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Effect of hydrothermal processing on the native starches of cassava (*Manihot esculenta*) and yam (*Dioscorea alata*)

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Efecto del proceso hidrotérmico en almidones nativos de yuca (*Manihot esculenta*) y ñame (*Dioscorea alata*)

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ABSTRACT

Currently, there is a need to develop starches with improved properties to enhance their applicability in food matrices. The effect of the hydrothermal treatment (HMT) on the physicochemical, morphological, and structural properties of native cassava and yam starches was evaluated. Native cassava and yam starches were subjected to low moisture (20 - 25%), a high temperature (90 °C), and a processing time of 4 hours. The results showed that HMT significantly decreased in cold water solubility (CWS), in cassava starch while increasing its water absorption capacity (WAC) and degree of crystallinity (DC). In contrast, yam starch displayed the opposite effects. Furthermore, the modification increased amylose content and paste stability. Additionally, microphotography revealed significant changes in granular morphology. In conclusion, hydrothermal treatment of tuber starches is a promising technology for improving the hydrophilic properties and pasting characteristics of cassava and yam starches, supporting the development of clean-label products.

Keywords:
Gelatinization
Heat-moisture treatment
Retrogradation
Tubers

RESUMEN

En la actualidad, surge la necesidad de desarrollar almidones con propiedades mejoradas para aumentar su aplicabilidad en matrices alimentarias. Se evaluó el efecto del tratamiento hidrotérmico (HMT) sobre las propiedades fisicoquímicas, morfológicas y estructurales de los almidones nativos de yuca y ñame. Los almidones nativos de yuca y ñame se sometieron a baja humedad (20 - 25%), alta temperatura (90 °C) y un tiempo de procesamiento de 4 horas. Los resultados mostraron que el HMT disminuía significativamente la solubilidad en agua fría (CWS), al tiempo que aumentaba la capacidad de absorción de agua (WAC) y el grado de cristalinidad (DC) de los almidones de yuca. En cambio, en el ñame se produjo el efecto contrario. Además, la modificación aumentó el contenido de amilosa y la estabilidad de las pastas. Adicionalmente la microfotografía reveló cambios significativos en la morfología granular. En conclusión, el tratamiento hidrotérmico en almidones de tubérculos es una tecnología prometedora para mejorar las propiedades hidrofílicas y las características de empastamiento de los almidones de yuca y ñame, garantizando el desarrollo de productos de etiqueta limpia.

Palabras clave:
Gelatinización
Tratamiento calor-humedad
Retrogradación
Tubérculos

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Starch is a polysaccharide deposited in birefringent semicrystalline aggregates that are insoluble in cold water and serve as the main source of energy storage (Bernal et al. 2022). This polymer is of great interest across various industries due to its versatility as a thickening, gelling, and texturizing agent. However, native starch exhibits functional limitations in its physicochemical and morphological properties, including low shear resistance, insolubility in cold water, thermal degradation, and a high level of retrogradation, which restrict its use in diverse products (Barragán et al. 2016). These limitations can be addressed by employing new technologies to enhance desirable properties or inhibit certain undesirable properties of native starch.

As a result, various methods—physical, chemical, and enzymatic—have been applied to modify starches and increase their industrial utility. Although chemical modification methods are widely used in industry, there is growing concern about their environmental impact, driving researchers to explore innovative, eco-friendly alternatives rooted in clean technologies (Maniglia et al. 2021). For this reason, physical modification methods have gained attention, as they are more environmentally friendly and can improve the intrinsic properties of starch while preserving the general structure of the granules without inducing gelatinization, a key factor in industrial applications (Sobowale et al. 2022; Solarte-Montúfar et al. 2019).

In this context, heat-moisture treatment (HMT) is regarded as one of the most environmentally friendly and low-cost alternative technologies. HMT enhances the physicochemical, rheological, and structural properties of starches without altering granular morphology (Klein et al. 2013; Yeh and Lai 2021). Recent studies have shown that HMT applied to tuber starches increases thermal stability, affects gelatinization temperatures, and introduces variations in the semicrystalline arrangement of starch granules (Barua et al. 2021; Dudu et al. 2020; Jia et al. 2022).

Given the limitations of native tuber starches, this study proposes the implementation of physical modification processes, such as hydrothermal treatment, to develop starches with enhanced hydrophilic capacity and high resistance to thermal stress. This research aims to determine the impact of heat-moisture treatment on the physicochemical, morphological, and structural properties of native cassava and yam starches as a technological alternative in developing innovative and eco-friendly starch modification processes for tuber-derived materials.

MATERIALS AND METHODS

Native cassava starch (NCS), variety “M-TAI” was supplied by the company Almidones de Sucre S.A.S. The yam “Criollo” was purchased at the local market in Sincelejo, Sucre, and native yam starch (NYS) was extracted in the unit operations plant of the Universidad de Sucre, following the methodology proposed by Salcedo-Mendoza et al. (2018) with some modifications. Specifically, chemical extraction (ammonia solution) was replaced by physical processes, and centrifugation washes were implemented to remove the mucilaginous material. Standards for potato amylose (A0512, USA) and corn amylopectin (10120, USA) were acquired from Sigma-Aldrich®. All reagents used in the research were of analytical grade.

Modification by heat-moisture treatment (HMT)

Cassava and yam starches were hydrothermally modified following the method proposed by Klein et al. (2013), with slight modifications. Initially, 30 g samples (d.b.) were hydrated to a moisture content of 20 and 25% (w/w), and then stored at room temperature for 24 h to ensure homogenization. Subsequently, the hydrated samples were subjected to 90 °C for 4 h in a forced convection oven (FD115, BINDER, Germany).

Amylose content and molecular order by FTIR-ATR

Amylose Content and Molecular Order by FTIR-ATR. The amylose content was estimated following the methodology proposed by Seña-Rambauth et al. (2024). FTIR-ATR spectra were recorded from 500 to 4,000 cm^{-1} with 32 scans at a resolution of 4 cm^{-1} using a Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (Spectrum, PerkinElmer, USA). The degree of molecular order (OM) was calculated as the absorbance ratio in the bands 1,047/1,022 cm^{-1} and 995/1,022, expressed as a percentage according to de Dios-Avila et al. (2022).

Diffraction pattern (XRD) and relative degree of crystallinity (DC)

The XRD was estimated using an X-ray diffractometer (Panalytical, X’Pert MPD, Switzerland). Spectra were acquired over a range of 4-40 °, operating at 1.8 kW and 40 mA (Davoudi et al. 2022). The relative degree of crystallinity (DC) was determined by calculating the ratio of the absorption peaks in the crystalline regions to the total area, using MATLAB for data processing.

Morphological characteristics

The morphology and birefringence capacity of the starch granules were examined using a trinocular polarized light microscope with bright field capabilities (Optika, B-383POL, Italy) (Seña-Rambauth et al. 2024).

Physicochemical properties

Water absorption capacity (WAC) was analyzed following the method proposed by Cao and Gao (2019). Cold water solubility (CWS) was determined using the method proposed by Salcedo-Mendoza et al. (2018), with slight modifications. For this, 0.125 g of starch was weighed and mixed with 12.5 mL of distilled water, homogenized for 5 min and centrifuged at 1,701 x g for 15 min. Cold water solubility (%) was calculated by weight difference and estimated based on mass gain. Swelling power (SP) was analyzed according to the methodology of Li et al. (2011) with slight modifications. A 0.5 g starch sample was added to 12.5 mL of distilled water preheated to 60 °C. Samples were placed in a water bath at 60 °C for cassava starch and 70 °C for yam starch for 30 min. After this time, they were centrifuged at 1,701 x g for 15 min. The supernatant was discarded, and the weight of the tube containing the gel was recorded. The weight of the gel and the amount (g) of dry solids recovered by evaporation were determined.

Pasting and gelatinization properties

Pasting properties were determined using the methodology proposed by Ramos-Villacob et al. (2023). Gelatinization properties were assessed through temperature scanning using a rheometer (Anton Paar MCR 302, Austria) using parallel plate geometry. Initially, the linear viscoelastic region was determined by performing an amplitude sweep. Subsequently, a temperature sweep was conducted between 30 and 90 °C at a constant frequency of 1 Hz and a strain of 0.5%. (Cham and Suwannaporn 2010). The values of the storage modulus (G′ [Pa]) and the loss modulus (G″ [Pa]) were obtained during the process

Experimental design and statistical analysis

A categorical one-factor design was established with six levels corresponding to the type of starch, as described in Table 1 The results were analyzed using analysis of variance (ANOVA) and Tukey's test for mean comparison at a significance level of 5%, using the statistical software Statgraphics (Centurion XVI, Statgraphics Inc., version XVI, USA).

Table 1. Experimental design implemented in the hydrothermal modification of starches.

Treatment	Nomenclature
Native cassava starch	NCS
Cassava starch with 20% w/w moisture content, modified by HMT	SCH-20
Cassava starch with 25% w/w moisture content, modified by HMT	SCH-25
Native yam starch	NYS
Yam starch with 20% w/w moisture content, modified by HMT	SYH-20
Yam starch with 25% w/w moisture content, modified by HMT	SYH-25

RESULTS AND DISCUSSION

Amylose content (AC)

The CA results for cassava and yam starches are presented in Table 2. The CA of NCS ranged between 18 and 20%, differing from the 24% reported for cassava starch by Ramos-Villacob et al. (2023). This difference is likely associated with cassava variety and crop conditions, such as harvest times and weather. The CA of NYS fluctuated between 24 and 25%, similar to the result obtained for yam starch by Salcedo-Mendoza et al. (2018).

After treatment, CA increased significantly in the modified starches (*P*<0.05), except for the SHY-25 treatment, which did not show significant differences compared to its native counterpart. Additionally, it was observed that the HMT treatment conducted at 20% moisture induced higher CA in cassava and yam starches (Table 2). These results are consistent with those reported for cassava starch treated with HMT by Liu et al. (2016). The authors suggest that such changes may be associated with chain disorder and a reduction in amylose leaching. They also reported that the degradation of amylopectin during HMT could explain the increase in amylose content after HMT treatment.

Table 2. Percentage of amylose content, relative degree of crystallinity and molecular order in native and modified starches.

Treatment	Amylose (%)	OM_1 (%)	OM_2 (%)	DC (%)
NCS	19.45±0.45[a]	0.737±0.00[ac]	1.184±0.02[a]	47.46±0.53[a]
SCH-20	22.94±0.09[b]	0.695±0.03[b]	1.233±0.03[bc]	49.56±0.46[b]
SCH-25	21.84±0.11[c]	0.727±0.00[ba]	1.202±0.02[ab]	50.65±0.41[b]
NYS	24.94±0.26[d]	0.749±0.00[ac]	1.281±0.00[c]	45.10±0.30[c]
SYH-20	25.60±0.12[e]	0.755±0.00[ac]	1.337±0.04[c]	42.80±0.08[d]
SYH-25	24.94±0.41[d]	0.777±0.02[c]	1.281±0.00[c]	40.50±0.45[e]

AC: amylose content; DC: relative degree of crystallinity; NCS: native cassava starch; SCH-20: cassava starch with 20% w/w moisture content, modified by HMT; SCH-25: cassava starch with 25% w/w moisture content, modified by HMT; NYS: native yam starch; SYH-20: yam starch with 20% w/w moisture content, modified by HMT; SYH-25: yam starch with 25% w/w moisture content, modified by HMT; MO_1: estimated molecular order between bands 1,047/1,022; MO_2: estimated molecular order between bands 995/1,022. Means with different lowercase letters in the same column indicate statistically significant differences according to Tukey's test ($P \leq 0.05$).

Furthermore, Liu et al. (2021) argue that HMT may cause thermal degradation of the outer linear chains of amylopectin, which could convert into amylose chains, forming complexes with other amylose chains or lipids. This would account for the increase in amylose content following hydrothermal treatment. Additionally, this effect may be due to less steric hindrance near the α-(1,6) glycosidic bond compared to the α-(1,4) bond, as the HMT treatment effectively broke the α-(1,6) glycosidic bond and disrupted the side chain of amylopectin, thereby producing short-chain amylose.

Molecular Order (MO)

The absorption peaks in the 1,200 to 900 cm^{-1} regions of the FTIR spectra are shown in Table 2. These spectra have been attributed to three main vibrational zones with maximum absorbance at 1,047, 1,022 and 995 cm^{-1}, providing insights into the structural organization of the chains, crystallinity, and retrogradation of starch (Varatharajan et al. 2010; Zheng et al. 2023). The ratio between the bands at 1,047/1,022 cm^{-1} corresponds to ordered and amorphous domains and was used to quantify the degree of molecular order (MO_1) in the starch granules (Table 2). Native cassava and yam starches after HMT showed similar vibrations in the absorption peaks corresponding to the C-H, C-O and O-H groups, possibly associated with the formation of new bonds during molecular reorganization (Mina et al. 2013). The MO_1 values in the cassava starches after the HMT treatment (SCH-20) showed a significant decrease (P<0.05) compared to native starch, which may be attributed to the dissociation of double helices in the crystalline lamellae that form the crystalline matrix of the starch granules (Yu et al. 2021) . In contrast, the MO_1 values of yam starches did not show significant changes (P<0.05) compared to the native counterpart. This indicates that the characteristic peaks of the treatments did not show a representative shift, and no new absorption peaks appeared or disappeared, suggesting that no chemical bonds or functional groups were formed or broken during hydrothermal treatment (Batista et al. 2023).

On the other hand, the ratio between the sharp peaks 995/1,022 cm^{-1} primarily results from the bending vibrations of the C-O-H group, which are sensitive to water content and reflect the water-starch interaction (Yu et al. 2021). This ratio was used to determine the degree of molecular order (MO_2) in the starch granules (Table 2). After hydrothermal treatment, the OM_2 value in cassava starch significantly increased (P<0.05) in the SCH-20 treatment compared to the native counterpart. This result is consistent with an increase reported by Batista et al. (2023) in breadfruit starch treated with hydrothermal treatment (annealing). The author suggests that the treatment promoted the unraveling and dissociation of the double helix within the crystallites, likely due to increased water content associated with the growth of amorphous regions in the granule. Meanwhile, OM_2 in SCH-25 and SYH-25 did not show significant differences (P<0.05). These variations in molecular order values may be attributed to differences in amylose content, as previously observed.

X-ray diffraction (XRD) and relative degree of crystallinity (DC)

The diffraction patterns of cassava and yam starches are shown in the diffractograms in Figure 1. The results indicate that NCS exhibited characteristic crystalline peaks of A-type polymorphism (Figure 1A), consistent with those reported for native cassava starch by Ramos-Villacob et al. (2023). In contrast, NYS showed a B-type pattern (Figure 1B), similar to yam starch reported by Meaño-Correa et al. (2015). After treatment, the cassava and yam starches showed angles similar to those of the native samples, indicating that the A-type and B-type crystalline structures of the treated samples were not modified.

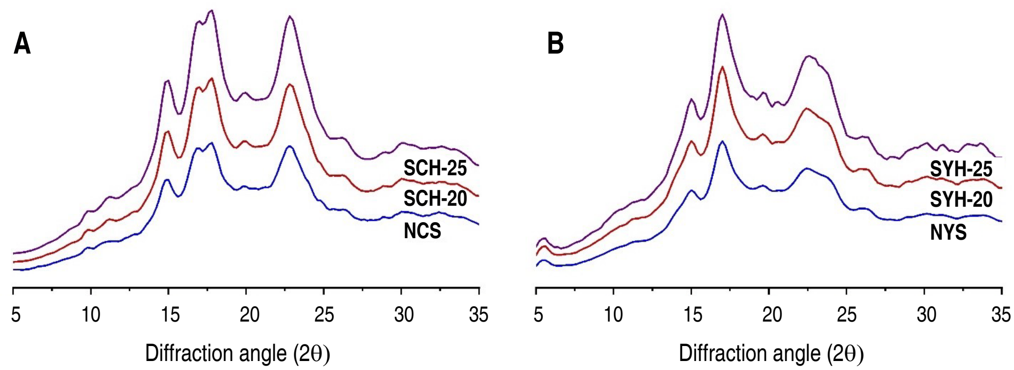

Figure 1. X-ray diffraction patterns (XRD) of. A) native and modified cassava starches, B) native and modified yam starches. NCS: native cassava starch; SCH-20: cassava starch with 20% w/w moisture content, modified by HMT; SCH-25: cassava starch with 25% w/w moisture content, modified by HMT; NYS: native yam starch; SYH-20: yam starch with 20% w/w moisture content, modified by HMT; SYH-25: yam starch with 25% w/w moisture content, modified by HMT.

The effect of HMT on DC is presented in Table 2. NCS showed a DC of 47.46%, consistent with findings reported by Figueroa-Flórez et al. (2019). After HMT, a significant increase (P<0.05) was observed in SCH-20 and SCH-25. Similar results were reported in cassava starch treated with HMT by Moraes et al. (2014), who argued that HMT leads to a reorganization of starch molecules, enhancing molecular interactions and thereby increasing crystallinity (Van et al. 2017). Meanwhile, NYS presented DC similar to that reported for yam starch (Arroyo-Dagobeth et al. 2023). After HMT, a decrease in DC was observed, proportional to the increase in moisture content in the SYH-20 and SYH-25 treatments. This decrease in DC is more evident at higher moisture levels, as water may contribute to the disruption of intra- and intermolecular hydrogen bonds within the starch granule (Liu et al. 2016).

Morphological characteristics

The morphological characteristics of native and modified starches from cassava and yam can be visualized through the analysis of bright-field and polarized light micrographs (Figure 2A, B). Native cassava starch granules exhibited a semi-spherical morphology with a smooth surface, free of pores, and truncated ends. These characteristics are possibly associated with the extraction process, during which starch granules may suffer lacerations due to handling and the physical conditions to which they are subjected, such as grating or crushing the cassava (Figueroa-Flórez et al. 2023). The granules starch had an average granular size of 10.5 µm, similar to that reported for cassava starch extracted from *Manihot esculenta cranz* by Ramos-Villacob et al. (2023).

Native cassava starches, after undergoing hydrothermal treatment, did not exhibit any morphological damage to the granules. However, the HMT treatment led to granular agglomeration, likely due to partial swelling and breakage of the starch granules in the presence of water molecules (Asranudin et al. 2023). Additionally, the treatment caused a 3.5% increase in granular size. These results are consistent with those reported by Moraes et al. (2014) for cassava starch granules, which maintained their morphology after being subjected to hydrothermal treatment under conditions of 30-35% moisture and 90 °C.

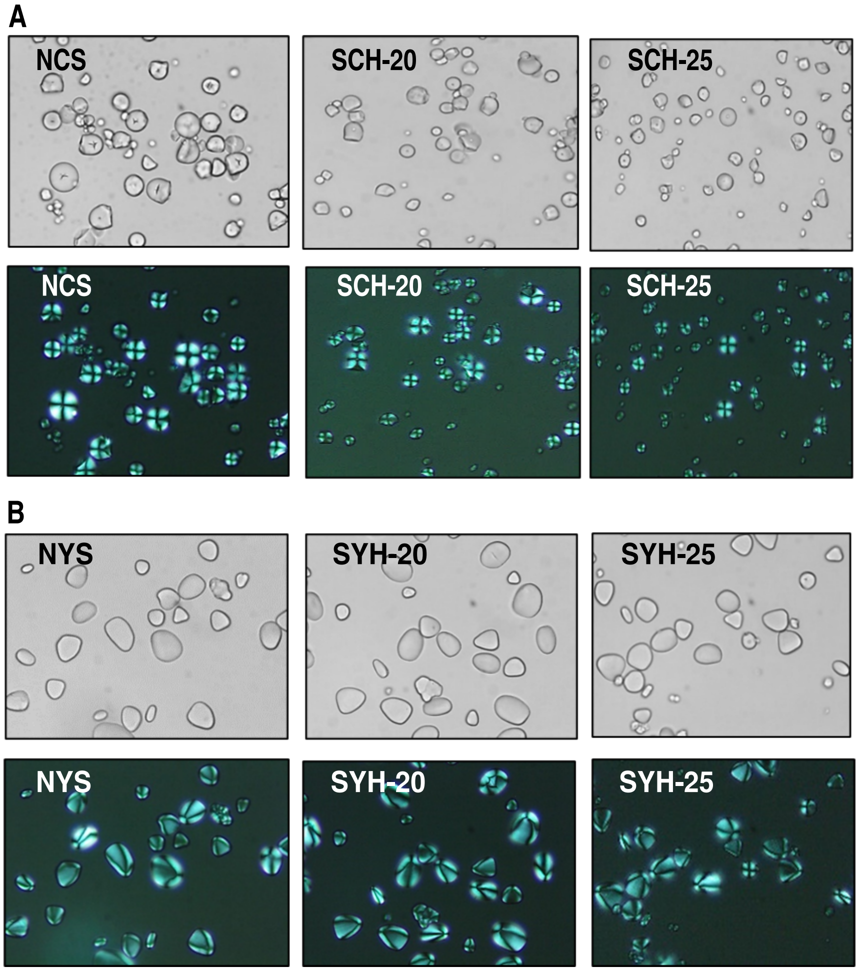

Figure 2. Bright-field and polarized light micrographs of. A) native and modified cassava starches, B) native and modified yam starches. NCS: native cassava starch; SCH-20: cassava starch with 20% w/w moisture content, modified by HMT; SCH-25: cassava starch with 25% w/w moisture content, modified by HMT; NYS: native yam starch; SYH-20: yam starch with 20% w/w moisture content, modified by HMT; SYH-25: yam starch with 25% w/w moisture content, modified by HMT.

The native yam starch granules (NYS) exhibited an oval morphology with a smooth, pore-free surface and an average particle size of 21 μm (Figure 2A). Similar results have been reported by Meaño et al. (2016). Both native and modified starches displayed a maltase cross extending towards the periphery of the granule, with characteristic birefringence typical of starch granules exhibiting a B-type diffraction pattern (Arroyo-Dagobeth et al. 2023). Additionally, the orientation suggests that the position of the 'hilum' is decentralized, which is characteristic of starch granules derived from rhizomes (Chakraborty et al. 2021).

After HMT treatment the morphology of the yam starch granules was preserved, with the presence of granular agglomerations similar to those observed in yam starch treated at 25% moisture and 110 °C, as reported by Indrianti and Pranoto (2018). An increase in granule size was also noted. Chen et al. (2022) suggest that this increase could be attributed to the thermal energy released during HMT, which may cause migration within the starch chain.

Physicochemical properties

(CWS), and swelling power (SP) of cassava and yam starches are shown in Table 3. NCS exhibited a WAC in the range of 70–75%, similar to results reported for cassava starch by Salcedo-Mendoza et al. (2017). After HMT treatment, cassava starches showed higher WAC (P<0.05), consistent with results reported by Liu et al. (2016) for HMT-treated starch. These authors suggest that such changes in WAC are likely associated with stronger interactions between hydroxyl and water molecules in HMT-treated samples compared to their native counterparts. NYS exhibited WAC in the range of 95–98%, consistent with values reported by Otegbayo et al. (2011) for yam starch. After HMT, yam starches showed a significant decrease (P<0.05) in WAC (Table 3).

Some studies have linked the reduction in WAC and swelling of starch granules to potential intragranular molecular reorganization, which reduces water accessibility to amorphous regions. This result aligns with the decrease in DC, as the lower WAC observed after HMT is attributed to the denser crystalline structure, which limits the starch's capacity to absorb water and swell (Liu et al. 2016; Oyeyinka et al. 2021).

Table 3. Physicochemical properties of native cassava and yam starches and HMT-treated starches.

Treatment	WAC (%)	SP(g/g)	CWS (%)
NCS	71.51±0.95^{a}	2.95±0.15^{a}	4.06±0.06^{a}
SCH-20	75.83±0.43^{b}	2.12±0.04^{b}	3.68±0.04^{ba}
SCH-25	76.83±0.81^{b}	2.28±0.09^{b}	3.65±0.04^{b}
NYS	97.62±0.42^{c}	2.16±0.02^{b}	5.31±0.24^{c}
SYH-20	93.37±0.28^{d}	2.17±0.01^{b}	4.60±0.25^{d}
SYH-25	94.48±0.16^{e}	2.16±0.02^{b}	4.78±0.03^{d}

WAC: Water absorption capacity; CWS: Solubility in cold water. SP: Swelling power. TG: Granule size. NCS: native cassava starch; SCH-20: cassava starch with 20% w/w moisture content, modified by HMT; SCH-25: cassava starch with 25% w/w moisture content, modified by HMT; NYS: native yam starch; SYH-20: yam starch with 20% w/w moisture content, modified by HMT; SYH-25: yam starch with 25% w/w moisture content, modified by HMT. Means with different lowercase letters in the same column indicate statistically significant differences according to Tukey's test ($P \leq 0.05$).

Native cassava starch exhibited SP values between 2.0 and 4.0 aligning with the ranges reported for various cassava varieties (Figueroa-Flórez et al. 2019). Following HMT, the SP of cassava starches decreased significantly (P<0.05), consistent with findings by Moraes et al. (2014) for HMT-modified cassava starch. This decrease in SP may be attributed to a loss of starch granule integrity upon high swelling, as the treatment could increase crystallinity, reduce starch hydration, and enhance interactions between amylose and amylopectin molecules (Sobowale et al. 2022; Suriya et al. 2019).

In contrast, native yam starch showed SP values ranging from 2.1 to 2.3%, consistent with those reported for *Dioscorea bulbifera L.* starch by Meaño et al. (2018). The HMT-modified yam starch did not show significant differences (P<0.05) compared to the native starch. This suggests that hydrothermal treatment did not affect the granular morphology of yam starch, resulting in limited granule swelling. This finding is supported by the micrographs (Figure 2B) in this study, which indicate that the structure and size of the granules remained similar to those of the native starch.

The cold-water solubility (CWS) of native cassava and yam starches was within the ranges reported for cassava starch by Figueroa-Flórez et al. (2023) and yam starch by Arroyo-Dagobeth et al. (2023). Following treatment at varying moisture levels, the CWS of cassava and yam starches decreased significantly (P<0.05). These results align with the study on HMT-treated yam starch conducted by Suriya et al. (2019), which suggests that a decrease in CWS may result from increased interactions between amylose-amylose and amylopectin-amylopectin chains due to heat treatment.

Pasting properties

The viscosity behaviors of native and modified starches are presented in Table 4. The NYS treatment showed a significantly higher (P<0.05) pasting temperature (TP) compared to NCS. A higher TP suggests greater internal stability of the starch granule, an increased presence of semicrystalline regions, and is generally associated with a higher amylose content (Salgado et al. 2019). Regarding viscosities, NCS exhibited a higher peak viscosity (PV) than NYS. Additionally, the BV values indicated greater stability for the NYS treatment, while the SV was higher in NYS compared to the NCS treatment. Similar findings on cassava and yam starches were reported by Arroyo-Dagobeth et al. (2023), who concluded that differences in these starchy materials are influenced by crystalline pattern type, as starches with a B-type diffraction pattern exhibit greater retrogradation compared to those with an A-type pattern (Klein et al. 2013).

Table 4. Pasting profiles of native cassava and yam starches and HMT-treated starches.

Treatment	PT (°C)	PV (Cp)	BV (Cp)	SV (Cp)
NCS	68.17±0.25[a]	2688±1.15[a]	935.7±19.0[a]	31.7±18.5[a]
SCH-20	70.43±0.15[b]	2574±1.15[b]	26.7±6.11[b]	364±4.16[b]
SCH-25	74.40±0.20[c]	2263±1.00[c]	2.0±1.00[b]	193±2.89[c]
NYS	82.80±0.20[d]	1724±1.53[d]	286±34[c]	1439±32.0[d]
SYH-20	87.53±0.76[e]	159.1±8.31[e]	125±6.54[d]	1020±2.08[e]
SYH-25	87.80±0.20[e]	183.1±4.96[f]	129±0.47[d]	671±6.12[f]

PT: Pasting temperature; PV: Peak viscosity; BV: Breakthrough viscosity; SV: Settling viscosity. NCS: native cassava starch; SCH-20: cassava starch with 20% w/w moisture content, modified by HMT; SCH-25: cassava starch with 25% w/w moisture content, modified by HMT; NYS: native yam starch; SYH-20: yam starch with 20% w/w moisture content, modified by HMT; SYH-25: yam starch with 25% w/w moisture content, modified by HMT. Means with different lowercase letters in the same column indicate statistically significant differences according to Tukey's test ($P \leq 0.05$).

After HMT treatment, the pasting temperature (PT) significantly increased (P<0.05) in both cassava and yam starches. This result may be linked to increased cross-linking of starch chains within the granular matrix, which requires more heat for structural degradation and gel formation. The peak viscosity (PV) of HMT-treated cassava and yam starch granules was significantly lower than that of the native controls (Table 4). Similar results have been reported in the literature for HMT-treated wheat starch by Liu et al. (2015), who suggested that the decrease in PV could be due to the loss of some branched chains during the modification process, leading to less swelling of the starch granules during heating (Li et al. 2017).

Conversely, cassava and yam starches exhibited a significant decrease (P<0.05) in breakdown viscosity (BV) after HMT treatment compared to their native counterparts. A similar decrease was observed by Indrianti and Pranoto (2018) in HMT-treated sweet potato starch, who argued that the reduction in BV enhances paste stability and could be associated with a decrease in swelling power. This is likely due to the strengthening of the gel matrix structure and amylose, which improves stability during shearing (Chung et al. 2009). Additionally, this decrease may result from associations between chains in the amorphous regions of the granule and changes in crystallinity during hydrothermal treatment (Trung et al. 2017).

In contrast, modified cassava starches showed an increase in setback viscosity (SV), indicating a greater tendency for retrogradation due to increased suspension viscosity during cooling (Paternina et al. 2016; Suriya et al. 2019). Meanwhile, modified yam starches exhibited a significant decrease (P<0.05) in SV compared to the native starch. This decrease in viscosity could be associated with an increased amylose-to-amylopectin ratio; starches with higher amylose content are likely to exhibit greater structural stability due to the stronger attraction between polymeric chains (Solarte-Montúfar et al. 2019).

Gelatinization properties

In this study, oscillatory dynamic tests were conducted to establish the gelatinization temperatures (Table 5). The results showed that elastic moduli (G') predominated over viscous moduli (G''), suggesting that the starch hydrogels exhibit an elastic structure (Glorio et al. 2009). The thermal effect in the range of 20 to 90 °C can disrupt the short-range double helices formed between amylopectin/amylopectin or amylopectin/amylose complexes, defining the boundaries of swelling and granular gelatinization processes. The gelatinization temperatures obtained align with those estimated by Barua et al. (2022) and Van et al. (2017) for native cassava and yam starches. From these findings, it can be inferred that rheological testing with a temperature sweep within the linear viscoelastic region is an effective method for determining gelatinization properties (Seña-Rambauth et al. 2024).

The gelatinization temperatures of native and modified starches are presented in Table 5. Initially, native yam starch (NYS) exhibited higher gelatinization temperatures than native cassava starch (NCS). These results are consistent with studies on cassava and yam starch reported by Van et al. (2017) and Martínez et al. (2019). These temperature differences are likely related to the crystalline pattern of each starchy material. NYS exhibits a B-type pattern, which contains abundant amylopectin chains with a high degree of polymerization, potentially requiring greater thermal energy to initiate gelatinization in NYS compared to NCS (Klein et al. 2013).

Table 5. Gelatinization properties estimated by oscillatory temperature sweeps on native and HMT-treated starches.

Treatment	To (°C)	Tp (°C)	Tc (°C)	Tc- To (°C)
NCS	61.74±0.01[a]	68.83±0.00[a]	75.94±0.02[a]	14.95±0.01[a]
SCH-20	62.72±0.03[b]	70.85±0.04[b]	77.99±0.00[b]	15.27±0.03[b]
SCH-25	63.75±0.00[c]	73.92±0.00[c]	79.40±0.00[c]	15.65±0.00[c]
NYS	74.91±0.00[d]	82.04±0.00[d]	86.13±0.00[d]	11.22±0.00[d]
SYH-20	83.07±0.01[e]	86.05±0.08[e]	90.17±0.00[e]	7.1±0.01[e]
SYH-25	86.11±0.00[f]	88.14±0.00[f]	90.20±0.00[e]	4.09±0.00[f]

To: initial temperature; Tp: peak gelatinization temperature; T_c: final temperature. NCS: native cassava starch; SCH-20: cassava starch with 20% w/w moisture content, modified by HMT; SCH-25: cassava starch with 25% w/w moisture content, modified by HMT; NYS: native yam starch; SYH-20: yam starch with 20% w/w moisture content, modified by HMT; SYH-25: yam starch with 25% w/w moisture content, modified by HMT. Means with different lowercase letters in the same column indicate statistically significant differences according to Tukey's test (P<0.05).

Following HMT treatment, the gelatinization temperatures (To, Tp, Tc) of cassava and yam starches significantly increased (P<0.05) compared to their native counterparts. The increase in gelatinization temperatures of the modified starch granules could be attributed to structural changes within the starch granules, such as the destabilization of crystalline regions and the leaching of amylose chains (Sun et al. 2014).

The differential temperature (Tc-To) in HMT-treated cassava starches (SCH-20 and SCH-25) increased significantly (P<0.05), while it decreased in other HMT-treated starches. This increase in differential temperature likely reflects the degree of heterogeneity among crystallites within the starch granules (Pardo et al. 2013). This property varies based on amylose content, as well as the size, shape, and distribution of the starch granules, and their internal interactions (Liu et al. 2021). Furthermore, changes in the thermal properties of cassava starch granules may be attributed to the formation of amylose-lipid inclusion complexes and enhanced amylose-amylopectin interactions during hydrothermal treatment. These interactions could lead to a reduction in amorphous regions and an increase in melting temperatures (Liu et al. 2016; Xie et al. 2019).

CONCLUSION

Hydrothermal treatment (HMT) facilitated the development of modified cassava and yam starches, resulting in structural alterations without significant changes in granular morphology compared to native starches. In cassava starch, HMT led to an increase in amylose content and molecular ordering, enhancing cold water solubility and reducing breakdown viscosity. Similarly, HMT in yam starch increased amylose content, altering the semicrystalline order of the granules and significantly affecting hydrophilic properties and pasting viscosities. Furthermore, hydrothermal treatment at 25% moisture (HMT) modified the hydrophilic properties, resulting in starches with stable breakdown viscosities and a lower tendency to retrogradation. Thus, hydrothermally treated starches could be suitable for use in baked goods or pastries. However, further studies are recommended, such as evaluating resistant starch or slow-digesting starch content through simple hydrothermal processes or repeated cycles.

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