



Article

Mechanochemical Effects of High-Intensity Ultrasound on Dual Starch Modification of Mango Cotyledons

Ramiro Torres-Gallo ^{1,2,*} , Ricardo Andrade-Pizarro ³ , Diego F. Tirado ⁴ , Andrés Chávez-Salazar ⁵ and Francisco J. Castellanos-Galeano ⁶

¹ Department of Agroindustrial Engineering, School of Engineering, Universidad del Atlántico, Puerto Colombia 081001, Colombia

² Doctorates in Engineering, Universidad de Caldas, Manizales 170001, Colombia

³ Department of Food Engineering, School of Engineering, Universidad de Córdoba, Montería 230002, Colombia; rdandrade@correo.unicordoba.edu.co

⁴ Biological Engineering Program, Dirección Académica, Universidad Nacional de Colombia, Sede de La Paz, La Paz 202017, Colombia; dtiradoa@unal.edu.co

⁵ Ci2DT2 Research Center, Department of Food Engineering, School of Artificial Intelligence and Engineering, Universidad de Caldas, Manizales 170001, Colombia; andres.chavez@ucaldas.edu.co

⁶ Technological Development Center for Bioprocess and Agroindustry Plant, Department of Food Engineering, School of Artificial Intelligence and Engineering, Universidad de Caldas, Manizales 170001, Colombia; francisco.castellanos@ucaldas.edu.co

* Correspondence: ramirotorres@mail.uniatlantico.edu.co

Abstract: The starch modification of mango cotyledons with both single ultrasound (US) and dual (US followed by octenyl succinic anhydride, OSA) was optimized by response surface methodology (RSM). The mechanochemical effects of ultrasound on amylose content, particle size, and dual modification efficiency were assessed. In addition, the structural, thermal, morphological, and functional properties were evaluated. After optimization with single US (41 min and 91% sonication intensity), sonication induced starch granule fragmentation, altering amorphous and partially crystalline regions, which increased amylose content (34%), reduced particle size ($D_{x50} = 12 \mu\text{m}$), and modified granule surface morphology. The dual modification (the subsequent OSA reaction lasted 4.6 h under the same conditions) reached a degree of substitution of 0.02 and 81% efficiency, imparting amphiphilic properties to the starch. OSA groups were mainly incorporated into amorphous and surface regions, which decreased crystallinity, gelatinization temperature, and enthalpy. The synergistic effect of the modification with US and OSA in the dual modification significantly improved the solubility and swelling power of starch, resulting in better dispersion, functionality in aqueous systems, and chemical reactivity. These findings highlight the potential of dual modification to transform mango cotyledon starch into a versatile ingredient in the food industry as a thickener, a stabilizer in soups and sauces, an emulsifier, a carrier of bioactive and edible films; in the cosmetic industry as a gelling and absorbent agent; and in the pharmaceutical industry for the controlled release of drugs. Furthermore, valorizing mango cotyledons supports circular economy principles, promoting sustainable and value-added food product development.

Keywords: optimization; OSA modification; response surface methodology (RSM); degree of substitution; amylose



Academic Editor: Ayesha Sarker

Received: 14 May 2025

Revised: 6 June 2025

Accepted: 11 June 2025

Published: 13 June 2025

Citation: Torres-Gallo, R.; Andrade-Pizarro, R.; Tirado, D.F.; Chávez-Salazar, A.; Castellanos-Galeano, F.J. Mechanochemical Effects of High-Intensity Ultrasound on Dual Starch Modification of Mango Cotyledons. *AgriEngineering* **2025**, *7*, 190. <https://doi.org/10.3390/agriengineering7060190>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Mango (*Mangifera indica* L.) is the second most produced tropical fruit in the world, with a production exceeding 61 million tons in 2023 and a production yield of 10 t/ha [1].

However, this process generates between 24% and 40% of residues with respect to the weight of the fresh fruit, mainly composed of seeds [2]. It is estimated that around 20 million tons of these by-products are discarded annually, contributing to water and air pollution, affecting vegetation, and emitting greenhouse gases [3]. Despite this environmental impact, mango seeds represent a valuable source of starch, with content ranging from 58.80 g/100 g dry matter to 80 g/100 g dry matter [4,5]. This richness makes seed residues an attractive alternative for obtaining non-conventional starches within a circular economy approach.

Starch is a key ingredient in the food and chemical industries. It is biodegradable, renewable, and low-cost. It is used as a thickener, emulsifier, gelling agent, stabilizer, adhesive, and fat substitute [6,7]. However, native starch has a low solubility, strong shear thinning behavior, low paste clarity, lack of emulsification, thermal resistance, high tendency to retrograde, and low stability in food matrices [8,9]. To overcome these limitations, enzymatic, chemical, or physical processes are employed [10]. These processes alter the molecular structure of starch, conferring new physical, chemical, and functional properties. As a result, modified starches can be tailored for diverse industrial applications, adapting to specific functional requirements [11].

Among the emerging technologies for starch modification, high-intensity, low-frequency ultrasound treatment (i.e., 20 kHz–100 kHz) has become more attractive for being environmentally friendly and effective in saving energy [12]. US cavitation is the main mechanism involved in US-assisted extraction. Cavitation bubble implosion causes the accumulation of energy in hot spots, leading to extreme pressures and temperatures (i.e., 1000 atm and up to 5000 K), which produce micro-jets, shear energy waves, and very large turbulences in the cavitation zone, causing various effects such as cracking, pores, erosion and molecular disruption [13,14]. The application of ultrasound can cause the breakdown of amylose and amylopectin chains, altering the physical, morphological, and structural characteristics of starch granules, and enhancing their functional, thermal, and pasting properties, thereby making them more versatile for industrial applications [15].

Currently, there is a growing trend towards the use of dual treatments, which combine ultrasound with other modification technologies [8]. Among these, modification with octenyl succinic anhydride (OSA) following sonication has shown promising results. This technique allows for obtaining amphiphilic starches with improved properties such as emulsifiers, stabilizers, and encapsulating agents in the food, cosmetic, and pharmaceutical industries [16,17]. In addition, OSA-modified starch retains its biodegradability and shows improved characteristics such as solubility, swelling capacity, viscosity, and translucency, while reducing the gelatinization temperature.

However, the OSA–starch reaction is a challenging event that is influenced by many process conditions (e.g., pH, temperature, time, catalyst) and the properties of the starch to be modified (e.g., granule size, amylose content, crystallinity) [18]. The reaction between OSA and starch occurs in an aqueous alkaline dispersion. One carboxyl group of OSA reacts with hydroxyl groups of starch to form an ester bond. The other carboxyl group forms sodium carboxylate. In aqueous suspension systems, OSA tends to form large oily droplets. This morphology limits its penetration into starch granules. As a result, the reaction efficiency is low and the distribution of octenyl succinic groups within the starch is uneven [9]. Recent studies indicate that sonication can improve the degree of substitution in OSA modification [17,19,20]. However, there is still no consensus on the mechanochemical effects of ultrasound on the esterification process and its influence on reaction times, which makes it difficult to establish optimal operating conditions.

Considering the research gap, this study focused on obtaining the optimal conditions in the modification process of mango cotyledon starch by US and double modification (US before OSA esterification). The mechanochemical effect of ultrasound on the structure and

properties of starch was studied, as well as its impact on the efficiency of the esterification reaction. The final purpose was to improve its properties as an emulsifier and encapsulating agent, with a view to its application in the food industry. The results obtained allowed for a better understanding of the effects of ultrasound on the physical and chemical modification processes of starches. In addition, they enabled the development of guidelines for the development of functional starches derived from agro-industrial waste.

2. Materials and Methods

2.1. Reagents and Materials

Octenyl succinic anhydride (OSA, 97% *v/v*, Sigma-Aldrich, Burlington, MA, USA), isopropyl alcohol ($\geq 99.7\%$ *v/v*, Sigma-Aldrich, St. Louis, MO, USA), dimethyl sulfoxide (DMSO, $\geq 99\%$ *v/v*, Sigma-Aldrich, St. Louis, MO, USA), hydrochloric acid (HCl, 37% *w/w*, analytical, Sigma-Aldrich, St. Louis, MO, USA), sodium hydroxide (NaOH $\geq 98\%$ *w/w*, anhydrous pellets, Sigma-Aldrich, St. Louis, MO, USA), potassium iodide ($\geq 99\%$ *v/v*, Sigma-Aldrich, St. Louis, MO, USA), and iodine ($\geq 99.8\%$ *v/v*, Sigma-Aldrich, St. Louis, MO, USA) were used.

Starches were extracted from mango (*Mangifera indica* L.) cotyledons of the Magdalena River variety at ripeness stage 4–5 [21], generously provided by a commercial entity from the Atlántico (Colombia). The starches were obtained in previous studies conducted by our research group, with an amylose content of $(25.7 \pm 0.1)\%$ *w/w* [22].

2.2. Ultrasonic (US) Modification

The modification with US was performed following the methodology described by Rahaman et al. [23]. Mango cotyledon starch was dispersed in distilled water in a 1:2 *w/v* ratio in a beaker and shaken uniformly for 15 min to acquire a homogeneous suspension. The suspension was subjected to ultrasonication in an Elmasonic P30H series ultrasonic bath (Elma Schmidbauer®, Singen, Germany) with a maximum ultrasonic power of 318 W, varying the time and intensity of the sonication power, according to the experimental design explained below, but not exceeding 30 °C. Subsequently, it was centrifuged for 10 min at 3500 rpm. The obtained cake was dried for 24 h at 40 °C in a tray dehydrator (WT-75-0201-W, Weston®, Weston, FL, USA), sieved (100-mesh), and stored until use.

An ultrasonic bath was used instead of a probe to modify the starch, as the former allows for a greater uniformity of treatment [24], as well as enabling modifications to the functional properties of starch without causing gelatinization or destruction [8,23].

2.3. Dual Modification

Dual modification was performed according to the methodology proposed by Ferraz et al. [16], with modifications. US-modified starch from mango cotyledons was dispersed in distilled water at a 1:3 *w/v* ratio. The pH of the suspension was adjusted to 8.5 with a solution of NaOH at 1.0 M. A solution of OSA with a 3% *w/w* dry basis to starch weight, previously diluted to 1:3 *v/v* in absolute ethanol, was slowly added. The reaction was monitored at 35 °C for the required reaction time according to the experimental design detailed below. After completion of the reaction, the pH was adjusted to 6.5 with a 1 M HCl solution. The dispersion was centrifuged at 3500 rpm for 10 min. The obtained cake was dried for 24 h at 40 °C in a tray dehydrator (WT-75-0201-W, Weston®, Weston, FL, USA), passed through a 100-mesh sieve, and stored until use.

2.4. Starch Modification Process Optimization

Optimal conditions for the US and dual modifications of mango cotyledon starch were achieved by using the response surface methodology (RSM). A general quadratic model

was formulated, offering a face-centered central composite design ($\alpha = 1$). The factors studied for the optimal conditions of US modification were US time (5 min and 55 min) and intensity of sonication power (40% and 100%); the response variables were apparent amylose content (to be maximized) and particle size (to be minimized). Meanwhile, the factors for the optimal dual modification conditions were sonication time (5 min and 55 min), sonication power intensity (40% and 100%), and reaction time (2 h and 7 h). The response variables were degree of substitution (to be maximized) and reaction efficiency (to be maximized).

Numerical optimization was performed using desirability techniques. Optimization criteria, such as importance and weight, were established based on the ranges of the response variables within the experimental region. An analysis of variance (ANOVA) was performed to examine the validity of the models using Design Expert 6.0.4[®] software (Stat-Ease, Inc., Minneapolis, MN, USA).

Additionally, three experiments were performed under the optimum modification conditions as well as for modification with OSA alone, at a reaction time equal to the optimum obtained in dual modification, to evaluate the effects of modifications on the physical, morphological, and thermal properties. All samples were analyzed in triplicate and values have been presented as mean $\pm$ standard deviation. ANOVA and Tukey's multiple comparison test were used to measure statistically significant differences ($p \leq 0.05$) using Statgraphics Centurion 19 (Statgraphics Technologies, Inc., The Plains, VA, USA).

2.5. Apparent Amylose Content (AAC) and Particle Size of US Modified Starches

Apparent amylose content (AAC) was quantified spectrophotometrically (UV-Vis 2550[®], Shimadzu, Japan) by the iodine colorimetric method. The determination was performed with a calibration curve using corn amylopectin and potato amylose, as described by Chen et al. [6]. For the analysis, 0.1 g of starch was accurately weighed on a dry basis and dissolved in DMSO. The dissolution was heated for 15 min at 85 °C on a hot plate with continuous stirring using a magnetic stir bar. Subsequently, it was brought to a final volume of 25 mL with deionized water in a volumetric flask. From this solution, a 1 mL aliquot was taken and diluted with 50 mL of deionized water. Then, 5 mL of a solution of iodine (0.0025 mol/L) in potassium iodide (0.0065 mol/L) was added. The mixture was left to react in the dark for 20 min, and finally, the absorbance was measured at 600 nm.

Starch granule size was measured by dynamic light scattering (DLS) using a Malvern Mastersizer 3000 particle analyzer (Malvern Panalytical[®], Malvern, UK). Measurements were performed in quadruplicate at room temperature. Refractive indices of 1.33 for water and 1.54 for starch were used, as reported by Torres-Gallo et al. [22]. The mean diameter was defined in terms of the 50th percentile (Dx50), the area-weighted mean, D [3.2], and the volume-weighted mean, D [4.3].

2.6. Degree of Substitution (DS) and Reaction Efficiency (RE) of Dual Modified Starch

The DS was measured according to the methodology described by Ferraz et al. [16]. For that, 5 g of modified starch was stirred at 100 rpm for 30 min in 25 mL 2.5 M HCl solution in isopropyl alcohol. Then, 100 mL isopropyl alcohol was added and stirred for 10 min. The dispersion was centrifuged at 5000 rpm for 5 min and the residue was washed with 100 mL isopropyl alcohol and water until Cl^- was absent. Subsequently, the residue was dispersed in 300 mL of deionized water and heated at 100 °C for 20 min. The dispersion was then titrated with 0.1 M NaOH using phenolphthalein as an indicator. Additionally, the same processing was performed for native starch, which was then used as blank. The

DS was calculated using both Equations (1) and (2) [25]; meanwhile, RE was found using Equation (3) [26].

$$OSA (\%) = \frac{210 \times (V_m - V_b) \times N}{W_m} \times 100\% \quad (1)$$

$$DS = \frac{162 \times OSA}{(210 \times 100) - (209 \times OSA)} \quad (2)$$

$$RE (\%) = \frac{DS}{DS_{Theoretical}} \quad (3)$$

where OSA was the weight percentage of OSA in the modified starch; V_m and V_b were the titration volumes of NaOH (mL) used with modified starch and native starch, respectively; N was the molarity of the standard NaOH solution; W_m was the weight of modified starch on a dry basis; $DS_{Theoretical}$ was calculated assuming that all added OSA reacted with starch; 162, 210, and 209 were the molecular weights of the glucose unit, octenyl succinyl group, and octenyl succinyl group minus the molecular weight of the hydrogen atom, respectively. Finally, 100 was the conversion factor.

2.7. Fourier Transform Infrared (FTIR) Spectroscopy

The molecular structure was analyzed according to Torres-Gallo et al. [22] by using a Nicolet iS20 FTIR spectrometer (Thermo Fisher Scientific®, Waltham, MA, USA) coupled with an ATR micro sampler. Spectra were acquired at a resolution of 4 cm^{-1} from 400 cm^{-1} to 4000 cm^{-1} . Subsequently, a baseline correction was performed and deconvoluted in the range of 800 cm^{-1} to 1200 cm^{-1} , using Origin® Version 2015 software (OriginLab Corporation, Northampton, MA, USA). Two spectral ratios were calculated from the deconvoluted spectra as follows: the value of $1047 \text{ cm}^{-1}/1022 \text{ cm}^{-1}$ (i.e., short-range order index) represents the ordered crystalline region of the amorphous region in starch; meanwhile, $995 \text{ cm}^{-1}/1022 \text{ cm}^{-1}$ (i.e., molecular disorder or degree of double helix) is the change of the double helix structure within the starch granule [27,28].

2.8. X-Ray Diffraction (XRD) Analysis

The XRD patterns of the starches were acquired using Panalytical Empyrean equipment with $\text{CuK}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$). The measurements of the radiation intensities of the equilibrated diffraction angle (2θ) were performed from 5° to 60° , with 0.02° step width. The relative crystallinity (RC) was calculated as a percentage of the ratio between the crystalline and total areas obtained from the diffractogram using the OriginPro 15 software (OriginLab Corporation, Northampton, MA, USA) according to the procedure described by Dome et al. [29].

2.9. Morphology Analysis

For the morphological analysis, a 1% w/v aqueous suspension of starch was prepared with distilled water. A drop of this suspension was placed on a slide and covered with a coverslip. The shape of the granules and the presence of the Maltese cross were examined by polarized light and normal light microscopy using an Optika B-510BF4K® microscope (Optika Science, Bergamo, Italy) equipped with an Optika C® series camera with a CMOS sensor (Optika Science, Bergamo, Italy). Optika Proview® 4.11 software was used to digitize the images. Additionally, a scanning electron microscope (SEM, Quanta 250 FEG®, FEI Company, Hillsboro, OR, USA) was used to study the starch's surface microstructure. The micrographs were taken at magnifications of $500\times$, $2000\times$, and $5000\times$ [22].

2.10. Thermal Properties

A differential scanning calorimeter (DSC-250 Discovery[®], TA Instruments, New Castle, DE, USA) was used. Starch–water dispersions (1:4 *w/v* ratio) were heated from 30 °C to 120 °C at 10 °C/min, with an empty aluminum tray used as the reference. All experiments were conducted in triplicate [22].

3. Results and Discussion

3.1. Optimization

3.1.1. Validity of the Models

The fitted models, expressed in coded process factors, for the response variables AAC and particle diameter—volume-weighted mean diameter ($D[4;3]$), area-weighted mean diameter ($D[3;2]$), and mean particle diameter at 50% of cumulative volume ($Dx50$), in the case of US modification—are represented as Equations (4)–(7), respectively. Meanwhile, in the case of dual modification, these models for the response variables DS and RE are represented via Equation (8) and Equation (9), respectively.

$$AC (\%) = 22.0625 + 0.4485A + 0.1119B - 0.0064A^2 \quad (4)$$

$$D[3,2] (\mu\text{m}) = 13.1095 - 0.0269A - 0.0101B + 0.0002AB \quad (5)$$

$$D[4,3] (\mu\text{m}) = 13.7166 - 0.01613A - 0.0054B \quad (6)$$

$$Dx50 (\mu\text{m}) = 13.1095 - 0.0269A - 0.0101B + 0.0002AB \quad (7)$$

$$DS = 8.6 \times 10^{-3} + 8.6 \times 10^{-5}A + 1.8 \times 10^{-5}B + 3.3 \times 10^{-3}C - 7.8 \times 10^{-6}AC - 8.9 \times 10^{-7}A^2 - 3.1 \times 10^{-4}C^2 \quad (8)$$

$$RE (\%) = 37.6406 + 0.3718A + 0.0775B + 14.3699C - 0.0342AC - 0.0039A^2 - 1.3535C^2 \quad (9)$$

where A is the ultrasonication time, B is the power intensity, and C is the dual modification reaction time. To obtain a more parsimonious model, the factors that did not present a significant effect ($p > 0.05$) according to the ANOVA (see Supplementary Data, Table S1) were excluded, except for the main factor B (power intensity), to maintain the hierarchy of the model.

The ANOVA (see Supplementary Data, Table S1) shows that the experimental models were statistically significant ($p \leq 0.05$). The models were able to adequately explain the experimental data, given the high values of the coefficient of determination (R^2), adjusted R^2 , and predicted R^2 . The lack-of-fit test indicates that the predicted model fitted the experimental data well ($p \leq 0.05$). In addition, the high value of precision (i.e., >4) and the coefficient of variance (CV) were relatively low (i.e., $<3\%$), indicating the high precision, accuracy, and reliability of the experiment [30].

3.1.2. Effects of US Modification on Starch

Figure 1 shows the response surface plots of the dependent variables AAC (see Figure 1a), $D[3;2]$ (see Figure 1b), $D[4;3]$ (see Figure 1c), and $Dx50$ (see Figure 1d), as functions of the independent variables US time and power intensity, when single US modification was carried out.

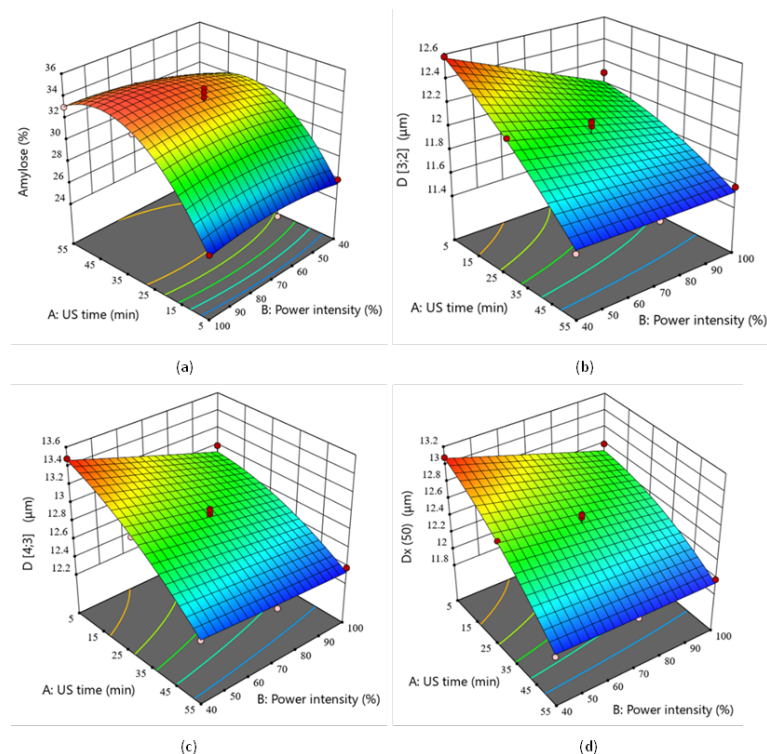


Figure 1. Response surfaces of the combined effects of sonication time and power intensity on (a) apparent amylose content (%); (b) area-weighted mean diameter ($D[3;2]$); (c) volume-weighted mean diameter ($D[4;3]$); and (d) mean particle diameter at 50% of cumulative volume ($Dx50$) values for the single ultrasound (US)-modified starch.

The AAC was statistically significant ($p \leq 0.05$) with respect to the main and quadratic factors of US time (A). The mean values ranged from 25.8% to 34.6%. The impact of US time on AAC was evident, as illustrated in Figure 1a. However, prolonged sonication led to its progressive decrease. This phenomenon could be attributed to two key factors: cavitation and local/microscopic effects [8,13,15].

The increase in AAC with sonication time in Figure 1 can be attributed to the mechanochemical effects caused by ultrasonic cavitation. The bubble implosion during the phase of rarefaction generated high pressures and temperatures, which culminated in the production of liquid microjets, shear forces, and the formation of free radicals, favoring the granular breakdown of starch. As a result, the selective depolymerization of the branched amylopectin chains (at the α -4 glycosidic linkages close to 1,6 linkages) and the molecular cleavage and release of long amylose chains occurred [13,15,27]. Finally, a prolonged period of sonication caused the excessive depolymerization of amylose, forming shorter chains (<20 glucose units). This affected the structural organization of starch, losing part of the helical stature and reducing the ability to form stable complexes with iodine [31,32]. This resulted in a drop in AAC.

These results agreed with the findings reported for wheat starch [6], teff grains [33], rice starch [14], and white millet [34], where the influence of sonication time on the molecular structure of starches was studied. The authors reported that at short sonication times (e.g., 10 min), the degradation of starches occurred in the amorphous region, resulting from cleavage at the glycosidic α -(1,4) linkages of amylose and amylopectin, while longer sonication times (e.g., 30 min) caused depolymerization to a lesser extent in amylopectin via cleavage of the α -(1,6) bonds. However, they did not report a decrease in amylopectin content resulting from excessive exposure to the US for longer than 30 min.

D[3;2], D[4;3], and Dx50 were statistically significant ($p \leq 0.05$) with respect to the independent variables US time (A), power intensity (B), and the AB interaction, except for the AB interaction in D[4;3] with a $p = 0.0552$. Particle diameters showed a decrease at higher levels of US time, with a lower influence of power intensity with increasing US time (see Figure 1b–d).

D[3;2], D[4;3] and Dx50 showed similar behaviors with low fluctuations, as follows: $(11.5 \pm 1.2) \mu\text{m} - (12.6 \pm 0.1) \mu\text{m}$, $(12.4 \pm 1.7) \mu\text{m} - (13.5 \pm 10.1) \mu\text{m}$, and $(11.9 \pm 1.7) \mu\text{m} - (13.1 \pm 10.1) \mu\text{m}$, respectively. This observed reduction in the sonicated sample can be explained by a fragmentation induced by the cavitation phenomenon, as the collapse of the bubbles leads to material fatigue, followed by a gradual tearing of the microscopic particles [14]. Another possible explanation is more likely to be related to the disintegration of large starch agglomerates rather than individual granules [13]. However, this was not evident in the SEM images.

These results agree with those reported for starches from kiwifruit [35], lychee [27], and rice [14]. However, with sweet potato [36] and pea [37] starches, US produced an increase in starch granule size, and we can attribute this behavior to the agglomeration (reaggregation) of starch granules or surface adhesiveness between granules. Meanwhile, Mohammad Amini et al. [38] and Falsafi et al. [39] reported that US had no significant effects on the sizes of corn and oat starch granules, respectively. It is suggested that these behaviors may be attributed to differences in the particular properties of starches from different sources [35].

3.1.3. Effects of Dual Modification on Starch

Figure 2 shows the response surfaces of the dependent variables *DS* (see Figure 2a,b) and *RE* (see Figure 2c,d) as functions of the independent variables time, US power intensity, and reaction time when the dual modification was performed.

The *DS* and *RE* were statistically significant ($p \leq 0.05$) with respect to the main and quadratic factors of US time (A) and reaction time (C). The mean values ranged from 0.1458% to 0.01919% and from 63.39% to 83.48%, respectively. The impacts of US time and reaction time on *DS* and *RE* were evident for the dual-modified starch, as shown in Figure 2.

The ultrasound (US) treatment time had a positive effect on both the degree of substitution (*DS*) and the reaction efficiency (*RE*) in the dual modification (US–OSA). This behavior could be attributed to the mechanochemical effect caused by ultrasound treatment before reaction with OSA [9].

Ultrasonic cavitation facilitated the entry of water and OSA groups into the internal structure of starch. In addition, the possible generation of free radicals by ultrasonic cavitation may have increased the active sites available for the reaction with OSA. The above is consistent with that reported by Chen et al. [6] for modified corn starch.

Several studies have already reported that AAC has a positive impact on *RE* [40,41], which reinforces the hypothesis that OSA modification takes place mainly in the amorphous parts of starch granules, dominated by amylose chains [36,41].

According to Figure 2, the impact of reaction time positively affected the *DS* and *RE*. The increased reaction time was able to enhance the diffusion and dissolution of reagents and cause a swelling of the starch granules, thus improving the uptake of the reagent by the molecules of starch, and consequently, the OSA was able to remain longer in the reaction medium [42]. However, the prolongation of the reaction time led to its progressive decrease. The depletion of the anhydride required for esterification likely promoted the hydrolysis of OSA, as well as the potential partial hydrolysis of the starch, due to the presence of NaOH used to maintain the reaction pH. These results agree with previous reports [43–45]

that have stated that long reaction times did not necessarily produce a high *DS* value. The saponification reaction of laterally formed esters competes with esterification in the production of OSA starch. Eventually, the side reactions become dominant.

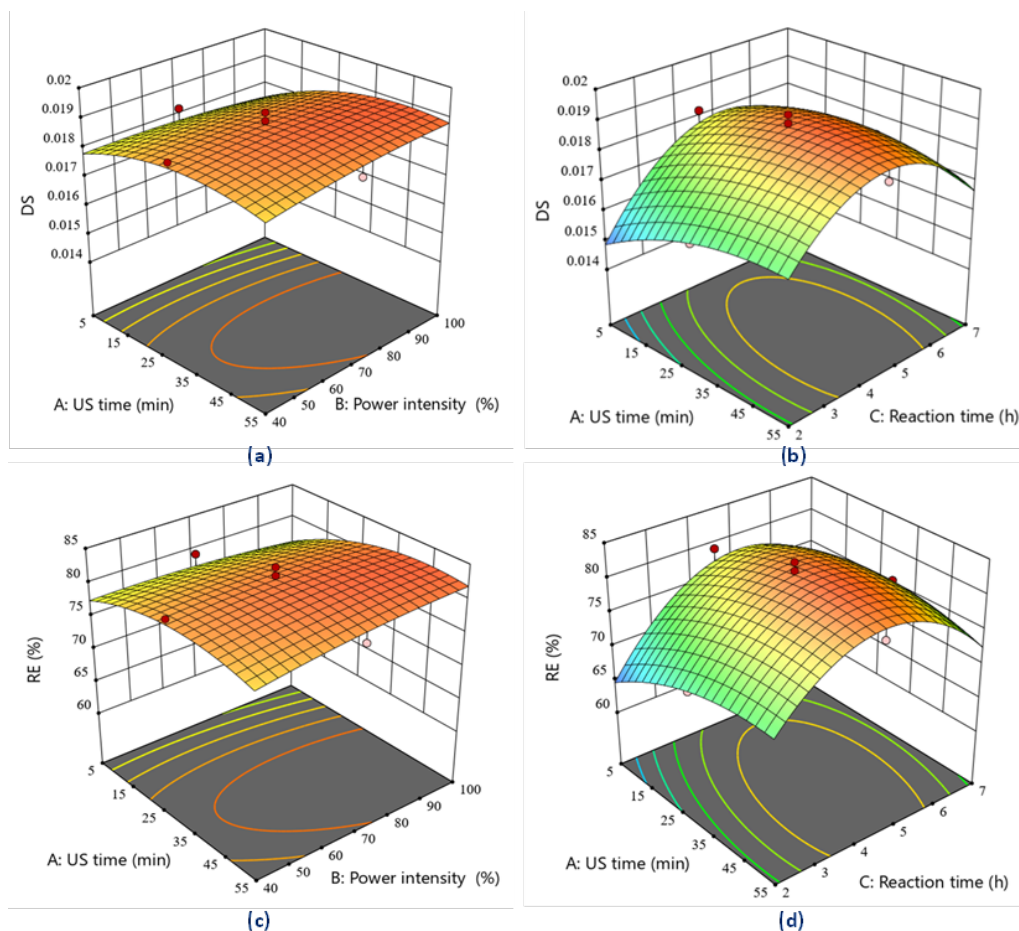


Figure 2. Response surface of the combined effects of sonication time and power intensity (a,b) and sonication time and reaction time (c,d) on the degree of substitution (*DS*) and reaction efficiency (*RE*) values for the dual-modified starch.

The depletion of the anhydride required for esterification likely promoted the hydrolysis of OSA, as well as the potential partial hydrolysis of the starch, due to the presence of the NaOH used to maintain the reaction's pH.

3.1.4. Predictive Model Verification

According to the results previously obtained, a multiple response optimization was planned, setting the criteria, weights, and impacts, as described in Table 1. The optimum conditions determined for starch modification by US were as follows: US time of 41.05 min and power intensity of 91.35%. Meanwhile, in the case of dual modification, the US time was 42.98 min, the power intensity was 92.34%, and the reaction time was 4.61 h. The values predicted by the model (theoretical value) and the experimental values of the response variables are shown in Table 1. The values of the relative mean error (RME) were all <5%, indicating that the models obtained were adequate and reliable for use in practical predictions.

Table 1. Experimental optimization of modified starch.

Variable	Criteria	Impact	Weight	Theoretical Value	Experimental Value	RME (%)
Single US modification						
AAC (%)	Maximize	5	7	34.3	33.6 ± 1.9	2.29
Dx50 (μm)	Minimize	3	3	11.8	12.1 ± 0.2	1.23
D[3;2] (μm)	Minimize	3	3	12.6	11.6 ± 0.2	1.20
D[4;3] (μm)	Minimize	3	3	12.2	12.7 ± 0.1	1.23
Dual modification						
DS	Maximize	3	3	0.0190	0.018 ± 0.0002	4.97
RE (%)	Maximize	3	3	82.3	80.7 ± 0.9	1.98

RME, relative mean error; AAC, apparent amylose content; Dx50, particle size as 50th percentile; D[3;2], particle size as area-weighted mean; D[4;3], particle size as volume-weighted mean; DS, degree of substitution; RE, reaction efficiency.

3.2. Properties of Modified Starches

3.2.1. FTIR

The effects of US and dual modifications on the chemical structures of starches were investigated by FTIR spectra. To directly compare the intensities of the bands, the original FTIR spectra were pooled, as shown in Figure 3.

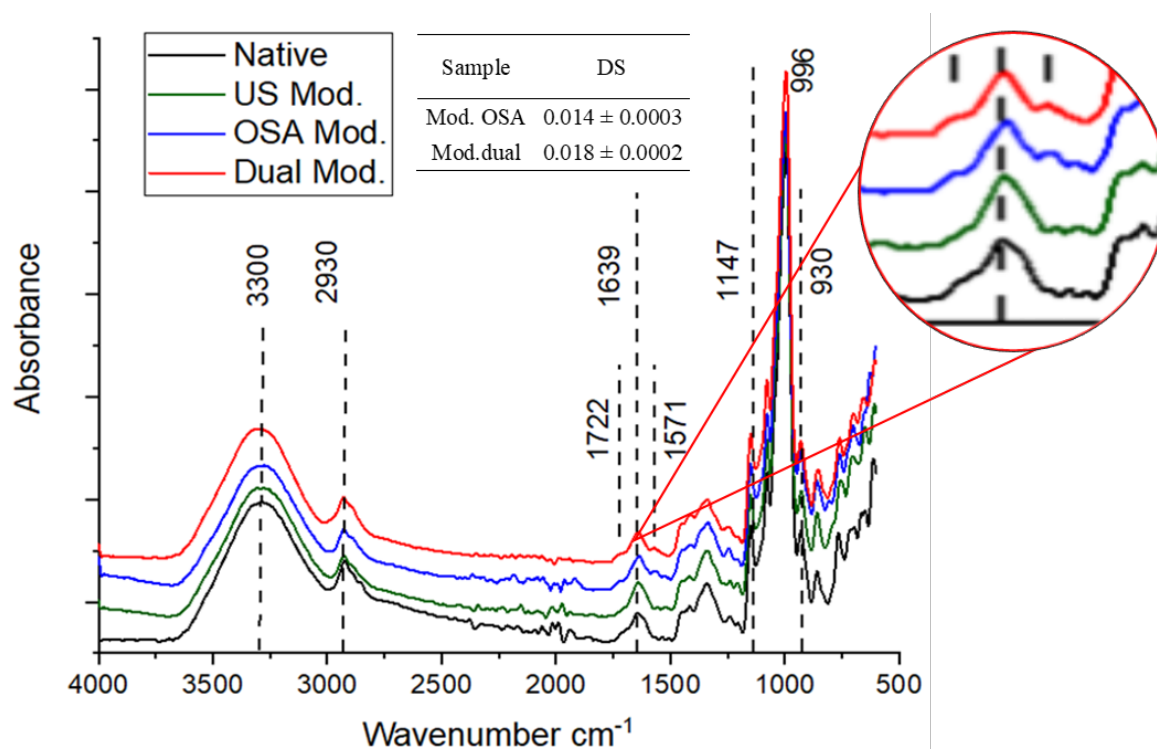


Figure 3. FTIR spectra for native and modified starches. **Key:** Native, native starch; US Mod., single ultrasound (US) modification; OSA Mod., single octenyl succinic anhydride (OSA) modification; Dual Mod., dual modification (modification US followed by OSA).

The peaks at 3300 cm^{-1} and 2930 cm^{-1} in Figure 3 are characteristic of the stretching and angular deformation of hydroxyl groups in the glucose units and strongly bound water, respectively. Such an amplitude is indicative of the formation of intermolecular and intramolecular hydrogen bonds [46]. The 2930 cm^{-1} band corresponds to glucose C–H stretching. The amylose/amylopectin ratio is reflected in the intensity variations.

The 1147 cm^{-1} peaks denote the asymmetric CO–C stretching, typical of glycosidic linkages [22].

Additionally, in Figure 3, the noticeable intensity of the wideband OH signal in the 3300 cm^{-1} range, along with its Gaussian profile, indicates a higher density of strong hydrogen bonding interactions and a reduced degree of freedom of water molecules within the interhelical space, typical of type A starches. Such an assumption is supported by the strong bands at 1147 cm^{-1} , 990 cm^{-1} , and 930 cm^{-1} , due to CO and CC stretching, with some COH contributions [46].

As can be seen in Figure 3, US-modified starch showed similar spectra to those of native starch. Nonetheless, the intensity fluctuations of the absorption peaks suggest changes in the ratio between amylose and amylopectin, as well as in the equilibrium between the crystalline and amorphous regions [47]. Meanwhile, OSA-modified and dual-modified starches displayed two new absorption bands at 1722 cm^{-1} and 1572 cm^{-1} , corresponding to the stretching vibration of the carbonyl (C=O) group of the ester and the carboxylate (RCOO⁻), respectively. This result aligns with the degree of substitution (DS) observed in both OSA-modified and dual-modified starches (Figure 3). Similar findings have been reported for sorghum OSA [36], mango seed OSA [16], and potato OSA starches [48].

As shown in Table 2, the ratio $1047\text{ cm}^{-1}/1022\text{ cm}^{-1}$ for the modified starches decreased significantly ($p \leq 0.05$) after the modification. On the other hand, the ratio $1022\text{ cm}^{-1}/995\text{ cm}^{-1}$ showed the opposite trend ($p \leq 0.05$). A lower value of the ratio of $1047\text{ cm}^{-1}/1022\text{ cm}^{-1}$ indicates lower RC, whereas a higher ratio $1022\text{ cm}^{-1}/995\text{ cm}^{-1}$ refers to a higher proportion of amorphous structure zones ordered in starch granules. These changes indicate that the US affected the short-range molecular order of starch, causing the degradation of helical structures and short-range ordered structures [13,14]. These results agree with those reported for modified sweet potato [49], cassava [50], and rice [13] starches.

Table 2. Structural characteristics given by FTIR.

Sample	IR Ratio $1047\text{ cm}^{-1}/1022\text{ cm}^{-1}$	IR Ratio $1022\text{ cm}^{-1}/995\text{ cm}^{-1}$
Native	0.72 ± 0.01^a	0.88 ± 0.03^a
US modification	0.68 ± 0.01^b	0.95 ± 0.02^b
OSA modification	0.67 ± 0.01^b	0.98 ± 0.02^b
Dual modification	0.64 ± 0.01^c	1.05 ± 0.03^c

Different letters within the same column represent values with statistically significant differences at 5% ($p \leq 0.05$); Native, native starch; US modification, single ultrasound (US) modification; OSA modification, single octenyl succinic anhydride (OSA) modification; Dual modification, modification US followed by OSA.

Finally, the decrease in the ratio $1047\text{ cm}^{-1}/1022\text{ cm}^{-1}$ (see Table 2) of the dual starch, concerning the US-modified starches, could be explained by the incorporation of OSA groups in the starch chains. These OSA groups interfered with the regular packing of the amylopectin chains, thus reducing the crystalline order and causing a higher structural disorder, which was also reflected in the increase in the ratio $1022\text{ cm}^{-1}/995\text{ cm}^{-1}$ [51,52], as can be seen in Table 2, which would indicate a higher proportion of ordered amorphous regions [51,52]. This behavior was also evident in starches modified with OSA compared to native starches. This agrees with what was reported for corn starches with high AAC [53], where the destruction of the ordered crystalline structure may have occurred slightly faster than that of the amorphous structure during OSA modification, possibly because the esterification reaction may also occur internally.

3.2.2. X-Ray Diffraction (XRD)

As can be seen in Figure 4, all starches exhibited a typical A-type polymorph. Two well-defined peaks were identified at approximately 15.1° and 23.0° (2θ), and an unresolved

doublet at 17.1° and 18.0° (2θ). Figure 4 also shows a peak at 19.9° (2θ), indicating the presence of an amylose–lipid complex. The result suggests that US irradiation and OSA modification did not alter the crystalline pattern of the modified starches. However, compared to native starch, a clear reduction in the intensities for the four diffraction peaks in the XRD patterns was observed in the modified starches, which is reflected in the decrease in their RC.

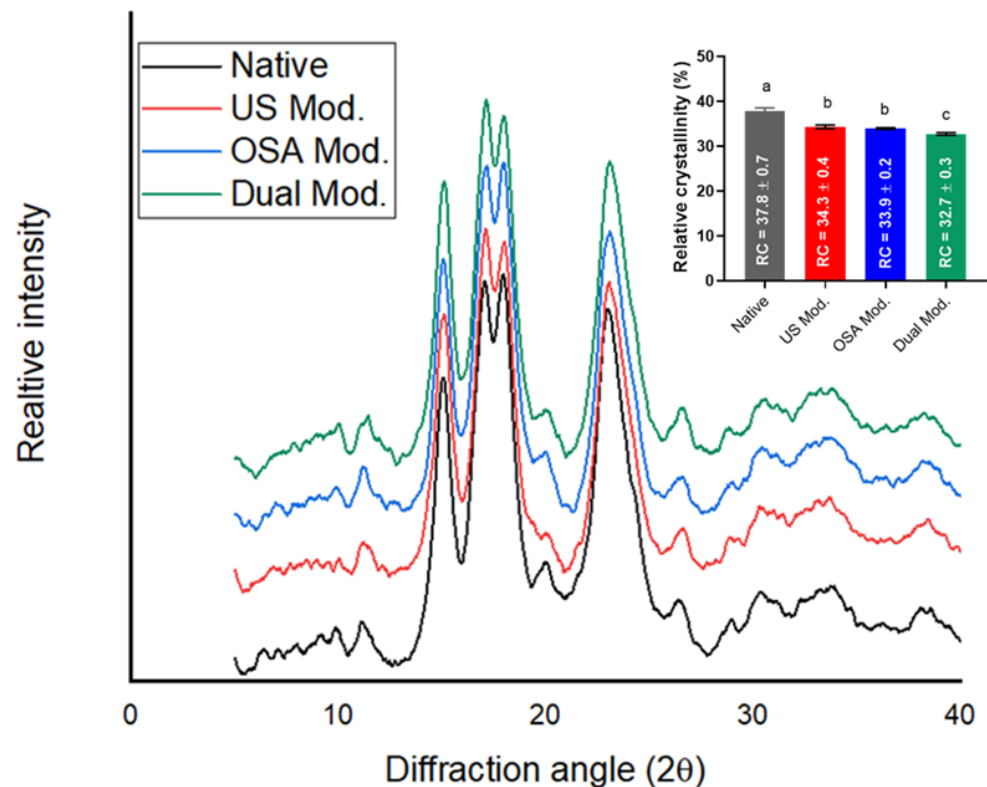


Figure 4. X-ray analysis for native and modified starches (i.e., Mod. US, Mod OSA and Mod. Dual). **Key:** RC, relative crystallinity; Native, native starch; US Mod., single ultrasound (US) modification; OSA Mod., single octenyl succinic anhydride (OSA) modification; Dual Mod., dual modification (modification US followed by OSA). Different letters in columns represent values with statistically significant difference at 5% ($p \leq 0.05$).

The RC values of the modified starches show a significant reduction with respect to native starch: 9.3% for the US-modified starch (see Figure 4). This effect can be attributed to the mechanochemical forces generated during the ultrasound (US) treatment, which weakened the double helical bonds and reduced both intermolecular and intramolecular forces within the starch granules. This caused the disruption of the amorphous regions and the depolymerization of the amylopectin chains, all of which contributed to a reduction in starch crystallinity [9]. This agrees with what was reported for modified starches from sorghum [47], sweet potato [15], taro [54], cassava, and corn [23], where sonication mainly affected the amorphous regions and partially altered the crystalline domains.

In OSA-modified starch, the RC decreased by 10.3%, which was associated with the insertion of OSA groups inside the granule, which would have altered the original structure. The depolymerization of the starch or gelatinization of the surface during modification could also have occurred. Previous studies documented comparable effects in starches of maize [53], adlay seed [52], sorghum [36], rice, cassava, oats [55], waxy maize, and potato worm [18].

Finally, the dual-modified starch showed the greatest decrease in RC, of 13.5%. The reduction of RC in the dually modified starch was probably because pretreatment with

the US altered the starch granule's surface and broke the branched chains of amylopectin. This facilitated the penetration of the OSA groups within the starch's amorphous structure, resulting in damage to the crystalline regions during the process of esterification. During esterification, the reaction in basic medium would have caused additional effects such as depolymerization and gelatinization. As a result, the esterification took place predominantly in the amorphous instead of in the crystalline domains, although it also weakened the strength of the crystalline regions.

The findings from the FTIR and XRD analyses suggest that ultrasonic modification more significantly affected the short-range molecular order (as evaluated by FTIR) compared to the reduction in long-range crystallinity (as measured by XRD). The decrease in the $1047/1022\text{ cm}^{-1}$ absorbance ratio was substantial and was accompanied by an increase in the $1022/995\text{ cm}^{-1}$ ratio, indicating local molecular disorganization. Regarding the RC, as derived from XRD, although a decrease was observed, it was relatively moderate (9–13%) when compared to the more pronounced internal structural rearrangement detected by FTIR. This is consistent with the results of previous studies reporting that ultrasonic treatment in starches preferentially disrupts amorphous regions and affects double helices, rather than completely breaking down the ordered crystalline network [8,15,56]. Similar patterns have been observed in modified starches of sorghum [36], rice, cassava, oats [55], waxy maize, potato and pea [18].

3.2.3. Morphological Characteristics

Polarized light microscopy showed most of the starch granules with well-defined Maltese crosses (see N1, U1, O1 and D1 in Figure 5), indicating that the starches were largely undamaged. However, in the US-modified, OSA-modified and dual-modified starches, some granules with small surface pores could be observed, with no visible changes in the morphology of the starch granules. It is evident that US and dual modification mainly affected the fine structure of the starch chains while keeping the solid structures of the starch granules intact. This agrees with what was reported for pea starches [37] and lychee starches [27].

Most of the native starch granules showed an oval shape (see N2 and N3 in Figure 5), while a smaller fraction showed a spherical shape, with smooth and intact surfaces without cracks. The US-modified starches, on the other hand, had pores, cracks, and depressions on the surface of their granules (see U2 and U3 in Figure 5). Ultrasonic cavitation caused hot spots and strong shear forces, including micro-shear and shock waves. In addition, starch granules were subjected to attack by hydroxyl radicals generated from the decomposition of water molecules through sonochemical effects, which could induce the scission of molecular chains, thus contributing to the degradation of starch granule integrity and rigidity [9]. Similar results were reported for sweet potato [15], cassava [23], and kiwifruit [35] starches.

For OSA starch, trivial collapses and cracks were observed (see O2 and O3 in Figure 5). These defects were linked to hydrolysis induced by the basic medium in which the modification occurred, and to esterification reactions [41]. In addition, a slight aggregation was observed, possibly due to the OSA-esterified amylose chains concentrating on the granule surface. This behavior agrees with observations in corn, potato, rice [57], rice, cassava, and oat starches [55].

The dual modification also yielded a notable difference in starch morphology, showing more uneven, rougher surfaces, with some corrosion and protrusions (see D2 and D3 in Figure 5), probably related to the aggregation of amylose chains esterified with OSA caused by the previous physical modification of the granules with US [53]. Such US modification facilitated OSA penetration and contact with starch hydroxyl groups, increasing starch reactivity, speed, and extent of modification [9]. Another plausible explanation could have

been the surface gelatinization in starch because of adding sodium hydroxide (NaOH) continuously to maintain the alkaline condition, because the addition of OSA reduced the pH [25]. However, it was not entirely clear whether the surface modifications were caused by esterification reactions or the mild hydrolysis resulting from preliminary treatment with NaOH [41]. These results agree with those reported for OSA-treated rice [40] and sorghum [36] starches.

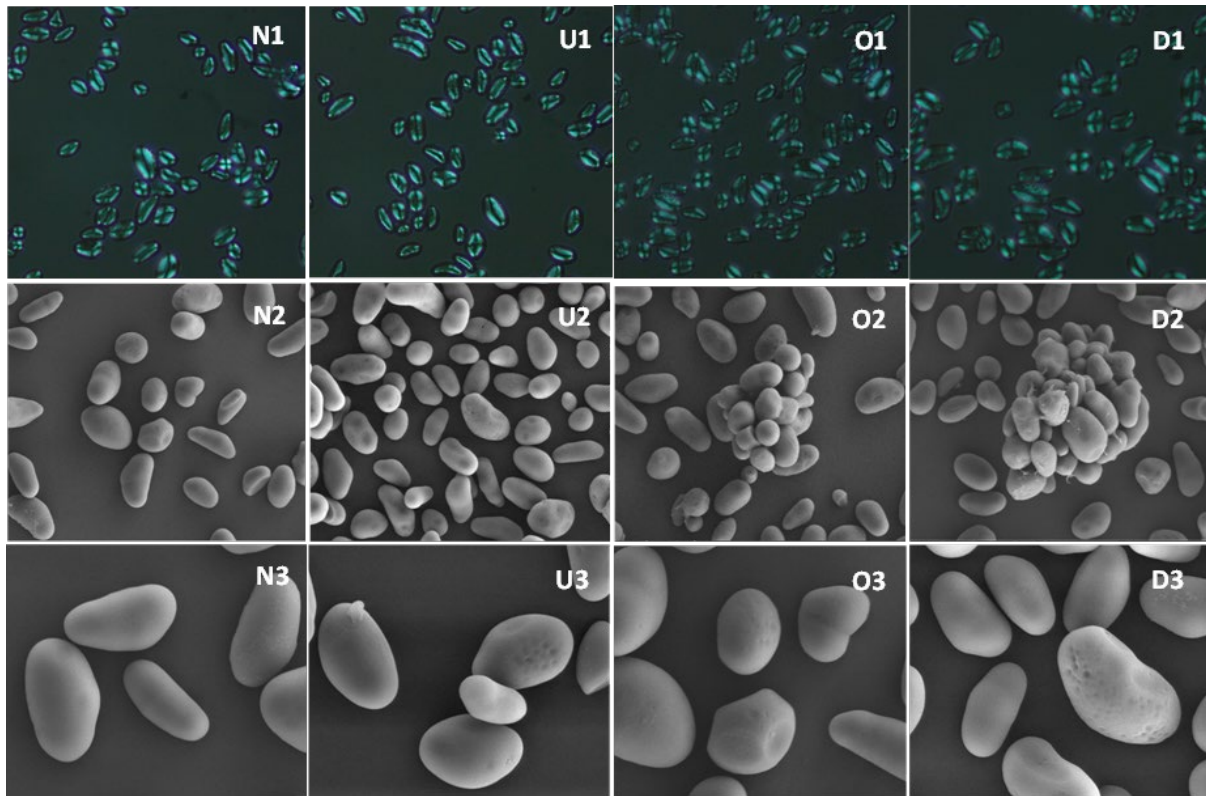


Figure 5. Micrograph at 40 $\times$ with polarized light (N1, U1, O1 and D1) and SEM of starch granules at 2000 $\times$ (N2, U2, O2 and D2) and 5000 $\times$ (N3, U3, O3 and D3) of native (N), US-modified (U), OSA-modified (O) and dual-modified (D) starches.

3.2.4. Thermal Properties

The thermal properties of the starch samples, including onset (T_0), peak (T_p), and conclusion (T_c) gelatinization temperatures, are summarized in Table 3. As seen in Table 3, the gelatinization temperatures of the US-modified, OSA-modified and dual-modified starches decreased compared to native starch ($p \leq 0.05$). This could be attributed to the breakdown of crystalline structures, the crumbling of double helices, and the breaking of hydrogen bonds within the starch granules. The results in Table 3 also reveal a decrease ($p \leq 0.05$) in the gelatinization temperature range after sonication, which indicates that the modified starches had weaker and more disordered crystalline structures. A similar gelatinization temperature behavior has been reported for starch from sorghum [47], sweet potato [15], corn [41], wheat, waxy maize, rice, and bean [57].

The lower ($p \leq 0.05$) gelatinization temperatures of starch modified with OSA observed in Table 3 could be due to the interruption of hydrogen bonds due to the replacement of polar hydrogens with the acyl groups of the succinyl-octenyl radical, showing weak inter- or intramolecular non-polar attractions, causing thermal instability of the starch and facilitating starch swelling at lower temperatures [58]. These findings agree with the observed reductions in crystallinity after dual modification determined by X-ray diffraction (see Section 3.2.2). This suggests that the internal ordering of starch granules was slightly

altered by OSA treatment. However, the effect might be more related to pH adjustment with NaOH in the modification process, agreeing with SEM results (see Section 3.2.3), rather than OSA reactions per se [25].

Table 3. Thermal properties of native and modified starches.

Sample	T_0 (°C)	T_P (°C)	T_C (°C)	ΔH_G (J/g)	Range
Native	71.7 ± 0.3^a	76.5 ± 0.1^a	81.4 ± 0.1^a	14.1 ± 0.4^a	9.7 ± 0.2^a
US modification	69.7 ± 0.2^b	75.8 ± 0.3^b	78.3 ± 0.2^b	11.1 ± 0.3^b	8.6 ± 0.2^b
OSA modification	69.3 ± 0.2^b	76.3 ± 0.2^a	77.7 ± 0.3^c	10.8 ± 0.3^c	7.9 ± 0.4^b
Dual modification	67.6 ± 0.4^c	73.5 ± 0.3^c	75.5 ± 0.4^d	9.7 ± 0.4^c	7.8 ± 0.5^c

Different letters within the same column represent values with statistically significant differences at 5% ($p \leq 0.05$). Native, native starch; US modification, single ultrasound (US) modification; OSA modification, octenyl succinic anhydride (OSA) modification; Dual modification, modification US followed by OSA; T_0 , onset gelatinization temperature; T_P , peak gelatinization temperature; T_C , conclusion gelatinization temperature; ΔH_G , gelatinization enthalpy; Range, $T_C - T_0$.

Beyond structural interpretation, the observed decreases in gelatinization temperatures in all modified starch samples, especially in double-modified starch, have practical significance in terms of processing and energy efficiency. This behavior is advantageous in industrial applications such as extrusion, baking, or spray-drying, where lower gelatinization temperatures can reduce heat input, energy costs, and processing times. In addition, the narrower gelatinization temperature range (i.e., from 9.7 °C in native starch to 7.8 °C in dual-modified starch) suggests a more uniform thermal response of the granules. This homogeneity improves the consistency of thermal behavior, which in turn favors product reproducibility and enables control over its texture and functionality [7,11].

The gelatinization enthalpy (ΔH_G) shown in Table 3 decreased ($p \leq 0.05$) in the modified US (i.e., 11%) and dual (i.e., 20%). These results indicate that some of the outer chains were destroyed, and the double helices were partially degraded after US irradiation. The major decrease in the dual starch was associated with the effect of esterification after ultrasound treatment. The substitution of hydrogen bonds by acyl groups of the succinyl-octenyl radical produced weaker nonpolar interactions, which decreased thermal stability and facilitated starch swelling at lower temperatures [18]. A similar behavior was observed in the OSA-modified starch, although the reduction in ΔH_G was less pronounced (18%).

Finally, the thermal changes observed in the dual treatment (see Table 3) suggest that OSA modification affected both the amylose chains and the organization of the amylopectin double helices, as proposed by Zhang et al. [36] and Lopez-Silva et al. [41].

3.2.5. Solubility and Swelling Power

According to Figure 6, the solubility and swelling power of the samples showed a clear pattern of variation as a function of the different treatments. The solubility of native starch was 10.6%. After ultrasound treatment, it increased to 12.3%. This increase was attributed to the partial disruption of the granular structure due to ultrasonic cavitation, which facilitated the release of amylopectin side chains and the cleavage of amylose chains [14,47]. Similar results were observed in sweet potato [15] and sorghum [47] starches.

Treatment with OSA increased the solubility up to 15.3%. This effect was related to the structural modification and the breaking of bonds in amorphous zones, because of the incorporation of OSA groups. These modifications generated a spatial barrier effect, which increased the interaction between the hydroxyl groups on the starch molecules and the surrounding water molecules [36]. As a result, the increased water permeability promoted the leaching of amylose from starch granules and resulted in increased solubility. This behavior was also reported in sorghum [36], maize [41], and corn [53] starches. The US +

OSA combination displayed the highest solubility value (i.e., 18.5%), showing a synergistic effect between the physical and chemical modifications of starch.

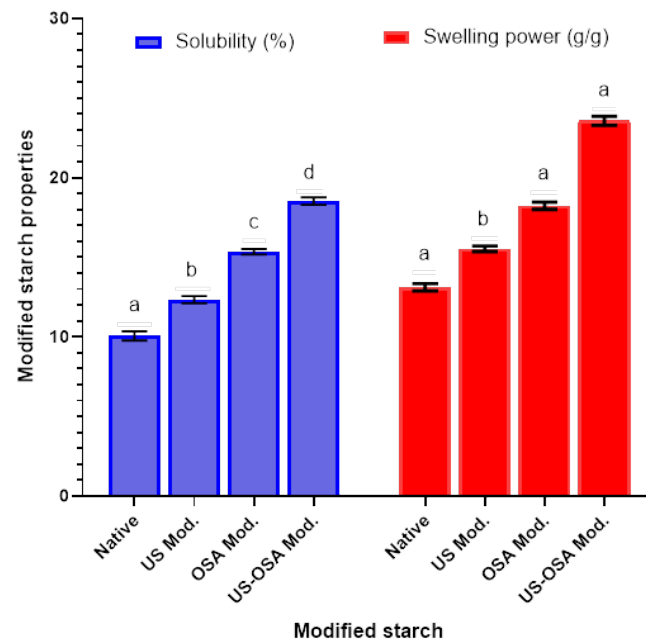


Figure 6. Solubility and swelling power, of native and modified starches. **Key:** Native, native starch; US Mod., single-ultrasound (US) modification; OSA Mod., single octenyl succinic anhydride (OSA) modification; Dual Mod., dual modification (modification US followed by OSA). Different letters in columns represent values with statistically significant difference at 5% ($p \leq 0.05$).

Swelling power followed the trend dual (i.e., 23.6%) > OSA (i.e., 18.2%) > US (i.e., 15.5%) > native (i.e., 13.1%). US treatment eased water penetration through microcracks. OSA, by increasing the affinity of starch for water, promoted the expansion of amylopectin chains and altered the amorphous regions by the spatial barrier effect, favoring water absorption and granule swelling [59]. Meanwhile, dual starch showed the highest solubility and water-holding capacity, making it suitable as an encapsulating, stabilizing, emulsifying, and thickening agent in foods, and for use in edible coatings and biodegradable films [11,58,60].

4. Conclusions

This study assessed the use of mango seed cotyledons and ultrasound (US) to obtain high-value-added starches. The ultrasonic treatment generated mechanochemical effects that significantly modified the physicochemical, morphological, and thermal properties of the starch. The optimal modification conditions allowed for reaching a high degree of substitution and reaction yield, validating the efficacy of the dual modification (i.e., (US followed by octenyl succinic anhydride, OSA). This modification conferred amphiphilic properties to the starch, which broadened its functionality.

It was found that OSA groups were incorporated mainly in amorphous and surface areas, reducing crystallinity, gelatinization temperature, and enthalpy. Increased amylose content, reduced particle size, and changes in surface morphology caused by US treatment reflected functional improvements.

The results demonstrate a synergistic effect between the modifications caused by the mechanochemical effects of US and OSA modifications, providing evidence of effective functionalization and process efficiency. The dual treatment significantly improved the techno-functional properties of the mango cotyledon starch, positioning it as a promising ingredient for the food industry in applications such as microencapsulants, emulsifiers,

stabilizers, thickeners, edible coatings, and biodegradable films. Meanwhile, it can be used in the cosmetic industry as a gelling and absorbent agent and in the pharmaceutical industry for the controlled release of drugs. In addition, the value of this technology for transforming agro-industrial waste into functional ingredients, promoting sustainability in the context of a circular economy, and making crops productive, while reducing the environmental burden, was highlighted.

For future research, complementary analyses such as those addressing water and oil absorption capacity, the rheological and textural properties of the modified starch gels, and their in vitro digestibility, could be employed to study in detail the impacts of the modifications on the gels' techno-functional properties and resistance to amylolytic reactions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agriengineering7060190/s1>, Table S1. ANOVA of the starch modification process optimization.

Author Contributions: Conceptualization, R.T.-G., R.A.-P., D.F.T., A.C.-S. and F.J.C.-G.; data curation, R.T.-G.; formal analysis, R.T.-G. and D.F.T.; funding acquisition, R.T.-G.; investigation, R.T.-G.; methodology, R.T.-G.; project administration, F.J.C.-G.; resources, R.A.-P., D.F.T. and F.J.C.-G.; supervision, A.C.-S. and F.J.C.-G.; validation, R.T.-G., D.F.T. and A.C.-S.; visualization, R.T.-G., D.F.T. and F.J.C.-G.; writing—original draft, R.T.-G.; writing—review and editing, R.T.-G., R.A.-P., D.F.T., A.C.-S. and F.J.C.-G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Science, Technology, and Innovation Fund (FCTI) of the Sistema General de Regalías (SGR), assigned for doctoral training of the first author, through the call of the Biennial Call Plan 2019 Court 2. BPIN framework project 2019000100035 “Formation of high-level human capital” University of Caldas—Colombia.

Institutional Review Board Statement: Ethics approval was not required for this research.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Acknowledgments: The authors express their gratitude to Universidad de Caldas, Universidad del Atlántico, Universidad de Córdoba, Universidad de Sucre, and Universidad Nacional de Colombia (Hermes 57862).

Conflicts of Interest: The authors have no competing interests to declare that are relevant to the content of this article.

References

1. FAO. FAOSTAT. 2025. Available online: <https://www.fao.org/faostat/es/#data/QCL/visualize> (accessed on 14 April 2025).
2. Musser, S.R.; Suhartini, S.; Melville, L. Methane from mango industrial waste: Influence of pH and co-anaerobic digestion. *Bioresour. Technol. Rep.* **2025**, *29*, 102056. [[CrossRef](#)]
3. García, M.N.; Enríquez, A.J.B.; Escobar, J.L.G.; Cruz, O.d.J.C.; Pérez, V.P.; Becerril, M.S. Phenolic Compounds in Agro-Industrial Waste of Mango Fruit: Impact on Health and Its Prebiotic Effect—A Review. *Pol. J. Food Nutr. Sci.* **2023**, *73*, 5–23. [[CrossRef](#)]
4. Bharti, I.; Singh, S.; Saxena, D.C. Exploring the influence of heat moisture treatment on physicochemical, pasting, structural and morphological properties of mango kernel starches from Indian cultivars. *LWT* **2019**, *110*, 197–206. [[CrossRef](#)]
5. Mutua, J.K.; Imathiu, S.; Owino, W.O. Evaluation of the proximate composition, antioxidant potential, and antimicrobial activity of mango seed kernel extracts. *Food Sci. Nutr.* **2016**, *5*, 349–357. [[CrossRef](#)]
6. Chen, H.; Su, Y.; Li, H.; Wang, Z.; Kan, J. Effects of synchronous intermissive multi-ultrasound and esterification dual modification on functionalities of starch and its emulsion stabilization ability. *Food Chem.* **2024**, *450*, 139412. [[CrossRef](#)]
7. Zheng, Y.; Fang, H.; Zhang, H.; Ye, X.; Tian, J. Effect of ultrasonic pre-treatments on the octenyl succinic anhydride substitution of potato starch and its physicochemical and emulsifying properties. *Int. J. Food Sci. Technol.* **2022**, *57*, 7286–7295. [[CrossRef](#)]
8. Vela, A.J.; Villanueva, M.; Ronda, F. Ultrasonication: An Efficient Alternative for the Physical Modification of Starches. *Flours Grains Foods* **2024**, *13*, 2325. [[CrossRef](#)]
9. Chakraborty, G.; Kumar, Y.; Sharanagat, V.S. Effect of ultrasonication on OSA esterified surface modification of sorghum (*Sorghum bicolor* (L.) Moench) starch. *Int. J. Biol. Macromol.* **2025**, *288*, 138634. [[CrossRef](#)]

10. Singh, R.; Sharanagat, V.S. Physico-functional and structural characterization of ultrasonic-assisted chemically modified elephant foot yam starch. *Int. J. Biol. Macromol.* **2020**, *164*, 1061–1069. [[CrossRef](#)]
11. Núñez-Bretón, L.C.; Torres-González, C.E.; Del Ángel-Zumaya, J.A.; Peredo-Lovillo, A.; Rivera-Villanueva, J.M.; Perea-Flores, M.d.J.; Guzmán-Gerónimo, R.I.; Manero, O.; González-Jiménez, F.E. Functionalization of starches from Mexican *Oxalis tuberosa* using dual chemical modification. *Food Hydrocoll.* **2024**, *149*, 109500. [[CrossRef](#)]
12. Torres-Gallo, R.; Bayuelo-Bonilla, S.; Carpio-Ortiz, L.; Barreto-Rodríguez, G.; Tirado, D.F. High-intensity ultrasound-assisted extraction of pectin from mango wastes at different maturity. *Int. J. Food Sci.* **2022**, *2022*, 4606024. [[CrossRef](#)] [[PubMed](#)]
13. Yang, W.; Kong, X.; Zheng, Y.; Sun, W.; Chen, S.; Liu, D.; Zhang, H.; Fang, H.; Tian, J.; Ye, X. Controlled ultrasound treatments modify the morphology and physical properties of rice starch rather than the fine structure. *Ultrason. Sonochem.* **2019**, *59*, 104709. [[CrossRef](#)] [[PubMed](#)]
14. Vela, A.J.; Villanueva, M.; Solaesa, Á.G.; Ronda, F. Impact of high-intensity ultrasound waves on structural, functional, thermal and rheological properties of rice flour and its biopolymers structural features. *Food Hydrocoll.* **2021**, *113*, 106480. [[CrossRef](#)]
15. Wang, H.; Xu, K.; Ma, Y.; Liang, Y.; Zhang, H.; Chen, L. Impact of ultrasonication on the aggregation structure and physicochemical characteristics of sweet potato starch. *Ultrason. Sonochem.* **2020**, *63*, 104868. [[CrossRef](#)]
16. Ferraz, C.A.; Fontes, R.L.S.; Fontes-Sant'Ana, G.C.; Calado, V.V.; López, E.O.; Rocha-Leão, M.H.M. Extraction, Modification, and Chemical, Thermal and Morphological Characterization of Starch from the Agro-Industrial Residue of Mango (*Mangifera indica* L.) var. Ubá. *Starch-Stärke* **2019**, *71*, 1800023. [[CrossRef](#)]
17. Gautam, G.; Talukdar, D.; Mahanta, C.L. Sonochemical effect on the degree of substitution of octenyl-succinic anhydride into waxy rice starch nanoparticles and study of gastro-intestinal hydrolysis using INFOGEST *in vitro* digestion method. *Food Res. Int.* **2023**, *165*, 112348. [[CrossRef](#)]
18. Wang, Q.; Tang, Z.; Li, Z.; Luan, Y.; Gu, C.; Liu, R.; Ge, Q.; Yu, H.; Wu, M. Effects of octenyl succinylation on the properties of starches with distinct crystalline types and their Pickering emulsions. *Int. J. Biol. Macromol.* **2023**, *230*, 123183. [[CrossRef](#)]
19. Silva, E.K.; Anthero, A.G.d.S.; Emerick, L.B.; Zabot, G.L.; Hubinger, M.D.; Meireles, M.A.A. Low-frequency ultrasound-assisted esterification of Bixa orellana L. seed starch with octenyl succinic anhydride. *Int. J. Biol. Macromol.* **2022**, *207*, 1–8. [[CrossRef](#)]
20. Vijayakumar, P.; Mounika, A.; Shanmugam, A.; Farzana, W. A comparative study on effect of succinylation on kodo millet and chickpea starch with ultrasound treatment. *Food. Biosci.* **2024**, *62*, 105104. [[CrossRef](#)]
21. Torres, R.; Montes, E.J.; Pérez, O.A.; Andrade, R.D. Relación del Color y del Estado de Madurez con las Propiedades Fisicoquímicas de Frutas Tropicales. *Inf. Tecnológica* **2013**, *24*, 51–56. [[CrossRef](#)]
22. Torres-Gallo, R.; Andrade-Pizarro, R.; Salcedo, J.; Chávez-Salazar, A.; Castellanos-Galeano, F.J. Optimization of ultrasound-assisted extraction of mango cotyledon starch: Physicochemical, structural, thermal and functional properties. *Int. J. Biol. Macromol.* **2025**, *285*, 138239. [[CrossRef](#)] [[PubMed](#)]
23. Rahaman, A.; Kumari, A.; Zeng, X.-A.; Farooq, M.A.; Siddique, R.; Khalifa, I.; Siddeeg, A.; Ali, M.; Manzoor, M.F. Ultrasound based modification and structural-functional analysis of corn and cassava starch. *Ultrason. Sonochem.* **2021**, *80*, 105795. [[CrossRef](#)] [[PubMed](#)]
24. Li, W.; Gamlath, C.J.; Pathak, R.; Martin, G.J.; Ashokkumar, M. Ultrasound—The Physical and Chemical Effects Integral to Food Processing. In *Innovative Food Processing Technologies: A Comprehensive Review*; Elsevier: Amsterdam, The Netherlands, 2021; pp. 329–358. [[CrossRef](#)]
25. Abiddin, N.Z.; Yusoff, A.; Ahmad, N. Effect of octenylsuccinylation on physicochemical, thermal, morphological and stability of octenyl succinic anhydride (OSA) modified sago starch. *Food Hydrocoll.* **2018**, *75*, 138–146. [[CrossRef](#)]
26. Shi, S.-S.; He, G.-Q. Process optimization for cassava starch modified by octenyl succinic anhydride. *Procedia Eng.* **2012**, *37*, 255–259. [[CrossRef](#)]
27. Morales-Trejo, F.; Trujillo-Ramírez, D.; Aguirre-Mandujano, E.; Lobato-Calleros, C.; Vernon-Carter, E.J.; Alvarez-Ramirez, J. Ultrasound-assisted extraction of lychee (*Litchi chinensis* Sonn.) seed starch: Physicochemical and functional properties. *Starch-Stärke* **2022**, *74*, 2100092. [[CrossRef](#)]
28. Zeng, F.; Zhu, S.; Chen, F.; Gao, Q.; Yu, S. Effect of different drying methods on the structure and digestibility of short chain amylose crystals. *Food Hydrocoll.* **2016**, *52*, 721–731. [[CrossRef](#)]
29. Dome, K.; Podgorbunskikh, E.; Bychkov, A.; Lomovsky, O. Changes in the crystallinity degree of starch having different types of crystal structure after mechanical pretreatment. *Polymers* **2020**, *12*, 641. [[CrossRef](#)]
30. Yang, L.; Zhou, Y.; Zheng, X.; Wang, H.; Wang, N. Determination of optimum experimental conditions for preparation and functional properties of hydroxypropylated, phosphorylated and hydroxypropyl-phosphorylated glutinous rice starch. *Int. J. Biol. Macromol.* **2017**, *105*, 317–327. [[CrossRef](#)]
31. Zhang, Y.; Dai, Y.; Hou, H.; Li, X.; Dong, H.; Wang, W.; Zhang, H. Ultrasound-assisted preparation of octenyl succinic anhydride modified starch and its influence mechanism on the quality. *Food Chem. X* **2020**, *5*, 100077. [[CrossRef](#)]
32. Pesek, S.; Silaghi-Dumitrescu, R. The Iodine/Iodide/Starch Supramolecular Complex. *Molecules* **2024**, *29*, 641. [[CrossRef](#)]

33. Vela, A.J.; Villanueva, M.; Li, C.; Hamaker, B.; Ronda, F. Ultrasound treatments of tef [*Eragrostis tef* (Zucc.) Trotter] flour rupture starch α -(1,4) bonds and fragment amylose with modification of gelatinization properties. *LWT* **2023**, *174*, 114463. [\[CrossRef\]](#)
34. Amarnath, M.; Muhammed, A.; Antony, A.K.; Malini, B.; Sunil, C. White finger millet starch: Physical modification (annealing and ultrasound), and its impact on physicochemical, functional, thermal and structural properties. *Food Humanit.* **2023**, *1*, 599–606. [\[CrossRef\]](#)
35. Wang, J.; Lv, X.; Lan, T.; Lei, Y.; Suo, J.; Zhao, Q.; Lei, J.; Sun, X.; Ma, T. Modification in structural, physicochemical, functional, and *in vitro* digestive properties of kiwi starch by high-power ultrasound treatment. *Ultrason. Sonochem.* **2022**, *86*, 106004. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Zhang, J.; Ran, C.; Jiang, X.; Dou, J. Impact of octenyl succinic anhydride (OSA) esterification on microstructure and physicochemical properties of sorghum starch. *LWT* **2021**, *152*, 112320. [\[CrossRef\]](#)
37. Li, G.; Ge, X.; Guo, C.; Liu, B. Effect of ultrasonic treatment on structure and physicochemical properties of pea starch. *Foods* **2023**, *12*, 2620. [\[CrossRef\]](#)
38. Amini, A.M.; Razavi, S.M.A.; Mortazavi, S.A. Morphological, physicochemical, and viscoelastic properties of sonicated corn starch. *Carbohydr. Polym.* **2015**, *122*, 282–292. [\[CrossRef\]](#)
39. Falsafi, S.R.; Maghsoudlou, Y.; Rostamabadi, H.; Rostamabadi, M.M.; Hamed, H.; Hosseini, S.M.H. Preparation of physically modified oat starch with different sonication treatments. *Food Hydrocoll.* **2019**, *89*, 311–320. [\[CrossRef\]](#)
40. Wang, W.; Liu, C.; Zhang, H.; Zhu, X.; Wang, L.; Zhang, N.; Yu, D. Properties of OSA-modified starch and emulsion prepared with different materials: Glutinous rice starch, japonica rice starch, and indica rice starch. *Food Res. Int.* **2022**, *161*, 111845. [\[CrossRef\]](#)
41. Lopez-Silva, M.; Bello-Perez, L.A.; Agama-Acevedo, E.; Alvarez-Ramirez, J. Effect of amylose content in morphological, functional and emulsification properties of OSA modified corn starch. *Food Hydrocoll.* **2019**, *97*, 105212. [\[CrossRef\]](#)
42. Han, S.Y.; Zhu, X.; Zhang, B. Optimization of reaction conditions of octenyl succinic anhydride potato starch and its morphology, crystalline structure and thermal characterization. *Adv. Mat. Res.* **2011**, *236–238*, 2279–2289. [\[CrossRef\]](#)
43. Song, X.; He, G.; Ruan, H.; Chen, Q. Preparation and properties of octenyl succinic anhydride modified early *Indica* rice starch. *Starch-Stärke* **2006**, *58*, 109–117. [\[CrossRef\]](#)
44. Segura-Campos, M.; Chel-Guerrero, L.; Betancur-Ancona, D. Synthesis and partial characterization of octenylsuccinic starch from *Phaseolus lunatus*. *Food Hydrocoll.* **2008**, *22*, 1467–1474. [\[CrossRef\]](#)
45. Abiddin, Z.; Yusoff, A.; Ahmad, N. Optimisation of reaction conditions of octenyl succinic anhydride (OSA) modified sago starch using response surface methodology (RSM). *Int. Food Res. J.* **2015**, *22*, 930–935.
46. Pozo, C.; Rodríguez-Llamazares, S.; Bouza, R.; Barral, L.; Castaño, J.; Müller, N.; Restrepo, I. Study of the structural order of native starch granules using combined FTIR and XRD analysis. *J. Polym. Res.* **2018**, *25*, 266. [\[CrossRef\]](#)
47. Jafari, M.; Koocheki, A. Impact of ultrasound treatment on the physicochemical and rheological properties of acid hydrolyzed sorghum starch. *Int. J. Biol. Macromol.* **2024**, *256*, 128521. [\[CrossRef\]](#)
48. Wang, J.; Su, L.; Wang, S. Physicochemical properties of octenyl succinic anhydride-modified potato starch with different degrees of substitution. *J. Sci. Food Agric.* **2010**, *90*, 424–429. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Hu, A.; Li, Y.; Zheng, J. Dual-frequency ultrasonic effect on the structure and properties of starch with different size. *LWT* **2019**, *106*, 254–262. [\[CrossRef\]](#)
50. Monroy, Y.; Rivero, S.; García, M.A. Microstructural and techno-functional properties of cassava starch modified by ultrasound. *Ultrason. Sonochem.* **2018**, *42*, 795–804. [\[CrossRef\]](#)
51. Velásquez-Barreto, F.F.; Bello-Pérez, L.A.; Yee-Madeira, H.; Sánchez, C.E.V. Esterification and characterization of starch from Andean tubers. *Starch-Stärke* **2019**, *71*, 1800101. [\[CrossRef\]](#)
52. Xu, L.; Bai, Z.; Feng, J.; He, L.; Ren, J.; Chai, S.; Chen, X. Effects of the degree of substitution of octenyl succinic anhydride on the physicochemical characteristics of adlay starch. *Int. J. Biol. Macromol.* **2023**, *241*, 124535. [\[CrossRef\]](#)
53. Li, J.; Wang, Q.; Blennow, A.; Herburger, K.; Zhu, C.; Nurzikhan, S.; Wei, J.; Zhong, Y.; Guo, D. The location of octenyl succinate anhydride groups in high-amylose maize starch granules and its effect on stability of pickering emulsion stability. *LWT* **2022**, *169*, 113892. [\[CrossRef\]](#)
54. Martins, A.; Beninca, C.; Bet, C.D.; Bisinella, R.Z.B.; de Oliveira, C.S.; Hornung, P.S.; Schnitzler, E. Ultrasonic modification of purple taro starch (*Colocasia esculenta* B. Tini): Structural, psychochemical and thermal properties. *J. Therm. Anal. Calorim.* **2020**, *142*, 819–828. [\[CrossRef\]](#)
55. Zhou, F.; Dong, M.; Huang, J.; Lin, G.; Liang, J.; Deng, S.; Gu, C.; Yang, Q. Preparation and physico-chemical characterization of OSA-modified starches from different botanical origins and study on the properties of Pickering emulsions stabilized by these starches. *Polymers* **2023**, *15*, 706. [\[CrossRef\]](#) [\[PubMed\]](#)
56. Kaur, H.; Gill, B.S. Effect of high-intensity ultrasound treatment on nutritional, rheological and structural properties of starches obtained from different cereals. *Int. J. Biol. Macromol.* **2019**, *126*, 367–375. [\[CrossRef\]](#)
57. Bajaj, R.; Singh, N.; Kaur, A. Properties of octenyl succinic anhydride (OSA) modified starches and their application in low fat mayonnaise. *Int. J. Biol. Macromol.* **2019**, *131*, 147–157. [\[CrossRef\]](#)

58. Quintero-Castaño, V.D.; Castellanos-Galeano, F.J.; Álvarez-Barreto, C.I.; Lucas-Aguirre, J.C.; Bello-Pérez, L.A.; Rodríguez-García, M.E. Starch from two unripe plantains and esterified with octenyl succinic anhydride (OSA): Partial characterization. *Food Chem.* **2020**, *315*, 126241. [[CrossRef](#)]
59. Wu, X.; Zhang, J.; Wu, X.; Yan, X.; Zhang, Q.; Zhang, B. Octenyl succinic anhydride tigernut starch: Structure, physicochemical properties and stability of curcumin-loaded Pickering emulsion. *Int. J. Biol. Macromol.* **2024**, *275*, 133475. [[CrossRef](#)]
60. Prakruthi, L.Y.; Krishnan, H.; Medha, T.; Kumarakuru, K.; Kumari, P.V.; Surekha, C.; Alavilli, H.; Kaushik, D.; Hashem, A.; Alotaibi, N.H.; et al. Enhancing starch properties through dual modification: Ultrasonication and acetic acid treatment of non-conventional starches. *Ultrason. Sonochem.* **2025**, *115*, 107301. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.