

Review

Morphological, thermal and rheological properties of starches from different botanical sources

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Abstract

Corn, rice, wheat and potato are the main sources of starches which differ significantly in composition, morphology, thermal, rheological and retrogradation properties. Cereal starches contain a significant quantity of phospholipids, while potato starch is rich in esterified phosphorus. Potato starch exhibits higher swelling power, solubility, paste clarity and viscosity than wheat, rice or corn starches. Morphological characteristics, such as shape and size of the starch granules, exhibit significant differences. Potato starch granules are smooth-surfaced, oval and irregular or cuboidal-shaped while corn, rice and wheat starch granules are angular, pentagonal and angular; and spherical and lenticular-shaped, respectively. Corn, rice and wheat starch granules are less smooth-surfaced than potato starch granules. Potato starch granules are largest ($<110\text{ }\mu\text{m}$) in size followed by wheat ($<30\text{ }\mu\text{m}$), corn ($<25\text{ }\mu\text{m}$) and rice ($<20\text{ }\mu\text{m}$) starches. Gelatinization temperatures (T_o , T_p , T_c) and enthalpies of gelatinization (ΔH_{gel}) of starches from different sources also differ significantly. Corn and rice starches generally show higher transition temperatures than wheat and potato starches while the ΔH_{gel} values are higher for potato and wheat starches. Potato starch shows a higher tendency towards retrogradation than the cereal starches. The rheological properties, such as storage modulus (G') and loss modulus (G'') of the starches from the different sources increase to a maximum and then drop during heating of all the starches. Potato starch shows highest peak G' , G'' and lower $\tan \delta$ than corn, rice and wheat starches during the heating cycle.

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Keywords: Potato; Corn; Rice; Wheat; Starch; Morphology; Gelatinization; Retrogradation; Thermal; Rheology

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1. Introduction

Starches from various plant sources, such as corn, potato, wheat, and rice, have received extensive attention in relation to structural and physico-chemical properties (Madsen & Christensen, 1996). Identification of native starch sources is required for desired functionality and unique properties (Duxbury, 1989). The physico-chemical properties and functional characteristics that are imparted by the starches to the aqueous systems and their uniqueness in various food applications vary with the biological origin (Svegmark & Hermansson, 1993). Starch contributes greatly to the textural properties of many foods and has many industrial applications as a thickener, colloidal stabilizer, gelling agent, bulking agent, water retention agent and adhesive. Interest in new value-added products to the industry has resulted in many studies being carried out on the morphological, rheological, thermal and textural properties of corn and potato starches (Evans & Haisman, 1979; Kim, Wiesenborn, Orr, & Grant 1995; Lii, Tsai, & Tseng, 1996; Wiesenborn, Orr, Casper, & Tacke, 1994). 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, Young, & Rocca, 1988), small angle neutron scattering (Jenkins, 1994) and Kofler hot stage microscope (Watson, 1964) have been used to study the gelatinization behaviour of starches. Stevens and Elton (1971) apparently first used DSC for measuring gelatinization and retrogradation of starch. Since then, it has proven to be an extremely valuable tool to quantify crystallinity in both native and retrograded starches, to determine retrogradation kinetics, and to study the effects of factors influencing retrogradation (Eliasson, 1985; Fearn & Russell, 1982; Jang & Pyun, 1997; Obanni & BeMiller, 1997). DSC has been of great value in studying both the loss of crystallite order during gelatinization, which occurs when the starch paste materials are heated in the presence of water, and the re-ordering of such systems during aging. This technique can detect both first order (melting) and second order (glass) thermal transitions (Russel & Oliver, 1989). Starch transition temperatures and gelatinization enthalpies, measured by DSC, may be related to characteristics of the starch granule, such as degree of crystallinity (Krueger, Knutson, Inglett, & Walker, 1987). However, it has been shown (by NMR and by X-ray diffraction) that the enthalpic transition is primarily due to the loss of double helical order rather than crystallinity (Cooke & Gidley, 1992). Rheological and thermal techniques have been applied to study the aging of starch gels. Starch exhibits unique viscosity behaviour with change of temperature, concentration and shear

rate (Nurul, Azemi, & Manan, 1999). The Brabender Visco-amylograph, rapid visco-analyser (RVA) and rotational viscometers have been extensively used for measuring starch paste viscosity (Wiesenborn et al., 1994). Many researchers have also used the dynamic rheometer for studying the viscoelastic or rheological properties of starches (Tsai, Li, & Lii, 1997; Hsu, Lu, & Huang, 2000; Lii et al., 1996). By determining the rheological properties of gels obtained under well controlled thermomechanical conditions, one can effectively investigate the relationships between pasting properties of various starches and rheological properties of their respective gels. Also, examining the microstructure of starch gels/pastes is essential for gaining better understanding of the relationship between chemical composition, viscoelastic properties and microstructure. The structure and the physicochemical properties of corn, rice, wheat and potato starches have been well documented. Scanning electron microscopy (SEM) has been used to relate granule morphology to starch genotype (Fannon, Hauber, & BeMiller, 1992a). SEM has also been used to relate paste structures to paste properties (Fannon & BeMiller, 1992; Fannon, Hauber, & BeMiller, 1992b). Laser light scattering has been used to characterize granule diameter, based on the assumption that granules are spherical, but this technique may not be accurate for potato starch granules which are slightly oblong, irregular or cuboidal (Wiesenborn et al., 1994).

In this review, we re-examine the information on composition, morphological, thermal and rheological characteristics of starches from some important plant sources.

2. Composition, transmittance, swelling and solubility

Starch is the major polysaccharide in plants and is in the form of granules that exist naturally within the plant cells. Starch is semicrystalline in nature with varying levels of crystallinity. The crystallinity is exclusively associated with the amylopectin component, while the amorphous regions mainly represent amylose (Zobel, 1988a, 1998b). Amylose is a linear polymer composed of glucopyranose units linked through α -D-(1-4) glycosidic linkages, while the amylopectin is a branched polymer with one of the highest molecular weights known among naturally occurring polymers (Karim, Norziah, & Seow, 2000). The packing of amylose and amylopectin within the granules has been reported to vary among the starches from different species. X-ray diffraction diffractometry has been used to reveal the presence and characteristics of the crystalline structure of the starch granules (Hoover, 2001). The cereal starches exhibit the typical A-type X-ray pattern, whereas, the tuber starches show the B-form and legumes, the mixed state pattern 'C'.

In normal and waxy starches, the branched molecule, amylopectin constitutes the crystallites. The branches of the amylopectin molecule form double helices that are arranged in crystalline domains (Sarko & Wu, 1978). The 'A', 'B', and 'C' pattern are thus, the different polymeric forms of the starch that differ in the packing of the amylopectin double helices. Starch paste behaviour in aqueous systems depend on the physical and chemical characteristics of the starch granules, such as mean granule size, granule size distribution, amylose/amylopectin ratio and mineral content (Madsen & Christensen, 1996). The amylose content of the starch granules varies with the botanical source of the starch (Table 1) and is affected by the climatic conditions and soil type during growth (Asaoka, Okuno, & Fuwa, 1985; Inatsu, Watanabe, Maida, Ito, & Osani, 1974; Juliano, Bautista, Lugay, & Reyes, 1964; Morrison & Azudin, 1987; Morrison, Milligan, & Azudin, 1984). Amylose content of potato starch varies from 23% to 31% for normal potato genotypes (Kim et al., 1995; Wiesenborn et al., 1994). However waxy potato genotypes, essentially without amylose, have also been reported (Hermansson & Svegmarm, 1996). Amylose content of rice is specified as waxy, 0–2%; very low, 5–12%; low, 12–20%; intermediate, 20–25%; and high 25–33% (Juliano, 1992). The amylose content of wheat

starch varies from 18 to 30% (Deatherage, MacMasters, & Rist, 1955; Medcalf & Gilles, 1965; Soulaka & Morrison, 1985). The activity of the enzymes involved in starch biosynthesis may be responsible for the variation in amylose content among the various starches (Krossmann & Lloyd, 2000). The variation in amylose contents among the starches from different and similar plant sources, in various studies may also be attributed to the different starch isolation procedures and analytical methods used to determine amylose content (Kim et al., 1995). In many instances, the amylose contents of the starches have been determined by colorimetric methods without prior defatting and/or by not taking into account the iodine complexing ability of the long external chains of tuber starches (Banks & Greenwood, 1975; Morrison & Karkalas, 1990). Thus, leading either to an underestimation (failure to remove amylose complexed lipids) or to an overestimation (failure to determine amylose content from a standard curve containing mixtures of amylose and amylopectin in various ratios) of the amylose content (Hoover, 2001).

Phosphorus is one of the non-carbohydrate constituents present in the starches, which significantly affects the functional properties of the starches. Phosphorus content varies from 0.003% in waxy corn starch to 0.09% in potato starch (Schoch, 1942a). Phosphorus

Table 1
Physicochemical properties of starches from different botanical sources

Starch source	Amylose content (%)	Swelling power (g/g) (°C)	Solubility (%) (°C)	Organic phosphorus contents (% dsb) ^l			Light transmittance ^p (% at 650 nm)
				Mono-P ^m	Lipid-P ⁿ	Inorganic-P	
Normal potato	20.1–31.0 ^a	1159 (95) ⁱ	82 (95) ^l	0.086±0.007	ND ^o	0.0048±0.0003	96
Normal corn	22.4–32.5 ^b	22 (95) ⁱ	22 (95) ^l	0.003±0.001	0.0097±0.0001	0.0013±0.0007	31
Waxy corn	1.4–2.7 ^c	–	–	0.0012±0.0006	ND ^o	0.0005±0.0001	46
High amylose corn	42.6–67.8 ^c	6.3 (95) ⁱ	12.4 (95) ^j	0.005±0.001	0.015±0.003	0.0076±0.0006	–
Normal rice	5–28.4 ^d	23–30 (95) ⁱ	11–18 (95) ^j	0.013	0.048	–	24
Waxy rice	0–2.0 ^d	45–50 (95) ⁱ	2.3–3.2 (95) ^j	0.003	ND ^o	–	–
High amylose rice	25–33 ^e	–	–	–	–	–	–
Normal wheat	18–30 ^f	18.3–26.6 (100) ^k	1.55 (100) ^k	0.001	0.058±0.002	Trace	28
Wheat A-granules	28.4–27.8 ^g	–	–	–	–	–	–
Wheat B-granules	27.5–24.5 ^g	–	–	–	–	–	–
Waxy wheat	29.10.8–0.9 ^h	–	–	–	–	–	–

^a Kim et al., 1995 and Wiesenborn et al., 1994.

^b Morrison et al., 1984 and Biliaderis, Maurice, and Vose, 1980.

^c Morrison et al., 1984.

^d Juliano, 1992 and Jane et al., 1996.

^e Juliano, 1992.

^f Deatherage et al., 1955, Medcalf and Gilles, 1965 and Soulaka and Morrison, 1985.

^g Tester and Morrison, 1990.

^h Sasaki et al., 2000.

ⁱ Leach, McCowen, and Schoch, 1959.

^j Lii, Tsai, and Tseng, 1996 and Lii, Shao, and Tseng, 1995.

^k Sasaki and Matsuki, 1998.

^l From Lim, Kasemsuwan, Jane, 1994 and Kasemsuwan and Jane, 1996, calculated based on integrated area of P-signals.

^m Phosphate monoesters P-signals located at 4.0–4.5 ppm relative to external 80% orthophosphoric acid.

ⁿ Phospholipids P-signals located at –0.4–1.2 ppm.

^o Not detectable.

^p From Jane et al. (1996), calculated using 1% starch paste.

is present as phosphate monoesters and phospholipids in various starches. The phosphate monoesters are covalently bound to the amylopectin fraction of the starch and increase starch paste clarity and viscosity, while the presence of phospholipids results in opaque and lower-viscosity pastes (Craig, Maningat, Seib, & Hoseney, 1989; Schoch, 1942a, 1942b). Phosphate groups, esterified to the amylopectin fraction of potato starch, contribute to the high viscosity and also to a high transparency, water binding capacity and freeze thaw stability (Craig et al., 1989; Swinkels, 1985). Phospholipid content of the starch is proportional to the amylose content of the starch (Morrison et al., 1984; Morrison, Tester, Snape, Law, & Gidley, 1993). Phospholipids present in starch have a tendency to form a complex with amylose and long branched chains of amylopectin, which results in limited swelling. Wheat and rice starches have higher phospholipid contents and produce starch pastes with lower transmittance than corn and potato starches with lower phospholipid contents (Table 1).

Potato starch, with a higher phosphate monoester content, results in pastes with higher transmittance than the other starches (Table 1). The phosphorus content and form in potato starch has been reported to be influenced by growing conditions, temperature and storage (Smith, 1987). The percentages of phosphorus in different forms for various starches are shown in Table 1. It has been shown that 61% of the starch phosphate monoesters in potato starch are bound on the C-6 of the glucose units, with 38% phosphate monoester on C-3 of the glucose and possibly 1% of monoester on the C-2 position (Jane, Kasemsuwan, Chen, & Juliano, 1996). Defatting of the starch has been reported to reduce the pasting temperature of rice starch and soften the starch gel (Maningat & Juliano, 1980). Free fatty acids in rice and maize starches contribute to their higher transition temperatures and lower retrogradation (Davies, Miller, & Procter, 1980) which is due to amylose–lipid complex formation. More than 90% of the lipids inside wheat starch granules are lysophospholipids and have been thought to occur in the form of inclusion complexes with amylose. Wheat starch lipids constitute 1% of the granular weight, having surface lipids to the extent of 0.05% (Eliasson, Karlsson, Larlsson, & Miezi, 1981; Morrison, 1988). The lipids are present at lower levels and significantly affect the swelling of wheat starch (Morrison et al., 1993). It has also been reported that surface lipids oxidize and contribute to the so-called cereal odour of wheat starch. The swelling power and solubility of the starches from different sources differ significantly (Table 1). 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. Potato starch has much higher swelling power and solubility than other starches. Potato starch exhibits the highest average swelling power, while it is lowest for wheat starch. The higher swelling power and solubility of potato starch is probably due to a higher content of phosphate groups on amylopectin (repulsion between phosphate groups on adjacent chains will increase hydration by weakening the extent of bonding within the crystalline domain) (Galliard & Bowler, 1987). The presence of lipids in starch may have a reducing effect on the swelling of the individual granules (Galliard & Bowler, 1987). Since corn, rice and wheat starch granules contain more lipids than potato starch granules, this may possibly explain the difference in the swelling power of these starches. The swelling power and solubility provide evidence of the magnitude of interaction 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). The differences between swelling powers and solubilities of starches from different sources may also be due to differences in morphological structure of starch granules. Kaur, Singh, and Sodhi (2002) reported a higher swelling power and lower solubility for potato starches having large and irregular or cuboidal granules. The large and irregular or cuboidal granules may be helpful in immobilizing the starch substance within the granule, even at very high levels of swelling, which results in lower solubility levels. Granules continue to swell as the temperature of the suspension is increased above the gelatinization range. According to deWilligen (1976a, 1976b), corn and wheat granules may swell up to 30 times their original volume and potato starch granules up to 100 times their original volume, without disintegration. It has been suggested that amylose plays a role in restricting initial swelling because this form of swelling proceeds more rapidly after amylose has first been exuded. The increase in starch solubility, with the concomitant increase in suspension clarity is seen mainly as the result of granule swelling, permitting the exudation of the amylose. The extent of leaching of solubles mainly depends on the lipid content of the starch and the ability of the starch to form amylose–lipid complexes. The amylose–lipid complexes are insoluble in water and require higher temperatures to dissociate (Morrison, 1988; Raphaelides & Karkalas, 1988). The amylose involved in complex formation with lipids is prevented from leaching out (Tester & Morrison, 1990). The cereal starches contain enough lipids to form lipid-saturated complexes (Karkalas & Raphaelides, 1986) with 7–8% amylose in the starch; hence the maximum amylose leached is about 20% of the total starch (Tester & Morrison,

1990). The differences of the swelling and solubility behaviour of the starches between botanical sources and among the cultivars of any one botanical source are caused by the differences in the amylose and the lipid contents, as well as the granule organization. The granules become increasingly susceptible to shear disintegration as they swell, and they release soluble material as they disintegrate. The hot starch paste is a mixture of swollen granules and granule fragments, together with colloiddally- and molecularly-dispersed starch granules. The mixture of the swollen and fragmented granules depends on the botanical source of the starch, water content, temperature and shearing during heating.

3. Morphological properties

Morphological characteristics of starches from different plant sources vary with the genotype and cultural practices. The variation in the size and shape of starch granules is attributed to the biological origin (Svegmark & Hermansson, 1993). The morphology of starch granules depends on the biochemistry of the chloroplast or amyloplast, as well as physiology of the plant (Badenhuizen, 1969). The granular structures of potato, corn, rice and wheat starches show significant variations in size and shape when viewed by SEM. Scanning electron micrographs of the starch granules from various plant sources are illustrated in Fig. 1. The granule size is variable and ranges from 1 to 110 μm (Hoover, 2001). The average granule size ranges from 1 to 20 μm for small and 20 to 110 μm for large potato starch granules. The extent of variation in the granular structure of starches from cultivar to cultivar is significantly higher in potatoes. The average size of individual corn starch granules ranges from 1 to 7 μm for small and 15 to 20 μm for large granules. The rice starch granules range from 3 to 5 μm in size. Potato starch granules have been observed to be oval and irregular or cuboidal in shape. The starch granules are angular-shaped for corn, and pentagonal and angular-shaped for rice. At maturity, wheat endosperm contains two types of starch granules: large A- and small B-type (Baum & Bailey, 1987). A-type granules are disk-like or lenticular in shape with diameters ranging from 10 to 35 μm . On the other hand, B-type starch granules are roughly spherical or polygonal in shape, ranging from 1 to 10 μm in diameter (Baum & Bailey, 1987). When observed under a scanning electron microscope, the surfaces of the granules from corn, rice and wheat appear to be less smooth than potato starch granules. Li, Vasanathan, Rosnagel, and Hoover (2001) observed the presence of “pin holes” and equatorial grooves or furrows in large-sized corn starch granules. Baldwin (1995) has shown the presence of large protruberances (200–500 μm) on the surface of potato starch granules, using atomic force microscopy.

The individual granules, in the case of rice starch, develop into compact spherical bundles or clusters, known as compound granules, which fill most of the central space within the endosperm cells. Physico-chemical properties, such as percent light transmittance, amylose content, swelling power and water-binding capacity were significantly correlated with the average granule size of the starches separated from different plant sources (Kaur, Singh, & Sodhi, *in press*; Singh & Singh, 2001; Zhou, Robards, Glennie-Holmes, & Helliwell, 1998).

4. Gelatinization and retrogradation properties

The crystalline order in starch granules is often the basic underlying factor influencing functional properties. Collapse of crystalline order within the starch granules manifests itself as irreversible changes in properties, such as granule swelling, pasting, loss of optical birefringence, loss of crystalline order, uncoiling and dissociation of the double helices, and starch solubility (Atwell, Hood, Lineback, Varriano-Martson, & Zohel, 1988; Hoover, 2001; Stevens & Elton, 1981). The order-disorder transitions that occur on heating an aqueous suspension of starch granules have been extensively investigated using DSC (Donovan, 1979; Jenkins, 1994; Lelievre & Mitchell, 1975). Starch transition temperatures and gelatinization enthalpies by DSC may be related to characteristics of the starch granule, such as degree of crystallinity (Krueger et al., 1987). This is influenced by chemical composition of starch and helps to determine the thermal and other physical characteristics of starch. Starches from different botanical sources, differing in composition, exhibited different transition temperatures and enthalpies of gelatinization. Kim et al. (1995) have studied the thermal properties of starches from 42 potato cultivars and correlated these properties with the physicochemical characteristics. Gelatinization starts at the hilum of the granule and swells rapidly to the periphery. Gelatinization occurs initially in the amorphous regions, as opposed to the crystalline regions, of the granule, because hydrogen bonding is weakened in these areas. Gelatinization temperatures and enthalpies associated with gelatinization endotherms vary between the starches from different sources (Table 2). The differences in transition temperatures between the different starches may be attributed to the differences in the degree of crystallinity. High transition temperatures have been reported to result from a high degree of crystallinity, which provides structural stability and makes the granule more resistant towards gelatinization (Barichello, Yada, Coffin, & Stanley, 1990). Tester (1997) has postulated that the extent of crystalline perfection is reflected in the gelatinization temperatures. The gelatinization and swelling

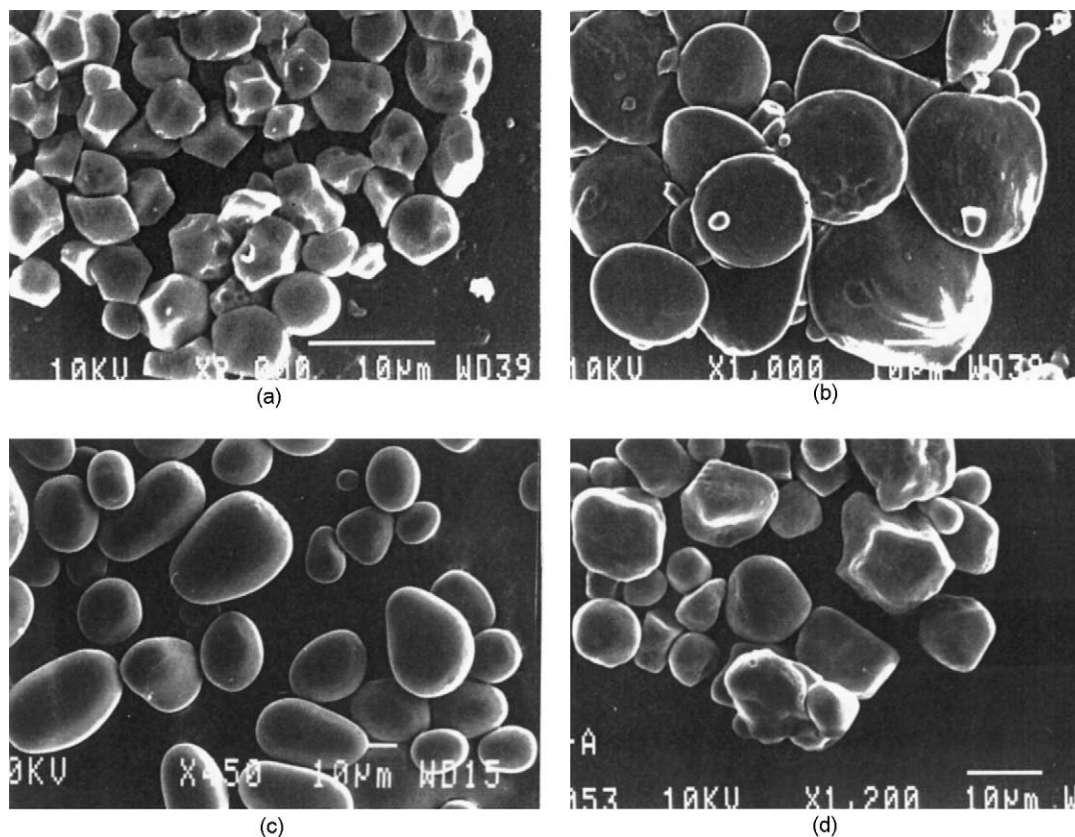


Fig. 1. Scanning electron micrographs (SEM) of starches separated from different sources: (a) rice, (b) wheat, (c) potato, (d) corn (bar = 10 µm).

Table 2

Gelatinization parameters of the starches from different botanical sources

Source	Methodology	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J/g)
Potato ^a	DSC:S:W 1:2:3	59.72–66.2	62.9–69.6	67.28–75.4	12.55–17.9
Potato ^b	DSC:S:W 1:3:3	57.0–68.3	60.6–72.4	66.5–78.0	13.0–15.8
Potato ^c	DSC:S:W 1:1.5	57.2	61.4	80.3	17.4
Normal corn ^c	DSC:S:W 1:1.5	62.3	67.7	84.3	14.0
Normal corn ^d	DSC:S:W 1:3	64.1	69.4	74.9	12.3
Normal corn ^e	DSC:S:W 1:9	65.7	71.0	–	12.0
Waxy corn ^e	DSC:S:W 1:9	66.6	73.6	–	14.2
Waxy corn ^d	DSC:S:W 1:3	64.2	69.2	74.6	15.4
High amylose corn ^e	DSC:S:W 1:9	66.8	73.7	–	13.7
Rice ^c	DSC:S:W 1:1.5	62.0	67.4	97.5	11.0
Rice ^e	DSC:S:W 1:9	57.7	65.1	–	11.5
Rice ^f	DSC:S:W 1:2:3	66.0–67.26	69.74–71.94	74.08–78.04	8.16–10.88
Rice ^d	DSC:S:W 1:3	70.3	76.2	80.2	13.2
Waxy rice ^g	DSC	66.1–74.9	70.4–78.8	–	7.7–12.1
Wheat ^c	DSC:S:W 1:1.5	51.2	56.0	76.0	9.0
Wheat ^h	DSC:S:W 1:2:3	46.0–52.4	52.2–57.6	57.8–66.1	14.8–17.9
Wheat ^d	DSC:S:W 1:3	57.1	61.6	66.2	10.7

Enthalpy values are expressed in J/g of the dry starch; S, starch; W, water. T_o = onset temperature, T_p = peak temperature; T_c = final temperature; ΔH_{gel} = Enthalpy of gelatinization (dsb, based on dry starch weight).

^a Kim et al., 1995 and Singh and Singh, 2001.

^b Cottrell, Duffins, Paterson, and George, 1995 and Jane et al., 1999.

^c Jenkins and Donald, 1998.

^d Jane et al., 1999.

^e Li and Yeh, 2001.

^f Sodhi and Singh, 2002.

^g Jane et al., 1996.

^h Sasaki et al., 2000.

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) (Tester, 1997). T_p gives a measure of crystallite quality (double helix length). Enthalpy of gelatinization (ΔH_{gel}) gives an overall measure of crystallinity (quality and quantity) and is an indicator of the loss of molecular order within the granule (Cooke & Gidley, 1992; Hoover & Vasanathan, 1994; Tester & Morrison, 1990). Gernat, Radosta, Anger, and Damaschun (1993) have stated that the amount of double-helical order in native starches should be strongly correlated to the amylopectin content and granule crystallinity increases with amylopectin content. This suggests that the ΔH_{gel} values should preferably be calculated on an amylopectin basis. However, the ΔH_{gel} values for different starches, given in Table 2 are not calculated in this manner. Granule shape, percentage of large and small granules and presence of phosphate esters have been reported to affect the gelatinization enthalpy values of starches (Stevens & Elton, 1971; Yuan, Thompson, & Boyer, 1993). Yamin, Lee, Polak, and White (1999) reported that a starch with low T_o and broad gelatinization range (R) might have irregularly shaped granules. Singh and Singh (2001) and Kaur, Singh, and Sodhi (2002) also reported lower transition temperatures and higher ΔH_{gel} for large and irregular or cuboidal potato starch granules. The variation in T_o , ΔH_{gel} and gelatinization temperature range in starches from different cultivars may be due to difference in amounts of longer chains in amylopectins. These longer chains require a higher temperature to dissociate completely than that required for shorter double helices (Yamin et al., 1999). Noda, Takahata, Sato, Ikoma, and Mochida (1996) also reported that DSC parameters are influenced by the molecular architecture of the crystalline region, which corresponds to the distribution of amylopectin shorter chains. The higher transition temperatures for corn and rice starch may result from the more rigid granular structure and the presence of lipids (Singh & Singh, in press). 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 starting gelatinization (Flipse, Keetels, Jacobson, & Visser, 1996). More energy is needed to initiate melting in the absence of amylose-rich amorphous regions (Kreuger et al., 1987). This correlation indicates that the starch with higher amylose content has more amorphous region and less crystalline region which thus, lowers the gelatinization temperatures (Sasaki, Yasui, & Matsuki, 2000). Potato amylopectin starches were reported to exhibit higher endothermic temperatures as well as higher enthalpies than normal potato starches. The amorphous amylose in the normal

potato starches decreases the relative amount of crystalline material in the granule (Svegmark et al., 2002). Similarly, Sasaki et al. (2000) reported higher transition temperatures for waxy wheat starches. However, high amylose starches with longer average chain length were reported to exhibit higher transition temperatures (Jane et al., 1999). The glass transition that precedes the gelatinization may also be affected by the absence/presence of the amylose in the starch granules. The existence of an effective glass transition has been observed for various granular starches by DSC (Slade & Levine, 1988). The gelatinization characteristics of intact A- and B-type starch granules in mature wheat endosperm have different temperature regimes (Eliasson & Karlsson, 1983; Soulaka & Morrison, 1985). Compared with the A-type starch granules, B-type starch granules started gelatinization at a lower T_o , but had higher T_p and T_c (Seib, 1994). A-type starch granules have higher ΔH_{gel} value than B-type starch granules.

The molecular interactions (hydrogen bonding between starch chains) after cooling of the gelatinized starch paste have been called retrogradation (Hoover, 2000). During retrogradation, amylose forms double-helical associations of 40–70 glucose units (Jane & Robyt, 1984) whereas amylopectin crystallization occurs by association of the outermost short branches (Ring et al., 1987). In the case of retrograded starch, the value of enthalpy provides a quantitative measure of the energy transformation that occurs during the melting of recrystallized amylopectin as well as precise measurements of the transition temperatures of the endothermic event (Karim et al., 2000). The endothermic peak of starches after gelatinization and storage at 4 °C appears at lower transition temperatures. Transition temperatures and retrogradation enthalpy (ΔH_{ret}) at the end of the storage period drop significantly, compared to transition temperatures and enthalpy (ΔH_{gel}) during gelatinization (Table 3). Starch retrogradation enthalpies are usually 60–80% smaller than gelatinization enthalpies and transition temperatures are 10–26 °C lower than those for gelatinization of starch granules (Baker & Rayas-Duarte, 1998; White, Abbas, & Johnson, 1989; Yuan et al., 1993). The crystalline forms are different in nature from those present in the native starch granules (Karim et al., 2000). Retrograded starches show lower gelatinization and enthalpy than native starches because they have weaker starch crystallinity (Sasaki et al., 2000). The extent of decrease in transition temperatures and enthalpy is higher in stored potato starch gels than in corn, rice and wheat gels. This may be attributed to the higher tendency of the potato starch gels towards retrogradation (Singh, Singh, & Saxena, 2002). The lower levels of retrogradation in corn, rice and wheat starches may be responsible for the lower decrease in transition temperatures and enthalpy. Recrystallization of amylopectin branch chains has been reported to

Table 3
Thermal properties during retrogradation of starches from different botanical sources

Source	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{ret} (J/g)	R (%) ^h
Potato ^a	59.72–60.70	63.26–64.58	67.28–70.34	6.42–8.61	51.50–62.16
Potato ^b	42.5	55.7	66.9	7.5	43.4
Normal corn ^b	39.0	50.1	59.4	5.8	47.6
Waxy corn ^b	40.2	51.3	60.2	7.3	47.0
High amylose corn ^b	44.1	ND ⁱ	115.4	9.9	61.0
Normal rice ^b	40.3	51.0	60.4	5.3	40.5
Normal rice ^c	37.05–38.43	49.80–52.59	62.42–65.92	–	–
Waxy rice ^c	36.72–37.25	50.65–51.26	62.56–62.93	–	–
Waxy rice ^b	43.2	50.6	55.2	0.8	5.0
Normal wheat ^b	38.6	47.6	55.7	3.6	33.7
Normal wheat ^{d,e}	29.8–31.7	41.8–42.7	–	7.0–8.5	–
Normal wheat ^{d,f}	30.9–32.6	41.2–42.6	–	8.1–9.7	–
Normal wheat ^g	20.4–20.6	33.2–33.7	50.0	10.1–10.6	–
Waxy wheat ^g	19.9–20.5	33.1–33.8	50.4–51.8	11.4–12.6	–

T_o = onset temperature, T_p = peak temperature; T_c = final temperature; ΔH_{ret} = Enthalpy of retrogradation (dw/b, based on starch weight).

^a Singh and Singh, 2001, after storage of the samples at 4 °C for 2 weeks.

^b Jane et al., 1999, storage at 4 °C for 7 days.

^c Lin and Lii, 2001, storage at 4 °C for 4 weeks.

^d Sasaki and Matsuki, 1998.

^e Storage at 5 °C for 2 weeks.

^f Storage at 5 °C for 4 weeks.

^g Sasaki et al., 2000, storage at 5 °C for 4 weeks.

^h Retrogradation (%) = $\Delta H_{gel}/\Delta H_{ret}$.

ⁱ Not detectable.

occur in a less ordered manner in stored starch gels as it is present in native form. This explains the observation of amylopectin retrogradation endotherms at a temperature range below that for gelatinization (Ward, Hosney, & Seib, 1994). The variation in thermal properties of starches after gelatinization and during refrigerated storage may be attributed to the variation in amylose to amylopectin ratio, size and shape of the granules and presence/absence of lipids. The amylose content has been reported to be one of the influential factors for starch retrogradation (Baik, Kim, Cheon, Ha, & Kim, 1997; Chang & Liu, 1991; Fan & Marks, 1998; Gudmundsson & Eliasson, 1990; Kaur, Singh, & Sodhi, 2002). Pan and Jane (2000) reported the presence of a higher amount of amylose in large-size maize starch granules. A greater amount of amylose has traditionally been linked to a greater retrogradation tendency in starches (Whistler & BeMiller, 1996) but amylopectin and intermediate materials also play an important role in starch retrogradation during refrigerated storage (Yamin et al., 1999). The intermediate materials with longer chains than amylopectin, may also form longer double helices during reassociation under refrigerated storage conditions. The retrogradation has been reported to be accelerated by the amylopectin with larger amylose chain length (Kalichevsky, Oxford, & Ring, 1990; Yuan et al., 1993). Shi and Seib (1992) showed that the retrogradation of waxy starches was directly proportional to the mole fraction of branches with degree of polymerisation (DP) 14–24, and inversely

proportional to the mole fraction of branches with DP 6–9. The low degree of retrogradation for waxy starches has been attributed to the high proportion of short chain branches of DP 6–9 (Lu, Chem, & Lii, 1997).

5. Rheological properties

During gelatinization, the starch granule swells to several times its initial size, ruptures and simultaneously amylose leaches out from inside the granule. A three dimensional network is formed by the leached out amylose (Eliasson, 1985; Hennig, Lechert, & Goemann, 1976; Tester & Morrison 1990). The swelling behavior of starch is the property of its amylopectin content, and amylose acts as both a diluent and an inhibitor of swelling (Tester & Morrison, 1990). Starch exhibits unique viscosity behaviour with change of temperature, concentration and shear rate (Nurul et al., 1999). This can be measured by the Brabender Viscoamylograph pasting curves. The shape of the Brabender peak is the reflection of the processes taking place during the pasting cycle. The height of the peak at a given concentration reflects the ability of the granules to swell freely before their physical breakdown. Starches that are capable of swelling to a high degree are also less resistant to breakdown on cooking and hence exhibit viscosity decreases significantly after reaching the maximum value. The shape of the peak is, however, strongly influenced by the initial concentration of the starch suspension. The

increase in viscosity during the cooling period indicates a tendency of various constituents present in the hot paste (swollen granules, fragments of swollen granules, colloiddally- and molecularly-dispersed starch molecules) to associate or retrograde as the temperature of the paste decreases.

The dynamic rheometer allows the continuous assessment of dynamic moduli during temperature and frequency sweep testing of the starch suspensions. The storage dynamic modulus (G') is a measure of the energy stored in the material and recovered from it per cycle while the loss modulus (G'') is a measure of the energy dissipated or lost per cycle of sinusoidal deformation (Ferry, 1980). The ratio of the energy lost to the

energy stored for each cycle can be defined by $\tan \delta$, which is an another parameter indicating the physical behaviour of a system. The G' of starch progressively increases at a certain temperature (TG') to a maximum (peak G') and then drops with continued heating in a dynamic rheometer. The initial increase in G' could be attributed to the degree of granular swelling to fill the entire available volume of the system (Eliasson, 1986) and intergranule contact might form a three-dimensional network of the swollen granules (Evans & Haisman, 1979; Wong & Lelievre, 1981). With further increase in temperature, G' decreases, indicating that the gel structure is destroyed during prolonged heating (Tsai et al., 1997). This destruction is due to the melting of the crystalline region remaining in the swollen starch granule, which deforms and loosens the particles (Eliasson, 1986). The rheological properties of the different starches vary to a large extent with respect to the granular structure (Table 4). Tsai et al. (1997) reported the effect of granular structure of rice starch on the pasting behaviour using the dynamic rheometer. The large and cuboidal or irregular shaped granules in potato starch exhibited higher storage and loss modulus and lower $\tan \delta$, than the small and oval granules (Singh & Singh, 2001). The presence of a high phosphate monoester content and the absence of lipids and phospholipids in the potato starch may also be responsible for high G' and G'' . Corn starch has a lower G' , G'' than potato starch. The phospholipids and the more rigid

Table 4
Rheological properties of starches from different botanical sources during heating from 30 to 75 °C, studied using dynamic rheometer

Source	TG' (°C)	Peak G' (Pa)	Peak G'' (Pa)	Breakdown in G' (Pa)	Peak $\tan \delta$
Potato ^{a,b}	62.7	8519	1580	3606	0.1565
Corn ^{c,d}	70.2	6345	1208	2329	0.1905
Rice ^{c,d}	72.4	4052	955	2831	0.1972
Wheat ^{d,e}	69.6	6935	1370	2730	0.1976

^a From Kaur, Singh, and Sodhi, 2002.

^b At 20% starch concentration.

^c Singh and Singh, 2002.

^d At 15% starch concentration.

^e Unpublished data.

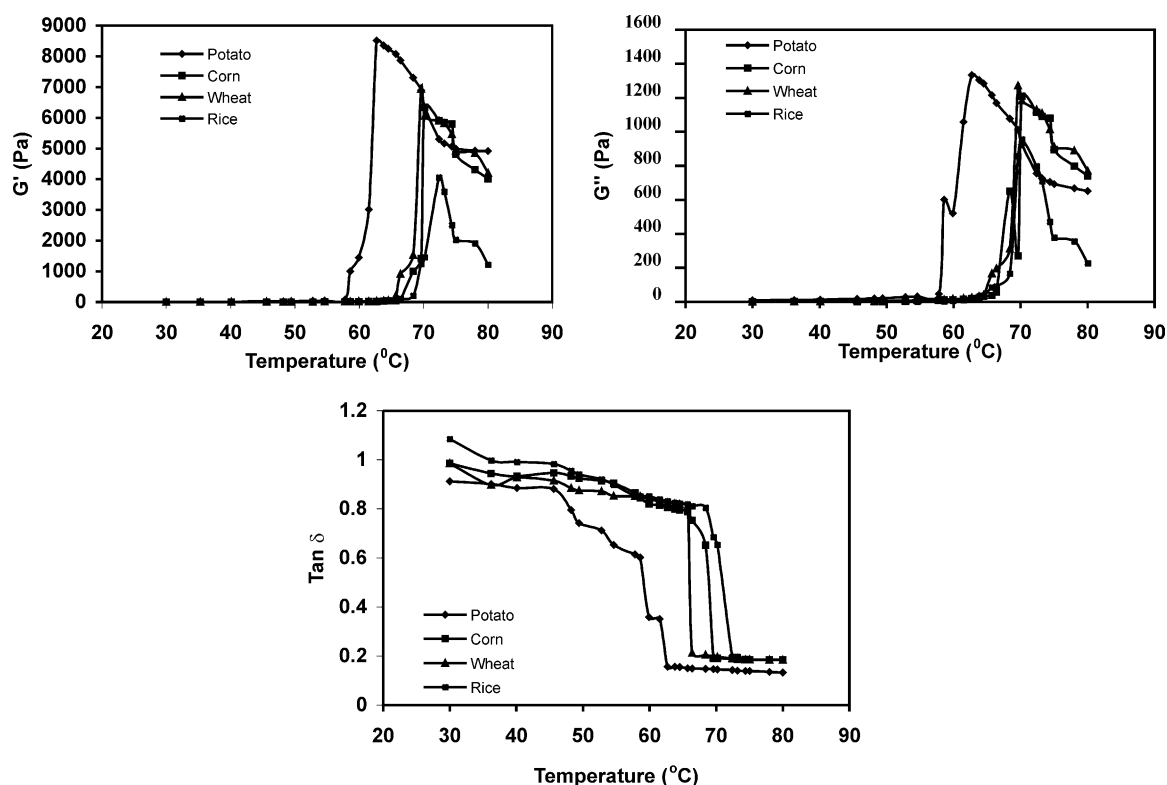


Fig. 2. Storage modulus (G'), loss modulus (G'') and loss factor ($\tan \delta$) of starches from different sources during heating on dynamic rheometer.

granules present in corn starch may be responsible for the lower G' of corn starch. The amylose-lipid complex formation during gelatinization of corn starch lowers the G' and G'' (Singh et al., 2002). The protein content of rice starch has been reported to be negatively correlated with peak viscosity and positively correlated with pasting temperature (Lim, Lee, Shin, & Lin, 1999). Sanchez, Torre, Osella, and Mancuello (1986) and Sabularse, Liuzzo, Rao, and Grodner (1992) reported that damaged starch was negatively correlated with peak viscosity. Wang and Wang (2001) suggested that damaged starch content plays a more important role than protein content in determining peak viscosity of starch. The extent of breakdown in starch pastes was calculated, and is a measure of degree of disintegration of starch granules (Singh et al., 2002). The breakdown in G' is the difference between peak G' at TG' and minimum G' at 75 °C. Potato starches show higher breakdown in G' than corn, rice and wheat starches. Differences in the breakdown values of starches may be attributed to the granule rigidity, lipid content and peak G' values. Corn, wheat and rice starches, being rich in lipids, show lower breakdown values. Similarly, wheat and rice starches, with large-sized granules, also show higher storage, loss modulus and lower $\tan \delta$ (Fig. 2). Amylose content is another factor, which significantly affects the rheological properties of the starch. Lii et al. (1996) reported the increase in G' and G'' of rice starch with the increase in amylose content during temperature sweep testing. Kaur, Singh, and Sodhi (2002) reported higher G' values for potato starches having higher amylose contents. Shewmaker et al. (1994) reported low paste viscosity for starch pastes made from potato genotypes with low amylose contents. Similarly, it has also been reported that the starches isolated from waxy potatoes show lower G' , G'' and higher $\tan \delta$ values (Kaur, Singh, Sodhi, and Gujral, 2002). Tsai et al. (1997) reported higher G' and G'' values for non-waxy rice and corn starches than the waxy corn and rice starches. They also reported an increase in G' with the addition of amylose to waxy rice and corn starches. Starches from waxy corn and rice varieties exhibited lower G' and G'' than normal corn and rice starch. In waxy starches, the phenomenon of gel formation is different from normal starch in which starch granules are embedded in a continuous network of amylose. The building up of gel network in waxy starch may involve swollen granules alone.

6. Conclusion

The starches from various plant sources differ significantly in physicochemical, rheological, thermal and retrogradation properties. Starches with specific functional properties are in great demand in the food

industry. Starches with desirable functional properties could play a significant role in improving the quality of different food products and could replace chemically-modified starches that are currently being used in a number of products.

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