

Physico-chemical and morphological characteristics of New Zealand *Taewa* (Maori potato) starches

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Abstract

The physico-chemical, morphological, thermal, pasting, textural, and retrogradation properties of the starches isolated from four traditional *Taewa* (Maori potato) cultivars (Karuparera, Tutaekuri, Huakaroro, Moemoe) of New Zealand were studied and compared with starch properties of a modern potato cultivar (Nadine). The relationships between the different starch characteristics were quantified using Pearson correlation and principal component analysis. Significant differences were observed among physico-chemical properties such as phosphorus content, amylose content, swelling power, solubility and light transmittance of starches from the different potato cultivars. The starch granule morphology (size and shape) for all the potato cultivars showed considerable variation when studied by scanning electron microscopy and particle size analysis. Starch granules from Nadine and Moemoe cultivars showed the presence of large and irregular or cuboid granules in fairly high number compared with the starches from the other cultivars. The transition temperatures (T_0 ; T_p ; T_c) and the enthalpies (ΔH_{gel}) associated with gelatinization suggested differences in the stability of the crystalline structures among these potato starches. The Moemoe starch showed the lowest T_0 , while it was higher for Tutaekuri and Karuparera starches. Pasting properties such as peak, final and breakdown viscosity and texture profile analysis (TPA) parameters of starch gels such as hardness and fracturability were found to be higher for Nadine and Huakaroro starches. The Nadine and Huakaroro starch gels also had lower tendency towards retrogradation as evidenced by their lower syneresis (%) during storage at 4 °C. Principal component analysis showed that the Tutaekuri and Nadine cultivars differed to the greatest degree in terms of the properties of their starches. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

The term *Taewa* is used to describe the varieties of potatoes that were introduced by the early settlers and whalers into New Zealand (Savage, Searle & Hellenas, 2000). *Taewa* became a major vegetable crop after the arrival of the first Europeans in New Zealand (Cambie & Ferguson, 2003). These potatoes, some of which have purple skin or flesh or both, are slightly bitter in taste, which has been suggested to be due to their higher anthocyanin and glycoalkaloid contents (Cambie & Ferguson, 2003).

Potatoes in general are an excellent source of starch, which contributes to the textural properties of many foods and is widely used in food and industrial applications as a thickener, colloidal stabiliser, gelling agent, bulking agent and water

holding agent. Potato starches have been studied extensively in relation to their structural, physico-chemical and functional properties, and it has been suggested that the extent of variation in these starch properties among different cultivars is considerably higher in potatoes than in other botanical starch sources (Kaur, Singh, & Singh, 2005; Singh, Singh, & Saxena, 2002; Singh, Singh, Kaur, Sodhi, & Gill, 2003; Singh, Kaur, & Singh, 2004; Tester & Karkalas, 2002; Yusuph, Tester, Ansell, & Snape, 2003); starches isolated from different potato cultivars exhibit significant variation in physico-chemical, morphological and functional properties (Kaur, Singh, & Sodhi, 2002; Kim, Wiesenborn, Orr, & Grant, 1995; Singh & Singh, 2001; Singh et al., 2003). Environmental factors such as temperature during growth, harvest date and storage temperature have been suggested to affect the properties of potato starch (Noda et al., 2004; Tester, Ansell, Snape, & Yusuph, 2005; Yusuph et al., 2003). Barichello and Yada (1991) studied the effects of genotype and cultural practices on potato starch pasting and physico-chemical characteristics. Similar studies (Kim et al., 1995; Wiesenborn, Orr, Casper, & Tacke, 1994)

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have been carried out to discover possible correlations between the physico-chemical and functional properties of starches isolated from different American potato cultivars.

The physico-chemical and morphological characteristics of native potato starches play a significant role during potato starch modifications (Kaur, Singh, & Singh, 2004; Singh & Singh, 2003; Singh et al., 2004). Also, it has been suggested that native starches selected from suitable cultivars with unique properties may have the potential to replace chemically modified starches (McComber, Osman, & Lohnes, 1988). Native starch characteristics, their correlation with different properties of starch based food products (such as starch noodles) and their interactions with different ingredients have been studied by different researchers (Azizi & Rao, 2005; Kaur et al., 2005; Singh, Singh, & Saxena, 2002a; Singh, Singh, & Sodhi, 2002b). Many techniques and methods for the characterization of starch have been developed that are suitable for screening large numbers of potato genotypes (Kim et al., 1995; Singh & Singh, 2001, 2003). Industrial interest in new value-added products has resulted in many studies being carried out on the characterization of starches isolated from different genotypes and novel sources (Kim et al., 1995; Romero-Bastida et al., 2005; Tavares et al., 2005; Wang, Gao, Chen, & Xiao, 2005).

In the present study, the physico-chemical, morphological and functional properties of the starches isolated from four traditional *Taewa* cultivars were compared with the properties of starch from a modern potato cultivar, and the correlations between different starch properties of all of these cultivars have been studied.

2. Material and methods

2.1. Materials

The tubers of four traditional New Zealand *Taewa* cultivars (*Solanum tuberosum* L. cv. Karuparera, Huakaroro, Tutaekuri, Moemoe) and one modern potato cultivar (Nadine) were procured from several local sources in New Zealand (2004 harvest). Uniformly sized tubers were selected from each cultivar batch before starch isolation. All the reagents used in the study were of analytical grade.

2.2. Potato starch isolation

Potato starch was isolated from each cultivar using a slight modification of the method described by Singh & Singh (2001). Potatoes were washed, brushed in warm water and peeled. The eyes and all bruises were pitted out. Immediately after peeling, the potatoes were cut into small pieces (4 cm²) and dipped in water containing a small amount of sodium metabisulphite (0.35 g/l). Pieces with dark spots were discarded. The juice was extracted from the potato pieces using a laboratory scale juicer. The juice was filtered through muslin cloth. The residue left on the muslin cloth was washed with distilled water, until only small amount of starch was passing through the cloth. The filtrate was collected in a glass beaker and the residue left on

the muslin cloth was discarded. The filtrate was passed through fine sieves (200 and 100 µm mesh size, respectively) and was left undisturbed for four hours. A solid layer of starch settled. The supernatant was decanted, the starch layer was reslurried in distilled water and, again, the starch was allowed to settle. This procedure was repeated for 4–5 times until the supernatant became transparent. The starch cake was collected and dried at a temperature of 40 °C in a hot-air cabinet drier.

2.3. Morphological properties

2.3.1. Granule size distribution

The starch granule size distribution was determined with a laser diffraction particle size analyzer (Malvern Mastersizer, Malvern Instruments Limited, UK). The starch sample (0.1125 g, dry weight basis) was mixed with 150 ml distilled water. The suspension was agitated at a very slow speed using a magnetic stirrer for 1 h at room temperature. The starch suspension was then filled into the small volume sample presentation unit of the Mastersizer to obtain an obscuration level of ~20%. Refractive indices of 1.530 and 1.330 were used for the starch and liquid phases, respectively, while the starch granule absorption was 0.1 (Nayouf, Loisel, & Doublier, 2003).

2.3.2. Scanning electron microscopy

Electron micrographs of the starches were obtained with a scanning electron microscope (Stereoscan 250 Mk3, Cambridge Instruments Limited, Cambridge, UK). Powdered starch samples were sprinkled on to double-sided sticky stick tape placed on an aluminum stub, and the starch was coated with gold.

2.4. Physico-chemical properties

2.4.1. Amylose and phosphorus content

The amylose content of starches isolated from the different cultivars was estimated using the method of McGrance, Cornell, and Rix (1998), as modified by Hoover & Ratnayake (2002). Starch (20 mg, dry weight basis) was dissolved in 90% dimethyl sulphoxide (8 ml) in 10 ml screw-cap reaction vials. The contents of the vials were vigorously agitated for 20 min and then heated in a water bath (with intermittent shaking) at 85 °C for 15 min. The vials were then cooled to ambient temperature, and the contents diluted with water to 25 ml in a volumetric flask. The diluted solution (1.0 ml) was mixed with water (40 ml) and 5 ml of iodine (I₂)/potassium iodide (KI) solution (0.0025 M I₂ and 0.0065 M KI) and the volume adjusted to a final value of 50 ml. The solution was allowed to stand for 15 min at ambient temperature prior to absorbance measurements at 600 nm. A standard curve was plotted for mixtures of amylose and amylopectin from potato.

The phosphorus content of the starches was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). 0.5 g of each starch sample was digested in capped polycarbonate tubes at 90 °C for 60 min with a mixture of 2.5 ml nitric acid and 0.5 ml hydrochloric acid. Samples were

then cooled and diluted to a final volume of 50 ml with deionised water. Phosphorus was analysed by ICP-OES at 1859 nm using standards prepared in a mixture of 5% (v/v) nitric acid and 1% (v/v) hydrochloric acid.

2.4.2. Swelling power, solubility and light transmittance

The swelling power and solubility of the starches were determined using 2% (w/v) aqueous suspension of starch at 90 °C by the method of Leach, McCowen and Schoch (1959). Light transmittance (%) of the pastes made from the starches was measured using the method described by Craig, Maningat, Seib, and Hosene (1989). A 1% (w/v) aqueous suspension of starch at near neutral pH was heated in a boiling water bath for 30 min with constant stirring. The suspension was cooled for 1 h at 25 °C. The samples were stored for 5 days at 4 °C and transmittance (%) was measured every 24 h at 640 nm against a water blank with a UV–Vis spectrophotometer.

2.4.3. Solubility and light transmittance in DMSO

The solubility of the starches in anhydrous dimethyl sulphoxide (DMSO) was measured after 18 h of stirring of starch by using the method of Yeh & Yeh (1993). The transmittance (%) of the starch suspensions (0.5%, w/v) in DMSO was measured at 640 nm against a DMSO blank with a UV–Vis spectrophotometer. The starch suspensions were shaken for 18 h to keep the starch granules continually suspended, and transmittance (%) was measured after shaking times of 2, 4, 6, 8, 12, 16, and 18 h.

2.5. Thermal properties

Thermal properties of the starches were analyzed using a DSC (Perkin Elmer Ltd, Norwalk, CT) equipped with a thermal analysis data station. Starch (~3.5 mg, dry weight basis) was weighed into a 40 µl aluminum pan, and distilled water was added using a Hamilton microsyringe to give a starch–water suspension containing 70% water. The pan was hermetically sealed and allowed to stand for 4 h at room temperature before being subjected to a heating scan in the DSC. The DSC was calibrated using indium, and an empty aluminum pan was used as the reference. Sample pans were heated at the rate of 10 °C/min from 20 to 100 °C. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of gelatinization (ΔH_{gel}) were calculated. The gelatinization temperature range (R) and the peak height index (PHI) were computed as described by Vasanathan & Bhatt (1996). Enthalpies were calculated on a dry starch basis.

2.6. Pasting properties

The pasting properties of the starches were measured using a Rapid Visco analyzer (RVA-4, Newport Scientific Pty Ltd, Warriewood, Australia). An aqueous dispersion of starch (7.4%, w/w; 27 g total weight) was equilibrated at 50 °C for 1 min, heated at the rate of 12.2 °C/min to 95 °C, held for 2.5 min, cooled to 50 °C at the rate of 11.8 °C/min and again held at 50 °C for 2 min. A constant paddle rotational speed

(160 rpm) was used throughout the entire analysis, except for rapid stirring at 960 rpm for the first 10 s to disperse the sample.

2.7. Textural properties of starch gels

The textural properties of RVA gels were evaluated by carrying out texture profile analysis (TPA) on a Texture Analyzer (TA-XT *plus*, Stable Micro Systems, Surrey, UK). The starch pastes formed in the canister by RVA testing were poured into cylindrical plastic tubes (20 mm diameter, 40 mm deep). After cooling at room temperature (25 °C) for 1 h, the tubes were covered and then stored at 4 °C for 24 h. The gel formed in the tube was used directly for texture profile analysis. Each gel sample was penetrated (to a depth of 16 mm) with a cylindrical probe 6 mm in diameter. Force–time curves were obtained at a crosshead speed of 1.0 mm/s during two penetration cycles. From the texture profile curve, *hardness*, *cohesiveness*, *adhesiveness*, *springiness*, *gumminess* and *chewiness* were calculated. TPA was performed on gels prepared in triplicate for each sample.

2.8. Retrogradation properties

2.8.1. Syneresis

Starch suspensions (2%, w/v) were heated at 90 °C for 30 min in a temperature controlled water bath with constant stirring, followed by rapid cooling to room temperature (in 6 min) using an ice water bath. The starch sample was stored for 7 days at 4 °C. Syneresis was measured at 1–4 and 7 days as the amount of water released (as a percentage by mass of the sample) after centrifugation at 3000 × *g* for 15 min.

2.9. Statistical analysis

The data reported are averages of triplicate observations. The data were subjected to statistical analysis using Minitab Release 14 Statistical Software (Minitab Inc., State College, PA). Pearson correlation coefficients (r) for relationships between various starch properties were calculated. A principle component analysis (PCA) of 28 measured starch properties was carried out to provide a ready means of visualizing the differences and similarities among the five potato cultivars in terms of these properties.

3. Results and discussion

3.1. Morphological properties

The full granule size distributions of the isolated starches from the different cultivars are shown in Fig. 1, and the distributions in terms of percentages of small, medium size and large granules in Table 1. There was significant variation among the starches of different cultivars. Starches from Nadine and Moemoe contained a fairly high percentage (79.2 and 70.5%, respectively) of large granules (>25 µm), whereas Tutaekuri had the lowest (48.5%). The percentages

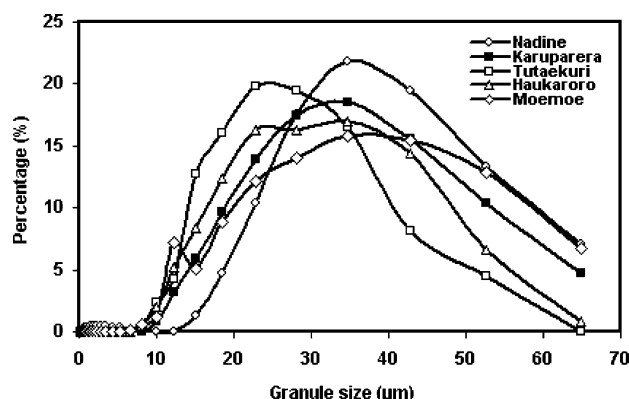


Fig. 1. Granule size distributions of potato starches isolated from different potato cultivars.

of small (1–10 μm) and medium size (11–25 μm) granules also varied to a significant extent among the starches of the different cultivars.

The mean granule volume of the Nadine starch was highest (10,648 μm^3) while the specific surface areas were lowest for Nadine (0.189 m^2/g) and Moemoe starches (0.188 m^2/g). The size of potato starch granules isolated from different cultivars has been reported to vary between 1 and 85 μm (Kaur et al., 2002, 2005; Singh & Kaur, 2004; Singh & Singh, 2001, 2003; Singh et al., 2002b, 2003a,b, 2004; Tester & Karkalas, 2002). The extent of variation in starch granule morphology and size distribution from cultivar to cultivar is significantly higher in potatoes compared to other botanical sources of starch (Singh et al., 2003). The granule size distribution of starch has been reported to change during the development of the storage organs of plants (Chojekci, Gale, & Bayliss, 1986).

Starches isolated from the different potato cultivars were viewed under SEM to study the differences in their morphological features (Fig. 2). The shape of the starch granules from all the potato cultivars varied from oval to irregular or cuboid. The small and medium size granules in the starches were found to be oval in shape, whereas the large granules were mostly irregular or cuboid. The starches from Nadine and Moemoe contained large irregular or cuboid granules in fairly high proportions. The granule surface of starches from all the cultivars was observed to be smooth except for the presence of a few small nodules or protuberances, and surface fragmentation, on some granules of Huakaroro and Karuparera starches (Fig. 3). The biochemistry of the chloroplast or amyloplast, as well as the physiology

of the plant, mainly dictates the morphology of starch granules (Badenhuizen, 1969). The membranes and the physical characteristics of the plastids may also be responsible for providing a particular shape or morphology to starch granules during granule development (Jane et al., 1994; Lindeboom, Chang, & Tyler, 2004). The presence of small nodules and protuberances on potato starch granule surfaces, ranging up to 1 μm in size, has been reported earlier (Baldwin, Adler, Davies, & Melia, 1998; Juszczak, Fortuna, & Krok, 2003).

3.2. Physico-chemical properties

The amylose and phosphorus contents of the four Taewa and the Nadine starches are presented in Table 2. The amylose content of all the starches ranged from 24.5 to 27.5%. The starch from Tutaekuri showed the highest amylose content (27.5%), and the starch from Huakaroro the lowest (24.5%). The differences among the amylose contents of the starches may be attributed to differences in the activities of the enzymes involved in the biosynthesis of linear and branched components within the starch granules (Krossmann & Lloyd, 2000). The amylose content of the starch granules has also been reported to be affected by climatic conditions and soil type during growth, and granule size distribution (Asaoka, Okuno, & Fuwa, 1985; Inatsu, Watanabe, Maida, Ito, & Osani, 1974; Juliano, Bautista, Lugay, & Reyes, 1964; Morrison & Azudin, 1987; Morrison, Milligan, & Azudin, 1984; Singh et al., 2003). The amylose content among the starches from different and similar plant sources has been reported to be affected by location, soil type, starch isolation procedures and analytical methods used to determine amylose content (Cottrell, Duffus, Paterson, & George, 1995; Kim et al., 1995; Singh et al., 2004).

Considerable differences in phosphorus content (0.032–0.056/100 g) were observed among the starches of the different cultivars, with Nadine starch possessing the highest phosphorus content, followed by Huakaroro starch (0.044/100 g). The Tutaekuri starch showed the lowest phosphorus content (0.032/100 g). The results obtained are comparable to data reported in the literature (Tester et al., 2005). In potato starch, the phosphorus is mainly present as phosphate monoesters, which are covalently bound to the amylopectin fraction of the starch (Craig et al., 1989; Schoch, 1942a,b). However, the phosphorus content and form in potato starch has been reported to be influenced by growing conditions (including temperature), storage conditions and the amylose/amylopectin ratio (Cottrell

Table 1
Morphological properties of starches from different potato cultivars: proportions of small, medium size and large granules, mean granule volume and granule specific surface area

Starch source	Small granules (%) (1–10 μm)	Medium size granules (%) (11–25 μm)	Large granules (%) (> 25 μm)	Mean volume (μm^3)	Specific surface area (m^2/g)
Nadine	4.4 ^c	16.4 ^a	79.2 ^c	10648 ^c	0.189 ^a
Karuparera	0.9 ^a	32.6 ^c	66.5 ^c	6859 ^d	0.198 ^b
Tutaekuri	2.7 ^b	52.8 ^c	48.5 ^a	3375 ^a	0.248 ^d
Haukaroro	2.7 ^b	42.1 ^d	55.2 ^b	4096 ^b	0.228 ^c
Moemoe	5.1 ^d	24.5 ^b	70.5 ^d	5832 ^c	0.188 ^a

Values with the same superscripts in a column did not differ significantly ($p < 0.05$).

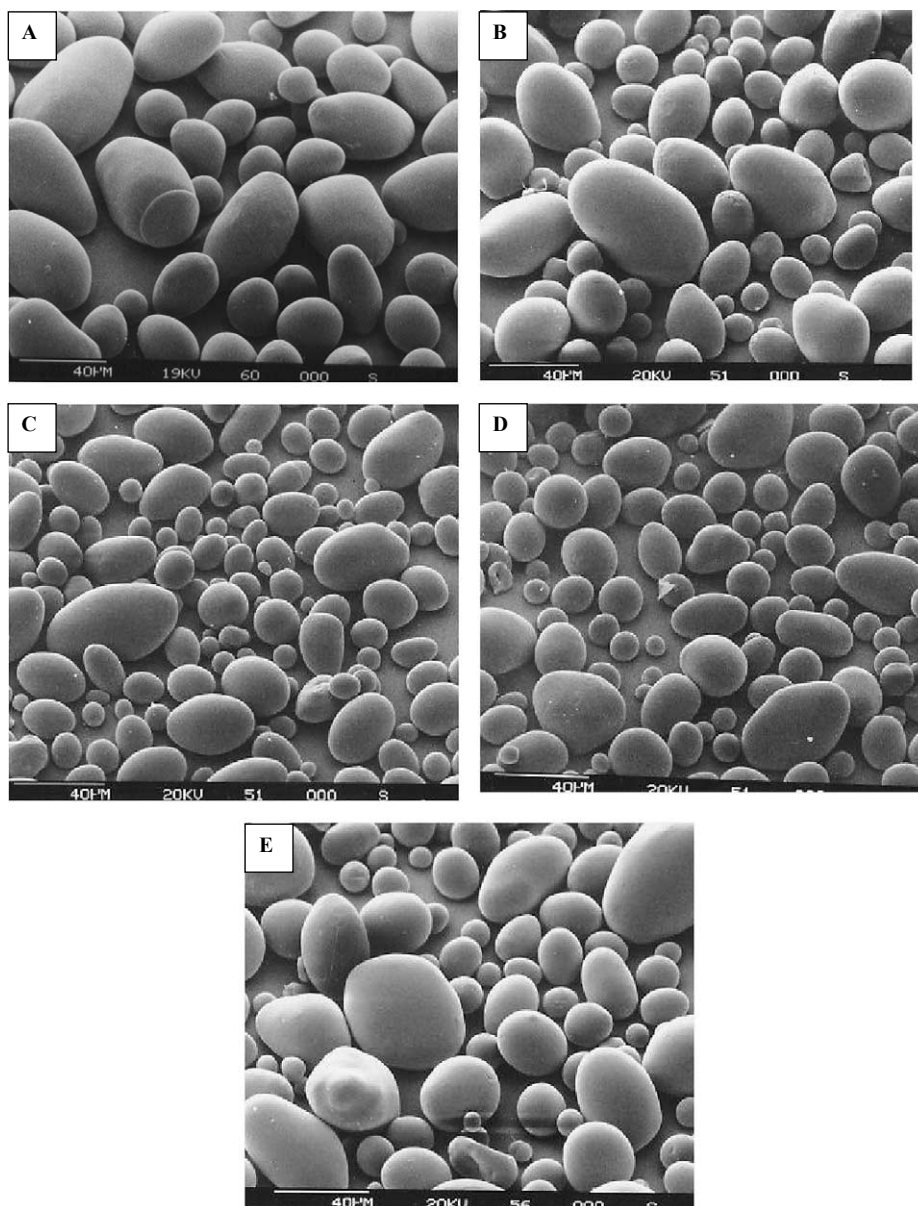


Fig. 2. Scanning electron micrographs (SEM) of potato starches (A) Nadine, (B) Karuparera, (C) Tutaekuri, (D) Huakaroro, (E) Moemoe ($\times 500$, bar = 40 μm).

et al., 1995; Smith, 1987). A weak negative correlation between amylose content and phosphorus content has been observed through Pearson correlation results ($r = -0.722$, Table 8). Also, the phosphorus and amylose contents run in opposite directions on PCA loading plot, suggesting a negative correlation between them (Fig. 10).

The swelling power, solubility and light transmittance (%) of starch pastes of the different cultivars varied to a greater extent (Tables 2 and 3; Fig. 4). Huakaroro and Moemoe starches, with relatively low amylose contents, showed higher swelling power and lower solubility, while the reverse was observed for Tutaekuri starch. The swelling power of Nadine starch was observed to be higher than for Tutaekuri and Karuparera starches. The significantly higher phosphorus content of the Nadine starch may have contributed to its fairly high swelling power. The weak internal organization caused by negatively

charged phosphate ester groups within starch granules has been reported to be responsible for the higher swelling power of potato starches (Kim, Wiesenborn, Lorenzen, & Berglund, 1996). However, Pearson correlation analysis showed the presence of a very weak positive correlation between phosphorus and swelling power (Table 8), which was not statistically significant. The hydration and swelling of starch during heating reflects the magnitude of interaction between the starch chains within the amorphous and crystalline domains (Liu, Ramsden, & Corke, 1999). The amylose to amylopectin ratio and the molecular weight/distribution of amylose and amylopectin may affect the extent of this interaction, resulting in variation in the swelling power and solubility of the starch. A strong negative correlation between amylose and swelling power has been revealed both by Pearson correlation analysis and PCA ($r = -0.925$, $p < 0.05$; Table 8, Fig. 10).

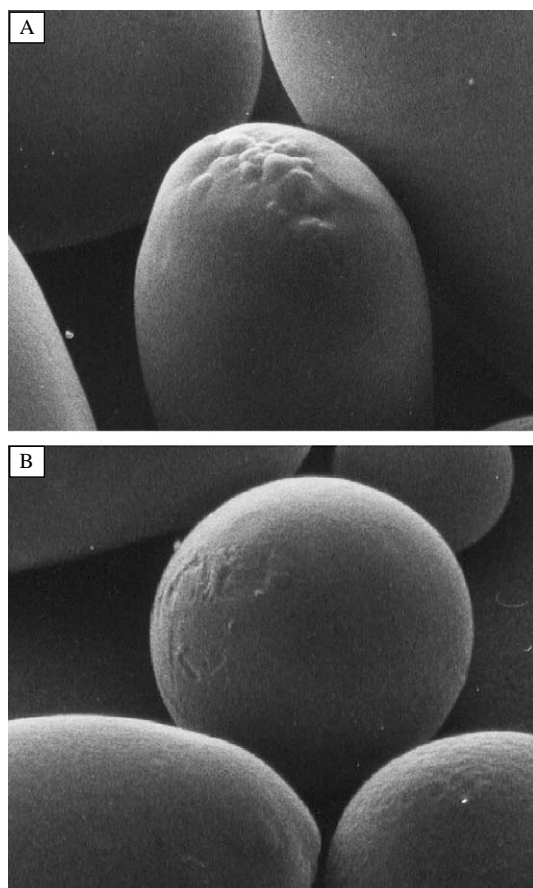


Fig. 3. Scanning electron micrographs (SEM) featuring (A) the presence of some small nodules or protuberances on some starch granules of the Karuparera cultivar and (B) surface fragmentation on some starch granules of the Huakaroro cultivar.

The light transmittance of the gelatinized starch pastes of different potato cultivars differed considerably (Fig. 4). Nadine and Moemoe starch pastes showed a higher initial light transmittance than those of the other starches. The light transmittance of all the starch pastes decreased progressively during refrigerated storage. However, this decrease was more pronounced during the initial 48 h (Fig. 4). The differences in phosphorus contents among the different starches may have affected the light transmittance of their pastes. Repulsion between adjacent starch molecules caused by the negatively charged phosphate groups apparently reduced interchain associations, and gave increased levels of hydrated molecules,

Table 2
Physico-chemical properties of starches from different potato cultivars: amylose content, phosphorus content and swelling power

Starch source	Amylose content (%)	Phosphorus content (g/100 g)	Swelling power (g/g)
Nadine	24.7 ^a	0.056 ^d	38.55 ^c
Karuparera	26.2 ^c	0.037 ^b	36.57 ^b
Tutaekuri	27.5 ^d	0.032 ^a	35.00 ^a
Haukaroro	24.5 ^a	0.044 ^c	40.56 ^d
Moemoe	25.0 ^b	0.037 ^b	40.41 ^d

Values with the same superscripts in a column did not differ significantly ($p < 0.05$).

Table 3
Physico-chemical properties of starches from different potato cultivars: solubility (in water) and solubility in DMSO

Starch source	Solubility (g/g)	Solubility (%) in DMSO
Nadine	0.0516 ^c	71.4 ^d
Karuparera	0.0492 ^c	60.3 ^c
Tutaekuri	0.0539 ^d	51.4 ^a
Haukaroro	0.0465 ^b	54.8 ^b
Moemoe	0.0435 ^a	62.1 ^c

Values with the same superscripts in a column did not differ significantly ($p < 0.05$).

resulting in enhanced paste clarity and higher light transmittance (Lim & Seib, 1993). The variation in light transmittance (%) among the starch pastes could also be attributed to the variation in the granule size distribution among the different starches (Singh et al., 2003). Light transmittance showed statistically significant correlations with mean granule volume and phosphorus content ($r = 0.943$ and $r = 0.896$, respectively; $p < 0.05$; Table 8). A positive correlation of light transmittance with large-size granules and mean volume can be observed in the PCA loading plot (Fig. 10). Starches with a higher proportion of large granules contain fewer granule remnants in their pastes, thus allowing the light to pass through instead of being refracted and/or scattered, resulting in higher light transmittance (Singh & Kaur, 2004; Singh & Singh, 2003).

The solubility and light transmittance of the different potato starches in DMSO varied significantly (Table 3, Fig. 5). Among the different starches, Nadine and Moemoe starches were observed to be the most soluble in DMSO (71.4 and 62.1%, respectively). The solubility values are in accordance with those reported earlier for potato starches (Kaur et al., 2004). The fairly high large granule percentage and higher mean granule volume may have resulted in the higher solubility of these starches in DMSO ($r = 0.978$ and 0.972 , respectively Table 8). Being a hydrogen bond acceptor, DMSO breaks associative hydrogen bonding in the starch molecules (Cooreman, van Rensburg, & Delcoul, 1995; French, 1984). Solubilization of the potato starch granules in DMSO has been reported to occur also through surface erosion (French, 1984).

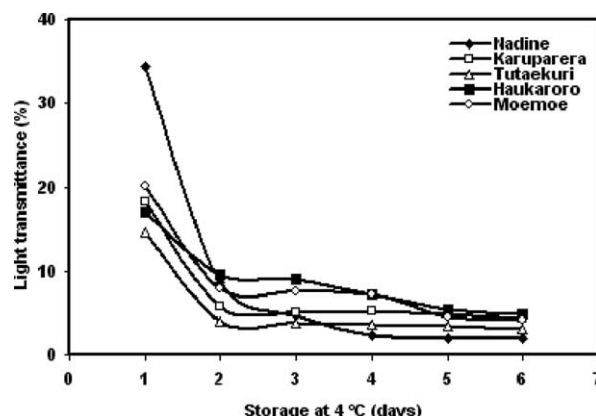


Fig. 4. Light transmittance (%) of potato starch pastes from the different potato cultivars.

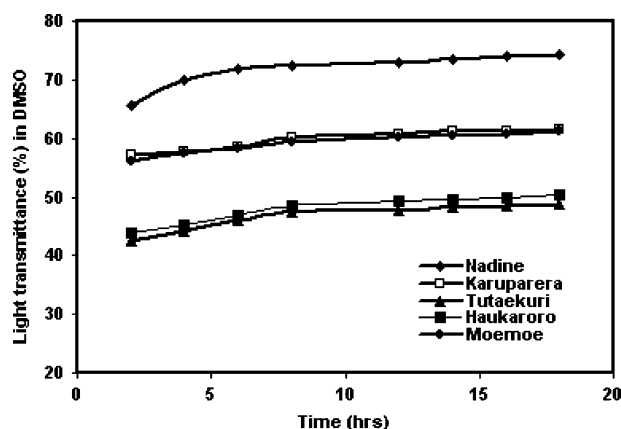


Fig. 5. Light transmittance (%) in DMSO of starch pastes from the different potato cultivars.

Sahai & Jackson (1996) reported that the extent of starch solubilization in DMSO varied significantly within a population of starch granules of different sizes, presumably reflecting inherent structural heterogeneity among the granules. The higher DMSO solubility of Nadine and Moemoe starches may reflect easier penetration of solvent molecules into their granule matrices.

The light transmittance (%) in DMSO of the starches increased steadily with time (Fig. 5). After 12 h, Nadine starch showed more than 70% transmittance in DMSO, while the starches from Tutaekuri and Haukaroro showed less than 50% even after 18 h.

3.3. Thermal properties

Thermal properties of starches from the different potato cultivars are presented in Table 4. These values are in accordance with the values for potato starches reported in the literature (Kim et al., 1995; Singh & Singh, 2001). The T_o values of starches from all the cultivars ranged from 60.2 to 62.9 °C. Among the five different starches, T_p and T_c varied in a pattern similar to that of T_o . Tutaekuri and Karuparera starches showed higher transition temperatures than did the other starches.

Variation in the thermal properties of different potato starches may be attributed to differences in starch phosphorus and amylose contents. The phosphorus content has been reported to be affected by the branching pattern in starch, and the latter influences the thermal behaviour (Wischmann et al.,

2005; Noda et al., 2005). The lower transition temperatures of the Nadine and Huakaroro starches may have been due to their higher phosphorus contents. The phosphate groups may destabilise the crystalline structures in the amylopectin regions of the starch granules, leading to lowering of the gelatinisation and melting temperatures of the starches (Wischmann et al., 2005). Higher phosphorus content is thus expected to give rise to lower gelatinization temperatures as monitored by DSC. Similarly, the crystalline parts of the granules in starches with less phosphate present would be expected to exhibit higher DSC temperature profiles owing to more stable amylopectin structures. Pearson correlation analysis and PCA showed a negative correlation between transition temperatures and phosphorus content, although these were weak and not statistically significant (Fig. 10; Table 8). However, the correlation between amylose content and T_c was highly significant ($r=0.967$; $p<0.01$; Table 8). The differences in transition temperatures among the different starches may also be attributed to differences in their degree of crystallinity. High transition temperatures have been reported to result from a high degree of crystallinity, which provides structural stability and makes the granules more resistant to gelatinization (Barichello et al., 1990).

The enthalpy of gelatinization was observed to be lowest for Tutaekuri starch (12.77 J/g), whereas it was highest for Moemoe starch (15.69 J/g). 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 that occurs on gelatinisation (Cooke & Gidley, 1992; Hoover & Vasanathan, 1994; Tester & Morrison, 1990). A lower ΔH_{gel} suggests a lower degree of organization in, or a lower stability of, the crystals (Chiotelli & Meste, 2002). The fairly high percentage of large granules in Nadine and Moemoe starches may have contributed to their relatively low transition temperatures; T_o , T_p and T_c were found to be negatively correlated to small granule percentage. It has been reported in earlier studies that starch granule size, phosphorus content, granule shape, amylopectin chain length, and crystalline regions of different stability and/or size mainly influence the thermal properties of starches (Noda et al., 1996; Singh & Kaur, 2004; Singh & Singh, 2001; Stevens & Elton, 1971; Wang et al., 2005; Yuan, Thompson, & Boyer, 1993). The PHI and R of the starches also varied to a considerable extent (Table 4). A higher PHI (5.02) was calculated for Tutaekuri starch, while a higher R was calculated for Moemoe starch.

Table 4

Thermal properties of starches from different potato cultivars: transition temperatures (T_o ; T_p ; T_c), enthalpy of gelatinization (ΔH_{gel}), peak height index (PHI) and gelatinization range (R)

Starch source	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J g ⁻¹)	PHI (J g ⁻¹ °C ⁻¹)	R (°C)
Nadine	61.7 ^b	65.0 ^b	70.3 ^a	14.25 ^b	4.37 ^b	8.5 ^a
Karuparera	62.7 ^c	66.5 ^c	72.3 ^b	14.84 ^b	3.90 ^a	9.6 ^b
Tutaekuri	62.9 ^c	65.4 ^b	72.8 ^b	12.77 ^a	5.02 ^c	10.0 ^b
Haukaroro	60.8 ^a	64.7 ^a	70.3 ^a	14.65 ^b	3.79 ^a	9.5 ^b
Moemoe	60.2 ^a	64.3 ^a	70.4 ^a	15.79 ^c	3.77 ^a	10.3 ^c

T_o , onset temperature; T_p , peak temperature; ΔH_{gel} , enthalpy of gelatinization (dw); R , gelatinization range ($T_c - T_o$); PHI, peak height index ($\Delta H_{gel}/(T_p - T_o)$). Values with the same superscripts in a column did not differ significantly ($p < 0.05$).

Table 5

Pasting properties of starches from different potato cultivars: peak viscosity, trough, breakdown, final viscosity and setback

Starch source	Peak viscosity (RVU)	Trough (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)
Nadine	489 ^d	233 ^d	256 ^d	266 ^d	33 ^b
Karuparera	407 ^b	220 ^c	187 ^b	254 ^c	34 ^b
Tutaekuri	338 ^a	193 ^b	119 ^a	230 ^{ab}	37 ^c
Haukaroro	421 ^c	209 ^c	212 ^{bc}	241 ^b	32 ^a
Moemoe	426 ^c	188 ^a	234 ^c	218 ^a	31 ^a

Values with the same superscripts in a column did not differ significantly ($p < 0.05$).

The differences in the R values among the starch cultivars may be due to the presence of small crystallites with slightly different crystal strengths in the crystalline regions of the starch granules (Banks & Greenwood, 1975).

3.4. Pasting properties

The pasting properties of all the potato starches are presented in the Table 5. The starches displayed significant variation in their pasting behaviour (Fig. 6). Peak viscosities varied from 338 to 489 RVU, being lowest for Tutaekuri and highest for Nadine. Tutaekuri starch showed a significantly lower breakdown value than those for the other starches. The trough and final viscosity (FV) were observed to be higher for Nadine and Karuparera starches. Hot paste viscosity has been reported to be influenced by the extent of amylose leaching, amylose-lipid complex formation, friction between swollen granules, granule swelling, and competition between leached amylose and remaining ungelatinized granules for free water (Liu, Ramsden, & Corke, 1997; Olkku & Rha, 1978). Tutaekuri starch showed the highest setback (37 RVU). The pasting temperature of the starches ranged from 67.1 °C for Moemoe to 68.6 °C for Tutaekuri (data not shown). The pasting temperatures for the starches from the various cultivars were observed to be ~2 °C higher than the peak transition temperatures of gelatinization measured using DSC.

Physico-chemical characteristics such as amylose content, phosphorus content and granule size distribution are the main determinants of the pasting and rheological properties of potato starches (Kaur et al., 2005; Liu, Weber, Currie, & Yada, 2003; Singh et al., 2003–2005; Wiesenborn et al., 1994). The higher

peak viscosity of the Nadine starch may be attributed to its lower amylose and higher phosphorus contents. Lower peak viscosities of potato starches having low phosphorus content have been reported earlier (Liu et al., 2003). A weak negative correlation between amylose and peak viscosity, and a positive correlation between phosphorus and peak viscosity were observed (Fig. 10; Table 8). Starch granules with low amylose and high phosphorus have been reported to swell much more freely than others (Kim et al., 1995, 1996). The presence of a fairly high percentage of large granules in Nadine and Moemoe starches may have contributed towards their higher peak viscosities. A significant correlation between peak viscosity and large granule percentage was found ($r = 0.880$, $p < 0.05$; Table 8). A higher peak storage modulus has been reported for potato starches having higher proportions of large granules in a number of studies (Kaur et al., 2002, 2004, 2005; Singh & Kaur, 2004; Singh & Singh, 2001; Singh et al., 2003, 2004). Liu et al. (2003) have suggested that the smaller granules may contribute to lower peak viscosity.

Breakdown and setback have been reported to have a close association with the amylose content (Singh et al., 2005). Amylose content was positively correlated with setback ($r = 0.909$, $p < 0.05$) and negatively correlated with breakdown ($r = -0.923$, $p < 0.05$; Table 8). Reassociation during cooling was poor in low amylose starches, while high amylose starches showed higher setback. The setback values have been found to be positively correlated with amylose content in many studies on starch pasting properties (Liu et al., 2003; Singh et al., 2005). Pearson correlation analyses and PCA used to explore interrelationships amongst the various RVA viscosity attributes suggest a positive correlation between PV and breakdown ($r = 0.959$, $p < 0.01$) and between FV and trough ($r = 0.991$, $p < 0.01$ Table 8).

3.5. Textural properties

The RVA starch gels were subjected to instrumental texture profile analysis after 24 h of refrigerated storage. The data obtained corroborated RVA results (Table 6; Fig. 7). Starch pastes with higher PV formed gels with higher hardness and fracturability ($r = 0.870$ and 0.875 , respectively Table 8). Statistically significant negative correlations of cohesiveness with peak viscosity and with breakdown were observed through Pearson correlation analysis and PCA ($r = -0.896$, $p < 0.05$ and -0.953 , $p < 0.01$ respectively) (Fig. 10, Table 8). Hardness values varied between 0.21 N for Tutaekuri and 0.4 N for Nadine starch gels. The higher fracturability and

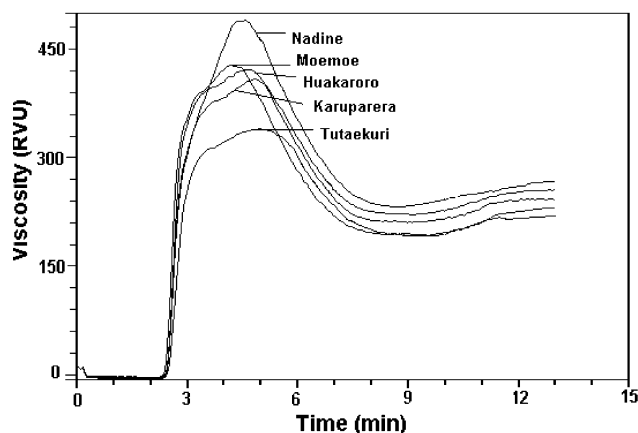


Fig. 6. Pasting properties of starches isolated from the different potato cultivars.

Table 6

Textural properties of starches from different potato cultivars: fracturability, hardness, cohesiveness, springiness, adhesiveness, gumminess and chewiness

Starch source	Fracturability (N)	Hardness (N)	Cohesiveness	Springiness (s)	Adhesiveness (Ns)	Gumminess (N)	Chewiness (Ns)
Nadine	0.34 ^d	0.40 ^d	0.57 ^a	0.95 ^{ab}	1.35 ^d	0.23 ^d	0.22 ^c
Karuparera	0.19 ^b	0.26 ^b	0.61 ^b	0.97 ^c	1.08 ^b	0.16 ^b	0.15 ^c
Tutaekuri	0.17 ^a	0.21 ^a	0.63 ^c	0.94 ^a	1.12 ^c	0.14 ^a	0.13 ^a
Haukaroro	0.22 ^c	0.30 ^c	0.61 ^b	0.96 ^b	0.95 ^b	0.18 ^c	0.17 ^d
Moemoe	0.23 ^c	0.25 ^b	0.57 ^a	0.93 ^a	0.41 ^a	0.14 ^a	0.14 ^b

Values with the same superscripts in a column did not differ significantly ($p < 0.05$).

hardness of Nadine and Moemoe starches, and their higher peak viscosities, may be attributed to the presence of a higher percentage of large granules, lower amylose content and higher phosphorus content.

Hardness was found to be positively correlated with phosphorus content and with mean granule volume ($r = 0.998$ and 0.827 , respectively). Cohesiveness and gumminess from all starch gels varied in the ranges 0.57 – 0.63 and 0.13 – 0.23 , respectively. The Nadine starch gel exhibited lower cohesiveness and higher gumminess and chewiness, whereas the reverse trend for these properties was observed for the Tutaekuri starch gel (Table 6). Starch gels with higher hardness showed lower cohesiveness and vice versa. However, the correlation between hardness and cohesiveness was not statistically significant ($r = -0.651$ Table 8). Springiness and adhesiveness were observed to be lower for Moemoe and Tutaekuri starch gels. The variations in textural properties

of starch gels are mainly influenced by variations in the rheological characteristics of the amylose matrix, the volume fraction and rigidity of gelatinized starch granules, and the phosphorus content, as well as the interactions between the dispersed and continuous phases of the gel (Biliaderis, 1998). These factors, in turn, have been reported to be dependent on the amylose and the structure of amylopectin (Yamin, Lee, Pollak, & White, 1999).

3.6. Retrogradation properties

The retrogradation properties (syneresis %) of gelatinized starch pastes are shown in Fig. 8. Tutaekuri starch paste showed the highest syneresis (9.0%) compared with the other starch pastes irrespective of the storage period, followed by Karuparera and Moemoe starch pastes (3.4 and 3.6%,

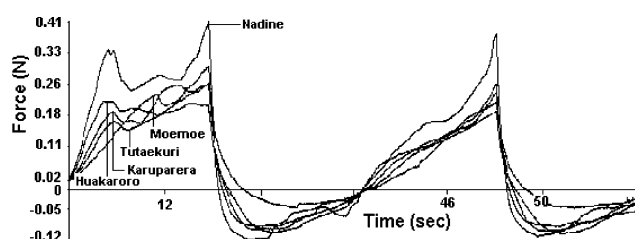


Fig. 7. Texture profile analysis (TPA) curves of starch gels from the different potato cultivars.

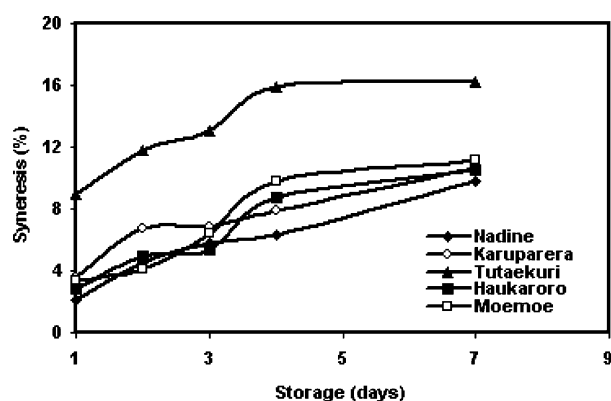


Fig. 8. Syneresis (%) of starch pastes from the different potato cultivars.

Table 7

Variables examined with PCA

Description	Variable
Granule size (1–10 μm)	1–10 μm
Granule size ($> 25 \mu\text{m}$)	$> 25 \mu\text{m}$
Mean granule volume	MV
Specific surface area of granule	SSA
Amylose content	Amylose
Phosphorus content	P
Swelling power	SP
Solubility in water	S
Light transmittance	LT
Solubility in DMSO	Sdmso
Onset transition temperature	T_o
Peak transition temperature	T_p
Conclusion transition temperature	T_c
Enthalpy of gelatinization	ΔH_{gel}
Gelatinization range	Range
Peak viscosity	PV
Trough viscosity	Trough
Breakdown viscosity	BD
Final viscosity	FV
Setback viscosity	Setback
Fracturability	Fr
Hardness	Hd
Cohesiveness	Coh
Springiness	Spr
Adhesiveness	Adh
Gumminess	Gmm
Chewiness	Chw
Syneresis	Syn

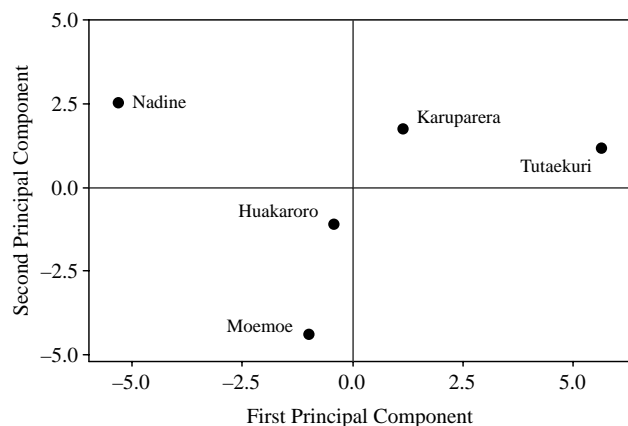


Fig. 9. Principal component analysis: score plot of PC1 and PC2 describing the overall variation among starches isolated from the different potato cultivars.

respectively) after 24 h. Syneresis (%) increased steadily during refrigerated storage. The tendency towards retrogradation was lower for Nadine and Huakaroro starch pastes. The lower syneresis (%) in these starch pastes may be attributed to their lower amylose content. The amylose content was positively correlated with syneresis (%) ($r=0.768$), but this correlation was not statistically significant. Amylose aggregation and crystallization have been reported to be complete within the first few hours of storage while amylopectin aggregation and crystallization occur at later stages (Miles, Morris, Orford, & Ring, 1985). The retrogradation properties of starches are also indirectly influenced by the structural arrangement of starch chains within the amorphous and crystalline regions of the ungelatinized granule, because this structural arrangement influences the extent of granule breakdown during gelatinisation and also influences the interactions that occur between starch chains during gel storage (Perera & Hoover, 1999). Statistically significant correlations were observed between syneresis and

the pasting properties peak viscosity, breakdown and setback ($r=-0.904$, -0.931 and 0.852 , respectively Table 8).

3.7. Principal component analysis (PCA)—an overview

The variables subjected to PCA are listed in Table 7, and the results of the analysis are shown in Figs. 9 and 10. The PCA plots provide an overview of the similarities and differences between the starches of the different cultivars, and of the interrelationships between the measured properties. The first and the second principal components (PC1 and PC2) explained 56 and 27%, respectively, of the overall variation. The distance between the locations of any two starches on the score plot is directly proportional to the degree of difference/similarity between them (Fig. 9). The Nadine starch is located at the far left of the score plot with a large negative score in PC1, while the Tutaekuri starch had a large positive score (Fig. 9). However, they differ only slightly in terms of PC2. Overall, these two starches exhibited the greatest differences in their properties, especially those properties whose curves in Fig. 10 lie relatively close to the PC1 axis. Karuparera starch was intermediate between Nadine and Tutaekuri in terms of these same properties (Table 8). The points in Fig. 9 for Huakaroro and Moemoe starches are located close to zero in PC1 and both showed negative scores in PC2, indicating that they differed mainly in terms of properties whose curves in Fig. 10 lie relatively close to the PC2 axis. The loading plot of the two PCs provided the information about correlations between measured physico-chemical, morphological, thermal, pasting and retrogradation parameters (Fig. 10). The properties whose curves lie close to each other on the plot are positively correlated while those whose curves run in opposite directions are negatively correlated. The principal components analysis discriminated between starches mainly on the basis of physico-chemical properties (amylose content, phosphorus content, solubility in DMSO), morphological features, variables related

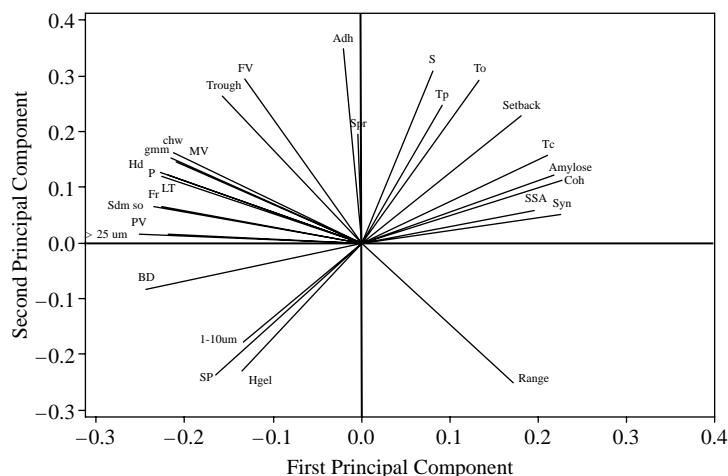


Fig. 10. Principal component analysis: loading plot of PC1 and PC2 describing the variation among the different properties of starches isolated from the different potato cultivars. A heavy solid line and a second line very close to it indicate two properties that are highly correlated.

Table 8
Pearson correlation coefficients for various properties of starches of different potato cultivars

	1–10 μm	> 25 μm	MV	Amy	P	SP	LT	Sdmso	T_o	T_p	T_c	ΔH_{gel}	PV	Trough	BD	FV	Setback	Fr	Hd	Coh	Spr	cAdh
> 25 μm	0.470																					
MV	0.312	0.924*																				
Amylose	−0.492	−0.582	−0.582																			
P	0.388	0.671	0.795	−0.722																		
SP	0.553	0.375	0.135	−0.925*	0.430																	
LT	0.521	0.849*	0.943*	−0.529	0.896*	0.239																
Sdmso	0.486	0.978**	0.972**	−0.568	0.781	0.315	0.940*															
T_o	−0.685	−0.313	−0.22	0.807	−0.263	−0.961**	−0.149	−0.236														
T_p	−0.863*	−0.105	0.081	0.573	−0.252	−0.736	−0.182	−0.112	0.846													
T_c	−0.685	−0.550	−0.399	0.967**	−0.700	−0.935*	−0.545	−0.549	0.875*	0.751												
ΔH_{gel}	0.295	0.575	0.254	−0.685	0.141	0.759	0.141	0.416	−0.739	−0.295	−0.616											
PV	0.476	0.880*	0.851*	−0.850*	0.901*	0.620	0.871*	0.904*	−0.483	−0.294	−0.805	0.536										
Trough	−0.213	0.553	0.781	−0.349	0.783	−0.026	0.704	0.647	0.265	0.401	−0.199	−0.021	0.669									
BD	0.576	0.849*	0.715	−0.923*	0.773	0.788	0.740	0.827	−0.694	−0.455	−0.897*	0.721	0.959**	0.453								
FV	−0.285	0.468	0.734	−0.227	0.726	−0.153	0.656	0.575	0.387	0.478	−0.080	−0.147	0.571	0.991**	0.333							
Setback	−0.498	−0.566	−0.293	0.909*	−0.413	−0.952**	−0.307	−0.468	0.906*	0.573	0.881	0.910*	−0.698	−0.059	−0.864*	0.077						
Fr	0.685	0.828	0.877*	−0.682	0.932*	0.434	0.976**	0.911*	−0.346	−0.365	−0.712	0.242	0.870*	0.629	0.833	0.562	−0.463					
Hd	0.376	0.702	0.827*	−0.706	0.998**	0.404	0.914*	0.809	−0.236	−0.215	−0.674	0.150	0.875*	0.804	0.776	0.747	−0.403	0.939*				
Coh	−0.682	−0.917*	−0.736	0.786	−0.637	−0.689	−0.739	−0.871*	0.664	0.455	0.798	−0.745	−0.896*	−0.310	−0.953**	−0.194	0.813	−0.804	−0.651			
Spr	−0.838	−0.005	0.142	0.001	0.107	−0.198	−0.081	−0.015	0.434	0.768	0.250	0.033	0.078	0.631	−0.046	0.647	0.093	−0.155	0.124	0.218		
Adh	−0.386	0.011	0.392	0.209	0.464	−0.533	0.400	0.182	0.699	0.518	0.281	−0.675	0.121	0.751	−0.160	0.829	0.566	0.276	0.474	0.284	0.473	
Syn	−0.252	−0.748	−0.636	0.768	−0.714	−0.756	−0.586	−0.707	0.589	0.218	0.799	−0.760	−0.904	−0.569	−0.931*	−0.452	0.852*	−0.671	−0.718	0.816	−0.295	0.088

* $p \leq 0.05$; ** $p \leq 0.01$. 1–10 μm = granule size (1–10 μm); > 25 μm = granule size (> 25 μm); MV, mean granule volume; Amy, amylose content; P, phosphorus content; SP, swelling power; LT, light transmittance; Sdmso, solubility in DMSO; T_o , onset transition temperature; T_p , peak transition temperature; T_c , conclusion transition temperature; ΔH_{gel} , enthalpy of gelatinization; PV, peak viscosity; Trough, trough viscosity; BD, breakdown viscosity; FV, final viscosity; Setback, setback viscosity; Fr, fracturability; Hd, hardness; Coh, cohesiveness; Spr, springiness; Adh, adhesiveness; Syn, syneresis.

to pasting and textural properties, and retrogradation (syneresis (%)).

4. Conclusions

Starch properties of all four *Taewa* (Maori potato) starches were generally similar in terms of physico-chemical and functional behaviour to those of the starch of the modern potato cultivar Nadine. However, a few small protuberances or nodules were observed on the granule surfaces of two *Taewa* starches. Depending on the percentages of large, medium and small size granules, the starches of different potato cultivars differ in chemical composition, which in turn influences their thermal and functional properties to a considerable extent. The amylose and phosphorus contents were observed to influence light transmittance (both in water and DMSO), solubility, swelling power and transition temperatures of the different potato starches. Similarly, pasting and textural properties of starches showed substantial dependence on granule size distribution, amylose and phosphorus contents.

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