

Extraction, Modification and Evaluation of Finger Millet Mucilage as Potential Natural Polymer for Pharmaceutical Applications

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Abstract—Starch, a biodegradable and renewable polysaccharide, is widely utilized in various industries due to its biocompatibility and functional versatility. Finger millet (*Eleusine coracana* L.), a nutrient-dense grain, is gaining recognition as a sustainable starch source with potential applications in pharmaceuticals and food industries. This study explores the extraction, modification, and characterization of finger millet starch to enhance its physicochemical properties. Among the extraction methods used—alkaline, acid, and water steeping—water steeping was found to be the most effective in yielding high-purity starch.

Index Terms—*Eleusine coracana*, Excipient, Finger Millet, Polymer, Starch.

To improve its functional attributes, the starch was subjected to cold-water swelling (CWS) and oxidation. Viscosity analysis revealed that CWS starch exhibited the highest thickening ability at lower concentrations, whereas oxidized starch demonstrated superior swelling properties, indicative of enhanced water absorption capacity. FTIR analysis confirmed structural modifications through changes in hydroxyl, carbonyl, and polysaccharide functional groups. The modified starches showed improved solubility, stability, and functional adaptability, making them suitable as pharmaceutical excipients and food additives. This study underscores the potential of finger millet starch as an eco-friendly and cost-effective alternative to conventional starch sources, contributing to sustainable food security and industrial applications. Further research on its large-scale processing and application in novel formulations is recommended.

I. INTRODUCTION

Starch The second most abundant substance in nature after cellulose is starch, a naturally occurring biodegradable renewable polysaccharide that is extensively present in plants. Typically, plants use the photosynthetic process to make starch, which stores solar chemical energy in various plant and algal sections and is advantageous to non-photosynthetic species like humans. Multiple units of amylose and amylopectin joined by glycosidic bonds make up starch. Potatoes, sweet potatoes, yams, rice, corn, and millets are rich sources of starch. etc.[6]

The constraints associated with traditional drug delivery systems, including issues of specificity, bioavailability, biocompatibility, biodegradability, and the need for parenteral administration, have been addressed through the introduction of nanomaterials as carriers for targeted drug delivery. This advancement aims to effectively combat both communicable and non-communicable diseases. Carbohydrate-based polymers have garnered significant attention as drug delivery systems (DDS) due to their biocompatibility, improved encapsulation efficiency, environmentally friendly characteristics, cost-effectiveness, and ability to facilitate controlled drug release. Starch, in particular, has emerged as a favored option for drug delivery, food packaging, and biomedical applications, serving as a filler, disintegrant, and binder. This preference is attributed to its enhanced loading efficiency and the gradual, sustained release of therapeutics, Siddha and Ayurvedic formulations, and bioactive compounds to targeted sites. The abundance, low cost, eco-friendliness, and biocompatibility of starch have further piqued the interest of researchers. Its affordability and safety make it a common excipient in the pharmaceutical sector. [2]

Commercial starches are derived from tubers like potatoes, roots like cassava, and cereals like corn, wheat, and rice. The viscosity, transparency, and water loss through gels (syneresis) of native starches derived from cereals and starchy root and tuber crops vary, however these properties can be altered by altering the native starch. [3]Therefore, in order to provide new qualities that will enhance their functional qualities and their application in pharmaceutical formulations, these starches may undergo physical, chemical, enzymatic, and genetic alterations.[4]

Starch is frequently used as a gelling agent, emulsion stabilizer, thickening, and water binder. If its suspension is heated, it possesses the unusual ability to absorb water and produce gel. However, due to their structural fragility, the native starches have limited functionality for usage in food applications. It is possible for native starch pastes and gels to retrograde or return to their insoluble state. Therefore, to create their range of functioning, starch must be modified or processed.[1]

The physical and chemical characteristics of starch are determined by its content and structure. Plant sources, growing climate, cultivation location, and soil type all affect the ratio of amylose to amylopectin and the overall structure of starch[7]. Native starch undergoes retrogradation, is hydrophilic, and is insoluble in water at room temperature. Furthermore, because it loses its mechanical integrity and degrades at relatively low temperatures, it cannot be melt-processed. These drawbacks have restricted its utilization in polymer applications that demand mechanical strength and thermal stability, particularly in the plastics industry where starch must typically be melted.

Finger millet

Millet starch is employed in various industries in its natural and modified forms. The natural constraints of unmodified millet starch restrict its use in industrial settings; however, both the unaltered and modified forms are frequently employed as thickening agents and binders in various products, including baked goods, meat products, and snack seasonings.[5]

Finger millet (*Eleusine coracana L.*), a member of the Poaceae family commonly referred to as "ragi," is a nutritious grain that is abundant in fiber, protein, and essential minerals. It possesses a sweet and subtly nutty taste, making it a popular ingredient in traditional cuisines of India and Africa, where it is utilized to prepare porridges, bread, and various other

dishes. This grain is significant among minor millets, as it enhances food security and nutritional stability in semi-arid regions.[4]

The seed coat of millets contains a substantial concentration of bioactive compounds, including phenolic acids such as ferulic acid, caffeic acid, vanillic acid, gallic acid, and quercetin. Numerous studies have established their importance and efficacy as antioxidants, anti-carcinogenic agents, anti-inflammatory substances, antiviral agents, and neuroprotective agents against severe health conditions, including cancer, cardiovascular diseases, diabetes, hypertension, high cholesterol, and neurodegenerative disorders. [5]The phenolic compounds found in millets have been extensively documented for their ability to counteract collagen glycation and cross-linking, nephritis, diabetes, wound healing, oxidative stress, enzyme inhibition, osteoporosis, and microbial activity. This highlights the in vitro and in vivo research conducted on the pharmacological significance of these compounds.[6] As a filler, glidant, thickening, binder, disintegrant, gelling, bulking, and water retention agent, starch is one of the most commonly used excipients in the food and pharmaceutical sectors. Starch's granular structure and functional characteristics have also been altered by physical and chemical means to remove some of their unwanted qualities and make them more appropriate for a given purpose.[7] With the versatility of starches in various drug dosage forms, there is the need to continue to develop new starch excipients with suitable properties to meet the special needs of drug formulators.

The alteration of finger millet starch via chemical means involves the incorporation of new chemical constituents or functional groups, resulting in a change in the starch's properties. Consequently, this modification affects the functional characteristics of the starch, such as its capacity to absorb water, swell, dissolve, and form gels. These chemical processes include substitution and elongation reactions.

Finger millet has the potential to replace major cereals as a sustainable raw source for the production of resistant starch, a type of starch that resists digestion in the small intestine however metabolized by gut microflora causing the production of short-chain fatty acids such as acetate, butyrate, propionate. Resistant starch behaves like dietary fiber, it helps to maintain gut health, control serum glucose level, and helps to

control body weight, making it a valuable ingredient for functional food product development.[4]

why modify starch?

- To improve the texture, structure, and consistency of food
- To increase shelf stability
- To create new functional properties
- To eliminate shortcomings of native starches that is modified starch used for
- Food: As a thickening agent, stabilizer, or emulsifier
- Pharmaceuticals: As a disintegrant, binder
- Coated paper: As a binder

II. MATERIALS AND METHOD

A. MATERIALS

Finger millet was collected from the local store from Solapur and checked for any miscellaneous object from the grains and cleaned

A well-maintained pH of distilled water was procured from lab for the steeping of the solution

A pH of 7 was maintained through the process with NaOH and 0.1N HCL

B. METHOD

Different methods of starch were used to extract the starch from the finger millet like alkaline, acid and water steeping method, out of which water steeping was found to be more productive in yield and all the constituents were observed in the starch which was confirmed with tests.

Starch preparation

The above methods were used to extract the finger millet starch, in which water steeping is more effective than alkaline method followed by acid steeping with all the constituents, Finger millet was grinded with mixer and flour was prepared.[9] The powder was taken in the ratio of 100gm :250ml. The solution was kept for 24 hrs to mix properly. The solution is mixed and centrifuged for 30min with 6000 rpm for 15 min with Remi's centrifugation machine till the starch is colourless and kept washing till it is white The starch is stored in dry place and used to carry out the reactions

III. MODIFICATION OF STARCH

Cold water starches

A distinct category of "instant" starches includes products that feature gelatinized, intact granules, specifically amorphous granules, which exhibit significant swelling when introduced into an aqueous environment at room temperature, without the need for cooking (BeMiller and Huber, 2015). These starches represent a unique form of pregelatinized starch and are commonly referred to as cold-water-soluble starches. However, traditional pregelatinized starches typically demonstrate greater solubility in room-temperature water (without shear application) compared to these particular products. Therefore, the author prefers the designation GCWS or simply cold-water-swelling (CWS) starches for this group. When incorporated into room-temperature aqueous systems, GCWS starches yield viscosities and gel properties that are more akin to those of cook-up starches than those of conventional pregelatinized starches.[7]

1. Procedure for preparing granular cold-water swelling starch on gram scale

GCWSS was produced by aqueous ethanol treatments at elevated temperature. The ethanol concentration ranged from 48 to 68% (v/v) and the treatment temperatures were 80, 85, 90, or 95 °C. Regular maize starch [20.0 g dry matter (dm) basis] (cf. Section 2.5) was suspended in a water:ethanol mixture [1/9 (w/w) starch dm/solvent] with varying ethanol concentration in a pressure resistant Schott bottle (250 ml) equipped with a leak proof screw cap. The bottles were hand shaken to disperse the starch and then continuously shaken in a water bath. After 30 min at the desired temperature, the suspensions were kept for 60 min at room temperature (RT), 200 ml ethanol was added and bottle contents were suspended. The starch suspensions were Büchner filtered and washed several times with ethanol. The resulting starch pellet was finely chopped with a spatula, spread over a paper filter sheet, airdried overnight at RT, sieved (mesh size: 150 m) and stored in air-tight plastic bottles. Sample codes are of the format ETSx%/y °C where ETS stands for ethanol treated starch, x% stands for the volume percentage of ethanol in the used water: ethanol mixture and y °C for the treatment temperature. The subscript 'waxy' is used when waxy instead of regular maize starch was used. An alternative treatment for overnight air-drying included

oven-drying for 60 min at 115 °C (ETSx%/y °C 115 °C).[8]

Oxidation of starch

Another technique for chemical alteration is oxidation. It leads to the substitution of carboxyl (R-COOH) and carbonyl (C=O) groups for hydroxyl groups, changing the structure of starch and affecting its properties [130–132]. The oxidized starch was found to have increased shear stability, swelling capacity, and solubility of starch because of a significant decrease in breakdown viscosity, depolymerization, and the presence of the hydrophilic group, respectively.

Procedure for oxidation

Starch oxidation was performed in accordance with the methodology established by Dias et al. (2011), incorporating specific modifications. A 200 g dry weight starch sample was suspended in 500 mL of distilled water within a 1 L glass reactor, which was then heated to 40 °C and treated with sodium hypochlorite. The pH of the starch slurry was adjusted to 7.0 using 0.5 mol equi/L NaOH and 0.5 mol equi/L HCl. After the addition of sodium hypochlorite, the pH was maintained at 7.0 with 0.5 mol equi/L NaOH for an additional duration of 60 minutes. The slurry was subsequently filtered through a Buchner filter funnel, washed with twice the volume of distilled water, and dried. Finally, the starch underwent FTIR analysis and was compared to standard FTIR results for starch.10

IV. RESULTS AND DISCUSSION

The presence of the starch was confirmed with the test of starch confirmatory test

The centrifuged extract was collected and mixed with the solution of KOH and results were observed. the change in the colour of the solution shows the presence of starch in the extract

Confirmatory Test for starch – Take aq. Extract 5% 5ml KOH solution binary colouration

Viscosity measurements are conducted to assess the quality and performance of products associated with fluid science. Various techniques exist for measuring viscosity, which depend on the materials involved and the specific conditions of the experiment. Choosing the appropriate viscometer for your study can be quite challenging. A wide range of viscometers is available for viscosity measurements; simpler models may involve timing the duration of a liquid drop from a stick, while more advanced instruments provide automated and precise recordings. This variety complicates the selection process for users aiming for accurate measurements. The viscosity was analyzed using a Brookfield viscometer equipped with spindle number 63. The results were obtained from different concentrations of starch mixed with water, which was heated until it dissolved, resulting in a homogeneous mixture.

Viscosity

1% Solution: At a 1% concentration, CWS starch has the highest viscosity of 115, followed by normal starch at 103, and oxidised starch at 96. This indicates that CWS starch forms a thicker solution compared to the other two at this concentration.

3% Solution: For the 3% solution, normal starch has the highest viscosity of 144, whereas CWS starch and oxidised starch have viscosities of 120 and 122, respectively. This suggests that normal starch forms a thicker solution at this concentration.

5% Solution: At a 5% concentration, CWS starch exhibits the highest viscosity of 344, significantly higher than both normal starch (247) and oxidised starch (230). This indicates that CWS starch has the most substantial thickening effect at higher concentrations.

Viscosity (spindle no. 63)	Normal Starch	CWS Starch	Oxidized Starch
1% solution	103	115	96
3% solution	144	120	122
5% solution	247	344	230

Table 1 Viscosity of different solutions

pH

pH is an important quantity that reflects the chemical conditions of a solution. The pH can control the availability of nutrients, biological functions, microbial activity, and the behaviour of chemicals. Because of this, monitoring or controlling the pH of soil, water, and food or beverage products is important for a wide variety of applications.

Solution	Normla starch	cws starch	Oxidised starch
1%solution	9.6	6	7.1
3%solution	10	6.8	6.1
5%solution	9.4	6.4	6.8

Table 2 pH OF Different solutions

Normal Starch: The pH values indicate that normal starch solutions are more alkaline across all concentrations.

CWS Starch: Cold Water Soluble (CWS) starch maintains a relatively lower pH compared to normal starch, making it slightly more acidic.

Oxidised Starch: The pH of oxidised starch remains fairly consistent across different concentrations, showing a moderate pH level.

Normal Starch: The pH values indicate that normal starch solutions are more alkaline across all concentrations.

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SWELLING INDEX

The swelling index is a measure of the ability of starch granules to absorb water and swell upon hydration. It is influenced by the structure and composition of the starch molecules. Here's a brief explanation of how the swelling index is determined:

Preparation: A 1% solution of each type of starch is prepared by dispersing the starch in water and allowing it to swell.

Measurement: The volume of the starch solution is measured before and after swelling. The swelling index is calculated as the ratio of the swollen volume to the original volume of the dry starch granules.

Comparison: The swelling index values are compared to understand the water absorption and swelling behaviour of different starches.

Swelling index	Normla starch	cws starch	Oxidised starch
1%solution	0.685	0.713	0.862

Table 3 Swelling index of different solutions

Normal Starch: The swelling index for the 1% solution of normal starch is 0.685. This indicates the extent to which normal starch granules absorb water and swell.

CWS Starch: Cold Water Soluble (CWS) starch has a swelling index of 0.713 for the 1% solution, which is slightly higher than that of normal starch. This

suggests that CWS starch has a better ability to absorb water and swell compared to normal starch.

Oxidised Starch: The oxidised starch shows the highest swelling index of 0.862 for the 1% solution. This means oxidised starch has the greatest capacity to absorb water and swell among the three types of starches.

FTIR of finger millet extracted starch

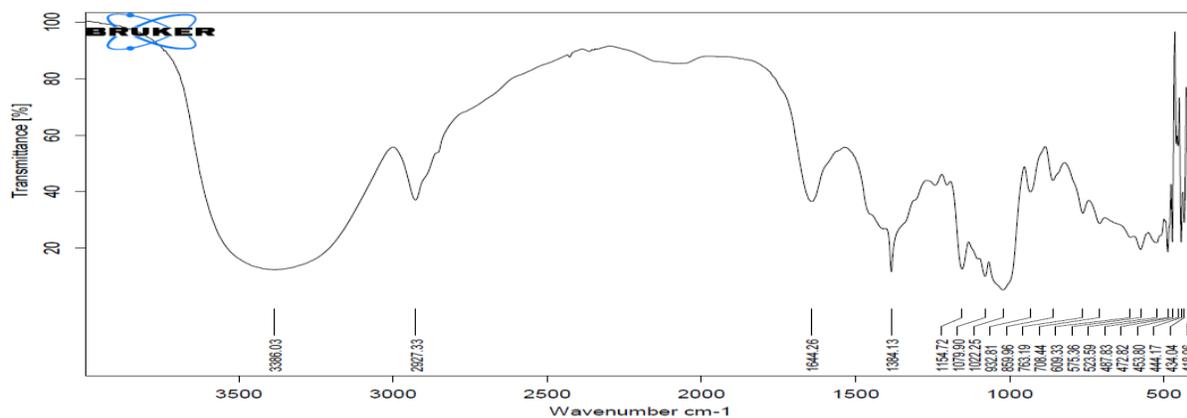


Figure 2. FTIR interpretation of finger millet extracted starch

Wavenumber (cm ⁻¹)	Possible Interpretation
3386.03 cm ⁻¹ :	O-H stretching vibrations, indicating the presence of hydroxyl groups.
2927.33 cm ⁻¹	C-H stretching vibrations, commonly found in alkanes.
1644.26 cm ⁻¹	C=O stretching vibrations, characteristic of carbonyl compounds
1384.13 cm ⁻¹	C-H bending vibrations, indicating the presence of alkanes.
1154.72 cm ⁻¹	C-O stretching vibrations, associated with alcohols, ethers, and esters
1079.90 cm ⁻¹	C-O stretching vibrations, commonly found in alcohols and ethers.
1022.25 cm ⁻¹	C-O stretching vibrations, typical of alcohols and ethers
932.81 cm ⁻¹ :	C-H bending vibrations, found in alkanes
859.96 cm	C-H bending vibrations, indicating the presence of alkane

Table 4 FTIR interpretation of finger millet extracted starch

FTIR of cold-water starch modified

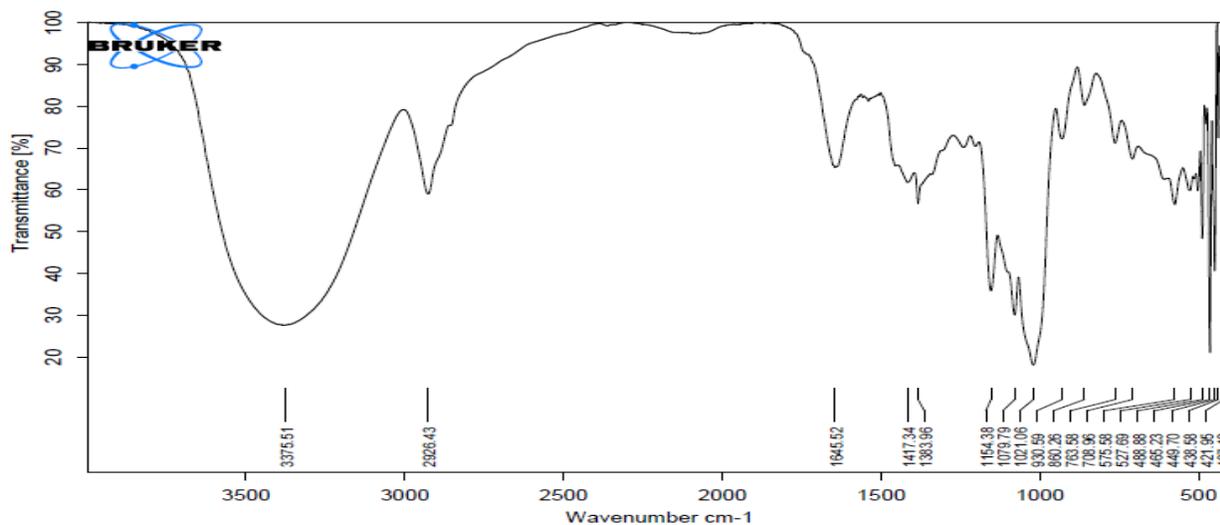


Figure 3 FTIR interpretation of cold-water starch modified

Wavenumber (cm ⁻¹)	Possible Interpretation
3375.51	O-H stretching vibrations (hydroxyl groups)
2926.43	C-H stretching vibrations (aliphatic chains)
1645.52	Bending vibrations of water molecules (absorbed water)
1417.34	C-H bending vibrations (carbohydrates)
1383.96	C-H bending vibrations (polysaccharides)
1154.38, 1079.79, 1021.06	C-O stretching vibrations (polysaccharides)
930.59	Skeletal vibrations of starch structure
860.26, 763.58, 708.96	Various bending and stretching vibrations (fingerprint region)
575.58, 527.69, 488.88, 465.23, 449.70, 438.58, 421.95, 407.12	Various bending and stretching vibrations (fingerprint region)

Table 5 FTIR interpretation of cold-water starch modified

FTIR interpretation of oxidized starch modified

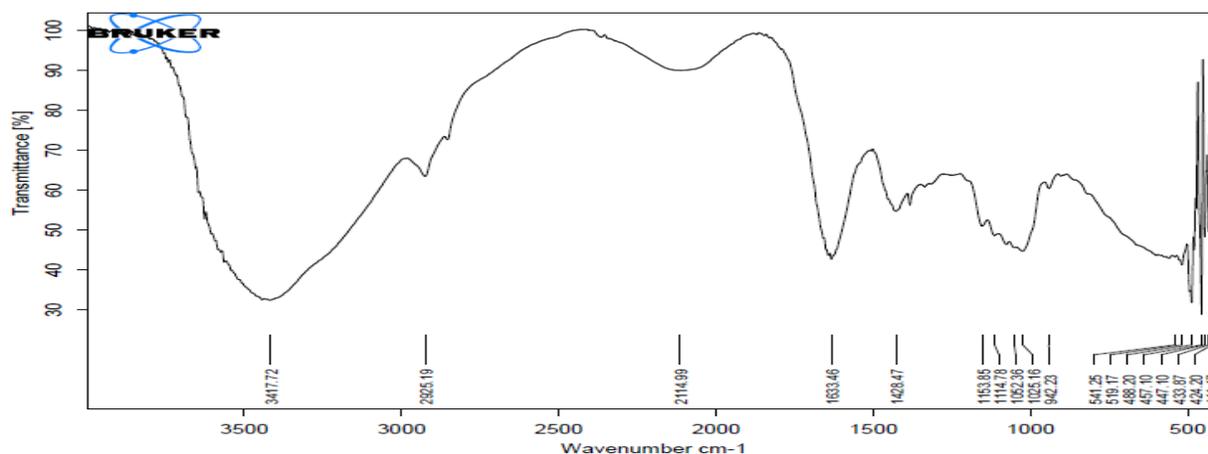


Figure 4 FTIR interpretation of oxidized starch modified

Wavenumber (cm ⁻¹)	Possible Interpretation
3417.72	O-H stretching vibrations (hydroxyl groups)
2925.19	C-H stretching vibrations (aliphatic chains)
2114.99	Possible specific functional groups introduced during oxidation
1633.46	Bending vibrations of water molecules (absorbed water)
1428.47	C-H bending vibrations (carbohydrates)
1153.85, 1114.78, 1052.36, 1025.16	C-O stretching vibrations (polysaccharides)
942.23	Skeletal vibrations of starch structure
541.25, 519.17, 488.20, 457.10, 447.10, 433.87, 424.20, 411.17	Various bending and stretching vibrations (fingerprint region)

Table 6 FTIR interpretation of oxidized starch modified

V. CONCLUSION

Finger millet starch has the potential to contribute to food security and sustainable development, particularly in regions where finger millet is widely cultivated. Finger millet starch is a good source of dietary fiber, resistant starch, and minerals, making it a nutritious and potential health promoting ingredient. Despite its high starch content, millet is often overlooked as a starch source because of limited awareness, its starch properties are not well understood.

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