

REVIEW ARTICLE

Starch digestibility: How single, double, and multiple physicochemical modifications change nutritional attributes of starch?

Hadis Rostamabadi¹  | Ilkem Demirkesen² | Behic Mert³ | Sreejani Barua⁴ |
Rosana Colussi⁵ | Sabrina Feksa Frasson⁶ | Yong Wang⁷ | Seid Reza Falsafi⁸ 

¹Department of Food Science and Technology, School of Nutrition and Food Science, Nutrition and Food Security Research Center, Isfahan University of Medical Sciences, Isfahan, Iran

²Department of Animal Health, Food and Feed Research, General Directorate of Agricultural Research and Policies, Ministry of Agriculture and Forestry, Ankara, Turkey

³Department of Food Engineering, Middle East Technical University, Ankara, Turkey

⁴Indian Institute of Technology Kharagpur, Kharagpur, India

⁵Center for Chemical, Pharmaceutical and Food Sciences, Federal University of Pelotas, Pelotas, Campus Universitário, Pelotas, Rio Grande do Sul, Brazil

⁶Department of Agroindustrial Science and Technology, Federal University of Pelotas, Pelotas, Rio Grande do Sul, Brazil

⁷School of Chemical Engineering, UNSW, Sydney, New South Wales, Australia

⁸Department of Agricultural Engineering, Food Science and Technology Division, Safiabad Agricultural Research and Education and Natural Resources Center, Agricultural Research, Education and Extension Organization (AREEO), Dezful, Iran

Correspondence

Seid Reza Falsafi, Isfahan Endocrine and Metabolism Research Center, Isfahan University of Medical Sciences, Isfahan, Iran.
Email: Falsafi.r@gmail.com

Abstract

The ever-increasing ranges of starch applications have been restricted by some of its inherent adverse characteristics like retrogradability, gel opacity, low resistibility to variations of pH, and elevated shear/temperatures. Starch modification through various physical, chemical, and enzymatic methods has been proposed as the most mature platform to tackle such drawbacks. Along with their outstanding potential in enhancing the starch's technofunctional characteristics, physicochemical modifications could remarkably customize starch nutritional/digestibility attributes. For instance, physical modifications could remarkably change starch digestibility by manipulating the granular architecture while chemical approaches change it by altering the chemical structure of starch molecules, making them unrecognizable to digestive enzymes. Such alterations could even be more challenging upon applying a combination of starch modifications. The changes in starch digestibility through its modification via single, double, and multiple modifications have been overviewed in this review.

KEYWORDS

digestibility, physicochemical modification, rapidly digestible starch, resistant starch, slowly digestible starch, starch

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial](https://creativecommons.org/licenses/by-nc/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

© 2024 The Authors. *Food Frontiers* published by Nanchang University, Northwest University, Jiangsu University, Zhejiang University, Fujian Agriculture and Forestry University and John Wiley & Sons Australia, Ltd.

1 | INTRODUCTION

Starch, as the most abundant nature-inspired carbohydrate in the human diet, naturally occurs in a broad range of food crops, that is, legumes, cereals, roots, tubers, fruits, as well as processed foods. By virtue of its promising characteristics, starch has been widely implicated in designing well-structured gels/films, developing foams, stabilizing emulsions, and thickening/texturizing foods (Chen et al., 2023). However, it is needless to say that the ever-growing food applications of starch have been challenged by some of its inherent shortcoming such as limited shear/temperature resistibility and unfavorable retrogradability/opacity of the paste. At present, starch modification via chemical, physical, and enzymatic approaches is the most mature platform to meet such bottlenecks where a partial change in chemical structure/physical architecture of the starch molecules could render starch granules resistant against applied shear upon heating, boost the paste clarity, customize the product rheology, as well as restrict the syneresis tendency of the gel by intensifying its water retention capacity (Falsafi, Maghsoudlou, Aalami, et al., 2019; Fan & Picchioni, 2020).

Nonetheless, aside from their substantial impacts on physicochemical and technofunctional attributes, starch modification could also provoke remarkable variations in starch digestibility (Olawoye & Gbadamosi, 2020). From the digestion point of view and given the great importance of controlling the absorbed glucose following the consumption of starchy foods in the context of community health, numerous efforts have been made to classify starches based on their digestion behavior. Englyst et al. (1992) have been the pioneers in studying the digestibility of starch. They developed the most famous method of classifying starches based on their digestion rate where the starch was digested in a simulated gastric/intestinal phase and the extent of released glucose was measured in various time intervals. According to this method, starch was compartmentalized into three distinctive fractions that is (i) rapidly digestible starch (RDS, a starch fraction that hydrolysis upon the first 20 min of digestion and results in a fast increase in blood glucose level); (ii) slowly digestible starch (SDS, a starch portion that hydrolysis completely but at a slower rate (20–120 min); and (iii) resistant starch (RS, a starch fraction that is not digested upon gastric and intestinal phase and transferred intact to the colon, where it can be fermented by probiotic bacteria) (Englyst et al., 1992).

As mentioned earlier, starch digestibility can be deliberately/inadvertently manipulated upon starch modification. For instance, hydrothermal treatments (i.e., annealing [ANN] and heat-moisture treatment [HMT]) have long been recognized as efficient approaches for enhancing the RS content of starch (Lee et al., 2012; Xu et al., 2018). Likewise, among chemical modification strategies, cross-linking has been a potent tool commercially utilized for the production of RS (Falsafi, Maghsoudlou, Aalami, et al., 2019). However, hydroxypropylation provoked variable changes in starch digestibility where it intensified the digestion rate of ungelatinized starch but hindered the digestibility of gelatinized counterparts (Dreher et al., 1984). In this regard, the starch source, the type of modification

applied, as well as the modification condition are determinant factors governing the starch digestibility.

Considering the inevitable role of starch on human health, in almost all recent studies on starch modification, along with other physicochemical attributes, the digestion behavior of starch is also investigated (Han et al., 2020; Punia, 2020). There are also some valuable efforts on assessing the digestibility of starch within the food/food matrices (Singh et al., 2010). However, the current literature lacks a comprehensive overview of the impact of different modifications on nutritional aspects of starch. With this perspective, in the present paper, we first focus on recent advances in the approaches employed for determining starch digestion behavior. We further comprehensively discuss the impact of physical, chemical, dual, and multiple modifications on starch digestibility.

2 | DETERMINATION OF STARCH DIGESTIBILITY VIA VARIOUS IN VITRO AND IN VIVO APPROACHES

2.1 | In vitro methods

2.1.1 | Static methods

There have been numerous in vitro techniques in the past to measure the extent of starch digestibility via hydrolysis, which vary in terms of sample preparation, the use of amylases and proteases, and the validation of results upon in vivo methods (Figure 1). Englyst et al. (1992) simulated the digestive behavior of starch in the small intestine using glucoamylase and categorizes it based on its biological availability into RDS (digested within 20 min), SDS (digested within 20–120 min), and RS (resistant to digestive enzymes in the small intestine). This has become one of the classic in vitro methods widely adopted for studying starch digestion. Another classic method is the use of 3,5-dinitrosalicylic acid, which is simple to operate (using only pancreatic amylase) but has complex hydrolysis products that introduce uncertainty in the analysis results (Falsafi, Maghsoudlou, Aalami, et al., 2019). Recently, Englyst et al. (2018) conducted an interlaboratory validation of the methods for determining RDS and SDS, and the results showed acceptable measurement uncertainty and validated the transferability of the approach among laboratories. This provides a credible basis for the evaluation of different types of starch, especially SDS, in food and the human body.

2.1.2 | Dynamic methods (human-mimicking/near-real)

Dynamic methods for studying starch digestibility involve the use of systems that mimic the human digestive process in order to more accurately understand how starch is digested and absorbed in the body. These methods can provide valuable information on the factors that influence starch digestibility and can be used to optimize the diges-

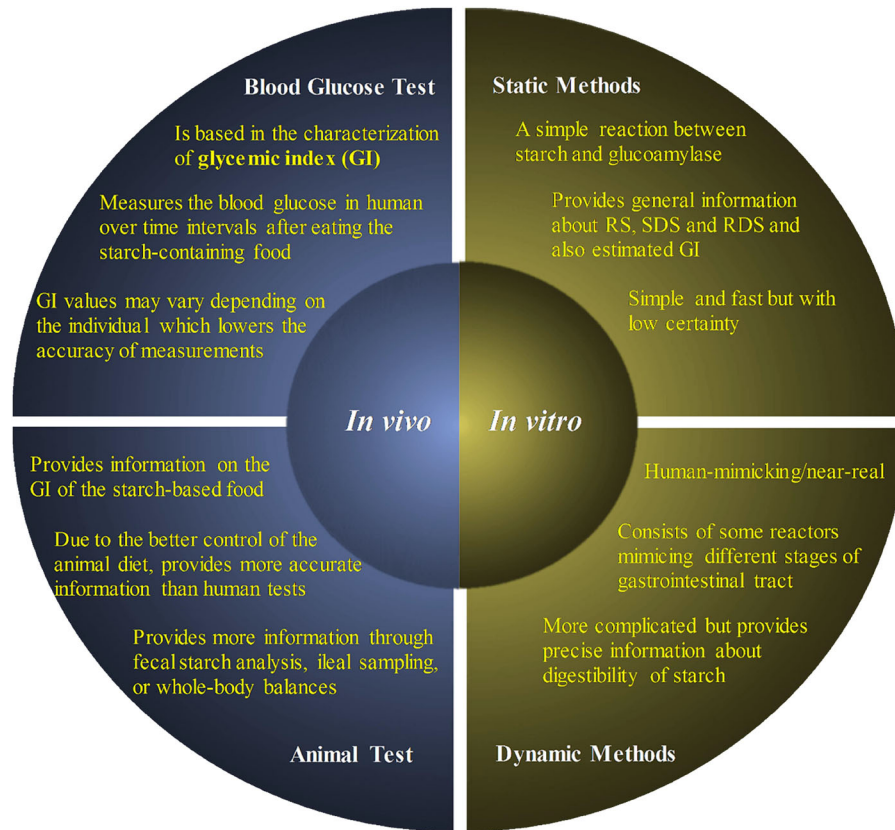


FIGURE 1 Determination of starch digestibility via various in vitro and in vivo approaches.

tion and absorption of starch in various food products. One dynamic method for studying starch digestibility is the near-real dynamic in vitro human stomach system developed by researchers at Soochow University in China (Wang, Wu, et al., 2019). This system consists of a series of reactors that mimic the different stages of digestion in the human stomach, including the presence of hydrochloric acid and pepsin in the first stage and the action of bile and pancreatic enzymes in the second stage. This system allows researchers to study the effects of various factors, such as pH and enzyme activity, on the digestion and absorption of starch. Another dynamic method for studying starch digestibility is the model stomach system developed by Paul Singh and colleagues at the University of California, Davis, which mimic the different stages of digestion in the human stomach and small intestine (Kong & Singh, 2010). The digestion system developed by the Riddet Institute in New Zealand is another dynamic method for studying starch digestibility with the focus on mimicking human stomach digestion (Ferrua & Singh, 2015). The TNO digestion system is a dynamic method for studying starch digestibility that was developed by the Netherlands Organization for Applied Scientific Research (TNO) (Wu & Chen, 2020). The system has also been used to study the effects of food processing methods on starch digestibility as well as to investigate the potential of different food ingredients to modify starch digestibility. There are more dynamic digestion systems developed by researchers in Belgium, the United Kingdom, and France, which are also emerging.

2.2 | In vivo methods

2.2.1 | Human blood glucose test

Typically, the in vivo method for determining starch digestibility in humans is characterized by the glycemic index (GI) (Lal et al., 2021). This method involves testing blood sugar levels in a minimum of 10 young healthy volunteers who have fasted for around 10 h. The volunteers are given either 50 g of d-glucose in 200 mL of water or an equal amount of available carbohydrates in the form of a test food. The experiments with the test food and reference food (d-glucose or white bread) are conducted on various intervals and repeated to obtain an average value. The volunteers are instructed to consume the food or glucose at a comfortable pace, and the test meals are served with a drink that does not contain sugar. Blood sugar levels are measured at 30-min intervals for 4 h, and the data is plotted on a graph to obtain the incremental area under the curve (IAUC) for the reference food and test food. The GI rating is then calculated as the IAUC for the test food divided by the IAUC for the reference food, multiplied by 100. The in vitro method for determining GI involves simulating the digestive process in the mouth, stomach, and small intestine using enzymes and measuring the release of free glucose at various time points.

New blood glucose testing methods, such as continuous glucose monitoring system that can detect glucose levels for several days

and provide real-time feedback, can greatly facilitate *in vivo* starch digestibility studies by eliminating the need for repeated blood sampling and testing (Falsafi et al., 2022). Other noninvasive methods, such as smart watches that display blood sugar levels, are also being developed, although their accuracy still needs to be improved (Sehgal et al., 2021). These advancements allow for more convenient and efficient testing of starch digestibility in humans.

Although the GI method is widely used and provides valuable information about the digestibility of starch in the human body, it has some limitations. It only measures the effect of the starch on blood sugar levels and does not consider other factors such as the effect on insulin levels or the effect on satiety. In addition, the GI values may vary depending on the individual, the amount and type of other foods consumed with the test food, and other factors such as the physical form of the food and the cooking method.

2.2.2 | Animal test

To evaluate starch digestibility using animal as *in vivo* method, a sample of the starch source is fed to the animal and the amount of starch that is digested is measured over a specific time period (Martens et al., 2019). This can be done using various techniques, such as fecal starch analysis, ileal sampling, or whole-body balances. The advantage of this method is that it allows for the evaluation of the digestibility of the starch in the context of the entire diet and the digestive physiology of the animal. However, this method can be time-consuming and may not be suitable for all types of starch sources.

3 | CHANGES IN STARCH DIGESTIBILITY UPON SINGLE MODIFICATIONS

3.1 | Impact of single physical modifications on starch digestibility

Physical modification of starch is simple, inexpensive, and safe, as it does not use chemicals or biological reagents (Colussi et al., 2020). The most popular physical modifications are pre-gelatinization and hydrothermal treatments as ANN, HMT, steaming, and extrusion (Fonseca et al., 2021; Garcia-Valle et al., 2021). Recently, new methods involving emerging technologies (i.e., ultrasonication [US], high-pressure processing [HPP], microwave, radio frequency treatments, pulsed electric field, ionizing radiation, cold plasma treatment, and ozonation) have been widely developed. Although all the methods mentioned above are physical modifications, depending on the treatment condition and the intensity applied, various changes in the physical and chemical structure of the starch granule may occur. For instance, modification by gamma irradiation could result in the formation of carbonyl compounds (e.g., formaldehyde, acetaldehyde, acetone, dihydroxyacetone, and acids); UV-irradiation results in crosslinking, oxidative photodegradation (in the air), depolymerization, and dextrinization via free radical generation; cold plasma induces free radicals

on starch molecules, and ozonation may form carbonyl and carboxyl groups (BeMiller & Huber, 2015). Overall, wherever the starch modification boosts the access of enzymes to starch molecules, a higher digestibility (higher RDS and less RS contents) is expected. On this ground, the alterations in physicochemical and structural attributes of starch through physicochemical modifications could induce changes in starch digestibility through various phenomena, such as (i) increasing the starch digestibility due to the loss of granule integrity and/or disintegration of starch granular structure, (ii) enhancing the starch resistibility to digestion due to the formation of amylose-amylose or amylose-amylopectin double helices with a higher degree of crystallinity, (iii) increasing the RS content following the rearrangement of starch molecules within granules into architectures with more perfection, and (iv) reducing the starch digestibility due to the formation of new chemical bonds (through cross-linking, esterification [ES], oxidation, or etherification), as the new bonds cannot be recognized by amylolysis enzymes, and they also block the move of enzymes over the backbone of starch molecules.

3.1.1 | Starch pre-gelatinization

The pre-gelatinization process is based on gelatinization, followed by drying under conditions that enable low or any molecular reorientation. The process can be done by direct heating or extrusion (Agama-Acevedo et al., 2018; Garcia-Valle et al., 2021) and the resulted starch becomes soluble in water at room temperature. This modification has indicated to significantly increase the starch digestibility.

Garcia-Valle et al. (2021) studied the effect of pre-gelatinization using extrusion on mango and amaranthus flours and verified its effects on texture, pasting properties, and *in vitro* starch digestibility. After modification, mango starch presented 56.3% of gelatinization and amaranth starch 51.3% (Table 1). For both flours, the extrusion process promotes a sharp increase in the maximum extent of hydrolysis, with higher hydrolysis for amaranth than mango flour. The lower digestibility of mango starch despite its higher percentage of gelatinization was explained by the more intact granular structure, which made it difficult for enzymes to access it during the *in vitro* digestion process. Agama-Acevedo et al. (2018) pregelatinized high-amylose starch by autoclaving and found a marked reduction in RDS and SDS levels. However, the greatest reduction was seen in the levels of RS, where in amylo maize V, it went from 69.1 to 21.1 and in amylo maize VII, from 81.2 to 30.6.

3.1.2 | Granular cold water swelling starch

The granular, cold-water swelling starch is intact gelatinized granules that swell extensively (without heating) when put in an aqueous medium, working as pregelatinized starch. There are several processes for the elaboration of this type of modified starch. Majzoubi and Farahnaky (2021), in their review paper, explain in detail the differences between each method, all of which aim to maintain the granular struc-

TABLE 1 An overview of the impact of physical modifications on starch digestibility. Rice starch with high amylose, medium amylose, and low amylose

Type of modification	Starch source	Modification condition	Digestibility determination method	Major findings relevant to starch digestion	Reference
Pre-gelatinization	High amylose maize (H-Ylon VII)	Starch: water ratio 1:2.5 (w/w) autoclave conditions: 121°C for 30 min During condition: hot air at 40°C for 24 h or freeze dried	In vitro Englyst et al. (1992)	<ul style="list-style-type: none"> RDS and SDS increased upon treatment RS content diminished by about 25% Oven drying resulted in more compact granular structures (Figure 1j–s) and was more effective in enhancing the RS than freeze-drying (Figure 2s) 	Agama-Acevedo et al. (2018)
	Mango and amaranth flour	Starch: 35% moisture Soaking for 18 h in a plastic bag Single screw-extruder for 50°C for all zones	In vitro	<ul style="list-style-type: none"> Increases in in vitro starch digestibility and changes on functional properties Reduction of resistant starch Increase in RDS Reduction in SDS for amaranth flour and increase for mango starch 	Garcia-Valle et al. (2021)
Granular cold water swelling starch	Maize	Mixture of 20 g starch with 40 mL of 50% ethanol (v/v) Incubation at 80°C for 30 min Storage at room temperature for 3 h Washing twice with 50% ethanol Freeze-drying	In vitro	<ul style="list-style-type: none"> Ethanol treatment disrupts the crystallinity of granules Increasing in the amyolytic susceptibility The content of RDS increased considerably There is a reduction in the content of RS 	Zhong et al. (2022)
Heat-moisture treatment	Rice starch with high amylose, medium amylose, and low amylose	Starches moisture of 15%, 20%, and 25% Heating in an autoclave at 110°C for 1 h	In vitro	<ul style="list-style-type: none"> Loss of physical integrity of low-amylose starch granules treated at 25% moisture Increasing of enzymatic susceptibility Reduction of the relative crystallinity The higher moisture content of the treatment lead to a higher enzymatic susceptibility, regardless of the amylose content 	da Rosa Zavareze (2012)
	Potato	Starches moisture of 15%, 20%, and 25% Heating in oven at 110°C for 16 h	In vitro	<ul style="list-style-type: none"> Reduction in the glucose release rate Higher moistures during HMT enhanced digestibility Reduction of 12% of digestion in the 90 of simulated small intestine 	Colussi et al. (2020)

(Continues)

TABLE 1 (Continued)

Type of modification	Starch source	Modification condition	Digestibility determination method	Major findings relevant to starch digestion	Reference
Heat-moisture treatment and annealing	Sohpliang	Heat-moisture treatment Starches moisture 20%, 25%, and 30% Heating in oven air oven at 100°C for 16 h. Annealing Starches moisture 70%, 75%, and 80% Heating air oven at 50°C for 24 h	In vitro Huang et al. (2016)	<ul style="list-style-type: none"> Reduction of RDS and an increase in SDS and RS Development of SDS and RS Changes in physicochemical properties Promotion of amylose-amylose and amylose-amylopectin interactions Formation of amylose-lipid complex Compact structure and the high stability Restriction of the availability of starch to enzymatic hydrolysis 	Marboh et al. (2022)
Steaming	Wheat	Starches were processed in a sample processor using superheat steam at temperature of 130, 150, and 170°C Time of processing: 1 and 4 min, respectively Cooling during 3 h at 25°C	In vitro	<ul style="list-style-type: none"> RDS decreased 12.3% from native starch to the treated at 150°C for 1 min SDS and RS values increased 6.6% and 6.5% at 150°C for 1 min comparing to native starch Treatment conditions had no significant effect on the digestibility of starch samples Decreasing of hydrolysis rate 	Ma et al. (2021)
Extrusion	Corn Waxy, normal, and high-amylose maize	Equipment: extruder hot-melt twin-screw Starch moisture: 40% Screw speed: 150 rpm Temperature profiles: 35, 45, 60, 80, 100, and 120°C Moisture: 16.4%–22.5% Crew speed: 250–600 rpm Barrel temperature: 100–160°C	In vitro Englyst et al. (1992) In vitro Englyst et al. (1992)	<ul style="list-style-type: none"> Increasing the RDS and SDS Reduction of RS Formation of amylose-lipid complexes Alteration in digestion kinetics Development of different secondary structures in the extrudates The amylose content significantly impacts on the degree of modification The content of SDS was 27.5% in the high amylose starch During the treatment, a loose crystalline order of waxy maize starch leads to a fully and rapidly digestible amorphous structure 	Liu et al. (2023) Robin et al. (2016)

(Continues)

TABLE 1 (Continued)

Type of modification	Starch source	Modification condition	Digestibility determination method	Major findings relevant to starch digestion	Reference
Ultrasound	Banana	Starch dispersion of 1.0%, w/v Ultrasonic processor at 20 kHz Time: 10 min (pulsed mode) Amplitudes: 40%, 60%, 80%, and 100%	In vitro	<ul style="list-style-type: none"> Hydrolysis degree reduced The contents of RDS and RS increased The content of SDS decreased Presence of pores and cracks increasing contact surface 	Sun et al. (2022)
	Maize and potato	The starch suspension of 10%, w/v Ultrasonic processor at 20 kHz and 500 W Time: 60 min	In vitro	<ul style="list-style-type: none"> Presence of pores and cracks that lead to an increase in the granule contact surface, making starch more susceptible to hydrolysis Type-B modified starch presented lower enzymatic hydrolysis Increasing the RDS and decreasing the SDS and RS Significant increasing in starch digestibility The solubility, water and oil absorption capacities, and freeze-thaw stability increased for maize and potato 	Zhou et al. (2023)
High-pressure processing	Potato	Suspension of 75 g of starch in 225 mL of water Processing: 400 and 600 MPa for 3 and 6 cycles of 10 min Retrogradation studies: storage at 4°C for 7 days	In vitro	<ul style="list-style-type: none"> 6 cycles of HPP was more efficient in reducing the digestibility HPP followed by retrogradation increased RC compared to only HPP The recrystallization of amylopectin during retrogradation reduced the starch digestion rate The HPP plus retrogradation allows the production of starch with different functional characteristics The HPP associated with retrogradation lowered glucose release 	Colussi et al. (2018)
	Rice flour	Starch suspension was placed in packed without air Processing: 200, 400, and 600 MPa at 25°C for 10 min	In vitro	<ul style="list-style-type: none"> All pressures applied increased the resistant starch fraction 	Park et al. (2021)

(Continues)

TABLE 1 (Continued)

Type of modification	Starch source	Modification condition	Digestibility determination method	Major findings relevant to starch digestion	Reference
Microwave	Water calltrop	Starch moisture 30% Processing time: 20, 30, or 50 s	In vitro Li et al. (2019) and Englyst et al. (1992)	<ul style="list-style-type: none"> The amylose content, crystallinity, and RS content increased Solubility and swelling power decreased The surface showed depression and roughness and small holes appears in some granules The XRD peaks intensified, and pattern transformed from C-type to A-type The RS increased and RDS decreased; thus, the eGI was reduced The solubility, water and oil absorption capacities, and freeze-thaw stability increased for both sources 	Wei et al. (2020)
	Maize and potato	Starch suspension 10%, w/v Microwave power: 60 Processing time: 90 s	In vitro	<ul style="list-style-type: none"> The RS increased and RDS decreased; thus, the eGI was reduced The solubility, water and oil absorption capacities, and freeze-thaw stability increased for both sources 	Zhou et al. (2023)
Pulsed electric field	Oat flour	Flour suspension 8% Processing conditions: 2.1–2.2/4.2–4.5 kV/cm; 1.2–9.7 J; 42–53/421–438 kJ/kg	In vitro	<ul style="list-style-type: none"> The condition of 48–249 kJ/kg using electric field strength of 4.3–4.5 kV/cm promoted flours less susceptible to digestive enzymes High levels of specific energy input increased starch digestibility Elevated specific energy input levels result in deformation of starch granules and increase the particle size and decreased the relative crystallinity 	Duque et al. (2022)
	Waxy rice	Starch suspension 10%, w/w Processing condition: 50 mS/cm; 30, 40, and 50 kV/cm Processing time 60 mL/min	In vitro Englyst et al. (1992)	<ul style="list-style-type: none"> Increasing of RDS Decreasing of SDS, RS, relative crystallinity, and diffraction intensity High PEF intensity decreasing the gelatinization temperature and enthalpy 	Zeng et al. (2015)

(Continues)

TABLE 1 (Continued)

Type of modification	Starch source	Modification condition	Digestibility determination method	Major findings relevant to starch digestion	Reference
Ionizing radiation	Maize	Granular starch UV light dose: 2.88 J/cm ² Processing time: 30 min	In vitro Zhang et al. (2017)	<ul style="list-style-type: none"> Increasing in SDS and a reduction in RS Little change was obtained in relative crystallinity, water absorption capacity and solubility 	Kurdziel et al. (2020)
	Kithul	Granular starch ⁶⁰ Co gamma irradiation Radiation doses: 0.5, 1, 2.5, 5, and 10 kGy Dose rate: 2 kGy/h Room temperature: 21 ± 2°C	In vitro Englyst et al. (1992)	<ul style="list-style-type: none"> Relative crystallinity decreased when the irradiation doses were increased There is the formation of large fissures and cracks on starch granules surface High radiation doses promote an increasing in solubility and a reduction in the swelling index and viscosity. Consequently, the in vitro starch digestibility showed the same behavior 	Sudheesh et al. (2019)
Cold plasma	Aria	Granular starch with a layer of ~3 mm	In vitro	<ul style="list-style-type: none"> Damage on granule surface, increased the surface area The gelatinization temperature and retrogradation reduced RDS increased and a SDS decreased Conversion of SDS in RDS The RS was not affected by different voltages 	Carvalho et al. (2021)
		Plasma generation voltage: 7, 10, 14, and 20 kV Excitation frequency: 200 Hz Processing time: 15 min Pressure: 101 kPa Distance between the aluminum electrodes: 15 mm			
Ozonation	Finger millet	Granular starch spread as a layer of ~3 mm	In vitro	<ul style="list-style-type: none"> Increasing of RDS and RS and decreasing of SDS The use of 200 Hz promoted the highest RDS and lowest SDS values Higher frequencies promote an increasing the RS values 	da Costa Pinto et al. (2023, p. 20)
		Excitation frequencies: 50, 100, 200, 350, and 550 Hz using 20 kV Processing time: 15 min Distance between electrodes: 15 mm			
Ozonation	Finger millet	Spread starch keep in contact with ozone for 10 min	In vitro	<ul style="list-style-type: none"> Increasing of RS Decreasing of starch digestibility Presence of cracks and imperfections on the surface of the granules by SEM Low solubility Formation of V-type pattern 	Wang et al. (2022)
		Residual ozone was digested for 10 min			

Abbreviations: HMT, heat-moisture treatment; HPP, high-pressure processing; PEF, pulse electric field; RDS, rapidly digestible starch; RS, resistant starch; SDS, slowly digestible starch; SEM, scanning electron microscopy; WAC, water absorption capacity; XRD, X-ray diffraction.

ture. All the processes employed have specificities, which alter the starch granule in a specific way. BeMiller and Huber (2015) explained that one of the processes can be done by heating the normal starch in aqueous ethanol up to 60°C, which degrades the crystalline lattice and promotes a partial swell of the granule, resulting in the development of amylose–ethanol V-complexes. The interlinking of amylose and amylopectin maintains some integrity of the granules. Finally, the ethanol is omitted via washing or evaporation at elevated temperatures (140–180°C). This process is believed to increase digestibility but not as much as in pregelatinized starch. Information about the digestibility of this type of starch is still scarce, but Zhong et al. (2022) prepared maize granular cold water swelling starch to increase the maltogenic α -amylase and branching enzyme efficiencies in the modification. As a result, they verified a great increase in enzyme efficiency.

3.1.3 | Hydrothermal treatments

Heat–moisture treatment (HMT) and annealing

The heat–moisture and ANN treatments are hydrothermal processes where the proportion of starch, moisture content, temperature, and heating time are controlled (Pratiwi et al., 2018). The techniques are differentiated as they use different amounts of water and temperatures. HMT is performed under limited moisture content (10%–30%) and temperatures that reach 90–120°C, while ANN involves water in excess (50%–80%) and temperatures below the gelatinization point. Both modifications alter starch's chemical and physical properties and do not destroy its granular structure (Fonseca et al., 2021).

According to Fonseca et al. (2021) the most significant architectural changes attained by HMT and ANN include lengthening the double helix's length, reducing the double helical content, solidifying the bonds between amylose and amylopectin, and generating semicrystalline lattices of more heterogeneity. Thereby, after modification, the starch structure (RS) turns more organized. The more organized the structure, the more difficult the access of enzymes during the digestion process; consequently, the less the digestion. On the other hand, it should be taken into account that each source of starch can present a different behavior in the face of modification due to granule size, amylose content, relative crystallinity pattern, and among others. Studies report the formation of SDS and RS and the reduction of RDS upon such treatments (Pratiwi et al., 2018). In another attempt, Colussi et al. (2020) verified the effect of HMT on potato starch. In their study, the author used 15%, 20%, 25% moisture, and 110°C for 16 h in the oven to conduct HMT, and after the treatment, the starch granules retained their granular structure. The HMT reduced the glucose release during the small intestinal digestion compared to the native starches, and such alterations were more noticeable at higher moisture contents. Huang et al. (2016) showed higher RDS and SDS contents and lower RS content in the modified starch samples by repeated HMT. In contrast to the changing trend of the RS, the elevated levels of SDS were observed as the HMT cycles increased, and the highest SDS was observed at three cycles of HMT and thereafter reduced. The finding of this study showed that rather than HMT duration, cycling periods were an essential factor

that significantly influenced the concentration of SDS in sweet potato starch. The damage to starch molecules caused a lower RS and higher SDS and RDS contents when HMT was applied for over three cycles. On the other hand, the diminished RDS and SDS and the higher content of RS for three-cycle HMT samples could be caused by the associations between starch chains and the perfect crystallite near the granule's surface, which prevents the disruption of starch molecule (Huang et al., 2016).

Marboh et al. (2022) studied the impact of HMT (100°C, at 20%, 25%, and 30% moisture for 16 h) and ANN (50°C, at 70%, 75%, and 80% moisture for 24 h) on physicochemical properties and in vitro digestibility of sohphlang (*Flemingia vestita*) tuber starch. In all treatments, the authors verified a reduction of RDS and increasing SDS and RS; however, the more intense change was found in HMT-modified starches. The content of RS in native starch was 11.30%, which increased to 16.71%–22.48% and 17.36%–21.58% for HMT and annealed starch, respectively. The promotion of SDS and RS during HMT and ANN results from the rearrangement in amylose/amylopectin architecture. As previously mentioned, several factors related to the process and the source and characteristics of starch influence digestibility of starch upon HMT and ANN modifications.

Steaming

Steaming is a viable thermophysical technology to modify starch upon employing dry and wet heat treatment (Hu et al., 2017). Aside from its potential to enhance product quality and consumer acceptability, steaming could also boost starch's SDS and RS content. Ma et al. (2021) mentioned that steam technology is a promising strategy applied to starch modification; once in their study, the SDS and RS content of wheat starch increased from 10.6% to 7.9% in native starch to 17.2% and 13.6% following steaming (150°C, 1 min). Hu et al. (2017) reported that steaming increased wheat flour's SDS and RS contents. Wu et al. (2016) described that superheated steam treatment was an appropriate technique for processing rice due to its ability to increase SDS and RS contents.

Extrusion process

The extrusion process involves the thermomechanical treatment of starch at limited moisture. It causes an ordered to disordered phase transition in starch, where the inter/intramolecular starch–starch hydrogen bonds are substituted by starch–water molecules –OH bindings. Divers processing conditions produce different structures, improving starch functional properties, such as pasting properties, water absorption, solubility, cold pasting viscosity, and reduced digestibility (BeMiller & Huber, 2015; Liu et al., 2023). After employing the extrusion process (moisture content of 40%, a screw speed of 150 rpm, and temperature profiles of 35, 45, 60, 80, 100, and 120°C, using a hot-melt twin-screw extruder), Liu et al. (2023) found that the process decreased RDS and SDS contents while increase the RS. The formation of starch–lipid complexes is responsible for the increase in RS levels. Robin et al. (2016) studied the impact of screw speed (250–600 rpm), barrel temperature (100–160°C), and water content (16.4%–22.5%) on RDS, SDS, and RS content of waxy, normal, and

high-amylose maize starches. Their investigation revealed that the natural RS in high-amylose native corn starch (CS) gives rise to enhanced SDS following extrusion. Its digestion behavior can be ascribed to some granular fragments that can endure the extrusion process and the development of secondary structures, such as amylose–lipid complexes and retrograded starch molecules.

3.1.4 | Novel physical modification approaches

Ultrasonication

US is a safe technology that produces mechanical actions and liquid cavitation bubbles that attack the starch granules and alter their properties (Barua et al., 2021). The main changes observed in ultrasonically modified starches are granular damage, especially on surfaces (cracks, pores, and imperfections), molecular depolymerization, which promotes alterations on starch properties (Sun et al., 2022; Zhou et al., 2023). At greater exposures of granules to US, more pores and cracks are created leading to an increase in the granule contact surface, which makes them more susceptible to hydrolysis. Most studies using US report an increase in digestibility. Zhou et al. (2023) applied 500 W, 20 kHz, 60 min on maize and potato starch and verified that the rate of starch hydrolysis elevated after the modification. The authors justify the higher rate to the fact that US destroys the physical barricade of the granules, resulting in an extra upsurge in the interaction between the starch and the enzyme. Another relevant point reported in the study was the differences in digestibility of A-type and type-B crystallinity patterns. The digestibility percentage of A-type (CS) was higher than B-type (potato starch). The same behavior was reported in other studies. B-type starches were less susceptible to enzymatic digestion due to their granular architecture. Contrary to the above studies, Ding et al. (2019) observed a reduction in starch digestibility when applied elevated powers of ultrasound (300–600 W) on type 3 resistant starch (RS3) (Figure 2). In detail, they outlined that at low powers of ultrasound (100–200), the degradation of granules and the emergence of cracks and pores on surface (Figure 2a,b) facilitate starch digestion. However, under higher powers of ultrasound (300–600 W), sonication treatment was accompanied by a remarkable rise in the temperature of the media. Upon cooling, the degraded starch fractions within the sonicated mixture were rearranged into V-type crystallite structures (Figure 2i) with less susceptibility to digestive enzymes (Figure 2h).

High-pressure processing (HPP)

During the HPP processing, reversible hydration of the amorphous regions occurs, followed by irretrievable destruction of the crystalline segments of starch granules. During the process, normally, the granular structure of starch is disrupted. The packing architecture of the amylose and amylopectin within the granules plays an important role in defining the behavior of starch under HPP and its consequent digestibility (BeMiller & Huber, 2015).

The main factors that interfere with the digestibility of starches submitted to HPP treatment are the botanical source, the treatment's intensity, and the starch's amylose content. In addition, the high

pressure disturbs the starch's internal structure, leading to a loss of structural integrity and vulnerability to enzymatic hydrolysis. However, immediately after the HPP process, retrogradation begins, which leads to the elevation of RS content. Park et al. (2021) investigated the effect of HPP on starch digestibility in both flours and starches extracted from flours. It was reported that HPP treatment of rice flour at 200–600 MPa for 10 min increased the RS fraction. A-type starches are less resistant to HPP than B-type starches, and C-type starches are intermediate where the A-type polymorphic RS is more compact and lower in water content. In contrast, the B-type polymorphic structure has a more open structure with a hydrated helical core (BeMiller & Huber, 2015). Colussi et al. (2018) studied different pressures, cycles of pressurization and depressurization, retrogradation behavior, and their influences on the functional properties and digestibility of potato starch. The authors mentioned that the HPP, in combination with retrogradation, facilitates the production of starch with different useful features that, after cooking, provide less digestibility during in vitro gastrointestinal digestion and a slower release of glucose.

Microwave and radio frequency treatments

Microwave and radio frequency are carried out using specific forms of irradiation in specific equipment. Samples must be as a suspension or moisture-adjusted samples followed by microwave heat treatment and cooling. Microwave promotes heating uniform across all starch specimen via vibrating polar substances (i.e., water molecules or ionic ingredients). However, this process can cause several changes in starches' functional and physicochemical properties (Zailani et al., 2023).

Wang et al. (2019) applied microwave irradiation on corn, potato, and chestnut starch. They observed that after microwave treatment, starches' digestibility and physicochemical properties changed. The in vitro starch digestibility elevated after microwave irradiation; while after retrogradation for 24 h, the digestibility of starch declined, and the RS content was greater than that of native starches. Upon studying the levels of RDS, SDS, and RS of the water caltrop starch treated by microwave, Wei et al. (2020) verified that the behavior of treated starches had significant differences with the extension of modification time (20, 30, or 50 s). The levels of RDS and SDS diminished when increasing the microwave treatment. This may be caused by the increment in amylose content and relative crystallinity, so the consolidated double-helical architectures avoid the enzymes activity. On the contrary, the RS content elevated gently and remarkably differed from the content in unmodified samples. The microwave treatment accelerates the degradation of hydrogen bindings, promotes molecular reorientation, and improves water distribution of the starch enhancing the quantity of bound water, conditions that can directly interfere with starch digestibility. Single microwave treatments in maize and potato starch incremented the RS and declined RDS and eGI (Zhou et al., 2023).

Pulse electric field (PEF)

The pulse electric field (PEF) can be used for starch modification. Its actuation mechanism happens through short pulses of high voltage

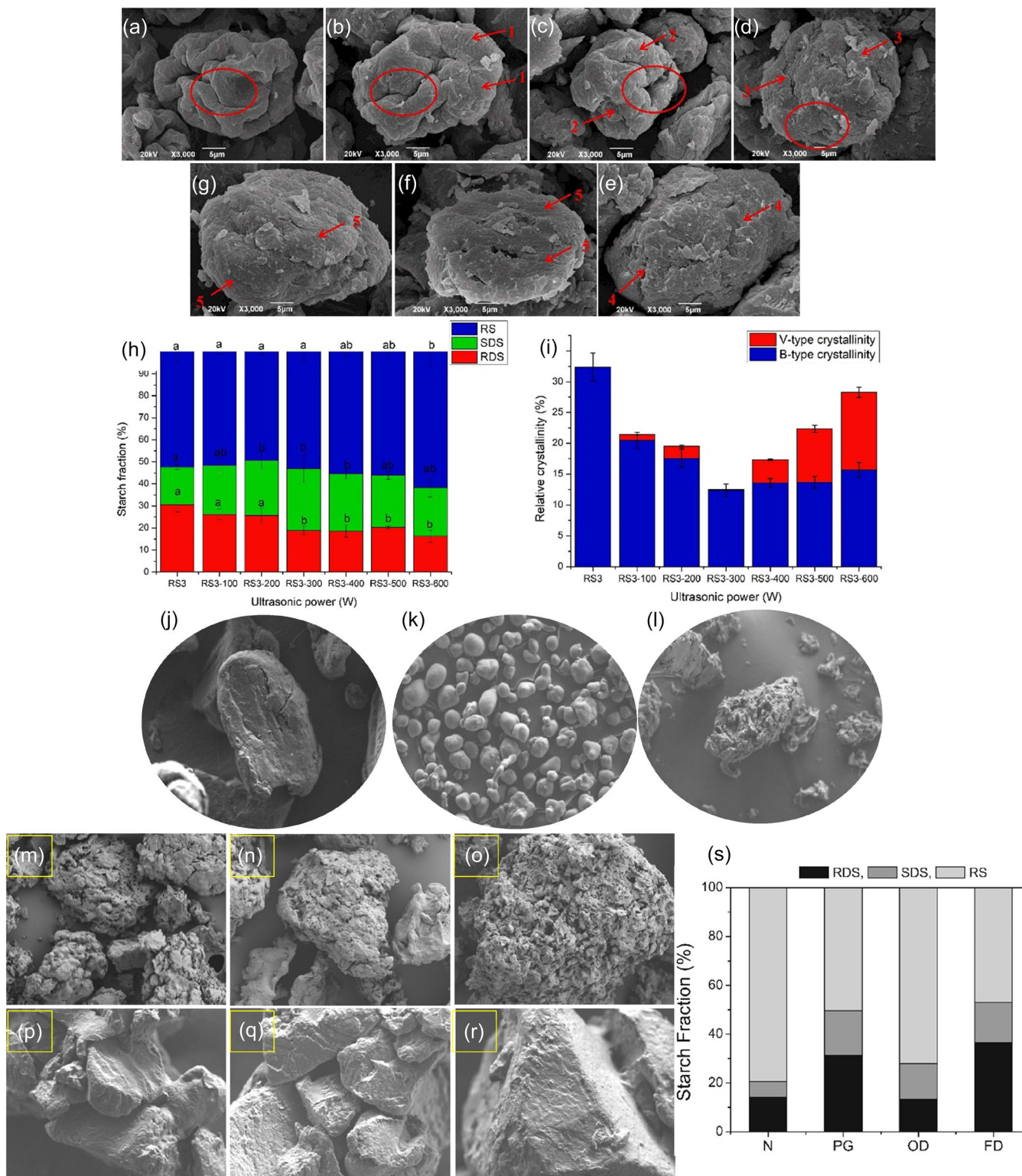


FIGURE 2 Scanning electron microscopy (SEM) images of normal type 3 resistant starch (a) and type 3 resistant starch (RS3) samples treated via ultrasound at various powers of 100 (b), 200 (c), 300 (d), 400 (e), 500 (f), and 600 W (g); starch fractions (h) and crystalline fragments (i) of RS3 starches treated at various ultrasound powers. SEM images of normal Hylon VII starch (j), oven dried (OD) Hylon VII (k), and freeze-dried (FD) Hylon VII (l) starches; FD samples hydrothermally treated for 3 (m), 12 (n), 24 (o), OD samples hydrothermally treated for 3 (p), 12 (q), and 24 h (r); starch fractions in normal, pregelatinized, OD and FD Hylon VII starch (s). Source: (a–i) Reprinted with permission from Ding et al. (2019); (j–s) reprinted with permission from Agama-Acevedo et al. (2018).

with very short period to avoid heating. In a study by Duque et al. (2022), PEF treatment (2.1–2.2/4.2–4.5 kV/cm; 1.2–9.7 J; 42–53/421–438 kJ/kg) was applied on oat flour. They outlined that PEF using high electric field strength and energy (<216 kJ/kg) was desirable for hindering starch digestion, where RS enhanced from 77% to 84%–85%, whereas RDS diminished from 15% to 7%–10%. The PEF treatment in waxy rice with varied intensities (30, 40, and 50 kV/cm) showed a gradual increase in starch digestibility as the intensity was increased.

Ionizing radiation

Radiation treatment has been widely used for food preservation as well as modification of various starches. Because of their high energy, ionizing gamma rays and UV radiation can destroy starch chains (Kurdziel et al., 2020). Sudheesh et al. (2019) modified kithul starch (*Caryota urens*) with gamma irradiation at different doses (0.5, 1, 2.5, 5, and 10 kGy). Increasing the irradiation doses enhanced the solubility while declining the relative crystallinity, swelling index, and viscosity and induced large imperfections on the surface of granules. The in vitro starch digestibility increased with radiation doses. In the study by Kurdziel et al. (2020), in the maize starch irradiated with UV light for 30 min, an increase in SDS and a decrease in RS were observed, whereas RDS content was not different.

Cold plasma

Besides being a physical treatment, plasma processing promotes various reactive species, inducing chemical changes. The extent of changes in the chemical composition relies on the starch type, plasma, and experimental conditions. The main changes in starch are the reduction in moisture, amylose content, crystallinity, and the formation of functional groups linked to the molecules (BeMiller & Huber, 2015). Moreover, the size, granule's lamellar structure, swelling power, solubility, pasting, thermal, and digestibility properties can be altered (da Costa Pinto et al., 2023). Upon Studying the impact of different high voltages of plasma (7, 10, 14, and 20 kV) on Aria starch, Carvalho et al. (2021) reported that the application of plasma caused a remarkable increment in RDS and a decline in SDS values. SDS consists of compressed amorphous segments and weak helical architecture that may be influenced by reactive species of plasma, depolymerizing the starch chains and transforming them to RDS. Although there are no variations in the RS content, the authors believe that there may have been formation of type 2 RS after modification. da Costa Pinto et al. (2023) also studied the cold plasma but with different frequencies (50, 100, 200, 350, and 550 Hz) at 20 kV for 15 min and verified that RDS and RS were remarkably enhanced; for another hand, the SDS diminished with cold plasma treatment. The excitation frequency of 200 Hz revealed the maximum RDS and minimum SDS content, and it can be explained because the presence of lower molecular weight residues led to an upsurge in starch hydrolyzability.

Ozonation

The ozonation is performed by incorporating the ozone into the starch dispersion in water, resulting in an oxidation reaction, which is considered a process of starch modification. Two key reactions occur upon

starch ozonation. First, the oxidation of –OH groups of the amylose and amylopectin (C–OH) to carbonyl (C=O) and carboxyl (HO–C=O) groups, mainly on the carbons located at 2, 3, and 6 positions of glucose. The starch molecules are depolymerized in the second reaction by cleaving glycosidic bonds (Castanha et al., 2017). Wang et al. (2022) modified finger millet starch (*Eleusine coracana* L.) with ozone gas. On scanning electron microscopy, the granules showed deep cracks, showing that ozone promoted erosion on the surface of starch granules. The solubility is minimal, generated by the crosslinking between starch molecules after the oxidation by ozone. On XRD, V-type crystal patterns starch emerged. In vitro starch digestibility revealed the formation of RS and a decrease in digestibility where the tighter V-type crystalline structures hindered the action of digestive enzymes.

3.2 | Impact of single chemical modification on starch digestibility

Starch characteristics can be customized by incorporating functional groups into its molecular structure. The stability of intramolecular and intermolecular bonds at various sites and locations is aided by such alterations. The functional and chemical characteristics of the modified starches are influenced by factors like the starch source, reaction conditions, degree of substitution, type, and distribution of substituting agent along the starch molecule (Falsafi, Maghsoudlou, Rostamabadi, et al., 2019). The five basic categories of chemical modifications are cross-linking, oxidation, ES, etherification, and acid hydrolysis. In addition to their remarkable impacts on physicochemical attributes, these chemical modifications are potent strategies for inducing different digestion behavior in starch (Wang et al., 2022, p. 20). A detailed overview of the digestibility of chemically modified starches has been provided in the following section.

3.2.1 | Starch cross-linking

Upon cross-linking modification, starch is subjected to a cross-linking agents, such as sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin, or phosphoryl chloride (POCl₃). Cross-linking alters the functional properties and digestibility of starch by fusing covalent bonds with preexisting hydrogen linkages in starch granules (Sharma et al., 2020). However, the impact of crosslinking can vary depending on the extent of modification, plant-based sources of starch, and the type of crosslinking agents employed during modification. Crosslinking treatment generates intra- and intermolecular connections in the granules, which, along with stabilizing their structure, results in an increase in their resistance against digestion (Park et al., 2018). This resistant starch fraction is referred to as RS4. It is worth noting that although a limited number of cross-linked spots could hugely affect the physicochemical properties of starch, they barely change its digestibility. For POCl₃ which is a rapid-reacting ingredient, it is not practicable to achieve enough cross-links to provoke resistance to digestion as the maximum authorized level of POCl₃

in foods is 0.1%. Woo and Seib (2002) outlined that the RS was almost negligible in POCl_3 cross-linked starch with 0.1% phosphorous content. Currently, the blends of STMP/STPP have been extensively engaged in producing type 4 RS where the maximum permitted level of phosphorous is 0.4%. However, conversely to POCl_3 , STMP/STPP is rather sluggish in reacting resulting in more time-consuming processes. This challenge has been the focus of different studies and almost tackled by performing cross-linking reactions under ultrasound or extrusion conditions (Falsafi, Maghsoudlou, Aalami, et al., 2019). Nevertheless, conflicting information is available in the literature regarding the impact of phosphorylation-induced crosslinking on starch digestibility. According to some researches, cross-linking with phosphorylation may slow down the pace of digestion (Shukri et al., 2015), whereas some others have found negligible changes in starch digestibility following cross-linking (Park et al., 2018). In a recent attempt, Dong and Vasanthan (2020) studied the digestion behavior of regular corn, faba bean, and field pea starches cross-linked via POCl_3 -aqueous (1%–2%), STMP/STPP semidry (99:1, w/w, 2%–4%), and STMP/STPP aqueous (99:1, w/w, 5%–12%) on digestion behavior. Upon similar reaction times, POCl_3 -treated samples possessed greater resistance against digestion. Moreover, both the starch source and the cross-linking reagent imparted significant changes in the digestion behavior of starches. In another attempt, Falsafi et al. (2019) studied the digestibility of CS cross-linked via different concentrations of SRMP–STPP (5%–15%) under conventional and ultrasound conditions. Compared with the conventional reaction systems, starch cross-linking under sonication almost doubled the RS content of starch.

3.2.2 | Starch esterification

For starch ES, carboxymethyl, hydroxypropyl, and/or hydroxyethyl groups substitute with reactive hydroxyl groups (using sodium hydroxide as a catalyst) under an alkaline media. The chemical agents commonly used in starch ES are reactive derivatives of carboxylic acids (i.e., formic acid, acetic acid, and propionic acid) and their anhydrous counterparts (Wang et al., 2022). According to Egharevba (2019) esterified starches are used as stabilizing ingredients in a variety of meals, including gravies, dips, sauces, fruit pie fillings, and puddings. The orientation of starch molecules, the distribution of the amorphous and crystalline segments, and the varied botanical sources all influence the active zones where the ES of starch occurs (Chen et al., 2018). During ES, the hydrocarbon moiety of the organic ester is added to starch chains, which degrade the starch granule structure and deteriorate the inter and intramolecular hydrogen linkages. As a result, a change in the access of water to starch molecules occur which further affects starch gelatinization and retrogradation leading to the alteration in starch digestion. The presence of larger functional groups on amylose and the outer branch of amylopectin, on one hand, improves the molecular interfacial function while, on the other hand, restricts the ability of digestive enzymes to attach to the starch molecules (Chen et al., 2018). Numerous studies in recent years have focused on the ES of several starch types with octenyl succinic anhydride (OSA) to

create an amphiphilic starch (Mirzaaghaei et al., 2022). In comparison to other chemical modifications, such as cross-linking, octenylsuccinylation of starch was reported to enhance rates of SDS content. This may be related to the physical impediment brought on by the presence of substantial octenylsuccinylation groups that covered the starch molecules and may have been able to delay the enzymatic hydrolysis. The octenylsuccinylation groups may also potentially have a role as a noncompetitive inhibitor of amyloglucosidase and pancreatic α -amylase. However, the limited permitted amount of OSA (3% maximum for starch modification) and the inevitable use of organic solvents during the modification process are some of the difficulties associated with the ES of starch using OSA. According to Lopez-Silva et al. (2020), enhancement in hydrophobicity and reduction in digestibility was found in esterified starch using OSA. In addition, the Food and Drug Administration (FDA) has certified fatty acid chloride (FAC) as an acceptable alternative agent to produce modified starch with no specific limits (FDA) (García-Tejeda et al., 2018). Recently, increasing attention has been paid to esterifying starch using FAC instead of organic solvents, which has been considered an environmentally friendly method (Mirzaaghaei et al., 2022). Shorter reaction times, non-toxicity of by-products (water and NaCl), and the lack of a solvent requirement for the precipitation of modified starch are just a few of the noteworthy benefits of using water as a reaction medium rather than organic solvents (Leal-Castañeda et al., 2018). In an attempt, Zhang et al. (2017) outlined that the extents of SDS and RS fractions are directly proportional to the degree of substitution in OSA-treated starches. This finding is intriguing because it establishes a connection between the molecular structure of starch chains and their digestibility characteristics. The digestibility of different esterified starches has been studied, which are summarized in Table 2.

3.2.3 | Starch etherification

Etherified starches are one of the most widely used derivatives of starch. For starch etherification, hydroxyalkyl groups are introduced inside the starch chains. However, in water, starch can be etherified with fatty epoxides or alkyl chlorides (Gilet et al., 2018). Upon etherification, some of the hydroxyl groups in the anhydroglucose units of starch are replaced with ether groups, which can prevent the creation of H bonds among the $-\text{OH}$ groups of starch and improve water resistance (Clasen et al., 2018). Given the new features of modified starch, etherification widens the application of starches particularly in the realm of food packaging and encapsulation of low water-soluble bioactive compounds. Although numerous research teams have comprehensively characterized various attributes of etherified starches (e.g., crystallinity, freeze-thaw stability, gelation, thermal properties, pasting/rheological behavior, retrogradation, chemical structure, and physical architecture) via conventional and novel instrumental approaches (i.e., XRD, NMR, FT-IR, and DSC), extremely limited attention has been given to their digestion behavior (Bakouri & Guemra, 2019; Charoenthai et al., 2022; Clasen et al., 2018). In an attempt, Lawal (2011) obtained a similar increase in digestibility of

TABLE 2 An overview of the impact of chemical modifications on starch digestibility.

Type of modification	Starch source	Modification condition	Digestibility determination method	RDS	SDS	RS	OD	Major findings relevant to digestion	Reference
Crosslinking	Faba bean	<ul style="list-style-type: none"> STMP was added to the slurry in different concentrations (1.0%, 3.0%, and 5.0%) 	Englyst et al. (1992)	↓	↓	↑	↓	<ul style="list-style-type: none"> RS increased from 49.8% to 51.3%–61.1% with increasing the crosslinking agent 	Sharma et al. (2020)
	Waxy maize	<ul style="list-style-type: none"> 99:1 mixture of STMP/STPP (5%, 10%, and 12%) was used for modification 	Englyst et al. (1992)	↓	–	↑	↓	<ul style="list-style-type: none"> RS increased by 7.6%, 14.8%, and 16.6% with increasing the concentration of STMP/STPP from 5% to 15% due to the restricted swelling of starch 	Park et al. (2018)
	Faba bean	<ul style="list-style-type: none"> Aqueous solution of STMP/STPP with 5%, 10%, and 12% w/w (99:1) was added in starch slurries (20 g/30 mL) 	Englyst et al. (1992)	↓	↓	↑	↓	<ul style="list-style-type: none"> Aqueous STMP/STPP: RS levels increased from 25.8% ± 0.4% to 32.8% ± 0.7% 	Dong and Vasanthan (2020)
	Corn	<ul style="list-style-type: none"> Semi dry reaction with 2% and 4% of 99:1 (w/w) STMP/STPP mixture in starch slurries (20 g/30 mL) Aqueous solution of STMP/STPP with 5%, 10%, and 12% w/w (99:1) was added in starch slurries (20 g/30 mL) 	Englyst et al. (1992)	↑	↓	↑	↓	<ul style="list-style-type: none"> STMP-semidry enhanced RDS and RS and declined SDS content in specimens. The increase in RDS was due to the heat treatment applied upon modification Aqueous STMP/STPP: RS levels increased from 19.7% ± 1.1% to 25.7% ± 1.1% 	Dong and Vasanthan (2020)
	Field pea	<ul style="list-style-type: none"> POCl₃ (1% and 2%) was added in the starch slurries (20 g/30 mL) Aqueous solution of STMP/STPP with 5%, 10%, and 12% w/w (99:1) was added in starch slurries (20 g/30 mL) 	Englyst et al. (1992)	↓	↓	↑	↓	<ul style="list-style-type: none"> RS content was 20.5% ± 0.8%, 26.6% ± 0.5%, and 28.0% ± 1.4% in native FP; 1% POCl₃-aqueous FP, and 2% POCl₃-aqueous, respectively Aqueous STMP/STPP: RS levels increased from 20.46% to 27.3% ± 1.1% 	Dong and Vasanthan (2020)
	Cardaba banana	<ul style="list-style-type: none"> POCl₃ (0.05% on dry weight basis) was added in starch slurries (30 g in 48 mL) 	In Vitro	↓	↑	↑	↓	<ul style="list-style-type: none"> RS fraction was increased from 31.99% ± 0.16% to 34.66% ± 0.17% 	Olawoye and Gbadamosi (2020)
Esterification	Waxy corn	<ul style="list-style-type: none"> 3% (dry basis) OSA was added to starch slurries (30 g/100 mL) 	Lopez-Silve et al (2020)	–	–	↑	↓	<ul style="list-style-type: none"> RS fraction was increased from 27.22% ± 0.93% to 36.26% ± 0.43% 	Lopez-Silve et al. (2020)
	Normal corn	<ul style="list-style-type: none"> 3% (dry basis) OSA was added to starch slurries (30 g/100 mL) 	Lopez-Silve et al (2020)	–	–	↑	↓	<ul style="list-style-type: none"> RS fraction was increased from 34.66% ± 0.67% to 43.65% ± 0.36% 	Lopez-Silve et al. (2020)
	Hylon VII	<ul style="list-style-type: none"> 3% (dry basis) OSA was added to starch slurries (30 g/100 mL) 	Lopez-Silve et al (2020)	–	–	↑	↓	<ul style="list-style-type: none"> RS fraction was increased from 74.84% ± 0.96% to 87.27% ± 1.45% 	Lopez-Silve et al. (2020)
	Cassava	<ul style="list-style-type: none"> 1.5%, 3%, and 6% (dry basis) OSA was added to starch slurries (30% w/w) 	Englyst et al. (1992)	↓	↑	↑	↓	<ul style="list-style-type: none"> Decrease in RDS from 75.75% to 41.83% and increase in RS fraction from 11.79% to 53.13% was observed 	Zhang et al. (2017)

(Continues)

TABLE 2 (Continued)

Type of modification	Starch source	Modification condition	Digestibility determination method	RDS	SDS	RS	OD	Major findings relevant to digestion	Reference
	Cassava	<ul style="list-style-type: none"> Phenolic acids and <i>N,N'</i>-carbonyldiimidazoles (CDI) solution in DMSO (80 mL) were added into starch slurries (2 g/20 mL of DMSO) 	Englyst et al. (2018)	↓	↓	↑	↓	<ul style="list-style-type: none"> Up to 12.3%, 6.0%, and 17.0% of starch fractions were transformed from RDS to SDS and RS (Figure 3g) The steric hindrance of phenolic acid residues, the compacter structure of the complexes, and the enhanced hydrophobicity resulted in diminished digestibility (Figure 3h–k) 	Xu et al. (2022)
	Wheat (A type)	<ul style="list-style-type: none"> 10 mL of citric acid (40%, dry basis) was added into 10 g of starch 	Englyst et al. (1992)	↓	↓	↑	↓	<ul style="list-style-type: none"> RDS was decreased from 24.72% to 17.92%, whereas RS increased from 49.42% to 77.29% 	Li et al. (2019)
	Wheat (B type)	<ul style="list-style-type: none"> 10 mL citric acid (40%, dry basis) was added into 10 g of starch 	Englyst et al. (1992)	↓	↓	↑	↓	<ul style="list-style-type: none"> RDS was decreased from 25.96% to 21.54%, whereas RS increased from 53.97% to 76.72% 	Li et al. (2019)
	Plantain	<ul style="list-style-type: none"> 70 mL citric acid (400 g/kg/70 mL) was dissolved in 100 g of flour 	Englyst et al. (1992)	↓	↓	↑	↓	<ul style="list-style-type: none"> RDS was decreased from 9.22% ± 0.77% to 4.44% ± 0.22% RS fraction was increased from 85.67% ± 0.77% to 93.87% ± 0.16% 	Sánchez-Rivera et al. (2017)
Oxidation	Potato	<ul style="list-style-type: none"> Sodium hypochlorite was added with starch slurry (50 g/450 g) until reaching 0.1%, 0.2%, 1%, 2%, 3%, and 4% of active chlorine concentration 	In vitro	↓	↑	↑	↓	<ul style="list-style-type: none"> RS fraction was increased from 2.61 to 11.9 after oxidation, whereas RDS diminished from 92.7% to 72.6% 	Zhou et al. (2016)
	Corn	<ul style="list-style-type: none"> Air oxidation was performed with corn starch (50 g) at different temperatures (20, 100, 120, 140, and 160°C) for 4 h 	Englyst et al. (1992)	↓	↓	↑	↓	<ul style="list-style-type: none"> Increase in the RS fraction was observed from 26.36% to 47.34% 	Reyes et al. (2021)
	Kithul palm	<ul style="list-style-type: none"> Starch concentration: 10% w/w pH: 9–10 Temp: 35°C Time: 30 min Active chlorine content: 0.06–2 g/50 g starch 	Englyst et al. (1992)	↓	↓	↑	↓	<ul style="list-style-type: none"> Oxidation resulted in an increase in resistant starch content and declined the overall starch digestibility The steric hindrance caused by the presence of bulky carbonyl and carboxyl residues in modified samples diminished the enzyme accessibility 	Sudheesh et al. (2019)

(Continues)

TABLE 2 (Continued)

Type of modification	Starch source	Modification condition	Digestibility determination method	RDS	SDS	RS	OD	Major findings relevant to digestion	Reference
Acid hydrolysis	<i>Cynanchum auriculatum</i>	<ul style="list-style-type: none"> Starch (2%, w/v) was suspended in 2.2 M HCl and kept at 35°C for 1–9 days 	In vitro	NC	NC	NC	NC	<ul style="list-style-type: none"> No significant alterations in the starch digestion fractions were found 	Wang et al. (2017)
	Maize	<ul style="list-style-type: none"> Starch was dispersed in citric acid solutions (0.1, 0.5, and 1 M) in the ratio of 2:3 (w/w, starch : citric acid solution) and heated at 50°C for 1, 4, and 8 h 	Englyst et al. (1992)	↓	↑	↓	↓	<ul style="list-style-type: none"> Although RS was reduced upon the sole application of citric acid, the combination of citric acid with heat treatment (140°C, –30 min) remarkably enhanced the RS and SDS and reduced RDS content 	Liu et al. (2014)

Abbreviations: FP, field pea; NC, not changed; POCl₃, phosphoryl chloride; RDS, rapidly digestible starch; RS, resistant starch; STMP, sodium trimetaphosphate; STPP, sodium tripolyphosphate; SDS, slowly digestible starch; OSA, octenyl succinic anhydride; OS, overall digestibility.

hydroxypropylated pigeon pea starch cussed by the weakened starch granules following the incorporation of large hydroxyalkyl groups into the starch molecular backbones. Indeed, the loosened architecture of the etherified starches facilitated the accessibility of starch molecules to enzyme attack.

3.2.4 | Starch oxidation

Usually, starch oxidation is performed when a starch slurry and an oxidizing agent (e.g., NaOCl, N₂O₄, and hydrogen peroxide) are combined under controlled pH and temperature conditions. Oxidation converts the three accessible hydroxyl groups at the C-2, C-3, and C-6 positions to carbonyl and/or carboxyl groups. Such reactions yield chain cleavage and result in the production of starch molecules of less molecular weight. However, depolarization is directly related to oxidation efficiency, which depends on several variables, such as the type of reaction, the chemicals utilized, and the molecular composition and granular structure of starch (Zhang et al., 2012). Generally, the quantity of carboxyl and carbonyl groups in the oxidized starch shows the degree of oxidation. However, the type of oxidative process and reagents used during the process also determine the nature and attributes of the produced starch derivative (Masina et al., 2017). Oxidized starches are mostly known as hydrophobic derivatives with low viscosity at high solid concentrations and are widely applied in producing well-structured thin films/textiles/papers where their physical, chemical, and technofunctional attributes are described in detail (Vanier et al., 2017). However, the nutritional aspect of oxidized starches is barely reported in the recent literature. In a very recent attempt, Hu et al. (2022) employed gaseous ozone as a green technique to produce oxidized tartary buckwheat starch. In the case of samples ozonated for 2.5 and 5 min, the in vitro digestibility results indicated a remarkable decrease in the RDS content of the starch, whereas RS content was significantly enhanced (Figure 3f). However, increasing the treatment time up to 15 and 20 min elevated the starch digestibility with a decrement in RS content. In fact, widening the superficial pores and internal channels at elevated times of ozonation (Figure 3a–e) facilitated the accessibility of digestive enzymes to the internal portions of the starch granules.

3.2.5 | Acid hydrolysis

Acid hydrolysis is one of the key modification techniques among other chemical modification for the preparation of thin boiling starches with customized viscosity and widely used in various realms of food, paper, and textile industries. Acid hydrolysis, in general, is the process whereby protic acid is utilized to dissolve a chemical bond through a nucleophilic substitution reaction with the addition of a water molecule (Haq et al., 2019). The microstructure and functional characteristics of starch may be impacted by the starch nature, acid concentration, type, and hydrolysis time. Typically, acid hydrolysis at mild conditions (namely acid thinning) prior to heating processes (i.e.,

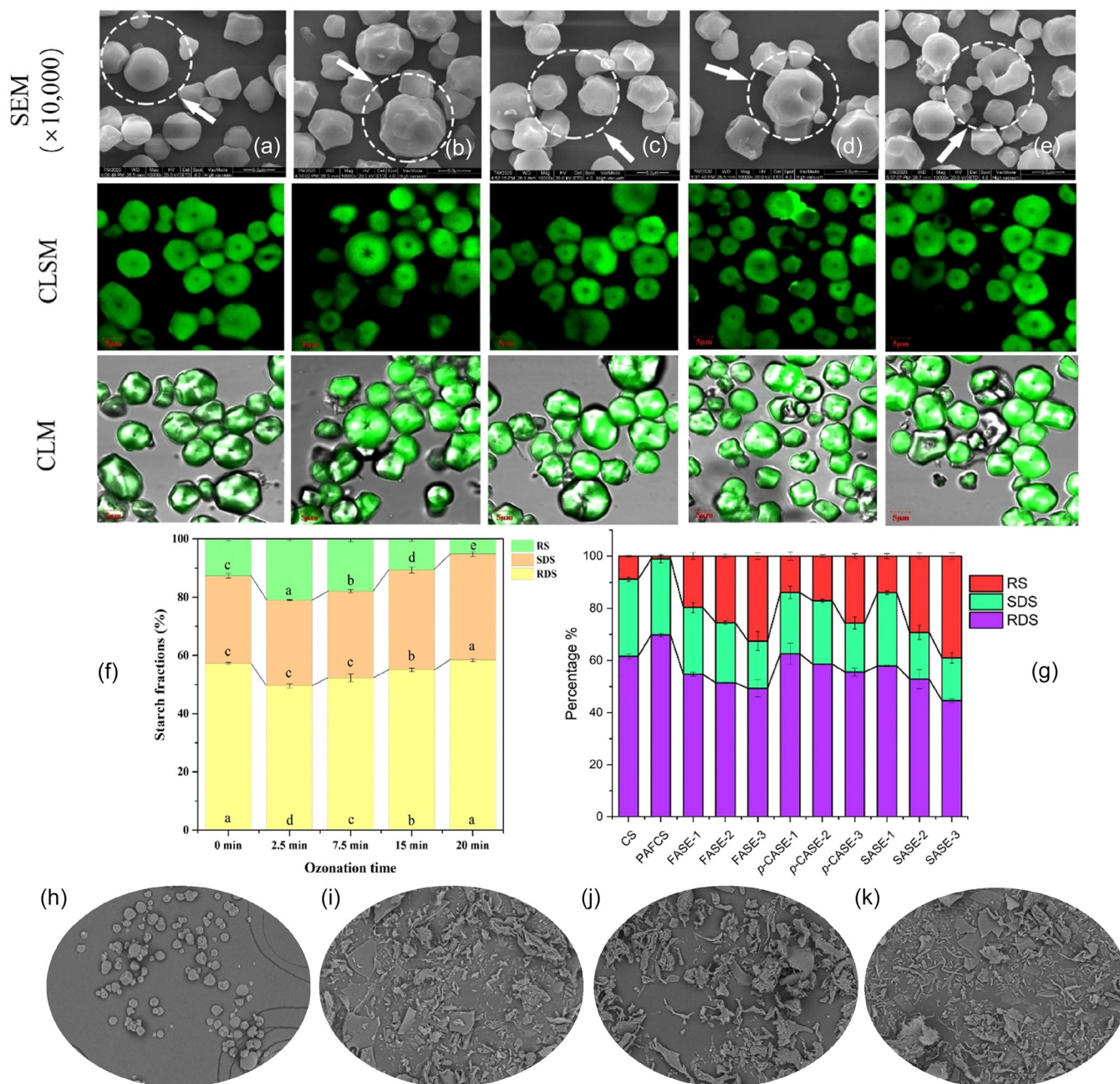


FIGURE 3 Scanning electron microscopy (SEM), CLSM (confocal laser scanning microscope), and CLM (complex light microscope) images of tartary buckwheat starch (TBS) ozonated for (a) 0, (b) 2.5, (c) 7.5, (d) 15, (e) 20 min, scale bar = 5 μ m; starch fractions in native and ozonated TBS (f). Starch fractions in cassava starch (CS) and its esters with ferulic acid, ferulic acid starch ester, p-coumaric acid, p-coumaric acid starch ester, sinapic acid, and sinapic acid (g); SEM images of cassava starch (h), ferulic acid starch ester (i), caffeic acid starch ester (j), and sinapic acid starch ester (k). Source: (a–f) Reprinted with permission from Hu et al. (2022); (g–k) reprinted with permission from Xu et al. (2022).

autoclaving in the presence of excess water or HMT at limited content of available water) has been introduced as a potent pretreatment for inducing the generation of retrograded RS3. Reportedly, amylopectin side chains located in amorphous portions of granules are more prone to acid hydrolysis leading to the formation of numerous linear short-chain amylose-like structures (Van Hung et al., 2016). As stated by Van Hung et al. (2016) such small structures are more mobile through heat treatments (e.g., HMT) and could reassemble into ordered crystallite

architecture with less susceptibility to enzyme digestion. A remarkable increase in thermostable RS content of yam, sweet potato, rice, and cassava starches following the combined treatment of starches with partial acid hydrolysis and HMT has been reported in the literature (Van Hung et al., 2014, 2017). However, in the case of citric acid, apart from its role as a hydrolyzing reagent, it could also efficiently contribute to cross-linking reactions where the starch molecules of the heated granules are comfortably attacked by citric acid and the OH

groups of glucose units could be replaced by citric anhydride acting as a junction zone (Van Hung et al., 2016). In a recent attempt, Li et al. (2020) made an effort to modify the pea and maize starches' digestibility through acid thinning, debranching, and recrystallization processes. The consecutive performance of acid thinning and debranching led to a remarkable increase in the RS content up to 68.1% and 59.6% for pea and maize starches, respectively. This might result from the extremely compacter structure of modified starches that has restricted the ingress of enzymes into the RSs and diminished their accessibility for hydrolysis actions.

4 | IMPACT OF DUAL/MULTIPLE MODIFICATIONS ON STARCH DIGESTIBILITY

The application of starch in its native form has been challenged by some obstacles, such as its insolubility in cold water, low gelatinization temperature, ease of syneresis, and the high tendency for retrogradation (Rostamabadi, Demirkesen, et al., 2023). Although the modification of starch through various physical and chemical approaches is able to improve its physicochemical characteristics, some drawbacks still exist (Falsafi et al., 2023). For instance, although the succinylated starches possess some advantages, such as high solubility in cold water, improved thickening power, high viscosity, increased paste clarity, retarded retrogradation, and freeze-thaw stability, they are unstable during shearing at high temperatures. The succinylated starches have some benefits, like high solubility in cold water, improved thickening power, high viscosity, enhanced paste clarity, slowed retrogradation, and freeze-thaw stability. However, they become unstable when exposed to high temperatures and shearing. Hence, dual or multiple modifications have been offered to enhance the functionality of single-modified starches for more specific food/nonfood purposes (Ashogbon, 2021). In this context, the plausible alterations in starch digestibility following the simultaneous application of double/multiple modifications could be complicated and depend on various factors such as the type of starch, the concentration of chemical compounds used, and the order of modifications applied.

4.1 | Dual modifications

In general, dual modifications can be categorized as homogenous modifications, such as dual chemical, dual physical, and dual enzymatic methods, or as dual heterogeneous modifications, which involve combining different individual single methods, such as dual chemical-physical, chemical-enzymatic, and physical-enzymatic. However, most of the studies in the literature have been focused on dual homogenous modifications.

4.2 | Dual chemical modification

Chemical modification requires the addition of various functional groups (such as ester, carboxylic, ether, and amino groups) to the

molecules while leaving their size and shape unchanged. Chemical approaches, including oxidation, esterification, and etherification, comprise binding of reactive sites of -OH groups of starch with chemical groups, altering the chemistry of the starch matrix. However, there are limitations on these methods because of environmental and consumer safety concerns (Ashogbon, 2021). In a dual chemical modification, two different chemical processes are used, such as acid hydrolysis and succinylation, cross-linking (CL) and acetylation (AC), oxidation and CL, and so on (Table 3). Chemically modified starch generally slows down the rate of starch digestion by hindering the binding of α -amylase to the glycosidic linkages. For instance, Cai et al. (2019) studied the structure and digestibility of rice starches modified via ES, AC, hydroxypropylation (HP), CL, and dual-modification (HP-CL and AC-CL) under extrusion condition. They outlined that implementing the cross-linking reactions on AC and HP starches resulted in the formation of granules of less size and more compact structures (Figure 4a-h) with greater resistance against water percolation and enzyme hydrolysis. Compared with native and single-modified starches, rice starches modified via HP-CL approach possessed the greatest extent of RS (15.3%) and offered the least GI (88.1) value. These results were similar to the finding of Zaman et al. (2022) who confirmed the potency of dual modification in customizing the starch digestibility and obtained a remarkable increase in RS content (70%) upon the simultaneous modification of sago starch via phosphorylation and AC. The increases in RS content of rice starches with the use of AC and HP have been stated in the study of Iftikhar et al. (2022). Reduced enzyme digestibility results from the cross-linking bridges that prevent digestive enzymes from moving through the interior area of swollen cross-linking starch granules. In the study of Sriprabloom et al. (2023), native cassava starch was chemically modified by octenylsuccinylation followed by cross-linking and cross-linking followed by octenylsuccinylation. The dual modification significantly reduced RDS and SDS contents but enhanced RS content as compared to native and single modified cassava starches. The lowest RDS content (51.25%–52.35%) and the highest RS content (19.48%–22.00%) among all the starch samples were obtained for dual modified starches. This could be explained by the starch granules being stronger as a result of the crosslinking agents combined with the physical resistance posed by the bulky octenylsuccinylation groups, which prevented digestive enzymes from entering the granules and reduced their enzymatic digestibility (Sriprabloom et al., 2023).

4.3 | Dual physical modification

During physical treatments, heat, steam, pressure, sound, and electricity are used; thus, physical modifications are changes made to the characteristics of starches without affecting the free -OH groups at sites C2, C3, and C6 on the glucose units of amylose and amylopectin. Dual physical modification, such as ANN/HMT, HMT/US, ANN and autoclave retrogradation, ANN/US, US/microwave, US/high voltage electric field (HV), and microwave/cold plasma, has extensively been used in different studies (Table 3) (Rostamabadi, Bajer, et al., 2023). Typically, during the first modification, architectural changes such as

TABLE 3 An overview of the impact of double and multiple modifications on starch digestibility.

Type of modification	Starch source	Key findings	References
Homogenous/Chemical modification			
Retrogradation and AC	Corn starch	<ul style="list-style-type: none"> ○ 52.32% digested of native corn starch was found after 30 min of reaction ○ The degree of digestion of retrograded starch was 34.31% after 30 min of reaction ○ The degree of digestion for retrograded acetylated starch was 25.88% after 30 min of reaction ○ A drastic decrease in the digestion rate of dual modified starch was observed 	Gangopadhyay et al. (2022)
AC and HP	Rice starch	<ul style="list-style-type: none"> ○ Modification diminished enzymatic hydrolysis resulted in higher RS and SDS (up to 20% of each) with the modification 	Iftikhar et al. (2022)
CL and esterification with octenylsuccinylation	Cassava starch	<ul style="list-style-type: none"> ○ The increased content of RS in cassava starch treated with two modifications was a result of the combined effect of functional groups added during both the first and second modifications 	Sriprabhom et al. (2023)
Esterification with octenylsuccinylation and CL with epichlorohydrin	Banana starch	<ul style="list-style-type: none"> ○ Dual modified starch had the lowest SDS and the highest RS content ○ The ungelatinized specimens showed low RDS (4.23%–9.19%), whereas the modified samples revealed an increment in SDS (from 10.79% to 16.79%) and possessed high RS content (74.07%–85.07%) ○ After cooking, the starch that had been esterified showed the highest SDS content at 21.32%, with cross-linked starch following at 15.13% 	Carlos-Amaya et al. (2011)
Carboxymethylation and CL with epichlorohydrin	Rice starch	<ul style="list-style-type: none"> ○ Non-cross-linked and lower cross-linked rice starches were mostly hydrolyzed within the first 20 min of digestion, which have a high amount of RDS and very small amounts of SDS and resistant starch ○ At higher cross-linking levels, the lower values of RDS in these samples (81%–90%) were obtained ○ As time progressed, the SDS values and the RS contents increased ○ As higher concentrations of ECH (3%–10%) were utilized, the amounts of RDS reduced and the amounts of SDS and RS enhanced 	Kittipongpatana and Kittipongpatana (2013)
Phosphorylation and heat treatment	Taipot starch	<ul style="list-style-type: none"> ○ The improved RS content of starch modified with dual treatments (phosphorylation and heat treatment and phosphorylation and autoclaving) 	Aaliya et al. (2021)
Phosphorylation and autoclaving			

(Continues)

TABLE 3 (Continued)

Type of modification	Starch source	Key findings	References
Homogenous/Physical modification			
Repeated HMT	Sweet potato starch	<ul style="list-style-type: none"> ○ The damage to starch molecules and the fewer extra linkages among starch chains led to formation of higher SDS and RDS contents and lower RS content by repeated heat-moisture treatments for three times ○ More additional bindings among starch chains and the perfect crystallite near the granule's surface, which prevent the disruption of starch molecules resulted in lower SDS and RDS and higher content of RS produced HMT cycling beyond three times 	Huang et al. (2016)
HMT and ANN	Cassava starch	<ul style="list-style-type: none"> ○ Increases in RS content and decreases in SDS content were observed for all hydrothermally treated samples ○ The process of annealing after HMT led to larger, more uniform crystal sizes and an increased content of RS ○ The HMT after annealing resulted in a smaller peripheral crystal size with an improved melting temperature 	Boonna and Tongta (2018)
HMT and ANN	Pea, lentil, and navy bean starches	<ul style="list-style-type: none"> ○ In granular starches, annealing and HMT increased SDS and decreased RS content in all starches ○ In gelatinized starches, annealing and HMT decreased the RDS level and increased the SDS content and RS level. The alterations described above were more noticeable in starches that had undergone dual modifications 	Chung et al. (2010)
HMT and ANN	Water caltrop starch	<ul style="list-style-type: none"> ○ Higher RS content was obtained with dual modification 	Liu et al. (2021)
HMT and ANN	Lotus rhizome starch	<ul style="list-style-type: none"> ○ All hydrothermal treatment increased the damaged starch and decreased the RS 	Yeh and Lai (2021)
HMT and ANN	Waxy rice starch	<ul style="list-style-type: none"> ○ Increases in SDS content with HMT and dual modification were obtained. However, RS levels reduced in all single- and dual-treated starches when compared with native starch 	Zeng et al. (2015)
ANN and autoclave retrogradation	Potato starch	<ul style="list-style-type: none"> ○ Compared to unmodified starch, the modified starches showed a reduced glyceemic load and glyceemic index 	Akanbi et al. (2019)
US and ANN	Foxtail millet starch	<ul style="list-style-type: none"> ○ US prior to ANN increased the amylose content and RS level ○ US prior to ANN led to the formation of A-type diffraction pattern and increased crystallinity, likely due to the more ordered arrangement of double helix chains 	Babu et al. (2019)
US and ANN	Waxy maize starch	<ul style="list-style-type: none"> ○ RS content was increased upon dual modification ○ The modification treatment led to an increase in the relative crystallinity and a change in retrogradation enthalpy. This indicated the structural rearrangement of debranched molecules 	Chang et al. (2021)

(Continues)

TABLE 3 (Continued)

Type of modification	Starch source	Key findings	References
US and HMT	Maize starch	<ul style="list-style-type: none"> The dual-modification treatment increased the rearrangement of the starch structure, resulting in increases in the RS content and the formation of thermostable, SDS, and RS 	Flores-Silva et al. (2018)
US and microwave	Maize starch and potato starch	<ul style="list-style-type: none"> The single treatment of microwave led to the formation of the amylose–lipid complex resulting in increases in RS and decreases in RDS US treatment and dual treatment caused to the loosening of the internal structure of starch by ultrasound and hence it increased the starch digestibility 	Zhou et al. (2023, p. 20)
US and high voltage electric field (HV)	Native potato starch	<ul style="list-style-type: none"> The higher RS content of HV–US than US–HV due to the interactions between different chains of starch or different microconstituents and the rearrangement and creation of hydrogen bonds of the starch inner structure, which provided the highest relative crystallinity, leading to a higher RS and SDS Lower RS content of US–HV samples caused by the partial disruption of the ordered chains, which facilitated enzymatic breakdown 	Cao and Gao (2020)
Twin-screw extrusion and cold plasma	Potato starch	<ul style="list-style-type: none"> A short treatment time led to crystallite perfection and resulted in reduced vulnerability to enzymatic digestion. Hence, a lower RDS and higher RS content of starch modified by cold plasma compared with native A long treatment time destroyed the outer and inner parts of starch granules. Hence, the degree of hydrolysis increased, leading to the formation of more RDS and less RS content The destruction of starch granules by twin-screw extrusion treatment led to formation of higher RDS and lower RS content 	Sun et al. (2021)
Microwave and cold plasma	Rice starch	<ul style="list-style-type: none"> The amylose molecules in rice starch were polymerized to form larger molecules with microwave and cold plasma treatments RS increased first, but it reduced as the cold plasma treatment time extended 	Sun et al. (2022)
Dual-frequency power US (20/40, 40/60, and 20/60 kHz)	Arrowhead starch	<ul style="list-style-type: none"> The digestion resistance of the V-type complexes was higher than that of the unsonicated and native complexes because a portion of RDS was converted into RS All sonicated samples had higher RS contents and lower RDS contents. The V-type complex formation led to higher resistance to digestion SDS increased with the increasing sonication time 	Raza et al. (2022)

(Continues)

TABLE 3 (Continued)

Type of modification	Starch source	Key findings	References
Homogenous/Enzyme modification			
β -Amylase and transglucosidase	Oat starch	<ul style="list-style-type: none"> ○ The dual enzyme modification resulted in the creation of an intermittent, densely packed, fibrous structure with multiple surface cracks ○ Dual enzyme-modified starches had a change in the pattern from A-type to A + V type and decreased in crystallinity ○ Dual enzyme-modified starches enhanced branch density and RC and increased RS content 	Shah et al. (2018)
β -Amylase and transglucosidase	Maize starch	<ul style="list-style-type: none"> ○ Dual-enzyme treatment led to the cleavage of α-1,4 linkage of starch and hence decreased the molecule weight and increased the amount of short chains and α-1,6 linkages. As a result, higher SDS content was obtained 	Miao et al. (2014)
α -Amylase and pullulanase	Corn starch	<ul style="list-style-type: none"> ○ Dual-enzyme treatment led to a decrease in the degree of polymerization of the enzyme-modified starch as compared to that of native starch, and the maximum RS content was obtained 	Liu et al. (2022)
1,4- α -Glucan branching enzymes from <i>Rhodothermus obamensi</i> STB05 and <i>Geobacillus thermoglucosidans</i> STB02	Corn starch	<ul style="list-style-type: none"> ○ The dual enzyme modification process led to higher branching densities, more abundant short branches, and shorter external chains, resulting in decreases in the RDS fraction in corn starch 	Yu et al. (2021)
Heterogenous/Psychical and chemical modification			
US and acetylation (AC) by acetic acid	Cassava starch	<ul style="list-style-type: none"> ○ Higher RS and SDS contents were observed in the modified starches compared to native starch ○ Lower RDS and higher RS were obtained for US-AC samples than AC-US group ○ If acetic acid treatment is performed prior to US, the starch molecule undergoes some removal of acetyl groups already attached to it, degradation of starch chains that contain these acetyl groups, and enhanced enzyme accessibility, resulting in elevated digestibility ○ The decline in digestible starch content and increment in SDS and RS contents following modification showed that much of the RDS content converted to SDS and RS contents 	Khurshida et al. (2021)
Autoclaving-retrogradation	Oat starch	<ul style="list-style-type: none"> ○ Dual autoclaving-retrogradation treatment elevated the RS content 	Shah et al. (2016)
Autoclaving-retrogradation	Rice starch	<ul style="list-style-type: none"> ○ The highest RS content in starch with high amylose content ○ Higher RS contents of treated rice starches than native starches ○ The process of dual autoclaving and retrogradation resulted in a restructuring of both the amylose and amylopectin components of starch, leading to improvements in its physicochemical characteristics and digestibility 	Ashwar et al. (2016)
Retrogradation and ANN	Rice starch	<ul style="list-style-type: none"> ○ ANN transformed SDS to RS fractions by enhancing the structural integrity of SDS 	Iftikhar and Dutta (2019)

(Continues)

TABLE 3 (Continued)

Type of modification	Starch source	Key findings	References
HMT, ANN, and dual retrogradation	Banana starch	<ul style="list-style-type: none"> ○ HMT gave the highest SDS and RS ○ HMT and ANN increased the RC, but dual retrogradation decreased the RC ○ HMT and dual retrogradation altered XRD patterns from B to A and A + B type, respectively, but annealing did not change the XRD patterns ○ A more porous surface with HMT and dual retrogradation provided higher digestibility 	Cahyana et al. (2019)
Oxidation, AC, AC after oxidation (dual modification), and physical modification such as ANN	Kithul palm starch	<ul style="list-style-type: none"> ○ ANN increased the RC and hence the structural stability ○ More variations in all physicochemical and digestibility properties of starch subjected to dual modification were obtained compared to starch subjected to single modifications like oxidation, AC, and ANN ○ Higher RS and lower digestibility of all modified starches were obtained compared to native starch 	Sudheesh et al. (2019)
ANN and CL	Maize starch	<ul style="list-style-type: none"> ○ CL followed by ANN induced a synergistic effect in the amorphous segments of starch, consolidating the internal structure of starch and decreasing enzymatic hydrolysis. This provided an anti-retrogradation effect and gave the highest RS content ○ A prior ANN process hindered the occurrence of CL of starch; hence, RDS and SDS contents to those of starch modified by ANN alone were obtained ○ CL led to less impairment to the starch structure and restricted the accessibility of amylase to starch than native starch with no effect on the RDS content the RS increased and SDS declined in CL reactions 	Jia et al. (2022)
HMT and CL	Waxy maize starch	<ul style="list-style-type: none"> ○ CL-HMT induced the formation of RS. However, this was not observed in HMT-CL treatment 	Park et al. (2018)
Dry-heat and phosphorylation, heat-moisture and phosphorylation, and autoclave and phosphorylation	Talipot starch	<ul style="list-style-type: none"> ○ An improve in RS content was obtained with the use of HMT-phosphorylation and autoclave-phosphorylation ○ The highest degree of crosslinking was obtained with the autoclave pretreated phosphorylated talipot starch sample ○ The highest RS content was obtained with the application of autoclave treatment before phosphorylation 	Aaliya et al. (2021)

(Continues)

TABLE 3 (Continued)

Type of modification	Starch source	Key findings	References
Heterogenous/Psychical and enzymatic modification			
Pullulanase and temperature-cycling	Sago starch	<ul style="list-style-type: none"> The modification increased SDS and reduced RDS 	Bunyasetthakun et al. (2020)
Amylosucrase and hydrothermal treatment	Rice starch	<ul style="list-style-type: none"> B-type crystalline structures were observed in starches modified with amylosucrase Hydrothermal treatment increased the RC with moisture level Decreases in RDS content in normal and waxy starches modified with amylosucrase after hydrothermal treatment were observed Effective use of amylosucrase and hydrothermal treatment in waxy rice starch than normal rice starch lowered the digestibility 	Kim et al. (2016)
Heterogenous/Enzymatic and chemical modification			
α -amylase and AC	Corn starch	<ul style="list-style-type: none"> The incorporation of both enzymatic hydrolysis and AC techniques resulted in an increased resistance to starch digestibility, primarily because of the abundant acetyl groups attached to the C2 position of the glucose units within the starch molecule, which imparted a bulkier structure 	Sahnoun et al. (2016)
Pullulanase and esterification with propionate	Rice starch	<ul style="list-style-type: none"> Increases in RS content of dually modified starches led to lower digestion hydrolysis rate 	Wang et al. (2021)
Multiple homogenous and heterogenous modifications			
Maltogenic amylase, glucan branching enzyme, pullulanase	Maize starch	<ul style="list-style-type: none"> The diffraction peaks of inclusion complexes intensified after the modification of maize starch-lauric acid complex by dual- and triple-enzymes Transglycosylation of maize starch by maltogenic amylase and glucan branching enzymes prior to pullulanase modification resulted in an increase in the number of α-1,6 glycosidic bonds within the starch molecule, as well as an increase in its branch density. This, in turn, led to the formation of a V-type complex and a more ordered structure, although to a limited extent Compared to the starch that underwent single modification, those that underwent dual and triple enzyme modifications were found to be less vulnerable to digestion 	Liu et al. (2020)
α -Amylase, pullulanase, and HMT	Indica starch	<ul style="list-style-type: none"> The modification treatment led to structural modifications offering 47.0% of RS content and positively impact intestinal health 	Zhou et al. (2014)
β -Amylase, transglucosidase, and esterification with octenylsuccinic anhydride	Maize starch	<ul style="list-style-type: none"> A decrease in digestibility was observed for native starch nanoparticles treated with β-enzymes as compared to native starch nanoparticles The dual-enzyme modification of starch resulted in a decrease in the overall rate of starch digestion due to the higher presence of shorter chains (DP 2–12) and a greater branch density (represented by the percentage of α-1,6 linkages). Furthermore, the esterification process involving octenylsuccinic anhydride led to a physical hindrance or the creation of a hydrophobic microenvironment by the bulky group of the anhydride, further contributing to the reduction in starch digestibility. Hence, the glucose yield for both starch nanoparticles treated with enzymes and native starch nanoparticles was reduced 	Lu et al. (2016)

(Continues)

TABLE 3 (Continued)

Type of modification	Starch source	Key findings	References
Pullulanase and microwave, citric acid esterification	Corn starch	<ul style="list-style-type: none"> Enzymatic debranching increased the amylose content and paste clarity, while declined the in vitro digestibility and RC of native starch Microwave assisted citric acid esterification decreased amylose content, in vitro enzymatic digestibility and RC compared to native starch. The digestion resistance of microwave assisted citric acid debranched starch > microwave assisted citric acid esterification treatment > debranched starch > native starch The A-type crystalline pattern of normal starch and microwave assisted citric acid debranched starch altered to B-type crystalline pattern after microwave assisted citric acid esterification treatment 	Hu et al. (2021)
Autoclaving/autoclaving and pullulanase and autoclaving and β -amylase, transglucosidase and pullulanase	Rice starch	<ul style="list-style-type: none"> The lowest glycemic index was obtained in starch treated with autoclaving and β-amylase, transglucosidase and pullulanase Dense structure and high short-chain ratio were obtained after autoclaving and sequential triple enzyme modification 	Li et al. (2020)
Acid hydrolysis, autoclaving-cooling cycles, and HMT	Cassava starch	<ul style="list-style-type: none"> The native starch underwent a single modification process (5% citric acid at 45°C for 3 h) and subsequently a dual modification process involving autoclaving-cooling cycles and HMT The application of multiple modification processes resulted in the complete removal of the granular structure of the starch, leading to the retrogradation of amylose linear chains within the starch granules and the formation of a more crystalline structure. As a result, the starch exhibited higher levels of RS 	Adhiyamaan and Parimalavalli (2020)
Single-retrogradation, dual-retrogradation, and triple-retrogradation	Waxy wheat starch	<ul style="list-style-type: none"> When subjected to a retrogradation time interval of 48 h, the dual-treated starch demonstrated a maximum yield of 44.41% for SDS The X-ray diffraction patterns of the treated starches shifted from an A-type pattern to a B-type pattern The relative crystallinity of modified starch decreased because of the interaction between amylose-amylose and/or amylose-amylopectin chains 	Hu et al. (2014)
Triple retrogradation cycle with time intervals of 24, 48, and 72 h	Chickpea starch	<ul style="list-style-type: none"> Higher RS content and lower SDS content were observed in triple retrograded starch with increasing retrogradation time 	Jagannadham et al. (2017)
Autoclaving-cooling cycles (single, triple, five)	Cowpea starch	<ul style="list-style-type: none"> Autoclaving-cooling led to increases in the amylose content and RS content due to increases in crystallite and double helix in modified starch The crystalline structure of cowpea starch underwent a transformation from a C-type structure to a combination of B-type and V-type structures 	Ratnaningsih et al. (2020)

Abbreviations: CL, crossing-linking; ECH, epichlorohydrin; HP, hydroxypropylation; HMT, heat-moisture treatment; RS, resistant starch; RDS, rapidly digestible starch; SDS, starch slowly digestible starch; US, ultrasonication.

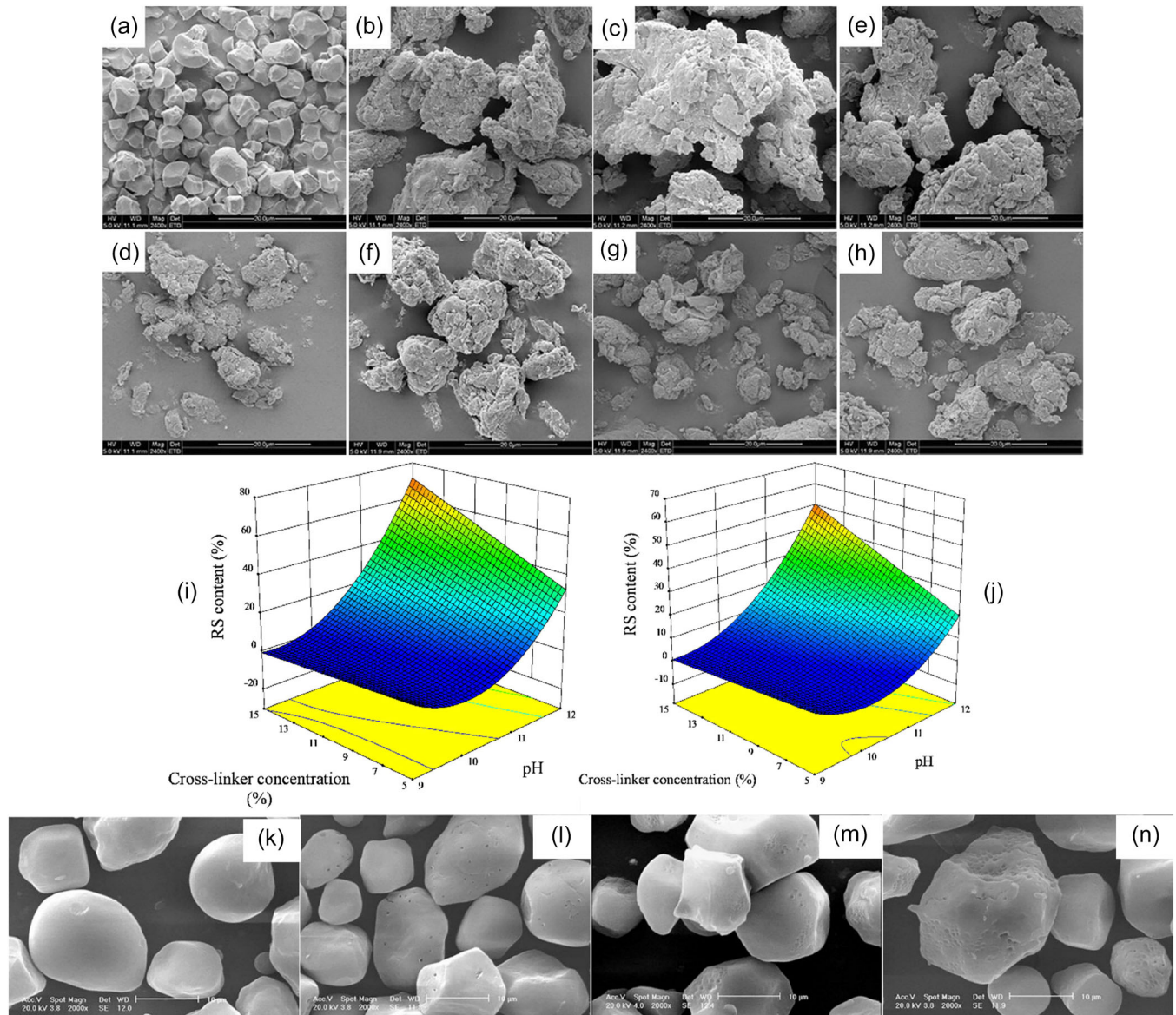


FIGURE 4 Scanning electron micrographs of native rice starch (a), control (b), OSA (c), hydroxypropylation (HP) (d), acetylation (AC) (e), crossing-linking (CL) (f), HP-CL (g), AC-CL (h). Response surface plots of resistant starch (RS) content of corn starch cross-linked under sonicated condition (i) and conventional condition (j); scanning electron microscopy (SEM) images of normal corn (k), ultrasound treated corn (l) conventional cross-linked (m) and sonicated cross-linked (n). *Source:* (a–h), reprinted with permission from Cai et al. (2019), (i–n) reprinted with permission from Falsafi et al. (2019).

emerging pores, cracks, indentations, and holes on granular surfaces, weakening of starch chains, and repositioning of amylose/amylopectin molecules happen, which maximizes the impact of the second alteration (Ashogbon, 2021). In a study performed by Boonna and Tongta (2018), the cassava starch digestibility was successfully manipulated by physical HMT and ANN treatments where dual modification resulted in greater starch resistibility against digestion. Based on their results the use of ANN after HMT was found to be more effective at providing the highest RS yield due to the production of a larger lateral crystal size with better homogeneity. Zeng et al. (2015) found increased SDS content when starch was modified by HMT and ANN, but RS levels

reduced in all treated starches relative to native starch. These might be related to the flawed crystalline structures that could not be further improved and were found to be consistent with the crystallinity data. In another work performed by Babu et al. (2019), foxtail millet starch was altered via US, ANN, and dual modifications (i.e., US-ANN and ANN-US). Although the sole application of sonication did not affect starch digestibility, its combination with ANN resulted in a remarkable reduce in RDS and enhancement in SDS and RS. In fact, the breakages in long chains of starch molecules facilitate their reorientation/rearrangement upon subsequent ANN process resulting in more resistibility against digestive enzymes.

4.4 | Dual enzyme modification

Debranching enzymes like pullulanase and isoamylase hydrolyze 1–6 links of amylopectin to generate linear chains, which are subsequently retrograded to enhance SDS or RS fractions, allowing for the creation of enzymatic modifications. Exo-corrosion and endo-corrosion are the two mechanisms by which the native starch granules undergo enzymatic depolymerization. Exo-corrosion entails the enzymatic degradation of granules' outer surface and the formation of distinctive fissures and pits. On the contrary, endo-corrosion refers to the creation of a pathway toward the hilum of the granule, leading to a decrease in the granule's structural strength and resulting in its disintegration (Ashogbon, 2021). Oat starches from three different varieties were modified with both β -amylase and transglucosidase and their physicochemical and nutritional attributes were investigated by Shah et al. (2018). The dual enzyme modification resulted in the formation of granules with an uneven and dense fibrous structure, which contained multiple surface cracks. In dual enzyme modified starches, the pattern changed from A-type to A + V type, accompanied by a reduction in crystallinity. Furthermore, the dual modification increased RS content, which might be attributed to the improved density of branching and crystalline structures. Similarly, Miao et al. (2014) showed that dual-enzymes treatment (β -amylase and transglucosidase) led to a decrease in the molecular weight as a result of increased number of short chains and an increase in α -1,6 linkages resulting in the slow digestion property of starch.

4.5 | Dual physical/chemical modification

A typical approach to induce the formation of RS in starch granules is applying the consecutive processes of acid hydrolysis-hydrothermal treatments, where a mild acid hydrolysis prior to heat treatment results in the generation of starch molecules with less molecular weight. Such starch fractions are more mobile and could feasibly rearrange into crystallite structures of less susceptibility to hydrolysis during the subsequent heating-cooling treatments (Van Hung et al., 2017). Falsafi et al. (2019), in an interesting attempt, tried to customize CS digestibility via its modification through a combination of sonication and cross-linking reactions. When compared with conventionally cross-linked samples, sonication remarkably diminished the starch digestibility due to its potential in intensifying the chemical reactions through mechanical agitation and increasing the pressure and temperature of the media. Furthermore, sonication provokes the creation of crack surfaces and pores, which eases the entering of cross-linked molecules into the starch granules (Figure 4i–n). In another attempt, Khurshida et al. (2021) outlined that dual modification by US and AC via acetic acid could change the digestibility of cassava starch. The order in which the modifications were carried out had a considerable impact on the properties of the starches that underwent dual enzyme modification. When US was applied before AC, the amount of RDS decreased substantially more than when AC was done before

US. Similarly, the RS content of starch exposed to US before AC was found to be significantly higher. Following US, the disruption of granules and starch molecules allows a greater number of acetyl groups to be linked which limits the activity of enzymes. Conversely, if AC was carried out before US, the application of sonication could potentially eliminate some of the previously attached acetyl groups from the starch molecule, which would make the enzymes more accessible and enhance digestibility. Similarly, Jia et al. (2022) reported the significant role of the sequence of modifications on the digestibility of starches. The authors reported that crosslinking followed by ANN strengthened the internal structure of starch and decreased enzymatic hydrolysis (Table 3). Iftikhar et al. (2022) stated that in the dual modified samples, ANN partially transformed SDS into RS fractions by enhancing the structural integrity of SDS.

In addition to crystalline perfection, granule morphology also affects the extent of digestibility. Cahyana et al. (2019) stated that compared to annealed and heat moisture treated flour, dual retrogradation provided a more porous surface, which made starch molecules more easily accessible for the amylase, resulting in higher digestibility. The amylose content has a noticeable effect on the digestibility of starches. The impact of ES on waxy, normal, gelose 50, and gelose 80 maize starches with 1%, 23%, 50%, and 80% amylose concentrations was examined by Hong et al. (2018). The ES (both by conventional and dual modification) brought about changes in the glycemic digestibility of the starches, resulting in a decrease in RDS and an increase in SDS and RS fractions. It was postulated that starch granules with a greater amylose content (higher than 50%) were more susceptible to ES because these granules had visible deformation and roughness after ES. This could be explained by the fact that the amorphous region was easily attacked by acetyl groups and that a larger area of amorphous sections resulted from increased amylose content. The higher the amylose content, the more the AC reactions. As a result, acetylated starch with 80% amylose content had better glycemic digestibility than 56.7% RS. Besides, more remarkable damages, shape roughness, and serious deformation of particles that appeared on the surface upon PEF-assisted ES compared to conventionally esterified starches made starch more susceptible to enzyme digestion, resulting in a higher RDS.

4.6 | Dual physical/enzymatic modification

Amylosucrase was applied to maximize the SDS and RS fractions in the study of Kim et al. (2016). The extent of lengthy branched chains tends to grow with the degree of retrogradation, which suggests that the lengthening of branched chains by amylosucrase may be a significant factor in augmenting the SDS and/or RS. Hydrothermal treatment reduced the content of RDS by transforming it to SDS as well as RS, and the yield of this conversion was found to be higher after the use of hydrothermal treatment under high moisture contents. On the other hand, RDS and SDS of amylosucrase-modified waxy starch were concomitantly transformed to RS, making them less available to digestive enzymes. At 40% moisture level, hydrothermal treatment led to an

almost complete conversion of RDS to RS in amylosucrase-modified waxy starch. The higher content of SDS than RS in amylosucrase and HMT modified rice starch indicated the crystalline network that formed during HMT was insufficiently perfect to produce RS. In contrast, waxy rice starch modified with amylosucrase and HMT was more favorable for RS fabrication and showed a 20%–50% rise in RS with a 25%–40% water addition. A more ordered semicrystalline structure may be produced by waxy starch modified with amylosucrase and HMT, suggesting that dual modification of starch from different sources led to different crystalline architectures and thereby different starch digestibility. The treatment of indica rice starch (IRS) with α -amylase prior to HMT has also been proposed by Zhou et al. (2014) as a potent tool to customize starch digestibility with a remarkable increase in RS content. The RS content of IRS, HMT-IRS, and dual modified IRS were 2%, 15.3%, and 47%, respectively, which was ascribed to the formation of compact double-strand structures from short starch fractions produced upon enzyme pretreatment. Wang et al. (2023) performed an interesting attempt to intensify the RS content of CS via sonication-assisted enzyme hydrolysis (USE), microwave assisted enzyme hydrolysis, and sonication-microwave-assisted enzyme hydrolysis (USME). Their results revealed the effectual influence of USME combined treatment in RS content from 4.7% (CS) to 40.71%, whereas SDS and RDS diminished from 20.99% to 13.18% and 74.29% to 45.26%, respectively.

4.7 | Dual chemical/enzymatic modification

The synthesis and characterization of rice starch following dual modification with pullulanase debranching and propionic anhydride propionylation (for 3, 6, 12, 24, 48, and 72 h) were performed in the study of Wang et al. (2021). Debranching elevated the amylose content of starch, which showed a positive correlation with the extent of debranching reactions, indicating more –OH groups have become available for propionylation reactions. This was in accordance with the digestibility results where dual-modified starch showed less susceptibility to digestion and possessed the greatest RS content. Particularly, the prolonged debranching treatment favors the accumulation of short chain molecules, which then form a compact crystal structure through hydrogen bonding with other molecules and become less digestible. On the other hand, a short debranching treatment is more likely to increase the effectiveness of propionylation while partially impeding the production of a double helix structure, which is detrimental to the formation of an ordered crystal structure. While the increases in debranching time led to increases in RS content, SDS content also decreased with the elevated debranching time. This result suggested that RS could be formed through a tightly packed crystal structure, which is created by the ordered arrangement of short chains. In contrast, SDS could be comprised of a small portion of the partially arranged crystal area, and the majority of the disordered amorphous region.

4.8 | Multiple modifications

There are few studies on the impact of multiple modifications on starch digestibility in the literature (Table 3). The influences of single-retrogradation, dual-retrogradation, and triple-retrogradation treatments on the *in vitro* digestibility and physicochemical attributes of waxy wheat starch were studied by Hu et al. (2014). The starch samples treated with single-retrogradation increased the conversion of RDS to SDS reaching to a highest amount of 38.19% after 48 h of retrogradation. This indicates that the disorderly crystal structure was observed to become more structured during the process of recrystallization/retrogradation. On the other hand, SDS transformed into RS with an increment in retrogradation time as the RS content started to rise as the crystal structure became ever more organized. Although there was no obvious change in the content of RDS, the samples retrograded twice had a higher content of SDS and a lower content of RS compared to starch samples retrograded once or three times for the same duration. Although there was no obvious change in RDS content, the samples retrograded dually showed higher SDS and lower RS contents than single and triple retrograded starch specimens with the same retrogradation time. This result was caused by the effect of dual retrogradation on the disruption of crystallites and the reorientation or generation of linkages among amylose and amylopectin.

Liu et al. (2020) stated that the dual and triple enzyme-modified specimens showed less susceptibility to digestive enzymes than the single enzyme-modified starch. In the study of Lu et al. (2016), native starch nanoparticles were subjected to enzymatic pretreatment using β -amylase and transglucosidase and then esterified with OSA. Compared to untreated native starch nanoparticles, those treated with β -enzymes showed reduced digestibility. The overall starch digestion rate was significantly decreased, leading to higher levels of SDS and RS after dual-enzyme modification. This effect was attributed to an increase in the proportion of short chains (DP 2–12) and branch density (percentage of α -1,6 linkages). The ES with OSA starch nanoparticles because of the physical hindrance or creation of hydrophobic microenvironment resulted from the bulky group of OSA. Similarly, Li et al. (2020) found that the lowest GI was obtained in starch treated physically (autoclaving) and sequentially with triple enzyme modification (α -amylase, transglucosidase, and pullulanase) due to the dense structure and high short-chain ratio of starches.

Hu et al. (2021) investigated the digestibility of CS that was modified through different methods, including enzymatic debranching, microwave-assisted citric acid ES, and microwave-assisted citric acid debranching. Pullulanase destroyed the crystalline regions of granules and increased the amorphous sections, as shown by the changes in relative crystallinity and enthalpy of gelatinization. Enzymatic debranching increased the amount of amylose, which was then converted into enzyme-resistant double helical structures with greater crystallinity during digestion. In the case of microwave-assisted citric acid-esterified starch, the hydroxyl groups of the molecules were esterified with the citric anhydride groups, increasing the molecular weight of the

starch. This could lead to changes in the shape and positioning of starch molecules, creating obstacles that delay their breakdown by enzymes. The amorphous, crystalline, and surface regions of starch granules may be destroyed by microwaves, making them more amylase-sensitive and hastening the digestion process. The decreased digestibility of starch treated with microwave-assisted citric acid debranching, compared to microwave-assisted citric acid ES was due to the impact of enzymatic debranching on the starch's susceptibility to enzymatic digestion.

5 | CHALLENGES AND FUTURE ASPECTS

Starch, as the most important carbohydrate in human diet, has always been subjected to various modifications to provide novel physicochemical and technofunctional attributes. As discussed in this review, the digestion behavior of starch upon modification is complicated, manipulated by the interplay among inherent starch attributes and extrinsic modification parameters. Hitherto, the remarkable influence of modification conditions on starch digestibility has been well discussed in the current literature. However, on the contrary, the fundamental role of inherent starch attributes (e.g., the interactions of starch with other constituents like lipids/proteins, and long/short range ordered structure of glucan chains) needs further investigation. Overall, it is been reported that increasing the starch interactions with lipids/proteins could hinder its digestibility via declining substrate accessibility to digestive enzymes but further investigations are required to substantiate this hypothesis. Enhancing our knowledge of the simultaneous impact of inherent parameters and extrinsic modification factors on starch digestibility could help in developing novel starch products with tuned digestion properties to deliver starch-based foods with higher dietary fiber content and acceptable organoleptic attributes.

Another substantial concern in this realm that needs to be resolved is that in many studies conducted on starch modification, the changes made in their digestibility are not properly addressed. The methods utilized to determine starch digestibility have been improving over the years (Dartois et al., 2010; Englyst et al., 1992; Flores et al., 2014; Huang et al., 2016; Minekus et al., 2014; Serrano & Franco 2005; Zhong et al., 2021). However, despite the advances already verified, there are still many challenges that researchers still have to overcome. It is perceived that the most recent works that analyze the digestibility of starch employ *in vitro* methods. The main reason for this option is that when using *in vivo* models, there are many variations, ranging from age, sex, weight, and even the metabolism of the individual, which varies from animal to animal. Due to this limitation, more recent studies have focused on *in vitro* digestibility (Tables 1–3).

In vitro digestion aims to simulate the digestive process of humans; however, digestion in humans is very complex, so, perfect simulations are not yet possible (Dartois et al., 2010; Englyst et al., 1992; Flores et al., 2014; Huang et al., 2016; Minekus et al., 2014; Serrano & Franco 2005; Zhong et al., 2021). Besides, it can be observed that different methodologies have employed different concentrations and types of enzymes. As enzymes from the human body are difficult to extract or expensive to purchase, other enzymes from mammals or microorgan-

isms are usually used (Dartois et al., 2010). In addition to enzymes, *in vitro* digestibility employs conditions similar to the human body, such as pH, temperature, and peristaltic movements. More importantly, there is a wide variation of methods in the literature for measuring starch digestibility which often makes it difficult to compare data between studies. The main limitations found are as follows:

Sample preparation: some studies do not subject the starch to gelatinization, which does not make the result factual as the cooking process makes the starch available for obtaining energy by the human body. Only special cases, such as pregelatinized starches, are not subjected to cooking before consumption. The digestibility values obtained by techniques that did not subject starch to gelatinization prior to digestibility do not reflect the real digestibility.

Method standardization: Some studies do not employ the digestion steps in the mouth, stomach, and small intestine. The sequence is important because, although the digestion time in the mouth is short, it is known that digestion starts in the mouth by chewing (particle size reduction) and mixing with saliva that contains amylases and lipases. Despite not being highly digestible, this process will strongly impact subsequent stages. Therefore, protein digestion that mainly takes place in the stomach is extremely important; once it is done, it will make the starch more "available" for digestion in the small intestine.

Isolated starch or in a food matrix: The digestibility behavior is completely different in isolated starch and the food matrix. Thus, it is recommended that the digestibility be done in the best way that represents the starch application.

In the future, more comparative methods with *in vivo* and *in vitro* digestibility should be performed. Furthermore, the *in vitro* digestibility methods should be standardized by the same types of gastric and intestinal juices, containing the same volumes, amount of sample, and types of enzymes. Moreover, all stages of the digestive process should be conducted (mouth, stomach, and small intestine) so that the results can be compared and better discussed.

6 | CONCLUDING REMARKS

The use of native starches is restricted by their insolubility in cold water, low gelatinization temperature, ease of syneresis, high tendency for retrogradation, and loss of viscosity. Additionally, when subjected to processing conditions of high temperature, stress, and pH, the paste and gel of native starches become unstable. Besides, their cooking results in unpleasant gels and cohesive and rubbery pastes. Moreover, the high hydrophilicity, solubility, and low tensile strength of native starches prevent them from being used as food packaging components. Modification of starches via single, double, and multiple modifications has been the most developed platform to tackle such drawbacks that could improve their physical, optical, morphological, and barrier qualities. But whether like it or not, starch's nutritional attributes and digestibility could also be changed through its modification. Therefore, in all studies investigating the changes in starch attributes over its modification, this vital character should also be appropriately determined by performing reliable *in vitro* and *in vivo* experiments. Physical

modifications alter starch digestibility through changing the structural orientation of amylose and amylopectin molecules; for instance, sonication intensifies starch digestibility by inducing pores and channels on granules facilitating the access of digestive enzymes.

ACKNOWLEDGMENTS

Not available.

CONFLICT OF INTEREST STATEMENT

The authors report there are no conflicts of interest to declare.

FUNDING INFORMATION

No funding was received for conducting this study.

ORCID

Hadis Rostamabadi  <https://orcid.org/0000-0003-0786-3813>

Seid Reza Falsafi  <https://orcid.org/0000-0002-5056-4459>

REFERENCES

- Aaliya, B., Sunooj, K. V., Rajkumar, C. B. S., Navaf, M., Akhila, P. P., Sudheesh, C., George, J., & Lackner, M. (2021). Effect of thermal pretreatments on phosphorylation of *Corypha umbraculifera* L. stem pith starch: A comparative study using dry-heat, heat-moisture and autoclave treatments. *Polymers*, 13(21), 3855.
- Adhijamaan, P. S., & Parimalavalli, R. (2020). Effect of dual modification on crystalline formation of resistant starch from cassava. *Journal of Food Measurement and Characterization*, 14(6), 3520–3528.
- Agama-Acevedo, E., Pacheco-Vargas, G., Bello-Pérez, L. A., & Alvarez-Ramirez, J. (2018). Effect of drying method and hydrothermal treatment of pregelatinized Hylon VII starch on resistant starch content. *Food Hydrocolloids*, 77, 817–824.
- Akanbi, C. T., Kadiri, O., & Gbadamosi, S. O. (2019). Kinetics of starch digestion in native and modified sweetpotato starches from an orange fleshed cultivar. *International Journal of Biological Macromolecules*, 134, 946–953.
- Ashogbon, A. O. (2021). Dual modification of various starches: Synthesis, properties and applications. *Food Chemistry*, 342, 128325.
- Ashwar, B. A., Gani, A., Wani, I. A., Shah, A., Masoodi, F. A., & Saxena, D. C. (2016). Production of resistant starch from rice by dual autoclaving-retrogradation treatment: In vitro digestibility, thermal and structural characterization. *Food Hydrocolloids*, 56, 108–117.
- Babu, A. S., Mohan, R. J., & Parimalavalli, R. (2019). Effect of single and dual-modifications on stability and structural characteristics of foxtail millet starch. *Food Chemistry*, 271, 457–465.
- Bakouri, H., & Guemra, K. (2019). Etherification and cross-linking effect on physicochemical properties of *Zea mays* starch executed at different sequences in 1-butyl-3-methylimidazolium chloride [BMIM] Cl ionic liquid media. *International Journal of Biological Macromolecules*, 125, 1118–1127.
- Barua, S., Tudu, K., Rakshit, M., & Srivastav, P. P. (2021). Characterization and digestogram modeling of modified elephant foot yam (*Amorphophallus paeoniifolius*) starch using ultrasonic pretreated autoclaving. *Journal of Food Process Engineering*, 44(11), e13841.
- BeMiller, J. N., & Huber, K. C. (2015). Physical modification of food starch functionalities. *Annual Review of Food Science and Technology*, 6, 19–69.
- Boonna, S., & Tongta, S. (2018). Structural transformation of crystallized debranched cassava starch during dual hydrothermal treatment in relation to enzyme digestibility. *Carbohydrate Polymers*, 191, 1–7.
- Bunyasetthakun, T., Huang, Q., Sureepisan, K., Suphantharika, M., Tangsrianugul, N., & Wongsagonsup, R. (2020). Effects of dual pullulanase-debranching and temperature-cycling treatments on physicochemical properties and in vitro digestibility of sago starch and its application in Chinese steamed buns. *Starch—Stärke*, 72(9–10), 2000034.
- Cahyana, Y., Wijaya, E., Halimah, T. S., Marta, H., Suryadi, E., & Kurniati, D. (2019). The effect of different thermal modifications on slowly digestible starch and physicochemical properties of green banana flour (*Musa acuminata* colla). *Food Chemistry*, 274, 274–280.
- Cai, C., Wei, B., Tian, Y., Ma, R., Chen, L., Qiu, L., & Jin, Z. (2019). Structural changes of chemically modified rice starch by one-step reactive extrusion. *Food Chemistry*, 288, 354–360. <https://doi.org/10.1016/j.foodchem.2019.03.017>
- Cao, M., & Gao, Q. (2020). Effect of dual modification with ultrasonic and electric field on potato starch. *International Journal of Biological Macromolecules*, 150, 637–643. <https://doi.org/10.1016/j.ijbiomac.2020.02.008>
- Carlos-Amaya, F., Osorio-Diaz, P., Agama-Acevedo, E., Yee-Madeira, H., & Bello-Pérez, L. A. (2011). Physicochemical and digestibility properties of double-modified banana (*Musa paradisiaca* L.) starches. *Journal of Agricultural and Food Chemistry*, 59(4), 1376–1382. <https://doi.org/10.1021/jf1035004>
- Carvalho, A. P. M. G., Barros, D. R., da Silva, L. S., Sanches, E. A., da Costa Pinto, C., de Souza, S. M., Clerici, M. T. P. S., Rodrigues, S., Fernandes, F. A. N., & Campelo, P. H. (2021). Dielectric barrier atmospheric cold plasma applied to the modification of resistant starches from *Goepertia allouia* starch: Effect of plasma generation voltage. *International Journal of Biological Macromolecules*, 182, 1618–1627. <https://doi.org/10.1016/j.ijbiomac.2021.05.165>
- Castanha, N., da Matta Junior, M. D., & Augusto, P. E. D. (2017). Potato starch modification using the ozone technology. *Food Hydrocolloids*, 66, 343–356. <https://doi.org/10.1016/j.foodhyd.2016.12.001>
- Chang, R., Lu, H., Bian, X., Tian, Y., & Jin, Z. (2021). Ultrasound assisted annealing production of resistant starches type 3 from fractionated debranched starch: Structural characterization and in-vitro digestibility. *Food Hydrocolloids*, 110, 106141. <https://doi.org/10.1016/j.foodhyd.2020.106141>
- Charoenthai, N., Sanga-ngam, T., Kasemwong, K., Sungthongjeen, S., & Puttipipatkachorn, S. (2022). Characterization of hydroxypropyl tapioca starch and its pregelatinized starch as tablet disintegrants. *Starch—Stärke*, 74(5–6), 2100263. <https://doi.org/10.1002/star.202100263>
- Chen, Y., McClements, D. J., Peng, X., Chen, L., Xu, Z., Meng, M., Ji, H., Long, J., Qiu, C., Zhao, J., & Jin, Z. (2023). Research progresses on enzymatic modification of starch with 4- α -glucanotransferase. *Trends in Food Science & Technology*, 131, 164–174. <https://doi.org/10.1016/j.tifs.2022.11.025>
- Chen, Y.-F., Kaur, L., & Singh, J. (2018). Chemical modification of starch. In M. Sjöö & L. Nilsson (Eds.), *Starch in food* (2nd ed., pp. 283–321). Woodhead Publishing. <https://doi.org/10.1016/B978-0-08-100868-3.00007-X>
- Chung, H.-J., Liu, Q., & Hoover, R. (2010). Effect of single and dual hydrothermal treatments on the crystalline structure, thermal properties, and nutritional fractions of pea, lentil, and navy bean starches. *Food Research International*, 43(2), 501–508. <https://doi.org/10.1016/j.foodres.2009.07.030>
- Clasen, S. H., Müller, C. M. O., Parize, A. L., & Pires, A. T. N. (2018). Synthesis and characterization of cassava starch with maleic acid derivatives by etherification reaction. *Carbohydrate Polymers*, 180, 348–353. <https://doi.org/10.1016/j.carbpol.2017.10.016>
- Colussi, R., Kaur, L., da Rosa Zavareze, E., Dias, A. R. G., Stewart, R. B., & Singh, J. (2018). High pressure processing and retrogradation of potato starch: Influence on functional properties and gastro-small intestinal digestion in vitro. *Food Hydrocolloids*, 75, 131–137. <https://doi.org/10.1016/j.foodhyd.2017.09.004>
- Colussi, R., Kringel, D., Kaur, L., da Rosa Zavareze, E., Dias, A. R. G., & Singh, J. (2020). Dual modification of potato starch: Effects of heat-moisture and high pressure treatments on starch structure and functionalities. *Food Chemistry*, 318, 126475. <https://doi.org/10.1016/j.foodchem.2020.126475>

- da Costa Pinto, C., Sanches, E. A., Clerici, M. T. P. S., Rodrigues, S., Fernandes, F. A. N., de Souza, S. M., Teixeira-Costa, B. E., de Araújo Bezerra, J., Lamarão, C. V., & Campelo, P. H. (2023). Modulation of the physicochemical properties of *Aria (Goeppertia allouia)* starch by cold plasma: Effect of excitation frequency. *Food and Bioprocess Technology*, 16(4), 768–784. <https://doi.org/10.1007/s11947-022-02970-6>
- da Rosa Zavareze, E., Mello El Halal, S. L., de los Santos, D. G., Helbig, E., Pereira, J. M., & Guerra Dias, A. R. (2012). Resistant starch and thermal, morphological and textural properties of heat-moisture treated rice starches with high-, medium- and low-amylose content. *Starch-Stärke*, 64(1), 45–54.
- Ding, Y., Luo, F., & Lin, Q. (2019). Insights into the relations between the molecular structures and digestion properties of retrograded starch after ultrasonic treatment. *Food Chemistry*, 294, 248–259. <https://doi.org/10.1016/j.foodchem.2019.05.050>
- Dong, H., & Vasanthan, T. (2020). Amylase resistance of corn, faba bean, and field pea starches as influenced by three different phosphorylation (cross-linking) techniques. *Food Hydrocolloids*, 101, 105506. <https://doi.org/10.1016/j.foodhyd.2019.105506>
- Dreher, M. L., Dreher, C. J., Berry, J. W., & Fleming, S. E. (1984). Starch digestibility of foods: A nutritional perspective. *C R C Critical Reviews in Food Science and Nutrition*, 20(1), 47–71. <https://doi.org/10.1080/10408398409527383>
- Duque, S. M. M., Leong, S. Y., Agyei, D., Singh, J., Larsen, N., Sutton, K., & Oey, I. (2022). Understanding the mechanism of how pulsed electric fields treatment affects the digestibility and characteristics of starch in oat flour. *Applied Sciences*, 12(20), 20. <https://doi.org/10.3390/app122010293>
- Egharevba, H. O. (2019). Chemical properties of starch and its application in the food industry. In *Chemical properties of starch*. IntechOpen. <https://doi.org/10.5772/intechopen.87777>
- Englyst, H. N., Kingman, S. M., & Cummings, J. H. (1992). Classification and measurement of nutritionally important starch fractions. *European Journal of Clinical Nutrition*, 46, (Suppl 2), S33–S50.
- Englyst, K., Goux, A., Meynier, A., Quigley, M., Englyst, H., Brack, O., & Vinoy, S. (2018). Inter-laboratory validation of the starch digestibility method for determination of rapidly digestible and slowly digestible starch. *Food Chemistry*, 245, 1183–1189. <https://doi.org/10.1016/j.foodchem.2017.11.037>
- Falsafi, S. R., Maghsoudlou, Y., Aalami, M., Jafari, S. M., & Raeisi, M. (2019). Physicochemical and morphological properties of resistant starch type 4 prepared under ultrasound and conventional conditions and their in-vitro and in-vivo digestibilities. *Ultrasonics Sonochemistry*, 53, 110–119. <https://doi.org/10.1016/j.ultsonch.2018.12.039>
- Falsafi, S. R., Maghsoudlou, Y., Aalami, M., Jafari, S. M., Raeisi, M., Nishinari, K., & Rostamabadi, H. (2022). Application of multi-criteria decision-making for optimizing the formulation of functional cookies containing different types of resistant starches: A physicochemical, organoleptic, in-vitro and in-vivo study. *Food Chemistry*, 393, 133376. <https://doi.org/10.1016/j.foodchem.2022.133376>
- Falsafi, S. R., Maghsoudlou, Y., Rostamabadi, H., Rostamabadi, M. M., Hamed, H., & Hosseini, S. M. H. (2019). Preparation of physically modified oat starch with different sonication treatments. *Food Hydrocolloids*, 89, 311–320. <https://doi.org/10.1016/j.foodhyd.2018.10.046>
- Falsafi, S. R., Topuz, F., & Rostamabadi, H. (2023). Dialdehyde carbohydrates – Advanced functional materials for biomedical applications. *Carbohydrate Polymers*, 321, 121276. <https://doi.org/10.1016/j.carbpol.2023.121276>
- Fan, Y., & Picchioni, F. (2020). Modification of starch: A review on the application of “green” solvents and controlled functionalization. *Carbohydrate Polymers*, 241, 116350. <https://doi.org/10.1016/j.carbpol.2020.116350>
- Ferrua, M. J., & Singh, R. P. (2015). Human gastric simulator (Riddet model). In K. Verhoeckx, P. Cotter, I. López-Expósito, C. Kleiveland, T. Lea, A. Mackie, T. Requena, D. Swiatecka, & H. Wichers (Eds.), *The impact of food bioactives on health: In vitro and ex vivo models*. Springer. <http://www.ncbi.nlm.nih.gov/books/NBK500155/>
- Flores-Silva, P. C., Alvarez-Ramirez, J., & Bello-Perez, L. A. (2018). Effect of dual modification order with ultrasound and hydrothermal treatments on starch digestibility. *Starch—Stärke*, 70(5–6), 1700284. <https://doi.org/10.1002/star.201700284>
- Fonseca, L. M., Halal, S. L. M. E., Dias, A. R. G., & da Rosa Zavareze, E. (2021). Physical modification of starch by heat-moisture treatment and annealing and their applications: A review. *Carbohydrate Polymers*, 274, 118665. <https://doi.org/10.1016/j.carbpol.2021.118665>
- Gangopadhyay, A., Bose, A., Rout, S. S., & Mohapatra, R. (2022). Application of dual modified corn starch as a polymer for the colon targeted direct compressible budesonide tablet. *Journal of Drug Delivery Science and Technology*, 74, 103556. <https://doi.org/10.1016/j.jddst.2022.103556>
- García-Tejeda, Y. V., Salinas-Moreno, Y., Barrera-Figueroa, V., & Martínez-Bustos, F. (2018). Preparation and characterization of octenyl succinylated normal and waxy starches of maize as encapsulating agents for anthocyanins by spray-drying. *Journal of Food Science and Technology*, 55(6), 2279–2287. <https://doi.org/10.1007/s13197-018-3145-7>
- García-Valle, D. E., Agama-Acevedo, E., Nuñez-Santiago, M. d. C., Alvarez-Ramirez, J., & Bello-Pérez, L. A. (2021). Extrusion pregelatinization improves texture, viscoelasticity and in vitro starch digestibility of mango and amaranth flours. *Journal of Functional Foods*, 80, 104441. <https://doi.org/10.1016/j.jff.2021.104441>
- Gilet, A., Quettier, C., Wiatz, V., Bricout, H., Ferreira, M., Rousseau, C., Monflier, E., & Tilloy, S. (2018). Unconventional media and technologies for starch etherification and esterification. *Green Chemistry*, 20(6), 1152–1168. <https://doi.org/10.1039/C7CG03135A>
- Han, Z., Shi, R., & Sun, D.-W. (2020). Effects of novel physical processing techniques on the multi-structures of starch. *Trends in Food Science & Technology*, 97, 126–135. <https://doi.org/10.1016/j.tifs.2020.01.006>
- Haq, F., Yu, H., Wang, L., Teng, L., Haroon, M., Khan, R. U., Mehmood, S., Bilal-Ul-Amin, Ullah, R. S., Khan, A., & Nazir, A. (2019). Advances in chemical modifications of starches and their applications. *Carbohydrate Research*, 476, 12–35. <https://doi.org/10.1016/j.carres.2019.02.007>
- Hong, J., Zeng, X.-A., Buckow, R., & Han, Z. (2018). Structural, thermodynamic and digestible properties of maize starches esterified by conventional and dual methods: Differentiation of amylose contents. *Food Hydrocolloids*, 83, 419–429. <https://doi.org/10.1016/j.foodhyd.2018.05.032>
- Hu, A., Chen, X., Wang, J., Wang, X., Zheng, J., & Wang, L. (2021). Effects on the structure and properties of native corn starch modified by enzymatic debranching (ED), microwave assisted esterification with citric acid (MCAE) and by the dual ED/MCAE treatment. *International Journal of Biological Macromolecules*, 171, 123–129. <https://doi.org/10.1016/j.ijbiomac.2021.01.012>
- Hu, J., Li, X., Cheng, Z., Fan, X., Ma, Z., Hu, X., Wu, G., & Xing, Y. (2022). Modified Tartary buckwheat (*Fagopyrum tataricum* Gaertn.) starch by gaseous ozone: Structural, physicochemical and in vitro digestible properties. *Food Hydrocolloids*, 125, 107365. <https://doi.org/10.1016/j.foodhyd.2021.107365>
- Hu, X.-P., Xie, Y.-Y., Jin, Z.-Y., Xu, X.-M., & Chen, H.-Q. (2014). Effect of single-, dual-, and triple-retrogradation treatments on in vitro digestibility and structural characteristics of waxy wheat starch. *Food Chemistry*, 157, 373–379. <https://doi.org/10.1016/j.foodchem.2014.02.065>
- Hu, Y., Wang, L., Zhu, H., & Li, Z. (2017). Modification of physicochemical properties and in vitro digestibility of wheat flour through superheated steam processing. *Journal of Cereal Science*, 74, 231–237. <https://doi.org/10.1016/j.jcs.2017.02.012>
- Huang, T.-T., Zhou, D.-N., Jin, Z.-Y., Xu, X.-M., & Chen, H.-Q. (2016). Effect of repeated heat-moisture treatments on digestibility, physicochemical and structural properties of sweet potato starch. *Food Hydrocolloids*, 54, 202–210. <https://doi.org/10.1016/j.foodhyd.2015.10.002>
- Van Hung, P., My, N. T. H., & Phi, N. T. L. (2014). Impact of acid and heat-moisture treatment combination on physicochemical

- characteristics and resistant starch contents of sweet potato and yam starches. *Starch—Stärke*, 66(11–12), 1013–1021. <https://doi.org/10.1002/star.201400104>
- Van Hung, P., Vien, N. L., & Lan Phi, N. T. (2016). Resistant starch improvement of rice starches under a combination of acid and heat-moisture treatments. *Food Chemistry*, 191, 67–73. <https://doi.org/10.1016/j.foodchem.2015.02.002>
- Iftikhar, S. A., & Dutta, H. (2019). Status of polymorphism, physicochemical properties and in vitro digestibility of dual retrogradation-annealing modified rice starches. *International Journal of Biological Macromolecules*, 132, 330–339. <https://doi.org/10.1016/j.ijbiomac.2019.03.206>
- Iftikhar, S., Chakraborty, S., & Dutta, H. (2022). Effect of acetylation, hydroxypropylation and dual acetylation-hydroxypropylation on physicochemical and digestive properties of rice starches with different amylose content. *Biointerface Research in Applied Chemistry*, 12, 6788–6803. <https://doi.org/10.33263/BRIAC125.67886803>
- Jagannadham, K., Parimalavalli, R., & Surendra Babu, A. (2017). Effect of triple retrogradation treatment on chickpea resistant starch formation and its characterization. *Journal of Food Science and Technology*, 54(4), 901–908. <https://doi.org/10.1007/s13197-016-2308-7>
- Jia, S., Yu, B., Zhao, H., Tao, H., Liu, P., & Cui, B. (2022). Physicochemical properties and in vitro digestibility of dual-modified starch by cross-linking and annealing. *Starch—Stärke*, 74(1–2), 2100102. <https://doi.org/10.1002/star.202100102>
- Khurshida, S., Das, M. J., Deka, S. C., & Sit, N. (2021). Effect of dual modification sequence on physicochemical, pasting, rheological and digestibility properties of cassava starch modified by acetic acid and ultrasound. *International Journal of Biological Macromolecules*, 188, 649–656. <https://doi.org/10.1016/j.ijbiomac.2021.08.062>
- Kim, J. H., Kim, H. R., Choi, S. J., Park, C.-S., & Moon, T. W. (2016). Production of an in vitro low-digestible starch via hydrothermal treatment of amylosucrase-modified normal and waxy rice starches and its structural properties. *Journal of Agricultural and Food Chemistry*, 64(24), 5045–5052. <https://doi.org/10.1021/acs.jafc.6b01055>
- Kittipongpatana, O. S., & Kittipongpatana, N. (2013). Physicochemical, in vitro digestibility and functional properties of carboxymethyl rice starch cross-linked with epichlorohydrin. *Food Chemistry*, 141(2), 1438–1444. <https://doi.org/10.1016/j.foodchem.2013.04.030>
- Kong, F., & Singh, R. P. (2010). A human gastric simulator (HGS) to study food digestion in human stomach. *Journal of Food Science*, 75(9), E627–E635. <https://doi.org/10.1111/j.1750-3841.2010.01856.x>
- Kurziel, M., Królikowska, K., Łabanowska, M., Pietrzyk, S., & Michalec, M. (2020). The effect of thermal and irradiation treatments on structural and physicochemical properties of octenyl succinate maize starches. *Food Chemistry*, 330, 127242. <https://doi.org/10.1016/j.foodchem.2020.127242>
- Lal, M. K., Singh, B., Sharma, S., Singh, M. P., & Kumar, A. (2021). Glycemic index of starchy crops and factors affecting its digestibility: A review. *Trends in Food Science & Technology*, 111, 741–755. <https://doi.org/10.1016/j.tifs.2021.02.067>
- Lawal, O. S. (2011). Hydroxypropylation of pigeon pea (*Cajanus cajan*) starch: Preparation, functional characterizations and enzymatic digestibility. *LWT—Food Science and Technology*, 44(3), 771–778. <https://doi.org/10.1016/j.lwt.2010.05.025>
- Leal-Castañeda, E. J., García-Tejeda, Y., Hernández-Sánchez, H., Alamilla-Blrán, L., Téllez-Medina, D. I., Calderón-Domínguez, G., García, H. S., & Gutiérrez-López, G. F. (2018). Pickering emulsions stabilized with native and lauroylated amaranth starch. *Food Hydrocolloids*, 80, 177–185. <https://doi.org/10.1016/j.foodhyd.2018.01.043>
- Lee, C. J., Kim, Y., Choi, S. J., & Moon, T. W. (2012). Slowly digestible starch from heat-moisture treated waxy potato starch: Preparation, structural characteristics, and glucose response in mice. *Food Chemistry*, 133(4), 1222–1229. <https://doi.org/10.1016/j.foodchem.2011.09.098>
- Li, H., Gui, Y., Li, J., Zhu, Y., Cui, B., & Guo, L. (2020). Modification of rice starch using a combination of autoclaving and triple enzyme treatment: Structural, physicochemical and digestibility properties. *International Journal of Biological Macromolecules*, 144, 500–508. <https://doi.org/10.1016/j.ijbiomac.2019.12.112>
- Li, L., Yuan, T. Z., & Ai, Y. (2020). Development, structure and in vitro digestibility of type 3 resistant starch from acid-thinned and debranched pea and normal maize starches. *Food Chemistry*, 318, 126485. <https://doi.org/10.1016/j.foodchem.2020.126485>
- Li, M.-N., Xie, Y., Chen, H.-Q., & Zhang, B. (2019). Effects of heat-moisture treatment after citric acid esterification on structural properties and digestibility of wheat starch, A- and B-type starch granules. *Food Chemistry*, 272, 523–529. <https://doi.org/10.1016/j.foodchem.2018.08.079>
- Liu, H., Liang, R., Antoniou, J., Liu, F., Shoemaker, C. F., Li, Y., & Zhong, F. (2014). The effect of high moisture heat-acid treatment on the structure and digestion property of normal maize starch. *Food Chemistry*, 159, 222–229. <https://doi.org/10.1016/j.foodchem.2014.02.162>
- Liu, J.-L., Tsai, P.-C., & Lai, L.-S. (2021). Impacts of hydrothermal treatments on the morphology, structural characteristics, and in vitro digestibility of water caltrop starch. *Molecules (Basel, Switzerland)*, 26(16), 4974. <https://doi.org/10.3390/molecules26164974>
- Liu, P., Fang, Y., Zhang, X., Zou, F., Gao, W., Zhao, H., Yuan, C., & Cui, B. (2020). Effects of multienzyme treatment on the physicochemical properties of maize starch-lauric acid complex. *Food Hydrocolloids*, 107, 105941. <https://doi.org/10.1016/j.foodhyd.2020.105941>
- Liu, Q., Shi, J., Jin, Z., & Jiao, A. (2023). Development and characterization of resistant starch produced by an extrusion–debranching strategy with a high starch concentration. *Food Hydrocolloids*, 136, 108276. <https://doi.org/10.1016/j.foodhyd.2022.108276>
- Liu, Y., Jiang, F., Du, C., Li, M., Leng, Z., Yu, X., & Du, S.-K. (2022). Optimization of corn resistant starch preparation by dual enzymatic modification using response surface methodology and its physicochemical characterization. *Foods (Basel, Switzerland)*, 11(15), 2223. <https://doi.org/10.3390/foods11152223>
- Lopez-Silva, M., Bello-Perez, L. A., Castillo-Rodriguez, V. M., Agama-Acevedo, E., & Alvarez-Ramirez, J. (2020). In vitro digestibility characteristics of octenyl succinic acid (OSA) modified starch with different amylose content. *Food Chemistry*, 304, 125434. <https://doi.org/10.1016/j.foodchem.2019.125434>
- Lu, K., Miao, M., Ye, F., Cui, S. W., Li, X., & Jiang, B. (2016). Impact of dual-enzyme treatment on the octenylsuccinic anhydride esterification of soluble starch nanoparticle. *Carbohydrate Polymers*, 147, 392–400. <https://doi.org/10.1016/j.carbpol.2016.04.012>
- Ma, Y., Zhang, W., Pan, Y., Ali, B., Xu, D., & Xu, X. (2021). Physicochemical, crystalline characterization and digestibility of wheat starch under superheated steam treatment. *Food Hydrocolloids*, 118, 106720. <https://doi.org/10.1016/j.foodhyd.2021.106720>
- Majzoobi, M., & Farahnaky, A. (2021). Granular cold-water swelling starch: properties, preparation and applications, a review. *Food Hydrocolloids*, 111, 106393. <https://doi.org/10.1016/j.foodhyd.2020.106393>
- Marboh, V., Gayary, M. A., Gautam, G., & Mahanta, C. L. (2022). Comparative study of heat-moisture treatment and annealing on morphology, crystallinity, pasting, and thermal properties of sohphlang (*Flemingia vestita*) starch. *Starch—Stärke*, 74(7–8), 2100294. <https://doi.org/10.1002/star.202100294>
- Martens, B. M. J., Flécher, T., de Vries, S., Schols, H. A., Bruininx, E. M. A. M., & Gerrits, W. J. J. (2019). Starch digestion kinetics and mechanisms of hydrolysing enzymes in growing pigs fed processed and native cereal-based diets. *The British Journal of Nutrition*, 121(10), 1124–1136. <https://doi.org/10.1017/S0007114519000503>
- Masina, N., Choonara, Y. E., Kumar, P., du Toit, L. C., Govender, M., Indermun, S., & Pillay, V. (2017). A review of the chemical modification techniques of starch. *Carbohydrate Polymers*, 157, 1226–1236. <https://doi.org/10.1016/j.carbpol.2016.09.094>
- Miao, M., Xiong, S., Jiang, B., Jiang, H., Cui, S. W., & Zhang, T. (2014). Dual-enzymatic modification of maize starch for increasing slow

- digestion property. *Food Hydrocolloids*, 38, 180–185. <https://doi.org/10.1016/j.foodhyd.2013.12.006>
- Mirzaaghaei, M., Nasirpour, A., Keramat, J., Goli, S. A. H., Dinari, M., Desobry, S., & Durand, A. (2022). Chemical modification of waxy maize starch by esterification with saturated fatty acid chlorides: Synthesis, physicochemical and emulsifying properties. *Food Chemistry*, 393, 133293. <https://doi.org/10.1016/j.foodchem.2022.133293>
- Olawoye, B., & Gbadamosi, S. O. (2020). Digestion kinetics of native and modified cardaba banana starch: A biphasic approach. *International Journal of Biological Macromolecules*, 154, 31–38. <https://doi.org/10.1016/j.ijbiomac.2020.03.089>
- Park, E. Y., Ma, J.-G., Kim, J., Lee, D. H., Kim, S. Y., Kwon, D.-J., & Kim, J.-Y. (2018). Effect of dual modification of HMT and crosslinking on physicochemical properties and digestibility of waxy maize starch. *Food Hydrocolloids*, 75, 33–40. <https://doi.org/10.1016/j.foodhyd.2017.09.017>
- Park, J. W., Seo, J. H., Hong, C. Y., Kim, M. Y., Lee, Y. J., Chun, A.-R., Lee, Y. R., Lee, J., & Jeong, H. S. (2021). Physicochemical properties of rice flour suspension treated by ultrahigh hydrostatic pressure. *Journal of Food Quality*, 2021, e8838131. <https://doi.org/10.1155/2021/8838131>
- Pratiwi, M., Faridah, D. N., & Lioe, H. N. (2018). Structural changes to starch after acid hydrolysis, debranching, autoclaving-cooling cycles, and heat moisture treatment (HMT): A review. *Starch—Stärke*, 70(1–2), 1700028. <https://doi.org/10.1002/star.201700028>
- Punia, S. (2020). Barley starch modifications: Physical, chemical and enzymatic—A review. *International Journal of Biological Macromolecules*, 144, 578–585. <https://doi.org/10.1016/j.ijbiomac.2019.12.088>
- Ratnaningsih, N., Suparmo Harmayani, E., & Marsono, Y. (2020). Physicochemical properties, in vitro starch digestibility, and estimated glycemic index of resistant starch from cowpea (*Vigna unguiculata*) starch by autoclaving-cooling cycles. *International Journal of Biological Macromolecules*, 142, 191–200. <https://doi.org/10.1016/j.ijbiomac.2019.09.092>
- Raza, H., Liang, Q., Ameer, K., Ma, H., & Ren, X. (2022). Dual-frequency power ultrasound effects on the complexing index, physicochemical properties, and digestion mechanism of arrowhead starch-lipid complexes. *Ultrasonics Sonochemistry*, 84, 105978. <https://doi.org/10.1016/j.ultsonch.2022.105978>
- Reyes, I., Hernandez-Jaimes, C., Vernon-Carter, E. J., Bello-Perez, L. A., & Alvarez-Ramirez, J. (2021). Air oxidation of corn starch: Effect of heating temperature on physicochemical properties and in vitro digestibility. *Starch—Stärke*, 73(3–4), 2000237. <https://doi.org/10.1002/star.202000237>
- Robin, F., Heindel, C., Pineau, N., Srichuwong, S., & Lehmann, U. (2016). Effect of maize type and extrusion-cooking conditions on starch digestibility profiles. *International Journal of Food Science & Technology*, 51(6), 1319–1326. <https://doi.org/10.1111/ijfs.13098>
- Rostamabadi, H., Bajer, D., Demirkesen, I., Kumar, Y., Su, C., Wang, Y., Nowacka, M., Singha, P., & Falsafi, S. R. (2023). Starch modification through its combination with other molecules: Gums, mucilages, polyphenols and salts. *Carbohydrate Polymers*, 314, 120905. <https://doi.org/10.1016/j.carbpol.2023.120905>
- Rostamabadi, H., Demirkesen, I., Hakgüder Taze, B., Can Karaca, A., Habib, M., Jan, K., Bashir, K., Nemçanu, M. R., Colussi, R., & Reza Falsafi, S. (2023). Ionizing and nonionizing radiations can change physicochemical, technofunctional, and nutritional attributes of starch. *Food Chemistry: X*, 19, 100771. <https://doi.org/10.1016/j.fochx.2023.100771>
- Sahnoun, M., Ismail, N., & Kammoun, R. (2016). Enzymatically hydrolysed, acetylated and dually modified corn starch: Physico-chemical, rheological and nutritional properties and effects on cake quality. *Journal of Food Science and Technology*, 53(1), 481–490. <https://doi.org/10.1007/s13197-015-1984-z>
- Sánchez-Rivera, M. M., Núñez-Santiago, M. d. C., Bello-Pérez, L. A., Agama-Acevedo, E., & Alvarez-Ramirez, J. (2017). Citric acid esterification of unripe plantain flour: Physicochemical properties and starch digestibility. *Starch—Stärke*, 69(9–10), 1700019. <https://doi.org/10.1002/star.201700019>
- Sehgal, S., De Bock, M., Williman, J., Taylor, B., Elbalshy, M., Galland, B., Hall, R., Paul, R., Boucsein, A., Jones, S., Frewen, C., & Wheeler, B. J. (2021). Study protocol: Safety and efficacy of smart watch integrated do-it-yourself continuous glucose monitoring in adults with Type 1 diabetes, a randomised controlled trial. *Journal of Diabetes and Metabolic Disorders*, 20(2), 2103–2113. <https://doi.org/10.1007/s40200-021-00923-y>
- Shah, A., Masoodi, F. A., Gani, A., & Ashwar, B. (2018). Dual enzyme modified oat starch: Structural characterisation, rheological properties, and digestibility in simulated GI tract. *International Journal of Biological Macromolecules*, 106, 140–147. <https://doi.org/10.1016/j.ijbiomac.2017.08.013>
- Shah, A., Masoodi, F. A., Gani, A., & Ashwar, B. A. (2016). In-vitro digestibility, rheology, structure, and functionality of RS3 from oat starch. *Food Chemistry*, 212, 749–758. <https://doi.org/10.1016/j.foodchem.2016.06.019>
- Sharma, V., Kaur, M., Sandhu, K. S., & Godara, S. K. (2020). Effect of crosslinking on physico-chemical, thermal, pasting, in vitro digestibility and film forming properties of faba bean (*Vicia faba* L.) starch. *International Journal of Biological Macromolecules*, 159, 243–249. <https://doi.org/10.1016/j.ijbiomac.2020.05.014>
- Shukri, R., Zhu, L., Seib, P. A., Maningat, C., & Shi, Y.-C. (2015). Direct in-vitro assay of resistant starch in phosphorylated cross-linked starch. *Bioactive Carbohydrates and Dietary Fibre*, 5(1), 1–9. <https://doi.org/10.1016/j.bcdf.2014.11.001>
- Singh, J., Dartois, A., & Kaur, L. (2010). Starch digestibility in food matrix: A review. *Trends in Food Science & Technology*, 21(4), 168–180. <https://doi.org/10.1016/j.tifs.2009.12.001>
- Sripriyabom, J., Tatikunakorn, P., Lerdpriyanun, P., Suphantharika, M., & Wongsagnosup, R. (2023). Effect of single and dual modifications with cross-linking and octenylsuccinylation on physicochemical, in-vitro digestibility, and emulsifying properties of cassava starch. *Food Research International*, 163, 112304. <https://doi.org/10.1016/j.foodres.2022.112304>
- Sudheesh, C., Sunooj, K. V., & George, J. (2019). Kithul palm (*Caryota urens*) as a new source of starch: Effect of single, dual chemical modifications and annealing on the physicochemical properties and in vitro digestibility. *International Journal of Biological Macromolecules*, 125, 1084–1092. <https://doi.org/10.1016/j.ijbiomac.2018.12.179>
- Sun, X., Saleh, A. S. M., Sun, Z., Ge, X., Shen, H., Zhang, Q., Yu, X., Yuan, L., & Li, W. (2022). Modification of multi-scale structure, physicochemical properties, and digestibility of rice starch via microwave and cold plasma treatments. *LWT—Food Science and Technology*, 153, 112483. <https://doi.org/10.1016/j.lwt.2021.112483>
- Sun, X., Sun, Z., Guo, Y., Zhao, J., Zhao, J., Ge, X., Shen, H., Zhang, Q., & Yan, W. (2021). Effect of twin-xuscrew extrusion combined with cold plasma on multi-scale structure, physicochemical properties, and digestibility of potato starches. *Innovative Food Science & Emerging Technologies*, 74, 102855. <https://doi.org/10.1016/j.ifset.2021.102855>
- Van Hung, P., Huong, N. T. M., Phi, N. T. L., & Tien, N. N. T. (2017). Physicochemical characteristics and in vitro digestibility of potato and cassava starches under organic acid and heat-moisture treatments. *International Journal of Biological Macromolecules*, 95, 299–305. <https://doi.org/10.1016/j.ijbiomac.2016.11.074>
- Vanier, N. L., El Halal, S. L. M., Dias, A. R. G., & da Rosa Zavareze, E. (2017). Molecular structure, functionality and applications of oxidized starches: A review. *Food Chemistry*, 221, 1546–1559. <https://doi.org/10.1016/j.foodchem.2016.10.138>
- Wang, M., Liu, G., Li, J., Wang, W., Hu, A., & Zheng, J. (2023). Structural and physicochemical properties of resistant starch under combined treatments of ultrasound, microwave, and enzyme. *International Journal of Biological Macromolecules*, 232, 123331.
- Wang, J., Wu, P., Liu, M., Liao, Z., Wang, Y., Dong, Z., & Chen, X. D. (2019). An advanced near real dynamic in vitro human stomach system to study

- gastric digestion and emptying of beef stew and cooked rice. *Food & Function*, 10(5), 2914–2925. <https://doi.org/10.1039/C8FO02586J>
- Wang, L., Chen, J., Lu, S., Xiao, P., Li, C., & Yi, C. (2022). Structural characterization, physicochemical properties and in vitro digestion of finger millet-resistant starch prepared by different methods. *International Journal of Food Science & Technology*, 57(1), 416–425. <https://doi.org/10.1111/ijfs.15432>
- Wang, M., Sun, M., Zhang, Y., Chen, Y., Wu, Y., & Ouyang, J. (2019). Effect of microwave irradiation-retrogradation treatment on the digestive and physicochemical properties of starches with different crystallinity. *Food Chemistry*, 298, 125015. <https://doi.org/10.1016/j.foodchem.2019.125015>
- Wang, R., Li, M., Liu, J., Wang, F., Wang, J., & Zhou, Z. (2021). Dual modification manipulates rice starch characteristics following debranching and propionate esterification. *Food Hydrocolloids*, 119, 106833. <https://doi.org/10.1016/j.foodhyd.2021.106833>
- Wang, X., Wen, F., Zhang, S., Shen, R., Jiang, W., & Liu, J. (2017). Effect of acid hydrolysis on morphology, structure and digestion property of starch from *Cynanchum auriculatum* Royle ex Wight. *International Journal of Biological Macromolecules*, 96, 807–816. <https://doi.org/10.1016/j.ijbiomac.2017.01.002>
- Wei, H.-X., Liang, B.-D., Chai, Y.-R., Xue, L.-P., Wang, X.-Q., & Yin, X.-M. (2020). Effect of different heat treatments on physicochemical properties and structural and digestibility of water caltrop starch. *Starch—Stärke*, 72(9–10), 1900275. <https://doi.org/10.1002/star.201900275>
- Woo, K. S., & Seib, P. A. (2002). Cross-linked resistant starch: Preparation and properties. *Cereal Chemistry*, 79(6), 819–825. <https://doi.org/10.1094/CCHEM.2002.79.6.819>
- Wu, P., & Chen, X. D. (2020). On designing biomimic in vitro human and animal digestion track models: Ideas, current and future devices. *Current Opinion in Food Science*, 35, 10–19. <https://doi.org/10.1016/j.cofs.2019.12.004>
- Wu, J., McClements, D. J., Chen, J., Hu, X., & Liu, C. (2016). Improvement in nutritional attributes of rice using superheated steam processing. *Journal of Functional Foods*, 24, 338–350.
- Xu, M., Saleh, A. S. M., Gong, B., Li, B., Jing, L., Gou, M., Jiang, H., & Li, W. (2018). The effect of repeated versus continuous annealing on structural, physicochemical, and digestive properties of potato starch. *Food Research International*, 111, 324–333. <https://doi.org/10.1016/j.foodres.2018.05.052>
- Xu, T., Zhong, Y., Chen, Q., Wu, L., Ji, S., Yang, B., Zhang, Y., Shen, J., & Lu, B. (2022). Modulating the digestibility of cassava starch by esterification with phenolic acids. *Food Hydrocolloids*, 127, 107432. <https://doi.org/10.1016/j.foodhyd.2021.107432>
- Yeh, Y., & Lai, L.-S. (2021). Effect of single and dual hydrothermal treatments on the resistant starch content and physicochemical properties of lotus rhizome starches. *Molecules (Basel, Switzerland)*, 26(14), 4339. <https://doi.org/10.3390/molecules26144339>
- Yu, L., Kong, H., Gu, Z., Li, C., Ban, X., Cheng, L., Hong, Y., & Li, Z. (2021). Two 1,4- α -glucan branching enzymes successively rearrange glycosidic bonds: A novel synergistic approach for reducing starch digestibility. *Carbohydrate Polymers*, 262, 117968. <https://doi.org/10.1016/j.carbpol.2021.117968>
- Zailani, M. A., Kamilah, H., Husaini, A., Awang Seruji, A. Z. R., & Sarbini, S. R. (2023). Starch modifications via physical treatments and the potential in improving resistant starch content. *Starch—Stärke*, 75(1–2), 2200146. <https://doi.org/10.1002/star.202200146>
- Zaman, S. A., Kamilah, H., Seruji, A. Z. R. A., Pa'ee, K. F., & Sarbini, S. R. (2022). Physicochemical properties and the functional food potential of resistant sago (*Metroxylon sagu*) starch type IV produced by phosphorylation/acetylation treatment. *Journal of Food Measurement and Characterization*, 16(2), 1702–1709. <https://doi.org/10.1007/s11694-021-01263-4>
- Zeng, F., Ma, F., Kong, F., Gao, Q., & Yu, S. (2015). Physicochemical properties and digestibility of hydrothermally treated waxy rice starch. *Food Chemistry*, 172, 92–98. <https://doi.org/10.1016/j.foodchem.2014.09.020>
- Zhang, B., Mei, J.-Q., Chen, B., & Chen, H.-Q. (2017). Digestibility, physicochemical and structural properties of octenyl succinic anhydride-modified cassava starches with different degree of substitution. *Food Chemistry*, 229, 136–141. <https://doi.org/10.1016/j.foodchem.2017.02.061>
- Zhang, Y.-R., Wang, X.-L., Zhao, G.-M., & Wang, Y.-Z. (2012). Preparation and properties of oxidized starch with high degree of oxidation. *Carbohydrate Polymers*, 87(4), 2554–2562. <https://doi.org/10.1016/j.carbpol.2011.11.036>
- Zhong, Y., Herburger, K., Xu, J., Kirkensgaard, J. J. K., Khakimov, B., Hansen, A. R., & Blennow, A. (2022). Ethanol pretreatment increases the efficiency of maltogenic α -amylase and branching enzyme to modify the structure of granular native maize starch. *Food Hydrocolloids*, 123, 107118. <https://doi.org/10.1016/j.foodhyd.2021.107118>
- Zhou, F., Liu, Q., Zhang, H., Chen, Q., & Kong, B. (2016). Potato starch oxidation induced by sodium hypochlorite and its effect on functional properties and digestibility. *International Journal of Biological Macromolecules*, 84, 410–417. <https://doi.org/10.1016/j.ijbiomac.2015.12.050>
- Zhou, Y., Meng, S., Chen, D., Zhu, X., & Yuan, H. (2014). Structure characterization and hypoglycemic effects of dual modified resistant starch from indica rice starch. *Carbohydrate Polymers*, 103, 81–86. <https://doi.org/10.1016/j.carbpol.2013.12.020>
- Zhou, Y., Wang, M., Wang, L., Liu, L., Wu, Y., & Ouyang, J. (2023). Comparison of the effect of ultrasound and microwave on the functional properties and in vitro digestibility of normal maize starch and potato starch. *Journal of Food Process Engineering*, 46(2), e14222. <https://doi.org/10.1111/jfpe.14222>

How to cite this article: Rostamabadi, H., Demirkesen, I., Mert, B., Barua, S., Colussi, R., Frasson, S. F., Wang, Y., & Falsafi, S. R. (2024). Starch digestibility: How single, double, and multiple physicochemical modifications change nutritional attributes of starch?. *Food Frontiers*, 1–35. <https://doi.org/10.1002/fft2.396>