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Functional characteristics of Bambara groundnut starch-catechin complex formed using cyclodextrins as initiators

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Abstract

Bambara groundnut (BGN) starch extracted from BGN flour was modified through complexation methods using alpha and beta cyclodextrin. Complexation methods used included the microwave, co-evaporation and kneading methods. Cyclodextrin (alpha and beta) were used as initiators for grafting catechin to the BGN starch molecule. The functional properties of native and modified BGN starches were assessed. The swelling capacity of BGN starches increased with an increase in temperature. The swelling capacities of BGN starches ranged from 0.36 g/g (BGN starch modified through the co-evaporation method, beta cyclodextrin + catechin) to 4.84 g/g (BGN starch modified through the microwave method, beta cyclodextrin + catechin). Complexation methods significantly reduced the swelling capacity of native BGN starch. Temperatures had a significant ($p \leq 0.05$) effect on the swelling capacity of BGN starches. The solubility of BGN starches ranged from 0.61 g/100 g (native BGN starch) to 46.04 g/100 g (BGN starch modified through the kneading method, alpha cyclodextrin); using water as a solvent. The water absorption of native and modified BGN starches ranged from 0.23 to 1.17 g/g, respectively. Starches complexed with β-cyclodextrin showed increased water absorption capacity in

comparison to the starches complexed with alpha cyclodextrin. The modification methods had a significant ($p \leq 0.05$) effect on the water absorption capacities of BGN starches. There was no significant difference in the oil absorption capacities of BGN starches and they ranged from 1.02 to 1.07 g/g. Pasting properties of BGN starches were assessed using a rapid visco analyser (RVA). The modified starches exhibited lower breakdown, setback, and final viscosities as well as significant increase in gelatinisation temperature compared to the native BGN starch.

Keywords: Food analysis, Food technology, Food science

1. Introduction

Among carbohydrate polymers, starch has increased attention due to its usefulness in different food products. Starch is used in many industrial and food applications because of its ability to impart a wide range of functional properties to both food and non-food products as well as its affordability and abundance (Bertolini, 2009). Starch is used in the food industry as a food ingredient, especially for its functional properties and as new food products are developed. Starch being a significant functional biopolymer it greatly influences properties of various food products (Singh and Kaur, 2004). It modifies the texture and consistency of food products. Furthermore, it plays a vital role in the textural characteristics of various food products as it has many functions. However, a thorough knowledge of the starch structure as well as its functional properties is needed for the development of starch value-added products. Expanding starch requirements together with its extending industrial usage call for the use of starch from underutilised legumes such as Bambara groundnut (BGN). This is because main sources of modified starches used in the food industry are from cereal and tuber starches therefore more costs are incurred in exporting the product. Hence it is of utmost importance to utilize the alternative products which are feasible to manufacture locally with little or no modifications to improve/boost the economy, while adding value and marketing BGN. Additionally, BGN was chosen for this research because of the legumes' affordability and availability. BGN is a native African crop mainly grown for its seeds by female subsistence farmers. BGN has high nutritive value containing 53−65% carbohydrate, about 20% protein, 6.5% fat, 6.1% fibre, 3.4% ash, as well as appreciable amounts of calcium, iron, sodium and potassium (Baryeh, 2001; Bamshaiye et al., 2011; Mensah, 2011; Afolabi, 2012; Gabriel et al., 2013). The high carbohydrate content of BGN makes it a good source of starch. Adebowale and Lawal (2002) reported that BGN is a promising source of starch, because of its excellent nutrient and caloric content and its high yielding potential. BGN starches contain varying

amounts of amylose in the range 21−35% depending on source and variety (Sirivongpaisal, 2008; Kaptso et al., 2015; Oyeyinka et al., 2015).

Functional properties such as viscosity, foaming, gelation, texture, emulsification, oil and water absorption capacity have a significant effect on the sensory characteristics of food. A few studies have been reported on the functional characteristics of Bambara groundnut starch. The swelling capacity of BGN starch has been reported to increase with an increase in temperature (Adebowale et al., 2002). Starch being a major dietary carbohydrate, it therefore serves as a source of energy. However, starchy diets have a downside of having higher glycemic response which then leads to different chronic diseases like obesity, diabetes and cardiovascular diseases. One way of overcoming this, could be the use of phenolic compounds such as catechin, to reduce starch digestibility (Guzar, 2012).

Cyclodextrins (alpha and beta) were used as initiators to graft catechin on to the BGN starch molecule. Cyclodextrins are known as cyclic oligomers of α-D-glucopyranose comprising of glucose units linked by α-(1,4) glycosidic bonds (Singh et al., 2002; Astray et al., 2009; Yavuz et al., 2010; Celebioglu et al., 2014; Mura, 2014). Cyclodextrins can form solid inclusion complexes (host-guest complexes) with a very wide range of compounds (Singh et al., 2002; Del Valle, 2004; Astray et al., 2009). From a microscopical point of view, cyclodextrins form inclusion complexes by encompassing the guest molecule thereby resulting in the micro-encapsulation of the molecule. As a result, beneficial chemical and physical changes arise in the guest molecule properties. There are reports of cyclodextrin inclusion complexes in the pharmaceutical and cosmetic industry. However, there is no documented study that reports the use of BGN starch to form complexes with cyclodextrin and catechin. Cyclodextrins are applied in the food processing and as food additives with a variety of aims. These aims include but not limited to solubilising vitamins, suppressing undesirable tastes and/or odours as well as controlling the release of certain food components. Uyanzindile (2014) reported that application of cyclodextrins in the food industry mounts to about 14%, therefore the BGN starch-catechin complex formed using cyclodextrin as initiators will aid in increasing their (cyclodextrin) use/application in the food industry. Hence, the need to investigate the effect of cyclodextrin as initiators on the functional properties of the BGN starch-catechin complex. The objective of this study was to establish the functional characteristics of the new BGN starch-catechin complex formed using cyclodextrin as initiators.

2. Materials and methods

2.1. Source of materials

Bambara groundnuts were purchased from Triotrade, Johannesburg, Gauteng province, South Africa. Catechin was purchased from Sigma Aldrich, Johannesburg, South Africa. Chemical reagents were of analytical grade.

2.2. Production of Bambara groundnut flour

Whole BGN seeds were screened and sorted to eliminate the defective ones and any physical hazards like stones and twigs. The seeds were then washed and dried at 50 °C for 24 h in the cabinet dryer (Cabinet dryer, Model 1069616, Geiger klotzbücher, Cape town, South Africa). They were then milled using the hammer mill (Trapp TRF 40, Animal ration shredder/Hammer mill foliage, Jaraqua do sul-sc, Brasil) with sieve of 250 μm. The flour was then stored in plastic bags (zip lock bags) and kept in the refrigerator at 4 °C before use.

2.3. Extraction of Bambara groundnut starch

The method reported by Gabriel et al. (2013) was used to extract starch from Bambara groundnut flour.

2.4. Formation of BGN starch-catechin complex using cyclodextrin (alpha and beta) as an initiator

Three different methods were employed to complex cyclodextrin, BGN starch and catechin. These methods were kneading, co-evaporation and microwave irradiation and are discussed in the following sections.

2.5. Kneading method

The kneading method adapted from Liu and Zhu (2006) and Yavuz et al. (2010) with slight modifications was used. Equal amounts 1:1 molar ratio of BGN starch and cyclodextrin were accurately weighed. Thereafter, 3% water was mixed with cyclodextrin (alpha and beta) in a mortar and pestle thus forming a homogeneous paste. While grinding, BGN starch was then slowly added, a small amount (5%) of hydro-alcoholic solution (ethyl alcohol) (1:1 ratio) was added to facilitate dissolution of BGN starch. The obtained mass was then dried at 40−50 °C in a vacuum oven for 24 hours. The dried complex was ground to a fine powder. This was repeated in the same manner; however, 1% catechin was now added to the cyclodextrin and BGN starch.

2.6. Co-evaporation method

The co-evaporation method adapted from Ribeiro et al. (2008) with slight modifications, was used. Equimolar amounts 1:1 molar ratio of cyclodextrin (alpha and beta) and BGN starch were dissolved in 15 ml ethanol and hydro-alcoholic solution (1:4 ethanol-water), respectively. These two solutions were then mixed to obtain a molecular dispersion of BGN starch and cyclodextrin (alpha and beta). The mixture was stirred at 300 rpm using magnetic stirrer at 37 °C for 24 h, until a clear solution was obtained. The solvents were then air-dried in a vacuum oven at 45−50 °C (Laborota 40001, Heidolph, Germany) to a constant weight. The resultant solids were then ground. This was repeated in the same manner; however, 1% catechin was now added to the cyclodextrin and BGN starch.

2.7. Microwave irradiation method

The microwave irradiation method adapted from Savjani et al. (2012) with some modifications, was used. Ethanol and water solution (1:1 water: ethanol v/v) were used to dissolve BGN starch and cyclodextrin (alpha and beta) in a 250 ml glass beaker. The mixture was reacted in a microwave oven (MODEL: MS-2027C, LG, South Africa) at a temperature of 60 °C for 90 min. When the reaction was complete, a sufficient amount of solvent mixture was used to remove residual, un-complexed BGN starch and cyclodextrin from the reaction by thoroughly rinsing the beaker with the solvent mixture. Obtained precipitate was then separated using Whatman No. 1 filter paper; thereafter it was dried for 48 h in a vacuum oven at 40 °C. This was repeated in the same manner; however, 1% catechin was now added to cyclodextrin and BGN starch.

2.8. Characterization of the modified BGN starch and BGN starch-catechin complex

2.8.1. Scanning electron microscopy

Starch granule morphology was examined using the scanning electron microscopy. The samples were transferred onto double-sided conductive carbon tape and mounted onto an aluminum SEM stubs. A thin layer of gold was used to coat the stubs to enhance conductivity. Thereafter, the sample was loaded into a Zeiss MERLIN Field Emission Scanning Electron Microscope (Carl Zeiss Microscopy, Munchen, Germany) at the Electron Microbeam Unit. A Zeiss Inlens Secondary Electron (SE) Detector, Zeiss Backscatter Electron (BSE) Detectors and Zeiss Smart SEM software were used to generate images, while the samples were chemically quantified by quantitative Energy Dispersive X-Ray Spectrometry (EDS) using an Oxford Instrument® X-Max 20 mm^2 detector and Oxford Aztec software (Oxford

Instruments, Oxfordshire OX13 5QX, United Kingdom). The starch samples were examined at 3 kV.

2.8.2. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy analysis of the modified BGN starch and BGN starch-catechin complex samples was carried out using the method reported by Afolabi (2012). The samples were milled using a coffee mill. Finely powdered sample and dry KBr (1:100, sample to KBr ratio) were accurately weighed and mixed. The mixing was completed in 5 mins and it was done in a vibratory ball mill capsule. The ground mixture was then transferred to a specadie, which then resulted in an 8.5 mm diameter film being produced, which was then analyzed in the beam of the FTIR spectrophotometer (Nicolet Magna IR 750, series II, Thermo Scientific, Portsmouth, NH, USA). The spectrum was analyzed in the resolution interval of $400-4000$ cm^{-1}.

2.8.3. Powder X-ray diffraction

The method adapted from Ribeiro et al. (2008) and Afolabi (2012) was used to determine the structure of modified BGN starch and BGN starch-catechin complex using powder X-ray diffraction. X-ray diffractograms of the powdered BGN starch (1 g) were acquired with an X-ray diffractometer (Empyrean, PANalytical Netherlands) with Bragg-Brentano geometry. The settings used were the diffraction angle-scanning region from 3 to 40°, target voltage 40 kV, target current 100 mA, ageing time 5 min and radiation wavelength of 0.1542 nm.

2.9. Evaluation of the functional properties of BGN starch-catechin complex

2.9.1. Effect of temperature on solubility and swelling

The method reported by Adebowale and Lawal (2002); Adebowale et al. (2002); Adebowale and Lawal (2003) and Lawal et al. (2004) was employed to establish the effect of temperature on solubility and swelling of modified BGN starch and BGN starch-catechin complex formed using cyclodextrins as initiators. A 1 g sample was accurately weighed and quantitatively transferred into a clean dried test tube which was then re-weighed (W1). Then 50 ml of distilled water was used to dissolve the starch until slurry was obtained. The slurry was then heated at temperatures of 60 °C, 70 °C, 80 °C and 90 °C for 30 min in a temperature-regulated water bath. The mixture was then cooled to room temperature and centrifuged at 26 × g, for 15 min. Thereafter, 5 ml of the supernatant was dried to a constant weight at 110 °C. The residue obtained after drying the supernatant represented the amount of starch solubilised in water. Solubility was calculated

as g per 100 g of sample on dry weight basis. The residue obtained after centrifugation with the water it retained was quantitatively transferred to a clean dried test tube which was weighed and recorded as W2. Swelling capacity was calculated by dividing the difference between W2 and W1 by the original sample weight.

2.9.2. Oil and water absorption capacities

Oil and water absorption capacities were determined by the method reported by Adebowale and Lawal (2002); Adebowale and Lawal (2003); Adebowale and Lawal (2004) and Lawal et al. (2004). A 10 ml aliquot of distilled water or oil was added to 1 g sample (native or modified BGN starches). The mixture was then mixed thoroughly in a Variwhirl mixer (fast mixer) (Model A901. Salver Chem, Chicago, USA) for 30 s. This was then allowed to stand at room temperature for 30 min, after which it was centrifuged at $2627 \times$ g for a min. Graduated 10 ml cylinder was used to measure the volume of the supernatant. Absorbed oil or water mass was expressed as gg^{-1} starch on a dry weight basis.

2.9.3. Pasting properties

The pasting properties of modified BGN starch and BGN starch-catechin complex were determined using a rapid visco analyser (RVA) (RVA 4500 Perten instruments, SIN 214 31208-45A, Australia). The method adapted from Afolabi (2012); Jan et al. (2013) was used to determine the pasting properties. A suspension of 3 g starch in 25 ml distilled water was subjected under controlled heating and cooling cycles under constant shear. During this cycle it was held at 50 °C for a minute, heated from 50 to 95 °C at 6 °C/min, held at 95 °C for 5 minutes, cooled to 50 °C at 6 °C/min, and held at 50 °C for 5 minutes. The pasting temperature, peak, trough, breakdown, final and setback viscosities were obtained from the RVA curves and viscosities were expressed as Pascal second (Pa. s).

2.10. Statistical analysis

All analyses were performed in triplicate. All results were reported as means ± standard deviation of three independent trials. Multivariate analysis of variance (MANOVA) was used to establish differences between initiators and methods of complexation. Duncan's multiple range tests was used to separate means where significant difference existed (IBM SPSS version 22, 2013).

3. Results and discussion

3.1. Morphology of native and modified BGN starches

Scanning electron microscopy (SEM) was used to determine the morphology of native and modified BGN starches. There was a significant difference between granular morphology of native and modified BGN starches. Native BGN starches displayed round, oval and elliptical shapes (Fig. 1) which is typical of legume starches. This results concurs with reports made by Adebowale and Lawal (2002), Sirivongpaisal (2008), Kaptso et al. (2015), Oyeyinka et al. (2015) and Ma et al. (2017) for BGN starch granular morphology. The granule surfaces all appeared to have smooth surfaces with no evidence of ruptures.

The SEM images of complexed BGN starches (Fig. 1) show clearly the characteristic BGN starch granules with cyclodextrin particles adhered to their surface, thus indicating the inclusion complex formation. The X-ray diffraction results for complexed BGN starches (shown in Figs. 4 and 5) concurred with the SEM image findings, showing that all the complexed BGN starches retained their crystallinity.

3.2. Structure of native and modified BGN starches determined by Fourier transform infrared spectroscopy

The FTIR spectrum of native BGN starch is shown in Fig. 2 with a broad peak at 3285.34 cm^{-1} that is in the range of 3200−3600 cm^{-1}. This is characteristic of OH stretching due to the hydrogen bonded hydroxyl groups contributing to the vibrational stretches associated with intra and intermolecular bound hydroxyl groups which make up the gross starch structure (Zhang and Han, 2006; Afolabi, 2012; Oyeyinka et al., 2015). Afolabi (2012) and Oyeyinka et al. (2015) reported similar results for BGN starches. The sharp peak at 2931.69 cm^{-1} is attributed to the C-H stretching. The sharp bend at 1634.36 cm^{-1} was attributed to the water bending vibrations. The tightly bound water absorbed by the amorphous regions in the starch
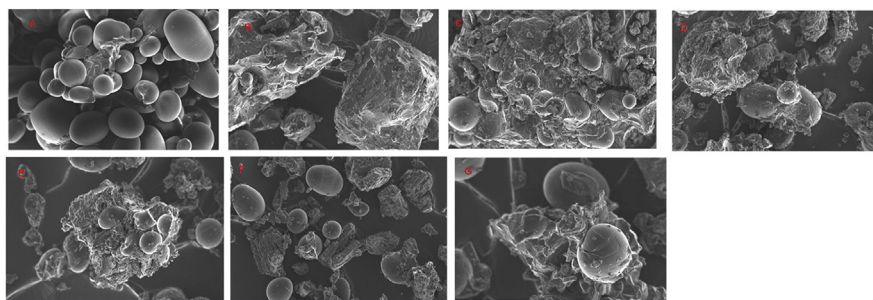

Fig. 1. Scanning electron micrographs of (A) native BGN starch, BGN starch-catechin complexes modified through; (B) microwave method using alpha cyclodextrin, (C) microwave method using beta cyclodextrin, (D) kneading method using alpha cyclodextrin, (E) kneading method using beta cyclodextrin, (F) co-evaporation method using alpha cyclodextrin, (G) co-evaporation method using beta cyclodextrin.
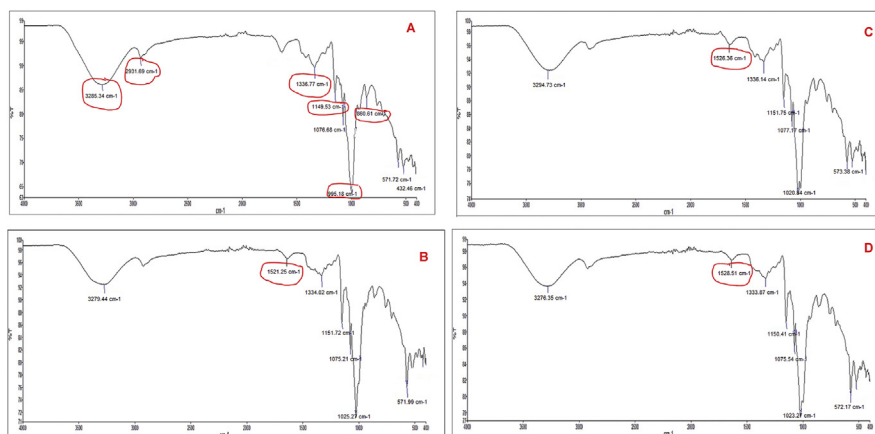
Fig. 2. FTIR spectrum of (A) native BGN starch, BGN starch-catechin complexes modified through; (B) co-evaporation method using alpha cyclodextrin, (C) co-evaporation method using beta cyclodextrin, (D) microwave method using alpha cyclodextrin.

molecules gives rise to these vibrations. Comparable results have been reported for pea and BGN starch by Zhang and Han (2006) and Oyeyinka et al. (2015), respectively. The wavelength of 1336.77 cm^{-1} is attributed to the stretching vibrations of C-O and C-C bonds which are found in the wavelength region of 800−1300 cm^{-1} (Oyeyinka et al., 2015; Wang et al., 2015).

The peak at 1149.53 cm^{-1} in the native BGN starch is due to the C-O, C-C and C-O-H stretching. Comparable results have been reported by Oyeyinka et al. (2015) and Warren et al. (2016). Zhang and Han (2006) reported the peaks at 1076.68 cm^{-1} and 995.18 cm^{-1} to be characteristic of the anhydroglucose ring O-C stretch. Furthermore, the peak at 995 cm^{-1} is known to be sensitive to water. The peak at 860.61 cm^{-1} is attributed to the C-O stretching in the native BGN starch as well as to the deformation of C-H vibrations. The native BGN starch exhibited complex vibrations at wavelengths below 800 cm^{-1}, that is, 571.72 and 432.46 cm^{-1} thus owing to the glucose pyranose ring skeletal mode vibration. This result is in agreement with reports made by Oyeyinka et al. (2015). Native BGN starch is therefore made up of glucose molecules just like all the other starches. In addition, it confirms that it is made up of carbon, hydrogen and oxygen atoms which make up the gross starch structure just like other starches.

The modified starches with catechin all showed a new absorption peak in the range 1520−1560 cm^{-1}. The new absorption peaks were attributed to the C-C stretching within the catechin aromatic ring. This result is in agreement with reports made by Spizzirri et al. (2010) in which they awarded the 1557 and 1525 cm^{-1} peaks to the C-C stretching found within the catechin aromatic ring. In addition, similar results were reported by Curcio et al. (2009) where a new absorption peak at 1558 cm^{-1} was awarded to the aromatic C-C stretch. This then suggests that catechin was grafted

onto the BGN starch molecules. Following modification of native BGN starch some spectral bands disappeared as well as the appearance of new peaks. However, since BGN starch, beta and alpha cyclodextrin are all carbohydrates this therefore means that they have similar groups. This resulted in the spectral peaks of BGN starch being covered by similar groups of cyclodextrins (alpha and beta). This explains the similarity of modified BGN starch spectral peaks with those of modified BGN starch complexed with cyclodextrin (alpha and beta).

3.3. Structure of modified BGN starch by complexation

3.3.1. Co-evaporation

Co-evaporation resulted in a shift in some spectral bands of the native BGN starch. Complexed BGN starches using beta cyclodextrin increased the broad peak at 3285 cm^{-1} in native BGN starch to 3294 cm^{-1} and 3298 cm^{-1} (with catechin) in complexed BGN starches. The spectral band at 1149 cm^{-1} in the native BGN starch which is a characteristic C-O, C-C and C-O-H stretching shifted to 1151 cm^{-1} in all complexed BGN starches. In addition, the characteristic hydroglucose ring O-C stretch at 1077 cm^{-1} in the native BGN starch decreased to 1075 cm^{-1} in alpha cyclodextrin complexed BGN starches. There was a disappearance of the 860 cm^{-1} peak in beta cyclodextrin complexed BGN starches. On the other hand, new peaks were observed in the complexed BGN starches in comparison to the native BGN starch. The new peaks ranged from 1020 to 1025 cm^{-1} which are found in the amorphous regions of the complexed BGN starches. In addition, new peaks at low wavelengths were also observed and they ranged from 521 to 526 cm^{-1} which is attributed to skeletal mode vibrations within the starch molecules. Lastly, the peaks at 1521.25 cm^{-1} (Fig. 2B) and 1526.36 cm^{-1} (Fig. 2C) found in the alpha and beta cyclodextrin catechin complexed BGN starches with catechin, respectively, were characteristic of the C-C stretching of catechin aromatic ring. These peaks gave an indication that catechin was successfully grafted to the BGN starch resulting in the formation of new complexes.

3.3.2. Microwave

Microwave as a complexation method resulted in some spectral bands within the native BGN starch shifting in the complexed BGN starches as well as the formation of new peaks indicating that BGN starch was complexed with cyclodextrin (alpha and beta) and catechin in others. The broad peak at 3285 cm^{-1} in native BGN starch decreased to 3276 cm^{-1} in alpha cyclodextrin + catechin complexed BGN starch while it increased to 3288 and 3298 cm^{-1} in beta cyclodextrin and beta cyclodextrin + catechin complexed BGN starches, respectively. It was speculated that the addition of catechin and cyclodextrin (alpha and beta) to the BGN starch contributed to the vibrational stretches within the intra and intermolecular bound hydroxyl groups

making up the gross structure of starch. The 860 cm^{-1} peak which was found in the native BGN starch was not observed in all complexed BGN starches modified through the microwave method. Some peaks in the native BGN starch shifted in the complexed BGN starch. The 1149 cm^{-1} peak in native BGN starch which is attributed to the C-O, C-C and C-O-H stretching appeared at 1151 cm^{-1} in complexed BGN starches. Furthermore, the characteristic hydroglucose ring O-C stretch at 1077 cm^{-1} in native starch appeared at 1075 cm^{-1} in alpha cyclodextrin complexed starches. In addition, new peaks were observed in the complexed BGN starches which gave an indication that new complexes were formed. The peaks at low wavelengths attributed to the skeletal mode vibrations ranged from 404 to 526 cm^{-1}. The peaks in amorphous regions of complexed BGN starches were in the range of 1020−1023 cm^{-1}. Finally, the new peaks observed at 1528.51 (Fig. 2D) and 1530.08 cm^{-1} (Fig. 3E) within the alpha and beta cyclodextrin catechin complexed BGN starches is a characteristic C-C stretching of catechins' aromatic ring. This gave an indication of catechin grafting to the BGN starch.

3.3.3. Kneading

Kneading also resulted in a shift in some spectral bands in the native BGN starch as well as the appearance of new peaks in the complexed BGN starches. The broad peak at 3285 cm^{-1} in the native BGN starch reduced to 3269 and 3275 cm^{-1} (with catechin) in alpha cyclodextrin complexed BGN. However, in the beta cyclodextrin complexed BGN starches it increased to 3292 and 3295 cm^{-1} (with catechin). The 860 cm^{-1} peak found in the native BGN starch disappeared in all complexed BGN starches through the kneading method with exception of the alpha cyclodextrin + catechin complexed BGN starch. New peaks at lower wavelengths
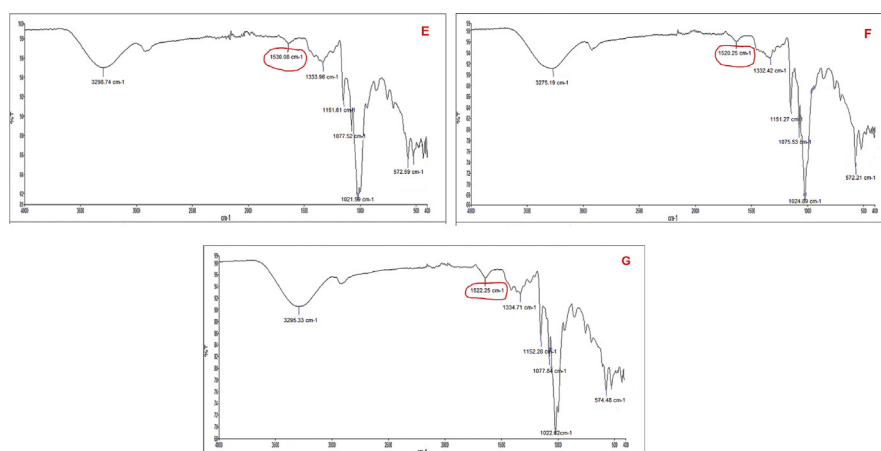

Fig. 3. FTIR spectrum of BGN starch-catechin complexes modified through; (E) microwave method using beta cyclodextrin, (F) kneading method using alpha cyclodextrin, (G) kneading method using beta cyclodextrin.

were observed in the range of $520-528$ cm^{-1} and these are known to be due to the skeletal mode vibrations within the starch molecule. Furthermore, new peaks in the range of $1022-1024$ cm^{-1} were also observed and these are found in the amorphous regions of the complexed BGN starches. The characteristic hydroglucose ring O-C stretch peak at 1075 cm^{-1} in the native BGN starch appeared at 1077 cm^{-1} in the alpha cyclodextrin complexed BGN starches. The 1149 cm^{-1} peak in native starch just like in other complexation methods appeared at 1151 cm^{-1} in complexed BGN starches. Lastly, the new peaks observed at 1520.25 (Fig. 3F) and 1522.25 cm^{-1} (Fig. 3G) within the alpha and beta cyclodextrin catechin complexed BGN starches were a characteristic of catechin aromatic ring C-C stretch. These gave an indication that catechin was grafted to the BGN starch.

3.4. Starch crystallinity

The powder X-ray diffraction patterns of native and modified BGN starches are presented in Figs. 4 and 5. Native BGN starch had diffraction peaks at 2θ values of 15°, 17° and 23° exhibiting a typical C type crystallinity. This means that BGN starch (legume starch) has lower digestibility in comparison to cereal starches. It therefore promotes moderate and slow insulin and postprandial glucose responses (Sandhu and Lim, 2008). Furthermore, the lowest digestibility and low GI values of BGN starch makes it suitable for diabetic patients. Type C starch crystallinity has been reported to be a mixture of A- and B- types. The packing arrangement of the amylopectin double helices as well as their hydration level differentiates between the A- and B- types. The A-type is more compact and its hydrated in-between each double
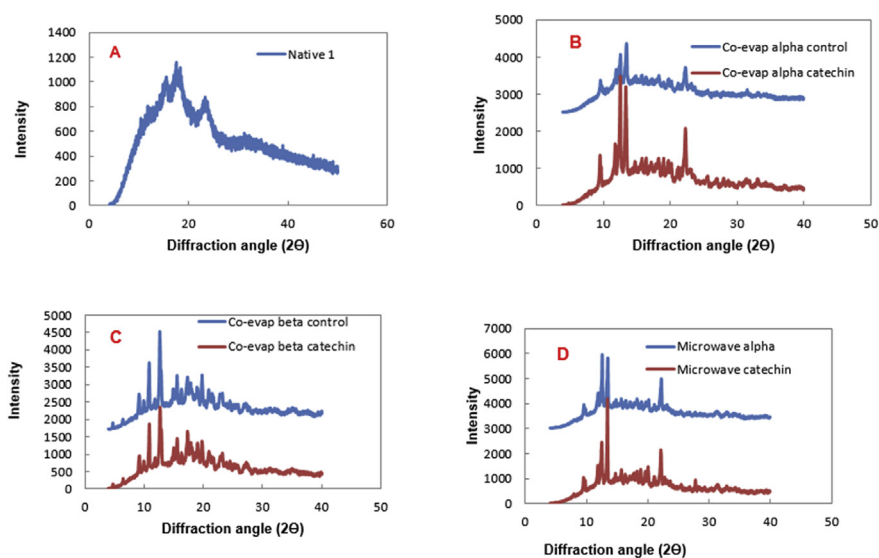

Fig. 4. Powder X-ray diffraction patterns of (A) native BGN starch, BGN starch-catechin complexes modified through; (B) co-evaporation method using alpha cyclodextrin, (C) co-evaporation method using beta cyclodextrin, (D) microwave method using alpha cyclodextrin.
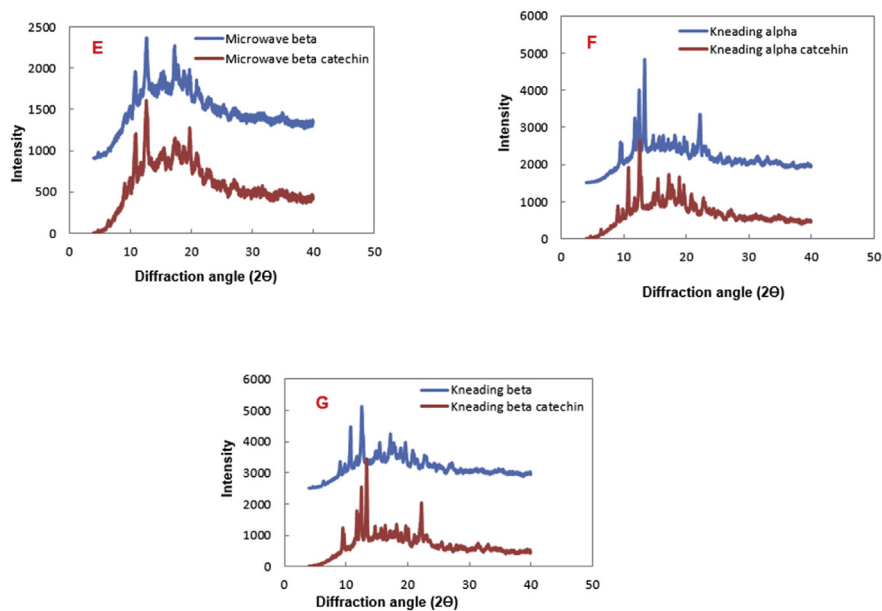
Fig. 5. Powder X-ray diffraction patterns of (E) microwave method using beta cyclodextrin, (F) kneading method using alpha cyclodextrin, (G) kneading method using beta cyclodextrin.

helix, while the B-type is more hydrated in the central cavity and loosely packed and (Oyeyinka et al., 2015). In addition type C is characteristic for legume starches (Hoover et al., 2010). This result concurs with the reports made by Afolabi (2012) and Oyeyinka et al. (2015) of native BGN starch exhibiting type C crystallinity. However, some researchers reported the A-type crystallinity for some varieties of BGN (Sirivongpaisal, 2008; Kaptso et al., 2015).

There was an increase in the starch crystallinity in all complexed BGN starches (Figs. 4 and 5) irrespective of the methods (co-evaporation, microwave, kneading). This was evidenced by an increase in the X-ray diffraction peaks in comparison to those of native BGN starch. Sharper peaks were an indication of increased starch crystallinity following complexation. In addition, Sapana and Shashikant (2014) reported the appearance of new peaks, shifting of some peaks as well as the sharpening of X-ray diffraction peaks due to the formation of complexes. The X-ray diffraction patterns of complexed BGN starches had (1) sharper peaks in comparison to the native BGN starch, (2) new peaks displayed and (3) some peaks shifted from the original existing ones prior to complexation. This is a confirmation that native BGN starch was successfully complexed with cyclodextrins (alpha and beta). The highly ordered crystalline structures of the complexed BGN starches were because of the intra- and intermolecular hydrogen bonds within the starch molecules.

3.5. Effect of temperature on native and modified BGN starch swelling capacity

The effect of temperature on swelling power of Bambara groundnut (BGN) starches (native and modified) indicates the different molecular organisation within starch granules. The swelling of starches was found to be a function of temperature (Fig. 6). The swelling power of native and modified BGN starches increased with an increase in temperature. Adebowale and Lawal (2002), reported a similar trend of increased swelling power with increase in temperature for BGN starch. This trend concurs with reports of Adebowale et al. (2002); Adebowale and Lawal (2003) that the swelling power of legume starches increases with an increase in temperature. The swelling capacities of BGN starches ranged from 0.36 to 4.84 g/g. The swelling capacities of BGN starches were highest at 80 °C and 90 °C because starch granules gradually swell as the temperature increases. This could be attributed to the rupturing of the intermolecular hydrogen bonds of the amorphous regions in the starch granule thereby resulting in irreversible and continuous absorption of water (Adebowale and Lawal, 2003).

The complexation methods (co-evaporation, microwave and kneading) reduced the swelling power of native BGN starch. This reduction may be due to the increased crystallinity of those starches as crystalline granules limit starch swelling capacity (Adebowale and Lawal, 2002). This increased starch crystallinity is confirmed by the sharper X-ray diffraction peaks (Figs. 4 and 5) of these starches in comparison to those of native BGN starch. In comparison to BGN native starch, all modification methods had a significant effect ($p \leq 0.05$) on the starch swelling capacity. However, the kneading and co-evaporation methods did not give significantly different results. All initiators had a significant impact on the swelling capacity of BGN starches (native and modified). Furthermore, the initiators significantly differed ($p \leq 0.05$) from each other with the exception of alpha cyclodextrin which did not differ
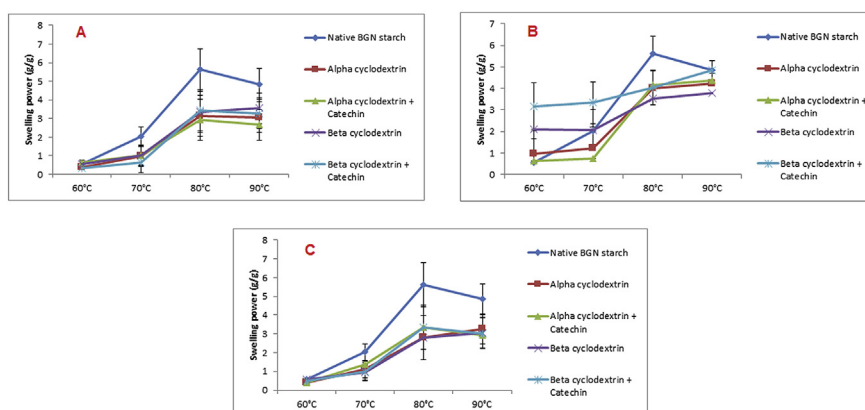

Fig. 6. Effect of temperature on swelling of native and modified Bambara groundnut starches. A: Co-evaporation, B: Microwave, C: Kneading.

significantly from beta cyclodextrin and alpha cyclodextrin + catechin. Temperatures had a significant effect ($p \leq 0.05$) on the starch swelling capacity and they significantly differed from each other. However, high temperatures (80 °C and 90 °C) did not significantly differ in the swelling power of native and modified BGN starches. This may be due to gelatinisation when the starch granules are heated and they absorb water and gradually swell; however, at temperatures higher than gelatinisation temperature the starch granules do not continue to swell because the starch granule structure will be essentially lost.

3.6. Effect of temperature on native and modified BGN starch solubility

Starch solubility for native and modified BGN starches indicated solubility to be inversely proportional to temperature as shown in Fig. 7. Water was used as solvent for the solubility test. Solubility of these starches was maximal at lower temperature (60 °C) and it decreased with an increase in temperature. The solubility of BGN starches ranged from 0.61 to 46.04 g/100 g. Native BGN starch had the least solubility (0.61 g/100 g) and BGN starch modified through the kneading method with alpha cyclodextrin had the maximum solubility (46.04 g/100 g). Complexation methods significantly increased the water solubility of native BGN starch at all studied temperatures. High temperatures had increased solubility because an increase in temperature resulted in the weakening of the starch intermolecular binding forces thereby enhancing the leaching of starch granular particles (leading to the increased solubility) (Adebowale and Lawal, 2002; Lawal et al., 2004). Starches complexed with alpha cyclodextrin had higher solubility in comparison to those complexed with beta cyclodextrin because beta cyclodextrin is less soluble than alpha cyclodextrin. Del Valle (2004) reported beta cyclodextrin to be at least 9 times less soluble than other cyclodextrins. The lower solubility of beta cyclodextrin in water is driven by the less favourable entropy.
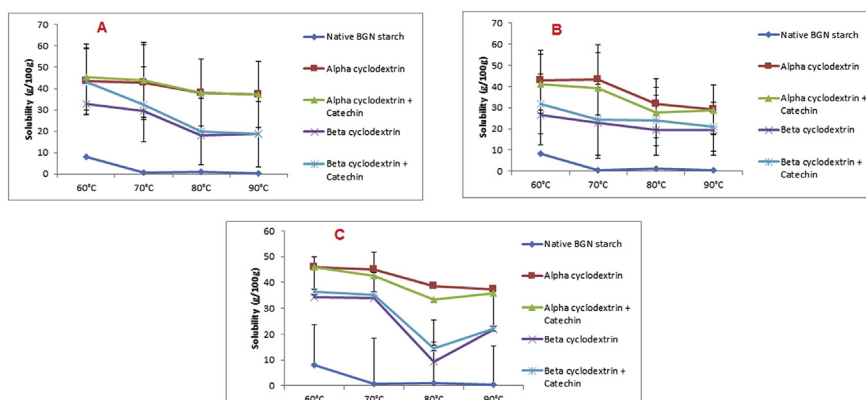

Fig. 7. Effect of temperature on solubility of native and modified Bambara groundnut starches. A: Co-evaporation, B: Microwave, C Kneading.

In comparison to native BGN starch, all modification methods had a significant effect ($p \leq 0.05$) on the starch solubility. However, kneading and co-evaporation methods did not differ significantly from each other. The initiators all had a significant impact on the starch solubility. Furthermore, the initiators significantly differed ($p \leq 0.05$) from each other with the exception of alpha cyclodextrin which did not differ significantly from alpha cyclodextrin + catechin. At higher temperatures there was enhanced starch mobility which resulted in increased dispersion of starch granules thus leading to increased starch solubility. Starches modified through the microwave method were more soluble in water when compared to the ones modified through co-evaporation and kneading methods. This is because co-evaporated and kneaded methods did not involve heat hence the starch granules were not completely gelatinised thus restricting their solubility in cold water.

3.7. Water and oil absorption capacities of native and modified BGN starches

Water absorption capacity is a function of water holding ability of the starch sample. Water absorption properties of native and modified BGN starch ranged from 0.23 − 1.17 g/g (Table 1). The complexation methods significantly ($p \leq 0.05$) reduced the water absorption capacity of the native BGN starch. BGN starch complexed with beta cyclodextrin absorbed more water when compared to the ones complexed with alpha cyclodextrin. This may probably be due to the higher hydrophilicity of beta cyclodextrin in comparison to alpha cyclodextrin. Furthermore, most BGN starches complexed with cyclodextrin + catechin absorbed more water than those without catechin. This may be because catechin hydroxyl groups increased the complexes' hydrophilicity property hence an increase in the water absorption capacity.

Table 1. Water and oil absorption capacities of native and modified Bambara groundnut starch.[a]

Modification method	Initiators	Water absorbed (g/g)	Oil absorbed (g/g)
Native BGN starch	Native starch	1.17 ± 0.71^{a}	1.06 ± 0.03^{a}
Microwave	Alpha cyclodextrin	0.58 ± 0.05^{a}	1.09 ± 0.01^{a}
	Alpha cyclodextrin + catechin	0.44 ± 0.04^{b}	1.04 ± 0.03^{a}
	Beta cyclodextrin	0.91 ± 0.02^{c}	1.07 ± 0.02^{a}
	Beta cyclodextrin + catechin	1.02 ± 0.04^{d}	1.07 ± 0.03^{a}
Co-evaporation	Alpha cyclodextrin	0.24 ± 0.03^{a}	1.07 ± 0.03^{a}
	Alpha cyclodextrin + catechin	0.23 ± 0.04^{a}	1.05 ± 0.04^{a}
	Beta cyclodextrin	0.62 ± 0.18^{b}	1.03 ± 0.02^{a}
	Beta cyclodextrin + catechin	0.76 ± 0.04^{b}	1.02 ± 0.02^{a}
Kneading	Alpha cyclodextrin	0.44 ± 0.07^{a}	1.03 ± 0.02^{a}
	Alpha cyclodextrin + catechin	0.46 ± 0.11^{a}	1.05 ± 0.03^{a}
	Beta cyclodextrin	0.73 ± 0.03^{b}	1.05 ± 0.02^{a}
	Beta cyclodextrin + catechin	0.69 ± 0.01^{b}	1.06 ± 0.04^{a}

[a] Mean values of triplicate determinations ± standard deviation. Means within a column (under the same row heading) followed by the same superscript are not significantly different.

The initiators within each method were significantly ($p \leq 0.05$) different. In the microwave method, all initiators significantly ($p \leq 0.05$) differed from each other. In addition, beta cyclodextrin + catechin complex had the maximal water absorption (1.02 g/g) while alpha cyclodextrin + catechin complex absorbed the least (0.44 g/g).

Among the co-evaporation method, beta cyclodextrin + catechin complex had the highest water absorption (0.76 g/g) while alpha cyclodextrin + catechin had the lowest (0.23 g/g). The initiators used significantly differed from each other. However, alpha cyclodextrin initiators did not differ significantly from each other; and this trend applies to the beta cyclodextrin initiators.

Among the kneading method, beta cyclodextrin complex had the highest water absorption (0.73 g/g) while alpha cyclodextrin had the lowest (0.44 g/g). The initiators significantly differed from each other. However, alpha cyclodextrin initiators did not differ significantly from each other; and this trend applies to the beta cyclodextrin initiators.

Oil absorption capacity works on the principle of physically entrapping oil through capillary attraction. Oil absorption capacity plays an important role in food products by retaining flavour, improving palatability, as well as extending the shelf life of the food product especially in meat and bakery products. The oil absorption properties of BGN starches (native and modified) ranged from 1.02−1.07 g/g. BGN starch complexes (beta cyclodextrin and beta cyclodextrin + catechin) in the microwave method and BGN starch complex (alpha cyclodextrin) in the co-evaporation methods had the maximal oil absorption capacity of 1.07 g/g. On the other hand, BGN starch complex (beta cyclodextrin + catechin) in the co-evaporation method absorbed the least oil at 1.02 g/g. Native BGN starch absorbed 1.06 g/g oil and this is lower than 1.76 g/g reported by Adebowale et al. (2002). However, it was higher than 1.01 g/g reported by Sirivongpaisal (2008). There was no significant difference in the oil absorbed in all BGN starches (native and modified) irrespective of the modification used. The oil absorption capacities within the complexation methods (microwave, co-evaporation and kneading) were higher than water absorption capacities. This may be due to the higher level of hydrophobicity compared to hydrophilicity in the complexed starches.

3.8. Pasting properties of native and modified BGN starches

The pasting characteristics of native and modified BGN starches are presented in Table 2. Pasting temperature is the temperature at which starch granules start to swell, and it gives an indication of the minimum temperature required to initiate starch gelatinisation (Shimelis et al., 2006; Jan et al., 2013). The pasting temperature of native and modified BGN starches ranged from 79.9 °C to 85.7 °C. BGN starch

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Table 2. Pasting properties of native and modified Bambara groundnut starch.[a]

Modification method	Initiators	Peak viscosity	Trough viscosity	Breakdown viscosity	Final viscosity	Set back	Peak time (min)	Pasting temp (T°C)
Native	Native starch	4.767 ± 177.49[a]	3.013 ± 8.72[a]	1.654 ± 22.61[a]	4.876 ± 180.27[a]	1.957 ± 16.50[a]	4.70 ± 0.03[a]	79.90 ± 0.00[a]
Microwave	α-cyclodextrin	0.562 ± 21.52[a]	0.463 ± 11.93[a]	0.111 ± 1.73[a]	0.974 ± 20.98[a]	0.514 ± 9.29[a]	7.00 ± 0.00[a]	85.67 ± 0.03[a]
	α-cyclodextrin + Catechin	0.344 ± 10.41[b]	0.267 ± 10.79[b]	0.076 ± 1.53[b]	0.603 ± 17.21[b]	0.326 ± 10.58[b]	7.00 ± 0.00[a]	85.70 ± 0.00[a]
	β-cyclodextrin	0.704 ± 74.63[c]	0.641 ± 83.46[c]	0.088 ± 1.00[c]	1.114 ± 72.69[c]	0.473 ± 24.09[c]	6.98 ± 0.04[a]	84.57 ± 0.58[b]
	β-cyclodextrin + Catechin	0.543 ± 9.85[a]	0.448 ± 10.50[a]	0.097 ± 1.15[d]	0.893 ± 12.50[d]	0.442 ± 2.00[d]	7.00 ± 0.00[a]	85.10 ± 0.58[a,b]
Co-evaporation	α-cyclodextrin	0.812 ± 2.52[a]	0.801 ± 3.21[a]	0.010 ± 0.58[a]	1.430 ± 7.51[a]	0.628 ± 4.51[a]	5.36 ± 0.15[a]	82.48 ± 0.08[a]
	α-cyclodextrin + Catechin	0.714 ± 4.73[b]	0.692 ± 21.38[b]	0.012 ± 1.73[a]	1.249 ± 11.36[b]	0.558 ± 16.65[b]	6.96 ± 0.04[b]	81.62 ± 0.03[b]
	β-cyclodextrin	0.882 ± 11.72[c]	0.831 ± 14.18[c]	0.055 ± 0.58[c]	1.473 ± 16.82[c]	0.645 ± 5.51[a]	5.20 ± 0.00[c]	81.85 ± 0.52[b]
	β-cyclodextrin + Catechin	0.678 ± 4.58[d]	0.647 (10.54)[d]	0.036 ± 0.00[d]	1.151 ± 4.51[d]	0.510 ± 0.00[c]	7.00 ± 0.00[b]	82.43 ± 0.06[a]
Kneading	α-cyclodextrin	0.863 ± 21.01[a]	0.867 ± 24.01[a]	0.002 ± 0.58[a]	1.574 ± 45.65[a]	0.730 ± 23.12[a]	6.12 ± 0.36[a]	81.55 ± 0.00[a]
	α-cyclodextrin + Catechin	0.907 ± 6.11[b]	0.891 ± 0.58[a]	0.015 ± 5.51[b]	1.655 ± 10.07[b]	0.765 ± 9.71[b]	5.74 ± 0.14[b]	80.62 ± 0.03[b]
	β-cyclodextrin	0.894 ± 9.45[b]	0.886 ± 10.21[a]	0.003 ± 0.58[a,c]	1.647 ± 15.13[b]	0.757 ± 5.29[a,b]	6.21 ± 0.13[a]	81.50 ± 0.00[c]
	β-cyclodextrin + Catechin	0.809 ± 14.05[c]	0.799 ± 14.50[b]	0.008 ± 0.58[c]	1.457 ± 34.21[c]	0.651 ± 18.00[c]	6.93 ± 0.07[c]	80.65 ± 0.00[d]

[a] Mean values of triplicate determinations ± standard deviation. Means within a column (under the same row heading) followed by the same superscript are not significantly.

modified through microwave (alpha cyclodextrin + catechin) had the highest pasting temperature (85.7 °C) while native BGN starch had the lowest pasting temperature (79.9 °C). All complexation methods were observed to increase the pasting temperature of native BGN starch. This increase may be attributed to cyclodextrin's tendency to increase the crystallinity region due to the reorientation of starch granules. This resulted in strengthened starch intramolecular bonds allowing starch to require more heat before paste formation and structural disintegration (Olu-Owolabi et al., 2014). In addition, higher pasting temperatures are an indication of higher resistance towards swelling and this concurs with the results of swelling ability of the complexed starches as shown in Fig. 6.

Peak viscosity is the maximum viscosity obtained during starch gelatinisation and it indicates the starch granules' water binding capacity. It is therefore used as an important parameter in the processing of starch. The peak viscosity ranged from 0.3443 to 4.767 Pa. s. The peak viscosity (4.767 Pa. s) of native BGN starch was significantly higher than the modified starches. Starch modification significantly reduced the peak viscosity of native starch, with BGN starch modified through the microwave method (alpha cyclodextrin + catechin) having the least peak viscosity of 0.3443 Pa. s. Within the microwave method, the peak viscosity significantly ($p \leq 0.05$) differed while that of alpha cyclodextrin and beta cyclodextrin + catechin did not differ significantly from each other. The initiators within the co-evaporation method had a significant effect ($p \leq 0.05$) on the starches' peak viscosity. Among the kneading method, the initiators significantly differed from each other with exception of alpha cyclodextrin + catechin and beta cyclodextrin that did not have a significant effect on the peak viscosity. The higher peak viscosity of native BGN starch in comparison to modified starches could be attributed to the lack of new functional groups and the native starch's unrestricted swelling property (Adebowale et al., 2002). The results show that the peak viscosity of all BGN starches (native and modified) differs from each other and this might be due to the differences in the rate at which starch granules swell and absorb water when heated (Falade et al., 2014; Wu et al., 2015). According to Wu et al. (2015), high peak viscosity is an indication that the starch has high water binding capacity; therefore it can be concluded that native BGN starch can swell easily and form a paste in comparison to the modified BGN starches. Furthermore, Falade et al. (2014) and Sanni et al. (2001) reported that there is a strong correlation between peak viscosity and starch damage, high starch damages results in high peak viscosity.

Breakdown viscosity gives an indication of the starch organisation structure. The starch granules susceptibility to disintegrate is known as breakdown viscosity (Jan et al., 2013; Falade et al., 2014; Wu et al., 2015). The breakdown viscosity of native and modified BGN starches ranged from 0.0023 to 1.654 Pa. s. Native BGN starch had a significantly higher breakdown viscosity (1.654 Pa. s) while BGN starch modified through kneading with alpha cyclodextrin had the lowest breakdown viscosity

(0.0023 Pa. s). All modification methods were observed to reduce native starch breakdown viscosity. Among the microwave method, all initiators had a significant ($p \leq 0.05$) effect on the breakdown viscosity of starch. Within the co-evaporation method, all initiators significantly differed ($p \leq 0.05$) from each other with exception of alpha cyclodextrin and alpha cyclodextrin + catechin which did not differ significantly from each other. Within the kneading method, all initiators had a significant ($p \leq 0.05$) effect on the starches' breakdown viscosity.

However, beta cyclodextrin did not differ significantly either from alpha cyclodextrin or beta cyclodextrin + catechin. Complexation methods were observed to have a significant effect in reducing the breakdown viscosity of BGN native starch more especially the kneading method. According to Falade et al. (2014), higher breakdown viscosity means that the starch has lower ability to withstand heating and shear stress during cooking. Low breakdown viscosity indicates thermal stability while high values indicate relatively low heat stability. Therefore, native BGN showing higher breakdown viscosity will have a lower ability to withstand shear stress and heating during cooking in comparison to starches with lower breakdown viscosity. Therefore, modified starches are preferred at higher temperatures due to their high thermal stabilities. In addition, higher breakdown viscosity gives an indication of starch which has undergone a higher degree of swelling and subsequent disintegration.

When starch pastes start to cool down there is re-association of the solubilised amylose and amylopectin molecules which results in increased viscosity. This rise in viscosity is known as the setback viscosity. Setback viscosity measures the starch tendency towards retrogradation (Jan et al., 2013; Falade et al., 2014; Olu-Owolabi et al., 2014). The setback viscosity of native and modified BGN starches ranged from 0.326 to 1.9567 Pa. s. Native BGN starch had the highest setback viscosity (1.9567 Pa. s) while BGN starch modified through microwave method (alpha cyclodextrin + catechin) had the lowest setback value of 0.326 Pa. s. Native BGN starch had a significantly higher setback viscosity when compared to modified starches. This shows that native BGN starch has a high tendency towards retrogradation. On the other hand, modification methods decreased the setback viscosity of native starch. This is because modification processes involve the introduction of functional groups which then prevent the starch molecules from re-associating after cooling thereby resulting in lower setback viscosity (Adebowale et al., 2002; Adebowale and Lawal, 2003; Lawal et al., 2004). Among the microwave method, the initiators had a significant effect on the setback viscosity as they all significantly ($p \leq 0.05$) differed from each other. Within the co-evaporation method, the initiators significantly ($p \leq 0.05$) differed from each other; however, alpha and beta cyclodextrin did not differ significantly. Within the kneading method, the initiators significantly ($p \leq 0.05$) differed from each other except for beta cyclodextrin which did not differ significantly either from alpha cyclodextrin or alpha cyclodextrin + catechin.

Final viscosity is used to determine starch quality and stability of the cooked starch paste in food products. Final viscosity gives an indication of the starch ability to form a gel or viscous paste after cooking and cooling (Shimelis et al., 2006; Jan et al., 2013). The final viscosities of native and modified BGN starches ranged from 0.6033 to 4.8763 Pa. s. Native BGN starch had the highest final viscosity of 4.8763 Pa. s while BGN starch modified through microwave method (alpha cyclo-dextrin + catechin) had the lowest final viscosity value of 0.6033 Pa. s.

4. Conclusion

Starch modification significantly improved functional characteristics of native BGN starch. The high breakdown viscosity of native BGN starch gave an indication that native BGN starch has a lower ability to withstand shear stress and heat during cooking processes. The modified starches will withstand high shear stress and temperatures during processing. Modification processes were observed to minimise starch retrogradation. The lower setback viscosities of modified starches are an advantage in retarding retrogradation.

Declarations

Author contribution statement

Nontobeko Benhilda Gulu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Victoria Jideani: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Ayesha Jacobs: Conceived and designed the experiments; Analyzed and interpreted the data.

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The authors declare no conflict of interest.

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