

## Functional properties of cowpea (*Vigna unguiculata* L. Walp) flours and pastes as affected by $\gamma$ -irradiation

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### Abstract

Cowpea flours and pastes were irradiated at 2, 10 and 50 kGy and analysed for their functional properties. At low dose irradiation (2 kGy), most of the protein-related functional properties of cowpea flours and pastes were unaffected. At 10 and 50 kGy, however, all protein-related functional properties, except for water absorption capacity, were significantly ( $p \leq 0.05$ ) affected. Nitrogen solubility index decreased significantly ( $p \leq 0.05$ ), probably due to protein denaturation and/or aggregation, whereas oil absorption capacity increased significantly ( $p \leq 0.05$ ), possibly due to exposure of previously buried non-polar protein sites. Starch-related functional properties, such as swelling and pasting properties, were decreased significantly ( $p \leq 0.05$ ) in a dose-dependent manner, most likely due to starch degradation.

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### 1. Introduction

Cowpea (*Vigna unguiculata* L. Walp) is an important protein source in protein-deficient sub-Saharan Africa. Most of the traditional African cowpea food products, such as *akara* and *moi-moi* (fried and steamed cowpea pastes, respectively), come from West Africa, which is by far the largest producer and consumer of cowpeas (FAO, 2003). Processing of cowpea seeds, to readily hydrateable cowpea flour, has been achieved to minimize difficulties such as high energy and time constraints encountered by the traditional cowpea paste preparation process (Dovlo, Williams, & Zoaka, 1976; Kethireddipalli, Hung, McWatters, & Phillips, 2002). In addition to cowpea foods, such as *akara* and *moi-moi*, several

other food uses of cowpea flour have been extensively reviewed by McWatters (1990).

Some desirable functional properties of cowpea flour, intended for the preparation of food products such as *akara*, have been documented. The ability of inherent proteins to absorb water and to trap air within the batter is very important in cowpea flours, since incorporation of air during whipping to obtain pastes confers the characteristic spongy texture to *akara* (Kethireddipalli et al., 2002). Good foaming ability, on the other hand, is known to correlate positively with cowpea protein content and solubility (Aluko & Yada, 1993; Okaka & Potter, 1979; Phillips, Chinnan, Branch, Miller, & McWatters, 1988). Physicochemical changes in proteins, such as denaturation, may affect functional properties such as water and fat absorption capacities, protein solubility, foaming and, subsequently, cowpea product characteristics (Kerr, Ward, McWatters, & Resurrection, 2000), whereas changes, such as starch degradation

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and debranching, are believed to affect functional properties such as viscosity (Rombo, Taylor, & Minnaar, 2001).

Low dose  $\gamma$ -irradiation has been applied to cowpea seeds, resulting in desirable outcomes such as insect and pest infestation prevention (Diop, Marchioni, Ba, & Hasselmann, 1997) and increased cowpea flour protein digestibility (Dario & Salgado, 1994). However, the effects of  $\gamma$ -irradiation on the functional properties of cowpeas are not known. Gamma-irradiation has been shown to increase water and oil absorption capacities and to decrease emulsion and foam capacities (FCs) in peanut flour (Rahma & Mostafa, 1988) as well as decrease protein solubility in soy (Byun & Kang, 1995; Hafez, Mohamed, Singh, & Hewedy, 1985) and red kidney bean proteins (Dogbevi, Vachon, & Lacroix, 1999). Various reasons were advanced for these irradiation-induced changes, such as protein denaturation, dissociation, exposure of polar and non-polar protein sites, deamination and hydrophobicity. Decreased viscosity, probably due to starch amylopectin depolymerisation, has also been reported for irradiated bean flour in our laboratories (Rombo et al., 2001, Rombo, Taylor, & Minnaar, 2004).

Proteins are believed to be largely responsible for functional properties, such as foaming, emulsification, nitrogen solubility, oil and water absorption (Kinsella, 1979), while viscosity and swelling characteristics are starch-related (Bressani, Singh, & Rachie, 1985). Therefore, changes in the physicochemical properties of protein and starch due to irradiation treatment may lead to modification of functional properties of cowpea flours and pastes. The extent and type of change may depend on irradiation dose employed as well as on the secondary effects of irradiation-induced water radiolysis (Urbain, 1986). Ultimately, the choice of irradiated cowpea flours or pastes as ingredients in food products would rely largely on their functional properties.

The objective of this research therefore, was to determine the effects of low, medium and high dose  $\gamma$  irradiation, under dry (flour) and wet (paste) conditions, on the functional properties of cowpea flours and pastes.

## 2. Materials and methods

### 2.1. Preparation of cowpea flours and pastes

Cleaned cowpea seeds (*Bechuana White* variety), provided by a commercial farm in Potchefstroom, South Africa, were soaked (25 °C, 3 h) in distilled water, oven-dried (50 °C, 18 h), dehulled using a rotary laboratory grain dehuller (50 g per cup, 30–35 s) and milled to pass through a 0.8-mm screen. Cowpea flour particle size was determined using a method described by Phillips et al. (1988). Flour (100 g) was agitated for 1 h on

stacked sieves of decreasing apertures on a mechanical agitator. Retained flour per sieve was weighed and expressed as percentage of original flour weight. The particle size distribution showed that approximately 73% of flour particles were in the 45–180  $\mu\text{m}$  and 27% in the 250–500  $\mu\text{m}$  size range. This particle size range is suitable for preparing *akara* since McWatters (1983) found that at least 66% of cowpea flour particles intended for *akara* processing, should have a particle size range of 45–150  $\mu\text{m}$ .

The cowpea flours used in this study comprised  $9.7 \pm 0.11\%$  moisture,  $1.3 \pm 0.02\%$  crude fat,  $23.7 \pm 0.35\%$  crude protein,  $3.5 \pm 0.06\%$  ash and  $61.8 \pm 0.29\%$  total carbohydrate on a wet basis.

Cowpea pastes were prepared by hydrating appropriate quantities of flours to obtain final moisture contents of 58% since this is the recommended moisture content for pastes intended for *akara* preparation from flours (McWatters, 1983). Water activities of cowpea flours ( $a_w = 0.3$ ) and pastes ( $a_w = 0.9$ ) were obtained by measuring the equilibrium relative humidity (ERH) of samples using a Novasina Thermoconstanter (Novasina AG, Zurich, Switzerland) where  $a_w = \text{ERH}/100$ .

### 2.2. Irradiation of cowpea flours and pastes

Cowpea flour and paste samples (200 g) were sealed in polyethylene bags (ca. 80  $\mu\text{m}$  thick) and kept chilled in ice-cooler boxes prior to and during irradiation. Samples were irradiated at Isotron SA in Isando, South Africa using a  $^{60}\text{Co}$  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.

### 2.3. Functional properties

#### 2.3.1. Nitrogen solubility index

Nitrogen solubility is considered useful in predicting water-lipid interactions (Kinsella, 1976; Mattill, 1971). Nitrogen solubility index (NSI) was determined by the AACC method 46–23 (AACC, 2000). One gramme of sample was stirred for a minimum of 1 h in 0.1 M NaCl solution (1:4 w/v) at pH 7 using an automated sample changer (Metrohm 730) and titrating unit (Metrohm Titrino SM 702) with interchangeable unit operated by a Tinet 2 software programme. Samples were then quantitatively transferred into 50 ml flasks and made to volume using 0.1 M NaCl. About 20 ml of sample suspension was centrifuged at 20,000g (15 min, 15 °C), followed by filtering the clear supernatant obtained through a Whatman No. 1 filter paper. The nitrogen contents of the filtered supernatants were determined by the Dumas method using a nitrogen analyser (model FP-2000; LECO Corp., Warrendale, PA, USA). The protein content was obtained by multiplying nitrogen

contents by the 6.25 conversion factor. The values obtained were expressed as a percentage of sample protein content.

### 2.3.2. Water and oil absorption capacities

Water and oil absorption capacities (WAC and OAC) were determined using the AACC method 56–20 (AACC, 2000) with slight modifications. Two grammes (dry weight basis) of sample was dispersed in 40 ml distilled water or refined canola vegetable oil, vortexed intermittently for 10 min and centrifuged at 1000g (15 min, 20 °C). The aqueous supernatant or clear oil obtained after centrifuging was decanted and the test tubes were inverted and allowed to drain for 5 min on a paper towel. By weighing the residue, WAC and OACs were calculated as grammes of water or oil absorbed per gramme of sample, respectively.

### 2.3.3. Foam capacity

The method described by Akubor, Isolokwu, Ugbanne, and Onimawo (2000) was used with modifications. In the modified method, 5% (w/v) sample dispersions were foamed using a Hobart 50-N kitchen machine. Foam formation was achieved by whipping for 8 min at 20 °C. Foam volume was measured by transferring the foam quantitatively to a 250-ml measuring cylinder and noting the volume. Foam volume was expressed as a percentage of the volume occupied by the sample prior to whipping.

### 2.3.4. Emulsion capacity

Emulsion capacity (EC) was determined using a method described by Marshall, Dutson, and Carpenter (1975). This method involves continuous addition of oil to an oil-in-water emulsion to the point of phase inversion detected by an abrupt breakdown in electrical conductivity. One percent (w/v) sample dispersions were prepared in tap water and titrated with refined canola vegetable oil. A Tinet 2 software programme employing changes in sample voltage (mV), was used. Oil was gradually added from a dispensing unit to a cooled (18 °C) double-jacketed reactor system containing the sample dispersion under the mixing action of an Ultra-Turrax T25 homogeniser (Janke & Kunkel, Staufen, Germany). The endpoint was that point where sample mV dropped sharply below 10 mV and the total volume of oil required to reach this point was regarded as the emulsion capacity of the sample and expressed as ml oil/g sample.

### 2.3.5. Swelling index

The swelling index (SI) of cowpea flour and paste was determined using the method described by Prinyawiwatkul, McWatters, Beuchat, and Phillips (1997), with some modifications. One gramme of sample was weighed into a test tube containing 20 ml water and the test tube was screw-capped and vortexed for 1

min. The tubes were then heated in a water bath (90 °C, 30 min) with intermittent mixing followed by cooling in a bowl of water for 30 s and in ice for 10 min to accelerate gel formation. After centrifuging (4500g, 10 min at 20 °C), cooled samples were allowed to stand for 5 min at ambient temperature and the clear supernatant carefully decanted. The weight of the residue was then noted. SI was considered as the ratio of the final residue weight to the initial sample weight.

### 2.3.6. Gel strength

A preliminary gel-forming test was carried out on all samples. At 18% (w/v) concentration, cowpea flour and paste samples were found to yield strong, firm and stable gels, a prerequisite for strength analysis using the texture analyser. Eighteen 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 (GS) 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<sup>2</sup>, penetration depth of 2.0 cm and punch speed of 0.2 cm/s was employed. Force measurements (maximum penetration force) were then obtained from the displayed force curve. The penetrating force required to destroy the gel structure was regarded as a measure of the GS (N/cm<sup>2</sup>).

### 2.3.7. 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, samples were heated from an initial temperature of 50–95 °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 measured were peak viscosity, trough viscosity, breakdown viscosity, final viscosity and setback viscosity.

### 2.3.8. Colour

Colour was measured using a Hunter Laboratory Instrument Model CIE 1996 (Hunter Associates Laboratory, Inc., Reston, VA, USA) and expressed on the *L*, *a* and *b* tristimulus scale as in the method described by Nnanna, Phillips, McWatters, and Hung (1990).

## 2.4. Amino acid composition and available lysine

### 2.4.1. Amino acid composition

The Pico-Tag method, described by Bidlingmeyer, Cohen, and Tarvin (1984), was used to determine the amino acid composition of non-irradiated (control) and 50 kGy, irradiated cowpea flours. This method involved three main steps: hydrolysis of the protein and peptides to yield free amino acids, pre-column

derivatization of sample and analysis by reverse phase HPLC. The Pico-Tag column part no. 88131 (3.9 mm × 15 cm) was employed and the wavelength detector was operated at 254 nm. The amino acids were then grouped according to their acidic, basic, polar and non-polar side chains, following the scheme reported by McMurry and Castellion (1996).

#### 2.4.2. Available lysine

The furosine method, described by Bujard and Finot (1978), was employed to determine the available lysine in cowpea flours. In this method, blocked lysine was calculated according to the equation: blocked lysine = (3.1 furosine/lysine after acid hydrolysis) + 1.86 furosine.

#### 2.5. Statistical analyses

All analyses were performed in triplicate ( $n = 3$ ) unless otherwise indicated. Analysis of variance (ANOVA), followed by the least significant difference test (LSD test), was applied to all data obtained. Correlation coefficients ( $r$ ) of functional properties were also obtained. The level of significance used was 95%.

### 3. Results and discussion

#### 3.1. Protein-related functional properties, amino acid composition and available lysine

##### 3.1.1. Nitrogen solubility index

NSI (Table 1) was on average, 8.2% higher in non-irradiated (control) cowpea pastes than in irradiated flours, probably because of the longer exposure of paste to water during its preparation. The NSI range recorded for non-irradiated cowpea flours and pastes in the present study compares reasonably well with that reported

(95%) for raw dehulled cowpea cotyledons (Okaka & Potter, 1979).

Irradiation caused significant ( $p \leq 0.05$ ) decreases in NSI of cowpea flours at 10 and 50 kGy but was unaffected at 2 kGy. On the other hand, NSI values of cowpea pastes were significantly decreased at 2 and 10 kGy doses but no subsequent decrease was observed at 50 kGy. Decreases in NSI have also been reported by Hafez et al. (1985) for irradiated soybean seeds and El-Din and Farag (1999) for sunflower meal, as well as decreased protein solubility and aggregation in irradiated soybean protein (Afify & Shousha, 1988). Protein denaturation may result in decreased solubility, due to the exposure of hydrophobic groups, followed by aggregation of the unfolded protein molecules (Cheftel, Cuq, & Lorient, 1985). Since irradiation effects are believed to be similar to those caused by heat treatment (Urbain, 1986), reasons for the observed decreases in nitrogen solubility may include irradiation-induced partial protein denaturation or protein–protein aggregation. In addition, proteins may react with other components in Maillard-type reactions during irradiation, leading to less soluble reaction products.

The  $L$  values for cowpea flours and pastes (Table 5) decreased in a consistent manner with increased irradiation doses. This supports the suggested link between possible Maillard browning reactions and decreases in NSI. However, the observed decrease in available lysine (which is usually associated with Maillard-type reactions) of cowpea flours after irradiation treatments was not statistically significant (Table 4). Under favourable conditions of water activity (such as was recorded in the present research), reducing sugars, and to some extent non-reducing sugars, as well as carbohydrate polymers, may take part in non-enzymatic Maillard browning reactions, leading to the formation of new compounds and a decrease in lysine availability (Smith & Friedman, 1984).

Table 1  
Effect of  $\gamma$ -irradiation, at 2, 10 and 50 kGy, on protein-related functional properties of cowpea flours and pastes

Irradiation dose (kGy)	Nitrogen solubility index (%)	Water absorption capacity (g water/g sample)	Oil absorption capacity (g oil/g sample)	Foam capacity (%)	Emulsion capacity (ml oil/g sample)
<b>Flours</b>					
0	82.6 <sup>c</sup> (0.0)	1.13 <sup>c</sup> (0.06)	0.83 <sup>a</sup> (0.06)	345.0 <sup>c</sup> (5.0)	530.0 <sup>c</sup> (5.0)
2	82.2 <sup>bc</sup> (0.0)	1.10 <sup>bc</sup> (0.00)	0.83 <sup>a</sup> (0.06)	341.0 <sup>abc</sup> (1.7)	520.0 <sup>d</sup> (0.0)
10	82.1 <sup>b</sup> (0.7)	1.13 <sup>c</sup> (0.06)	1.13 <sup>b</sup> (0.06)	337.3 <sup>a</sup> (2.3)	515.0 <sup>d</sup> (0.0)
50	81.4 <sup>a</sup> (0.0)	1.13 <sup>c</sup> (0.06)	1.10 <sup>b</sup> (0.00)	337.0 <sup>a</sup> (1.7)	496.7 <sup>c</sup> (2.9)
<b>Pastes</b>					
0	90.8 <sup>f</sup> (0.0)	1.00 <sup>a</sup> (0.00)	1.30 <sup>c</sup> (0.00)	338.7 <sup>ab</sup> (2.3)	500.0 <sup>c</sup> (0.0)
2	89.8 <sup>e</sup> (0.0)	1.03 <sup>ab</sup> (0.06)	1.30 <sup>c</sup> (0.00)	338.7 <sup>ab</sup> (2.3)	476.7 <sup>a</sup> (2.9)
10	85.2 <sup>d</sup> (0.0)	1.00 <sup>a</sup> (0.00)	1.47 <sup>d</sup> (0.06)	338.7 <sup>ab</sup> (2.3)	486.7 <sup>b</sup> (2.9)
50	85.6 <sup>d</sup> (0.1)	1.03 <sup>ab</sup> (0.06)	1.53 <sup>d</sup> (0.06)	342.3 <sup>bc</sup> (2.5)	490.0 <sup>b</sup> (5.0)

Values are means and standard deviations (in parentheses) of three determinations ( $n = 3$ ).

Values followed by different superscript letters in a column are significantly ( $p \leq 0.05$ ) different from each other.



As expected, the lowering effect of irradiation on NSI was more pronounced in cowpea paste than flour because of the secondary radiolytic effects (Urbain, 1986) of water incorporated during the paste preparation step.

### 3.1.2. Water absorption capacity

The WACs (Table 1) of non-irradiated cowpea flours and pastes compare reasonably well with reported values for cowpea flours (Kerr et al., 2000; Sosulski, Kasi-rye-Alemu, & Sumner, 1987). The significantly ( $p \leq 0.05$ ) lower WAC values for cowpea pastes than for flours, in general, may be as a result of partial water saturation of cowpea protein and starch during paste preparation (Prinyawiwatkul et al., 1997).

Irradiation had no apparent effect on WAC of cowpea flours and pastes. This may be due to the counter-acting effects of irradiation on protein and starch components present in cowpeas. These components both have a potential affinity for water (Narayana & Rao, 1982; Prinyawiwatkul et al., 1997). On the one hand, irradiation-induced unfolding and the ensuing exposure of non-polar protein sites may have led to a reduction in the availability of polar amino groups for water binding (Zayas, 1997), resulting in decreased WAC. A slight decrease in polar amino groups after irradiation at 50 kGy was observed (Table 3). On the other hand, WAC could have increased due to depolymerisation of starch (as shown by decreases in viscosity, Table 2), resulting in short chain dextrans with a higher affinity for water (Whistler & Daniel, 1985).

### 3.1.3. Oil absorption capacity

OACs of non-irradiated cowpea paste and flour samples (Table 1) compare reasonably well with those values reported for whole cowpea flour before and after six months of storage (Abu, Arogba, & Ugwu, 1999) but were lower than those reported for dehulled cowpea seed

Table 3  
Effect of  $\gamma$ -irradiation, at 50 kGy, on amino acid composition (g/100 g sample) of cowpea flour

Amino acid	Non-irradiated cowpea flour (0 kGy)	Irradiated cowpea flour (50 kGy)
<i>Acidic side chains</i>		
Aspartic	2.76 <sup>a</sup> (0.03)	2.59 <sup>b</sup> (0.00)
Glutamic	4.29 <sup>a</sup> (0.01)	4.08 <sup>b</sup> (0.03)
Sub-total	7.05	6.67
<i>Basic side chains</i>		
Histidine	0.73 <sup>a</sup> (0.01)	0.66 <sup>b</sup> (0.01)
Arginine	1.69 <sup>a</sup> (0.01)	1.59 <sup>a</sup> (0.05)
Lysine	1.66 <sup>a</sup> (0.02)	1.53 <sup>b</sup> (0.03)
Sub-total	4.08	3.78
<i>Polar side chains</i>		
Tryptophan	0.08 <sup>a</sup> (0.01)	0.08 <sup>a</sup> (0.01)
Serine	1.41 <sup>a</sup> (0.00)	1.33 <sup>b</sup> (0.01)
Threonine	1.06 <sup>a</sup> (0.00)	0.99 <sup>a</sup> (0.04)
Tyrosine	0.68 <sup>a</sup> (0.01)	0.79 <sup>b</sup> (0.01)
Cysteine	0.23 <sup>a</sup> (0.00)	0.21 <sup>b</sup> (0.01)
Sub-total	3.46	3.40
<i>Non-polar side chains</i>		
Alanine	1.10 <sup>a</sup> (0.01)	1.05 <sup>b</sup> (0.00)
Proline	1.03 <sup>a</sup> (0.01)	0.97 <sup>b</sup> (0.01)
Valine	1.12 <sup>a</sup> (0.00)	1.04 <sup>b</sup> (0.01)
Methionine	0.35 <sup>a</sup> (0.01)	0.30 <sup>b</sup> (0.01)
Isoleucine	0.93 <sup>a</sup> (0.01)	0.88 <sup>b</sup> (0.01)
Leucine	1.84 <sup>a</sup> (0.01)	1.74 <sup>b</sup> (0.01)
Phenylalanine	1.38 <sup>a</sup> (0.01)	1.31 <sup>b</sup> (0.01)
Glycine	0.93 <sup>a</sup> (0.01)	0.86 <sup>b</sup> (0.01)
Sub-total	8.69	8.15

Values are means and standard deviations in (parentheses) of duplicate determinations ( $n = 2$ ).

Values followed by a different superscript letter in a row are significantly ( $p \leq 0.05$ ) different from each other.

flour and wet-processed cowpea protein concentrate (Sosulski et al., 1987). The mechanism of oil absorption involves the physical entrapment of oil by food components and the affinity of non-polar protein side chains for lipids (Kinsella, 1979; Sathe, Deshpande, & Salunkhe, 1982).

Table 2  
Effect of  $\gamma$ -irradiation, at 2, 10 and 50 kGy, on the pasting properties, swelling index and gel strength of cowpea flours and pastes

Irradiation dose (kGy)	Peak viscosity (cP)	Trough viscosity (cP)	Breakdown viscosity (cP)	Final viscosity (50 °C) (cP)	Setback viscosity (cP)	Swelling index	Gel strength (N/cm <sup>2</sup> )
<b>Flours</b>							
0	4807.7 <sup>c</sup> (148.3)	1974.0 <sup>c</sup> (142.2)	2833.7 <sup>e</sup> (288.7)	4708.7 <sup>f</sup> (15.0)	2734.7 <sup>c</sup> (140.6)	9.39 <sup>f</sup> (0.24)	4.70 <sup>f</sup> (0.10)
2	2888.3 <sup>d</sup> (145.2)	1298.0 <sup>c</sup> (67.2)	1590.3 <sup>f</sup> (210.4)	2940.7 <sup>d</sup> (132.2)	1642.7 <sup>d</sup> (192.6)	8.00 <sup>e</sup> (0.08)	3.93 <sup>d</sup> (0.06)
10	1573.0 <sup>c</sup> (96.6)	636.0 <sup>b</sup> (65.8)	937.0 <sup>bc</sup> (51.0)	1260.7 <sup>b</sup> (91.2)	624.7 <sup>b</sup> (37.2)	6.33 <sup>c</sup> (0.15)	3.20 <sup>c</sup> (0.00)
50	448.7 <sup>a</sup> (66.2)	113.7 <sup>a</sup> (15.9)	335.0 <sup>a</sup> (50.5)	229.7 <sup>a</sup> (28.6)	116.0 <sup>a</sup> (13.5)	2.12 <sup>a</sup> (0.02)	2.53 <sup>a</sup> (0.06)
<b>Pastes</b>							
0	7598.0 <sup>f</sup> (8.5)	6591.0 <sup>e</sup> (8.5)	1007.0 <sup>cde</sup> (17.0)	7586.5 <sup>e</sup> (2.1)	995.5 <sup>c</sup> (6.4)	8.21 <sup>c</sup> (0.22)	5.33 <sup>e</sup> (0.06)
2	2868.5 <sup>d</sup> (620.1)	2254.0 <sup>f</sup> (308.3)	614.5 <sup>ab</sup> (311.8)	3821.0 <sup>c</sup> (837.2)	1567.0 <sup>d</sup> (528.9)	7.96 <sup>c</sup> (0.19)	4.67 <sup>f</sup> (0.06)
10	2610.0 <sup>d</sup> (166.9)	1627.5 <sup>d</sup> (87.0)	982.5 <sup>bd</sup> (79.9)	2353.0 <sup>c</sup> (161.2)	725.5 <sup>bc</sup> (74.2)	7.26 <sup>d</sup> (0.09)	4.53 <sup>e</sup> (0.06)
50	1147.5 <sup>b</sup> (47.4)	481.0 <sup>b</sup> (12.7)	666.5 <sup>abc</sup> (34.6)	662.0 <sup>a</sup> (33.9)	181.0 <sup>a</sup> (21.2)	5.19 <sup>b</sup> (0.11)	3.03 <sup>b</sup> (0.06)

Values are means and standard deviations (in parentheses) of three determinations ( $n = 3$ ).

Values followed by different superscript letters in a column are significantly ( $p \leq 0.05$ ) different from each other.

Table 4  
Effect of  $\gamma$ -irradiation, at 2, 10 and 50 kGy, on total and available lysine of cowpea flours

Irradiation dose (kGy)	Total lysine (g/g sample)	Available lysine (g/g sample)
0	1.58 <sup>a</sup> (0.04)	1.56 <sup>a</sup> (0.04)
2	1.56 <sup>a</sup> (0.01)	1.55 <sup>a</sup> (0.01)
10	1.57 <sup>a</sup> (0.05)	1.56 <sup>a</sup> (0.05)
50	1.53 <sup>a</sup> (0.01)	1.52 <sup>a</sup> (0.01)

Values are means and standard deviations (in parentheses) of duplicate determinations ( $n = 2$ ).

Values followed by the same superscript letter in a row are not significantly ( $p > 0.05$ ) different from each other.

Table 5  
Effect of  $\gamma$ -irradiation, at 2, 10 and 50 kGy, on colour ( $L$ ,  $a$ ,  $b$  values) of cowpea flours and pastes

Irradiation dose (kGy)	$L$	$a$	$b$
<i>Flours</i>			
0	92.5 <sup>c</sup> (0.3)	-5.0 <sup>a</sup> (0.1)	15.2 <sup>a</sup> (0.5)
2	91.8 <sup>c</sup> (0.3)	-5.1 <sup>a</sup> (0.1)	15.2 <sup>a</sup> (0.5)
10	91.0 <sup>c</sup> (0.5)	-4.9 <sup>a</sup> (0.1)	15.5 <sup>a</sup> (0.5)
50	88.7 <sup>d</sup> (1.2)	-4.0 <sup>b</sup> (0.2)	16.5 <sup>b</sup> (0.1)
<i>Pastes</i>			
0	75.1 <sup>bc</sup> (4.5)	-3.4 <sup>c</sup> (0.8)	22.0 <sup>c</sup> (0.9)
2	73.1 <sup>a</sup> (5.5)	-3.1 <sup>d</sup> (0.6)	21.2 <sup>d</sup> (1.4)
10	73.7 <sup>ac</sup> (5.1)	-2.7 <sup>e</sup> (0.4)	20.5 <sup>c</sup> (1.9)
50	73.6 <sup>ab</sup> (2.6)	-2.3 <sup>f</sup> (0.7)	20.5 <sup>c</sup> (2.1)

Values are means and standard deviations (in parentheses) of nine determinations ( $n = 9$ ).

Values followed by the same superscript letter in a column are not significantly ( $p > 0.05$ ) different from each other.

$L$  = Lightness (0 = black, 100 = white),  $+a$  = redness,  $-a$  = greenness,  $+b$  = yellowness,  $-b$  = blueness.

When compared to WAC, the higher OAC values may imply that non-polar amino acid residues predominate in cowpea flour and paste proteins. This is consistent with the amino acid profile of cowpea flour reported in Table 3.

Although irradiation at 2 kGy did not change OAC significantly, irradiation at 10 kGy significantly ( $p \leq 0.05$ ) increased OAC values in both cowpea flours

and pastes. No further increases in OAC were found at the higher dose level. Increases in OAC up to 10 kGy may be due to unmasking of non-polar protein residues as a result of irradiation-induced denaturation (Urbain, 1986). Increased hydrophobicity due to irradiation exposure of previously buried non-polar protein sites has also been reported for red kidney bean proteins at 2 kGy (Dogbevi et al., 1999). It is interesting to note that cowpea pastes had higher OAC than their flour counterparts before and after irradiation, possibly due to changes in the proteins of the pastes as a result of different preparation procedures used.

### 3.1.4. Foam capacity

Foaming capacities of cowpea flours and pastes, before and after irradiation (Table 1), were higher than those reported for dehulled cowpea flour and air classified protein concentrates at their native pH (Sosulski et al., 1987). Perhaps differences in the chemical compositions of cowpea cultivars and protein solubility might have accounted for the observed differences in FC.

Irradiation at 10 kGy decreased the FC of cowpea flours significantly ( $p < 0.05$ ), probably owing to extensive protein denaturation. It has been suggested that foaming properties are negatively related to protein denaturation in that native proteins have higher foaming abilities than denatured proteins (Yasumatsu et al., 1972). Although higher protein denaturation would have been expected, given the additional radiolytic effect of added water, cowpea pastes were seemingly unaffected ( $p > 0.05$ ) by up to 50 kGy irradiation. A combination of both protein aggregation and fragmentation, occurring more in cowpea pastes, could have resulted in proteins with low (protein aggregates) as well as high (peptides and amino acids) foaming capacities, respectively. These counteracted each other with regard to foaming ability, leading to the observed insignificant change in FC of cowpea pastes on irradiation. Positive correlations ( $r = 0.56$ ) between foaming properties and nitrogen solubility, such as was observed in cowpea flours (Table 6a) have been reported elsewhere for cow-

Table 6a  
Correlation coefficients ( $r$ ) for cowpea flour functional properties

Functional property	WAC	OAC	FC	EC	SI	GS	NSI	PEAK $\mu$	FINAL $\mu$
WAC		0.23	0.08	-0.02	-0.13	-0.04	-0.31	-0.07	-0.08
OAC	0.23		-0.59*	-0.68*	-0.75*	-0.82*	-0.56	-0.82*	-0.85*
FC	0.08	-0.59*		0.75*	0.64*	0.79*	0.56	0.79*	0.79*
EC	-0.02	-0.68*	0.75*		0.97*	0.95*	0.82*	0.93*	0.92*
SI	-0.13	-0.75*	0.64*	0.97*		0.95*	0.83*	0.92*	0.92*
GS	-0.04	-0.82*	0.79*	0.95*	0.95*		0.79*	0.99*	0.99*
NSI	-0.31	-0.56	0.56	0.82*	0.83*	0.79*		0.79*	0.78*
PEAK $\mu$	-0.07	-0.82*	0.79*	0.93*	0.92*	0.99*	0.79*		1.00*
FINAL $\mu$	-0.08	-0.85*	0.79*	0.92*	0.92*	0.99*	0.78*	1.00*	

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

Table 6b  
Correlation coefficients (*r*) for cowpea pastes functional properties

Functional property	WAC	OAC	FC	EC	SI	GS	NSI	PEAK $\mu$	FINAL $\mu$
WAC		0.00	0.16	-0.17	-0.18	-0.31	-0.04	-0.29	-0.24
OAC	0.00		0.34	0.04	-0.87*	-0.81*	-0.90*	-0.69*	-0.81*
FC	0.16	0.34		0.10	-0.61*	-0.60*	-0.34	-0.37	-0.42
EC	-0.17	0.04	0.10		-0.02	0.18	0.14	0.63*	0.47
SI	-0.18	-0.87*	-0.61*	-0.02		0.97*	0.74*	0.72*	0.82*
GS	-0.31	-0.81*	-0.60*	0.18	0.97*		0.72*	0.82*	0.88*
NSI	-0.04	-0.90*	-0.34	0.14	0.74*	0.72*		0.77*	0.87*
PEAK $\mu$	-0.29	-0.69*	-0.37	0.63*	0.72*	0.82*	0.77*		0.98*
FINAL $\mu$	-0.24	-0.81*	-0.42	0.47	0.82*	0.88*	0.87*	0.98*	

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

pea (Okaka & Potter, 1979) and winged bean flour (Narayana & Rao, 1982).

### 3.1.5. Emulsion capacity

The emulsifying properties (Table 1) of non-irradiated cowpea flours and pastes employed in the present study were found to be superior to that of soy flour (Okaka & Potter, 1979) and unpublished values for soy and lupin protein isolates obtained from Fraunhofer IVV laboratory in Freising, Germany. This may partly be explained by the higher NSI values of the cowpea flours and pastes used in this study.

Irradiation at 2, 10 and 50 kGy caused significant ( $p \leq 0.05$ ) decreases in EC of cowpea flours and pastes when compared with the non-irradiated (control) samples, consistent with the decreases in NSI (Table 1). A significant positive correlation ( $r = 0.82$ ) was recorded between EC and NSI in cowpea flours but not with the pastes. The decreases in EC might be related to the changes in proteins previously described for NSI. Changes, such as protein aggregation as well as surface hydrophobicity and charge characteristics, affect emulsifying capacity in different ways (Cheftel et al., 1985). Significant positive correlations between protein hydrophobicity and emulsifying properties of five different proteins have also been reported (Kato, Osako, Matsuomi, & Kobayashi, 1983).

### 3.1.6. Amino acid composition

Table 3 shows non-irradiated (control) and irradiated cowpea flours to be rich in glutamic and aspartic acid, moderate in terms of the essential amino acids, lysine, phenylalanine, leucine, valine and threonine but low in tryptophan, cysteine, and methionine. A similar amino acid profile has been reported for cowpea proteins (Sosulski et al., 1987). Based on the values in Table 3, the calculated acidic, basic, polar and non-polar amino acids in non-irradiated (control) cowpea flour were 7.05, 4.08, 3.46 and 8.69 (g/100 g sample), respectively.

With the exception of tyrosine, that increased significantly ( $p \leq 0.05$ ), the amino acids in cowpea flour decreased significantly ( $p \leq 0.05$ ) at 50 kGy. Decreases in

arginine, and tryptophan were, however, statistically insignificant ( $p > 0.05$ ).

### 3.1.7. Available lysine

Most (98.7%) of the total lysine (Table 4) in non-irradiated cowpea flour was available. Irradiation up to 50 kGy dose did not cause a significant reduction in lysine availability ( $p > 0.05$ ), although decreases (about 1%) in available lysine with 2, 10 and 50 kGy irradiation doses were recorded, similar to the decreases in the amino acid profile of 50 kGy irradiated cowpea flour (Table 4). The decreases in available lysine, coupled with the colour results, seem to suggest that some browning may have occurred in cowpea flours and pastes with irradiation treatment.

## 3.2. Starch-related functional properties

### 3.2.1. Swelling index and gel strength

The SIs of cowpea flours were decreased by 14.8%, 32.6% and 77.4% and pastes by 3.1%, 11.6% and 36.8% with 2, 10 and 50 kGy irradiation doses, respectively (Table 2). Irradiation also reduced the GS of cowpea flours and pastes in a dose-dependent manner (Table 2). The values for swelling index correlated positively ( $r = 0.95$  and  $0.97$ ) with the GS values in cowpea flours and pastes, respectively (Tables 6a and 6b). Irradiation-induced decreases in swelling and GS in cowpea flours and pastes might be direct consequences of viscosity decreases owing to starch degradation (Rombo et al., 2001, 2004). Degradation of starch in cowpea flours and pastes may have inhibited the ability of the starch granules to trap water and to swell during gelatinisation, leading to the observed decreases with irradiation (Whistler & Daniel, 1985).

### 3.2.2. Pasting properties

In most cases, the pasting properties (peak, trough, breakdown, final and setback viscosities) of cowpea flours and pastes decreased significantly ( $p \leq 0.05$ ) with increased irradiation doses (Table 2). For example, final viscosities of cowpea flours decreased by 37.5%, 73.2%

and 95.1% and pastes by 49.6%, 69.0% and 91.3% after 2, 10 and 50 kGy irradiation doses, respectively. Similar observations were made with irradiated rice (Wu, Shu, Wang, & Xia, 2002), maize and kidney bean flours (Rombo et al., 2001). The observed decreases in pasting properties with irradiation were probably due to starch molecular changes, such as starch degradation and debranching to simpler units (Rombo et al., 2001, 2004).

High positive correlations (Tables 6a and 6b) were observed between peak viscosity and SI, and peak viscosity and GS for cowpea flours ( $r = 0.92$  and  $0.99$ , respectively) and pastes ( $r = 0.72$  and  $0.82$ , respectively). Similar correlations were found between final viscosity, SI and GS for both cowpea flours and pastes. Crosbie (1991) also observed a high positive correlation between starch swelling volume and starch paste peak viscosity for wheat flour. SI, being a simpler and less expensive technique, might therefore, be a useful alternative index to paste peak viscosity measurements for characterising the performance of starch in starch-based food products.

#### 4. Conclusions

At low dose irradiation (2 kGy), most of the protein-related functional properties of cowpea flours and pastes are not affected. However, higher doses (i.e. 10 and 50 kGy) affect NSI, OAC, FC, and EC of cowpea flours and pastes significantly. Decreases in NSI may be due to irradiation-induced protein denaturation and/or protein aggregation, whereas increases in OAC may be due to exposure of previously buried non-polar protein sites.

Starch-related functional properties of cowpea flours and pastes, such as SI, GS and viscosity, are significantly decreased at all irradiation doses in a dose-dependent manner, presumably because of starch degradation.

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#### References

Abu, J. D., Arogba, S. S., & Ugwu, F. M. (1999). The effects of post harvest handling on physical, chemical and functional properties of

- cowpea (*Vigna unguiculata* L. Walp) seed. *Journal of the Science of Food and Agriculture*, 79, 1325–1330.
- Afify, A. M. R., & Shousha, M. A. (1988). Effect of low-dose irradiation on soybean protein solubility, trypsin inhibitor activity and protein patterns separated by polyacrylamide gel electrophoresis. *Journal of Agricultural and Food Chemistry*, 36, 810–813.
- Akubor, P. I., Isolokwu, O., Ugbane, O., & Onimawo, I. A. (2000). Proximate composition and functional properties of African breadfruit kernel and flour blends. *Food Research International*, 33, 707–712.
- Aluko, R. E., & Yada, R. Y. (1993). Relationship of hydrophobicity and solubility with some functional properties of cowpea (*Vigna unguiculata*) protein isolate. *Journal of the Science of Food and Agriculture*, 62, 331–335.
- American Association of Cereal Chemists, AACC (2000). *Approved Methods of the AACC* (10th ed.) St Paul, MN: AACC.
- Bidlingmeyer, B. A., Cohen, S. A., & Tarvin, T. L. (1984). Rapid analysis of amino acids using pre-column derivatization. *Journal of Chromatography*, 336, 93–104.
- Bressani, R., Singh, S. R., & Rachie, K. O. (1985). In *Cowpea research, production and utilization* (pp. 353–359). New York: Wiley.
- Bujard, E., & Finot, P. A. (1978). Mesure de la disponibilité et du blocage de la lysine dans les laits industriels. *Annales de la Nutrition et de l'Alimentation*, 32, 291–305.
- Byun, M., & Kang, I. (1995). Properties of soya milk and tofu prepared with  $\gamma$ -irradiated soyabeans. *Journal of the Science of Food and Agriculture*, 67, 477–483.
- Cheftel, J. C., Cuq, J. L., & Lorient, D. (1985). In O. R. Fennema (Ed.), *Food chemistry* (2nd ed., pp. 245–369). New York: Marcel Dekker.
- Crosbie, G. B. (1991). The relationship between starch swelling properties, paste viscosity and boiled noodle quality. *Journal of Cereal Science*, 13, 145–150.
- Dario, A. C., & Salgado, J. M. (1994). Effect of thermal treatments on the chemical and biological value of irradiated and non-irradiated cowpea bean (*Vigna unguiculata* L. Walp) flour. *Plant Foods for Human Nutrition*, 46, 181–186.
- Diop, Y. M., Marchioni, E., Ba, D., & Hasselmann, C. (1997). Radiation disinfestation of cowpea seeds contaminated by *Callosobruchus maculatus*. *Journal of Food Processing and Preservation*, 21, 69–81.
- Dogbevi, M. K., Vachon, C., & Lacroix, M. (1999). Physico-chemical properties of dry red kidney bean proteins and natural microflora as affected by gamma irradiation. *Journal of Food Science*, 64, 540–542.
- Dovlo, F.D., Williams, C.E & Zoaka, L. (1976). In *Cowpeas, Home preparation and use in West Africa*. International Development Research Center (IDRC – 055e). Ottawa, Canada.
- El-Din, M. D., & Farag, H. (1999). Effect of radiation and other processing methods on protein quality of sunflower meal. *Journal of the Science of Food and Agriculture*, 79, 1565–1570.
- Food and Agricultural Organisation (FAO). (2003). Food and Agricultural Organisation World Dry Cowpea Production Figures. <http://faostat.fao.org/faostat/> accessed in June, 2004.
- Hafez, Y. S., Mohamed, A. I., Singh, G., & Hewedy, F. M. (1985). Effects of gamma irradiation on proteins and fatty acids of soybean. *Journal of Food Science*, 50, 1271–1274.
- Kato, A., Osako, Y., Matsudomi, N., & Kobayashi, K. (1983). Changes in the emulsifying and foaming properties of proteins during heat denaturation. *Agricultural and Biological Chemistry*, 47, 33–37.
- Kerr, W. L., Ward, C. D. W., McWatters, K. H., & Resurreccion, A. V. A. (2000). Milling and particle size of cowpea flour and snack chip quality. *Food Research International*, 34, 39–45.
- Kethireddipalli, P., Hung, Y.-C., McWatters, K. H., & Phillips, R. D. (2002). Effect of milling method (wet and dry) on the functional



- properties of cowpea (*Vigna unguiculata*) pastes and end product (akara) quality. *Journal of Food Science*, 67, 48–52.
- Kinsella, J. E. (1976). Functional properties of proteins in foods: a survey. *CRC reviews in Food Science and Nutrition*, 7, 219.
- Kinsella, J. E. (1979). Functional properties of soyproteins. *Journal of the American Oil Chemists' Society*, 56, 242–258.
- Marshall, W. H., Dutson, T. R., & Carpenter, Z. L. (1975). A simple method for emulsion end-point determination. *Journal of Food Science*, 40, 896–897.
- Mattill, K. F. (1971). The functional requirements of proteins in foods. *Journal of the American Oil Chemists Society*, 48, 477.
- McMurry, J., & Castellion, M.E. (1996). *Fundamentals of general, organic, and biological chemistry*. (p. 517) New Jersey, USA: Prentice-Hall.
- McWatters, K. H. (1983). Compositional, physical, and sensory characteristics of Akara processed from cowpea paste and Nigerian cowpea flour. *Cereal Chemistry*, 60, 333–336.
- McWatters, K. H. (1990). Functional characteristics of cowpea flours in foods. *Journal of the American Oil Chemists' Society*, 67, 272–275.
- Narayana, K., & Rao, N. M. S. (1982). Functional properties of raw and heat processed winged bean (*Psophocarpus tetragonolobus*) flour. *Journal of Food Science*, 42, 534–538.
- Nnanna, I. A., Phillips, D. R., McWatters, K. H., & Hung, Y. C. (1990). Effect of germination on the physical, chemical, and sensory characteristics of cowpea products; flour, paste, and akara. *Journal of Agricultural and Food Chemistry*, 38, 812–816.
- Okaka, J. C., & Potter, N. N. (1979). Sensory, nutritional and storage properties of cowpea powders processed to reduce beany flavour. *Journal of Food Science*, 44, 1539–1542.
- Phillips, R. D., Chinnan, M. S., Branch, A. L., Miller, J., & McWatters, K. H. (1988). Effects of pretreatment on functional and nutritional properties of cowpea meal. *Journal of Food Science*, 53, 805–809.
- Prinyawiwatkul, W., McWatters, K. H., Beuchat, L. R., & Phillips, R. D. (1997). Functional characteristics of cowpea (*Vigna unguiculata*) flour and starch as affected by soaking, boiling and fungal fermentation before milling. *Food Chemistry*, 58, 361–372.
- Rahma, E. H., & Mostafa, M. M. (1988). Functional properties of peanut flour as affected by different heat treatments. *Journal of Food Science and Technology*, 25, 11–15.
- Rombo, G. O., Taylor, J. R. N., & Minnaar, A. (2001). Effect of irradiation, with and without cooking of maize and kidney bean flours, on porridge viscosity and in vitro starch digestibility. *Journal of the Science of Food and Agriculture*, 81, 497–502.
- Rombo, G. O., Taylor, J. R. N., & Minnaar, A. (2004). Irradiation of maize and kidney bean flours: effects on starch physicochemical properties. *Journal of the Science of Food and Agriculture*, 84, 350–356.
- Sathe, S. K., Deshpande, S. S., & Salunkhe, D. K. (1982). Functional properties of winged bean proteins. *Journal of Food Science*, 47, 503.
- Smith, G. A., & Friedman, M. (1984). Effect of carbohydrates and heat on the amino acid composition and chemically available lysine content of casein. *Journal of Food Science*, 49, 817–820.
- Sosulski, F. W., Kasirye-Alemu, E. N., & Sumner, A. K. (1987). Microscopic, nutritional and functional properties of cowpea flours and protein concentrates during storage. *Journal of Food Science*, 52, 700–706.
- Urbain, W.M. (1986). *Food irradiation*. (pp. 37–81) New York: Academic Press.
- Whistler, R. L., & Daniel, J. R. (1985). In O. R. Fennema (Ed.), *Food Chemistry* (2nd ed., pp. 69–125). New York: Marcel Dekker.
- Wu, D., Shu, Q., Wang, Z., & Xia, Y. (2002). Effect of gamma irradiation on starch viscosity and physicochemical properties of different rice. *Radiation Physics and Chemistry*, 65, 79–86.
- Yasumatsu, K., Sawada, K., Moritaka, S., Misaki, M., Toda, J., Wada, T., & Ishii, K. (1972). Whipping and emulsifying properties of soybean products. *Agricultural and Biological Chemistry*, 36, 719.
- Zayas, J.F (1997). *Functionality of proteins in food*. (p.81) New York: Springer.