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Effect of γ-irradiation on some physicochemical and thermal properties of cowpea (*Vigna unguiculata* L. Walp) starch

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Abstract

Previously, we reported that starch-related functional properties of cowpea flours and pastes were modified by 2, 10 and 50 kGy γ-irradiation doses. To elucidate some of the effects of γ-irradiation specifically on cowpea starch as well as the actual contribution of starch to the observed functional modifications at the flour and paste level, starch was isolated from irradiated cowpea flours and pastes and studied using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Fourier Transform Infra-Red (FTIR) spectroscopy, Rapid Visco-Analyser (RVA) pasting properties, and some functional properties. Pasting (peak, trough, breakdown, final, and setback viscosities) and swelling properties were significantly decreased in a dose-dependent manner. DSC of cowpea starch showed increases in peak gelatinisation temperature with increasing irradiation dose. SEM (2500×) microphotographs showed that up to 50 kGy irradiation did not present any visible physical effect on the cowpea starch granule. FTIR indicated that starch granule surface order (crystallinity) was not affected by the irradiation doses employed.

Keywords: Cowpea starch; γ-Irradiation; DSC; SEM; FTIR; RVA pasting properties; Functional properties

1. Introduction

In addition to the use of cowpea-based foods as important sources of protein for a vast majority of people in sub-Saharan Africa, the low fat content of cowpea, coupled with the moderate amounts of protein (ca. 25%) and high starch (ca. 55%) contents (Dario & Salgado, 1994; Deshpande & Damodaran, 1990), makes cowpea an important potential source of functional ingredients for the food and non-food industries. The low fat content of cowpea makes defatting prior to protein isolation optional. For this reason, and given the right functional properties, the use of cowpea protein, to complement soy protein that requires defatting, may be enhanced.

Starch is an often-overlooked by-product after protein isolation from cowpeas and other legumes. This might in part be due to the relatively high amylose content of legume starches (Whistler & Daniel, 1985) that tends to confer poor functional properties in many food applications as compared to the more popular maize and root starch sources. However, with the advances made so far in starch modification (Nagasawa, Yagi, Kume, & Yoshii, 2004; Swinkels, 1985), it is possible to re-structure virtually all starches by means of various agents of modification to meet specific and targeted use. Such a modification may enhance the use of legume starches such as cowpea starch and reduce

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over-dependence on the more familiar starch sources. The main traditional use of starch in food systems is as thickeners (Whistler & Daniel, 1985). Non-food applications of starch and its derivatives include their use as biodegradable plastic material (Iman, Gordon, Mao, & Chen, 2001; van Soest, Tournois, deWit, & Vliegenthart, 1995), and in medicines and cosmetics (Choi & Kerr, 2003; Husband, 1998; Thevis, Opfermann, & Schänzer, 2000).

γ-Irradiation is an ionic, no-heat process that continues to receive attention as a preservation and functional modification agent in polymer research and application. γ-Irradiation has been applied to cowpeas in the past for reasons other than for the modification of functional properties (Dario & Salgado, 1994; Diop, Marchioni, Ba, & Hasselmann, 1997). γ-Irradiation has also been used to modify the properties of maize starch extrudates (Sokhey & Chinnaswamy, 1992) and the possibility of modifying the functional properties of cowpea flours and pastes using irradiation has recently been reported (Abu, Muller, Duodu, & Minnaar, 2004). Such modifications were obviously achieved primarily through the effects of irradiation on the major cowpea macromolecules namely, starch and protein. The effects of various doses of irradiation on starch have been shown to include depolymerisation and degradation (Anathaswamy, Vakil, & Sreenivasan, 1970; Sokhey & Hanna, 1993), often resulting in decreased viscosity (Rombo, Taylor, & Minnaar, 2001) or cross-linking (Chatakanonda, Varanivit, & Chinachoti, 2000; Nagasawa et al., 2004). Since the functionality of an individual biopolymer in foods may be affected by its interactions with other food components (Dickinson, 2003), studies on isolated starch might provide a better understanding of the mechanisms involved in irradiation-induced modification of starch-related functionality in multi-component cowpea flours and pastes. To our knowledge, information on the effects of γ-irradiation on cowpea starch physicochemical properties is lacking.

Techniques such as differential scanning calorimetry (DSC), X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), size exclusion HPLC and Fourier transform infrared (FTIR) spectroscopy have been used to study starch molecular and thermal properties (Hohlberg & Stanley, 1987; Rombo, Taylor, & Minnaar, 2004; Sevenou, Hill, Farhat, & Mitchell, 2002; Sokhey & Hanna, 1993; van Soest et al., 1995). Usually, two or more of these methods are used in combination, since none is capable of providing adequate information for describing starch molecular and thermal properties.

Depending on their properties, irradiation-modified cowpea starch may find application in a wide range of industries. Here, we report the physicochemical and thermal properties of starch isolated from 2, 10 and 50 kGy irradiated cowpea flours and pastes.

2. Materials and methods

2.1. Preparation and irradiation of cowpea flours and pastes

Cowpea flour and paste samples (200 g) were sealed in polyethylene bags (ca. 80 μm thick) and kept chilled in ice-cooler boxes prior to and during irradiation. Samples were irradiated at Isotron S.A. in Isando, South Africa, using a ^{60}Co source. Target doses were 2, 10 and 50 kGy. Non-irradiated (control) and irradiated samples were stored at −18 °C. Cowpea pastes were freeze-dried and milled through a 0.8-mm mesh prior to analyses.

2.2. Starch granule isolation

Starch granules were extracted from non-irradiated (control) and irradiated cowpea flours and pastes according to the method described by Taylor, Dewar, Taylor, and von Ascheraden (1997) with some modifications. About 20 g cowpea flour or paste were extracted thrice for salt-soluble proteins with 100 ml of 0.1 M NaCl by stirring (4 °C) for 1 h intervals. The resultant slurry was washed thrice with 100 ml distilled water to extract water-soluble proteins and to rid the slurry of salt. Thereafter, the slurry was passed through a wet mill (Retsch, Haan, Germany) with a 250-μm screen. The liquid containing the starch was centrifuged (800*g*) for 2 min and the fibrous residue on the screen was discarded. After the supernatant was decanted off, the dark protein layer was scraped off. The white pellet left behind was freeze-dried to obtain starch samples.

2.3. Particle size analysis

Starch particle size was determined by a laser diffraction technique, using a long-bench Mastersizer S (Malvern instrument Ltd, Worcester, UK). In this wet dispersion method, ca. 0.1 g sample in 100 ml butanol (dispersion liquid) was pumped at 2000 rpm. Several snapshots of sample were recorded within one measurement and then transformed to a distribution of particle size data using the accompanying software (Mastersizer Sv2.19) according to the Mie theory. The particle size measurement range was 0.05–900 μm. Measurements were made 3 min after loading sample into the dispersion unit. Each sample was measured twice, after which the dispersion unit was cleaned with butanol, followed by analyses of subsequent samples. The mean values for irradiated and non-irradiated cowpea starch samples were noted.

2.4. Functional properties

2.4.1. Water and oil absorption capacities (WAC and OAC)

The water absorption and oil absorption capacities of cowpea starch samples were determined using the AACC method 56–20 (AACC, 2000) as described by Abu et al. (2004).

2.4.2. Swelling index

Starch swelling index was determined using the method of Prinyawiwatkul, McWatters, Beuchat, and Phillips (1997) with modifications, as previously described (Abu et al., 2004).

2.4.3. Gel strength

Gel strength was determined using the method described by Abu et al. (2004). Fourteen percent (w/v) sample dispersions in tap water were heated (90 °C, 30 min) in a water bath, cooled in ice baths for 15 min and stored overnight at 5 °C. Gel strength was then determined using a TA-XT Plus Texture Analyzer (Stable micro systems, Goldalming, Surrey, UK). A 9-mm diameter spindle with a punch area of 0.636 cm^2, penetration depth of 2.0 cm and punch speed of 0.2 cm/s was employed. Force measurements (maximum penetration force) were obtained from the displayed force curve. The penetrating force required to destroy the gel structure was regarded as a measure of the gel strength (N/cm^2).

2.4.4. Pasting properties

Pasting properties were determined using a Rapid Visco-Analyser (RVA model 3D, Newport Scientific, Sydney, Australia). The standard profile 2 of the RVA was employed. With this profile, 2 g samples in 25 ml distilled water were heated from an initial temperature of 50 to 95 °C in 7.3 min, held at this temperature for 5 min and cooled to 50 °C in 7.3 min at a speed of 160 rpm for the first 10 s and 960 rpm for the remainder of the cycle. The pasting properties considered were peak, trough, breakdown, final and setback viscosities.

2.5. Differential scanning calorimetry

DSC was carried out with a micro-DSC III system (Setaram, Caluire, France). Ten percent (w/v) starch samples, dispersed in distilled water, were scanned from 24 to 115 °C at 1 °C/min. The reference pan was filled with distilled water. Peak gelatinisation temperatures and enthalpy values were noted.

2.6. Scanning electron microscopy

Starch samples were fixed on a cylindrical microscope stub covered with carbon strip and coated with a thin layer of gold, followed by observation under a scanning electron microscope (Model ABT-55, Tokyo, Japan). A magnification of 2500× was used.

2.7. Fourier transform infrared

Fourier Transform Infrared measurements were made with a Perkin–Elmer 2000 GX FT-IR Spectrometer adapted with a Perkin–Elmer auto-image microscope system operated in the attenuated total reflectance (ATR) mode. ATR-FTIR is a surface analytical method that can acquire information on the outer region of a starch sample up to a penetration depth of ~2 μm (Sevenou et al., 2002). Samples were placed between high-pressure diamond optics and measured under the microscope in absorbance mode. A deconvolution factor of 2 was used. The absorbances at 1042 and 1024 cm^{-1}were noted from the deconvoluted spectra. Instead of single intensity measurements, ratios of absorbance intensities were used to compensate for path-length differences between samples that might arise from incomplete coverage of the ATR technique, as suggested by van Soest et al. (1995). The infrared ratio of 1042/1024 was calculated per sample to estimate the degree of order (crystallinity) of starch granules at the surface, as described by several workers (Rubens, Snauwaert, Heremans, & Stute, 1999; van Soest et al., 1995) with some modifications.

2.8. Statistical analyses

Functional properties (WAC, OAC, SI and GS), and FTIR were determined at least in triplicate ($n = 3$). Pasting properties, DSC and SEM were determined in duplicate ($n = 2$). Analysis of variance (ANOVA), followed by the least significant difference test (LSD-test), was applied in selected cases. The level of significance used was 95%. Correlations of selected physicochemical and thermal properties were obtained.

3. Results and discussions

3.1. Effect of irradiation on functional and pasting properties of cowpea starch

Irradiation at 2 kGy caused a significant increase in water absorption capacity (WAC) of cowpea starch (Table 1). The increase in WAC with irradiation may in part be due to irradiation-induced damage or degradation of cowpea starch to simpler molecules such as dextrins and sugars that have higher affinity for water than starch (Whistler & Daniel, 1985). Other workers (Sabularse, Liuzzo, Rao, & Grodner, 1992; Sokhey & Hanna, 1993; Wu, Shu, Wang, & Xia, 2002) have also reported depolymerisation of various starches

Table 1
Effect of irradiation (2, 10 and 50 kGy) on functional properties of starch isolated from cowpea flours and pastes

Irradiation dose (kGy)	Water absorption capacity (g water/g sample)	Oil absorption capacity (g oil/g sample)	Swelling index	Gel strength (N/cm^2)
Starch isolated from cowpea flours				
0	1.70^{a} (0.00)	0.78^{a} (0.03)	18.37^{g} (0.12)	9.73^{f} (0.12)
2	1.90^{b} (0.01)	0.83^{b} (0.01)	15.33^{d} (0.06)	7.33^{e} (0.12)
10	1.90^{b} (0.01)	0.95^{d} (0.01)	11.10^{b} (0.26)	4.93^{c} (0.12)
50	1.90^{b} (0.00)	1.10^{g} (0.03)	8.53^{a} (0.15)	3.57^{a} (0.12)
Starch isolated from cowpea pastes				
0	1.90^{b} (0.00)	0.90^{c} (0.01)	18.00^{f} (0.20)	9.80^{f} (0.17)
2	2.00^{c} (0.05)	0.94^{d} (0.01)	16.80^{e} (0.40)	7.47^{e} (0.06)
10	2.00^{c} (0.06)	0.98^{e} (0.00)	13.23^{c} (0.06)	6.47^{d} (0.06)
50	2.10^{d} (0.00)	1.06^{f} (0.02)	11.30^{b} (0.10)	3.87^{b} (0.06)

Values are means ± SD (in parentheses) of three determinations ($n = 3$).
Values followed by the same superscript letter in a column are not significantly ($p > 0.05$) different from each other.

Table 2
Effect of irradiation on pasting properties (cP) of cowpea starch isolated from cowpea flours and pastes irradiated at 2, 10, and 50 kGy

Irradiation dose (kGy)	Peak viscosity	Trough viscosity	Breakdown viscosity	Final viscosity	Setback viscosity
Starch isolated from cowpea flours					
0	1689^{f} (13.0)	1243^{fg} (7.0)	446^{d} (6.0)	2721^{g} (30.0)	1478^{e} (23.0)
2	1081^{d} (20.0)	680^{e} (10.0)	401^{cd} (11.0)	1034^{e} (23.0)	354^{c} (13.0)
10	563^{b} (2.0)	264^{b} (4.0)	299^{bc} (2.0)	385^{b} (3.0)	121^{ab} (1.0)
50	211^{a} (8.0)	141^{a} (5.0)	70^{a} (3.0)	222^{a} (6.0)	81^{a} (1.0)
Starch isolated from cowpea pastes					
0	1653^{f} (19.0)	1168^{f} (136.0)	485^{d} (156.0)	2660^{g} (21.0)	1493^{e} (158.0)
2	1546^{e} (35.0)	1337^{g} (40.0)	208^{b} (6.0)	2327^{f} (70.0)	990^{d} (30.0)
10	1032^{c} (15.0)	560^{d} (16.0)	472^{d} (0.0)	804^{d} (21.0)	244^{bc} (6.0)
50	566^{b} (24.0)	415^{c} (22.0)	152^{ab} (2.0)	605^{c} (24.0)	191^{ab} (2.0)

Values are means ± SD (in parentheses) of duplicate determinations ($n = 2$).
Values followed by the same superscript in a column are not significantly ($p > 0.05$) different from each other.

following irradiation application. At 10 and 50 kGy irradiation doses, however, further increases in WAC did not occur (Table 1). The main chemical effects of ionising radiation on polymers include cross-linking and degradation via chain scission (Nagasawa et al., 2004). According to Chapiro (1962), both processes occur simultaneously and their yields determine the final results of irradiation. It is possible that starch cross-linking occurred more at higher irradiation doses. This possibly counteracted the increases in WAC occasioned by starch degradation at the lower dose since cross-linked starches (having a strong starch-starch association) may be expected to possess lower WACs than their native counterparts. Elevated cross-linking of maize and bean starches through the formation of β-bonds has been reported at high irradiation doses (Rombo et al., 2004).

Oil absorption capacity (OAC) of cowpea starch increased with irradiation in a dose-dependent manner (Table 1). Oil absorption in starch relies predominantly on the physical entrapment of oil within the starch structure, since starch does not possess non-polar sites akin to those found in proteins. The increases in OAC may be related to an increased ability of degraded and/or cross-linked starch to entrap more oil, physically, with increasing irradiation dose.

Table 3
Effect of irradiation on selected bands and band ratios of starches isolated from cowpea flours and pastes as determined by Fourier transform infrared spectroscopy (FTIR)

Irradiation dose (kGy)	Infrared band height		Infrared band ratios
	1042 cm^{-1}	1024 cm^{-1}	1042/1024
Starch isolated from cowpea flours			
0	1.35 (0.02)	1.67 (0.03)	0.81^{a} (0.01)
2	1.38 (0.07)	1.68 (0.02)	0.82^{a} (0.03)
10	1.38 (0.06)	1.67 (0.05)	0.83^{a} (0.03)
50	1.40 (0.04)	1.67 (0.03)	0.84^{a} (0.02)
Starch isolated from cowpea pastes			
0	1.38 (0.03)	1.68 (0.03)	0.82^{a} (0.02)
2	1.35 (0.05)	1.61 (0.05)	0.84^{a} (0.02)
10	1.32 (0.06)	1.61 (0.08)	0.82^{a} (0.02)
50	1.39 (0.03)	1.69 (0.02)	0.82^{a} (0.02)

Values are means ± SD (in parentheses) of five determinations ($n = 5$).
Values followed by the same superscript letter are not statistically different.

At all the doses studied, irradiation caused significant ($p \leqslant 0.05$) reductions in swelling index (SI) and gel strength (GS) of cowpea starch samples (Table 1). Swelling results from the ability of starch to trap and retain water within its structures, prior to and during gelatinisation (Whistler & Daniel, 1985). Such capability is decreased markedly once starch degradation occurs through irradiation application. Since the amylopectin fraction of starch is believed to be primarily responsible for swelling (Tester & Morrison, 1990), the decrease in SI may be related to a high reduction in amylopectin with irradiation. De Kerf, Mondelaers, Lahorte, Vervaet, and Remon (2001) found a significant reduction in amylopectin fraction of various starches with irradiation application. The decrease in GS with irradiation is obviously a direct consequence of reduced starch viscosity (Table 2). SI, being a less expensive method and having high significant correlations with most properties studied (Table 4), may therefore be employed as a rapid qualitative indicator of functional and thermal properties of irradiated cowpea starch with relative success.

As expected, pasting properties (peak, trough, breakdown, final and setback viscosities) were decreased significantly ($p \leqslant 0.05$) by irradiation (Table 2). Similar irradiation-induced decreases in pasting properties have been reported for rice starch (Wu et al., 2002), maize and bean flours (Rombo et al., 2001). Decreases in pasting properties, such as breakdown and setback values, result primarily from irradiation-induced starch degradation and may present opportunities such as ease of cooking and reduced starch retrogradation, respectively (Sabularse et al., 1992).

In general, the extent of irradiation-induced decrease in pasting properties, such as peak, final and setback viscosities (Table 2), as well as SI and GS (Table 1), was greater in starches isolated from irradiated cowpea flours than in those isolated from pastes. This may be due in part to starch cross-linking, occurring more in the pastes during irradiation than in the flours. Highly cross-linked starches may be expected to have relatively higher viscosity than their less cross-linked counterparts. Nagasawa et al. (2004) found that the paste-like condition (40–50% moisture content) was very favourable for irradiation-induced cross-linking of carboxyl methyl starch. It may be inferred, therefore, that irradiation should be carried out under dry conditions if the primary aim is to decrease viscosity of cowpea starch.

3.2. Effect of irradiation on physical properties of cowpea starch granules

Cowpea starch granule sizes were analysed to characterise and determine the effect of irradiation on starch granule size, since granule size is partly important in starch pasting and retrogradation properties (Swinkels, 1985). The results of starch granule size analyses

Table 4
Correlation coefficients (r) of physicochemical and thermal properties of starches isolated from irradiated cowpea flours and pastes

Property	Irradiation dose	PGT	Enthalpy	1042 IR Band	1024 IR Band	1042/1024 Ratio	WAC	OAC	SI	GS	Peak (viscosity)	Trough (viscosity)	Breakdown (viscosity)	Final (viscosity)	Setback (viscosity)
Irradiation dose	1.00	0.71*	−0.33	0.56	0.32	0.32	0.46	0.86*	−0.82*	−0.84*	−0.82*	−0.71*	−0.80*	−0.67	−0.62
PGT	0.71*	1.00	−0.11	0.46	0.03	0.72*	0.24	0.83*	−0.87*	−0.79*	−0.82*	−0.74*	−0.73*	−0.69	−0.63
Enthalpy	−0.33	−0.11	1.00	−0.53	−0.31	−0.33	−0.18	−0.19	0.01	0.18	0.04	−0.17	0.65	−0.17	−0.16
1042 IR Band	0.56	0.46	−0.53	1.00	0.80	0.28	0.06	0.35	−0.45	−0.44	−0.53	−0.45	−0.56	−0.35	−0.26
1024 IR Band	0.32	0.03	−0.31	0.80*	1.00	−0.34	−0.23	−0.05	−0.15	−0.10	−0.26	−0.28	−0.10	−0.13	−0.02
1042/1024 Ratio	0.32	0.72*	−0.33	0.28	−0.34	1.00	0.34	0.60	−0.48	−0.52	−0.43	−0.27	−0.72*	−0.33	−0.37
WAC	0.46	0.24	−0.18	0.06	−0.23	0.34	1.00	0.68	−0.42	−0.56	−0.38	−0.32	−0.42	−0.44	−0.52
OAC	0.86*	0.83*	−0.19	0.35	−0.05	0.60	0.68	1.00	−0.84*	−0.85*	−0.78*	−0.68	−0.75*	−0.68	−0.66
SI	−0.82*	−0.87*	0.01	−0.45	−0.15	−0.48	−0.42	−0.84*	1.00	0.97*	0.99*	0.95*	0.69	0.94*	0.90*
GS	−0.84*	−0.79*	0.18	−0.44	−0.10	−0.52	−0.56	−0.85*	0.97*	1.00	0.96*	0.88*	0.79*	0.92*	0.91*
Peak viscosity	−0.82*	−0.82*	0.04	−0.53	−0.26	−0.43	−0.38	−0.78*	0.99*	0.96*	1.00	0.97*	0.68	0.96*	0.91*
Trough viscosity	−0.71*	−0.74*	−0.17	−0.45	−0.28	−0.27	−0.32	−0.68	0.95*	0.88*	0.97*	1.00	0.48	0.97*	0.92*
Breakdown viscosity	−0.80*	−0.73*	0.65	−0.56	−0.10	−0.72*	−0.42	−0.75*	0.69	0.79*	0.68	0.48	1.00	0.51	0.52
Final viscosity	−0.67	−0.69	−0.17	−0.35	−0.13	−0.33	−0.44	−0.68	0.94*	0.92*	0.96*	0.97*	0.51	1.00	0.98*
Setback viscosity	−0.62	−0.63	−0.16	−0.26	−0.02	−0.37	−0.52	−0.66	0.90*	0.91*	0.91*	0.92*	0.52	0.98*	1.00

Values with asterisks (*) are significantly correlated ($p \leqslant 0.05$).

indicate that both irradiated and control cowpea starch granules ranged from ca. 20–38 to 15–40 μm, obtained by the laser diffraction method (not shown) and SEM (Fig. 3), respectively. These size ranges for cowpea starch granules compare fairly with those reported for horsebean (17–31 μm), wrinkled pea (30–40 μm) (Blanshard, 1987) and for several varieties of cowpea (7.5–37.3 μm) (Agunbiade & Longe, 1999) starches. The laser diffraction data (not shown) and SEM microphotographs show that starch granule size was apparently unaffected by irradiation.

Because of the high reduction in starch viscosity, coupled with the generally held belief that starch degradation occurred with irradiation, we took microphotographs of starch granules obtained from control (0 kGy) and irradiated (50 kGy) cowpea flours using scanning electron microscopy (SEM) at 2500 magnification for evidence of starch granular fissures or splitting. SEM results (Fig. 3) show that cowpea starch granules are made up of several shapes (oval to kidney). Irradiation apparently did not cause fissures or splitting in cowpea starch granules. Sokhey and Hanna (1993) also reported the absence of evidence of physical damage to waxy maize starch granules irradiated at 31 kGy using SEM. Perhaps, irradiation damage to starch granules exist only in the form of changes to the structure of starch molecules (MacArthur & D'Appolonia, 1984).

Irradiated and non-irradiated cowpea starch granules were studied using FTIR spectroscopy for possible irradiation-induced changes in starch granule surface order (crystallinity), using the method described by van Soest et al. (1995). The bands at 1047 and 1022 cm^{-1} are known to be sensitive to changes in the crystalline and amorphous properties of starch, respectively, and their respective ratios indicate the degree of starch order (Sevenou et al., 2002; van Soest et al., 1995). In this study, we assumed that the bands obtained at approximately 1042 and 1024 cm^{-1} (which shifted slightly with irradiation) correspond to the 1047 and 1022 cm^{-1} bands reported by van Soest et al. (1995) for potato starch. Our results seem to suggest that the degree of starch granule surface order (crystallinity) was not affected by up to 50 kGy irradiation dose, given that the ratio of absorbance values at 1042 and 1024 cm^{-1} did not change with irradiation (Table 3). The value of these ratios (ca. 0.8) in general, seems to suggest that cowpea starch is more amorphous than crystalline at the granule surface.

3.3. Effect of irradiation on thermal properties of cowpea starch

Fig. 1 shows the effect of irradiation on cowpea starch peak gelatinisation temperature (PGT) as studied by differential scanning calorimetry (DSC). The PGT values observed for control and irradiated cowpea

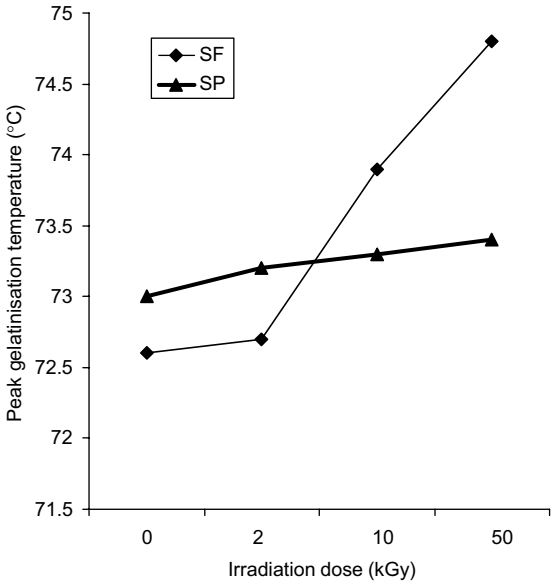

Fig. 1. Effect of irradiation on peak gelatinisation temperature of starch isolated from irradiated cowpea flours (SF) and pastes (SP).

starch samples (Fig. 1) fall within the range (67–78 °C) estimated as gelatinisation temperature for cowpea starch (Okechukwu, Rao, Ngoddy, & McWatters, 1991). Irradiation caused a dose-dependent increase in PGT of cowpea starch. Increases in PGT with irradiation may be related to decreases in the overall crystallinity of starch (Hohlberg & Stanley, 1987). Rayas-Solis (1987) also found an increase in gelatinisation temperature of great northern bean starch irradiated at 20 kGy and attributed this increase to a more disordered (decreased crystallinity) starch granule structure. However, no changes in starch crystallinity could be determined from the FTIR data. Perhaps, the contribution of starch granule surface crystallinity, as determined by FTIR in this work, to the overall starch crystallinity recorded with the DSC, is insignificant. This may imply that measurement of starch granule surface crystallinity using the

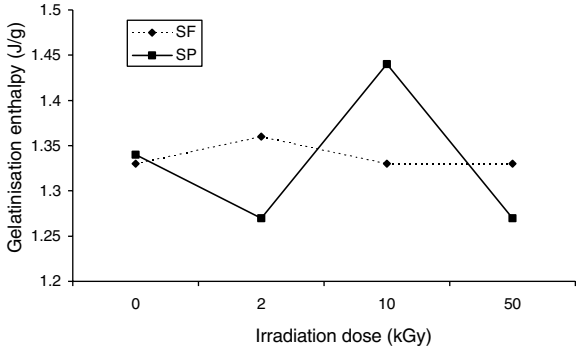

Fig. 2. Effect of irradiation on gelatinisation enthalpy of starch isolated from irradiated cowpea flours (SF) and pastes (SP).

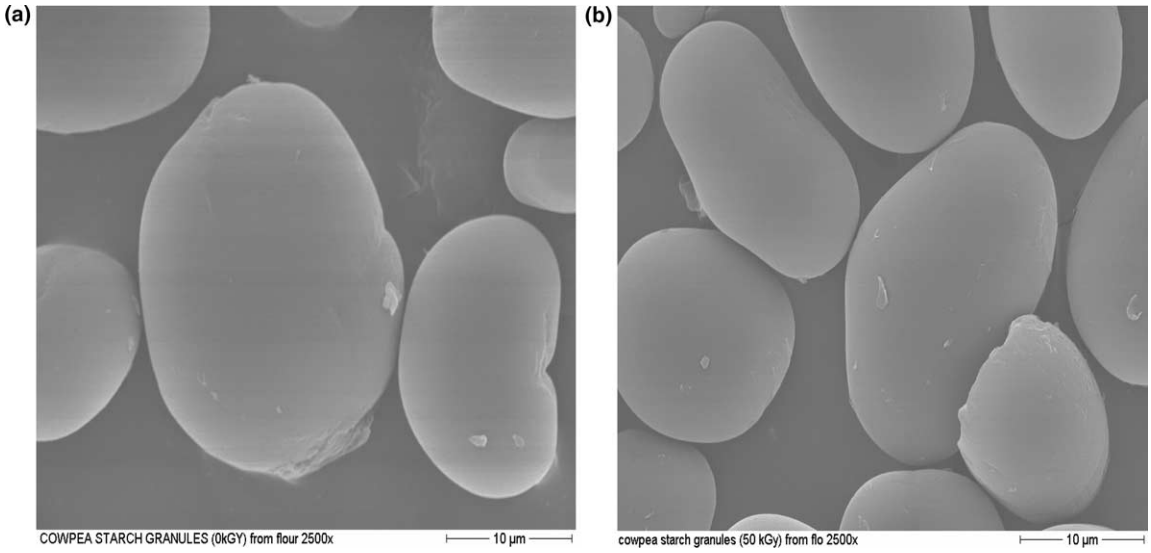

Fig. 3. Scanning electron microscopy (SEM) microphotographs of starch granules isolated from control (a) and 50 kGy-irradiated (b) cowpea flours (2500× mag).

ATR–FTIR might not be sufficient in revealing the effect of irradiation on cowpea starch granules.

The effect of irradiation on cowpea starch gelatinisation enthalpies was not clear-cut (Fig. 2). The fluctuations in enthalpy values with irradiation may be related to the differences in irradiation dose effects on cowpea starch. As mentioned previously, depending on irradiation dose, starch may degrade or cross-link. Chatakanonda et al. (2000) suggested that cross-linking of starch tends to increase the onset temperature of gelatinisation and to decrease the endothermic enthalpy of gelatinisation. Unlike the significant correlations obtained with peak gelatinisation temperature and most irradiated cowpea starch functional properties, no significant correlation was found between cowpea starch enthalpies and the functional properties studied (Table 4). Krueger, Knutson, Inglett, and Walker (1987) showed gelatinisation enthalpy to be highly variable between maize starch varieties while peak temperature showed less variation. Consequently, changes in starch gelatinisation temperatures may be a more useful measure of irradiation-induced changes in cowpea starch than their corresponding enthalpy values.

4. Conclusions

Our data show that γ-irradiation, as low as 2 kGy, significantly modified all cowpea starch pasting and functional properties studied. Swelling index (SI) and peak gelatinisation temperature (PGT) present significant correlations with most cowpea starch physicochemical properties. Differential scanning calorimetry (DSC) shows increase in PGT of cowpea starch, possibly indicating a progressive decrease in overall starch order (crystallinity) with increasing irradiation dose. However, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) seem to suggest that cowpea starch granule physical properties and surface crystallinity respectively, are not affected by γ-irradiation up to 50 kGy.

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