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ORIGINAL ARTICLE

Physicochemical properties of Bambara groundnut (*Vigna subterranea*) starch annealed at different temperatures

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Abstract

Bambara groundnut is a starchy grain that could serve as a starch source for the industry. In the native form, starches are generally unsuitable for most industrial applications and hence are modified. Physical modification methods including annealing are preferred for starch modification because they are environmentally friendly. Previous studies on the annealing of Bambara starch focused on single-temperature treatment. This study investigated the physicochemical properties of Bambara starch annealed at varying temperatures of 45, 50, 55, and 60°C for 24 h. The amylose contents of the starches varied between 27.18% and 28.53%. Annealed Bambara starches showed significantly lower swelling and solubility values than the native starch. Furthermore, except for the time to peak (4.05–4.44 min), pasting temperatures (81.95–84.00°C), gelatinization temperatures (70.47–77.23°C), and gelatinization enthalpies (3.95–4.41 J/g) which increased the pasting properties of the annealed starches decreased. The result of this study should guide researchers on the specific annealing temperature to use for specific food and industrial applications.

Novelty impact statement: Bambara grains are rich in starch which could be used as an alternative and cheap starch source to the conventional corn and potato sources. This study report for the first time the impact of different annealing temperatures on the physicochemical properties of Bambara starch. Annealing was chosen because it is an environmentally friendly method of starch modification. Results from this study show that the modified starch would have varying applications in the food industry, for example as a thickener, and as a stabilizer.

1 | INTRODUCTION

Bambara groundnut is an underutilized grain legume which is widely grown in Africa and some areas in Asia, Northern Australia, and South America (Diedericks et al., 2019). The Bambara plant is highly tolerant to drought (Oyeyinka et al., 2015) and produces better yield under poor agronomic conditions (Mazahib et al., 2013). The annual production of Bambara grains is estimated to be approximately 200,000 t from an area of about 250,000 ha worldwide (Majola et al., 2021). Globally, sub-Saharan Africa is the leading producer of Bambara groundnut, with West Africa as the largest producer (FAOSTAT, 2020). According to Bamshaiye et al. (2011), West Africa produces over 45% of the total production of Bambara groundnut in Africa, while this region reportedly contributes to about 74% of global production (FAOSTAT, 2020). Like other hard-to-cook legumes, efforts are being made to expand its utilization options (Akinwande et al., 2017). The grains of Bambara is regarded as an emerging source of plant-based protein (Yang et al., 2022) which could be explored as a functional ingredient in food products (Arise et al., 2016; Diedericks et al., 2019).

Bambara groundnut has an excellent nutritional profile including a relatively high level of protein (15%–27%) (Oyeyinka & Oyeyinka, 2018) and a good balance of essential amino acids which could be used to enhance the nutritional value of foods (Yao et al., 2015). Besides the protein content, the matured seeds are equally a good source of carbohydrate, the bulk being starch (Murevanhema & Jideani, 2013; Oyeyinka & Oyeyinka, 2018). Depending on the source and variety of the grain, the starch of Bambara groundnut may vary between 18% and 50% (Adebowale et al., 2002; Adebowale & Lawal, 2002; Afolabi, 2012; Oyeyinka et al., 2015; Oyeyinka, Singh, & Amonsou, 2017; Poulter, 1981; Sirivongpaisal, 2008). However, unmodified starches generally have inherent limitations such as insolubility in water, easy retrogradation, and unstable under high mechanical stress, pH, and temperature (Ashogbon, 2018), which makes them unsuitable for most industrial applications (Bangar et al., 2022).

Modification methods ranging from enzymatic, chemical, technological, and physical or combinations of these methods have been used to enhance the functionality and physicochemical properties of starches from various sources (Bangar et al., 2022; Oyeyinka & Oyeyinka, 2018). However, the use of physical methods such as microwave heating, heat moisture treatment, and annealing is gaining more acceptability due to their inexpensive, simple, safe, and easy-to-use nature (Raghunathan et al., 2021). Annealing is a hydrothermal treatment that has been safely used by different researchers for modifying starches of different botanical origins (da Rosa Zavareze & Dias, 2011). Annealed starches are suggested to have the potential for industrial use because of improved thermal stability and decreased rate of retrogradation (Adebowale et al., 2005). The application of starch in the industry is influenced by its physicochemical properties and hence it is important to determine the physicochemical properties of starch before and after modification.

Previous studies on the modification of Bambara groundnut starch used oxidation, acetylation (Adebowale et al., 2002), carboxymethylation (Afolabi, 2012), lipids (Oyeyinka et al., 2016a, 2016b; Oyeyinka, Singh, Venter, et al., 2017), microwaving (Oyeyinka et al., 2019), heat moisture treatment, annealing (Adebowale & Lawal, 2002; Afolabi et al., 2018), annealing and a combination of annealing and lipids (Oyeyinka et al., 2018). Annealing of Bambara starch at 50°C was found to result in a significant reduction in swelling power, peak, breakdown, and setback viscosities but an increase in final viscosity and pasting temperature (Afolabi et al., 2018; Ikegwu et al., 2011; Oyeyinka et al., 2018). The majority of the studies on the annealing of starches from different botanical sources focused on the use of single-temperature treatment (da Rosa Zavareze & Dias, 2011), which has made their applications readily known. However, some studies also used varying temperatures during the annealing of starch (Kohyama & Sasaki, 2006; Tester et al., 2000; Wang et al., 2017). The few studies described above on annealing of Bambara starch focused on the use of single-temperature of 50°C. No study has determined the effect of varying temperatures on the physicochemical properties of Bambara groundnut starch. Annealing of Bambara starch at varying temperatures may produce starch with different physicochemical properties that can be utilized for different industrial applications. Therefore, this study investigated the functional and physicochemical properties of Bambara starch annealed at different temperatures of 45, 50, 55, and 60°C. These temperatures were chosen because they are below the gelatinization temperature reported in the literature for Bambara starch (Oyeyinka & Oyeyinka, 2018) and also within the range of temperatures used for annealing (da Rosa Zavareze & Dias, 2011).

2 | MATERIALS AND METHODS

2.1 | Materials

Cream-colored Bambara groundnut seeds were obtained from the Bodija market in Ibadan, Oyo State, Nigeria. Native Bambara starch was extracted and annealed at the Food Processing Laboratory of the University of Ibadan, Oyo State, Nigeria. The reagents and equipment used for the analysis were available at the Central Research Laboratory (CRL) of the University of Ibadan, and the National Horticultural Research Institute (NIHORT) Ibadan, Oyo State, Nigeria.

2.2 | Starch extraction from Bambara groundnut seeds

Cleaned grains were soaked in water for 14 h to enhance the softening and loosening of the starch cells. Grains were manually dehulled, milled, and sieved with a muslin cloth. The Bambara chaff was discarded, the sieved mixture was allowed to settle for 12 h and the surface water was discarded. The starch was dissolved in 0.3% (w/v) NaOH to solubilize any adhering proteins and the slurry was stirred and allowed to settle. Burette reagent was used to test for the absence or presence of protein. After the test was negative for the presence of protein, the starch was neutralized with 0.1 N HCL and washed several times with distilled water. Extracted starch was dried in an oven (INESA DHG-9123) at 50°C for 10 h. Dried starch was milled using a manual grinder to enhance its fineness, sieved (sieve aperture size: 180 μm), and then packaged in Ziplock bags.

2.3 | Annealing of native Bambara starch

Annealing was carried out according to the method of Ikegwu et al. (2011) with slight modification. Starch was divided into four portions, each part (125 g) was placed in a foil-sealed beaker suspended in distilled water (1:2 w/v) and heated for 24 h in a sealed container placed in a water bath at varying annealing temperatures (45, 50, 55, and 60°C). The suspensions were then filtered through a Whatman No. 1 filter paper and oven-dried (INESA DHG-9123) at 50°C for 12 h.

Dried annealed starches ground with a SAISHO electric blender and sieved (sieve aperture size: 180 μm) to enhance their smoothness. They were then packaged in Ziplock bags before further analyses.

2.4 | Analyses

2.4.1 | Amylose content

The amylose content determination was carried out according to the method described by Oyeyinka et al. (2015). Briefly, the starch sample (20 mg) was weighed into a 100 ml flask and dispersed in 0.5 N of potassium hydroxide solution (10 ml) for 5 min. The dispersed sample was made up to the 100 ml mark with distilled water. The starch solution (10 ml) was mixed with 0.1 N hydrochloric acid (5 ml) and iodine reagent (0.5 ml) and the solution was brought to 50 ml with distilled water. The iodine reagent was prepared by dissolving 20 g of potassium iodide and 2 g of resublimed iodine in 100 ml of water. A 10 ml portion of the mixture was diluted in another flask and brought to 100 ml with distilled water. The absorbance was read at 620 nm using a UV–VIS Spectrometer (UV-1809PC, Shimadzu Corpor., Kyoto, Japan).

2.4.2 | Swelling power and solubility

The swelling power and solubility patterns of the annealed starches were determined as described by the method of Madruga et al. (2014) except that the starch samples were heated at 45, 60, 75, and 90°C for 30 min with constant stirring. For solubility measurement, the supernatant separated after the determination of swelling power was collected on a pre-weighed evaporating crucible dish and oven-dried (105°C for 12 h), and the dried residue was weighed. The solubility was then expressed as a percentage of the dried supernatant weight to the original sample weight.

2.4.3 | Paste clarity

The paste clarity was determined using the method described by Liu et al. (2014) except that 1 g of starch was used in 100 ml of water and the starch suspension was heated in a water bath at 90°C for 20 min (with occasional shaking). After cooling to room temperature, the transmittance (%) of each starch slurry was then measured at 650 nm using a UV–VIS Spectrometer (Uv-1809PC, Shimadzu Corpor., Kyoto, Japan).

2.4.4 | Freeze–thaw stability

The method described by Srichuwong et al. (2012) was used for the determination of the freeze–thaw stability of native and annealed starches. Starch gels (5% w/v) were prepared and repeatedly freeze–thawed for up to five cycles. The starches were suspended in distilled water, heated at 95°C for 30 min under constant mild agitation, and cooled to room temperature in an iced shaking water bath. Thereafter, 20 g of paste was taken, placed in a centrifuge tube, and subjected to a freeze–thaw cycle by storing first at −18°C for 21 h in a freezer, and then thawing at 30°C for 3 h. The tubes were centrifuged at 8000*g* for 10 min using a Beckman Coulter Centrifuge (Avant J-26 XPI, High-Performance Centrifuge, USA). The supernatant removed from the gel was weighed and syneresis (water release) from the thawed gel after the first, third, and fifth cycle was expressed as the percentage of separated liquid per total weight of the sample in the centrifuge tube.

2.4.5 | Pasting properties

The pasting properties of the annealed starches were determined using a Rapid Visco Analyzer (RVA) following the method of Akinwande et al. (2014) with slight modification. About 3.5 g of each sample (on a dry basis) was weighed and 25 ml of distilled water was dispersed into the canister, and both were mixed. A paddle was placed into the canister; this was placed centrally onto the paddle coupling and then inserted into the RVA machine. The measurement cycle was initiated by pressing the motor tower of the instrument. The profile was seen as it ran and displayed on the monitor of a computer connected to the instrument. The 13 min profile was used including heating from 50°C to 95°C in 3 min, 45 s and holding at 95°C for 2 min, 30 s. The sample was subsequently cooled to 50°C, over a 3 min, 45 s period followed by a period of 2 min where the temperature was controlled at 50°C.

2.4.6 | Thermal properties

The thermal properties of the starch samples were determined using a differential scanning calorimeter (SDT Q600, USA) as previously described (Oyeyinka et al., 2016b). Briefly, starch (3 mg) was weighed into the aluminium DSC pan, and distilled water (12 μl) was added before the pan was sealed. Pans were allowed to equilibrate, and samples were scanned at 10–110°C with an interval heating rate of 10°C/min. An empty pan was used as a reference for all measurements.

2.5 | Statistical analysis

All experiment was carried out in triplicate. Replicate data were analyzed using the statistical package for Social Sciences (SPSS) version 16 (IBM, Armonk, USA). Tukey's test SPSS program and statistical significance were determined by analysis of variance, while Duncan's test was used to separate the means. The differences were considered to be significant at a 95% confidence level ($p < .05$). Pearson correlation was further used to establish the relationship among functional, pasting, and thermal properties at 90% ($p < .01$) and 95% (0.05) levels of confidence.

3 | RESULTS AND DISCUSSION

3.1 | Effect of annealing temperature on amylose content

The annealed starch samples had similar amylose content (27.18%–28.53%) compared with the native starch (28.47%), though there was a slight but insignificant decrease after annealing (Table 1). The amylose content values observed for native and annealed starches agree with the studies on Bambara starch (Afolabi et al., 2018; Oyeyinka et al., 2015, 2019; Oyeyinka, Singh, & Amonsou, 2017). Previous researchers also found a decrease in amylose content for normal corn, high-amylose corn, potato (O'Brien & Wang, 2008), pea (Wang et al., 2013), and wheat starches after annealing (Lan et al., 2008). However, some studies reported that amylose content did not change after annealing of normal corn (Chung et al., 2009), potato, and wheat (Kohyama & Sasaki, 2006) as well as high amylose corn starches (Wang et al., 2014).

In this study, annealing temperatures of 45, 50, and 55°C had no significant ($p \geq .05$) effect on the amylose content when compared with the native starch, but the Bambara starch annealed at 60°C was significantly different from the native starch (Table 1). During annealing of starch, incubation temperature, incubation time, and starch to water ratio have been suggested to influence the annealing process by previous researchers (Krueger et al., 1987; Larsson & Eliasson, 1991; Wang et al., 1997). Wang et al. (1997) studied the effect of different annealing temperatures on the physicochemical properties of sago starch and found that the temperature of incubation was a critical factor for annealing. According to these authors, starch samples must be incubated up to about 55°C before significant evidence of annealing was observed (Wang et al., 1997). This seems to be the case in the current study where Bambara starch annealed at 60°C was significantly different from the native starch. Annealing treatment is thought to be a physical process that does not involve the leaching of amylose (Wang et al., 2014). Variation in the result for annealed starches would depend on the extent of interaction between amylose and amylose chains as well as amylose to amylopectin chain which presumably limit the extent of iodine binding (Lan et al., 2008).

3.2 | Effect of annealing temperature on swelling power and solubility

Annealing temperature significantly changed the swelling behavior (Figure 1) and solubility index (Figure 2) of annealed Bambara starches. For both native and annealed starches, there was a greater significant reduction in swelling power at higher test temperatures (>60°C). The swelling power of native and annealed starches generally increased with increasing heating temperature, especially above 75°C which could be due to the melting of starch crystallites (Hoover et al., 2010). The melting of starch crystallites presumably results from starch gelatinization during heating. However, annealing of the starch significantly reduced the ability of the starch samples to swell (Figure 1). Annealing generally reduced the swelling power of Bambara groundnut starch compared with its native counterparts. The swelling power of starch provides information on the degree of interaction between starch chains (amylose and amylopectin) in the amorphous and crystalline domains (Lan et al., 2008). Thus, a reduction in swelling power following annealing suggests a strengthening of these starch chains and an increase in crystallinity (Waduge et al., 2006). A higher annealing temperature would thus result in a greater strengthening of starch chains which may explain the higher reduction in swelling. The reduction in the swelling power of Bambara starches after annealing has also been reported in the literature (Adebowale & Lawal, 2002; Afolabi et al., 2018; Oyeyinka et al., 2018).

The impact of annealing temperature on the swelling power of Bambara starches showed that swelling power increased with annealing temperatures among the annealed starches. The swelling power was in order 45°C < 50°C < 55°C < 60°C, suggesting that lower temperatures resulted in a higher reduction in swelling power of the annealed Bambara starches. Furthermore, at lower test temperatures of 45 and 60°C, the swelling power for annealed starches was significantly different from each other and the native starch. However, at higher test temperatures of 75 and 90°C, the swelling power for the annealed starches was similar for some samples, further indicating the significance of annealing

TABLE 1 Amylose content and freeze–thaw (syneresis %) of native and annealed Bambara starches

Samples	Amylose content	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
NBS	28.47 ± 0.51^{a}	26.37 ± 0.02^{a}	27.03 ± 0.02^{a}	29.15 ± 0.02^{a}	30.07 ± 0.02^{a}	32.43 ± 0.02^{a}
ABS-45	28.53 ± 0.12^{a}	18.18 ± 0.08^{e}	18.46 ± 0.06^{e}	18.69 ± 0.06^{e}	19.27 ± 0.38^{e}	20.48 ± 0.48^{e}
ABS-50	27.59 ± 0.71^{ab}	20.14 ± 0.06^{d}	21.21 ± 0.68^{d}	22.97 ± 0.04^{d}	23.42 ± 0.07^{d}	24.18 ± 0.37^{d}
ABS-55	27.87 ± 0.25^{ab}	23.07 ± 0.03^{c}	23.66 ± 0.09^{c}	24.51 ± 0.08^{c}	25.99 ± 0.05^{c}	27.78 ± 0.10^{c}
ABS-60	27.18 ± 0.79^{b}	24.05 ± 0.02^{b}	25.22 ± 0.69^{b}	26.35 ± 0.04^{b}	27.87 ± 0.06^{b}	29.05 ± 0.03^{b}

Note: Means in the same column not followed by the same superscripts are significantly ($p < .05$) different.

Abbreviations: ABS-45, Bambara starch annealed at 45°C; ABS-50, Bambara starch annealed at 50°C; ABS-55, Bambara starch annealed at 55°C; ABS-60, Bambara starch annealed at 60°C; NBS, native Bambara starch.

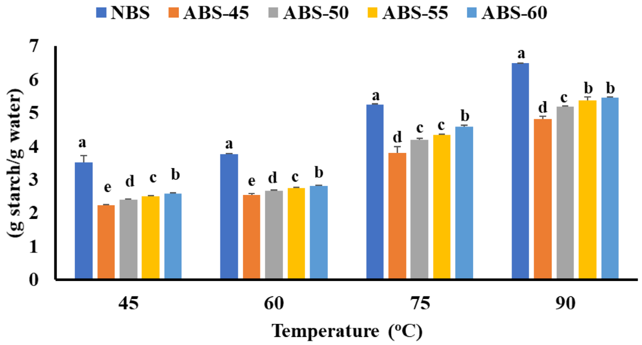

FIGURE 1 Swelling power of native and annealed Bambara groundnut starch. ABS-45, Bambara starch annealed at 45°C; ABS-50, Bambara starch annealed at 50°C; ABS-55, Bambara starch annealed at 55°C; ABS-60, Bambara starch annealed at 60°C; NBS, Native Bambara starch.

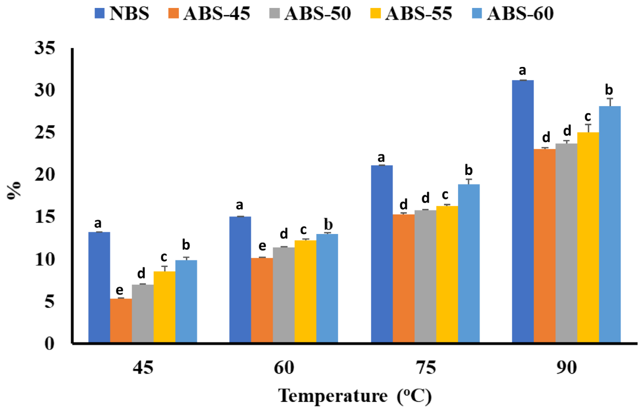

FIGURE 2 Solubility index of native and annealed Bambara groundnut starch. ABS-45, Bambara starch annealed at 45°C; ABS-50, Bambara starch annealed at 50°C; ABS-55, Bambara starch annealed at 55°C; ABS-60, Bambara starch annealed at 60°C; NBS, Native Bambara starch.

at lower temperatures (45-50°C). Dias et al. (2010) studied the effect of different annealing temperatures (45, 50, and 55°C) on the physicochemical properties of starches with low, medium, and high amylose rice starches and found that a higher annealing temperature of 55°C had a greater reduction in swelling compared with rice starch annealed at 45 and 50°C. However, the impact was reported to depend largely on the amylose content. Thus, amylose content of various starches can also influence the degree of interaction between the starch chains (amylose and amylopectin) during annealing treatment. The observed differences in the swelling ability of the starches in the current study compared with those reported by Dias et al. (2010) further suggest the impact of annealing conditions on the resulting functionality of annealed starches. For example, in this study, starch was hydrated at a ratio of 1 to 2, while Dias et al. (2010) used excess water in the ratio of 1 to 9 for starch and water, respectively. Future studies may also assess the impact of excess moisture on the physicochemical properties of annealed Bambara starch.

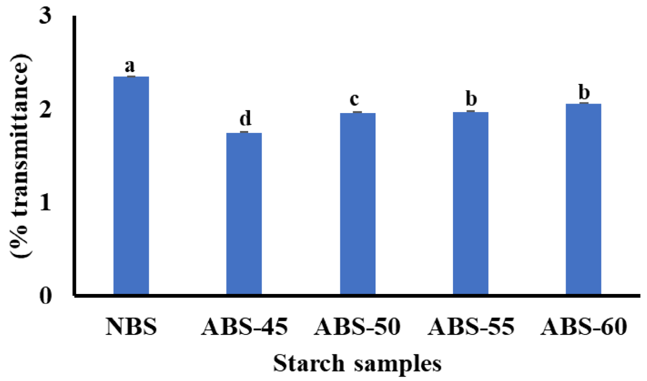

FIGURE 3 Paste clarity of native and annealed Bambara groundnut starch. ABS-45, Bambara starch annealed at 45°C; ABS-50, Bambara starch annealed at 50°C; ABS-55, Bambara starch annealed at 55°C; ABS-60, Bambara starch annealed at 60°C; NBS: Native Bambara starch.

The solubility data plotted as a graph of soluble content versus heating or test temperature showed that the solubility of native and annealed Bambara starches increased with an increase in temperature (Figure 2), similar to what was observed in the swelling power (Figure 1). However, the solubility values were much lower than the swelling power of the starches. Furthermore, there was a significant reduction in the solubility of the Bambara starch annealed at 45°C, 50°C, 55°C, and 60°C compared with the native starch. The solubility of the starches increased as the annealing temperature increased and agrees with the swelling power data (Figure 1). The behavior of the annealed starches at lower test temperatures (45 and 60°C) was different when compared with higher test temperatures (75 and 90°C). At lower test temperatures (45 and 60°C), starches annealed at lower temperatures of 45 and 50°C were different from starches annealed at 55 and 60°C, including the native starch. However, at higher test temperatures (75 and 90°C), starches annealed at lower temperatures (45 and 50°C) displayed similar solubility values. This further confirms that for annealing to substantially change the swelling and solubility properties of Bambara starch under low moisture levels (1:2 for starch to water) as used in this study, lower annealing temperatures (45 and 50°C) would be preferred. This may explain why previous studies used 50°C for annealing of Bambara starch (Adebowale & Lawal, 2002; Oyeyinka et al., 2018). This study has revealed that at low moisture levels, higher annealing temperatures (55 and 60°C) favored a lower reduction in swelling compared with lower annealing temperatures (45 and 50°C).

3.3 | Paste clarity

Generally, annealed starches showed significantly ($p < .05$) lower paste clarity than the native starch (Figure 3). Annealing temperature influenced the paste clarity values of the starches, but the effect was insignificant ($p \geq .05$) at 55 and 60°C since the values for these starches were similar. Paste clarity of starches is determined by measuring the passage of light through the cooked starch paste.

A higher transmittance value shows that the paste is clearer while lower transmittance shows the opposite. In this study, starches annealed at higher temperatures (55 and 60°C) had clearer pastes than those annealed at lower temperatures (45 and 50°C). This trend agrees with the solubility result (Figure 2) and amylose content data (Table 1). Bambara starch (annealed at 60°C) with the lowest amylose content showed the highest paste clarity. We hypothesize that the annealing process may have triggered thermal crosslinking of the amylose chains within the starch structure which presumably strengthens the starch chains leading to a reduced ability of the starch to swell, a lower amount of leached amylose (solubility), and hence a high paste clarity. Our result is in agreement with an earlier study where amylose content influenced the paste clarity of starch from Bambara genotypes (Oyeyinka et al., 2015). Previous studies similarly reported that starches with lower amylose content are readily dispersed and show higher paste clarity (Craig et al., 1989; Swinkels, 1985). An earlier study also reported that starch solubility correlated with paste clarity, indicating that the more soluble the starch, the more transparent is the paste (Nemtanu & Minea, 2006). Paste clarity is an important functional property of starches that determines their application in the food industry. For example, the starch used in fruit pie filling for thickening should ideally have a high paste clarity while those used in spoonable salad dressings should have low paste clarity (opaque) (Craig et al., 1989). Thus, the annealed starches produced in this study could have varied uses depending on the intended use.

3.4 | Freeze–thaw stability

The freeze–thaw stability is very important when formulating refrigerated and frozen foods. The water release from the thawed gels (syneresis) was calculated during a five-cycle freeze–thaw process and the values are presented in Table 1. In general, annealed starches showed significantly lower syneresis than the native starch samples for all the repeated cycles. Annealing temperature had a significant effect on the amount of exudate from the starches after the freeze–thaw cycles. Syneresis increased with an increase in annealing temperature. Bambara starch annealed at lower temperatures was more resistant to syneresis than those annealed at higher temperatures (Table 3). For example, for cycle 1 to cycle 5, the order of syneresis is in the order 45 > 50 > 55 > 60°C. The lower syneresis in the Bambara starch annealed at 45°C may explain its lower setback viscosity (Table 2) and suggest higher freeze–thaw stability. Setback value measures the retrogradation tendency or syneresis of starch, which implies the appearance of separate fluid droplets on starch gels (Adebowale et al., 2009). Previous studies found that annealing increased the syneresis of the starch paste compared with native starch paste (Adebowale et al., 2005; Yadav et al., 2013), which was different from the result of this study (Table 1). According to these authors, higher syneresis of annealed starches is presumably due to case hardening and disintegration of starch granules, resulting in lower water absorption of the granules (Yadav et al., 2013). Amylose content has been found to significantly influence the syneresis of starches. Starches with higher amylose content would normally show higher syneresis. Srichuwong et al. (2012) found that the amylose content of starches from different botanical sources showed a significant positive correlation with the syneresis rate for first, third, and fifth freeze–thaw cycles. However, in this study, the reverse was the case. Higher syneresis was found in starches with lower amylose content indicating that other factors may influence the syneresis of the annealed starches.

3.5 | Pasting properties

The pasting properties of native and annealed Bambara starches as influenced by annealing temperatures are shown in Table 2. Except for the time to peak and pasting temperatures which increased, all other pasting properties such as peak viscosity, trough viscosity, breakdown viscosity, setback viscosity, and final viscosity all decreased after annealing (Table 2). The increase in pasting temperatures of the annealed starches has been attributed to the strengthening of bonds within the starch granules (Gomes et al., 2004). Reduction in peak viscosity, trough viscosity, breakdown viscosity, setback viscosity, and final viscosity has been previously reported for Bambara starch after annealing (Adebowale & Lawal, 2002; Oyeyinka et al., 2018).

Annealing temperature had a varied effect on the pasting properties of the Bambara starches. For example, while peak, trough, and final viscosities increased with increasing annealing temperatures, the breakdown and setback viscosities decreased. The peak

TABLE 2 Pasting properties of native and annealed Bambara starches

Samples	PV (cP)	TV (cP)	BV (cP)	FV (cP)	SV (cP)	Peak time (min)	PT (°C)
NBS	5822.00 ± 2.12^{a}	3015.00 ± 1.41^{a}	3024.00 ± 1.41^{a}	6431.50 ± 2.12^{a}	3713.00 ± 1.41^{a}	4.05 ± 0.07^{c}	76.2 ± 0.14^{d}
ABS-45	5718.50 ± 255.27^{ab}	2916 ± 42.43^{b}	1713.00 ± 16.97^{c}	6149 ± 100.41^{ab}	2301.00 ± 4.24^{c}	4.40 ± 0.00^{ab}	81.95 ± 0.64^{c}
ABS-50	5436.50 ± 50.21^{b}	2852 ± 8.49^{bc}	1820.00 ± 53.74^{c}	5735 ± 367.69^{b}	2373.00 ± 36.77^{c}	4.30 ± 0.04^{bc}	82.40 ± 0.00^{c}
ABS-55	4514.00 ± 73.54^{c}	2801 ± 56.57^{c}	2584.00 ± 58.69^{b}	5225 ± 45.26^{c}	2931.50 ± 569.22^{bc}	4.44 ± 0.05^{a}	83.20 ± 0.00^{b}
ABS-60	4468.00 ± 18.37^{c}	2648 ± 35.36^{d}	2802.50 ± 297.69^{ab}	4949 ± 39.59^{c}	3525.50 ± 125.16^{ab}	4.27 ± 0.00^{c}	84.00 ± 0.07^{a}

Note: Means in the same column not followed by the same superscripts are significantly ($p < .05$) different.

Abbreviations: ABS-45, Bambara starch annealed at 45°C; ABS-50, Bambara starch annealed at 50°C; ABS-55, Bambara starch annealed at 55°C; ABS-60, Bambara starch annealed at 60°C; BV, breakdown viscosity; FV, final viscosity; NBS, native Bambara starch; PT, pasting temperature; PV, peak viscosity; SV, setback viscosity; TV, trough viscosity.

TABLE 3 Thermal properties of native and annealed Bambara starches

Samples	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
NBS	56.43 ± 0.15^e	64.80 ± 0.10^e	69.33 ± 0.15^e	3.73 ± 0.02^e
ABS-45	69.70 ± 0.20^a	77.23 ± 0.15^a	84.20 ± 0.10^a	3.95 ± 0.02^d
ABS-50	65.70 ± 0.20^b	74.60 ± 0.30^b	80.70 ± 0.20^b	4.20 ± 0.03^c
ABS-55	62.67 ± 0.15^c	71.73 ± 0.21^c	76.70 ± 0.26^c	4.31 ± 0.02^b
ABS-60	60.37 ± 0.15^d	70.47 ± 0.06^d	73.43 ± 0.21^d	4.41 ± 0.02^a

Note: Means in the same column not followed by the same superscripts are significantly ($p < .05$) different.

Abbreviations: ABS-45, Bambara starch annealed at 45°C; ABS-50, Bambara starch annealed at 50°C; ABS-55, Bambara starch annealed at 55°C; ABS-60, Bambara starch annealed at 60°C; NBS, native Bambara starch; T_c, conclusion gelatinization temperature; T_o, onset gelatinization temperature; T_p, peak gelatinization temperature; ΔH, enthalpy of gelatinization.

viscosity of the starches decreased by approximately 2%, 7%, 22%, and 23% for starch annealed at 45, 50, 55, and 60°C, respectively. The peak viscosity result indicates that higher temperature favored a greater reduction in peak viscosity. Annealing as a physical modification is thought to promote resistance of starch granules to deformation by strengthening its intragranular binding forces (Gomes et al., 2004; Song et al., 2014). Thus, higher temperatures seem to promote greater resistance to swelling than lower temperatures. The impact of annealing on the pasting properties of starch has been very controversial. For instance, while the peak viscosity of potato starch (Jacobs et al., 1995) and Bambara starch (Adebowale & Lawal, 2002; Oyeyinka et al., 2018) decreased after annealing, those of rice and wheat starches increased (Jacobs et al., 1996). A study by Wang et al. (2017) on the impact of annealing temperatures (30, 40, and 50°C) on pasting properties of wheat starch reported that annealing at lower temperatures (30 and 40°C) greatly increased the pasting viscosity, while annealing at 50°C decreased the pasting viscosity with a corresponding increase in pasting temperature. The same authors found that annealing increased the peak viscosity of yam starch but the same parameter decreased after annealing at 40 and 50°C (Wang et al., 2017). According to Fonseca et al. (2021), the effect of annealing on starch pasting properties depends on factors such as branch chain length distribution of amylopectin, granule swelling, and relative crystallinity. Other factors which may influence the pasting properties of annealed starches would depend on the botanical origin of the starch. We hypothesize that annealing at different temperatures of 45, 50, 55, and 60°C may have altered the internal structure of the starches differently, resulting in changes in the architecture of the amylopectin component of the annealed starches. This seems plausible since the branch chain length distribution of amylopectin changed after annealing, with annealed starches showing a higher proportion of A (DP 6–12) and B1 (DP 13–24) chains compared with B2 (DP 25–36) and B3 (DP > 37) chains (Su et al., 2020). Furthermore, the amylose contents and amylopectin branch chain-length distributions of starches have been reported to predominantly influence the pasting properties of starch (Jane et al., 1999). Thus, future studies are required to characterize the amylopectin branch chain-length distribution of native and annealed Bambara starches to fully understand the impact of annealing on the starch.

3.6 | Thermal properties

Native Bambara starch showed significantly different gelatinization temperatures (T_o: onset gelatinization; T_p: peak gelatinization temperature, and T_c: conclusion gelatinization) and gelatinization enthalpy (ΔH) compared with the annealed starches (Table 3). The T_p of the native starch (64.80°C) is much lower than the values (73.10–93.20°C) reported for Bambara starch in different studies (Afolabi, 2012; Kaptso et al., 2015; Oyeyinka, Singh, & Amonsou, 2017). After annealing, Bambara starch showed a significant increase in gelatinization temperatures and enthalpies (Table 3), which could be associated with the reductions in swelling power of the starches (Figure 1). A shift to higher gelatinization temperatures after annealing is thought to result from stronger interactions between starch chains, which presumably reduce the swelling of the starch and hence delayed gelatinization (da Rosa Zavareze & Dias, 2011). Oyeyinka et al. (2018) also reported higher gelatinization temperatures for annealed Bambara starch compared with the native starch.

Annealing temperature had a significant impact on the gelatinization properties of the annealed starches. The gelatinization temperatures (T_o, T_p, and T_c) and ΔH all decreased with an increase in annealing temperatures (Table 3). Differences in gelatinization temperatures of the annealed starches may be attributed to the modifications within the amylopectin chains. Noda et al. (1996) reported that longer amylopectin chain starch would display higher T_o, T_p, and T_c and ΔH compared with starches with more short chains. The amylopectin chain length distribution of native and modified Bambara starches has not been reported in the literature and it remains unclear if the amylopectin chains are modified in Bambara starch during annealing, suggesting future studies in this direction.

3.7 | Pearson correlation of selected variables

Pearson correlation was further used to assess the strength and the direction of relationship between selected variables such as amylose content, functional, pasting, and thermal properties of the starch samples, and the result is presented in Table 4. The amylose content

TABLE 4 Pearson correlation matrix between selected parameters for modified Bambara groundnut starch

	Amylose	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	PV	TV	BDV	FV	SV	Peak time	PT	PC	SP-75	SB-75
Amylose	1														
T_o (°C)	0.23	1													
T_p (°C)	0.12	0.98**	1												
T_c (°C)	0.21	0.99**	0.98**	1											
ΔH (J/g)	−0.57*	0.14	0.31	0.15	1										
PV	0.44	0.14	−0.01	0.14	−0.89**	1									
TV	0.54*	0.00	−0.17	0.01	−0.93**	0.87**	1								
BDV	−0.21	−0.94**	−0.92**	−0.95**	−0.05	−0.29	−0.08	1							
FV	0.52*	0.00	−0.16	0.01	−0.96**	0.93**	0.94**	−0.11	1						
SV	−0.22	−0.27	−0.16	−0.30	0.43	−0.47	−0.66**	0.19	−0.51	1					
Peak time	0.06	0.78**	0.83**	0.77**	0.56*	−0.43	−0.39	−0.62*	−0.049	−0.09	1				
Past temp	−0.38	0.51	0.65**	0.50	0.91**	−0.73**	−0.84**	−0.39	−0.83**	0.33	0.80**	1			
PC	−0.16	−0.97**	−0.98**	−0.95**	−0.33	0.10	0.21	0.85**	0.19	0.13	−0.88**	−0.68**	1		
SP-75	−0.11	−0.96**	−0.98**	−0.96**	−0.34	0.10	0.18	0.86**	0.21	0.17	−0.88**	−0.66**	0.98**	1	
SB-75	−0.14	−0.93**	−0.94**	−0.94**	−0.36	0.10	0.16	0.87**	0.22	0.21	−0.89**	−0.66**	0.93**	0.93**	1

Abbreviations: BDV, breakdown viscosity; FV, final viscosity; PT, pasting temperature; PV, peak viscosity; T_o, onset gelatinization temperature; T_c, conclusion gelatinization temperature; T_p, peak gelatinization temperature; TV, trough viscosity; SB-75, solubility at 75°C; SP-75, swelling power at 75°C; SV, setback viscosity; ΔH, enthalpy of gelatinization.

*Correlation is significant at the 0.05 level (2-tailed); **Correlation is significant at the 0.01 level (2-tailed).

of the starch samples positively correlated with the trough viscosity ($r = 0.54$, $p < .05$), final viscosity ($r = 0.52$, $p < .05$), but showed a negative but significant correlation with the enthalpy of gelatinization (ΔH) ($r = -0.57$, $p < .05$). Earlier studies also found higher viscosity for maize (Xie et al., 2009) or Bambara starch with a high amylose content (Oyeyinka et al., 2015), and this was also observed in this study (Table 1). The negative correlation of amylose with the ΔH further confirms that low amylose starch would exhibit high ΔH values. The crystalline region of starch granules is made up of the amylopectin chains that are packed together (Oyeyinka et al., 2021), and this region dictates the overall crystallinity of starch as well a loss of molecular order within the starch granule during gelatinization (Zhang et al., 2019). The ΔH values showed a significant positive correlation with peak time ($r = 0.56$, $p < .05$) and pasting temperature ($r = 0.91$, $p < .01$) (Table 4). Both peak time and pasting temperatures are an indication of the energy requirements during the cooking of starchy foods. The higher the pasting temperature and peak time values the greater the energy required for cooking. In this study, annealing increased both parameters (peak time and pasting temperature), and hence suggests the modified starches would require a longer time to cook and this may impact energy requirement. However, the benefit accruable from the modified starch may outweigh the cost of processing, for example, the modified starch would withstand higher temperatures as reflected in the improvement in the thermal properties (Table 3). The thermal properties T_o ($r = 0.96$, $p < .01$), T_p ($r = 0.98$, $p < .01$), and T_c ($r = 0.96$, $p < .01$), all showed a negative correlation with the swelling ability of the starches (Table 4). Thus, the reduction in swelling (Figure 1) after annealing slowed down the melting of starch crystallites, presumably due to thermal crosslinking and strengthening of the starch molecules as previously stated. Overall, starch composition (ratio of amylose to amylopectin) is an important factor which influences the physicochemical and functional properties of starches. However, it has been reported that the chain length distribution of the amylopectin component of starch contributes a greater influence on the physiochemical properties of starch than starch composition (Jane et al., 1999; Noda et al., 1996). Thus, future studies on the amylopectin component and its influence on the physicochemical properties of native and modified Bambara groundnut starch is required.

4 | CONCLUSION

This study investigated the impact of different annealing temperatures on the physicochemical properties of Bambara starch. Annealing temperatures significantly influenced the physicochemical properties of Bambara starch. Amylose content reduce with an increase in annealing temperature, but the increase was insignificant. However, the paste clarity, gelatinization temperature, peak viscosity, trough, final viscosity, and the peak time of Bambara starches significantly reduce with an increase in annealing temperature, possibly due to thermal crosslinking and strengthening of the starch molecules. The modified starches in this study could be explored in various food applications by selecting the appropriate annealing temperatures for the desired starch functionality. Future studies may be required to optimize the annealing conditions of temperature and time to suit the intended use. Furthermore, due to the greater impact of amylopectin chain length on the physiochemical and functional properties of starch, it is worthwhile to investigate the influence of annealing on the distribution of amylopectin chains of Bambara starch in future studies.

AUTHOR CONTRIBUTION

Faith O. Nwaogazie did data curation, analysis, and draft manuscript writing. Bolanle A. Akinwande did Research conceptualization, reading of draft manuscript, validation and funding. Samson Oyeyinka did data analysis, validation, draft manuscript, and revision of manuscript.

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CONFLICT OF INTEREST

Authors declare that there is no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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