International Journal of
Science, Architecture, Technology and Environment

Structure–Function Engineering of Arenga pinnata Starch via Dual Acylation and Phosphate Cross-Linking for Functional Food Systems

Jusman[1*], M. Mirzan[2], Nurakhirawati[3]

[1,2,3]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Tadulako University, Jl. Ir. Soekarno Hatta Km. 10, Tondo Palu 94117, Central Sulawesi, Indonesia)*

[*]*Corresponding author, jusman_palu04@yahoo.com*

Orchid : https://orcid.org/0000-0002-1275-8359

DOI: https://doi.org/10.63680/ijsate1125043.037

Abstract

Arenga pinnata is an abundant Indonesian starch resource with considerable potential for functional food applications; however, its utilization is limited by poor processing stability and pronounced retrogradation during storage. This study investigates an integrated chemical modification strategy combining sequential dual acylation (acetylation and butyrylation) with phosphate cross-linking to elucidate structure–function relationships in modified starch from Arenga pinnata. Native starch was dispersed in aqueous media and acetylated using acetic anhydride at varying concentrations (3–12%, w/w), followed by butyrylation with butyric anhydride under controlled alkaline conditions. The acylated starch was subsequently cross-linked using a sodium trimetaphosphate/sodium tripolyphosphate (STMP/STPP, 99:1) system at different levels. Chemical incorporation was quantified by acetyl content and degree of substitution (DS). At the same time, functional performance was evaluated by water- and oil-holding capacities, swelling power, solubility, and digestion–resistance–related parameters. Increasing acetylation levels resulted in a systematic increase in acetyl content and DS, demonstrating that substitution could be effectively tuned by reagent concentration. Higher substitution levels enhanced hydration capacity and swelling behavior, accompanied by reduced solubility, indicating modified intermolecular associations and increased hydrophobicity within the starch matrix. Phosphate cross-linking further contributed to structural stabilization and increased the proportion of digestion-resistant starch fractions compared with native starch. An optimal modification condition was identified at 12% STMP/STPP combined with acetylation within the studied range, yielding an acetyl content of 2.740% and an acetyl DS of 0.112, which provided a balanced combination of functional stability and hydration performance. These results demonstrate that dual acylation coupled with phosphate cross-linking is an effective strategy for engineering the functional properties of Arenga pinnata starch for functional food systems. Nevertheless, the nutritional relevance of digestion-resistant fractions should be further validated using standardized resistant starch assays in formulated food matrices.

Keywords: Arenga pinnata, acetylation, butyrylation, phosphate cross-linking, degree of substitution (DS), functional food

1. Introduction

Starch is a ubiquitous natural biopolymer and the dominant reserve carbohydrate in higher plants, thereby representing a strategically important renewable resource for both food and non-food value chains. It is primarily accumulated in tubers (e.g., cassava, sweet potato, potato), seeds (e.g., maize, rice, wheat), stems (e.g., palm/aren and sago), and fruits, and its wide availability has motivated sustained research on starch-based ingredients and materials for thickening/texturizing, encapsulation, and biopolymer-based products (Fu et al., 2022; Compart et al., 2023; Puri et al., 2025; Gupta et al., 2025). However, recent reviews consistently emphasize that native starches often exhibit operational limitations—such as thermal instability, poor solubility control, retrogradation during storage, and vulnerability to enzymatic degradation—that restrict performance under diverse processing and end-use conditions, thus necessitating targeted modification strategies to obtain application-specific functionality (Fu et al., 2022; Compart et al., 2023; Puri et al., 2025; Gupta et al., 2025).

Within this context, *Arenga pinnata* starch represents a strategically important yet underexplored indigenous starch resource in Indonesia, owing to its wide geographical distribution and reported yield potential. These attributes provide a practical foundation for developing localized starch-processing technologies and value-added ingredients for food and non-food applications. Beyond availability, *Arenga pinnata* starch exhibits intrinsic structural characteristics such as its amylose amylopectin distribution and distinctive granule morphology that differ from those of more extensively studied commercial starches, including cassava and potato. Such structural distinctions imply that the functional behavior of *Arenga pinnata* starch during processing and storage cannot be directly extrapolated from conventional botanical sources (Hehamahua et al., 2023; Supreethee & Vashisth, 2025; Palencia et al., 2025).

Reported extraction yields of approximately 16–26% further support the feasibility of Arenga pinnata starch valorization, while highlighting the importance of downstream modification strategies to translate raw starch availability into functionally stable, specification-compliant ingredients. Comparative studies indicate that, like many native starches, Arenga pinnata starch may exhibit pronounced retrogradation and limited thermal stability, which can limit its suitability for applications requiring stable paste properties, storage resilience, and predictable hydration behavior (Palencia et al., 2025). These constraints underscore the need to understand and deliberately tailor the structure function relationships of *Arenga pinnata* starch through targeted modification rather than relying on its native form for direct industrial use.

The main research problem addressed in this study is that native *Arenga pinnata* starch can exhibit physicochemical and functional limitations that reduce usability in targeted formulations; therefore, performance improvement generally requires deliberate structural modification rather than direct industrial deployment. For native palm and sago like starches, frequently discussed constraints include instability under shear and acidic environments, freeze thaw instability, limited paste clarity, and inadequate swelling/solubility balance, and these properties are commonly quantified using dynamic rheometry (shear stability), differential scanning calorimetry (DSC; thermal and freeze–thaw stability), and turbidimetry (paste clarity) (He et al., 2022). These limitations are particularly consequential in functional-food contexts because the ingredient must remain processable under manufacturing conditions while maintaining a defined nutritional functionality during consumption, storage, and digestion.

A general solution recognized in the recent literature is starch modification via physical, chemical, or enzymatic routes, each producing distinct outcomes and thus requiring selection aligned with the intended functional profile. Physical modification is often used to enhance thermal stability and adjust swelling behavior; chemical modification is used to tailor viscosity, hydration, and hydrolytic tolerance through targeted substitution or network formation; and enzymatic modification typically proceeds under milder conditions while improving specific textural and functional attributes in food systems (He et al., 2022; Bhati et al., 2025). Nevertheless, it is increasingly recognized that one-step treatments can yield incomplete or imbalanced property changes; for instance, stability improvements may be accompanied by reduced swelling or dispersibility, whereas increased hydration capacity may coincide with poor storage stability, implying that single-step modification may not reliably deliver the combined physical, chemical, and functional requirements of functional-food specifications (Compart et al., 2023; He et al., 2022).

From a chemical-design perspective, the anhydroglucose unit (AGU) of starch provides three hydroxyl (–OH) groups (at C2, C3, and C6), and therefore the theoretical maximum degree of substitution (DS) is 3. In practice, substitution is expected to be position-dependent because –OH accessibility and local steric environment differ across carbon positions, which can influence hydrogen bonding, chain packing, and ultimately the linkage between chemical incorporation and macroscopic functionality. Accordingly, chemical modification should be understood as a controlled perturbation of intermolecular interactions and molecular accessibility, thereby altering crystallinity, hydration, and compatibility with lipids and other formulation components.

In this context, combined (dual- or multi-step) modifications have been advanced as a rational strategy to achieve performance targets that are difficult to attain with single-step treatments alone. Mechanistically, dual modifications are proposed to generate synergy: cross-linking can increase resistance to shear, heat, and acidic environments, whereas acylation can introduce controlled hydrophobicity and reduce retrogradation, thereby broadening processing flexibility and stabilizing functionality across a wider operating window (Chandak et al., 2022; Subroto et al., 2023). Therefore, a combined “double–single” strategy is positioned here as a practical approach to tune aren starch toward the balanced property set required for functional-food applications.

In functional-food framing, resistant starch (RS) is commonly defined as the starch fraction that resists enzymatic digestion in the small intestine and is subsequently fermented in the colon. RS is frequently classified into types such as RS1–RS4 based on physical inaccessibility, native granular resistance, retrograded structures, and chemically modified forms, respectively (Luo et al., 2023). Recent literature has further used glycemic index (GI) assessment frameworks to support the expectation that RS enrichment may moderate the postprandial blood glucose response. However, these implications remain contingent on the food matrix, processing history, and individual metabolic variability (Thongkham et al., 2024). Importantly, RS-centered claims also warrant careful communication of limitations, including potential gastrointestinal discomfort in sensitive consumers and heterogeneous physiological responses to dietary fiber-like components, implying that functional positioning should be hedged and supported by appropriate labeling and consumer education (Wu et al., 2024).

Despite the progress above, a gap remains in systematically linking, for aren starch, the chemical extent of modification (e.g., reagent-group incorporation and DS) with structural evidence (e.g., functional-group signatures and crystalline order) and with functional proxies relevant to functional foods (e.g., water holding capacity, oil holding capacity, swelling, solubility, and RS quantified using standardized analytical references). This gap is practically important because industrial adoption typically requires reproducible property tuning within defined operating windows rather than qualitative confirmation of modification, and because aren

starch differs structurally from conventional starches, limiting direct extrapolation from other botanical sources (Hehamahua et al., 2023; Supreethee & Vashisth, 2025).

Accordingly, the objective of this study is to characterize and elucidate the physical, chemical, and functional properties of Arenga pinnata starch produced using a combined modification scheme (a "double–single" strategy) for functional-food applications. To our best knowledge, the integrated characterization framework applied here linking DS and reagent-group incorporation with spectroscopic and crystallographic evidence and with functional metrics relevant to hydration, lipid interaction, and digestion resistance provides a structured basis for evaluating whether a combined modification approach can yield an aren starch with a more desirable and practically usable property profile than native starch or single-step modified counterparts. The scope of the present work is therefore limited to chemical characterization and functional-property assessment; any broader physiological implications are discussed cautiously, as expectations that require further validation in formulated foods and, where relevant, in vivo studies.

2. Methodology

2.1 Materials and experimental design

Arenga pinnata starch (aren starch) was chemically modified using a combined, multi-step route comprising acetylation, butyrylation, and phosphate cross-linking. The procedure was implemented as a controlled-pH, room-temperature esterification sequence followed by alkaline phosphate cross-linking, where the cross-linking reagent level was treated as the primary experimental factor. Specifically, a mixture of sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) at a 99:1 (w/w) mass ratio was applied at four levels: 3, 6, 9, and 12% (w/w, starch basis), yielding five modified-starch treatments for subsequent characterization.

The esterification framework is consistent with recent reports in which starch acetylation/butyrylation is commonly performed using acetic anhydride or butyric anhydride under controlled pH, temperature, and reaction time to regulate acyl incorporation and degree of substitution (DS), while avoiding excessive hydrolysis that can decrease substitution efficiency (Chandak et al., 2022). The cross-linking approach aligns with contemporary combined-modification strategies for starch engineering, in which phosphate cross-linking is used to enhance processing stability and expand the functional operating window of modified starch systems (Subroto et al., 2023).

2.2 Preparation and combined chemical modification of aren starch

A starch suspension was prepared by dispersing aren starch (100 g) in distilled water (225 mL). The suspension was stirred on a magnetic stirrer at room temperature for one h to achieve uniform dispersion.

2.2.1 Acetylation

Acetylation was initiated by adding acetic anhydride at 12% (v/w) dropwise into the starch suspension. During addition and reaction, the pH was maintained at 8.0–8.5 by incremental addition of 3% (w/v) NaOH. The acetylation reaction was conducted at room temperature for 60 min under continuous stirring.

2.2.2 Butyrylation

Following acetylation, butyric anhydride (12% v/w) was added dropwise to the reaction mixture. The pH was

maintained at 10.0 with 3% (w/v) NaOH, and the butyrylation reaction was conducted at room temperature for 40 min under stirring.

2.2.3 Alkaline adjustment and phosphate cross-linking

After the butyrylation stage, the suspension pH was increased to 10.5 by adding 5% (w/v) NaOH while maintaining agitation. Phosphate cross-linking was then carried out by adding an STMP/STPP reagent mixture (99:1, w/w) at 3, 6, 9 or 12% (w/w, starch basis). After reagent addition, the suspension was stirred at room temperature for 30 min. The pH was subsequently adjusted downward to 5.5.

The cross-linking reaction was completed by incubating the suspension in a shaking incubator at 40°C and 200 rpm for 24 h. The reaction was terminated by adding 0.5 N HCl until the suspension reached pH 4.5.

2.3 Product recovery and post-treatment

Upon completion of the modification, the reaction mixture was subjected to precipitation and sequential washing to remove residual reagents and by-products. The modified starch was washed with distilled water three times and ethanol once. The washed material was dried in a cabinet dryer at 50°C for 12 h, until it reached a moisture content of 10–12%. The dried product was then milled and sieved through a 100-mesh screen to obtain a uniform modified-starch powder for analysis.

2.4 Physicochemical and functional characterization

A comprehensive characterization set was performed to link chemical incorporation, structural features, and functional performance.

2.4.1 Reagent-group percentage and degree of substitution (DS)

Reagent-group content (%) and DS were used as quantitative indicators of the extent of chemical substitution. In line with recent practice, DS was interpreted as the molar extent of acyl substitution relative to the starch backbone, while acknowledging that analytical bias can arise from moisture effects and spectral overlap when spectroscopic approaches are used (Chandak et al., 2022).

2.4.2 Water holding capacity (WHC) and oil holding capacity (OHC)

WHC and OHC were determined using standard gravimetric procedures and reported as grams of water (or oil) per gram of dry starch. Values were obtained from the mass difference before and after incubation/centrifugation and decanting, with controlled contact time and temperature to ensure comparability across treatments.

2.4.3 Swelling power and solubility

Swelling power and solubility were measured using controlled heating-based protocols. Swelling power was reported as grams of swollen starch per gram of original dry starch, while solubility was reported as percentage of solubilized starch at the specified test temperature/time.

2.4.4 Resistant starch (RS)

Resistant starch (RS) content was determined using AOAC-aligned procedures, as recommended in recent RS-focused functional-food literature. In particular, the approach is consistent with AOAC 2002.02-style methodology involving gelatinization and enzymatic digestion steps, and RS results were reported as grams of resistant starch per gram (or per 100 g) of sample on a defined basis (Luo et al., 2023).

2.5 Data reporting and quality control

All reagent levels, pH values, temperatures, reaction times, and centrifugation/incubation conditions were reported with units to ensure reproducibility. Functional and structural outcomes were interpreted cautiously, emphasizing trend-based comparisons across the cross-linking levels rather than overgeneralizing beyond the studied operating window.

3. Results and Discussions

3.1 Effect of Acetic Anhydride Concentration on Acetyl Content and Degree of Substitution

The results presented in Figure 1 demonstrate that acetic anhydride concentration plays a crucial role in determining the level of acetylation in sugar palm (*Arenga pinnata*) starch, as evidenced by progressive and statistically significant increases in both acetyl content (Ac, %) and degree of substitution (DS) within the tested concentration range of 3–12%. Quantitatively, acetyl content increased from 0.620% at 3% acetic anhydride to 2.740% at 12%, while DS increased from 0.021 to 0.112 across the same range (Figure 1).

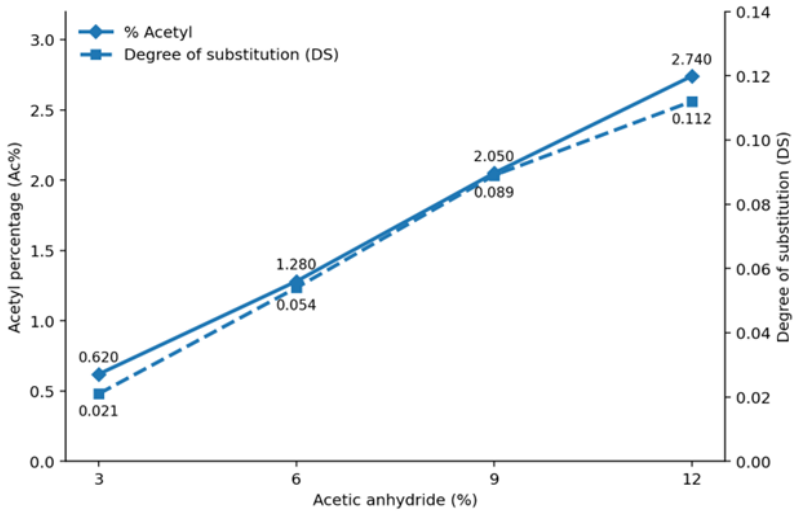

Figure 1. Percentage acetyl and DS of aren starch acetate at different acetic anhydride concentrations

This trend confirms that greater reagent availability is directly correlated with enhanced chemical substitution on the polysaccharide backbone. From a practical standpoint, these findings suggest that acetic anhydride concentration serves as an effective control variable for tuning the degree of substitution, and consequently modulating the functional properties of the modified starch. This is particularly relevant for the design of starch-based materials tailored to specific application requirements, where precise control over the extent of

chemical modification is desired.

Mechanistically, the observed increases in Ac and DS can be attributed to a higher probability of successful substitution reactions resulting from more frequent interactions between acetylating species and available hydroxyl groups. Beyond this kinetic rationale, the realized degree of substitution is also influenced by structural accessibility within the starch granule. Modification occurs more readily in surface-accessible and amorphous regions where diffusion is less restricted, while penetration into more crystalline domains is limited. As a result, at higher reagent concentrations, further increases in Ac and DS become progressively smaller (Ma et al., 2025; Taghavi et al., 2024).

This phenomenon is evident in the data, where the increase in DS between 9% and 12% is smaller than that observed in earlier concentration intervals. This suggests the onset of saturation or reduced substitution efficiency, potentially due to limited reactive sites remaining, competition with hydrolysis reactions, or internal diffusion barriers (Harush et al., 2025; Li et al., 2025). Therefore, the relationship between reagent concentration and substitution level should not be assumed to be indefinitely linear, but rather a system-specific response shaped by the interplay of reagent availability, reaction dynamics, and microstructural accessibility (Pasqualoni et al., 2024). The results confirm that increasing acetic anhydride concentration effectively enhances the acetylation level of sugar palm starch within the operating range studied. However, to achieve optimal reaction efficiency and avoid reagent wastage, structural and kinetic limitations inherent to the starch system during chemical modification must be carefully considered.

3.2 Water-holding capacity (WHC) and oil-holding capacity (OHC)

Figure 2 illustrates the effect of increasing acetic anhydride concentration (0–12%) on the water-holding capacity (WHC) and oil-holding capacity (OHC) of native and acetylated starch (*Arenga pinnata*). Overall, both WHC and OHC increased monotonically with higher levels of acetylation, confirming that chemical modification enhances the starch's ability to retain both aqueous and lipid phases within the tested concentration range.

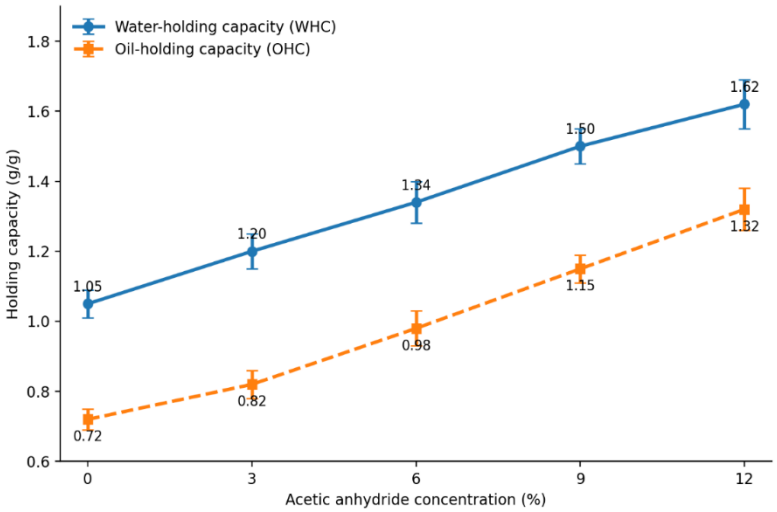

Figure 2. Water- and oil-holding capacity of native aren starch and acetylated aren starch at different acetic anhydride concentrations

Quantitatively, native starch (0% acetylation) exhibited a WHC of 1.05 g/g and an OHC of 0.72 g/g. Upon acetylation, WHC increased to 1.20 g/g (3%), 1.34 g/g (6%), 1.50 g/g (9%), and 1.62 g/g (12%), while OHC similarly increased to 0.82 g/g (3%), 0.98 g/g (6%), 1.15 g/g (9%), and 1.32 g/g (12%). The accompanying statistical annotations (a–e) indicate significant differences across all treatment levels, highlighting acetic anhydride concentration as an effective variable for tuning starch hydration and lipid-affinity properties.

The simultaneous enhancement of WHC and OHC is mechanistically consistent with the dual functional role of acetyl substituents. First, acetylation disrupts intra- and intermolecular hydrogen bonding within starch chains, thereby increasing molecular flexibility and reorganization potential, facilitating the entrapment of water and oil. Second, the acetyl group introduces both polar (carbonyl) and nonpolar (methyl) functionalities. The carbonyl group supports hydrophilic interactions through hydrogen bonding and dipole associations, while the methyl component contributes to hydrophobicity, thereby improving oil retention. These modifications may also be accompanied by changes in granule porosity, surface energy, or capillarity that further enhance binding capacity.

From a structure–function standpoint, the improved WHC and OHC likely reflect integrated molecular-level and mesostructural changes that accompany increasing substitution and acyl incorporation. This is consistent with previous findings showing that enhanced substitution leads to greater retention capacities due to disrupted hydrogen bonding, altered polarity distribution, and potential changes in microvoid or pore structures following drying (Pasqualoni et al., 2024; Li et al., 2025).

Functionally, these results suggest that acetylated sugar palm starches possess improved capabilities for stabilizing multiphase systems such as emulsions, fat-containing gels, or structured moisture systems due to their increased compatibility with both aqueous and lipid components. However, the practical benefits of enhanced WHC and OHC must be considered alongside other relevant properties, such as swelling power, paste viscosity, solubility, and thermal stability, to determine formulation-specific applicability and processing behavior.

3.3 Swelling power, solubility, and fiber-related outcome

3.3.1 Swelling power and solubility

Figure 3 shows the effect of acetic anhydride concentration (3–12%) on the swelling power and solubility of acetylated aren starch. Across the concentration range studied, swelling power increased consistently, whereas solubility decreased, indicating a characteristic divergence in hydration-related behavior attributable to acetylation.

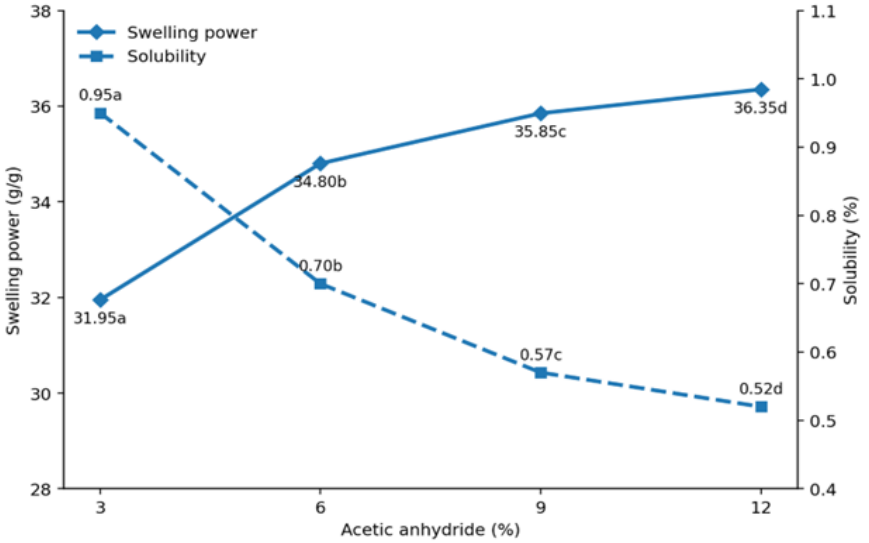

Figure 3. Swelling power and solubility of native aren starch and acetylated aren starch at different acetic anhydride concentrations

Quantitatively, swelling power increased from 31.95 g/g (3%) to 34.80 g/g (6%), 35.85 g/g (9%), and 36.35 g/g (12%). In contrast, solubility decreased from 0.95% (3%) to 0.70% (6%), 0.57% (9%), and 0.52% (12%). Statistical annotations (a–d) confirm that the differences between all treatments were significant for both parameters.

Mechanistically, this inverse relationship reflects two concurrent effects of acetyl substitution. On the one hand, the introduction of acetyl groups weakens intermolecular hydrogen bonding between starch chains, allowing greater water ingress and granule expansion upon heating, resulting in increased swelling power. On the other hand, the increased hydrophobicity of the acetyl groups reduces the solubility of starch components in the surrounding medium, likely due to diminished polar interactions and reduced molecular dispersibility.

This trade-off between swelling and solubility is well documented in chemically modified starch systems and is a central factor in determining the optimal concentration of modifying agents. In practical terms: higher swelling power supports applications requiring water structuring, thickening, and gel formation, especially under thermal processing, and Lower solubility may improve formulation stability against leaching, a desirable trait in processed food systems (e.g., freeze–thaw products, shelf-stable sauces), but may also limit starch dispersibility in cold systems or dilute aqueous phases.

From a functional-food formulation standpoint, these opposing trends underscore the importance of balancing performance attributes rather than maximizing a single metric. As emphasized in recent studies, optimal starch modification conditions are often determined by balancing texture development, stability, and processing tolerance (Cao et al., 2022; Sondari et al., 2022; Yisa et al., 2022; Zhang et al., 2024). Therefore, the swelling–solubility divergence observed in Figure 3 should be interpreted not as a limitation but as a design parameter that can guide application-specific optimization.

3.3.2. Fiber-Related Outcome and Implications for Functional-Food Positioning

Figure 4 presents the effect of increasing acetic anhydride concentration on the fiber content (%) of native and acetylated aren starch, showing an apparent monotonic increase in fiber content as acetylation level increased.

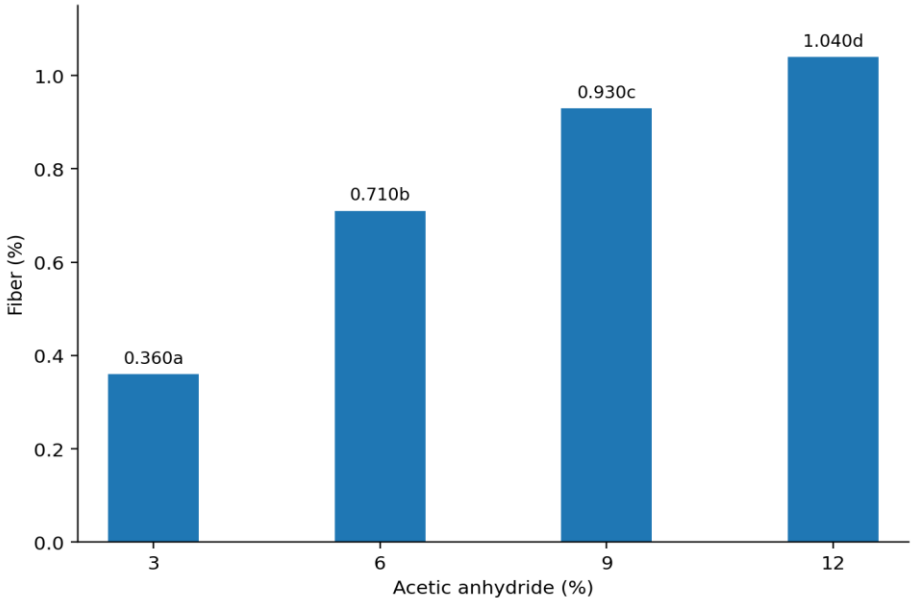

Figure 4 Fiber content of native aren starch and acetylated aren starch at different acetic anhydride concentrations

Fiber content **increased** from 0.360% at 3% acetic anhydride to 0.710% at 6%, 0.930% at 9%, and 1.040% at 12%, with statistically significant differences among treatments as indicated by distinct letter groupings (a–d). This trend suggests that higher degrees of acetyl substitution are associated with a progressively larger fraction of starch components that exhibit reduced enzymatic susceptibility under the analytical conditions employed, consistent with dietary fiber- or resistant starch (RS)-like behavior. Mechanistically, this response is consistent with previous reports indicating that acetylation of starch hydroxyl groups can hinder enzymatic access to glycosidic linkages and induce changes in granule organization, both of which contribute to decreased digestibility and are commonly discussed in relation to chemically modified RS4-type starches. However, recent studies emphasize that resistance to digestion and fiber classification are highly method-dependent. That unambiguous assignment to specific RS categories (e.g., RS2, RS3, or RS4) becomes challenging in systems where chemical substitution and structural reorganization occur simultaneously (Wang et al., 2023; Pasqualoni et al., 2024). Accordingly, although the increased fiber values observed in Figure 4 are directionally supportive of enhanced RS-related functionality, they should not be regarded as definitive evidence of dietary fiber classification without further validation through standardized RS quantification, comparison with native and commercial reference starches, and verification in realistic food matrices where processing history, ingredient interactions, and storage conditions can significantly influence digestibility outcomes (Yang et al., 2023; Kumar et al., 2025). From a functional-food development perspective, the observed increase in fiber content is promising, particularly when considered alongside concurrent improvements in water-holding capacity, oil-holding capacity, and swelling behavior (Figures 1–3), as these combined attributes may support multifunctional performance in formulated products. Nevertheless,

practical application requires careful consideration of sensory attributes, processing behavior, and regulatory acceptance, since increases in fiber content and hydrophobicity may also affect mouthfeel, dispersibility, and consumer perception. Furthermore, successful industrial adoption depends on reproducibility of substitution levels and fiber-related outcomes across batches, scalability of the acetylation process, and compatibility with target formulation matrices and shelf-life requirements (Agvaandorj et al., 2025; Cao et al., 2022). Overall, the results presented in Figure 4 support the conclusion that controlled acetylation can effectively tune sugar palm starch toward functional-food-relevant performance by increasing digestion resistance, while underscoring the need for complementary analyses and application-specific validation to ensure consistency, regulatory compliance, and consumer acceptance.

Conclusions

This study demonstrates that a combined chemical modification strategy involving acetylation, butyrylation, and phosphate cross-linking provides a practical approach to tailor the physicochemical and functional properties of *Arenga pinnata* starch beyond the inherent limitations of its native form. Increasing acetic anhydride concentration within the evaluated range resulted in a systematic increase in acetyl content and degree of substitution (DS), confirming that the substitution level can be reliably controlled by adjusting reagent availability under controlled reaction conditions. These chemical changes consistently translated into functional modifications, including enhanced water- and oil-holding capacities, increased swelling power, and reduced solubility, collectively indicating a shift in hydration behavior driven by weakened intermolecular associations and increased hydrophobic character upon acetyl incorporation.

In parallel, the observed increase in fiber-related outcomes relative to native starch suggests that chemical substitution altered starch accessibility, promoting the formation of starch-derived fractions that are more resistant to digestion under the applied analytical framework. From a functional-food perspective, this trend is directionally favorable; however, it should be interpreted cautiously, as definitive nutritional implications require validation through standardized resistant starch assays and assessment in real food matrices, where processing history and ingredient interactions may significantly influence digestibility and physiological responses. Importantly, the functional gains achieved through acylation must be considered alongside inherent trade-offs, particularly between swelling capacity and solubility, and between hydrophobicity and dispersibility, which together define an application-specific operating window.

Within the scope of this work, phosphate cross-linking further stabilized the modified starch structure, and an optimal condition was identified at 12% STMP/STPP, yielding an acetyl content of 2.740 % and an acetyl DS of 0.112, indicating promising potential for functional ingredient development. Overall, the findings support the conclusion that aren starch can be systematically engineered through combined modification to achieve balanced functional performance relevant to food applications. Nevertheless, successful translation to industrial and functional-food use will depend on reproducibility at scale, comprehensive safety and stability evaluation, and benchmarking against commercial modified starches to ensure that the engineered benefits are maintained under practical processing and storage conditions.

Acknowledgments

Acknowledge the people who have contributed directly or indirectly to your research.

Declaration of Conflicting Interests

The authors would like to acknowledge the administrative and technical support provided by the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Tadulako University. The authors also appreciate the material contributions and equipment support provided by the laboratory facilities.

Funding

The author received no financial support for the research, authorship and publication of this article.

References

Agvaandorj, A., Li, Y., & No, J. (2025). Effects of structural changes in cross-linked mung bean starch on freeze–thaw properties and in vitro digestibility. Foods, 14(4), Article 689. https://doi.org/10.3390/foods14040689

Bhati, N., Bhatt, P., Kumar, V., Tomar, S., Sethi, V., Mittal, A., & Tyagi, L. (2025). Eco-friendly enzymatic starch modification: Precision strategies for tailored industrial and biomedical functionalities. Starch – Stärke, 77(9). https://doi.org/10.1002/star.70087

Cao, C., Wei, D., Xuan, F., Deng, C., Hu, J., & Zhou, Y. (2022). Comparative study on the structure and physicochemical properties of waxy rice starch by phosphorylation, lactylation, and dual modification. Food Science and Technology, 42. https://doi.org/10.1590/fst.18622

Chandak, A., Dhull, S., Chawla, P., Fogarasi, M., & Fogarasi, S. (2022). Effect of single and dual modifications on properties of lotus rhizome starch modified by microwave and γ-irradiation: A comparative study. Foods, 11(19), Article 2969. https://doi.org/10.3390/foods11192969

Compart, J., Singh, A., Fettke, J., & Apriyanto, A. (2023). Customizing starch properties: A review of starch modifications and their applications. Polymers, 15(16), Article 3491. https://doi.org/10.3390/polym15163491

Fu, Y., Jiang, E., & Yao, Y. (2022). New techniques in structural tailoring of starch functionality. Annual Review of Food Science and Technology, 13(1), 117–143. https://doi.org/10.1146/annurev-food-102821-035457

Gupta, R., U., G., Kumar, S., Pipliya, S., Kaur, B., & Srivastav, P. (2025). Synergistic modification of starch polysaccharide via sequential treatments with ultrasonic and cold plasma technology. Journal of Food Processing and Preservation, 2025(1). https://doi.org/10.1155/jfpp/9063007

Harush, M., Levi, C., & Lesmes, U. (2025). Potential of process-induced modification of potato starch to modulate starch

digestibility and levels of resistant starch type III. Foods, 14(5), Article 880. https://doi.org/10.3390/foods14050880

He, M., Jiang, H., Kong, H., Li, C., Gu, Z., Ban, X., & Li, Z. (2022). Engineering starch by enzymatic structure design for versatile applications in food industries: A critical review. Systems Microbiology and Biomanufacturing, 3(1), 12–27. https://doi.org/10.1007/s43393-022-00139-y

Hehamahua, Z., Aziezah, E., Supriyadi, S., Ningrum, A., & Ardhi, A. (2023). Sugar palm starch (Arenga pinnata) modification using microwave and acetylation: Effect of moisture content and microwave power on physicochemical characteristics. Food Research, 7(5), 84–96. https://doi.org/10.26656/fr.2017.7(5).991

Kumar, R., Singh, N., & Khatkar, B. (2023). Effects of A- and B-type starch granules on composition, structural, thermal, morphological, and pasting properties of starches from diverse wheat varieties. Food Bioengineering, 2(4), 373–383. https://doi.org/10.1002/fbe2.12068

Li, X., Yan, J., Gao, J., Xing, F., Gu, Q., Zhao, C., & Liu, J. (2025). Structure, physicochemical properties, and in vitro digestibility of starch in corn flour with different milling processes. Food Chemistry X, 30, Article 102901. https://doi.org/10.1016/j.fochx.2025.102901

Luo, M., Gong, W., Zhang, S., Xie, L., Shi, Y., Wu, D., & Shu, X. (2023). Discrepancies in resistant starch and starch physicochemical properties between rice mutants similar in high amylose content. Frontiers in Plant Science, 14. https://doi.org/10.3389/fpls.2023.1267281

Ma, H., Yang, L., Zhang, D., Chen, H., & Kan, J. (2025). Functionalities of octenyl succinic anhydride wheat starch and its effect on the quality of model dough and noodles. Foods, 14(10), Article 1688. https://doi.org/10.3390/foods14101688

Palencia, M., Quintero, A., & Combatt, E. (2025). Biopolymers contained in cassava starch (Manihot esculenta): Amylose and amylopectin. Journal of Science with Technological Applications, 19, 1–9. https://doi.org/10.34294/j.jsta.25.19.110

Pasqualoni, I., Tolve, R., Simonato, B., & Bianchi, F. (2024). The impact of selected ingredients on the predicted glycemic index and technological properties of bread. Foods, 13(16), Article 2488. https://doi.org/10.3390/foods13162488

Puri, A., Mohite, P., Ramole, A., Verma, S., Kamble, M., Ranch, K., & Singh, S. (2025). Starch science advancement: Isolation techniques, modification strategies, and multifaceted applications. Macromol, 5(3), Article 40. https://doi.org/10.3390/macromol5030040

Sondari, D., Suwarda, R., Pratiwi, F., Muawanah, A., Pramasari, D., & Ahmad, A. (2022). Preparation of starch phosphate microparticle derived from cassava starch. IOP Conference Series: Earth and Environmental Science, 1024(1), Article 012039. https://doi.org/10.1088/1755-1315/1024/1/012039

Subroto, E., Cahyana, Y., Indiarto, R., & Rahmah, T. (2023). Modification of starches and flours by acetylation and its dual modifications: A review of impact on physicochemical properties and their applications. Polymers, 15(14), Article 2990. https://doi.org/10.3390/polym15142990

Supreethee, S., & Vashisth, R. (2025). Unlocking the potential of palm tree starch: A review on modification techniques and its application. International Journal of Food Science & Technology, 60(1). https://doi.org/10.1093/ijfood/vvaf009

Taghavi, E., Andriani, C., Nordin, N., Seruji, A., Rasdi, N., & Hadi, N. (2024). Rheological and stability of mayonnaise-based Pickering emulsions stabilised by modified rice starch granules as a plant-based emulsifier. International Journal of Food Science & Technology, 59(8), 5651–5663. https://doi.org/10.1111/ijfs.17292

Thongkham, C., Kongkachuichai, R., Charoensiri, R., Sahaspot, S., & Wunjuntuk, K. (2024). Reduction of the glycemic index in Thai layer cakes and butter cakes from sago flour. Hong Kong Journal of Social Sciences, (62). https://doi.org/10.55463/hkjss.issn.1021-3619.62.74

Wang, Z., Wang, S., Xu, Q., Kong, Q., Li, F., Lin, L., & Wei, Y. (2023). Synthesis and functions of resistant starch. Advances in Nutrition, 14(5), 1131–1144. https://doi.org/10.1016/j.advnut.2023.06.001

Wu, X., Zhang, J., Yan, X., Wu, X., Zhang, Q., & Luan, M. (2024). An in-depth overview of the structural properties, health benefits, and applications of resistant dextrin. Journal of Food Processing and Preservation, 2024, 1–14. https://doi.org/10.1155/2024/8055063

Yang, J., Meng, D., Wu, Z., Chen, J., & Xue, L. (2023). Modification and solubility enhancement of rice protein and its application in food processing: A review. Molecules, 28(10), Article 4078. https://doi.org/10.3390/molecules28104078

Yisa, B., Musa, D., Evans, E., Shaba, Y., & Amaechi, D. (2022). The effect of phosphorylation (sodium trimetaphosphate) of FARO 40 rice starch for the production of pharmaceutical-grade starch. Chemical Science International Journal, 31, 40–53. https://doi.org/10.9734/csji/2022/v31i5823

Zhang, Z., Feng, Y., Wang, H., & He, H. (2024). Synergistic modification of hot-melt extrusion and nobiletin on the multiscale structures, interactions, thermal properties, and in vitro digestibility of rice starch. Frontiers in Nutrition, 11. https://doi.org/10.3389/fnut.2024.1398380