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Some properties of potatoes and their starches II. Morphological, thermal and rheological properties of starches

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Abstract

The physico-chemical, morphological, thermal and rheological properties of the starches separated from different potato cultivars (Kufri Jyoti, Kufri Badshah and Pukhraj) were studied. The starches separated from the mealier cultivars (Kufri Jyoti and Kufri Badshah) showed lower transition temperatures (T_0 ; T_p and T_c), peak height indices (PHI), and higher gelatinization temperature range (R) and enthalpies of gelatinization (ΔH_{gel}) than the starch from the least mealy cultivar (Pukhraj). Swelling power, solubility, amylose content and transmittance values were observed to be higher for Kufri Jyoti and Kufri Badshah potato starches, while turbidity values were lower for these starches. The rheological properties of starches, measured using a dynamic rheometer, showed significant variation in the peak G', G" and peak tan δ values. Kufri Badshah and Kufri Jyoti starches showed higher peak G', G" and lower peak tan δ values than Pukhraj starch during heating and cooling cycles. Kufri Jyoti and Kufri Badshah starches showed higher breakdown in G' than starch from the Pukhraj potato cultivar. The large-sized granules of the starches from Kufri Badshah and Kufri Jyoti appeared to be associated with higher values of peak G' and G'' and consistency coefficient. Starch from the least mealy cultivar (Pukhraj) showed higher retrogradation, which increased progressively during storage at 4 °C for 120 h. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Potato; Starch; Morphology; Thermal; Rheology; Retrogradation

1. Introduction

Textural changes in cooked potatoes are mainly associated with the gelatinization, and retrogradation behaviour of starch (Jane, Chen, Lee, McPherson, Wong, Radosavl Jevic, & Kasemsuwan, 1999; Kim, Wiesenborn & Grant, 1997). The presence of starch in the cells and the size of the starch granules have been reported to be important for the final texture of potatoes (Barrios, Newsom, & Miller, 1963; Ridley & Hogan, 1976). The preparation and evaluation of potato starch pastes and gels is a key route for evaluating potato starch properties (Bohlin, Eliasson, & Mita, 1986; Muhrbeck & Eliasson, 1987). Hopkins and Gormley (2000) reported a good correlation between the textural properties of the cooked potatoes and rheological properties of pastes and gels made from starch separated from different Irish potato cultivars. Morphological, rheological and thermal characteristics of potato starch vary with the genotype and cultural practices. Kim, Wiesenborn, Orr, and Grant (1995) and Wiesenborn, Orr, Casper, and Tacke (1994) have studied the paste behavior of starch from various American potato cultivars and correlated the physicochemical characteristics with functional properties of starch separated from them. Potato starch properties depend on the physical and chemical characteristics of the starch, such as mean granule size, granule size distribution, amylose/amylopectin ratio and mineral content (Madsen & Christensen, 1996). Study of the texture of potato cells requires a methodology that enables monitoring of textural changes during heating (Shomer, Rao, Bourne, & Levy, 1993). Starch behaviour is an important factor in relation to texture due to several changes that take place upon gelatinization (Fleche, 1985; Swinkels, 1985b). Scanning electron microscopy (SEM) has been used to relate granule morphology to starch genotype, paste structure and

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paste properties (Fannon, Hauber, & Bemiller, 1992). Krueger, Knutson, Inglett, and Walker (1987) reported that characteristics of a starch granule, such as degree of crystallinity, are related to the transition temperature and enthalpy of gelatinization. The starch granule shapes, percentage of large and small granules and the presence of phosphate ester may also affect the gelatinization enthalpy values (Yuan, Thompson, & Boyer, 1993). Cottrell, Duffus, Paterson, and George (1995) found that genotype and growing conditions influence the properties of starch granules, such as gelatinization temperature, crystallinity, phosphorus and amylose content. Shewmaker et al. (1994) reported low paste viscosity for starch pastes made from potato genotypes with low amylose content. Dynamic shear tests are widely used to monitor changes in structure and texture without destroying the sample and with minimal disturbance (Ross-Murphy, 1984). Studies have been conducted on the increase in elasticity, as expressed by increased storage modulus during the formation of gel structure, by many biopolymers (Doublier & Choplin, 1989). During cooling, the starch chains in the gelatinized paste associate and lead to the formation of a more ordered structure which causes turbidity effects and reduces the light transmittance in the starch paste (Perera & Hoover, 1999). Craig, Maningat, Seib, and Hoseney (1989) suggested that the high light transmittance exhibited by potato starch pastes may be due to the absence of granule remnants.

In the present investigation, we have studied the physicochemical, morphological, thermal and rheological properties of the starches separated from different potato cultivars.

2. Materials and methods

2.1. Materials

The potatoes of three cultivars (Kufri Jyoti, Kufri Badshah and Pukhraj) were procured from Sangha Potato Farms, Jalandhar, India from the 2001 harvest. Uniform sized tubers were selected from each cultivar and washed thoroughly.

2.2. Starch isolation

Starch was isolated from the three potato cultivars as described earlier (Singh & Singh, 2001).

2.3. Physico-chemical properties of starch

2.3.1. Amylose content

Amylose content of the isolated starch was determined by using the method of Williams, Kuzina, and Hlynka (1970).

2.3.2. Swelling power (g/g) and solubility $(%$)

Swelling power and solubility were determined in triplicate, using the method of Leach, McCowen, and Schoch (1959).

2.3.3. Turbidity

Turbidity of starches from different potato cultivars was measured as described by Perera and Hoover (1999). A 2% aqueous suspension of starch from each potato cultivar was heated in a water bath at $90 °C$ for 1 h with constant stirring. The suspension was cooled for 1 h at 30 °C. The samples were stored for 5 days at 4 °C in a refrigerator and turbidity was determined every 24 h by measuring absorbance at 640 nm against a water blank with a Shimadzu UV-1601 spectrophotometer (Shimadzu Corporation, Kyoto, Japan).

2.3.4. Transmittance (%)

Transmittance of starches from different potato cultivars was measured as described by Craig et al. (1989). A 1% aqueous suspension of starch from each potato cultivar was heated in a water bath at $90 °C$ for 1 h with constant stirring. The suspension was cooled for 1 h at 30 °C. The samples were stored for 5 days at 4 °C in a refrigerator and transmittance was determined every 24 h by measuring absorbance at 640 nm against a water blank with a Spectronic-20D (Milton Roy Company, USA).

2.3.5. Water binding capacity (WBC)

WBC of the starches from different potato cultivars was determined using the method described by Yamazaki (1953), as modified by Medcalf and Gilles (1965). A suspension of 5 g starch (dry weight) in 75 ml distilled water was agitated for 1 h and centrifuged (3000 \times g) or 10 min. The free water was removed from the wet starch, drained for 10 min and wet starch was weighed.

2.4. Thermal properties

Thermal characteristics of isolated starches were studied by using a differential scanning calorimeter-821^e (Mettler Toledo, Switzerland) equipped with a thermal analysis data station. Starch (3.5 mg, dry weight) was loaded into a 40 µl capacity aluminium pan (Mettler, ME-27331) and distilled water was added with the help of a Hamilton microsyringe to achieve a starchwater suspension containing 70% water. Samples were hermetically sealed and allowed to stand for 1 h at room temperature before heating in the DSC. The DSC analyzer was calibrated using indium and an empty aluminium pan was used as reference. Sample pans were heated at a rate of $10 \degree C/$ min from 20 to $100 \degree C$. Onset temperature (T_0) ; peak temperature (T_n) ; conclusion temperature (T_c) and enthalpy of gelatinization (ΔH_{gel}) were calculated automatically. The gelatinization

temperature range (R) was computed as (T_c-T_o) , as described by Vasanthan and Bhatty (1996). Enthalpies were calculated on a starch dry basis. The peak height index (PHI) was calculated by the ratio $\Delta H/(T_p-T_o)$, as described by Krueger et al. (1987).

2.5. Morphological properties

Scanning electron micrographs were taken by a JEOL JSM-6100 scanning electron microscope (Jeol Ltd., Tokyo, Japan). Starch samples were suspended in ethanol to obtain a 1% suspension. One drop of the starchethanol solution was applied on an aluminium stub using double-sided adhesive tape and the starch was coated with gold-palladium (60:40). An accelerating potential of 10 kV was used during micrography.

2.6. Rheological properties

2.6.1. Dynamic rheometry

A small amplitude oscillatory rheological measurement was made for starches from each potato cultivar, with a dynamic rheometer (Carri-Med CSL²-100, TA Instruments Ltd., Surrey, England) equipped with parallel plate system (4 cm diameter). The gap size was set at 1000 μ m. The strain and frequency were set at 0.5% and 1 Hz, respectively, for all determinations. The dynamic rheological properties, such as storage modulus (G') , loss modulus (G'') and loss factor (tan δ) were determined for starches from different potato cultivars. Starch suspensions of 15% (w/w) concentration were loaded onto the ram of the rheometer and covered with a thin layer of low-density silicon oil (to minimize evaporation losses). The starch samples were subjected to temperature sweep testing and were heated from 30 to 75 °C at the rate of 2 °C/ min and cooled from 75 to 25 °C at the rate of 5 °C/ min.

2.6.2. Viscometry

An aqueous starch slurry (4%) was heated from 30 to 90 °C at a rate of 1.5 °C/min, held for 20 min at 90 °C, then cooled at 50 °C at a rate of 1.5 °C/min in brabender viscoamylograph (Brabender OHG Duisburg, Germany). The cooked paste was used to determine the consistency coefficients and flow behaviour indices on a Brookfield viscometer (Brookfield Inc. USA) using spindle No. 21.

2.7. Retrogradation (%)

Starch suspension (2%, w/w) was heated at 85 °C for 30 min in a temperature-controlled water bath, followed by rapid cooling in an ice water bath to room temperature. The starch sample was stored for 24, 48 and 120 h at 4 °C. Syneresis was measured as% amount of water released after centrifugation at $3000 \times g$ for 15 min.

2.8. Statistical analysis

The data reported in all the tables are averages of triplicate observations. The data were subjected to statistical analysis using Minitab Statistical Software (Minitab Inc., USA).

3. Results and discussion

3.1. Physico-chemical characteristics of potato starch

The starch from Kufri Jyoti potato cultivar showed highest amylose content, swelling power, and solubility, whereas the starch from Pukhraj potato cultivar showed the lowest values for these parameters (Table 1). Kufri Jyoti, Kufri Badshah, and Pukhraj starch showed amylose contents of 31.2, 29.8 and 25.2%, respectively. The higher amylose content of the starches from Kufri Jyoti and Kufri Badshah potato cultivars may be due to the presence of more large-sized granules. Peng, Gao, Abdel-Aal, Hucl, and Chibbar (1999) also reported higher amylose contents of the large-sized A-type granules in the six wheat cultivars. Unrau and Nylund (1957) and Barrios et al. (1963) reported that mealy potatoes have higher amylose contents than waxy potatoes. The ability of the starch to swell in excess water, as well as solubility, has been observed to be related to the mealy characteristics. The difference in swelling powers and solubility of different starches may be attributed to the difference in viscosity patterns and weak internal organization resulting from negatively charged phosphate groups within the potato starch granules (Kim, Wiesenborn, Lorenzen, & Berglund, 1996). The difference in morphological structures of granules may also be responsible for the difference in swelling power and solubilities of the three starches (Singh & Singh, 2001). The turbidity and % light transmittance values of gelatinized starch suspensions from the three potato cultivars differed significantly (Tables 2 and 3). Kufri Badshah and Kufri Jyoti starch pastes showed higher light transmittance and lower turbidity values than Pukhraj potato starch pastes. This may be due to the

Table 1

Swelling power, solubility, water binding capacity and amylose content of starches separated from different potato cultivars^a

Cultivar	Solubility $($ %)	Swelling power (g/g)	Water binding capacity $(\%)$	Amylose content $(\%)$
Pukhraj	0.093a	56.22a	99.8c	25.2a
Kufri Jyoti	0.127 _b	64.7c	93.4a	31.2c
Kufri Badshah	0.099a	59.74b	97.41b	29.8 _b

^a Values with similar letters in column do not differ significantly $(P < 0.05)$.

presence of fewer granule remnants in the starch paste, which in turn depends on the starch granule morphology. The covalently bound phosphate groups in potato starch granules also contribute to the differences in the light transmittance values (Banks & Greenwood, 1975). The light transmittance values of starch suspensions from all the potato cultivars decreased while turbidity values increased progressively during storage. The granule swelling, granule remnants, leached amylose and amylopectin, amylose and amylopectin chain lengths have been reported to be responsible for turbidity development in starches during storage (Jacobson, Obanni, & Bemiller, 1997). Starches from the mealy potato cultivars having larger sized granules showed higher transmittance and lower turbidity values. WBC of the three starches also differed significantly (Table 1). Pukhraj starch showed the highest WBC (99.8%) while it was lowest (93.4%) for Kufri Jyoti starch. The difference in WBC of starches separated from different potato cultivars may be attributed to the variation in granular structure. Loose association of amylose and amylopectin molecules in the native starch granules has also been reported to be responsible for high WBC (Soni, Sharma, Bisen, Srivastava, & Gharia, 1987).

3.2. Thermal properties of potato starches

Thermal properties of the three potato starches, measured by DSC, differed significantly. Endothermic peaks for starches from different potato cultivars appeared

Table 2

Effect of storage duration on the turbidity of starches separated from different potato cultivars^a

Cultivar	Turbidity (Absorbance at 640 nm)						
	0 h	24 _h	48 h	72 h	96 h		
Pukhraj Kufri Jyoti Kufri Badshah	1.25a 1.247a 1.238a	1.47 _b 1.33 _b 1.3 _{bc}	1.68c 1.44c 1.34cd	1.77d 1.5d 1.38d	1.81e 1.57e 1.43e		

^a Values with similar letter in a column do not differ significantly $(P < 0.05)$.

Table 3

Effect of storage duration on the transmittance $(\%)$ of starches separated from different potato cultivars^a

Cultivar	Transmittance at 640 nm $(\%)$						
	0 h	24h	48 h	72 h	96 h		
Pukhraj KufriJyoti Kufri Badshah	59.0e 65.6d 64.8d	24.6c 26.6c 30.6d	23.1c 25.2c 28.4c	19.6 _b 20.4 _b 22.2 _h	16.2a 17.8a 19.3a		

^a Values with similar letters in a column do not differ significantly $(P<0.05)$.

between 59.96 and 68.89 °C. The transition temperatures $(T_o, T_p$ and T_c), R, ΔH_{gel} and PHI of different potato starches are summarized in Table 4. Similar ranges of T_0 , T_p , T_c and ΔH_{gel} were reported by Kim et al. (1995) for different American potato cultivars. Kufri Badshah starch showed the highest ΔH_{gel} value of 12.16 J/g and Pukhraj starch showed the lowest ΔH_{gel} value of 11.88 J/g. Kufri Badshah and Kufri Jyoti cultivars with more mealy character had starch with lower T_0 , T_p, T_c , PHI and higher R values. These differences may be attributed to the difference in granular structure, amylose content and gelatinization temperature between these starches (Singh & Singh, 2001). The larger granules in the starches from Kufri Jyoti and Kufri Badshah potato cultivars may be responsible for the high ΔH_{gel} value. Eliasson and Karlsson (1983) and Saulaka and Morrison (1985) reported that large-sized A- type starch granules from the wheat cultivars had higher ΔH_{gel} than the small-sized B-type granules (Peng et al., 1999). The differences in the R values among the starches from different cultivars may also be due to the presence of crystalline regions of different strength in the granule (Banks & Greenwood, 1975). Kufri Jyoti and Kufri Badshah starches contain large granules, which may be responsible for the higher ΔH_{gel} and lower T_o , T_p and T_c (Singh & Singh, 2001; Vasanthan & Bhatty, 1996). The lower ΔH_{gel} for Pukhraj starch may also be attributed to the low amylose content (Shewmaker et al., 1994). McComber, Osman, and Lohnes (1988) reported that the starch granules from the mealy potatoes had lower gelatinization temperatures than waxy potatoes.

3.3. Morphological properties of potato starches

The granule size of potato starches from different cultivars ranged between 15 and $20 \mu m$ for small and $25-50$ µm for large granules (Fig. 1). The granule surface appeared smooth, oval and irregular-shaped. Kufri jyoti potato starch showed the presence of a fairly large number of large-sized, oval-shaped granules. Kufri Badshah starch also showed the presence of many largesized granules, while the Pukhraj starch had small-sized granules in a much larger number. The difference in the

Table 4

Thermal properties of starches separated from different potato cultivars^a

Cultivar	$T_{\rm o}$ $(^{\circ}C)$	$T_{\rm n}$ $(^{\circ}C)$	T_c $(^{\circ}C)$	$\Delta H_{\rm sel}$ (J/g)	PHI	R
Pukhraj Kufri Jyoti Kufri Badshah	61.61c 60.91b	64.10b 59.96a 63.37a 67.43a 12.16b 3.48c	64.58b 68.9b 11.88a 4.0a	68.34b 11.9a	3.73bc	7.28a 7.43b 7.47b

^a T_0 =onset temperature, T_p =peak temperature, R=gelatinization range (T_c-T_o) ; ΔH_{gel} = Enthalpy of gelatinization (dwb, based on starch weight), PHI=peak height index $\Delta H_{gel}/(T_p-T_o)$. Values with similar latters in a column do not differ significantly $(P<0.05)$.

granule morphology may be attributed to the biological origin, biochemistry of the amyloplast and physiology of the plant (Badenhuizen, 1969; Svegmark & Hermansson, 1993). These results agree with the previous findings of Geddes, Greenwood, and Mackenzie (1965) that the amylose content of the tuber starch is directly related to the granule size.

3.4. Rheological properties of potato starches

Among the three cultivars studied, Pukhraj starch showed the highest TG' of 62.7 °C during the heating cycle, whereas Kufri Badshah starch showed the lowest TG' of 60.1 °C, which proved the difference between gelatinization temperatures of these starches. The G' and G'' of all three potato starches increased progressively to a maximum and then dropped during the heating cycle (Figs. 2a, 3a, 4a). Kufri Badshah showed the highest G' , G'' and lowest tan δ among the three starches during heating, while these parameters were lowest for Pukhraj starch (Table 5). The difference in the G' , G'' and tan δ during the heating cycle may be attributed to the difference in the starch granular structure which in turn depends on their biological origin (Svegmark

& Hermansson, 1993). The extent of breakdown in G' was measured as the degree of disintegration of starch granules (Singh & Singh, 2001). Kufri Badshah starch showed maximum breakdown in G' , followed by Kufri Jyoti and Pukhraj starches. Pukhraj starch showed lowest G' breakdown values. The greater breakdown in Kufri Badshah and Kufri Jyoti starches may be attributed to the presence of more large-sized starch granules which are fragile in nature, while small-sized granules of Pukhraj starch may be responsible for the low G' breakdown values. During cooling of the heated starch pastes from 75 to 25 °C, G' and G'' values increased and tan δ value decreased (Table 6, Figs. 2b, 3b, 4b). Kufri Badshah starch showed the highest G' , G'' and lowest tan δ , which confirms the formation of the most rigid gel structure by this starch. A decrease in tan δ values during cooling of starches has been reported to be evidence of gel formation (Reddy & Seib, 2000). Kufri Jyoti potatoes with highest mealiness scores resulted in starch paste showing highest consistency coefficient and lowest flow behaviour index (Table 5). Pukhraj and Kufri Badshah starch pastes did not differ significantly. The mealiness of the cooked potatoes had been reported to correlated with the relative starch viscosities, measured

Fig. 1. Scanning electron micrographs (SEM) of starches separated from different potato cultivars (a) Pukhraj, (b) Kufri Jyoti, (c) Kufri Badshah.

Fig. 2. Storage modulus (G'), Loss modulus (G'') and Loss factor (tan δ) of starch from cv. Pukhraj during heating (A) and cooling (B).

Table 5 Rheological properties of starches measured using dynamic rheometer (during heating) and Brookfield viscometer^a

Cultivar	T G' (°C)	Peak G' (Pa)	Peak G'' (Pa)	Breakdown in $G'(\text{Pa})$	Peak $\tan \delta$	$(Pas\eta)$	N	R^2
Pukhraj	62.7c	8519a	2186a	3521a	0.2566c	25.0a	0.33a	0.997
Kufri Jyoti	61.5bc	'2804b	2471b	6894b	0.193 b	38.1c	0.29a	0.988
Kufri Badshah	60.1ab	16100c	2617c	9889c	0.1626a	26.0 _b	0.38 _b	0.995

^a Values with similar letters in a column do not differ significantly ($P < 0.05$).

Table 6 Rheological properties of starches separated from different potato cultivars during coolinga

Cultivar	Peak G' (Pa)	Peak G'' (Pa)	Peak $\tan \delta$
Pukhraj	107300a	19056a	0.1776c
Kufri Jyoti	16 10 10 b	2122 _b	0.1318b
Kufri Badshah	196300c	22947c	0.1169a

^a Values with similar letters in a column do not differ significantly $(P < 0.05)$.

Table 7

Effect of storage duration on the retrogradation of starches separated from different potato cultivarsa

Cultivar	Retrogradation $(\%)$					
	24h	48 h	120 _h			
Pukhraj	6.8a	8.2 _b	9.4c			
Kufri Jyoti	4.9a	6.7 _b	7.8c			
Kufri Badshah	5.7a	7.8b	8.9c			

^a Values with similar letters in a column do not differ significantly $(P<0.05)$.

Fig. 3. Storage modulus (G'), Loss modulus (G'') and Loss factor (tan δ) of starch from cv. Kufri Badshah during heating (A) and cooling (B).

Fig. 4. Storage modulus (G'), Loss modulus (G'') and Loss factor (tand) of starch from cv. Kufri Jyoti during heating (A) and cooling (B).

by the Brabender amylograph and Brookfield viscometer (Kuhn, Dosrosier, & Ammerman, 1959; Unrau & Nylund, 1957).

3.5. Retrogradation properties of potato starches

The extent of retrogradation in starches from the three potato cultivars differed significantly (Table 7). Starch separated from Pukhraj potatoes showed highest retrogradation (6.8–9.4%) during the 120 h of storage at 4 °C, while Kufri Jyoti and Kufri Badshah starches showed lower values of retrogradation, i.e 4.9 and 5.7%, respectively. The results clearly showed that the retrogradation vaules of starches vary with the mealiness scores of potatoes. Hopkins and Gormley (2000) also reported lower retrogradation values for starches from mealy potato cultivars. The difference in the amylose contents (Kim et al., 1997; Madsen & Christensen, 1996; Swinkels, 1985a) and granular structures (Singh & Singh, 2001) among the three potato cultivars might also have affected the retrogradation properties. The retrogradation in all three potato starches increased with the increase in the storage period. The retrogradation properties of the starches are indirectly influenced by the structural arrangement of starch chains within the amorphous and crystalline regions of the ungelatinized granules, which in turn influence the extent of granule breakdown during gelatinization and the interaction that occurs between starch chains during gel storage (Perera & Hoover, 1999).

4. Conclusion

The cooking, textural and rheological properties of potatoes were observed to be related to the physicochemical, morphological, thermal and rheological properties of their starches. The starches separated from the potatoes with higher Maxwell elastic moduli (E_0, E_1) and E_3), TPA hardness, fracturability, cohesiveness, adhesiveness, lower cooking time and viscous moduli $(\eta_1, \eta_2 \text{ and } \eta_3)$ exhibited greater granule size, swelling power, solubility, amylose content, peak G' , G'' , ΔH_{gel} , lower transition temperatures and retrogradation.

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