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Rheological and structural properties of starches from γ-irradiated and stored potatoes

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ABSTRACT

Starch was extracted from irradiated and stored potato tubers and the properties were compared to CIPC (chlorpropham) treated tubers. The granule properties and dynamic viscoelasticity in temperature ramp and frequency sweep modes were studied while heating the samples. Starch structural characteristics were investigated by high performance anion exchange chromatography (HPAEC) and Fourier transform infrared spectroscopy (FTIR). Gamma-irradiation of potato tubers at a dosage of 0.1 kGy induced some degradation of starch molecules, resulting in earlier swelling of starch granules, and greater extents of amylose and total carbohydrate leaching. The early swelling phenomenon was also enhanced with tuber storage time. The retrogradation rate and extent for a concentrated starch gel also increased with tuber storage time whereas γ-irradiation delayed the gel retrogradation. Sprout inhibiting methods could be selected based on the specific processing and texture requirements of the end products.

1. Introduction

Potatoes (*Solanum tuberosum* L.) are a staple food cultivated throughout the world and in most parts are harvested once a year, and thus have to be stored to ensure adequate supplies until the next harvest. Sprouting during potato storage is the most obvious manifestation of deterioration, which includes loss of marketable weight and nutritional value, and softening and shrinkage. The sprouts also contain the toxic glycoalkaloid solanine which may cause safety concerns (Friedman & McDonald, 1997). Therefore, successful storage of potatoes requires the use of a sprout inhibitor or irradiation and an optimal temperature regime (Thomas, 1984). Chlorpropham (CIPC, isopropyl 3-chlorocarbanilate) inhibits potato sprout development by interfering with spindle formation during cell division (Vaughn & Lehnen, 1991), and is the most potent and widely used chemical sprout inhibitor registered for use in potato storages (Jaarma, 1969; Lewis, Thornton & Kleinkopf, 1997; Mahajan, Dhatt, Sandhu & Garg, 2008). In practice, CIPC is applied as an aerosol or by dusting over the tubers, or as dip or spray in wax emulsions, and has been proven effective in allowing for long-term storage of potatoes at 7–10 °C (Thomas, 1984). The residual level of CIPC in whole tuber during storage must be below the U.S. Environmental Protection Agency established tolerance limit of 30 ppm (Kleinkopf, Oberg & Olsen, 2003); therefore, an adequate, consistent and homogeneous application technology is critical to the control of CIPC levels.

Irradiation using cobalt-60 is a preferred physical method for sprout inhibition (Ezekiel, Rana, Singh & Singh, 2007; Islam, Karim, Langerak & Hossain, 1985; Thomas, 1984), since its deeper penetration enables administering treatment to entire industrial pallets, reducing the need for material handling (Thomas, 1984). The most accepted explanation for the mechanism of sprout inhibition is that γ-irradiation affects the nucleic acid metabolism of potato tubers (Thomas, 1984). In 1999, the Food and Agriculture Organization of the United Nations (FAO)/International Atomic Energy Agency (IAEA)/World Health Organization (WHO) Study Group and International Conference stated that food irradiated to any dose appropriate to achieve technological objectives is both safe and nutritionally adequate (FAO/IAEA/WHO, 1997). However, in Canada, potato tubers are only permitted to be irradiated by cobalt-60 to a maximum absorbed dose of 0.15 kGy for the purpose of sprout inhibition during storage (Food and Drug Regulations, current to June 9, 2010).

Potato starch is extensively used as a thickener or as a gelling agent in a variety of food products because of its unique textural properties (Luallen, 2002). Rheological properties of starch are key factors determining their industrial usage. Tsai, Li and Lii (1997) suggested the integrity of swollen starch granules was the major factor determining the rheological properties of a starch paste or gel. They reported that the formation of gel structure was governed

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by the rigidity of swollen granules and that the hot-water soluble component could strengthen the elasticity of the starch gel or paste. Maximal swelling might also be related to the molecular weight and the shape of the amylopectin (Tester & Morrison, 1990b). Radiation treatment is known to affect the molecular size of potato starch (Greenwood & MacKenzie, 1963). The breaking of the glycosidic bond was considered the most important change caused by irradiation of starch (Urbain, 1986). At high radiation doses (from 9 to 600 kGy), a decrease in molecular weight (Michel, Raffi & Saintlebe, 1980) and a decrease in order in dried starch granules (Ciesla, Zoltowski & Mogilevski, 1992) were observed, which can influence its gelling properties (Ciesla & Eliasson, 2002). However, the impact of low doses of irradiation (<0.15 kGy) on the swelling properties of starch granules has not been fully elucidated, despite a few reports on thermal and pasting properties of isolated starches from potato tubers irradiated at a dosage of 0.1–0.5 kGy (Ezekiel et al., 2007).

In addition to its role as a gelling agent, starch imparts structure, texture, consistency, and appeal to many food systems (Rogols, 1986). The structure of the starch-based food matrix in return determines partially the accessibility of starch to digestion, and thus influences the postprandial blood glucose response (Riccardi, Clemente & Giacco, 2003). Irradiation can bring about structural modifications of foods (Rogols, 1986). The chemical bonds of starch can be hydrolyzed by γ-irradiation, leading to degradation of the polysaccharide chains. The starch granules themselves can also be damaged depending on the radiation dose which would eventually influence starch gelatinization, retrogradation properties and thus the gel texture. It is essential to elucidate the impact of γ-irradiation on rheological and structural properties of starch from potato tubers irradiated at dosages lower than 0.15 kGy.

In the present study, potato tubers were irradiated at a low dose (0.1 kGy) and stored at 8 °C, 80% RH for 90 days. The chemical composition, chain length distribution and crystallinity of starches; swelling factor, amylose and total carbohydrate leaching during heating of starch granules in excess water; and formed network of starch gels, were determined to characterize the structural changes at the molecular and granular levels of the isolated starch from irradiated and stored potatoes. The changes of rheological properties of the starches were discussed and compared to those from CIPC treated tubers (control).

2. Materials and methods

2.1. Materials, irradiation, CIPC treatment and storage

Potato (*S. tuberosum* L.) variety F03031 from the 2009 growing season was obtained from Agriculture and Agri-Food Canada's Potato Research Centre in Fredericton, New Brunswick, Canada. After storing at 12–13 °C for about 14 days for wound healing, the tubers (about 75% moisture content) were divided into two groups of 10 kg each.

The first group was packed in a polyethylene bag and irradiated using a ^{60}Co γ-source (C-188, MDS Nordion, Ottawa, ON, Canada) at an ambient temperature (20 ± 0.5 °C). The dose was controlled at 0.1 kGy at a dose rate of 0.54 Gy/min, which is lower than the maximum permitted absorbed dose (0.15 kGy) regulated by Food and Drug Regulations in Canada (current to June 9, 2010). The irradiation treatment was performed at the McMaster Nuclear Reactor, McMaster University (Hamilton, ON, Canada). The second group was treated with CIPC which served as a control. A 1% aqueous solution of CIPC was applied to the tuber surface by spraying. The dosage used was 35 ppm, the same as that applied commercially. Irradiated and CIPC treated (control) tubers were stored for 0–90 days at 8 °C, 80% relative humidity (RH) in a dark storage room. No tuber sprouting was observed during the three months of storage.

2.2. Starch extraction and chemical analysis

Starch was extracted from the tubers with different treatments and tuber storage times according to the method of Liu, Weber, Currie and Yada (2003). Apparent amylose content in potato starch was determined by an iodine colorimetric method described by Williams, Kuzina and Hlynka (1970). Starch damage was estimated using the Megazyme Starch Damage Assay Kit (Megazyme International Ireland Ltd., Wicklow, Ireland). Isoamylase debranching of whole starch accompanied by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was used to determine the branch chain length distribution of the amylopectin (Liu, Gu, Donner, Tetlow & Emes, 2007).

2.3. Swelling factor, amylose and total carbohydrate leaching during heating

The swelling factor of starch when heated at 90 °C for 0, 2, 4, 10 and 30 min in excess water was measured according to the method of Tester and Morrison (1990a). The swelling factor is reported as the ratio of the volume of swollen granules to the volume of dry starch.

For measurements of amylose and total carbohydrate leaching, starches (20 mg) in water (10 mL) were heated at 90 °C in sealed tubes for 0, 2, 4, 10 and 30 min with continuous shaking. The tubes were then cooled to room temperature and centrifuged at 2000 × *g* for 10 min. The supernatant (1.0 mL) was withdrawn and its amylose content and total carbohydrate content were determined as described by Williams et al. (1970) and Dubois, Gilles, Hamilton, Rebers and Smith (1956), respectively.

2.4. Dynamic viscoelasticity measurements

Dynamic viscoelasticity of the starches was measured in dynamic shear mode using a strain-controlled rheometer (ARES, TA Instruments, New Castle, DE, USA), operated with a parallel-plate geometry with a 25 mm diameter, as described in previous work (Lu et al., 2009a). A strain of 1.0% was used to assure that the tests were in the linear region defined by preliminary strain sweep tests. The frequency was 1.0 rad/s. Briefly, a 30% starch suspension was loaded on the lower fixture and the gap was set to 2.0 mm. Temperature ramp tests of the samples were conducted from 40 °C to 95 °C at a heating rate of 1.0 °C/min, held for 10 min, then cooled to 4 °C at a rate of 3 °C/min, and then held at 4 °C for 2 h. Storage modulus (G'), loss modulus (G'') and loss tangent ($\tan\delta = G''/G'$) were obtained using software (TA Orchestrator, ver 6.6.0B1, TA Instruments, New Castle, DE, USA). As described in the previous paper (Lu et al., 2009a), the following specific values were obtained from the storage moduli (G') curve: G'_{peak}, the peak value of G' during heating; $T_{G'\text{peak}}$, the corresponding temperature of G'_{peak}; $G'_{4,2}$, the G' value when held at 4 °C for 2 h.

After the temperature ramp test, a dynamic frequency sweep from 0.1 to 100 rad/s was conducted to determine the mechanical spectrum (G' and G'') against frequency (ω). The complex dynamic viscosity (η^*) was provided ($\eta^* = [(G')^2 + (G'')^2]^{1/2}/\omega$) from the measurement. Logarithmic plots of η^* *vs.* ω were fitted to power law Eq. (1) as below with respect to frequency (ω).

$$\eta^*(\omega) = a^*\omega^{-b^*} \quad (1)$$

The derived parameters ($\log a^*$ and $-b^*$) and the square correlation coefficient (R^2) for the fit were obtained (Paraskevopoulou, Kiosseoglou, Alevisopoulos & Kasapis, 1997). The value of $\log a^*$ represents the magnitude of the viscoelastic functions, i.e., is related to the system consistency. The b^* parameter reflects the type of gel structure by the dependence of the viscoelastic functions on frequency, i.e., is related to the type of structure built up by the system molecules (Paraskevopoulou et al., 1997).

2.5. Fourier transform infrared spectroscopy (FTIR)

Infrared spectra of starch were recorded on a Digilab FTS 7000 spectrometer (Digilab USA, Randolph, MA) according to the method used previously (Chung, Hoover & Liu, 2009). The moisture content of starch was equilibrated to 14% in a desiccator containing a saturated solution of ammonium nitrate for fourteen days before FTIR analysis. The amplitudes of absorbance for each spectrum at 1047 and 1022 cm^{-1} were measured.

2.6. Statistical analysis

All samples were tested at least in duplicate in each analytical technique. Statistics (one-way analysis of variance, ANOVA) was conducted with SAS (Version 9.2 for Windows, SAS Institute Inc., Cary, NC, USA). When appropriate, the difference among means was determined using Tukey's multiple comparisons. Statistical significance was set at the 5% level of probability.

3. Results

3.1. Chemical components of starch, starch damage and amylopectin chain length distribution

The apparent amylose content of starch, level of starch damage, average chain length and chain length distribution in amylopectin of starches from γ-irradiated and CIPC treated potatoes stored for 0 and 90 days (8 °C, 80% RH) are shown in Table 1. Gamma-irradiation at a dosage of 0.1 kGy resulted in a significant increase in apparent amylose content of starch (30.9–32.3%) and in the amount of starch damage (0.64–1.13%) compared to that of CIPC-treated control ($P \leq 0.05$), while no effect from tuber storage time was observed on amylose content within each of the treatments ($P > 0.05$). Although no significant difference could be seen in average chain length, or the percentage of amylopectin chains with DP ≤ 24 or DP ≥ 37, a small but significant decrease (15.0–14.6%) in the percentage of amylopectin chains with DP 25–36 was observed for the irradiated sample stored for 90 days ($P \leq 0.05$).

3.2. Swelling factor, amylose and total carbohydrate leaching during heating

The swelling factor, amylose and total carbohydrate leaching of starches from γ-irradiated and CIPC treated potatoes stored for 0, 30 and 90 days are shown in Fig. 1. As shown in Fig. 1(A), swelling factors of starch increased to a maximum when heating for 4–10 min and then decreased, indicating the bursting of the swollen starch granules after heating at 90 °C for 10 min. Before storage, the CIPC treated sample (control) had the lowest swelling factor at 2, 4 and 10 min, compared to the irradiated one, and the maximal swelling factor during heating appeared around 10 min. All of the γ-irradiated samples showed a sharp increase in swelling factor within 4 min of heating at 90 °C, indicating an earlier swelling than that of control, and thereafter the swelling factor decreased. Tuber storage time had a positive effect on the swelling factor, and the effect was more notable for CIPC treated samples when heating for 10 min, given that the CIPC treated sample stored for 90 days showed the highest swelling factor.

The amylose leaching during heating of starch samples is shown in Fig. 1(B). It increased with heating time for all samples. A sharp increase was observed within 10 min of heating. After that, the amylose leaching tended to slow down. Irradiated samples showed

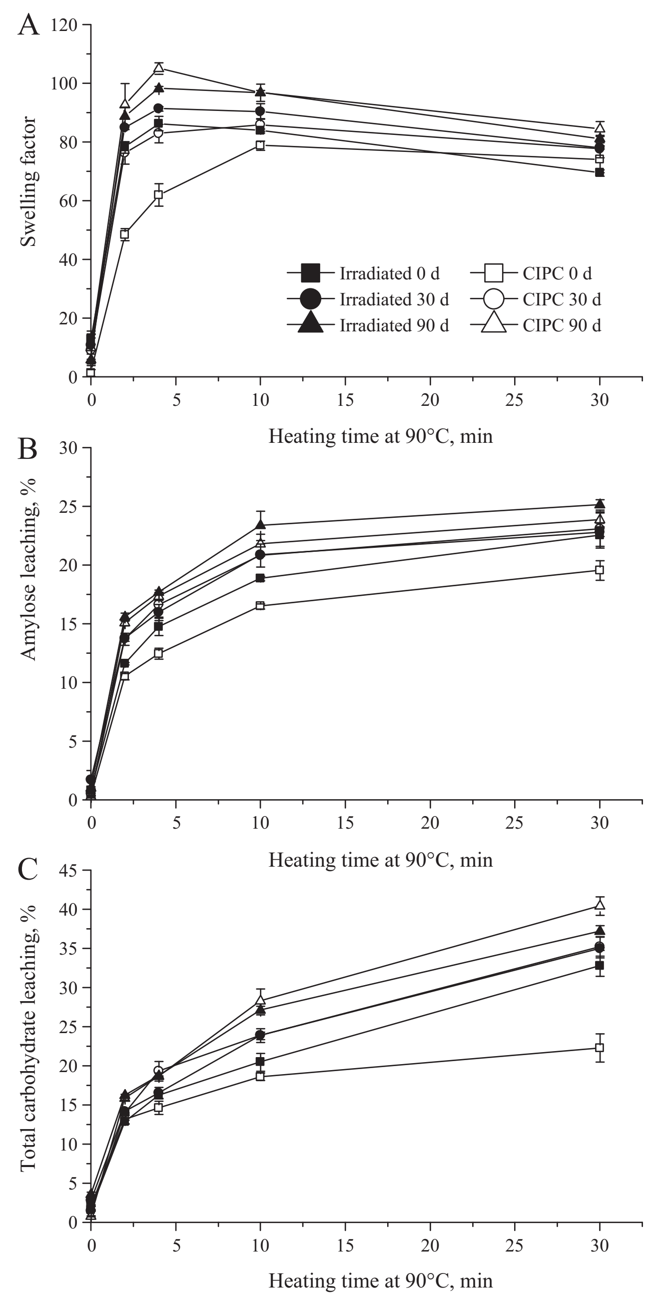

Fig. 1. (A) Swelling factor; (B) amylose leaching, and (C) total carbohydrate leaching of starches from γ-irradiated and CIPC treated potatoes stored for 0, 30 and 90 days (8 °C, 80% RH) during heating at 90 °C for 0, 2, 4, 10 and 30 min, respectively. □ and ■, 0 day; ○ and ●, 30 days; △ and ▲, 90 days; open symbols, CIPC treated; solid symbols, irradiated. Error bars represent standard deviation. $n = 3$.

higher amylose leaching than control at each heating interval. Amylose leaching also tended to increase with tuber storage time. The same trend was observed for the total carbohydrate leaching as shown in Fig. 1(C). The total carbohydrate leaching kept increasing with heating time, which was different from the amylose leaching profiles.

3.3. Rheological properties of starch gels

3.3.1. Temperature ramp test

Fig. 2 illustrates the storage moduli (G') of starch from irradiated and CIPC-treated potatoes stored for 0, 30 and 90 days, measured by a temperature ramp test. When heating from 40 °C, the value of G'

Table 1
Apparent amylose content, average chain length and chain length distribution in amylopectin of starches from γ-irradiated and CIPC treated potatoes stored for 0 and 90 days (8 °C, 80% RH).

Tuber storage time, day	Treatment	Apparent amylose, %	Starch damage, %	Average chain length	Distribution (%)			
					DP[a] 6–12	DP 13–24	DP 25–36	DP ≥ 37
0	CIPC-treated	30.9 ± 0.6	0.64 ± 0.02	21.4 ± 0.2	19.1 ± 1.4	53.0 ± 2.6	15.5 ± 0.1	12.4 ± 1.3
	Irradiated	32.3 ± 0.3*	1.13 ± 0.03*	21.6 ± 0.0	19.6 ± 1.3	51.4 ± 1.0	15.2 ± 0.9	13.7 ± 0.6
90	CIPC-treated	31.1 ± 0.9	0.67 ± 0.02	21.3 ± 0.1	20.7 ± 0.9	51.2 ± 1.7	15.0 ± 0.2	13.1 ± 0.6
	Irradiated	32.4 ± 0.7*	0.73 ± 0.03	21.6 ± 0.2	20.4 ± 1.1	51.0 ± 0.5	14.6 ± 0.2*	14.1 ± 0.7

Values denote means ± standard deviations.
[a] DP, degree of polymerization.
* indicates data are significantly different in same column at same tuber storage times as determined by *t*-test ($P \leq 0.05$). $n = 2$.

increased with the temperature until the peak value was reached; after that, the value decreased upon further heating to 95 °C. In the cooling stage, G' increased steadily.

The G' peak temperature ($T_{G'peak}$) and height (G'_{peak}) and final G' value ($G'_{4,2}$) varied among samples (Fig. 2). When the potatoes were stored for 0, 30 and 90 days, G'_{peak} values were 10.0, 10.3 and 25.7 kPa for CIPC-treated samples, while the values were 10.4, 10.7 and 13.8 kPa for irradiated samples, respectively. The corresponding temperatures of G'_{peak} ($T_{G'peak}$) were 69.1, 66.5 and 63.3 °C for CIPC-treated samples, while the temperatures were 66.2, 65.3 and 64.7 °C for irradiated samples, respectively. The final G' values ($G'_{4,2}$) were 118.0, 130.3 and 295.9 kPa for CIPC-treated samples, while they were 118.5, 127.2 and 178.4 kPa for irradiated samples, respectively (Fig. 2). Evidently, both irradiation and storage affected the storage modulus of dynamic viscoelasticity of the starch samples.

3.3.2. Frequency sweep test

Dynamic frequency sweep tests were conducted to evaluate the network structure of the gel obtained from the temperature ramp test after being held at 4 °C for 2 h. As shown in Fig. 3(A), the storage modulus (G') was generally independent of frequency for all samples within the testing frequency range of 0.1–100 rad/s, indicating well-formed gel structures, whereas the loss modulus (G'') was slightly frequency dependent. For each tuber storage time, irradiated samples showed a lower magnitude of G' than the control, indicating less rigidity of the starch gel from irradiated potatoes. Furthermore, the magnitude of the G' value increased with tuber storage time for both irradiated and control samples, with the increase more notable for the control.

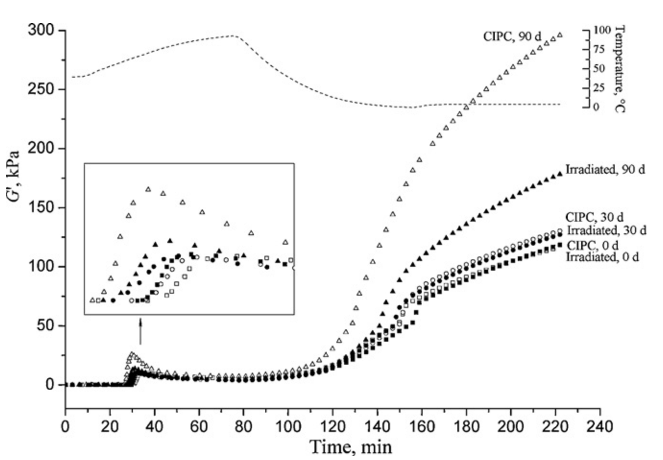

Fig. 2. Dynamic viscoelasticity of starch pastes during heating from sprout inhibited potatoes stored for 0, 30 and 90 days (8 °C, 80% RH). The inset graph is an enlarged display of G' peak during heating. □ and ■, 0 day; ○ and ●, 30 days; △ and ▲, 90 days; open symbols, CIPC treated; solid symbols, irradiated.

The evolution of complex dynamic viscosity (η^*) with frequency is shown in Fig. 3(B). In all cases, a linear decrease of η^* with frequency was observed, and all curves were parallel. Similar to the G' curves in Fig. 3(A), irradiated samples showed a lower magnitude of η^* than the control, and the magnitude of η^* increased with tuber storage time and was more notable for the CIPC-treated samples (control). The derived parameters (log a^* and b^*) and the square correlation coefficient (R^2) for the fit of complex viscosity to the power law Eq. (1) with respect to frequency are shown in Table 2.

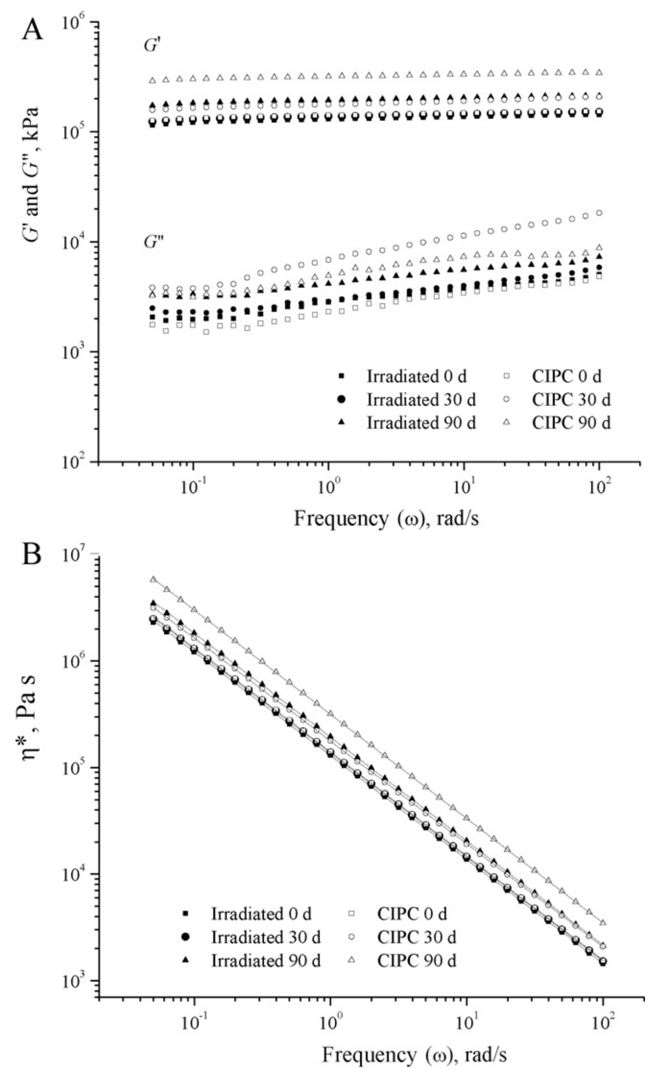

Fig. 3. (A) Frequency dependence of storage (G') and loss (G'') moduli, and (B) complex viscosity (η^*) of starch from CIPC treated and irradiated potatoes stored for 0, 30 and 90 days (8 °C, 80% RH). □ and ■, 0 day; ○ and ●, 30 days; △ and ▲, 90 days; open symbols, CIPC treated; solid symbols, irradiated.

Table 2
Power law parameters derived from Eq. (1) for the frequency dependence of η^*. The values of a^* are equal to η^* at 1 rad/s. Temperature of 4 °C, 1% strain, frequency range from 0.1 to 100 rad/s.

Treatment	Storage, day	Log a^*	b^*	R^2
CIPC treated	0	5.148	0.977	1.000
	30	5.250	0.966	
	90	5.501	0.979	
Irradiated	0	5.112	0.975	
	30	5.137	0.976	
	90	5.287	0.976	

It can be seen that the value of log a^* increased with tuber storage time in either case, irradiated or stored, and the log a^* of CIPC treated sample was slightly greater than that of irradiated sample at each tuber storage time. The value of b^* was around 0.97 in all cases, either irradiated or stored. The square correlation coefficient (R^2) for the fit of complex viscosity was 1.000 in all cases (Table 2).

3.4. *Fourier transform infrared spectroscopy (FTIR)*

The FTIR spectra of starches from potatoes after irradiation and CIPC treatment and storage for 0, 30 and 90 days are shown in Fig. 4(A), and the ratios between the bands at 1047/1022 cm^{-1} from each spectrum are shown in Fig. 4(B). As shown in Fig. 4(A), the FTIR spectra were similar for both sprout inhibiting treatments and tuber storage time, except different peak heights were observed for the bands at 1047 and 1022 cm^{-1}. As shown in Fig. 4(B), the degree of ordered structure in starch (ratio of peak height of the bands at 1047/1022 cm^{-1}) increased significantly after potatoes were stored for 30 days ($P \le 0.05$), but no significant change ($P > 0.05$) was seen after extended tuber storage time (from 30 to 90 days), either for irradiated or CIPC treated samples. Little difference was seen between irradiated samples and CIPC treated samples at each storage interval.

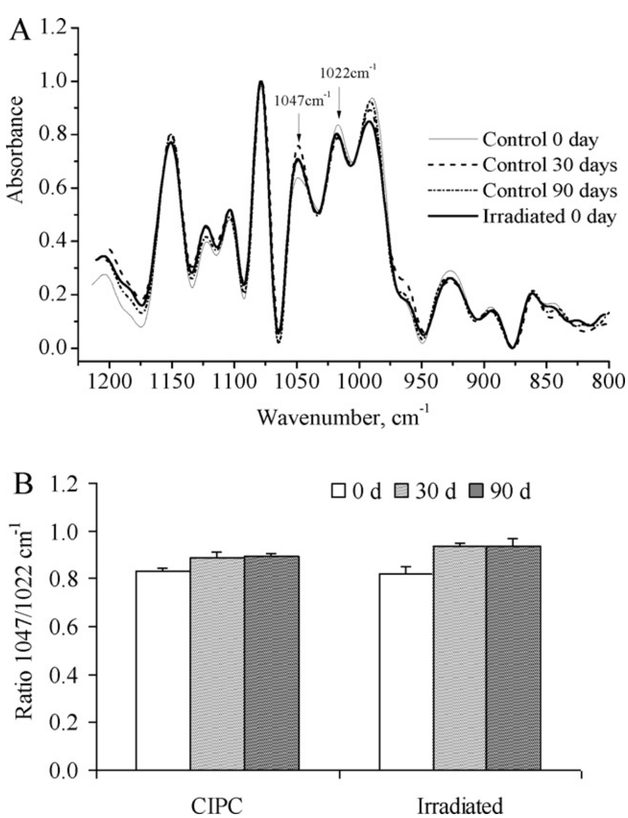

Fig. 4. (A) Deconvoluted Fourier transform infrared (FTIR) spectra and (B) the ratios of bands at 1047 and 1022 cm^{-1} of FTIR spectra of starches from irradiated and CIPC treated potatoes stored for 0, 30 and 90 days (8 °C, 80% RH). Error bars represent standard deviation. $n = 2$.

4. Discussion

Compared to control, γ-irradiation of potato tubers even at a low dosage (0.1 kGy) resulted in a significant increase in apparent amylose content of starch ($P \le 0.05$), a small but significant increase in starch damage ($P \le 0.05$) and a decrease in chain length of chains with DP 25–36 in amylopectin (Table 1) ($P \le 0.05$), indicating degradation in amylopectin molecules occurred by γ-rays. This result is consistent with previous work (Ezekiel et al., 2007), in which it was reported that starch separated from potatoes irradiated at levels of 0.1 and 0.5 kGy and stored at 8 °C showed 1–2% higher amylose content than control. The chain length of amylose and amylopectin displayed a progressive reduction as the irradiation dosage increased (Sokhey & Chinnaswamy, 1993). Bao, Ao and Jane (2005) have also claimed that γ-irradiation could depolymerize amylopectin and amylose into shorter chain molecules, with amylopectin affected more than amylose. Actually, the maximum length of branch chains detected by HPAEC in this study was less than DP 65. Jane et al. (1999) reported that the highest detectable DP was 85 in their HPAEC system, and found that amylopectin with very long branch chains (DP > 73), could display iodine affinity and affect starch pasting properties, like amylose. They also reported that starches displaying a B-type X-ray pattern, e.g. potato starch, had larger proportions of long amylopectin branch chains than the A- and C-type starches, and gave greater over-estimations of the amylose content. Unfortunately, the effect of γ-irradiation on the portion of chains over DP 73 could not be detected by HPAEC in this study. However, the slight increase in apparent amylose content and starch damage, and decrease in percentage of chain length of DP 25–36 in irradiated samples indicated at least some degradation of amylopectin chains occurred by γ-irradiation, and the effects on physicochemical and rheological properties of the starch could be predominant.

The degradation of starch molecules by γ-irradiation also influenced the starch granule properties. As shown in Fig. 1(A), the swelling factor of starch granules sharply increased and the peak value was achieved earlier (4 min *vs.* 10 min) immediately after irradiation when heating in excess water at 90 °C for 10 min, accompanied by a greater amount of amylose leaching (Fig. 1(B)) and total carbohydrate leaching (Fig. 1(C)), compared to starch from the CIPC treated potatoes (stored for 0 day). These changes could be due to loosened granule structure caused both by bond breakage and introduction of functional group dislocations after γ-irradiation (Bachman, Witkowski & Pietka, 1987). A greater swelling power indicates less resistance towards swelling (Al-Kahtani et al., 2000), thus the increase in swelling factor can possibly be attributed to the depolymerization of the starch due to irradiation. During amylose leaching measurement at 90 °C with extended heating to 30 min, a dark purple color developed upon addition of iodine reagent, indicating that starch granules began to burst and considerable amounts of branched components were leached from the starch granules. This was also confirmed by the sharp increase in the total carbohydrate leaching (Fig. 1(C)). The increase in swelling factor with extended tuber storage time might be attributed to the increased potato maturity during storage when the tuber sprouting potential was inhibited by γ-irradiation or CIPC treatment. Liu et al. (2003) have reported that the swelling factor of starch granules increased as potato growth time increased. It is possible that this change continued during storage of the sprout-inhibited tubers.

The earlier swelling and increased swelling capacity with γ-irradiation and tuber storage time were also evident during the heating stage in a temperature ramp test of dynamic viscoelasticity of a 30% starch suspension (inset of Fig. 2). The storage modulus (G') in viscoelastic materials measures the stored energy, representing the elastic portion. In this study, the increase in G' during heating appeared to be an indicator of starch granule swelling, and the peak of G' during heating (G'_{peak}) appeared to reflect the rigidity of starch granules during swelling. Tsai et al. (1997) reported that the integrity of the swollen starch granules is a major factor determining the rheological properties of a starch paste or gel. As mentioned above, the degradation of amylopectin molecules revealed by chain length distribution analysis, and loosened granule structure caused both by bond breakage and introduction of functional group dislocations after γ-irradiation (Bachman et al., 1987), could contribute to the earlier swelling of irradiated samples than control (CIPC treated and stored for 0 day). The significantly higher ($P \leq 0.05$) G'_{peak} of CIPC treated sample stored for 90 days could be explained by the maturity of starch granules as mentioned above when interpreting the data of swelling factor. However, this sample also showed the earliest swelling. We assume that the endogenous amylase activity in potato tubers was not fully inhibited by the single CIPC application, resulting in some starch hydrolysis during storage (Cottrell, Duffus, Paterson & Mackay, 1995), leading to earlier swelling. High gelatinization temperatures are thought to be indicative of more stable amorphous regions, a more ordered crystalline structure and/or a higher ratio of crystalline to amorphous regions (Barichello, Yada, Coffin & Stanley, 1990), thus the early swelling of starch during heating in water indicated that a less stable or ordered starch structure was present. Leached amylose is also a key factor affecting granule swelling, acting as both a diluent and an inhibitor of swelling, and inhibitor of the breakdown of swollen granules (Tester & Morrison, 1990a). The greater amount of leached amylose from the samples stored for 90 days (Fig. 1(B)), either irradiated or CIPC treated, might also play a role in the high G'_{peak} values.

The most notable difference among samples was the G' value when the starch gel was held at 4 °C for 2 h ($G'_{4,2}$) as shown in Fig. 2. The value of $G'_{4,2}$ reflects the retrogradation rate and extent of a starch gel, and is due largely to the re-crystallization of the amylopectin molecules (since the amylose molecules had likely finished re-crystallizing before being cooled to 4 °C), and a thermal transition peak was observed in the temperature range of 40–60 °C, the temperature range for melting retrograded amylopectin, when scanning the starch gel (cooled 2 h) from 25 to 90 °C by DSC (Lu, Sasaki, Kobayashi, Li & Kohyama, 2009b). In starch gels, the swollen granules (ghosts) act as fillers in the amylose network matrix. The increase in the modulus of starch gels is mainly linked to re-crystallization of amylopectin, which results in an increase in the rigidity of the granules and thus enhances their reinforcement of the amylose matrix (Miles, Morris, Orford & Ring, 1985). Higher proportions of longer chains in amylopectin molecules tend to result in a greater extent of retrogradation. Thus the degradation of amylopectin molecules (Table 1) in the irradiated sample may explain its lower $G'_{4,2}$ value than the CIPC treated one when stored for 90 days. It appeared that $G'_{4,2}$ value also increased with potato tuber storage time, either for irradiated or CIPC treated samples. This could also be related to the maturity of starch granules as the storage proceeded.

The above results are well supported by the dynamic frequency sweep test (Fig. 3(A)), given that the large magnitude and frequency independence of storage modulus (G') showed all samples formed strong gels (Lapasin & Pricl, 1999). The gel rigidity (magnitude of G' value) increased with tuber storage time, whereas it decreased after irradiation. The latter decrease should be related to a loss in polymer viscoelasticity that reveals a reduction of the gel structure after irradiation (Esteves, Raymundo, de Sousa, Andrade & Empis, 2002). As shown in Fig. 3(A), G'' curves did not follow the same trend of corresponding G' curves. G'' value could be ignored in the present study as it is no longer reliable when the ratio G''/G' is lower than 0.01 and the value depends on the instrumental resolution of the phase lag between sinusoidal stress and deformation (Lapasin & Pricl, 1999).

Another way of looking at these results is to follow the evolution of complex viscosity (η^*) with respect to the frequency (ω) for the starch gels (Fig. 3(B)) and to fit the curves to power law (Paraskevopoulou et al., 1997). Empirically, both moduli and complex viscosity traces are fitted to power law equations with respect to frequency, and derived parameters can be used as standards/indices for quality control and development of products (Paraskevopoulou et al., 1997). As shown in Table 2, irradiation of potato tubers induced a decrease in gel strength at each tuber storage time, expressed in terms of a consistent reduction in the magnitude of log a^*, whereas the gel strength steadily increased with tuber storage time. However, no change in the structure type was observed, since b^* was similar for all of the starch gels. The square correlation coefficient (R^2) for the fit of storage and loss moduli was in the range 0.94–0.99 (data not shown); however, R^2 of complex viscosity was 1.000 in all cases, indicating that the power law equation can be precisely and successfully applied in the fitting of complex viscosity of potato starch gels for either irradiated or stored potatoes.

The starch and gel samples displayed absorbance peaks at 1047 and 1022 cm^{-1} (Fig. 4(A and B)). The main band at 1047 cm^{-1} characterizes the degree of ordered structure in starch, and the band at 1022 cm^{-1} has been correlated with vibrational modes within the amorphous phase of starch. The ratio between the bands at 1047/1022 cm^{-1} has been used to quantify the degree of short-range ordering in starches (van Soest, Tournois, de Wit, & Vliegenthart, 1995). Similar FTIR spectral patterns were observed in the starch samples (Fig. 4(A)). However, the ratio of absorbance at 1047 cm^{-1} and 1022 cm^{-1} varied with irradiation and storage (Fig. 4(B)). It would appear that the degree of short-range ordering in starch increased significantly with storage ($P \leq 0.05$) but did not vary after irradiation. This result confirmed the results from dynamic viscoelasticity, which showed that starch from stored potatoes displayed enhanced re-crystallization during retrogradation (Fig. 2). Overall, the findings in this study imply that irradiated potatoes might be a good source to produce starch pastes or thickeners because of the easy bursting of the granules and low tendency of starch precipitation due to slow retrogradation, while starch from CIPC treated and stored potatoes might be suitable to use in gel foods such as starch noodles, etc., in which retrogradation of starch gel is an asset for noodle texture. For the starch industry, processing of newly irradiated potatoes should be avoided because of the large amount of starch damage.

5. Conclusion

Low dosage γ-irradiation of potato tubers induced degradation of starch molecules, resulted in greater leaching of granule contents during heating, and resulted in earlier swelling of starch granules compared to control. The early swelling phenomenon was also enhanced with longer tuber storage time. The retrogradation rate and extent of a concentrated starch gel increased with tuber storage time while irradiation seemed to delay retrogradation. The effects of potato irradiation and subsequent storage on starch properties were more evident by rheological measurements, whereas less notably by the chain length distribution of amylopectin molecules and ordered starch structure. The power law equation can be precisely and successfully applied in the fitting of complex viscosity of potato starch gels for either irradiated or stored potatoes. Further study is needed to fully clarify the impact of irradiation treatment on potato starch food applications, and it is suggested that a suitable sprout inhibiting method should be selected based on the processing and texture requirements of the end products.

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