., 2002; Singh and Singh, 2001; Zhou *et al*., 1998).

In general, starches isolated from legumes have variable granule dimensions, ranging from 4-80 µm (Table 5). The shape of the granules varies from oval, spherical, round and elliptical to irregularly shaped, depending on the source of the starch (Hoover and Sosulski, 1991). Mung bean and black bean have relatively small starch granules (Table 5).

Gelatinization and retrogradation properties. When the starch granule is heated up to the gelatinization temperature in excess water, heat transfer and moisture transfer phenomena occur (Lii *et al*., 1996). The term gelatinization has become established in connection with starch and refers to irreversible physical changes taking place upon the heating of starch in water involving the loss of molecular order, the melting of crystallites, granular swelling and disruption and starch solubilization (Biliaderis, 1998; Atwell *et al*., 1988). The degree of gelatinization can be determined qualitatively and quantitatively by physical, chemical and biochemical methods such as loss of birefringence (Liu *et al*., 2002), increase in viscosity (Wiesenborn *et al*., 1994), decrease in enthalpy (Steven and Elton, 1971), proton magnetic resonance (Cooke and Gidley, 1992; Gidley and Bociek, 1988, 1985), loss of X-ray diffraction pattern (Collison, 1968a,b), and differential scanning calorimetry (Marshall *et al*., 1993).

Table 5. Physical dimensions of granules of some legume starches (Hoover and Sosulski, 1991)

Starch source	Range (diameter)			Shape
	Width (µm)	Length (µm)	Unspecified (µm)	
Kidney bean	16-42	16-60	-	Elliptical, oval
Northern bean	12-40	12-62	-	Oval, irregular, round
Black bean	8-34	8-55	-	Oval, spherical
Mung bean	7-20	10-32	-	Oval, irregular, round
Smooth pea	-	-	20-40	Oval, round
Wrinkle pea	-	-	6-80	Round
Chick pea	-	-	8-54	Oval, spherical
Faba bean	12-24	20-48	-	Oval, spherical
Lentil	15-30	10-36	-	Oval, round, ellipsoid

Gelatinization starts at the hilum of the granule and progresses rapidly to the periphery (Singh *et al*., 2003). It occurs initially in the amorphous regions as opposed to the crystalline regions of the granule, because hydrogen bonding is weaker in the amorphous areas (Singh *et al*., 2003). Waxy starches swell more than starches having a normal amylose content (Tester and Debon, 2000). Tester and Morrison (1990) stated that the swelling behaviour of starch is primarily a property of its amylopectin content, and amylose acts as both a diluent and an inhibitor of swelling, especially in the presence of lipid. They also reported that maximal swelling might also be related to the molecular weight and the shape of the amylopectin molecules.Juhasz and Salgo (2008) concluded in their work that amylopectin was primarily responsible for uptake of water and associated low viscosities and restricted swelling of most legume starch granules to their high amylose content.

Ghiasi *et al*. (1982) indicated that starches with high amylopectin content, e.g., waxy starches have higher gelatinization temperatures than those with a higher amylose content because of the increased levels of crystalline structure associated with amylopectin. Because amylopectin plays a major role in starch granule crystallinity, the presence of amylose lowers the melting point of crystalline regions and the energy for initiation of gelatinization (Flipse *et al*., 1996).

Kreuger *et al*. (1987) postulated that more energy is needed to initiate melting in the absence of amylose-rich amorphous regions. This correlation is clearly seen in Table 6 which is derived from a study of the gelatinization of legume and non-legume starches using

DSC (Biliaderis *et al.*, 1980), and which indicates that starches with higher amylose contents have more amorphous regions and less crystalline regions, which thus lowers their gelatinization temperatures (Sasaki *et al.*, 2000). Hence, legume starches, which tend to have higher amylose contents, would be expected to have lower gelatinization temperature (Table 6). However, Vandeputte and Delcour (2004) indicated that whether amylopectin chains have a positive or negative influence on gelatinization temperature depends on the way they are packed into the lamellar structure of the starch granules. They also proposed that the short amylopectin chains may destabilize the lamellar structure in several ways. Chang *et al.* (2006) reported that the higher average chain length of amylopectin or lower proportion of its short chains might contribute to higher gelatinization temperature of starch granules. Tester (1997) has postulated that gelatinization and swelling properties are controlled, in part, by the molecular structure of amylopectin (unit chain length, extent of branching, molecular weight and polydispersity), starch composition (amylose to amylopectin ratio and phosphorus content), and granule architecture (crystalline to amorphous ratio). Amylopectin from cereals has also been shown to retrograde to a less extent than pea, potato and canna amylopectin, which has been attributed to shorter average chain length in the cereal amylopectin (Kalichevsky *et al.*, 1990; Orford *et al.*, 1987).

During DSC analysis of starch, single or double endothermic peaks are obtained depending on the water concentration during starch gelatinization. Starch gelatinization in excess water exhibits a single endothermic transition, whereas, when a starch-water dispersion is heated in the presence of a limited amount of water, two endothermic transitions are observed (Maaruf *et al.*, 2001; Donovan, 1979). In an extensive study carried out by Biliaderis *et al.* (1980) to investigate the influence of water content on the appearance of these two endotherms with smooth pea, adzuki bean and lentil starches, similar results were obtained for the three legume starches. When the starches were heated at high water concentrations, single endothermic transitions were observed at approximately 64°C, 75°C and 56°C for smooth pea, adzuki bean and lentil starch, respectively (Table 6). As the ratio of starch to water increased for each of the starches, the second endotherm started to develop at higher temperatures and became predominant at low water contents. This concentration

Table 6. Thermal characteristics and other physico-chemical properties of various starches (Biliaderis *et al.*, 1980)

Starch source	Phosphorus content (%)	Amylose content (%)	Initial pasting temp (°C)	Gelatinization temp (°C)	Starch conc. for DSC exp. (%, w/w)	Tp_0	Tp_1	Tp_2	Tm	ΔH (cal/g)
						°C				
Adzuki bean	0.013	34.9	78	83-(85)-89	47.7	69	75	89	112	4.4
Smooth pea	0.006	33.1	73	65-(67)-69	47.5	56	64	87	101	3.5
Acid-modified, 5.1[a]	-	26.8	-	-	47.8	60	73	95	103	2.4
Acid-modified, 9.6[a]	-	23.0	-	-	47.9	60	72	96	109	2.2
Garbanzo bean	0.010	34.1	75	65-(68)-71	45.6	68	72	96	108	3.1
Red kidney bean	0.016	35.0	73	64-(66)-68	46.3	61	68	86	100	2.6
Lentil	0.008	45.5	66	58-(59)-61	47.5	48	56	80	95	2.6
Navy bean	0.011	36.0	75	68-(71)-74	46.1	59	67	83	99	3.5
Mung bean	0.016	34.9	73	63-(65)-69	47.5	57	65	83	99	3.9
Faba bean	0.010	32.5	72	61-(63)-66	46.6	56	65	83	97	3.3
Potato, commercial	0.075	20.0	51	64-(65)-67	46.3	55	60	68	85	4.4
Corn, commercial	0.019	22.6	74	63-(65)-68	46.4	60	67	78	89	3.3[b]
Corn, lab prepared	0.012	22.4	73	62-(65)-67	47.3	53	63	75[c]	86	2.7
Acid-modified, 6.5[a]	-	22.6	-	-	47.9	54	73	99[c]	89	2.4
High-amylose corn comm.	0.029	50.3	96	82-(86)-99	48.2	71	82	105	114	4.2[b]
Waxy corn, commercial	0.002	00.0	72	64-(68)-70	47.6	64	71	88	97	4.0[b]

[a]Numbers represent percent lintnerization; [b]For calculation of ΔH values only p_1 and P_2 were used; [c]shoulder.

dependent shift and differences in the melting points of the three legume starches were proposed to be related to various factors, of which the granular organization and its inherent crystallinity are probably the most important (Biliaderis *et al*., 1980). The authors also identified factors such as differences in the degree of branching among the amylopectins of the starches. The order of increasing degree of branching was adzuki bean < smooth pea < lentil (Biliaderis *et al*., 1980). The branching is detrimental to crystallization and hence broadens the melting temperature range and lowers the melting temperature, as found in the field of synthetic polymers (Cowie, 1973). One would expect that the higher the degree of branching, the wider the melting temperature range and the less resistant the starch is to gelatinization (Biliaderis *et al*., 1980).

Ratnayake *et al*. (2001) studied the gelatinization transition temperatures [T_o (onset); T_p (midpoint); T_c (conclusion)] and the enthalpies of gelatinization (ΔH) of starches from four cultivars (Carneval, Carrera, Grande and Keoma) of field pea. They reported that the T_o, T_p, T_c and $\Delta H/\Delta P$ (enthalpy calculated on the basis of amylopectin content) did not vary significantly among the starches. In contrast, they indicated that the gelatinization temperature range ($T_c – T_o$) followed the order: Grande ~ Keoma > Carneval > Carrera. The T_o, T_p, T_c and ΔH of the field pea starches were within the range reported for other legume starches (Hoover and Sosulski, 1991).Additionally,Sandhu and Lim (2008) separated starches from pigeon pea,chick pea, field pea,kidney bean and black gram and reported their gelatinization temperature to be in the range of 68.3 to 69.3%.Abu *et al.* (2006) also reported gelatinization temperature of cowpea starch to range from 67.0-78.0°C. Nearly identical nature of the gelatinization transition temperatures and enthalpies indicates that the numbers of double helices (in the amorphous and crystalline domains) that unraveled and melted during gelatinization were nearly similar in the four starches (Ratnayake *et al*., 2001). However, the gelatinization temperature range ($T_c – T_o$) differed due to differences in the degree of heterogeneity of the starch crystallites within the granules (Ratnayake *et al*., 2001).

When gelatinized starch cools, the molecules begin to reassociate into an ordered structure, in a process called retrogradation (Orford *et al*., 1987). During retrogradation, amylose forms double helical associations of 40-70 glucose units (Jane and Robyt, 1984) whereas amylopectin crystallization occurs by association of the outermost short branches (Ring *et al*., 1987). The extent of reassociation (or retrogradation) depends on the botanical source of the starch (Gudmundsson, 1992; Gudmundsson *et al*., 1991; Kalichevsky *et al*., 1990; Roulet *et al.,* 1990; 6.Orford *et al*., 1987; Gudmundsson and Eliasson, 1989, 1991, 1992, 1993), the fine structure of amylopectin (Ward *et al*., 1994; Kalichevsky *et al*., 1990), water content (Gudmundsson, 1994; Zeleznak and Hoseney, 1986; Longton and LeGrys, 1981), storage temperature (Colwel *et al*., 1969, Mclver *et al*., 1968), and the presence of lipids and surfactants (Gudmundsson, 1992; Gudmundsson and Eliason, 1990; Eliasson and Ljunger, 1988a,b; Slade and Levine, 1987; Batres and White, 1986; Evans, 1986). A greater amount of amylose has traditionally been linked to a greater retrogradation tendency in starches (Whistler and BeMiller, 1996), but amylopectin and intermediate materials also play an important role in starch retrogradation during refrigerated storage (Yamin *et al*., 1999). In non-mutant-genotype starches, the amylose is responsible for short changes (Goodfellow and Wilson, 1990). The amylopectin molecule is responsible for longer term rheological and structural changes of starch gels (Gudmundsson, 1994). The roles of amylose and amylopectin depend on the composite nature of the starch gels where swollen gelatinized starch granules are embedded within an amylose-gel matrix (Steeneken, 1989; Russell, 1987; Christianson and Bagley, 1983; Eliasson and Bohlin, 1982; Ring and Stainsby, 1982).

The impacts of retrogradation in starch-based products can be beneficial or, more commonly, undesirable. There is general consensus that starch retrogradation contributes significantly to staling or undesirable firming of bread and other starch products (Del Nobile *et al*., 2003; Abd karim *et al*., 2000;Liu and Thompson, 1998a,1998b). Similarly, the vulnerability of legume starch (high amylose content, Table 1) gels to retrogradation and syneresis makes these types of starches unacceptable for products requiring low-temperature storage. In contrast, retrogradation is sometimes promoted to modify the structural, mechanical or organoleptic properties of certain starch-based products, for example; jam, gels, sauce, jelly, gravy, extruded snacks, vermicelli, soup, biscuit, and creamy desserts (Morikawa and Nishinari, 2000; Perera and Hoover, 1999; Yoshimura *et al*., 1999). Of considerable interest from a food point of view is that retrograded starch is resistant to the action of α-amylase in the ileum and is therefore not a source of blood glucose (Crapo *et al.*, 1977) but passes into the colon where it is acted upon by gut bacteria (Roder *et al.*, 2005). The retrograded starch shows a B-type X-ray diffraction pattern (Zobel, 1988b). Because starch retrogradation is a kinetically controlled process (Slade and Levine, 1987), the alteration of time, temperature and water content during processing can produce a variety of end products.

Starch retrogradation enthalpies are usually 60-80°C lower than gelatinization enthalpies, and transition temperatures are 10-26°C lower than those for gelatinization of starch granules (Baker and Rayas-Duarte, 1998; Yuan *et al*., 1993;White *et al*., 1989). The crystalline forms of retrograded starches are different in nature from those present in the native starch granules (Abd Karim *et al*., 2000). Retrograded starches show lower gelatinization temperatures and enthalpy than native starches because they have weaker starch crystallinity (Sasaki *et al*., 2000).

Tjahjadi and Breen (1984) reported that the degree of retrogradation, as measured by syneresis of Adzuki bean starch was greater than that of corn, wheat or potato starch gels. The authors also observed that the degree of syneresis decreased with increasing starch concentration. This behavior agreed with the results earlier obtained by Lii and Chang (1981) who reported that this pattern is characteristic of many legume starches. Ratnayake *et al*. (2001) studied the extent of retrogradation during gel storage and monitored it by determining changes in retrogradation enthalpy and in freeze-thaw stability. They indicated that in four field pea starches, T_o, T_p and T_c of retrograded gels were lower than those for the gelatinization endotherm, and $T_c - T_o$ for retrogradation was broader than for the gelatinization endotherm. These authors reported that the magnitude of ΔHR (enthalpy of retrogradation) followed the order: Carneval > Carrera > Grande > Keoma, whereas, $T_c - TO$ followed the order: Keoma > Grande > Carneval > Carrera. They implied that the wide melting temperature range ($T_c - T_o$) might be due to a large variation in the quantity and heterogeneity of the recrystallized amylopectin and explained differences in ΔH_R among starches on the basis of amylopectin unit chain length distribution (Lai *et al.*, 2000; Fredriksson *et al*., 1998; Lu *et al.*, 1997; Ward *et al*., 1994; Shi and Seib, 1992; Kalichevsky *et al.*, 1990).

Generally, legume starches retrograde significantly due to their relatively high amylose contents, although long term retrogradation, which has been blamed for deterioration in the quality of starch-based product, is attributed to short chains of amylopectin (Robin *et al*., 1974). Amylopectin has high water-binding capacity and slowly undergoes retrogradation, thus forming clear gels that are soft and flow well (Yuan *et al*., 1993).

Summary and conclusions. Inexpensive legumes are the major sources of dietary proteins, as animal proteins are expensive and beyond the reach of the poor. They are also rich in other nutrients such as starch, dietary fibre, vitamins, oils, phytochemicals and mineral elements.

Greater attention has been given to the protein component of legume seeds, despite the fact that the major component is starch. The protein found in this legumes is rich in lysine yet deficient in sulphur containing amino acids, hence the need to consume the products with cereal products to improve the quality of the protein. However, utilization of the starch fraction will be economically important if the proteins are used as food. Despite the current low production and utilization of legume starches in comparison with cereal starches, the former play important roles in the food industries because they affect the physical properties of many foods and are used as gelling agents, thickners, emulsion stabilizers and water binders. Legume starches differ in granule morphology, gelatinization temperature range and amylose content. They generally exhibit C-type X-ray patterns (mixture of A- and B- type X-ray patterns). The retrogadation and syneresis associated with legume starches can be reduced by physically or chemically modifying the native starches to make them more acceptable in food and non-food applications.

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