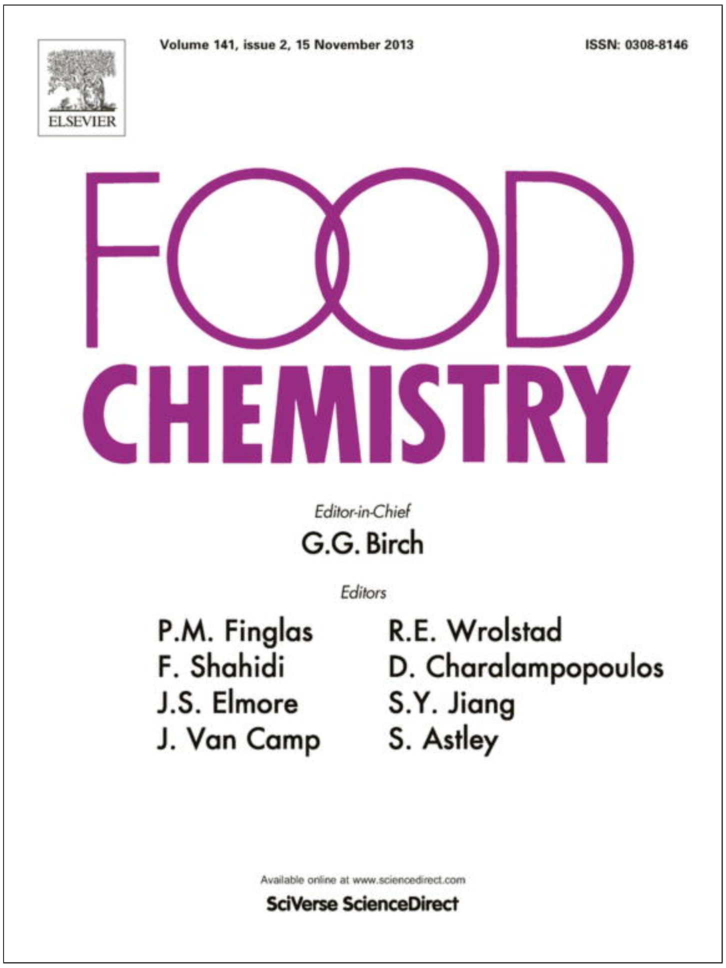

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Functional, thermal and molecular behaviours of ozone-oxidised cocoyam and yam starches

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ABSTRACT

Ozone-oxidised starches were prepared from the native starches isolated from white and red cocoyam, and white and yellow yam cultivars. The native and oxidised starches were evaluated for functional, thermal and molecular properties. The correlations between the amount of reacted ozone and carbonyl and carboxyl contents of the starches were positive, as ozone generation time (OGT) increased. Significant differences were obtained in terms of swelling power, solubility, pasting properties and textural properties of the native starches upon oxidation. The DSC data showed lower transition temperatures and enthalpies for retrograded gels compared to the gelatinized gels of the same starch types. The native starches showed C_B-type XRD patterns while the oxidised starches resembled the C_A-type pattern. As amylose content increased, amylopectin contents of the starches decreased upon oxidation. Similarly, an increase in M_w values were observed with a corresponding decrease in M_n values upon oxidation.

1. Introduction

Starch, a biocompatible, biodegradable, nontoxic polymer (Weslen & Weslen, 2002), which occurs widely in nature, has become one of the most important renewable resources for the food and non-food industries due to a host of advantages. These include low density, cost effectiveness, abundant supply and environmental amity (Oladebeye, Oshodi, Oladebeye, & Amoo, 2011). In its native form, starch is unusable for some applications. The undesirable behaviours of native starch can be reduced or eliminated through modifications; by reorganising the structural arrangement of the starch granules, resulting in enhanced physicochemical properties. Oxidation is one such modification. Oxidized starches have gained significant application in food products that require neutral taste and low-viscosity, such as salad cream, mayonnaise and lemon curd, and non-food products that require surface sizing and coating properties (Lawal, 2004; Lawal, Adebowale, Ogunsanwo, Barba, & Ilo, 2005).

During oxidation, starch hydroxyl groups are oxidised first to carbonyl groups and then to carboxyl groups, which is accompanied by depolymerization of starch molecules mainly by cleavage of amylose and amylopectin molecules at α-(1$\rightarrow$4)-glucosidic linkages (Wurzburg, 1986).

The commercial production of oxidised starch generally employs sodium hypochlorite as the oxidising agent. Besides the environmental issue created by oxidation of starch with alkaline hypochlorite, which has been reported (Kesselmans & Bleeker, 1997), Wing and Willett (1997) have also reported a low starch yield as a result of the loss of small molecules produced by starch breakdown.

To combat these challenges, the use of a green oxidant, such as ozone, has been studied and preferred as a good replacement for chemical oxidation (Kesselmans & Bleeker, 1997). The ozonated starches exhibited similar pasting properties compared with starches chemically oxidised at low concentration of sodium hypochlorite (An & King, 2009). No residues are observed when the ozonized starches are introduced to a food product (Chan, Bhat, & Karim, 2009). Recently, starches of corn, sago and tapioca were treated under similar ozone treatment conditions with ozone generation times (OGT) of 1, 3, 5 and 10 min. The results showed that the extent of starch oxidation varies among different types of starch (Chan, Bhat, Senan, Williams, & Karim, 2011; Chan et al., 2009). It was postulated that a sample treated at 10 min OGT will exhibit a significant difference in molecular mass compared to native starch. The data obtained compared favourably with those results obtained in oxidised starches, which are prepared by the conventional chemical method. Up to now, no other studies have been published on the use of other starch sources (such as potato and maize), which may be potential competitors for commercial starches in food and non-food applications. In this

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vein, roots and tubers, which are staple foods, were selected in this study as possible additional sources of starch for industrial applications in non-food products.

This work was designed to isolate and modify, via ozone-oxidation, native starches from cocoyam (*Colocasia esculenta*) and yam (*Dioscorea* spp.) cultivars, and investigate their functional, thermal and molecular behaviour. This is to ascertain the potential for these root and tuber crops to serve as possible alternative sources of starch, which demand as a value-added material in both industrial and domestic products is fast growing.

2. Materials and methods

2.1. Materials

Corms of white and red cocoyam cultivars, and tubers of white yam (*Dioscorea rotundata*) and yellow yam (*Dioscorea cayenensis*) were purchased at Uchi Market, Auchi, Nigeria. All reagents used in this work were of analytical grade. All chemicals were used directly without further purification.

2.2. Native starch extraction

Starches were extracted from the various roots and tubers by adopting the method described in a previous work (Oladebeye, Oshodi, & Oladebeye, 2009). The roots and tubers were washed with water, peeled, sliced, rewashed and grated to obtain the pulp, which was sieved through muslin bags. The filtrate (starch milk) was allowed to stand for 3–4 h for the starch to settle before decanting the supernatant to obtain wet starch cake. The wet starch cake was purified by adding more distilled water and allowed to settle before decanting. The resulting wet starch cakes were air-dried at 40 °C for 48 h before being ground into a fine powder, and packaged into transparent polyethylene bags and labelled prior to analysis.

2.3. Preparation of ozone-oxidised starch

Ozone-oxidised starches were prepared by a method originally employed by Chan et al. (2011) with some modifications. A starch sample in powder form was placed in the reaction vessel (a rotating vessel designed for an evaporator) that was connected to an ozone generator. O_3 was generated for 5, 10 and 15 min OGTs, and the reaction vessel was rotated at 150 rpm to ensure homogeneous contact between starch and O_3 during the reaction. Next, 10 min of contact time elapsed with both the gas inlet and outlet closed to allow the reaction (oxidation) to take place. Finally, O_2 was flushed through the vessel for 20 min to flush out any O_3 that did not react with the starch, which was then trapped by potassium iodide (KI) solutions. The amount of unreacted O_3 was determined by acidifying KI solutions with 2.0 M H_2SO_4 followed by titration with standardized 0.2 M $Na_2S_2O_3$, using starch solution as indicator. A blank test was carried out following the same procedure, but without starch to obtain the amount of O_3 generated. From the calibration curve, the amount of reacted O_3 was deduced.

2.4. Determination of carbonyl and carboxyl contents

The carbonyl content of ozone-oxidised starch was determined by following the titrimetric method of Smith (1967). Carbonyl content was calculated as follows:

$$\text{Carbonyl content (g/100 g)} = \frac{[\text{Blank} - \text{Sample}]\ \text{ml} \times \text{acid normality} \times 0.028}{\text{Weight of sample}} \times 100$$

The carboxyl content of ozone-oxidised starch was determined according to the modified procedure of Chattopadhyay, Singhal, and Kulkarni (1997). Carboxyl content was calculated as follows:

$$\text{Carbonyl content (g/100 g)} = \frac{[\text{Sample} - \text{Blank}]\ \text{ml} \times \text{mol. equiv./L of NaOH} \times 0.045}{\text{Weight of sample}} \times 100$$

2.5. Swelling power and solubility

Swelling power and solubility of starch samples were determined by adopting the method described by Leach, McCowen, and Schoch (1959). Swelling power is the ratio of the weight of the wet sediment to the initial weight of dry starch. The solubility is the ratio in weight of the dried supernatant to the initial weight of dry starch.

2.6. Pasting properties

The pasting profile of the starches (8% w/w, dry weight basis) was determined using the Rapid Visco Analyzer (model RVA-4, Newport Scientific Pvt. Ltd., Warriewood, Australia). The samples were equilibrated at 50 °C for 1 min and then raised to 95 °C in 3.75 min, held for 2.5 min, cooled to 50 °C in 3.75 min and held for 5 min. The paddle speed was set at 960 rpm for the first 10 s to evenly disperse the starch slurry, and reduced to 160 rpm throughout the remainder of the experiment. The units of viscosity were expressed as rapid visco units (RVUs).

2.7. Textural properties

The textural behaviours of the gels were investigated, using the method described by Gunaratne and Corke (2007) with some modifications. These were determined on the starch gel made in the RVA testing using a TA-XT2 texture analyzer (Stable Micro Systems, Godalming, England). After RVA testing, the paddle was removed and the starch paste in the canister was covered by Parafilm wrap and stored at 4 °C for 7 days for proper gel formation. The gel was allowed to equilibrate to room temperature and was compressed at a pre-set speed of 5 mm/s, test speed of 0.5 mm/s and post speed of 5 mm/s to a distance of 10 mm with a 6 mm cylindrical probe and trigger force of 5 g. The maximum force peak (hardness) in the TPA profile represents the gel strength, while other parameters such as gumminess, springiness, chewiness and cohesiveness were deduced by extrapolations from the TPA curve.

2.8. Thermal analysis

The gelatinization and retrogradation characteristics of the ozone-oxidised starches were studied using a Differential Scanning Calorimeter (DSC-Q100, TA Instruments, New Castle, DE, USA). To study the gelatinization profiles of the samples, starch slurries were prepared at 1:3 dry starch/water ratios, hermetically sealed using a DuPont encapsulation press (DuPont Co., Delaware, USA) and reweighed. Samples were heated at a rate of 5 °C/min from 20 to 100 °C. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of gelatinization (ΔH_{gel}) were calculated. Enthalpies were calculated on a dry starch basis. Thereafter, the gelatinized starch samples (in the original sealed pan) were stored at 4 °C for 7 days for retrogradation studies. After the storage period, the samples were removed and allowed to equilibrate at room temperature for 1 h before being rescanned using the DSC with the same heating programme.

2.9. X-ray diffraction

The X-ray diffraction studies were carried out using a Siemens D5000 X-ray Powder Diffractometer (20° Geometry, Madison, USA). The ozone-oxidised starch samples were equilibrated with distilled water in a dessicator for 48 h before attempts to improve the resolution of the X-ray diffractogram pattern. The fine samples were filled into a sample holder and packed as densely as possible. The finished surface was smoothed and flushed. The samples were mounted into a X-ray diffractometer and copper Kα, 2λ (λ = 1.540 μm and 1.544 Å; 40 kV; 35 mA) was generated to determine the X-ray pattern. The scan was acquired at a diffraction angle (2θ) of 1.5–600 at 0.05 step size with a count time of 3 s. From the resulting X-ray patterns, peak positions were identified using the instrument's software, and these peak positions were used to determine the crystalline nature of the starch samples.

2.10. Molecular mass distribution

The standard method described by Timpa (1991) was adopted for the GPC analysis of the starch samples with some modifications. Starch sample (45 mg) was added to 5 ml of dimethylacetamide (DMAC) in 10 ml Reacta-Vials (Pierce, Rockford, IL) in a heating block. The temperature was raised to 150 °C for 1 h 15 min, cooled to 100 °C and dried LiC1 (to 8% w/v) was added. A further decrease in temperature to 50 °C was ensured with continuous stirring overnight before incubating until clear solutions were obtained. The resulting solutions were quantitatively diluted to 50 ml with DMAC. Prior to injection, solutions were filtered *in vacuo* through Teflon solvent-resistant disposable filters (Millex SR, 0.5 pm, Millipore) using 4 ml glass vials (WISP, Waters) in a Baker 10 extraction apparatus fitted with glass syringes (10 cm^3). The mobile-phase solvent for GPC was DMAC containing 5% LiCl. The GPC system consisted of an automatic sampler (Waters WISP) with an HPLC pump (Waters Model 590), with detection by multi-angle laser light scattering (MALLS) (DAWN EOS, Wyatt Technology Corp, Santa Barbara, CA) and differential refractive index (RI) (Waters Corp., Milford, MA) detectors. The RI calibration constant was measured with a series of NaCl standards. The 90° photodiode detector of MALLS was calibrated using toluene (HPLC grade). This system was equipped with four columns (Ultra-styragel 10^3, 10^4 and 10^5 (Baxter, Muskegon, MI) and 10^6 (Phenomenex, Torrance, CA)) connected in series and preceded by a guard column (Phenogel, linear, Phenomenex). The system was maintained at 50 °C. Standard injection volume was 40 μl and the mobile phase was pumped at a rate of 1.0 ml min^{-1}. Run times were 60 min. The software package Unical based upon ASYST (Unical, Version 3.02, Viscotek) was used for data acquisition and analysis. The system was calibrated with polystyrene standards. Data were obtained from two dissolutions per sample with two GPC runs per dissolution.

The amylose contents were determined following the method described by Williams, Kuzina, and Hlynka (1970) and the amylopectin estimated (100% – % amylose content).

2.11. Statistical analysis

Duncan's least significant test was used to compare means at the 5% significance level. Simple Pearson's correlation and regression analysis was conducted using SPSS 17.0 software (SPSS, Inc., Chicago, IL).

3. Results and discussion

3.1. Amount of reacted ozone, carbonyl and carboxyl contents

Table 1 depicts the amount of ozone that reacted with the native starches (white cocoyam, red cocoyam, white yam and yellow yam), and the carbonyl and carboxyl contents of their ozone-oxidised derivatives. OGTs of 5, 10 and 15 min were used in this research work. There was significant and consistent increase in the amount of ozone that reacted with the starch samples as OGT increased. The amount of reacted ozone ranged from 0.60 to 1.83, 0.03 to 1.00, 0.50 to 1.53, 0.33 to 1.13 mmol for white cocoyam, red cocoyam, white yam and yellow yam starches, respectively. The white cultivars, both cocoyam and yam, exhibited higher levels of carbonyl and carboxyl groups than other cultivars at the same OGT time. This may account for difference in amylose and amylopectin contents of the cultivars of the same botanical source. The consistency of increase in the amount of reacted ozone and OGT obtained in this work compares favourably with the earlier reports of Chan et al. (2009) for starches of corn, sago and tapioca. In each sample, the highest amount of reacted ozone was obtained at 15 min OGT. Chan et al. (2011) had reported highest amount of reacted ozone at 10 min OGT for starches of corn, sago and tapioca. However, the results obtained in this work showed possible reaction between the starch molecules and ozone molecules at higher OGT.

The carbonyl and carboxyl contents are paramount for oxidation of starch, as they account for the depolymerization of amylose and amylopectin, and conversion of hydroxyls first to carbonyls, and then to carboxyls. There were significant increases in carbonyl and carboxyl contents of the starches with respect to increase in OGT. The range of carboxyl contents obtained in this work is appreciably less than the 1.1% reported by Wurzburg (1986) for most commercial starches oxidised with hypochlorite. The Pearson correlation analysis of the data obtained showed a significant positive relationship between the amounts of ozone reacted with the starches and carbonyl contents (white cocoyam, $r = 0.996$; red cocoyam, $r = 0.960$; white yam, $r = 0.921$; yellow yam, $r = 0.878$, $p < 0.01$). A significantly positive relationship existed between the amounts of ozone reacted with the starches and carboxyl contents (white cocoyam, $r = 0.811$; red cocoyam, $r = 0.934$; white yam, $r = 0.997$; yellow yam, $r = 0.913$, $p < 0.01$). These observations, invariably, showed that both carboxyl and carbonyl contents of these oxidised starches increased with increase in amounts of ozone that reacted with them. These observations are in league with the finding by Kuakpetoon and Wang (2001), who reported that both carboxyl and carbonyl contents of oxidised starch increased as the hypochlorite concentration increased.

3.2. Swelling power and solubility

Swelling power and solubility are measures of the magnitude of the interaction between starch chains within the amorphous and crystalline domains. The swelling power and solubility of the native and ozone-oxidised starches are presented in Table 2. A decrease in swelling power was obtained for ozone-oxidised starches of both white and red cocoyam cultivars as OGT increased, with significant exception at 15 min OGT for white cocoyam. The ozone-oxidised derivatives of white yam starches possessed higher swelling power than the native starch, although there was no orderly trend as OGT increased. Nevertheless, the ozone-oxidised derivatives of yellow yam had an orderly trend of increasing swelling power as OGT increased. The differences in the extent of swelling indicates structural differences among starches. The increase in swelling power of oxidised starch might be due to the introduction of hydrophilic carboxyl groups and the repulsion between negative charges. The reduction in the swelling power after oxidation may be due to structural disintegration within the starch granule during the process of modification (Lawal et al., 2005). A similar decrease in the swelling power upon oxidation was reported for the mucuna bean (Adebowale & Lawal, 2003). The inconsistency in swelling power of the starches could be attributed to the different rates of

Table 1
Amount of reacted ozone, carbonyl and carboxyl contents of starch samples.

Starch	OGT (min)	Reacted ozone (mmol)	Carbonyl content (%)	Carboxyl content (%)
White cocoyam	5	0.60 ± 0.06^{a}	0.322 ± 0.001^{a}	0.201 ± 0.001^{a}
	10	1.40 ± 0.75^{ab}	0.538 ± 0.001^{b}	0.254 ± 0.001^{b}
	15	1.83 ± 0.00^{b}	0.711 ± 0.002^{c}	0.311 ± 0.001^{c}
Red cocoyam	5	0.03 ± 0.00^{a}	0.320 ± 0.001^{a}	0.190 ± 0.001^{a}
	10	0.13 ± 0.00^{b}	0.542 ± 0.001^{b}	0.225 ± 0.001^{b}
	15	1.00 ± 0.06^{c}	0.623 ± 0.002^{c}	0.430 ± 0.001^{c}
White yam	5	0.50 ± 0.06^{a}	0.322 ± 0.001^{a}	0.182 ± 0.001^{a}
	10	1.30 ± 0.06^{b}	0.546 ± 0.001^{b}	0.223 ± 0.001^{b}
	15	1.53 ± 0.00^{c}	0.587 ± 0.001^{c}	0.280 ± 0.001^{c}
Yellow yam	5	0.33 ± 0.00^{a}	0.433 ± 0.002^{a}	0.224 ± 0.001^{a}
	10	0.50 ± 0.06^{a}	0.535 ± 0.001^{b}	0.264 ± 0.001^{b}
	15	1.13 ± 0.20^{b}	0.541 ± 0.001^{c}	0.270 ± 0.001^{c}

Results are expressed as means ± standard deviations ($n = 3$). Values in the same column with different superscript letters within a particular starch are significantly different ($p < 0.05$).

Table 2
Swelling power and solubility of native and ozone-oxidised starches.

Starch	OGT (min)	Swelling power (g/g)	Solubility (%)
White cocoyam	Native[A]	12.70 ± 0.06^{c}	11.58 ± 0.04^{a}
	5	10.38 ± 0.04^{a}	12.76 ± 0.04^{b}
	10	10.77 ± 0.04^{b}	13.38 ± 0.08^{c}
	15	13.65 ± 0.04^{d}	13.74 ± 0.03^{d}
Red cocoyam	Native	12.14 ± 0.05^{d}	12.20 ± 0.02^{a}
	5	10.71 ± 0.04^{b}	12.73 ± 0.03^{b}
	10	10.83 ± 0.03^{c}	13.84 ± 0.08^{d}
	15	10.44 ± 0.04^{a}	13.67 ± 0.08^{c}
White yam	Native	13.13 ± 0.14^{a}	2.77 ± 0.04^{a}
	5	14.78 ± 0.08^{d}	4.27 ± 0.07^{c}
	10	13.78 ± 0.06^{b}	3.80 ± 0.11^{b}
	15	14.10 ± 0.07^{c}	4.42 ± 0.05^{c}
Yellow yam	Native	13.89 ± 0.13^{bc}	2.29 ± 0.04^{a}
	5	12.90 ± 0.09^{a}	7.75 ± 0.11^{d}
	10	13.65 ± 0.09^{ab}	2.81 ± 0.02^{b}
	15	13.92 ± 0.04^{c}	6.33 ± 0.02^{c}

Results are expressed as means ± standard deviations ($n = 3$). Values in the same column with different superscript letters within a particular starch are significantly different ($p < 0.05$).

[A] Unmodified starch sample.

depolymerization of the polymer chains to form a carbonyl group, and oxidation of carbonyl group to carboxyl group at different OGTs. The Pearson correlation analysis of swelling powers and carbonyl contents for the oxidised starches was white cocoyam ($r = 0.890$, $p < 0.05$), red cocoyam ($r = -0.439$, $p < 0.01$), white yam ($r = 0.699$, $p < 0.01$) and yellow yam ($r = 0.970$, $p < 0.01$), and swelling powers and carboxyl contents white cocoyam ($r = 0.424$, $p < 0.05$), red cocoyam ($r = -0.888$, $p < 0.05$), white yam ($r = -0.586$, $p < 0.05$) and yellow yam ($r = 0.982$, $p < 0.01$). The swelling power of starches is of great significance in tablet and capsule formulations, as it is believed that disintegrants works through a swelling and wicking action (Adebayo & Itiola, 1998). As a result, starches with higher swelling power would be expected to release the active pharmaceutical ingredient from its compacts at a faster rate, where starch acts as a disintegrant.

Solubility represents the amount of solubilized starch molecules present at a certain temperature. Increase in solubility was favourably obtained for the native starches of white cocoyam, red cocoyam, white yam and yellow yam upon oxidation with gaseous ozone (Table 2). The increase in solubility after oxidation has been adduced to depolymerization and structural weakening of the starch granules (Hodge & Osman, 1996), which has been equally reported for normal corn starch and sago starch (Chan et al., 2009; Sandhu, Kaur, Singh, & Lim, 2008).

3.3. Pasting properties

The pasting profiles of the native and ozone-oxidised starches analysed with rapid visco analyzer (RVA) are shown in Table 3. There were significant reductions in the pasting temperatures of the oxidised derivatives of white and red cocoyam starches. White and yellow yam, however, showed significant elevation in paste temperature after oxidation, with deviations observed for white yam at 10 min OGT and yellow yam at 15 min OGT. The ranges of pasting temperature of the oxidised starches are 82.40–83.25 °C (white cocoyam), 82.48–83.29 °C (red cocoyam), 80.46–81.67 °C (white yam) and 84.86–85.77 °C (yellow yam), in comparison with the respective values of pasting temperature of native starches (83.89, 83.51, 81.62 and 84.92 °C). The reduction of pasting temperature following oxidation could be a consequence of structural weakening and disintegration during oxidation (Lawal, 2004).

Peak viscosity values for ozone-oxidised white and yellow yam starches were significantly lower than their corresponding native starches. White cocoyam experienced lowering in peak viscosity at 5 and 10 min OGTs, whereas the starch of red cocoyam remained unchanged after ozone-oxidation. The differences upon oxidation were more appreciable in terms of their hot paste viscosity and cold paste viscosity. The differences in peak viscosities were not,

Table 3
Pasting properties of native and ozone-oxidised starches.

Starch	OGT (min)	Peak viscosity (RVU)	Hot paste viscosity (RVU)	Breakdown (RVU)	Cold paste viscosity (RVU)	Setback (RVU)	Peak time (min)	Pasting temperature (°C)
White cocoyam	Native	75.31 ± 3.83^{b}	60.56 ± 4.51^{c}	14.75 ± 0.74^{a}	95.94 ± 6.14^{c}	35.39 ± 1.71^{d}	4.49 ± 0.08^{b}	83.98 ± 0.10^{c}
	5	64.08 ± 2.13^{a}	49.67 ± 2.44^{ab}	14.41 ± 0.41^{a}	74.58 ± 2.14^{b}	24.91 ± 0.30^{b}	4.45 ± 0.01^{b}	83.15 ± 0.05^{b}
	10	66.92 ± 1.86^{a}	50.58 ± 1.58^{b}	16.34 ± 1.53^{a}	77.50 ± 1.70^{b}	26.92 ± 0.12^{c}	4.25 ± 0.03^{a}	83.25 ± 0.09^{b}
	15	74.17 ± 3.83^{b}	45.00 ± 1.34^{a}	29.17 ± 2.49^{b}	67.83 ± 1.32^{a}	22.83 ± 0.02^{a}	4.18 ± 0.02^{a}	82.40 ± 0.06^{a}
Red cocoyam	Native	58.47 ± 2.84^{a}	48.89 ± 3.00^{c}	9.59 ± 0.29^{a}	81.47 ± 5.51^{c}	32.52 ± 2.53^{b}	4.76 ± 0.10^{b}	83.51 ± 0.94^{bc}
	5	56.67 ± 1.22^{a}	37.58 ± 1.13^{b}	19.08 ± 0.09^{b}	59.25 ± 1.04^{b}	21.67 ± 2.15^{a}	4.45 ± 0.03^{ab}	83.29 ± 0.10^{b}
	10	54.58 ± 1.14^{a}	33.83 ± 1.22^{a}	20.75 ± 0.08^{c}	53.75 ± 1.50^{a}	19.92 ± 0.28^{a}	4.38 ± 0.08^{a}	82.53 ± 0.04^{a}
	15	56.83 ± 2.40^{a}	32.83 ± 1.73^{a}	24.00 ± 0.67^{d}	51.67 ± 1.77^{a}	18.83 ± 0.04^{a}	4.45 ± 0.35^{ab}	82.48 ± 0.07^{a}
White yam	Native	126.55 ± 2.23^{b}	109.00 ± 1.84^{b}	17.56 ± 1.18^{a}	161.78 ± 3.61^{c}	52.78 ± 2.35^{d}	5.87 ± 0.04^{c}	80.78 ± 0.07^{a}
	5	128.00 ± 3.15^{b}	108.17 ± 2.35^{b}	19.83 ± 0.82^{b}	140.08 ± 5.03^{b}	31.92 ± 2.68^{c}	5.52 ± 0.01^{a}	81.62 ± 0.05^{b}
	10	121.00 ± 3.05^{a}	104.50 ± 1.60^{a}	16.50 ± 1.45^{a}	132.83 ± 2.62^{a}	28.33 ± 1.02^{b}	5.72 ± 0.01^{b}	80.46 ± 0.06^{a}
	15	116.92 ± 2.13^{a}	101.25 ± 1.87^{a}	15.67 ± 0.40^{a}	126.58 ± 1.37^{a}	25.33 ± 0.50^{a}	5.78 ± 0.01^{b}	81.67 ± 0.03^{b}
Yellow yam	Native	115.91 ± 0.88^{d}	111.08 ± 2.18^{d}	4.83 ± 1.51^{b}	159.55 ± 3.56^{a}	48.47 ± 1.63^{b}	6.16 ± 0.03^{a}	84.92 ± 0.05^{a}
	5	99.25 ± 0.80^{c}	97.25 ± 0.86^{c}	2.00 ± 0.06^{a}	124.50 ± 0.60^{c}	27.25 ± 0.26^{a}	6.72 ± 0.01^{c}	85.72 ± 0.03^{b}
	10	90.17 ± 0.83^{a}	87.75 ± 0.35^{a}	2.42 ± 0.48^{a}	113.17 ± 1.19^{a}	25.42 ± 0.84^{a}	6.52 ± 0.01^{b}	85.77 ± 0.05^{b}
	15	92.25 ± 0.50^{b}	90.33 ± 0.67^{b}	1.92 ± 0.17^{a}	117.17 ± 0.83^{b}	26.83 ± 1.50^{a}	6.92 ± 0.01^{d}	84.86 ± 0.05^{a}

Results are expressed as means ± standard deviations ($n = 3$). Values in the same column with different superscript letters within a particular starch are significantly different ($p < 0.05$).

in anyway, influenced by the carboxyl contents of the starches, as the Pearson correlation analysis of the starches showed both positive and negative relationships (white cocoyam, $r = 0.860$, $p < 0.05$; white yam, $r = -0.884$, $p < 0.01$ and yellow yam, $r = -0.715$, $p < 0.05$). The decrease in peak viscosity, hot paste viscosity and cold paste viscosity could be as a result of partial cleavage of the glycosidic linkage after treatment with gaseous ozone, resulting in a decrease in the molecular weight of starch molecules. This gives rise to a partially degraded network with weak shear resistance and failure to maintain the integrity of the starch granule, thereby resulting in a lower viscosity (Morton & Solarek, 1984)). This trend is in agreement with the results reported for ozone-oxidised corn starch by Chan et al. (2009) and for oxidised mucuna bean starch by Adebowale and Lawal (2003).

Breakdown viscosity is a measure of granule disruption, or lesser affinity of starch to resist shear force during heating. A gradual increase in breakdown viscosity was observed for white and red cocoyam cultivars upon ozone-oxidation as OGT increased, whereas a significant decrease was observed for white and yellow yam cultivars. The ozone-oxidised derivatives of yellow yam were significantly similar as OGT increased. The same observations were obtained for white yam at 10 and 15 min OGTs. The increased breakdown viscosity could be attributed to the weakened structure of the granules after treatment with gaseous ozone, which facilitated disruption of the granular structure. The reduction in breakdown viscosity has been adduced to the introduction of new substituent groups into the oxidised starches (Adebowale & Lawal, 2003). Carbonyl and carboxyl groups were introduced into the native starch through the oxidation of the starch hydroxyl groups by ozone molecules. Wurzburg (1986) had indicated C-2, C-3 and C-6 as those positions where oxidation of hydroxyl groups takes place, with further possibility of starch degradation by cleavage of amylose and amylopectin molecules at α-(1→4)-glucosidic linkages. Reports have been made of the increase in breakdown viscosity after oxidation of native starches with ozone (An & King, 2009; Chan et al., 2009). The different responses of these starches to ozone-oxidation may be adduced to variation in their botanical sources.

Setback viscosity is a measure of the degree of retrogradation of starch, mainly amylose (Karim, Norziah, & Seow, 2000), implying

Table 4
Textural properties of native and ozone-oxidised starch gels.

Starch	OGT (min)	Gel strength (N)	Springiness	Cohesiveness	Gumminess (N)	Chewiness (Nm)	Resilience
White cocoyam	Native	8.29 ± 0.62^{c}	0.99 ± 0.09^{b}	0.31 ± 0.02^{a}	1.69 ± 0.09^{b}	1.68 ± 0.87^{c}	0.040 ± 0.005^{a}
	5	7.22 ± 0.22^{b}	0.80 ± 0.05^{a}	0.59 ± 0.06^{b}	1.61 ± 0.05^{b}	1.29 ± 0.11^{b}	0.350 ± 0.010^{b}
	10	7.36 ± 0.12^{b}	0.98 ± 0.09^{b}	0.37 ± 0.02^{a}	1.12 ± 0.08^{a}	1.10 ± 0.08^{a}	0.050 ± 0.005^{a}
	15	2.83 ± 0.10^{a}	0.91 ± 0.11^{ab}	0.71 ± 0.06^{c}	1.13 ± 0.10^{a}	1.02 ± 0.06^{a}	0.440 ± 0.080^{c}
Red cocoyam	Native	5.39 ± 0.10^{d}	1.00 ± 0.11^{a}	0.34 ± 0.07^{a}	2.79 ± 0.10^{c}	2.78 ± 0.14^{c}	0.050 ± 0.002^{a}
	5	2.71 ± 0.05^{b}	0.98 ± 0.19^{a}	0.41 ± 0.08^{a}	2.95 ± 0.10^{c}	2.90 ± 0.12^{c}	0.040 ± 0.004^{a}
	10	3.00 ± 0.21^{c}	0.99 ± 0.16^{a}	0.32 ± 0.05^{a}	2.32 ± 0.20^{b}	2.30 ± 0.29^{b}	0.030 ± 0.003^{a}
	15	1.60 ± 0.15^{a}	0.88 ± 0.12^{a}	0.62 ± 0.04^{b}	1.76 ± 0.09^{a}	1.54 ± 0.07^{a}	0.370 ± 0.030^{b}
White yam	Native	6.25 ± 0.35^{d}	0.58 ± 0.11^{a}	0.33 ± 0.05^{a}	2.04 ± 0.11^{b}	1.17 ± 0.09^{c}	0.070 ± 0.004^{a}
	5	4.95 ± 0.46^{c}	0.81 ± 0.07^{b}	0.38 ± 0.12^{a}	1.88 ± 0.12^{b}	1.52 ± 0.08^{d}	0.110 ± 0.020^{b}
	10	4.20 ± 0.22^{b}	0.52 ± 0.06^{a}	0.35 ± 0.07^{a}	1.48 ± 0.05^{a}	0.76 ± 0.06^{b}	0.090 ± 0.005^{ab}
	15	3.35 ± 0.13^{a}	0.55 ± 0.05^{a}	0.33 ± 0.04^{a}	1.11 ± 0.06^{a}	0.61 ± 0.03^{a}	0.110 ± 0.010^{b}
Yellow yam	Native	2.35 ± 0.15^{b}	0.65 ± 0.13^{b}	0.39 ± 0.10^{a}	0.91 ± 0.18^{a}	0.59 ± 0.14^{b}	0.060 ± 0.001^{a}
	5	2.08 ± 0.12^{ab}	0.44 ± 0.09^{a}	0.39 ± 0.12^{a}	0.82 ± 0.05^{a}	0.36 ± 0.07^{a}	0.090 ± 0.002^{b}
	10	2.29 ± 0.16^{b}	0.43 ± 0.07^{a}	0.39 ± 0.12^{a}	0.90 ± 0.11^{a}	0.39 ± 0.12^{ab}	0.090 ± 0.002^{b}
	15	1.93 ± 0.10^{a}	0.40 ± 0.09^{a}	0.36 ± 0.11^{a}	0.69 ± 0.16^{a}	0.28 ± 0.11^{a}	0.080 ± 0.004^{a}

Results are expressed as means ± standard deviations ($n = 3$). Values in the same column with different superscript letters within a particular starch are significantly different ($p < 0.05$).

that a high setback viscosity value means a high tendency of starch to retrogradation. The values of setback viscosity of all the starches progressively decreased upon ozone-oxidation with respect to increase in OGT. During the cooling cycle of hot starch paste, the re-association tendency of the starch granules favoured an increase in viscosity. This phenomenon is largely favoured by the affinity of hydroxyl groups of one molecule for another. Oxidized starches, having been subjected to conformational reordering and rearrangement through the introduction of carboxyl groups, are less prone to such reassociations. The introduction of carboxyl groups to replace hydroxyl groups inhibits the formation of such binding forces.

The peak time implies a measure of the rate at which equilibrium is attained between swelling and polymer leaching, and rupture and polymer alignment. The peak times for the starches showed range of 3.38–4.49 min for white cocoyam, 3.45–4.76 min for red cocoyam, 3.40–5.87 min for white yam and 3.78–6.16 min for yellow yam. The peak times for white cocoyam, red cocoyam and white yam were significantly lowered after ozone-oxidation, with slight deviation observed for red cocoyam at 15 min OGT. Conversely, an opposite trend with significant increase in peak time was observed for yellow yam as OGT increased.

3.4. Textural properties

The textural properties of native and ozone-oxidised starches determined using the texture analyzer are shown in Table 4. Significant decrease in the values of gel strength (N), gumminess (N) and chewiness (Nm) were observed for all the starches upon ozone-oxidation, with exception observed for yellow yam starches in terms of chewiness. Springiness of the native starches appeared unaffected by ozone-oxidation, except for slight differences observed for yellow yam, white cocoyam and white yam (at 5 min OGT). The values of cohesiveness were insignificantly different for white and yellow yam cultivars, whereas slight differences were observed for white and red cocoyam cultivars. The starches behaved more resilient after oxidation with ozone with deviations observed for white cocoyam at 10 min OGT, white yam at 10 min OGT and yellow yam at 15 min OGT. However, within the starch types, the highest values of cohesiveness were observed for white cocoyam starch at 15 min OGT, red cocoyam starch at 15 min OGT and white yam starch at 5 min OGT. Ozone-oxidised starch gel of white cocoyam exhibited the highest gel strength (7.22 ± 0.22 N) at 5 min OGT, with the lowest (1.60 ± 0.15 N) observed for red cocoyam at 15 min OGT. Gel firmness is mainly caused by retrogradation of starch gels, which is associated with the syneresis of water and crystallisation of amylopectin, leading to harder gels (Miles, Morris, Orford, & Ring, 1985). The oxidised starches had ranges of springiness, cohesiveness, gumminess, chewiness and resilience as 0.40–0.99, 0.32–0.71, 0.69–2.95 N, 0.28–2.90 Nm and 0.03–0.37, respectively.

3.5. Thermal properties

The profiles of gelatinization and retrogradation (after 7 days storage) are depicted by Table 5. The gelatinization temperatures, T_o, T_p and T_c and enthalpies of gelatinization (ΔH_{gel}) of the ozone-oxidised starches were insignificantly different from those of the native starches. The gelatinization temperature and enthalpy of starches depends on the microstructure and degree of crystallinity within the granules, and also on the granule size and amylose-to-amylopectin ratio (Sandhu et al., 2008). The results obtained in this study could suggest that the process of gelatinization, that involves destruction of starch crystallite and loss of helical conformation, was not affected by OGTs. However, the ΔH_{gel} obtained for the ozone-oxidised starches of white and red cocoyam, and

Table 5
Gelatinization and retrogradation profiles of native and ozone-oxidised starches.

Starch	Gelatinization						Retrogradation				
	OGT (mins)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J/g)	R^A (°C)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J/g)	R^A (°C)
White cocoyam	Native	77.24 ± 0.11^{b}	79.52 ± 0.01^{b}	86.14 ± 0.58^{a}	15.19 ± 3.12^{a}	8.91 ± 0.69^{a}	43.32 ± 0.98^{a}	54.67 ± 0.11^{a}	69.86 ± 1.98^{a}	8.97 ± 1.92^{a}	26.55 ± 2.96^{a}
	5	76.57 ± 0.01^{a}	78.73 ± 0.11^{a}	86.16 ± 3.54^{a}	15.32 ± 1.90^{a}	9.59 ± 3.52^{ab}	43.57 ± 1.77^{a}	54.87 ± 0.00^{a}	70.29 ± 1.08^{a}	8.59 ± 0.73^{a}	26.72 ± 0.69^{a}
	10	76.44 ± 0.00^{a}	78.70 ± 0.04^{a}	91.30 ± 1.90^{a}	20.34 ± 2.29^{a}	14.86 ± 1.90^{b}	42.92 ± 0.56^{a}	54.84 ± 0.41^{a}	71.70 ± 0.81^{a}	9.83 ± 0.27^{a}	28.78 ± 0.87^{a}
	15	78.52 ± 0.04^{c}	80.90 ± 0.12^{c}	89.02 ± 0.88^{a}	15.00 ± 0.95^{a}	10.50 ± 0.84^{ab}	44.68 ± 0.88^{a}	56.24 ± 0.87^{b}	71.24 ± 1.44^{a}	8.41 ± 0.30^{a}	26.56 ± 2.32^{a}
Red cocoyam	Native	75.96 ± 0.07^{b}	78.66 ± 0.04^{b}	89.20 ± 0.13^{c}	13.61 ± 0.66^{a}	13.24 ± 0.21^{c}	43.27 ± 0.49^{a}	55.86 ± 0.54^{b}	70.31 ± 0.17^{a}	8.99 ± 0.01^{a}	27.04 ± 0.66^{a}
	5	75.40 ± 0.19^{a}	78.24 ± 0.26^{a}	84.91 ± 1.81^{b}	14.24 ± 1.39^{a}	9.44 ± 1.61^{b}	42.84 ± 1.27^{a}	54.75 ± 0.00^{ab}	70.16 ± 1.17^{a}	8.12 ± 0.69^{a}	27.33 ± 2.44^{a}
	10	75.38 ± 0.21^{a}	78.17 ± 0.08^{a}	84.29 ± 0.16^{ab}	13.17 ± 2.68^{a}	8.91 ± 0.37^{ab}	42.11 ± 0.93^{a}	54.18 ± 0.59^{a}	68.89 ± 2.85^{a}	8.02 ± 2.26^{a}	26.78 ± 3.78^{a}
	15	75.14 ± 0.12^{a}	78.13 ± 0.12^{a}	82.11 ± 0.23^{a}	14.68 ± 4.50^{a}	6.97 ± 0.35^{a}	42.63 ± 0.74^{a}	54.77 ± 0.00^{ab}	71.24 ± 0.12^{a}	8.94 ± 0.63^{a}	28.60 ± 0.86^{a}
White yam	Native	71.23 ± 0.01^{b}	74.52 ± 0.06^{c}	84.32 ± 3.03^{a}	13.94 ± 1.51^{ab}	13.09 ± 3.04^{a}	43.49 ± 0.27^{b}	56.33 ± 0.91^{a}	72.69 ± 1.09^{a}	6.98 ± 0.54^{b}	29.20 ± 0.82^{a}
	5	71.04 ± 0.01^{a}	73.90 ± 0.03^{a}	80.51 ± 1.61^{a}	11.99 ± 0.79^{ab}	9.47 ± 1.63^{a}	42.79 ± 0.12^{a}	55.15 ± 2.46^{a}	74.69 ± 0.13^{ab}	5.22 ± 0.81^{a}	31.90 ± 0.25^{ab}
	10	71.07 ± 0.04^{a}	74.28 ± 0.00^{b}	83.85 ± 0.32^{a}	14.43 ± 0.31^{b}	12.78 ± 0.28^{a}	43.19 ± 0.05^{ab}	57.86 ± 0.64^{a}	76.49 ± 0.86^{ab}	9.17 ± 0.12^{c}	33.30 ± 0.91^{ab}
	15	71.14 ± 0.06^{ab}	74.21 ± 0.01^{b}	79.49 ± 0.05^{a}	11.94 ± 0.06^{a}	8.35 ± 0.01^{a}	42.83 ± 0.35^{a}	57.83 ± 1.00^{a}	76.80 ± 2.39^{b}	8.87 ± 0.28^{c}	33.97 ± 2.74^{b}
Yellow yam	Native	71.55 ± 0.54^{b}	74.80 ± 0.17^{bc}	81.80 ± 1.15^{ab}	10.80 ± 0.57^{a}	10.25 ± 1.69^{a}	43.09 ± 0.04^{a}	64.09 ± 0.11^{b}	86.91 ± 0.49^{b}	11.70 ± 0.28^{b}	43.82 ± 0.54^{b}
	5	70.63 ± 0.28^{a}	74.59 ± 0.01^{ab}	81.27 ± 2.03^{ab}	15.43 ± 2.11^{b}	10.64 ± 1.75^{a}	44.58 ± 0.11^{c}	59.26 ± 2.61^{a}	78.77 ± 4.29^{a}	7.91 ± 1.50^{a}	34.19 ± 4.40^{a}
	10	71.13 ± 0.03^{ab}	74.93 ± 0.06^{c}	83.29 ± 0.36^{b}	10.84 ± 0.11^{a}	12.16 ± 0.33^{a}	43.50 ± 0.11^{ab}	56.74 ± 0.00^{a}	77.91 ± 1.27^{a}	7.87 ± 0.54^{a}	34.41 ± 1.38^{a}
	15	70.76 ± 0.14^{ab}	74.35 ± 0.14^{a}	79.70 ± 0.19^{a}	13.14 ± 0.04^{ab}	8.94 ± 0.50^{a}	44.17 ± 0.55^{bc}	58.54 ± 0.00^{a}	74.65 ± 0.21^{a}	8.83 ± 0.11^{a}	30.48 ± 0.76^{a}

Results are expressed as means ± standard deviations ($n = 3$). Values in the same column with different superscript letters within a particular starch are significantly different ($p < 0.05$).

[A] R = temperature range.

Table 6
Amylose contents, amylopectin contents and molecular mass distribution of native and ozone-oxidised starches.

Sample	OGT (min)	Amylose content (%)	Amylopectin content (%)	$M_w{}^A \times 10^6$	$M_n{}^B \times 10^6$	Polydispersity ratio
White cocoyam	Native	19.62 ± 0.05^a	80.39 ± 0.05^f	3.29 ± 0.01^b	1.07 ± 0.01^e	3.08 ± 0.01^{ab}
	10	25.31 ± 0.10^e	74.69 ± 0.10^b	5.88 ± 0.01^f	0.56 ± 0.01^c	10.59 ± 0.15^d
Red cocoyam	Native	20.75 ± 0.05^c	79.26 ± 0.05^d	3.59 ± 0.01^c	1.10 ± 0.01^f	3.27 ± 0.01^{bc}
	10	24.71 ± 0.05^d	75.30 ± 0.05^c	6.09 ± 0.01^h	0.59 ± 0.01^d	10.42 ± 0.15^d
White yam	Native	19.72 ± 0.10^a	80.28 ± 0.10^f	3.63 ± 0.01^d	1.06 ± 0.01^e	3.44 ± 0.03^c
	10	25.63 ± 0.05^f	74.38 ± 0.05^a	5.95 ± 0.01^g	0.52 ± 0.01^a	11.56 ± 0.13^e
Yellow yam	Native	20.05 ± 0.05^b	79.96 ± 0.05^e	3.18 ± 0.01^a	1.10 ± 0.01^f	2.91 ± 0.04^a
	10	25.52 ± 0.10^f	74.48 ± 0.10^a	5.70 ± 0.01^e	0.54 ± 0.01^b	10.66 ± 0.16^d

Results are expressed as means ± standard deviations ($n = 3$). Values in the same column with different superscript letters are significantly different ($p < 0.05$).
[A] M_w = weight average.
[B] M_n = number average.

white and yellow yam were higher than the range of 10.3–11.0 and 11.8 J/g reported for oxidised normal corn starches and oxidised waxy corn by Sandhu et al. (2008).

The thermal properties of the retrograded gels of native and ozone-oxidised starches after 7 days of storage at 4 °C were insignificantly different. However, the endothermic transition temperatures (T_o, T_p and T_c) and melting enthalpies of retrograded gels (ΔH_{ret}) were below the gelatinization temperatures and melting enthalpies of gelatinization (ΔH_{gel}). These observations were similar to previous studies on corn, sago, tapioca and waxy corn starches (Chan et al., 2011; Sandhu et al., 2008). These results imply that retrogradation results in reassociation of the gelatinized starch molecules, but in a less ordered and hence less stable way than those existing in the native starch granules (Karim et al., 2000).

3.6. X-ray diffraction

The X-ray diffraction patterns obtained for the native and ozone-oxidised starches are shown in Supplementary Figs. 1 and 2. Ozone-oxidised starches at 10 min OGT were analysed, because at this OGT, the ozone-oxidised starches competed favourably, in terms of pasting properties, with oxidised starches prepared by conventional alkaline hypochlorite method. Pasting properties of ozone-oxidised and alkaline hypochlorite oxidised starches have been compared (An & King, 2009).

X-ray diffraction peaks for the native starches appeared at 14.95°, 16.95° and 22.10° 2θ for white cocoyam, 15.25°, 17.30° and 17.40° 2θ for red cocoyam, 5.80°, 15.05° and 17.40° 2θ for white yam and 5.75°, 14.25° and 17.10° 2θ for yellow yam. The strongest and broadest diffraction peaks appeared at $2\theta = 16.95°$, 17.30°, 17.40° and 17.10° for native starches of white cocoyam, red cocoyam, white yam and yellow yam respectively. These reflections indicated that the native starches are of C_B-type crystalline nature. Starches of roots and tubers have been reported to exhibit maximum X-ray diffraction peaks at 17° 2θ (Hoover, 2001). Upon oxidation, at 10 min OGT, diffraction peaks appeared at $2\theta = 15.20°$, 17.30° and 23.35° (white cocoyam), 15.35°, 17.50°, 18.30° and 23.00° (red cocoyam), 5.85°, 17.35° and 23.40° (white yam), and 5.70°, 17.25° and 24.10° (yellow yam). These reflections were closely similar to C_A-type reported for sweetpotato starch at $2\theta = 15.4°$, 17.2°, 18.3° and 23.4° (Noda, Takahata, Sato, Hisamatsu, & Yamada, 1995; Osundahunsi, Fagbemi, Kesselman, & Shimoni, 2003).

3.7. Molecular behaviours

Table 6 depicts the amylose contents, amylopectin contents and molecular mass distribution of the native and ozone-oxidised starches. Among all the native starches, the highest (20.75 ± 0.05%) and lowest (19.62 ± 0.05%) amylose contents were obtained for red and white cocoyam respectively. Upon oxidation, at 10 min OGT, there was a gradual increase in amylose contents with corresponding decrease in amylopectin contents. This could imply that ozone-oxidation of the starches resulted in partial depolymerization of a portion of the crystalline lamellae, which mainly consist of amylopectin chains. The values of M_w of the oxidised starches increased significantly compared to the native starches. An opposite trend of general decrease in the values of M_n was observed for the native starches following oxidation at 10 min OGT. The relative increases in M_w of the oxidised starches to the native starches were 78.72%, 69.64%, 63.91% and 79.25% for white cocoyam, red cocoyam, white yam and yellow yam respectively. In the same vein, the relative decreases in M_n of the oxidised starches to the native starches were 47.66%, 46.36%, 50.94% and 50.91% for white cocoyam, red cocoyam, white yam and yellow yam respectively. Higher values of weight average, M_w of the oxidised starches could be indicative of the formation of intermolecular cross-links (Wang & Wang, 2003) between ozone gas and the amylose molecules, which is accompanied by depolymerization of portion of amylopectin chains as evident by their increased proportion of amylose. Polydispersity ratio, M_w/M_n is an indication of broadness of molecular weight distribution (Gowariker, Viswanathan, & Sreedhar, 1986, chap. 12). Polydispersity ratios of the oxidised starches were higher than the corresponding native starches. The ranges of polydispersity ratio were 2.91–3.44 and 10.59–11.56 for native and oxidised starches respectively.

4. Conclusion

Ozone-oxidation of starches is an alternative to the conventional chemical method of preparing oxidised starches. The data obtained from this study shows that ozone-oxidation affects the functional, thermal and molecular behaviours of the various starches when treated under the same conditions of ozonation. Generally, at 10 min OGT, the starches compare favourably with results reported for conventional alkaline method of oxidation of starches. The oxidised starches investigated in this study could serve as alternative sources of starch for the ever-increasing demand for starch in food and non-food applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2013.04.080.

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