Structural and physicochemical characterization of modified starch from arrowhead tuber (*Sagittaria sagittifolia* L.) using tri-frequency power ultrasound

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**A B S T R A C T**

*Sagittaria sagittifolia* L. is a well-known plant, belongs to the Alismataceae family. Sonication can improve the functional properties of starch; hence, the aim of this study was to develop ultrasonically modified arrowhead starch (UMAS) using a sophisticated and eco-friendly tri-frequency power ultrasound (20/40/60 kHz) method at 300, 600, and 900 W for 15 and 30 min. Significant (*p* < 0.05) increases in swelling power, solubility, and water and oil holding capacities were achieved. FTIR spectroscopy corroborated the ordered, amorphous, and hydrated crystals of the sonicated samples. Increases in sonication frequency and power led to significant (*p* < 0.05) increases in onset gelatinization temperatures. Scanning electron microscopic analysis of sonicated samples showed superficial cracks and roughness on starch granules appeared in a sonication power-dependent manner compared with that of untreated sample. Overall, the ultrasonically-treated samples showed improved physicochemical properties, which could be useful for industrial applications.

**1. Introduction**

Arrowhead (*Sagittaria sagittifolia* L.) is a well-known plant and a member of the Alismataceae family. It is also known by other names, such as swan potato, duck potato, Indian potato, *Jiandaocao*, *Yanweicao*, and *Wapato*. As a perennial aquatic herb, the arrowhead comprises arrow-shaped leaves growing in alternating fashion from a rhizome and is a rich source of macro and micronutrients [1]. This crop has been used as a restorative plant in traditional Chinese medicine since the Tang dynasty. The raw tubers of this plant require adequate processing to remove unpleasant and bitter tastes before consumption. The indigenous people of the Americas have also traditionally consumed arrowhead tubers. People in China, India, Bangladesh, Indonesia, Nepal, Malaysia, Sri Lanka, Thailand, Cambodia, and Vietnam consume arrowhead tubers in both raw and cooked forms [3]. Its taste resembles that of potatoes or chestnuts, and it can be cooked by roasting, frying, or boiling. Regarding its nutritional profile, arrowhead tuber comprises starch (54.6%), protein (16.4%), fat (0.47%), and ash (4.76%) [4]. Polysaccharides sourced from arrowhead tubers are increasingly receiving attention as biologically active ingredients [1,5].

Starch is one of the main active components of arrowhead tubers. Arrowhead tubers have been reported to have excellent health-promoting effects, such as antioxidant, hepatoprotective, and antineoplastic effects [1]. Arrowhead starch has also been employed recently as an encapsulating agent during spray drying. The arrowhead starch has been reported to exhibit great functionality for being applied as a hydrocolloid, gelling and thickening agent [6]. It has been revealed by modern research that arrowhead tuber comprises of rich amounts of non-starch polysaccharides which exhibit significant hypolipidemic, hypoglycemic, and antioxidant properties [7]. This is indicative of the fact that arrowhead tubers have promising potential for the relief and prevention of cardiovascular disease. Furthermore, arrowhead starch exhibits several unique functional properties, including a specific paste behavior, a small granule size, clustered granular structures, and a rich lipid profile. Starch sourced from this plant could be used as a functional film-forming component, filling ingredient during pill formation, and fat
substitute. However, the inherent limitations of native arrowhead starch, such as a high paste viscosity with low clarity and low resistance to shear stress, have limited its widespread application in the formulation of food products [8]. As a result, researchers have focused their attention on the physical modification of this starch owing to a growing customer understanding and concern regarding the side effects of chemical processing [9]. As far as the nutritional composition is concerned, arrowhead tubers are reported to comprise of starch (54.60%), protein (16.4%), ash (4.76%), and fat (0.47%). Overall, the amylose content in arrowhead tuber composition is found to be 30.73% [10]. In another report by Ahmed et al. [11], it was evident that three cultivars of arrowhead tubers exhibited amylose content in ranges of 26.6–31.3% and 28.2–29.9% determined by means of gel permeation chromatography (GMC) and amperometric iodosimetry, respectively. Moreover, it was evident from the published literature that carbohydrates dominate the nutritional profile of arrowhead tubers followed by total dietary fiber (TDF). Whereas, as far as the fiber content is concerned, insoluble dietary fiber fraction accounts for the large proportion of TDF in arrowhead starch [7]. Arrowhead starch comprises of almost 5 vitamins in its composition with the total vitamin content of 79.7 mg/kg, while individual vitamin content as follows: vitamin B1 (1.4 mg/kg), vitamin B2 (0.7 mg/kg), vitamin B3 (16 mg/kg), vitamin C (40 mg/kg) and vitamin E (21.6 mg/kg). Moreover, other nutritional composition parameters were found to be as; energy (940 kcal/kg), proteins, (46 g/kg), lipids (2 g/kg), carbohydrates (199 g/kg), TDF (162 g/kg), soluble dietary fiber (13.6 g/kg), insoluble dietary fiber (148 g/kg). In case of minerals, the arrowhead composition comprises of following 10 minerals, such as calcium (140 mg/kg), phosphorus (1.57 g/kg), potassium (7.07 g/kg), sodium (391 mg/kg), magnesium (240 mg/kg), iron (22 mg/kg), zinc (9.90 mg/kg), selenium (9.20 mg/kg), copper (2.20 mg/kg) and manganese (3.90 mg/kg). Overall, the arrowhead tuber contains a total of 18 amino acids, of which 8 amino acids are categorized as essential accounting for a total of 47.03%. The top three major amino acids in arrowhead composition are methionine (514 mg/kg), glycine (413 mg/kg), and aspartate (329 mg/kg) [7,10].

Power ultrasound has emerged as an eco-friendly tool for the physical modification of starches, with advantages over food processing, including reduced processing time and energy consumption, enhanced reaction rates, and high throughput [12]. Sonication leads to a series of changes in starches, including a decreased viscosity, increased transparency, and solubility, and the breakage of granular starch structures depending on the botanical origin, physical state, the slurry concentration of starches, and sonication parameters (time, temperature, frequency, and power) [13]. Presently, several studies on arrowhead flour have been conducted using γ-irradiation and roasting; some have reported changes in physicochemical properties using hydrolysis-microwave, subcritical water, ultrasound-subcritical water, autoclaving, and ultrasound-autoclaving [8,10,14]. In fact, it has already been reported that sonication may cause alterations in pore size and distribution, leading to the formation of new pores. Moreover, enhanced solubility, gel transparency, swelling power, and declining tendencies in pseudo-plasticity and gelatination enthalpy have been reported [8,12,15]. Additionally, cavitation bubbles’ collapse may cause the generation of high-intensity shear forces, shock waves, microjets, and sonication-induced turbulence leading to accelerated physicochemical alterations in starches [9,16]. However, reports on the preparation of physically modified starch using tri-frequency power ultrasound are currently lacking. In this study, the investigators were investigated to elucidate the effects of various ultrasonication times (15 and 30 min) and ultrasound powers (300, 600, and 900 W) in tri-frequency ultrasonic mode (20/40/60 kHz). There are already published reports available on the investigation of effects of mono-frequency ultrasound (e.g. 20 kHz, 40 kHz, and 60 kHz) and dual-frequency ultrasound (e.g. 20/40 kHz, 20/60 kHz, and 40/60 kHz) and tri-frequency (20/40/60 kHz), where the author discovered the use of tri-frequency (20/40/60 kHz) was more suitable for improving the physicochemical properties of starch-linoleic acid complex [17]. However, to the best of our knowledge, the reports on physical modification of arrowhead starch at variable ultrasonication times (15 and 30 min) and ultrasound powers (300, 600, and 900 W) in tri-frequency ultrasonic mode (20/40/60 kHz) are not available until now. Considering the ability of sonication to improve the functional properties of starch and the ability of power ultrasound to prepare physically modified starches, this study was aimed to develop ultrasonically modified arrowhead starch (UMAS) through a sophisticated and eco-friendly tri-frequency power ultrasound (TFPU, 20/40/60 kHz) method at 300, 600, and 900 W for 15 and 30 min. Thereafter, the structural, morphological, thermal, rheological, and physicochemical properties of native arrowhead starch (AS) and UMAS were investigated.

2. Materials and methods

2.1. Materials

Arrowhead tubers were purchased from a local market, JiangDa Farmer’s market, close to Jiangsu University in Zhenjiang, China. Arrowhead starch was extracted as described by [8]. The amylose content of the arrowhead starch was 30.77% as analyzed previously by Raza et al. [17].

2.2. Ultrasound modification of arrowhead starch

Arrowhead starch was dispersed in distilled water to obtain a 10% (w/v) suspension and transferred into high-pressure resistant polythene bags. The sealed bags were then sonicated at a tri-frequency 20/40/60 kHz using an ultrasound bath, as shown in Fig. 1 (model no. 20084798; Jiangsu University) at a power density of 300 W/L. The water temperature was controlled by a HH-6A digital-thermostatic bath (Zhongzheng Equip. Manufac. Co. Ltd., China) at 24 ± 1°C and the peristaltic pump to control the flow rate of water at 300 rpm as used by our research group in previous studies [18,19]. Furthermore, the discontinuous ultrasound was used with intervals of 10 s on and 4 s off to avoid the rise in the temperature and giving the machine enough rest for smooth running. The starch samples were named according to the sonication times (15 and 30 min) and ultrasound powers (300, 600, and 900 W), as shown in Table 1. The multi-frequency sonication equipment was designed by our research group at Jiangsu University [20]. This novel multi-frequency sonication equipment may work under three different frequency modes, such as mono-, dual- or tri-frequency modes. This particular structure produces resonance under the combination of various frequency modes, so it is easier to produce an ultrasonic cavitation effect by varying the operating modes.

2.3. Swelling power and solubility

The swelling behavior and solubility of the AS and UMAS at different sonication powers were calculated using the method described by Falsafi et al. [12] with few modifications. The samples were added and screw-capped tubes and mixed in distilled water to make 3% (w/v) dispersions. The tubes were then heated at 65, 80, and 95 °C for 30 min with continuous stirring. After heating, the suspensions were cooled down to room temperature and centrifuged for 20 min at 4000 rpm. The supernatant was separated and dried at 100 °C until a constant weight was obtained. The weight of the dried supernatant to the initial weight of dried starch was calculated as solubility (%), whereas the weight of wet pellet after centrifugation to the weight of initial starch was reported as the swelling power in grams of water/g of the initial weight of the starch sample.

2.4. Oil and water absorption capacity

The water holding capacity (WHC) and oil holding capacity (OHC) were determined using the method reported by Ashwar et al. [21]. Two
3 grams of AS and UMAS samples were placed in centrifugation tubes, and 10 mL of water or sunflower oil was added to each tube. The tubes were vortexed for 5 min, followed by centrifugation for 10 min at $3000 \times g$. After centrifugation, the supernatant was discarded, and the weight of the wet pellet in the tube was calculated. The results of the WHC and OHC were analyzed using Eq. 1:

$$\text{WHC or OHC} = \frac{\text{Weight of the wet pellet} - \text{the initial dry weight of the sample}}{\text{the initial dry weight of the sample}}$$  \hspace{1cm} (1)

2.5. Particle size distribution

A Mastersizer 3000 laser diffraction particle size analyzer (MS 3000; British Malvern Instruments Co., Ltd.) was used to measure the particle size distribution of the AS and UMAS samples. Almost 200 mg of the sample was dispersed in a 100 mL beaker and suspended in 50 mL of water. The bubble-free sample was poured into a Mastersizer 3000 for analysis.

2.6. Spectral analysis using FTIR

The spectral changes in the AS and ultrasonically modified arrowhead starches were analyzed using FT-IR (Nicolet™ IS™ 50, New York, USA). Dried starch samples were mixed and ground with potassium bromide (KBr) in the sample to a KBr ratio of 5:100. Then, the samples were converted into a transparent think-sheet using a hydraulic press. A total of 32 scans were performed in the wavelength range of 4000–400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.

2.7. X-ray diffractograms using XRD

An X-ray diffractometer (D8 ADVANCE; BRUKER, Germany) was used to measure the changes in the diffractograms and relative crystallinity of the samples after ultrasound treatment. The samples were scanned at 20 angles of 5–35°. The generator voltage and current of the diffractometer were 45 kV and 40 mA, respectively.

2.8. Analysis of rheological parameters

The rheology of the AS and UMAS was performed using a Discovery-3 rheometer (DHR3; TA Instruments Ltd., New Castle DE, USA). The plate was equipped with a parallel plate with a diameter of 40 mm. Starch samples (5% w/v) were analyzed for the steady shear sweep test at a shear rate of 1–100 (1/s) to evaluate the flow behavior.

2.9. Scanning electron microscopy (SEM)

The morphological changes in the native arrowhead and modified starch at different ultrasound powers and times were analyzed using a scanning electron microscope (S-3400 N; Hitachi High Technologies, Tokyo, Japan). The samples were coated with gold–palladium using a mini-sputter and photographed at an image resolution of 500–10000 ×.

2.10. Thermal properties

Thermal changes in AS and UMAS were measured using differential scanning calorimetry (DSC) (STA449C; NETZSCH, Germany). The samples (3–5 mg, db) were mixed with 16 μL of distilled water and hermetically sealed in stainless steel pans before equilibrating for 24 h at room temperature. After equilibration, scanning was performed at 25–150 °C at a rate of 10 °C/min. Thermal parameters, such as onset temperature (To) and conclusion temperature (Tc), and changes in
gelation enthalpy (ΔH) were measured. In addition, the range of the total gelation temperature (Tr) and peak height index (PHI) was calculated using Eq. (2) and (3):

\[ Tr = \left[ 2 \left( T_p - T_0 \right) \right] \] ........................................ (2)

\[ PHI = \frac{\Delta H}{(T_p - T_0)} \] ........................................ (3)

2.11. Statistical analysis

Statistical analysis of the AS and UMAS experimental data was performed by one-way analysis of variance (ANOVA) and Tukey’s test for statistical significance \( p < 0.05 \) using SPSS Statistics 19.0.

3. Results and discussion

3.1. Swelling power and solubility

Swelling power analysis of AS and sonicated samples (UMAS1 to UMAS6) was performed, and the effects of power ultrasound are illustrated in Fig. 2. The results showed that the swelling power of sonicated samples at 65 °C, 80 °C, and 95 °C was significantly different \( (p < 0.05) \) compared to that of the control (AS) samples at all temperatures. Increases in swelling power were observed at all temperatures with corresponding increases in sonication power, whereas the swelling power at 80 °C and 95 °C was significantly higher \( (p < 0.05) \) for all samples compared to samples analyzed for swelling power at 65 °C. At 65 °C, 80 °C, and 95 °C, the swelling power of all samples ranged from 4 to 7 g/g, 6–14 g/g, and 7–16 g/g, respectively. At a constant temperature, the increase in the swelling power of ultrasound-treated samples could be
attributed to the cavitation-induced increases in the temperature of the “internal matrices” of the modified starches. When AS was subjected to thermal constraints under power ultrasound, the starch granules were heated, and the internal matrices of the starch granules changed from an ordered state to a disintegrated condition owing to the absorption of water by amylopectin of AS, which led to increased swelling. The characteristics of amylopectin were indicative of the degree of swelling, and increases in ultrasound power led to a gradual loss of crystallinity in the microcrystalline bundled arrangement of amylopectin molecules. Similar results have been reported by Wang et al. [22], who noted that the sonication-induced disintegration of potato starch granules is accompanied by a loss of crystallinity in amylopectin.

Similar to the swelling power, the solubility of the AS and sonicated samples were also determined, the results of which are illustrated in Fig. 2. The solubility of all sonicated samples was higher than that of the control at all temperatures. At 65°C, the solubility ranged from 4% to 6%. Comparatively, no significant change (p > 0.05) in the solubility percentages of UMAS3, UMAS4, and UMAS5 was observed; however, the UMAS6 sample exhibited the highest solubility percentage among all sonicated samples. At 80°C and 95°C, the solubility of all samples ranged from 8.5 to 17% and 11.5–20%, respectively. At both 80°C and 95°C, the UMAS5 sample exhibited a slight decline in solubility, whereas further increases in sonication power led to enhanced solubility. The reason for the increased solubility of sonicated samples compared to that of the control may be the hydrolysis of starch granules caused by ultrasonic treatment. Increases in ultrasonic power led to the destruction of the granular structure or enhanced exposure of hydrogen bonds, which consequently caused an increase in the hydration capacity and solubility of starch granules because of the sonicated-induced accelerated degradation of AS. Increases in the hydration and solubility of starch from potatoes [22] and corn [23] have been reported in previous studies.

3.2. Water and oil holding capacities of ultrasonically modified arrowhead starch

The water and oil holding capacities (WHC and OHC) of AS and sonicated samples (UMAS1 to UMAS6) were determined, the results of which are tabulated in Table 3. Native AS exhibited WHC and OHC values of 47.07% and 45.62%, respectively. Overall, sonication power-dependent significant (p < 0.05) increases in WHC and OHC were observed in all ultrasound-irradiated samples. The WHC for all sonicated samples ranged from 60.46% to 67.47%. The highest WHC (67.47%) was found in the UMAS6 sample, which was significantly higher than that in the control samples (47.07%). Increases in the WHC of sonicated samples with corresponding increases in sonication frequency and power could be attributable to the high affinity of cavitation-induced small granules to water molecules. Cavitation caused the induction of void fractions in arrowhead starch molecules, leading to an increase in the WHC of sonicated starch samples. Furthermore, the increased WHC and OHC of sonicated samples could be explained by the cavitation-driven breakdown of starch molecules into small-sized granules, exhibiting enhanced exposed granule-specific areas when compared with those of native starch molecules. These results are in agreement with the findings of Falsafi et al. [12] for sonicated oat samples demonstrated a significant increase in (p < 0.05) WHC and OHC with a corresponding increase in sonication power. Similarly, the OHC ranged from 59.11 to 64.41% in the case of all sonicated samples. The highest OHC (64.41%) was found in the UMAS6 sample, which was significantly higher than that observed in the control samples (45.62%). UMAS2 and UMAS3 samples did not show any significant (p > 0.05) differences in OHC, whereas UMAS4 and UMAS5 samples exhibited comparable OHC. The gradual and slightly increasing trend in OHC with increasing sonication power could be due to two likely phenomena: (i) cavitation leading to an enhanced capillary entrapment of oil molecules in the void fraction; (ii) the filling of interstitial spaces between starch granules. Moreover, the sonication-induced increases in OHC may be correlated to the increased formation of pores and fissures in the granule microstructure (as evident from the SEM micrographs). These findings are in accordance with the results of Wang et al. [24] for sweet potato starch and Singh and Sharanagat [25] for ultrasonic-assisted modified starch of elephant foot yam.

3.3. Particle size distribution

The particle size distributions (PSDs) of the AS and sonicated samples (UMAS1 to UMAS6) were determined at volume distributions of D (3, 2)/μm, D (4, 3)/μm, D (10)/μm D (50)/μm, and D (90)/μm, and the results are shown in Fig. 3 and Table 2. D (3, 2) and D (4, 3) are indicative of the mean area diameter and mean volume diameter, respectively. D (10), D (50), and D (90) represented the quantities of starch granules that were smaller (i.e., 10%, 50%, and 90%) than the average starch granules in all samples. Starch granular sizes are closely associated with the degree of crystallinity of starch and the amylose to amylopectin ratio, which has been reported to significantly influence the physicochemical (theology, retrogradation, and gelatinization) and thermodynamic properties of starches. Overall, the PSD of the AS and sonicated samples exhibited a monomodal size distribution in terms of a single broad peak, whereas a slightly rising peak was observed at particle sizes ranging from 0.8 to 1 μm. At D (3, 2)/μm, the sonicated samples exhibited the following particle sizes; UMAS1 (7.54 μm), UMAS2 (7.52 μm), UMAS3 (6.89 μm), UMAS4 (6.90 μm), UMAS5 (7.12 μm), and UMAS6 (7.89 μm). At all PSD volume distributions, gradual decreasing tendencies were observed for all sonicated samples except the UMAS6 sample, with corresponding increases in applied ultrasound frequency and power. These findings corroborated that the sonication frequencies and power levels effectively led to the breakdown of relatively larger starch granule agglomerates rather than causing the disintegration of smaller starch granules. The particle sizes at all volume distributions in UMAS6 showed a slight increase compared with those in UMAS1. Compared to the control (AS) samples, all PSD fractions subjected to ultrasound irradiation showed relatively higher (p < 0.05) particle sizes. It was evident from the PSD results that sonication accelerated the degradation of starch granules in a positive manner and led to the destruction of large starch agglomerates. These destroyed starch granules exhibited high water and oil absorption capacities, accompanied by a higher swelling power. Consequently, ultrasound-treated samples exhibited larger particle sizes than the untreated control (AS) samples [26].

3.4. Molecular order degree measurement by FT-IR

FTIR usually provides valuable information regarding structural characteristics (double helical order, helicity, and chain conformation) in a short-range. The FTIR spectra of the AS and sonicated samples (UMAS1 to UMAS6) are shown in Table 4 and Fig. 4. Overall, from the results, it was evident that the positioning of the characteristic absorption peaks did not show any modification after subjecting the starch samples to sonication pre-treatments at various frequencies and power levels. This implied that there was no occurrence of a new absorption peak or loss of any absorption peak, which most likely resulted in no loss or formation of any new specific functional groups or chemical bonds. Native AS starch registered a band in the IR spectral region of 3321 cm⁻¹, which was indicative of the presence of stretching vibrations of hydroxyl functional groups (O–H). At the same time, a reduced band in the IR spectral region at 2924 cm⁻¹ corresponded to the stretching vibration owing to the presence of C–H groups. The sharp peaks observed in the IR spectral regions of 1021 cm⁻¹ and 1151 cm⁻¹ indicate the registered vibrations of the C–O–C functional groups. Furthermore, a characteristic shoulder peak was observed at 3189 cm⁻¹, which may be attributable to the O–H stretching of hydroxyl groups in intermolecular or intramolecular bonds in starches. The maximum absorption in the IR
the spectral regions of 1047, 995–1022 cm⁻¹, and 800–1200 cm⁻¹ were the main characteristic parameters in the FTIR spectra, which potentially corroborated the ordered, amorphous, and hydrated crystals, respectively, in the case of the sonicated (UMAS1 to UMAS6) samples. Hence, in accordance with a study by Qin et al. [8], intensity proportions of

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Table 2
Related parameters of the particle size distribution of arrowhead starch and ultrasonically modified arrowhead starch (UMAS).

| Sample   | D (3, 2)/μm | D (4, 3)/μm | D (10)/μm | D (50)/μm | D (90)/μm |
|----------|-------------|-------------|-----------|-----------|-----------|
| AS       | 6.41 ± 0.08d| 11.80 ± 0.06d| 10.50 ± 0.10d| 26.10 ± 0.08d|
| UMAS1    | 7.54 ± 0.38a| 14.10 ± 0.04a| 12.40 ± 0.06a| 24.60 ± 0.13a|
| UMAS2    | 7.52 ± 0.08b| 13.50 ± 0.24c| 12.00 ± 0.11a| 26.00 ± 0.10e|
| UMAS3    | 6.89 ± 0.08c| 15.30 ± 0.10a| 10.70 ± 0.11c| 23.80 ± 0.07c|
| UMAS4    | 6.90 ± 0.12c| 12.70 ± 0.11c| 11.30 ± 0.10d| 23.60 ± 0.07c|
| UMAS5    | 6.90 ± 0.18c| 13.00 ± 0.10c| 11.20 ± 0.03c| 24.50 ± 0.08e|
| UMAS6    | 7.89 ± 0.21abc| 15.90 ± 0.14bc| 12.20 ± 0.13c| 30.50 ± 0.13c|
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Values are means of triplicate determinations ± standard deviation. AS, arrowhead starch; UMAS1, 300 W, 15 min; UMAS2, 300 W, 30 min; UMAS3, 600 W, 15 min; UMAS4, 600 W, 30 min; UMAS5, 900 W, 15 min; UMAS6, 900 W, 30 min.

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Table 3
Changes in water and oil holding capacities of native (AS) and ultrasonically modified arrowhead starch (UMAS).

| Sample   | WHC (%) | OHC (%) |
|----------|---------|---------|
| AS       | 47.07 ± 0.40f | 45.62 ± 0.40d |
| UMAS1    | 60.46 ± 0.21e | 59.10 ± 0.28c |
| UMAS2    | 62.56 ± 0.14d | 60.81 ± 0.16b |
| UMAS3    | 63.58 ± 0.15c | 61.09 ± 0.35b |
| UMAS4    | 65.39 ± 0.38b | 63.15 ± 0.49a |
| UMAS5    | 66.20 ± 0.01b | 63.18 ± 0.87a |
| UMAS6    | 67.47 ± 0.60a | 64.40 ± 0.14a |
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Values are means of triplicate determinations ± standard deviation. AS, arrowhead starch; UMAS1, 300 W, 15 min; UMAS2, 300 W, 30 min; UMAS3, 600 W, 15 min; UMAS4, 600 W, 30 min; UMAS5, 900 W, 15 min; UMAS6, 900 W, 30 min.

The ratio of 1047/1022 cm⁻¹ (R1047/1022) may be employed to describe the degree of order (DO), and the spectral intensity ratio at 995/1022 cm⁻¹ (R995/1022) was indicative of internal structural and conformational changes in the degree of the double helix (DD). Overall, all sonicated samples showed significantly higher DO spectral intensity ratios, except UMAS6, compared to the control (AS) samples. UMAS6 showed a slightly increasing trend in DO ratio compared with that observed for the control. The DO was comparable for UMAS1, UMAS3, and UMAS5, whereas UMAS2 and UMAS4 samples exhibited similar DO spectral intensity ratios. In the case of DD ratios, the order was as follows: AS < UMAS3 < UMAS5 < UMAS4 < UMAS2 < UMAS1. These differences were not significant (p > 0.05), which implied that ultrasonication treatment at variable power levels (300, 600, and 900 W) and time intervals (15 and 30 min) did not result in a significant loss of molecular order, and the degree of helicity remained more or less stable. It could be further concluded that ultrasonic pre-treatment enhanced the number of double helices. Similar findings have been reported by Kaur and Gill [27] regarding the structural characterization of ultrasound-irradiated and physical modification of starches originating from different cereals, such as wheat, rice, maize, and barley. It was also reported by the authors that sonication treatment caused strengthening of band intensity as ultrasonic waves led to enhanced microstructural potential because of retention of bound water. The FTIR spectral regions
belonging to 1047 and 1080 cm\(^{-1}\) are reported to have linkage to the ordered structures of starch granules, whereas, FTIR band at 1022 cm\(^{-1}\) is found to be associated with that of amorphous regions of starch granules [28]. Ultrasound treatment of UMAS samples led to the modification of relative intensity of the FTIR band at spectral regions of 1047 and 1080 cm\(^{-1}\), which was indicative of the fact that ultrasound waves caused distortion in starch granules crystallinity.

The XRD analysis of native AS and sonicated samples (UMAS1 to UMAS6) was performed to elucidate the diffraction patterns and degree of crystallinity, the results of which are shown in Fig. 5. Overall, all diffractograms of the ultrasound-irradiated samples showed a resemblance to the control (AS) samples in peak positioning, height, and shape. The relative crystallinity (RC) and Bragg angles (2\(\theta\)) are listed in Table 4. The initial peak of the AS samples was observed at 5.51°, whereas UMAS2, UMAS4, UMAS5, and UMAS6 showed the emergence of initial peaks at 5.68°, 7.76°, 5.48°, and 7.44°, respectively. However, it was evident from the results that the ultrasound-irradiated samples showed slightly sonication power-dependent increases in Bragg’s angle with corresponding increases in sonication frequency and power compared with those of the control samples. This implied that cavitation-induced sonication pre-treatments led to slight modifications in the RC of the sonicated samples compared with that of the control. In terms of RC%, UMAS1 and UMAS5 sonicated samples showed similar RC compared to the control, whereas UMAS2 and UMAS3 exhibited significant increases in RC%, which implied that cavitation resulted in the induction of a relatively higher degree of crystallinity compared to the control (AS). However, further increases in the sonication frequency and power led to a decline in RC, which was subsequently comparable to that of the control. The declining tendencies observed in RC at higher sonication intensities are in agreement with the findings of Falsafi et al. [12]. These RC reductions in sonicated samples could be attributed to the cavitation-induced erosion of weak crystalline structural configurations in native AS starch after exposure to ultrasound irradiation. The degree of crystallinity is usually an indicator of amyllopectin content in starches as the crystalline structures of starches are generally formed by the side chains of amyllopectin [29], and ultrasound irradiation causes significant changes in amyllopectin chains at variable frequencies and power levels. As acoustic waves, ultrasounds operate at a frequency that exceeds the audible threshold of human hearing range. Ultrasound treatment has been regarded as the physical method of starch modification which has many advantages as an eco-friendly technique in terms of rendering high quality and selectivity accompanied by the reduced processing time and usage of organic chemicals [23]. All ultrasonically treated samples showed a higher degree of crystallinity in comparison with that of untreated control samples. This could be ascribed to the fact of ultrasonication-induced acoustic cavitation that possibly degraded the amylose-rich amorphous regions of the arrowhead starch. It could further be interpreted to the fact that the linear amylose chains are more susceptible to depolymerization by the incident sonication waves compare to the outer lamellae that are fragmented at longer sonication treatment times. The prolonged treatment with ultrasonic waves at increased power is prompted to attack the more crystalline inner lamellae rich in amyllopectin chains resulting in a decrease in relative crystallinity as in the case of UMAS5 and UMAS6 as shown in Table 4.

Pure arrowhead starch (AS) was used as reference material, and it was evident from the diffractograms of XRD analysis that pure starch exhibited a typical A-type crystalline arrangement. These slight variations in peak intensities might be ascribed to the sonication effect which probably enhanced the amylose content and improved dispersibility which consequently facilitated the formation of starch microbubbles [30]. Subsequently, effects of tri-frequency sonication treatment on relative crystallinity of pure starch, control, and ultrasonically-treated samples are given in Table 4 which imply that sonication-induced cavitation led to gradual variations in relative crystallinity (RC) of sonicated samples when compared to that of control. In terms of RC%, all sonicated samples exhibited rising tendencies in RC%. Specifically, UMAS1, UMAS2 and UMAS3 samples irradiated at ultrasonic power of 300 and 600 W exhibited significant (p < 0.05) increases in RC% which implied that cavitation caused induction of a relatively higher degree of crystallinity when compared to control (AS). However, further rises in sonication power (UMAS4, UMAS5, and
UMAS6) led to declining tendencies in RC of sonicated samples when compared to UMAS2 and UMAS3 samples. These results regarding RC declining tendencies at higher sonication power were in agreement with the findings of Falsafi et al. [28]. The degree of crystallinity is usually indicative of amylopectin content in starches because the crystalline structures of starches are usually formed by the side chains of amylopectin [29] and ultrasound-irradiation caused significant (p < 0.05) changes in amylopectin chains at variable ultrasonic power levels [31]. Multi-power ultrasound application at tri-frequency mode forced a double helix of swollen starch granules to open and damaged the native semi-crystalline structural configuration and exposed the internal laminated structures [32]. This caused a sufficient release of AS semi-crystalline structural configuration and exposed the internal crystallinity. The findings of increased relative crystallinity in sonicated samples as compared to untreated control samples [28,35] in this study, the patterns obtained for sonicated samples exhibited similar crystalline arrangement similar to that of native starch, which was indicative of the fact that ultrasound treatment did not exert significant influence in terms of reduction of diffraction intensities which implied that ultrasound treatment did cause significant damage to the amorphous regions of sonicated samples on crystallinity structure [28]. It has been also reported in the published literature that the sonication effect on crystallinity content is dependent on starch type as well as experimental conditions, since packing of amorphous and crystalline regions inside the granule may cause different susceptibilities to be attacked by ultrasounds, being found to increase [28], decrease [13], or not cause any significant change in the degree of crystallinity [34,35]. The relative crystallinity in this study indicated important changes. The findings of increased relative crystallinity in sonicated samples were in line with the previously published report about ultrasound-treated corn starch whereby the relative crystallinity exhibit increases from 25% in native corn starch to about 33% for sonicated-corn starch. This rising tendency in RC of ultrasound-treated samples may be ascribed to the fact of preferential degradation of amylose-rich amorphous regions of starch granules [28]. It was also evident that starch chains cleaved in amorphous regions led to the reordering of fragmented chains to some extent accompanied with a high degree of crystalline structure with sharper XRD patterns. Ultrasound waves are reported to cause more susceptibility to depolymerization in linear amylase chains and degradation of amylose-rich amorphous regions of starch granules led to higher relative crystallinity in sonicated samples as compared to untreated control samples [28,35]. In another report by Bernardo et al. [33] evaluated the effects of ultrasound treatment on Yam (Dioscorea bulbífera) starch. As compared to native Yam starch, sonicated Yam starch samples exhibited significant increases in relative crystallinity of about 21.52% when irradiated at 12% sonication amplitude for 3 min and the probable reason for the increase in RC was great sonication impact on amorphous starch granules owing to preferentially degradation of amorphous regions in linear chain amylase molecules. The results of XRD were further endorsed by results of FTIR spectra. The FTIR spectral regions belonging to 1047 and 1080 cm⁻¹ are reported to have linkage to the ordered structures of starch granules, whereas, FTIR band at 1022 cm⁻¹ is found to be associated with that of amorphous regions of starch granules [28]. Ultrasonic treatment of UMAS samples led to the modification of relative intensity of the FTIR band at spectral regions of 1047 and 1022 cm⁻¹, which was indicative of the fact that ultrasound waves caused distortion in starch granules crystallinity. The intensity ratio (R_{1047/1022}) was indicative of the RC index in terms of short-range crystallinity corresponding to the ratio of areas of deconvoluting curves for FTIR spectral peaks at 1047 and 1022 cm⁻¹, respectively. The decay of this intensity ratio (R_{1047/1022}) indicated sonication-induced disruption of short-range crystallinity owing to crack down in helical structures of starch granules [28].

3.6. Thermal properties of sonicated AS starches

DSC analysis was carried out for the control and sonicated samples, and the results are shown in the thermograms in Table 5. Useful information from DSC thermograms was extracted in terms of onset (T_o), peak (T_p), and conclusion (T_c) temperatures of gelatinization, reaction heat or enthalpy change (ΔH), and reference temperature (T_r). ΔH was determined by calculating the area under the curve between the onset and conclusion temperatures. The results showed that increases in sonication power led to significant (p < 0.05) increases in onset gelatinization temperatures (T_o) from 47.54 °C to 63.91 °C as compared to that of the control (AS) samples (37.27 °C). Significant (p < 0.05) increases in T_p (84.06–92.41 °C) and T_c (84.06–92.41 °C) showed sonication power-dependent gradual rises in UMAS1, UMAS2, and UMAS3 samples, while further increases in sonication power led to slight decreases.

Moreover, the ΔH of sonicated samples (UMAS1 to UMAS6) ranged from 3.41 to 4.92 J/g, which was significantly lower (p < 0.05) than the control (6.92 J/g). On the DSC thermograms, T_o was indicative of the gelatinization of less-ordered double-helical structures of starch granules. These weak structures with less ordered configurations within starch granules exhibited a higher disruption rate after exposure to high-intensity ultrasound irradiation. Hence, the UMAS6 sample showed gradually decreasing tendencies of T_o, T_p, and T_c in comparison with other sonicated samples. Sonication intensity and ΔH were shown to be negatively correlated, which may be ascribed to the probable phenomenon of double-helical structural disintegration of starch granules owing to the release of energy from cavitation-induced collapse of bubbles [28].

Moreover, the diffusion of water molecules resulted in increased mass transfer into swollen starch granules and reached crystalline lattices because of the formation of holes, fissures, cracks, and channels after exposure to ultrasound irradiation. The cavitation results in the sonochemical ionization of water molecules, which gives rise to an elevated release of H⁺ ions leading to the distortion of the crystalline regions of starch granules [22]. These results were in line with the findings of Jambark et al. [36] who also stated that decreasing tendency

| Sample | T_o (°C) | T_p (°C) | T_c (°C) | ΔH (J/g) | PHI (J/g) | T_c (°C) |
|--------|---------|---------|---------|---------|-----------|---------|
| AS     | 37.27 ± 1.308d | 79.63 ± 0.650d | 116.25 ± 0.55ab | 6.92 ± 0.55ab | 0.081 ± 0.002ab | 84.73 ± 3.917a |
| UMAS1  | 47.54 ± 0.926c | 84.06 ± 1.301c | 119.09 ± 0.41bc | 4.30 ± 0.41bc | 0.058 ± 0.006cd | 73.05 ± 0.749b |
| UMAS2  | 60.94 ± 0.424ab | 84.06 ± 0.860bc | 114.62 ± 0.28cd | 3.41 ± 0.28cd | 0.065 ± 0.004cd | 51.70 ± 0.424e |
| UMAS3  | 60.93 ± 0.622ab | 92.41 ± 0.537a | 121.59 ± 0.090cd | 3.64 ± 0.090cd | 0.057 ± 0.001ed | 62.96 ± 0.169c |
| UMAS4  | 60.92 ± 1.202ab | 89.70 ± 0.785ab | 118.11 ± 0.137cd | 3.89 ± 0.137cd | 0.067 ± 0.001cd | 57.55 ± 0.834d |
| UMAS5  | 63.91 ± 0.870a | 88.19 ± 1.358b | 115.63 ± 0.096cd | 3.54 ± 0.096cd | 0.072 ± 0.001bc | 48.00 ± 0.976e |
| UMAS6  | 57.98 ± 1.146b | 86.89 ± 0.983bc | 117.80 ± 0.926ab | 4.92 ± 0.926ab | 0.085 ± 0.008a | 57.81 ± 4.257 cd |

Values are means of triplicate determinations ± standard deviation. AS, arrowhead starch; UMAS1, 300 W, 15 min; UMAS2, 300 W, 30 min; UMAS3, 600 W, 15 min; UMAS4, 600 W, 30 min; UMAS5, 900 W, 15 min; UMAS6, 900 W, 30 min.
of gelatinization enthalpy (ΔH) after exposure to ultrasound treatments might be resulted owing to possible varying alignments of hydrogen bonding linkages within the sonicated starch granules as a result of distortion and sonication-induced disruptions in the amorphous regions of AS granules. Total gelation temperature (Tr) and peak height index (PHI) also showed significantly (p < 0.05) decreasing tendencies with rises in sonication power. PHI was ranged from 0.057 to 0.072 J/g in all sonicated samples (UMAS1 to UMAS5) as compared to that of control (AS) (0.081 J/g). Only UMAS6 exhibited comparable PHI to that of control. Moreover, all sonicated samples exhibited Tr in the range of 48 °C to 73.05 °C which was significantly (p < 0.05) lower as compared to that of control (84.73 °C). Such reduction of total gelation temperature (Tr) and peak height index (PHI) was indicative of structural reinforcement of starch granules after sonication treatment probably because of enhanced packing of crystalline leftovers after sonication-induced disruption of amorphous regions and melting of weakest starch granule crystallites due to cavitation [15,23].

3.7. Microstructural properties of sonicated AS starches

Scanning electron micrographs of the native (control) and sonicated AS starches are shown in Fig. 6. The SEM images revealed that native AS starch (control) samples exhibited shapes ranging from spherical, cuboid, round, and polygonal starch granules with smooth edges. The majority of the native AS granules showed smooth surfaces without fissures on the outer sides, which implied that the starch granules were prepared in an adequate manner. Some granules in the clusters were found to be polyhedral on one side, which implied that adjacent native granules in clusters affected the shapes. Micrographs of sonicated samples showed that the sonication frequency and intensity exerted slight to highly significant effects on granule morphology (UMAS1, UMAS2, and UMAS3). As the sonication intensity increased, superficial cracks and roughness on starch granules appeared in a sonication power-dependent manner (UMAS4, UMAS5, and UMAS6). The formation of fissures and pores on the surface was also observed in ultrasound-treated rice starch [37]. At the high intensity of ultrasound irradiation (UMAS4, UMAS5, and UMAS6), a relative size reduction in starch granules was observed after exposure to high-intensity ultrasound pre-treatments. The emergence of superficial cracks, fissures, and roughness on sonicated granules could be attributable to cavitation-induced bursting due to the energetic vibrations of ultrasound sound irradiation, leading to formation of ultrasound waves of high pressure and massive velocity to hit the starch granules and cause degradation. The sonochemical effect of power ultrasound caused the splitting of water molecules to yield OH radicals, which attacked starch granules and enhanced polymer degradation. A similar reduction in the size of sonicated starch granules has been reported for corn [36] and pinhao starches [38].

3.8. Rheological behavior of sonicated AS starches

The rheological properties of native (control) and sonicated AS starches were determined in terms of stress and viscosity against the shear rate. Flow curves were constructed for the control and sonicated starch samples, and the results are shown in Fig. 7. From the results, it was evident that the flow curves of the control and sonicated samples all exhibited shear-thinning behaviors over the entire range of measured shear rates from 1 to 100 s⁻¹, as declining tendencies were observed regarding the viscosity of all samples with corresponding increases in shear rate. This may be explained by the unidirectional motion of starch molecules and the intense shear action of high-intensity ultrasounds, which resulted in weakened intermolecular interaction forces. Initially, UMAS1, UMAS2, and UMAS4 exhibited shear-thinning behavior similar to that of the control (AS) starch samples. Further increases in shear rate caused increasing trends in the stress of the sonicated and control samples. Overall, all sonicated samples showed a lower degree of shear-thinning compared to the control. Similarly, viscosity exhibited declining tendencies with corresponding increases in the shear rate, regardless of sample type; however, UMAS3, UMAS5, and UMAS6 samples had a lower viscosity than the other sonicated and control samples. Compared with the control, UMAS1, UMAS2, and UMAS4 exhibited shear-thinning behaviors similar to those of the control (AS) starch samples. The lower viscosity of UMAS3, UMAS5, and UMAS6 samples compared to other sonicated and control samples could be ascribed to the dissolution of amylose molecules from starch granules, and the suspension became less viscous after exposure to high-intensity ultrasound irradiation. Furthermore, the sharp decrease in viscosity was evident with corresponding rises in sonication power and this might be ascribed to the possible rise in amylose content as well as amylepectin debranching owing to cavitation-induced disruption of C-O-C chain in AS starch [39]. The high degree of amylose exhibited more resistance to the sonication treatment because of chain aggregation. When the sonicated samples were subjected to ultrasonic heating and shearing, the linear amylose molecules possibly first dissolved from AS tubers with a corresponding rise in treatment temperature followed by dissolution of mild amylepectin molecules. It has already been reported that a high degree of temperature is needed for amylose gelatinization which consequently caused multiphase transformation and macromolecules winding between linear starch polymer chains [40,41]. This led to the high degree of shear stress of sonicated samples (Fig. 7). Sonication-induced bubble cavitation led to elevated temperatures, which may cause a reduction in the viscosity of gelatinized starch granules accompanied by increased fluidity. Similar results have been reported for corn starch [42], a novel native starch isolated from Rhizoma Castroideae [29].

3.9. Potential technological applications of ultrasonically modified starch

Ultrasonically modified starches may be exploited to impart several techno-functional properties, such as emulsification, gelling, and thickening. Modified starches in food industries can be utilized for several purposes: 1) modified starches are commonly used for stabilization, thickening, and enhancement of mouth feel of canned foodstuffs [43]; 2) as functional ingredients, modified pregelatinized starches may be employed in cookies manufacturing to control the degree of spread as well as in other bakery products like cake for glazing, softening and moisture retention; 3) in frozen batter foods for provision of better adhesion, improved crispiness and decreased oil pick-up during frying [29,43]; 4) for thickening of salad dressings especially in fat-replaced and fat-reduced dressings; 5) for thickening and provision of short texture to retorted baby foods [44]; 6) last but not the least they are also utilized in beverage emulsions for preventing flavor loss, sedimentation and creaming (phase separation) [43].

4. Conclusions

This study was aimed to develop ultrasonically-modified arrowhead starch (UMAS) using a sophisticated and eco-friendly tri-frequency power ultrasound (TPPU, 20/40/60 kHz) method at various power levels (300, 600, and 900 W) at different time intervals (15 and 30 min). Furthermore, the structural, morphological, thermal, rheological, and physicochemical properties of native arrowhead starch (AS) and UMAS were investigated. Significant (p < 0.05) increases in swelling power, solubility, WHC, and OHC were observed at all temperatures, with corresponding increases in the sonication power. At all PSD volume distributions, a gradual decrease was observed in all sonicated samples, except for UMAS6. In particular, the maximum absorption in the IR spectral regions of 1047, 995–1022 cm⁻¹ and 800–1200 cm⁻¹ were indicative of the main characteristic FTIR spectra, which possibly corroborated the ordered, amorphous, and hydrated crystals, respectively, in sonicated samples. In terms of RC%, sonicated samples, the rising tendency in relative crystallinity of ultrasound-treated samples may be ascribed to the fact of preferential degradation of amylose-rich
Fig. 6. Scanning electron micrographs of AS (A1-A3) as UMAS1 (B1-B3), UMAS2 (C1-C3), UMAS3 (D1-D3), UMAS4 (E1-E3), UMAS5 (F1-F3), and UMAS6 (G1-G3) where the numbers 1, 2, and 3 represent the size at 100 µm, 10 µm, and 5 µm, respectively.
Micrographs of sonicated samples showed that as the sonication in sonication-induced disruptions in the amorphous regions of AS granules. Linkages within the sonicated starch granules as a result of distortion and viscoelastic characteristics and properties of the starch in different botanical sources, Food Science Technology 35 (2015) 215-256.

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Fig. 7. Rheological behavior of AS and UMAS.

amorphous regions of starch granules. Decreasing tendency of gelatinization enthalpy (ΔH) were observed after exposure to ultrasound treatments owing to possible varying alignments of hydrogen bonding linkages within the sonicated starch granules as a result of distortion and sonication-induced disruptions in the amorphous regions of AS granules. Micrographs of sonicated samples showed that as the sonication intensity was increased, superficial cracks and roughness on starch granules appeared in a sonication power-dependent manner (UMAS4, UMAS5, and UMAS6) compared to the control (AS) samples. Overall, all sonicated samples showed a lower degree of shear-thinning and viscosity with corresponding increases in the shear rate. Our findings suggest that controlled TFU can be used to alter the morphology and physicochemical characteristics of starch, which could be used to develop new products with specified properties.

CRediT authorship contribution statement

Husnain Raza: Investigation, Methodology, Writing – original draft, Writing – review & editing. Kashif Ameer: Writing – review & editing. Haile Ma: Supervision, Writing – review & editing. Qiufang Liang: Supervision, Writing – review & editing, Funding acquisition. Xiaofeng Ren: Conceptualization, Funding acquisition, Project administration, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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