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# Low temperature post-harvest storage of New Zealand Taewa (Maori potato): Effects on starch physico-chemical and functional characteristics

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#### Abstract

Fresh tubers from four traditional Taewa (Maori potato) cultivars (Karuparera, Tutaekuri, Huakaroro and Moemoe) and one modern potato cultivar (Nadine) of New Zealand, were stored at 4 °C and 80–90% relative humidity for six months after harvest. Starch was isolated from tubers after every three month period, and its physico-chemical and functional properties measured. Considerable changes in these properties occurred during storage. The extent of changes varied significantly from cultivar to cultivar. Starch swelling power, solubility and light transmittance decreased during tuber storage while a slight increase was observed in starch amylose content. The starch granule size distribution shifted to smaller granule size during tuber storage. Scanning electron micrographs showed degradation/erosion and pitting on the surfaces of many of the starch granules isolated from stored tubers. Transition temperatures and enthalpies of gelatinization of the starches increased somewhat during tuber storage, suggesting that changes in the stability of starch crystalline structures had occurred. Pasting, viscoelastic and texture profile analysis (TPA) characteristics of starch gels were found to have been influenced by tuber storage time for all the cultivars, but to the greatest extent for Nadine and Huakaroro. Gels made from starches from the stored tubers had a reduced tendency towards retrogradation as evidenced by the decrease in syneresis (%) during gel storage at 4 °C.

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# 1. Introduction

Taewa are a unique resource cultivated and valued by Maori, the early settlers and natives of New Zealand. Taewa is a collective noun referring to the traditional cultivars of Solanum tuberosum that have been cultivated by Maori for at least 200 years, and were a staple food crop of Maori before the main European settlement in the mid-nineteenth century ([Roskruge, 1999\)](#page-13-0). The prolonged storage of potatoes at low temperature is required to ensure regular supplies throughout the year. Post-harvest cool storage provides a necessary environment to prevent loss

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of weight, spoilage and sprouting. The potato tuber is not a static entity during storage as physiological changes continue to occur owing to the constant release of sugars from the starch for respiration ([Burton, 1989](#page-13-0)). The carbohydrate composition in tubers has been observed to change during post-harvest storage, and this affects the eating quality as well as the processing traits of potato and its products [\(Herrman, Love, Shafaii, & Dwelle, 1996\)](#page-13-0). The quality of potatoes continues to change as a result of physiological activity owing to accumulation of reducing sugars and depletion of starch ([Nourian, Ramaswamy, & Kushal](#page-13-0)[appa, 2003a, 2003b](#page-13-0)). Therefore, sugar and starch are the main components affected by post-harvest metabolism in potato tubers, which ultimately affects potatoes' cooking, sensory and processing characteristics.

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Numerous studies based on the measurement of enzymic activity in tubers have suggested marked changes in starch as well as individual and total sugar concentrations during storage [\(Hagenimana, Vezina, & Simard, 1994; Takahata,](#page-13-0) [Noda, & Sato, 1995](#page-13-0)). The first step in the pathway of starch degradation is catalyzed by enzymes such as  $\alpha$ -amylase, which are capable of metabolizing polymers at the surfaces of the semicrystalline granules ([Smith, Zeeman, & Smith,](#page-13-0) [2005\)](#page-13-0). The rate of starch depletion and sugar accumulation depends largely on the cultivar and temperature of storage, possibly owing to variation in enzyme activities ([Kazami,](#page-13-0) [Tsuchiya, Kobayashi, & Ogura, 2000\)](#page-13-0). As no single potato cultivar has been shown to be appropriate for all food applications and storage stabilities, screening of cultivars is needed to determine their ability to provide optimum processing performance and product quality after low temperature storage. Therefore, the accumulation of reducing sugars in potato tubers stored at low temperatures is a phenomenon of great economic importance in the potato processing industry.

Potato starch is one of the most abundant industrially produced polymers. It is synthesized naturally in potatoes as a storage carbohydrate composed of linear (amylose) and branched (amylopectin) glucose polymers arranged in highly ordered, supramolecular structures, the starch granules. Potato starch is a highly versatile raw material in the manufacture of both food and non-food products. It has its own distinctive physico-chemical, thermal and rheological characteristics and is sufficiently bland to be incorporated easily into food preparations. The functional characteristics of potato starch depend on physical and chemical characteristics such as mean granule size, granule size distribution, amylose/amylopectin ratio and mineral content [\(Kaur, Singh, & Singh, 2005\)](#page-13-0). A few studies have been carried out to evaluate changes in the cooking quality of potato tubers as a function of storage conditions [\(Kazami](#page-13-0) [et al., 2000; Nourian et al. 2003a, 2003b](#page-13-0)). However, to our knowledge, no comprehensive study has been carried out to assess the effect of low temperature post-harvest storage on the starch characteristics of different potato cultivars. Hence, the present study was designed to evaluate changes in the starch characteristics of a number of New Zealand Taewa and a modern potato cultivar as a function of storage time at  $4^{\circ}$ C.

# 2. Materials and methods

# 2.1. Plant material

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). Twenty-five kilograms of tubers of uniform size of each cultivar were washed in running water to remove surface dirt, dried in air and stored at  $4^{\circ}$ C and 85–90% relative humidity for six months. The

tubers were stockpiled by using crates throughout the storage chamber to minimize the effects of differences in temperature and relative humidity, if any. At selected times, sample tubers were removed from storage for starch isolation and analysis.

#### 2.2. Starch isolation

Starch was isolated from each cultivar using a slight modification of the method described by [Singh and Singh](#page-13-0) [\(2001\)](#page-13-0). Tubers were washed, brushed in warm water and hand peeled. The eyes and all bruises were pitted out. Immediately after peeling, the tubers were manually cut into small cubes (approximately 4 cm<sup>3</sup>) and dipped in water containing sodium metabisulphite (0.35 g/l). Pieces with dark spots were discarded. The juice (containing starch) was extracted from the tuber pieces using a laboratory scale juicer (Model JE 90J, Breville Pty Ltd., Australia). The juice was filtered through a muslin cloth. The residue left on the muslin cloth was washed with distilled water until only a 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  $(200 \text{ and } 100 \mu \text{m} \text{ mesh size})$ respectively) and 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 4–5 times, until the supernatant became transparent. The starch cake was collected and dried at a temperature of 40 °C to a moisture content of  $6\%$  using a hot-air cabinet drier.

#### 2.3. Morphological characteristics

#### 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 100 rpm using a magnetic stirrer (MR 3000, Heidolph, Germany) 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  $\sim$ 20%. Refractive indices of 1.530 and 1.330 were set for the starch and liquid phases, respectively, while the starch granule absorption was set at 0.1 ([Singh, McCarthy, Singh,](#page-13-0) [Moughan, & Kaur, 2007a](#page-13-0)).

#### 2.3.2. Granule morphology

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

#### <span id="page-2-0"></span>2.4. Physico-chemical characteristics

#### 2.4.1. Amylose, phosphorus and fat

The amylose content  $(\%$ , w/w) of fresh and stored potato starches was estimated using iodine colorimetry by the method of [Hoover and Ratnayake \(2002\)](#page-13-0). The method is based on the iodine binding capacity and spectral properties of the amylopectin- and the amylose–iodine complexes, respectively. Starch (20 mg, dry weight basis) was dissolved in a solution (8 ml) containing 90% dimethyl sulphoxide and 10% deionised water using 10 ml screw-cap reaction vials. The contents of the vials were vigorously agitated using a rotary shaker for 20 min and heated in a water bath (with intermittent shaking to keep the starch granules suspended) at  $85^{\circ}$ C for 15 min. The vials were cooled to ambient temperature, and the contents diluted with water to 25 ml in a volumetric flask. An aliquot of the diluted solution (1.0 ml) was mixed with water (40 ml) and 5 ml of iodine  $(I_2)/$ potassium iodide (KI) solution  $(0.0025 \text{ M} I_2 \text{ and } 0.0065 \text{ M} \text{ K}I)$  and adjusted to a final volume of 50 ml. The contents were allowed to stand for 15 min at ambient temperature before absorbance measurement at 600 nm. A standard curve was plotted for mixtures of pure amylose and pure amylopectin.

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 cooled and diluted to a final volume of 50 ml with deionised water. Phosphorus was analyzed by ICP-OES at 1859 nm using standards prepared in a mixture of 5%  $(v/v)$  nitric acid and 1%  $(v/v)$  hydrochloric acid. The fat content  $(\%)$  of the starches was estimated following the [AOAC \(2000\)](#page-13-0) procedure (Soxhlet extraction, AOAC 920.39).

#### 2.4.2. Swelling power, solubility and light transmittance

The swelling power and solubility of the starches were determined using  $2\%$  (w/v) aqueous suspensions at 90 °C using the method of [Singh et al. \(2007a\).](#page-13-0) Light transmittance  $(\%)$  of the pastes made from the starches was measured using the method described by [Craig, Maningat, Seib, and Hose](#page-13-0)[ney \(1989\)](#page-13-0). 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  $^{\circ}$ C. The samples were stored for five days at  $4^{\circ}$ 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 by using the method of Yeh and Yeh (1993). The transmittance  $\left(\frac{0}{0}\right)$  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 characteristics

Thermal properties of the starches were measured using a differential scanning calorimeter (DSC, Perkin Elmer Ltd., Norwalk, CT) equipped with a thermal analysis data station. Starch ( $\sim$ 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  $\mathrm{^{\circ}C/m}$  from 20 to 100  $\mathrm{^{\circ}C}$ . Onset temperature  $(T<sub>o</sub>)$ , peak temperature  $(T<sub>p</sub>)$ , conclusion temperature  $(T<sub>c</sub>)$ and enthalpy of gelatinization  $(\Delta H_{gel})$  were calculated using Pyris DSC 7 (Perkin–Elmer Ltd., Norwalk, CT) software supplied with the DSC. Enthalpies were calculated on a dry starch basis. The gelatinization temperature range  $(R)$ and the peak height index (PHI) were computed as described by [Vasanthan and Bhatty \(1996\).](#page-13-0)

#### 2.6. Pasting characteristics

The pasting properties of the starches were measured using a Rapid Visco Analyser (RVA-4, Newport Scientific Pty Ltd., Warriewood, Australia). An aqueous dispersion of starch  $(7.4\% \text{ w/w}; 27 \text{ g total weight})$  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  $\degree$ C/min and held at 50  $\degree$ 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. Viscoelastic characteristics of gels

The gels prepared in the RVA (as described in Section 2.6) were subjected to small amplitude oscillatory rheological measurements using a dynamic rheometer (Physica MCR 301, Anton Paar Germany, GmbH, Germany) equipped with a cone and plate system (4 cm dia). The gap was set at  $1000 \mu m$ . Starch gel was loaded onto the lower plate of the rheometer (preheated to  $25 \degree C$ ). The edge of the sample was covered with a thin layer of low-density silicone oil (to minimize evaporative losses) before starting a measurement. The starch gels were held at  $25^{\circ}$ C for 20 min and then subjected to a frequency sweep test within the linear viscoelastic region using a frequency range of 0.1–20 Hz, with the strain set at 0.5%. Dynamic rheological parameters such as storage modulus  $(G')$ , loss modulus  $(G'')$ and loss tangent (tan $\delta$ ) were determined for all starches as functions of frequency.

# 2.8. Textural characteristics: texture profile analysis

The textural properties of cooked RVA pastes made (as described in Section [2.6\)](#page-2-0) 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 by RVA testing were poured into cylindrical tubes (20 mm diameter, 40 mm deep). After cooling at room temperature (25 °C) for 1 h, the tubes were covered and stored at 4  $^{\circ}$ C for 24 h. The gel formed in each 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, fracturability, hardness, cohesiveness, adhesiveness, springiness and gumminess were calculated.

# 2.9. 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  $^{\circ}$ C. Syneresis (%) was measured at 1, 2, 3, 4 and 7 days as the amount of water released (as a percentage by mass of the sample) after centrifugation at 3000g for 15 min.

#### 2.10. Statistical analysis

The data reported are means of triplicate observations except in [Table 7](#page-10-0); the data in [Table 7](#page-10-0) are means of eight replicates. All the data were subjected to statistical analysis using Minitab Release 14 Statistical Software (Minitab Inc., State College, PA). Two-way Analysis of Variance (ANOVA) and Tukey's test were performed. Significant differences were reported when  $p \le 0.05$ . Pearson correlation analysis (coefficients) and principle component analysis (PCA) of the measured starch characteristics were carried out to provide a means of visualizing the differences and similarities among the fresh and stored potato cultivars in terms of various starch properties.

#### 3. Results and discussion

# 3.1. Morphological characteristics

#### 3.1.1. Granule size distribution

The granule size distributions of the isolated starches from the different fresh and stored cultivars as percentages of small, medium and large granules are presented in Table 1. Starches of the fresh and stored Nadine cultivar had the highest percentages (52–61%) of large granules, whereas Tutaekuri starches had the lowest (22–29%). All the starches of fresh cultivars differed significantly from each other in terms of percent large granules. The percentages

of small and medium size granules also varied to a considerable extent among the starches of the different cultivars. The extent of variation in starch granule morphology and size distribution from cultivar to cultivar is significantly higher in potatoes (between 1 and  $85 \mu m$ ) than other botanical sources of starch [\(Singh & Singh, 2001; Singh, Kaur, &](#page-13-0) [McCarthy, 2007b](#page-13-0)).

Six months of storage of the cultivars at low temperature altered the granule size distribution of their starches (Tables 1 and 2). The starches isolated from cultivars stored for three and six months showed shifts of particle size range to smaller particle size. Storage thus resulted in decreases in the large granule percentage to a significant extent (Table 1). Moemoe and Nadine starches showed the largest decreases whereas the decrease was lowest for Huakaroro starch (Table 1). There were corresponding increases in the medium size granule percentages and, for all cultivars except Moemoe, in the small granule percentages also. The starch content of potatoes has been reported to decrease at low storage temperature through the process of starch conversion to sugars [\(Smith et al., 2005\)](#page-13-0). [Nourian](#page-13-0) [et al. \(2003a, 2003b\)](#page-13-0) reported that the starch content dropped considerably during prolonged storage of tubers at  $4-8$  °C. The enzymic conversion of starch during low temperature storage in the present work may have altered the granule size distributions of the starches of the different cultivars. The decrease in the percentages of in-tuber large granules implies the susceptibility of the large granule fraction to low-temperature-storage-induced conversion postharvest. The raw starches from various botanical sources have been reported to exhibit a shift of the granule size dis-

Table 1

Morphological properties of starches from the different potato cultivars (fresh and stored): proportions of small, medium and large size granules

Starch source	Small granules $(\% )$ $(1-10 \mu m)$	Medium size granules $(\% )$ $(11-30 \mu m)$	Large granules $(\%)$ (>30 µm)
Fresh			
Nadine	$4.4^\circ$	34.0 <sup>g</sup>	61.6 <sup>a</sup>
Karuparera	1.0 <sup>f</sup>	50.0 <sup>cd</sup>	$49.0^\circ$
Tutaekuri	$2.7^e$	$69.2^{\rm a}$	28.1 <sup>g</sup>
Huakaroro	$3.0^\circ$	$58.1^{b}$	$38.9^\circ$
Moemoe	5.1 <sup>b</sup>	39.9 <sup>ef</sup>	$55.0^{b}$
Stored (3 months)			
Nadine	$4.5^\circ$	36.6 <sup>f</sup>	$59.1^{\rm a}$
Karuparera	7.0 <sup>a</sup>	$48.5^{\rm d}$	$44.5^{\text{cd}}$
Tutaekuri	4.6 <sup>c</sup>	69.1 <sup>a</sup>	26.3 <sup>g</sup>
Huakaroro	$5.3^{b}$	$60.1^{\rm b}$	$34.6^{f}$
Moemoe	2.9 <sup>e</sup>	$50.3^{\text{cd}}$	$46.8^\circ$
Stored (6 months)			
Nadine	4.6 <sup>c</sup>	$43.3^\circ$	$52.1^{bc}$
Karuparera	$4.6^\circ$	$53.5^\circ$	41.9 <sup>d</sup>
Tutaekuri	4.8 <sup>bc</sup>	$72.6^{\rm a}$	$22.6^{\rm h}$
Huakaroro	5.1 <sup>b</sup>	$62.0^{b}$	32.9 <sup>f</sup>
Moemoe	$4.5^\circ$	$53.1^\circ$	$42.4^{\rm d}$

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

<span id="page-4-0"></span>Table 2 Analysis of variance results  $(p \text{ values})$ 

Source	d.f.	Solubility in <b>DMSO</b>	Large granules	Storage modulus	Peak viscosity	Final viscosity	Onset temperature $(T_{\rm o})$	Hardness
Cultivar	4	0.000	0.000	0.000	0.000	0.003	0.000	0.000
Storage time	∠	0.000	0.000	0.002	0.000	0.000	0.003	0.014
Cultivar $\times$ storage time	8	0.770	0.030	0.000	0.000	0.040	0.928	0.604
Error	30							
Total	44							

tribution to lower sizes after in vitro enzymic hydrolysis ([Kimura & Robyt, 1995\)](#page-13-0), although in-tuber enzymic degradation proceeds in a different manner and may not be entirely comparable.

# 3.1.2. Granule morphology

Starches isolated from the different potato cultivars were viewed under SEM to study differences in their morphological features and changes induced by low temperature postharvest storage (Fig. 1). The shape of the starch granules from all the potato cultivars varied from oval (small granules) to irregular or cuboid (large granules). The membranes and the physical characteristics of the plastids may be responsible for providing a particular shape or morphology to starch granules during granule development ([Lindebooma, Chang, & Tylera, 2004](#page-13-0)). The surfaces of starch granules from all of the fresh cultivars were observed to be mainly smooth with only very few small protuberances and only slight fragmentation visible on some granules of Karuparera and Huakaroro starches.



Fig. 1. Scanning electron micrographs. (A) Starch granules isolated from fresh Tutaekuri cultivar; (B) surface degradation of starch granules isolated from the Tutaekuri cultivar after three months of storage; (C) surface pitting on starch granule isolated from the Tutaekuri cultivar after six months of storage; (D, E) surface pitting and fragmentation of starch granules isolated from the Huakaroro cultivar after six months of storage.

The starch granules of the post-harvest stored tubers showed a slightly altered surface morphology when compared to their fresh counterparts. Many large irregular or cuboid granules became progressively less smooth and exhibited more surface fragmentation and/or pitting with increasing storage time. Some medium size and small granules also showed the same changes in their surface morphology. The extent of surface degradation/erosion and indentation was observed to be greater in starches of the stored Moemoe, Tutaekuri and Huakaroro cultivars [\(Fig. 1](#page-4-0)). The signs of degradation were spread over almost the whole of the granule surface and were shallow. No deep penetrations/indentations or holes were observed. Changes in the granule surface of the starches during storage at low temperature may be attributed to an increase in the activities of starch degrading enzymes ( $\alpha$ - and  $\beta$ -amylases) and debranching enzymes, which erode the outer granule layer [\(Cochrane, Duffus, Allison, & Mackay, 1991\)](#page-13-0). These enzymes hydrolyze the glucan linkages within starch polymers exposed on the surface of the granules, releasing glucans that become substrates for further degradation ([Smith](#page-13-0) [et al., 2005](#page-13-0)). The enzyme generally believed to do this in planta is the endoamylase  $\alpha$ -amylase. However, the role of an isoamylase gene amy 3, located in the chloroplast, has also been thought to catalyze the attack on the granule surface [\(Smith et al., 2005](#page-13-0)).

#### 3.2. Physico-chemical characteristics

The amylose content of all the starches ranged from 24.5% to 28% (Table 3). The starch from Tutaekuri showed the highest amylose content whereas Huakaroro had the

Table 3

Physico-chemical properties of starches from the different potato cultivars (fresh and stored): amylose content, phosphorus content, swelling power and fat content

Starch source	Amylose content $(\% )$	Swelling power $(g/g)$	Phosphorus content $(g/100 g)$	Fat $(\%)$
Fresh				
Nadine	24.7 <sup>d</sup>	$38.55^{\circ}$	$0.056^{\rm b}$	0.36 <sup>d</sup>
Karuparera	$26.2^{b}$	$36.57^e$	0.037 <sup>d</sup>	0.12 <sup>g</sup>
Tutaekuri	$27.5^{\rm a}$	35.00 <sup>f</sup>	$0.032^e$	0.49 <sup>b</sup>
Huakaroro	$24.5^\circ$	40.56 <sup>a</sup>	$0.044^c$	ND
Moemoe	25.0 <sup>cd</sup>	40.41 <sup>a</sup>	0.037 <sup>d</sup>	$0.04^{\rm h}$
Stored (3 months)				
Nadine	24.9 <sup>cd</sup>	$37.69$ <sup>d</sup>	$0.056^{\rm b}$	$0.53^{\rm a}$
Karuparera	$26.6^{ab}$	$35.69$ <sup>ef</sup>	0.037 <sup>d</sup>	0.09 <sup>h</sup>
Tutaekuri	$27.8^{\rm a}$	34.27 <sup>g</sup>	$0.032^e$	$0.32^e$
Huakaroro	$24.8^{d}$	39.88 <sup>ab</sup>	0.042 <sup>cd</sup>	ND
Moemoe	$25.2^{\circ}$	$39.34^{b}$	$0.037$ <sup>d</sup>	$0.07^{\rm h}$
Stored (6 months)				
Nadine	$25.1^\circ$	$37.75^{\rm d}$	$0.059^{a}$	$0.42^{\circ}$
Karuparera	$26.8^{ab}$	$34.85$ <sup>f</sup>	$0.035^{de}$	ND
Tutaekuri	28 <sup>a</sup>	$35.24$ <sup>ef</sup>	0.037 <sup>d</sup>	0.32 <sup>e</sup>
Huakaroro	25 <sup>cd</sup>	39.95 <sup>ab</sup>	$0.044^c$	ND
Moemoe	$25.2^{\circ}$	$38.45^{\circ}$	$0.037$ <sup>d</sup>	0.19 <sup>f</sup>

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

lowest, irrespective of storage period. The differences among the amylose contents of starches from various sources have been reported to depend on the activities of the enzymes involved in the biosynthesis of linear and branched components within the starch granules during growth of the plant ([Kossmann & Lloyd, 2000](#page-13-0)). The amylose content of starches has also been reported to be affected by climatic conditions during growth, soil type, and granule size distribution ([Asaoka, Okuno, & Fuwa,](#page-13-0) [1985; Singh et al., 2007b\)](#page-13-0). The amylose content of the starches isolated from stored tubers was slightly higher than that in the case of fresh tubers, as indicated by the intensity of the blue colour developed by iodine during colorimetric measurements. The activities of starch degrading and debranching enzymes during storage of potato tubers have been reported to increase, which may lead to the degradation of starch by hydrolytic attacks involving cleavage of  $\alpha$ -1,4 and  $\alpha$ -1,6 linkages [\(Cochrane et al., 1991\)](#page-13-0). Debranching enzymes such as limit dextrinase and isoamylase have been reported to hydrolyze  $\alpha$ -1,6 linked glucans during starch degradation, which may alter the amylose to amylopectin ratio ([Smith et al., 2005\)](#page-13-0). Although the increases in amylose content during storage reported here were not always statistically significant, noticeable changes in various parameters dependent on amylose content were observed during the present study.

Considerable differences in phosphorus content were observed among the starches of the different cultivars (Table 3). Nadine starch had the highest phosphorus content irrespective of storage period, followed by Huakaroro starch. The Tutaekuri starch showed the lowest phosphorus content. The effect of storage on the phosphorus content of starches was small and non-significant. The results obtained for phosphorus levels in the five starches are comparable to data reported in the literature [\(Kim, Wiesen](#page-13-0)[born, Orr, & Grant, 1995](#page-13-0)). 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](#page-13-0)). The activities of different proteins involved in starch metabolism may influence the biosynthesis of phosphate esters in starch granules. However, the phosphorus content and form in potato starch has also been reported to be influenced by growing conditions (including temperature) and the amylose/amylopectin ratio ([Cottrell, Duffus, Paterson, & George, 1995](#page-13-0)). A negative correlation between the amylose and phosphorus contents of fresh and stored starches was observed in this study  $(r = -0.634, p \le 0.05)$ . The storage of the different cultivars did not show any significant effect on the fat content of their starches.

The swelling power and solubility (in water) of the starch pastes from different cultivars varied to a greater extent (Tables 3 and 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 that of <span id="page-6-0"></span>Table 4 Physico-chemical properties of starches from the different potato cultivars (fresh and stored): solubility (in water) and solubility in DMSO



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

Tutaekuri and Karuparera starches. The significantly higher phosphorus content of the Nadine starch may have contributed to its relatively high swelling power and solubility. Higher swelling power and solubility have been reported for potato starches with higher phosphorus content ([Kim et al., 1995; Kim, Wiesenborn, Lorenzen, &](#page-13-0) [Berglund, 1996\)](#page-13-0). The swelling power and solubility of the starches isolated from the stored tubers decreased with an increase in storage time. The starches isolated from stored Karuparera and Moemoe cultivars showed greatest decreases in swelling power. The hydration and swelling of starch during heating reflects the magnitude of the interaction between the starch chains within the amorphous and crystalline domains [\(Liu, Ramsden, & Corke, 1999\)](#page-13-0). Changes in amylose to amylopectin ratio, granule size distribution and starch composition during storage may have affected the extent of this interaction, resulting in variation in the swelling power and solubility of the starches of the stored cultivars. A strong negative correlation between amylose and swelling power was revealed by both Pearson correlation analysis and PCA  $(r = -0.908, p \le 0.05;$ Fig. 2).

Starch molecules in pastes and gels are known to associate on aging, resulting in effects such as precipitation, gelation, and changes in concentration and opacity. The light transmittance of the gelatinized starch pastes of different potato cultivars differed considerably. Fig. 3 shows the changes in light transmittance of starches from fresh and six months stored Nadine and Tutaekuri cultivars, during 7 days of storage. The starch pastes of stored potato



Fig. 3. Light transmittance  $(\%)$  of starch pastes from fresh  $(0)$  and stored (for six months, 6) Nadine and Tutaekuri cultivars.



Fig. 2. Principal component analysis: loading plot of PC1 and PC2 showing 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.

cultivars showed lower light transmittance than starches of the fresh counterparts. The lower light transmittance of the starch pastes of stored cultivars can be attributed to the decreases in granule size and phosphorus content that occurred during storage. The repulsion between adjacent starch molecules caused by the negatively charged phosphate groups apparently reduced interchain associations and gave increased levels of hydrated molecules promoting high transparency [\(Lim & Seib, 1993](#page-13-0)). Pastes of starches of fresh cultivars with higher proportions of large granules would have contained fewer granule remnants (which scatter/refract light) than the pastes of starches from stored cultivars, whose starches contained higher proportions of small granules. Small granules result in pastes with a greater concentration of granule remnants, resulting in lower light transmittance.

The solubility of the different potato starches in DMSO varied significantly ([Table 4](#page-6-0)). Among the different starches, Nadine and Moemoe starches were observed to be the most soluble in DMSO. Solubility in DMSO decreased with storage time, probably because of the shifts in granule size distribution to smaller granule size ([Tables 4 and 2\)](#page-6-0). [Sahai](#page-13-0) [and Jackson \(1996\)](#page-13-0) reported that starch solubility in DMSO varied significantly within a population of starch granules of different sizes, presumably reflecting inherent structural heterogeneity among granules. The higher DMSO solubility of Nadine and Moemoe starches may reflect easier penetration of solvent molecules into their granule matrices. Fig. 4 shows the light transmittance changes in starch pastes of fresh as well as six months stored cultivars during 20 h of continuous shaking. The light transmittance  $(\%)$  in DMSO of the starches increased steadily with time. After 12 h, Nadine starch showed more than 70% transmittance in DMSO, while the starches from

Tutaekuri and Huakaroro showed less than 50% even after 18 h.

#### 3.3. Thermal characteristics

The DSC thermogram parameters of starches from the fresh and post-harvest stored cultivars are presented in [Table 5](#page-8-0). The transition temperatures  $(T_o; T_p; T_c)$ , range  $(T_c - T_o)$ , enthalpy of gelatinization  $(\Delta H_{gel})$  and peak height index (PHI) of starches from the different potato cultivars differed significantly ( $p < 0.05$ ).  $T_0$  and  $T_p$  ranged from 60.8 to 63.4 °C and 64.3 to 66.5 °C, respectively, whereas the range of  $T_c$  was found to be 70.3–73.5 °C. Similar ranges of the parameters of endothermic events for starches from different potato cultivars have been reported in the literature ([Kim et al., 1995; Singh, Kaur, & Singh,](#page-13-0) [2004; Singh et al., 2007b\)](#page-13-0). Double helical and crystalline structures are disrupted in starches during gelatinization. This order–disorder phase transition involves melting of crystals, which as shown by DSC thermograms generally occurs in the temperature range  $50-70$  °C for various native starches. Enthalpy  $(\Delta H_{gel})$  gives an overall measure of crystallinity (quality and quantity) and is an indicator of the loss of molecular (mainly double helical) order within the granule that occurs on gelatinization [\(Cooke & Gidley,](#page-13-0) [1992\)](#page-13-0). The  $\Delta H_{\text{gel}}$  of all the starches varied from 12.8 to 17.1. The starches of stored cultivars showed higher ranges of transition temperatures and higher enthalpies of gelatinization than the fresh counterparts. The Tutaekuri and Karuparera starches showed the highest  $T_0$ ,  $T_p$  and  $T_c$  values when the tubers were fresh. The transition temperatures of starches increased by  $\sim$  1–2 °C during six months of storage. Increased enthalpies of gelatinization were found for starches of the stored cultivars at the ends of



Fig. 4. Light transmittance (%) in DMSO of starch pastes from the different fresh and stored potato cultivars. (a) Starches of fresh cultivars (0); (b) starches of cultivars stored for six months (6).

<span id="page-8-0"></span>Table 5

Starch source  $T_o(^{\circ}C)$  $T_{\rm p}$  (°C)  $T_{\rm c}$  (°C)  $\Delta H_{\rm gel}$  (J  $\rm g^{-1})$ ) PHI (J  $g^{-1} {}^{\circ}C^{-1}$  $R(^{\circ}C)$ Fresh Nadine 61.7<sup>d</sup> 65.0<sup>e</sup> 70.3<sup>h</sup> 14.3<sup>h</sup> 4.4<sup>e</sup> 8.5<sup>g</sup> 8.5<sup>g</sup> **Karuparera** 62.7<sup>b</sup> 66.5<sup>a</sup> 72.3<sup>d</sup> 14.8<sup>f</sup> 3.9<sup>f</sup> 9.6<sup>c</sup> Tutaekuri 62.9<sup>b</sup> 65.4<sup>d</sup> 72.8<sup>c</sup> 12.8<sup>i</sup> 5.0<sup>c</sup> 5.0<sup>c</sup> 10.0<sup>b</sup> Huakaroro 60.8<sup>e</sup> 64.7<sup>f</sup> 70.3<sup>h</sup> 14.7<sup>g</sup> 3.8<sup>g</sup> 9.5<sup>c</sup> Moemoe 60.2f 64.3<sup>g</sup> 70.4<sup>h</sup> 15.8<sup>e</sup> 3.8<sup>g</sup> 3.8<sup>g</sup> 10.3<sup>b</sup> Stored (3 months) Nadine 62.0<sup>d</sup> 65.0<sup>e</sup> 71.0<sup>f</sup> 16.0<sup>c</sup> 5.3<sup>b</sup> 9.1<sup>de</sup> 9.1<sup>de</sup> **Karuparera** 63.2<sup>ab</sup> 66.3<sup>ab</sup> 72.3<sup>d</sup> 16.2<sup>c</sup> 5.2<sup>b</sup> 9.1<sup>de</sup> 9.1<sup>de</sup> Tutaekuri 62.9<sup>b</sup> 65.8<sup>c</sup> 73.2<sup>b</sup> 14.5<sup>gh</sup> 5.0<sup>cd</sup> 5.0<sup>cd</sup> 10.3<sup>a</sup> Huakaroro 60.9e 64.9f 70.8<sup>g</sup> 15.8d 4.0f 9.8b Moemoe 60.4<sup>f</sup> 64.7<sup>f</sup> 70.6<sup>g</sup> 16.0<sup>d</sup> 3.8<sup>g</sup> 10.2<sup>a</sup> 10.2<sup>a</sup> Stored (6 months) Nadine 62.9<sup>b</sup> 66.3<sup>ab</sup> 71.8<sup>e</sup> 17.0<sup>a</sup> 5.0<sup>cd</sup> 5.0<sup>cd</sup> 8.9<sup>e</sup> Karuparera 63.4<sup>a</sup> 66.2<sup>b</sup> 72.6<sup>c</sup> 16.6<sup>b</sup> 5.9<sup>a</sup> 5.9<sup>a</sup> 9.2<sup>d</sup> Tutaekuri 63.4<sup>a</sup> 65.3<sup>ab</sup> 73.5<sup>a</sup> 16.1<sup>c</sup> 5.8<sup>a</sup> 5.8<sup>a</sup> 9.9<sup>b</sup> Huakaroro 62.4<sup>c</sup> 65.7<sup>c</sup> 71.0<sup>f</sup> 16.6<sup>b</sup> 5.0<sup>c</sup> 5.7<sup>c</sup> 8.7<sup>f</sup> Moemoe 61.9<sup>d</sup> 65.5<sup>d</sup> 71.1<sup>f</sup> 17.1<sup>a</sup> 4.7<sup>d</sup> 9.2<sup>d</sup> 9.2<sup>d</sup>

Thermal properties of starches from the different potato cultivars (fresh and stored): transition temperatures ( $T_o$ ;  $T_p$ ;  $T_c$ ), enthalpy of gelatinization  $\Delta H_{\text{gel}}$ peak height index (PHI) and gelatinization range  $(R)$ 

 $T_{\rm o}$  = onset temperature,  $T_{\rm p}$  = peak temperature,  $T_{\rm c}$  = conclusion temperature,  $\Delta H_{\rm gel}$  = enthalpy of gelatinization (dwb),  $R$  = gelatinization range  $(=T_c - T_o)$ , PHI = peak height index  $(=\Delta H_{\text{gel}}/(T_p - T_o))$ . Values with the same letter in a column did not differ significantly (p < 0.05).

both storage stages (3 months and 6 months). Nadine, Karuparera and Huakaroro starches from stored cultivars showed higher enthalpies than those from the fresh cultivars. The relatively high percentage of large granules in Nadine and Moemoe starches may have contributed to their relatively low transition temperatures.

It has been reported in earlier studies that starch granule size and shape, phosphorus content, amylopectin chain length, and crystalline regions of different stability and/or size may influence the thermal properties of starches [\(Singh](#page-13-0) [& Singh, 2001; Singh et al., 2007b](#page-13-0)). Starches with higher amylose contents showed higher transition temperatures, whereas the reverse was observed for the starches with low amylose (Table 5). Low temperature storage changed the granule size distribution, amylose and phosphorus contents, and this may have increased the transition temperatures of gelatinization. The generally lower transition temperatures of the Nadine and Huakaroro starches may also be attributed to their higher phosphorus contents. The phosphate groups may destabilize the crystalline structures in the amylopectin regions of starch granules, leading to lowering of the gelatinization and melting temperatures of the starches ([Wischmann et al., 2005](#page-13-0)). 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. The differences in transition temperatures among the different starches may generally be attributed to the differences in their degree of crystallinity.

# 3.4. Pasting characteristics

Among the starches isolated from fresh potatoes, Nadine and Moemoe exhibited the highest peak viscosities (489 and 426 RVU, respectively) and Tutaekuri starch the lowest viscosity (338 RVU) [\(Table 6\)](#page-9-0). Pasting properties were found to have been influenced by storage at low temperature. The RVA pasting parameters peak viscosity and breakdown viscosity increased with increasing storage time, whereas the opposite was observed for the trough and final viscosities. The starches of Nadine, Karuparera and Huakaroro showed the greatest increases in peak viscosity during six months of low temperature tuber storage. During storage of potatoes, starch granules of large size gradually decrease in size and the number of small granules increases (Smith, 1987), which may have influenced the pasting behaviour of starches extracted from tubers stored at 4  $^{\circ}$ C.

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 ([Singh et al., 2007b](#page-13-0)). The higher peak viscosity of the Nadine starches may be attributed to lower amylose and higher phosphorus contents. Starch granules with low amylose and high phosphorus have been reported to swell much more freely than others [\(Kim et al.,](#page-13-0) [1995](#page-13-0)). The trough and final viscosity (FV) were observed to decrease for the starches of stored cultivars. Amylose leaching, amylose–lipid complex formation, friction between swollen granules, granule swelling, and competition between leached amylose and remaining ungelatinized granules for free water have been reported to affect the hot paste viscosity ([Liu, Ramsden, & Corke, 1997\)](#page-13-0). Tutaekuri fresh starch showed the highest setback, 37 RVU, and this decreased to 28 RVU during six months of tuber storage, which may be attributed to the overall shift in its granule size distribution. Breakdown and setback viscosities have also been reported to have a close association with the

<span id="page-9-0"></span>Table 6

Pasting properties of starches from the different potato cultivars (fresh and stored): peak viscosity, trough, breakdown, final viscosity and setback

Starch source	Peak viscosity (RVU)	Trough (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)
Fresh					
Nadine	489 <sup>e</sup>	233 <sup>a</sup>	256 <sup>e</sup>	$266^{\rm a}$	33 <sup>a</sup>
Karuparera	407 <sup>fg</sup>	$220^{\rm a}$	187 <sup>g</sup>	$254^{\mathrm{a}}$	34 <sup>a</sup>
Tutaekuri	338 <sup>h</sup>	193 <sup>b</sup>	119 <sup>h</sup>	230 <sup>b</sup>	37 <sup>b</sup>
Huakaroro	421 <sup>f</sup>	209 <sup>ab</sup>	$212$ <sup>fg</sup>	$241^{ab}$	32 <sup>a</sup>
Moemoe	426 <sup>f</sup>	$188^{bc}$	234 <sup>ef</sup>	$218^{bc}$	31 <sup>a</sup>
Stored (3 months)					
Nadine	634 <sup>b</sup>	196 <sup>b</sup>	478 <sup>a</sup>	226 <sup>b</sup>	$30^{bc}$
Karuparera	437 <sup>f</sup>	$178^{\circ}$	$246^\circ$	$205^{\circ}$	$27^{\circ}$
Tutaekuri	379 <sup>g</sup>	138 <sup>e</sup>	$241^{\circ}$	196 <sup>c</sup>	$28^{\circ}$
Huakaroro	435 <sup>f</sup>	191 <sup>b</sup>	$243^{\circ}$	$211^{bc}$	20 <sup>d</sup>
Moemoe	422 <sup>f</sup>	199 <sup>b</sup>	$223^t$	232 <sup>b</sup>	$32^{\rm a}$
Stored (6 months)					
Nadine	$664$ <sup>a</sup>	$176^{\circ}$	487 <sup>a</sup>	$204^{\circ}$	$27^{\circ}$
Karuparera	587 <sup>c</sup>	155 <sup>d</sup>	431 <sup>b</sup>	185 <sup>d</sup>	29 <sup>c</sup>
Tutaekuri	420 <sup>f</sup>	$173^{\circ}$	$247^{\circ}$	$200^{\circ}$	$27^{\circ}$
Huakaroro	554 <sup>d</sup>	$176^{\circ}$	$378^\circ$	196 <sup>c</sup>	20 <sup>d</sup>
Moemoe	$500^{\circ}$	163 <sup>cd</sup>	336 <sup>d</sup>	191 <sup>d</sup>	$27^{\circ}$

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

amylose content [\(Singh, Kaur, Ezekiel, & Gurraya, 2005\)](#page-13-0). Reassociation during cooling was poor in low amylose starches, whereas starches containing high amylose, generally showed higher setback, as observed for Tutaekuri fresh starch. Setback value has been found to be positively correlated with amylose content in many studies on starch pasting properties [\(Singh et al., 2005](#page-13-0)).

#### 3.5. Viscoelastic characteristics of starch gels

Amplitude sweeps were carried out to identify the linear viscoelastic region for the RVA cooked and cooled potato starch gels. The potato starch gels showed normal viscoelastic behaviour, with the storage moduli  $(G')$  being always higher than loss moduli  $(G'')$  during measurements (data not shown). Frequency sweeps were carried out at 25 °C using a strain of 0.5%, which was within the linear viscoelastic region for all gels. All of the rheological parameters showed considerable differences among the different starches with respect to frequency dependence [\(Fig. 5\)](#page-10-0).  $G'$ and  $G''$  increased with increasing frequency. [Fig. 5](#page-10-0) shows the frequency dependence of  $G'$  and  $G''$  for Nadine and Tutaekuri starch gels for fresh as well as stored tubers, at a temperature of 25 °C. For fresh tubers,  $G'$  and  $G''$  were observed to be higher for Tutaekuri and Karuparera starches, followed by Moemoe starch [\(Table 7](#page-10-0)).

The differences in viscoelastic behaviour among the starches of fresh cultivars may be attributed to variation in the aggregation of amylose and amylopectin in their gels. During cooling and resting in the rheometer at  $25 \degree C$ , the gels of Tutaekuri and Karuparera starches, which had somewhat higher amylose content than the other starches, may have retrograded to a greater extent, leading to the formation of more solid-like structures with higher values of the rheological parameters. It is noteworthy that this effect was much more noticeable at higher frequency [\(Fig. 5\)](#page-10-0). Differences in rheological properties between starches from different sources have been reported to vary with differences in granule size and shape, the content of phosphate esters and the amylose to amylopectin ratio ([Kim et al., 1995](#page-13-0)). A significant positive correlation between  $G'$  and starch phosphorus was observed in the present study  $(r = 0.705, p \le 0.05)$ ; [Fig. 2\)](#page-6-0). The viscoelastic parameters of the starch gels decreased considerably during the first three months of tuber storage, and further, small decreases occurred in the second three month period.

The loss tangent,  $\tan \delta (=G''/G')$  is a useful parameter for assessment of viscoelastic behaviour. A tan $\delta$  of less than unity indicates predominantly elastic behaviour while a tan $\delta$  greater than unity indicates viscous behaviour [\(Kaur et al., 2005\)](#page-13-0). In the present study, tan  $\delta$  varied from 0.332 to 0.649 ([Table 7\)](#page-10-0). tan  $\delta$  increased with storage time, possibly as the result of changes in starch granule size distribution and chemical composition.

#### 3.6. Texture profile analysis – textural characteristics

Gels made by heating RVA pastes of starches from the fresh and stored tubers showed considerable variation in textural parameters as measured by instrumental texture profile analysis (TPA) [\(Table 8\)](#page-11-0). The TPA test mimics the human chewing action by subjecting a starch gel to a compressive deformation followed by a relaxation and then a second compressive deformation ([Mishra & Rai, 2006\)](#page-13-0). The hardness, springiness and gumminess of starch gels decreased during tuber storage. Nadine starch gels showed higher hardness, regardless of storage time. Hardness values varied from 0.21 N for Tutaekuri to 0.4 N for Nadine starch gels originating from fresh tubers. The higher fractu-

<span id="page-10-0"></span>

Fig. 5. Viscoelastic characteristics of starches from the different fresh and stored potato cultivars. (a) Effect of post-harvest tuber storage on the frequency dependence of the storage modulus  $(G,$  closed symbols) and loss modulus ( $G''$ , open symbols) of Nadine starch (N); (b) effect of post-harvest storage on the frequency dependence of the storage modulus  $(G'$ , closed symbols) and loss modulus  $(G'')$ , open symbols) of Tutaekuri starch (T) during frequency sweep experiments; (c) effect of post-harvest tuber storage on the frequency dependence of the loss tangent (tan $\delta$ ) of Nadine (N) and Tutaekuri (T) starches. 1, 2 and 3 signify 0, 3 and 6 months of storage.

rability and hardness of Nadine starch gels compared with gels prepared with starches of the other cultivars 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 large granule percentage  $(r = 0.818$  and 0.792, respectively,  $p < 0.05$ ; [Fig. 2](#page-6-0)). Cohesiveness and gumminess for all starch gels varied in the ranges 0.49–0.65 and 0.10–0.23, respectively. Hardness and fracturability were found to be positively correlated  $(r = 0.925, p < 0.05;$  [Fig. 2](#page-6-0)). Nadine starch gels exhibited the lowest cohesiveness and highest gumminess for both fresh and stored tubers, whereas the reverse trend for these properties was observed for Tutaekuri starch gels ([Table 8\)](#page-11-0). Starch gels with highest hardness showed lowest cohesiveness. Adhesiveness was observed to be lower for Moemoe and Tutaekuri starch gels after a six month storage period than that observed after a three month storage period. 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 interactions between the dispersed and continuous phases of the gel [\(Biliaderis, 1998\)](#page-13-0).

#### 3.7. Syneresis

The syneresis  $(\%)$  of starch pastes from stored tubers was observed to be lower than in the case of fresh tubers. The syneresis (%) of gelatinized starch pastes of fresh and six months stored cultivars are shown in [Fig. 6](#page-11-0). The

Table 7

Viscoelastic characteristics of starches from the different potato cultivars (fresh and stored)

Starch source	G'	$G^{\prime\prime}$	$\tan \delta$
Fresh			
Nadine	121 <sup>b</sup>	$49.0^\circ$	$0.404^{gh}$
Karuparera	$162^{\rm a}$	$54.4^{\rm a}$	$0.336^{i}$
Tutaekuri	168 <sup>a</sup>	55.7 <sup>a</sup>	$0.332^{1}$
Huakaroro	116 <sup>c</sup>	47.6 <sup>d</sup>	0.411 <sup>g</sup>
Moemoe	$134^{\rm b}$	$52.5^{\rm b}$	0.392 <sup>h</sup>
Stored (3 months)			
Nadine	$78$ <sup>de</sup>	39.4 <sup>ef</sup>	$0.505$ ef
Karuparera	81 <sup>d</sup>	$41.3^\circ$	$0.511^e$
Tutaekuri	$79.5^{\rm d}$	$41.3^\circ$	$0.519^e$
Huakaroro	67 <sup>ef</sup>	36.0 <sup>f</sup>	$0.538$ <sup>d</sup>
Moemoe	$74^e$	37.0 <sup>f</sup>	0.500 <sup>f</sup>
Stored (6 months)			
Nadine	$63.3^g$	$41.1^\circ$	$0.649^{\rm a}$
Karuparera	$65.7^{f}$	37.7 <sup>f</sup>	$0.574^{\circ}$
Tutaekuri	60.9 <sup>h</sup>	$35.4^{8}$	$0.582^{\circ}$
Huakaroro	60.7 <sup>h</sup>	$35.2^{g}$	0.580 <sup>c</sup>
Moemoe	$64.3^{f}$	39.9 <sup>f</sup>	$0.622^b$

Values with the same letter in a column did not differ significantly  $(p \le 0.05)$ .  $G'$  = storage modulus,  $G''$  = loss modulus, tan $\delta$  = loss tangent. Rheological parameters at  $25^{\circ}$ C and  $20$  Hz.

<span id="page-11-0"></span>Table 8

Textural properties of starches from the different potato cultivars (fresh and stored): fracturability, hardness, cohesiveness, springiness, adhesiveness, gumminess and chewiness

Starch source	Fracturability (N)	Hardness (N)	Cohesiveness	Springiness (s)	Adhesiveness (Ns)	Gumminess (N)
Fresh						
Nadine	$0.34^{a}$	0.40 <sup>a</sup>	$0.57^{\rm h}$	0.95 <sup>cd</sup>	$1.35^{b}$	0.23 <sup>a</sup>
Karuparera	0.19 <sup>ef</sup>	0.26 <sup>e</sup>	0.61 <sup>e</sup>	0.97 <sup>b</sup>	1.08 <sup>d</sup>	$0.16$ <sup>de</sup>
Tutaekuri	0.17 <sup>g</sup>	0.21 <sup>g</sup>	0.63 <sup>c</sup>	0.94 <sup>d</sup>	1.12 <sup>cd</sup>	0.14 <sup>e</sup>
Huakaroro	$0.22^{\circ}$	0.30 <sup>d</sup>	0.61 <sup>e</sup>	0.96 <sup>c</sup>	0.95 <sup>f</sup>	$0.18^{d}$
Moemoe	0.23 <sup>c</sup>	$0.25^e$	0.57 <sup>h</sup>	0.93 <sup>e</sup>	0.41 <sup>h</sup>	0.14 <sup>e</sup>
Stored (3 months)						
Nadine	0.30 <sup>b</sup>	$0.37^{b}$	0.59 <sup>g</sup>	0.95 <sup>d</sup>	$1.44^{\rm a}$	$0.22^{\circ}$
Karuparera	0.20 <sup>d</sup>	0.23 <sup>f</sup>	$0.63^d$	0.92 <sup>f</sup>	1.05 <sup>d</sup>	$0.15^e$
Tutaekuri	0.19 <sup>f</sup>	0.24 <sup>f</sup>	$0.65^{\rm a}$	0.95 <sup>cd</sup>	1.17 <sup>vc</sup>	$0.15^{\text{de}}$
Huakaroro	$0.22^{\circ}$	0.24 <sup>ef</sup>	$0.59^{8}$	0.95 <sup>d</sup>	1.00 <sup>e</sup>	$0.14^e$
Moemoe	0.19 <sup>e</sup>	0.26 <sup>e</sup>	0.60 <sup>f</sup>	0.95 <sup>d</sup>	1.15 <sup>c</sup>	$0.16$ <sup>de</sup>
Stored (6 months)						
Nadine	0.29 <sup>b</sup>	$0.32^{\circ}$	$0.55^{1}$	0.99 <sup>a</sup>	$1.42^{\rm a}$	0.22 <sup>b</sup>
Karuparera	0.20 <sup>d</sup>	$0.27^e$	$0.49^{j}$	$0.83^{\rm h}$	$1.05^{\text{de}}$	0.13 <sup>f</sup>
Tutaekuri	$0.14^h$	$0.16^{\rm h}$	0.64 <sup>c</sup>	0.95 <sup>cd</sup>	0.58 <sup>g</sup>	0.10 <sup>g</sup>
Huakaroro	0.18 <sup>f</sup>	0.24 <sup>ef</sup>	$0.65^{\rm b}$	0.90 <sup>g</sup>	1.07 <sup>de</sup>	$0.16$ <sup>de</sup>
Moemoe	0.20 <sup>d</sup>	0.20 <sup>g</sup>	$0.50^{j}$	0.92 <sup>f</sup>	0.93 <sup>f</sup>	0.10 <sup>g</sup>

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

changes that occurred in granule size distribution may have affected syneresis, as pastes prepared from potato starches with higher percentages of small granules have been reported to exhibit lower syneresis ([Kaur et al., 2005; Singh](#page-13-0) [et al., 2004](#page-13-0)). For fresh tubers, Tutaekuri starch paste showed the highest syneresis (9.0% after 24 h) compared with starch pastes from the other cultivars, followed by Karuparera and Moemoe starch pastes (3.4% and 3.6%, respectively, after 24 h). Syneresis (%) decreased slowly during tuber storage, but the relative differences between cultivars remained substantially constant. The lower syneresis (%) exhibited by Nadine and Huakaroro starch pastes can be attributed to their lower amylose content. The tendency of the starch pastes to synerese was observed to be higher during the initial stages of paste storage. Amylose aggregation and crystallization have been reported to complete within the first few hours of storage while amylopectin aggregation and crystallization occur at later stages [\(Miles, Morris, Orford, & Ring, 1985\)](#page-13-0). 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](#page-13-0)).

# 3.8. Analysis of variance (ANOVA) and principal component analysis (PCA)

When the ANOVA results were examined, it was seen that the significantly affected starch parameters of the various cultivars were large granule population, peak and final viscosity, storage modulus of pastes and solubility of



Fig. 6. Syneresis (%) of refrigerated starch pastes from the different fresh and stored potato cultivars. (a) Starches of fresh cultivars (0); (b) starches of cultivars stored for six months (6).

Table 9 Variables examined with PCA

Description	Variable
Granule size $(1-10 \mu m)$	SG
Granule size $(>30 \mu m)$	LG
Granule size $(11-30 \mu m)$	MG
Amylose $(\% )$	Amy
Phosphorus content	P
Swelling power	<b>SP</b>
Solubility in water	Sol
Solubility in DMSO	SDmso
Onset transition temperature	$T_{\rm o}$
Peak transition temperature	$T_{\rm p}$
Conclusion transition temperature	$T_{\rm c}$
Enthalpy of gelatinization	Enth
Peak viscosity	PV
Trough viscosity	Tr
Breakdown viscosity	<b>B</b> dn
Final viscosity	FV
Setback viscosity	Sethk
Fracturability	Fr
Hardness	Hd
Cohesiveness	Ch
Springiness	Spr
Adhesiveness	Adh
Gumminess	Gum
Storage modulus	St Mod
Loss modulus	Ls Mod
Loss tangent	tan d

starch in DMSO ([Table 2](#page-4-0);  $p \le 0.05$ ). In terms of the interaction between the storage time and cultivars, the large granule population, storage modulus and peak and final viscosities showed highly significant effects ( $p < 0.05$ ) ([Table 2](#page-4-0)). The variables subjected to PCA are listed in Table 9, and the results of the analysis are shown in [Figs.](#page-6-0) [2 and 7.](#page-6-0) The PCA plots provide an overview of the similarities and differences among the starches of the different cultivars, and of the interrelationships between the measured properties. The first, second and third principal components (PC1, PC2 and PC3) explained 42.17%, 19.67% and 17.05%, 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. 7). 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 suggesting that these two starches exhibited the greatest differences in their characteristics. The loading plot of the two PCs provide information about correlations between measured physico-chemical, morphological, thermal, pasting and retrogradation parameters ([Fig. 2\)](#page-6-0). 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. PCA of the data obtained indicated that the starches of fresh and stored Nadine and Tutaekuri tubers exhibited the greatest differences in their starch properties.

#### 4. Conclusions

Post-harvest storage of potatoes was observed to be an important factor affecting the morphological, physicochemical, thermal and rheological characteristics of starches from different cultivars. Starches isolated from all of the cultivars showed a general shift in granule size distribution to smaller granule size, changes in the granule surface and a decrease in solubility with increasing low temperature storage time. In contrast, thermal parameters and peak viscosities increased with storage time. The extent of the changes in starch properties during post-harvest storage differed among the cultivars. The results of this study may prove useful in the selection of suitable storage times and cultivars with desirable starch characteristics for specific end-uses.



Fig. 7. Principal component analysis: score plot of PC1 and PC2 illustrating the overall differences among starches isolated from the different potato cultivars.

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