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Cutting-edge progress in green technologies for resistant starch type 3 and type 5 preparation: An updated review

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ABSTRACT

Resistant starch (RS) is a dietary fiber that resists starch hydrolysis in the small intestine, and is fermented in the colon by microorganisms. RS not only has a broad range of benefits in the food and non-food industries but also has a significance impact on health promotion and prevention of non-communicable diseases. RS types 3 and 5 have been the focus of research from an environment-friendly perspective. RS3 is normally formed by recrystallization after physical modification, whereas RS5 is obtained by the complexation of starch and fatty acids through the thermomechanical methods. This review provides updates and approaches to RS3 and RS5 preparations that promote RS content based on green technologies. This information will be useful for future research on RS development and for identifying preparation methods for functional food.

1. Introduction

Starch is an edible carbohydrate source composed of two glucose polymers: amylose and amylopectin. Most native starches, including rapidly digestible starch and slowly digestible starch (SDS), are digested and absorbed in the small intestine (Englyst, Kingman, & Cummings, 1992). However, the indigestible portion of starch, known as resistant starch (RS), cannot be hydrolyzed by digestive enzymes in the human body (Englyst et al., 1992).

RS is of great interest because of its function as dietary fiber and rich nutritional value (Ashwar, Gani, Shah, Wani, & Masoodi, 2016; Slavin, 2013) with low calories (1.6–2.8 Kcal g^{-1}) (Raigond, Dutt, & Singh, 2018). In the large intestine, RS is used by anaerobic gut bacteria through saccharolytic fermentation, resulting in the production of short-chain fatty acids such as acetic, butyric, and propionic acids, which regulate gastrointestinal diseases, metabolic disorders, and have neuroactive properties (Nugent, 2005; Silva, Bernardi, & Frozza, 2020; Zhang & Bao, 2021).

RS plays a crucial role in the prevention and control of non-communicable diseases by attenuating postprandial glycemia (Maziarz et al., 2017; Raben et al., 1994), inhibiting glucose and lipid synthesis (Shang, Si, Strappe, Zhou, & Blanchard, 2017; Zhou, Wang, Ren, Wang, & Blanchard, 2015), and increasing glucose tolerance, insulin sensitivity, lipid oxidation, glycogen synthesis, and cholesterol homeostasis (Keenan et al., 2015; Wang et al., 2019; Zhou et al., 2015).

According to its origin and structure, RS is divided into five categories (RS1-RS5). RS1 is a naturally encapsulated starch often found in grains, seeds, and legumes (Shen, Li, & Li, 2022). RS2 is a native starch granule with a tightly packed crystalline structure that is particularly abundant in raw potatoes and green bananas (Jiang, Du, Jiang, & Wang, 2020). RS3 is a physically modified or retrograded starch, and can naturally form during food processing through the recrystallization of starch polymers (Walsh, Lucey, Walter, Zannini, & Arendt, 2022). RS4 is a chemically modified starch obtained through substitution, esterification, and cross-linking reactions (Shen et al., 2022). RS5 is the complexation form of starch and lipids during heating and cooling coupled with the kinetics of hydrogen bonding and hydrophobic interactions (Wang et al., 2020). In addition, RS formation is regulated by several starch-synthesis-related genes (Shen et al., 2022). To improve RS content in natural source (RS1 and RS2), molecular genetics and genetic

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engineering combined with plant breeding have been applied (Blennow et al., 2020; Huang et al., 2023). However, the limitations of using molecular techniques and conventional breeding are time-consumption and the complexity of the plant genome (Ashkani et al., 2015).

As the global demand for RS has steadily increased, the levels of RS3, RS4 and RS5 in native sources have been intensively improved using starch modification methods (physical, chemical, and enzymatic) (Birt et al., 2013; Zhang & Bao, 2021). However, because empowering health and sustainability have been trendy agendas worldwide for more than a decade, chemical-free methods have become promising approaches for RS3 and RS5 preparation, providing several advantages such as simplicity, low cost, nontoxicity, affordability and sustainability (Raghunathan, Pandiselvam, Kothakota, & Mousavi-Khaneghah, 2021; Zhang & Bao, 2021).

This review provides an update on recent green methods for the preparation of RS3 and RS5, focusing on increasing RS content (Fig. 1). To expand the application of modified starch, dual modification and semi-green techniques that can increase the RS levels have also been included (Fig. 2). In addition, the major factors affecting RS improvement are listed. The

knowledge provided by this review can be advantageous for improving RS, food and non-food applications, and promoting disease prevention, health and well-being.

2. Common green technologies for preparation and improvement of RS3

The RS content in food is generally affected by the processing procedure, temperature, and storage time, which is highly related to starch gelatinization and retrogradation (Liu, Guo, Li, Wang, & lv, M., Peng, Q., & Wang, M., 2015). Physical modification is considered a common green technology for RS improvement and can be classified into three groups: thermal, hydrothermal, and non-thermal modifications (Punia, 2020). Recent studies on common green technologies with approved RS contents are listed in Table 1 and Fig.1.

2.1. Thermal treatment

Thermal treatment not only breaks non-covalent bonding (hydrophobic interactions and hydrogen bonds) but also disturbs the conformation of starch (Kim, Ye, & Baik, 2023).

2.1.1. Dry heat treatment (DHT)

DHT is a simple, safe, and healthy method for starch modification, generally performed at 100–150 °C for a period of time with a moisture content <10% (Liu et al., 2022). DHT changes the entire structure of starch by rearranging glucan chains and forming a defense-like structure at the active site of amylase, resulting in reduced enzyme hydrolysis (Chi et al., 2019). Oh, Bae, and Lee (2018) applied DHT to high-amylose rice starch (40.6% amylose) (Table 1) and found that all treatment conditions caused a higher RS content as compared to that of native starch, but there was no significant difference observed among the DHT starches, except the starch treated at 110 °C for 2 h, considering the peak RS content. In addition, the degree of DHT has been confirmed to have a strong impact on the starch digestion rate (Liu et al., 2022; Oh et al., 2018). Based on chestnut starch (Liu et al., 2022), DHT at 140 °C for 4 and 8 h resulted in significant increases in RS content as a result of retrograded DHT-treated starch during gelatinization. Moreover, the addition of xanthan gum (XG), a microbial polysaccharide extracted from *Xanthomonas* spp. (0.01%, 0.05%, and 0.2% *w/v*) mixing with chestnut-treated DHT starches (8% w/v) dramatically increased the RS content to 64.36% (DS8–0.2%XG) compared with that of the non-added sample (61.77% on DS8 sample) (Liu et al., 2022). This study showed a synergistic effect on the reduction in chestnut starch digestibility because of the tight and orderly structure of DHT and XG (Liu et al., 2022). The DHT technique prompts an increase in RS content, whereas the duration of DHT is not impacted by the starch source.

2.1.2. Autoclaving treatment

Autoclaving can increase RS content by heating the starch suspension in an autoclave, followed by cooling to generate retrograded amylose (Pratiwi, Faridah, & Lioe, 2018). During autoclaving, the internal structure of gelatinized starch granules changes with the degradation of long glucan chains, leading to increased availability of amylose

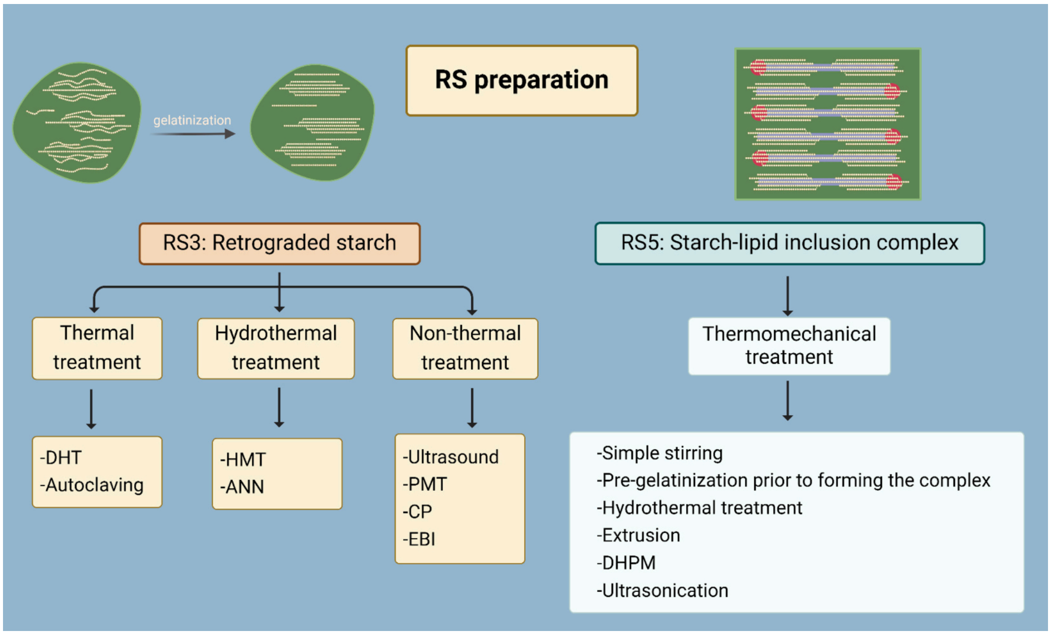

Fig. 1. Short mapping of update methods for RS3 and RS5 preparation explained in this article.
Abbreviations: ANN, annealing; CP, cold plasma; DHPM, dynamic high pressure microfluidization; DHT, dry heat treatment; EBI, electron beam irradiation; HMT, heat moisture treatment; PMT, pressure moisture treatment.

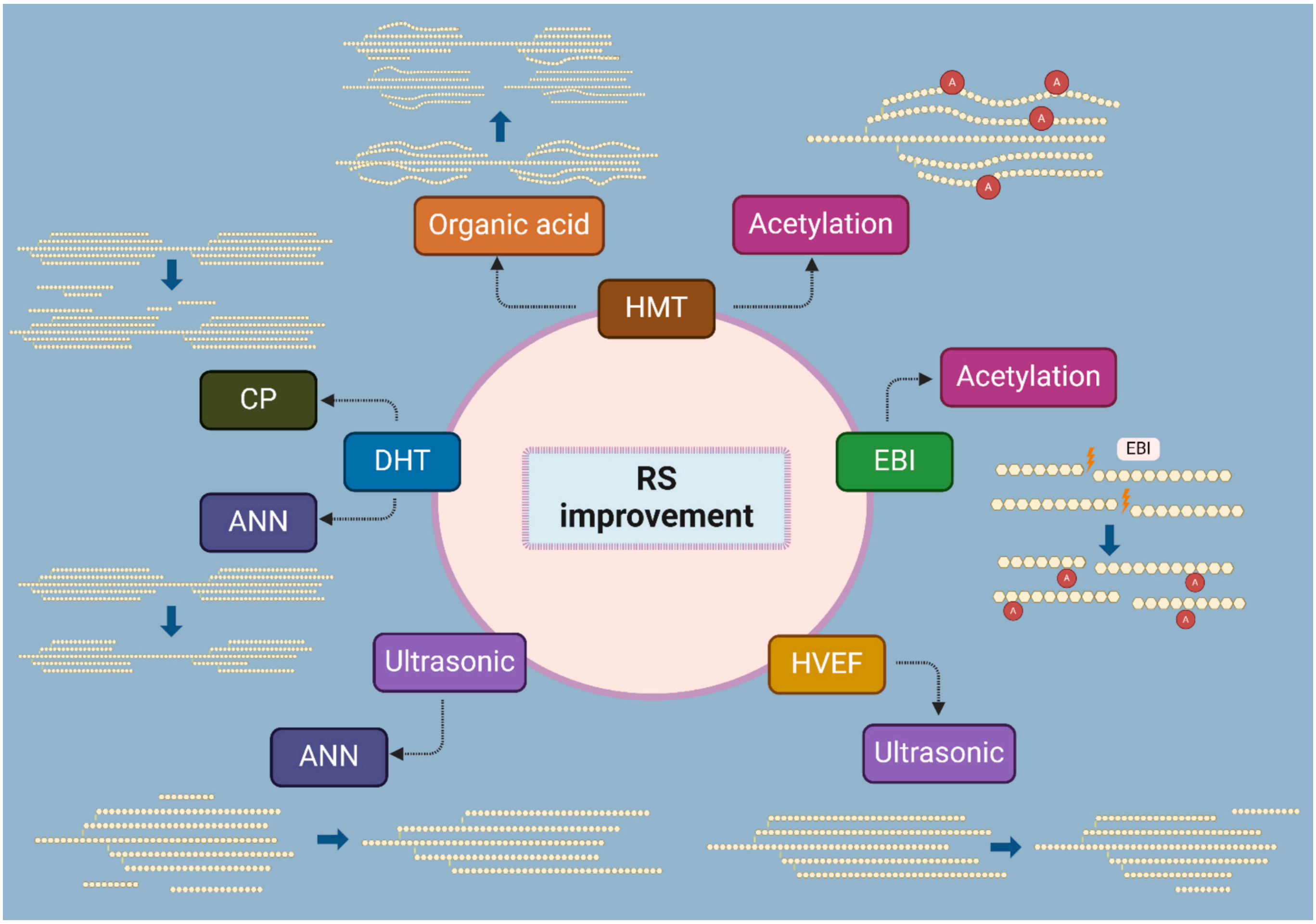

Fig. 2. Connecting of dual modification methods and semi-green techniques for promoting RS content listed in this study.
Abbreviations: ANN, annealing; CP, cold plasma; DHT, dry heat treatment; EBI, electron beam irradiation; HMT, heat moisture treatment; HVEF, high voltage electric field; RS, resistant starch. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as a free-curled-up molecule (Liu et al., 2013; Sun et al., 2022). In addition, owing to high temperature and pressure, the starch paste viscosity decreases along with higher intermolecular interactions in starch. After the temperature gradually decreases, starch retrogradation proceeds immediately with the formation of RS (Sun et al., 2022). Using autoclaving, the RS content can be increased by controlling the starch source, heating temperature, duration, and number of treatment cycles (Faridah et al., 2022). Recent studies showed that the autoclaving has a significant effect on rice and sweet potato starches by increasing the RS content after modification (Table 1). In addition, a meta-analysis showed that RS content has been dramatically increased after autoclaving treatment using a starch suspension at a 1:4 ratio of sample: water, performing two cycles of autoclaving-cooling and autoclaving at 121 °C for 30 min (Faridah et al., 2022).

2.2. Hydrothermal treatment

Hydrothermal treatments apply heat to starch in the presence of moisture to increase SDS and RS levels in post-gelatinized starch (Dupuis, Liu, & Yada, 2014; Liu et al., 2015). Well-known and effective hydrothermal treatments include heat-moisture treatment (HMT), and annealing (ANN) (Fig. 1). Both treatments can improve the RS content through a rubbery state, in which amylose and amylopectin form double helices and increase the stability of starch granules (Dupuis et al., 2014).

2.2.1. HMT

HMT is performed by treating starch granules with limited moisture content ($< 35\%$) at a range of gelatinization and transition temperatures (84–140 °C) for periods of time (1–16 h) (Fonseca, Halal, Dias, Zavareze, & d. R., 2021; Liu et al., 2015; Zhang & Bao, 2021). During HMT, intermolecular starch associations occur during modification without destroying the starch granules, but change the properties and functionality of starch (Acevedo, Villanueva, Chaves, Avanza, & Ronda, 2022) regarding the proportion of starch components (Damaiyanti, Faridah, Indrasti, Jayanegara, & Afandi, 2023), moisture content, heating duration (Sui et al., 2015), temperature (Piecyk & Domian, 2021), and starch origin (Fang, Liu, & Gao, 2023).

Wang et al. (2018) reported that the higher moisture content (MC) during HMT, the greater the SDS and RS contents. Recently, a meta-analysis revealed that an amylose content of starch and flour of 21–30% is optimal for achieving RS improvement (Damaiyanti et al., 2023). However, some studies have found that HMT can reduce digestible starch content (Acevedo et al., 2022; Wang et al., 2020).

2.2.2. ANN

ANN plays an important role in promoting starch thermostability, RS formation, relative crystallinity, and gelatinization temperature using simple procedures (Lan et al., 2008; Liu et al., 2015). In general, ANN is performed above the glass transition temperature and below the gelatinization temperature of starch under excess water conditions (40–70% v/v, moisture $>40\%$) for a certain period of time (Chung, Liu, & Hoover,

Table 1
List and detailed updates of common physical modifications for RS improvement.

Method	Treatment condition	Starch source	RS of native sample (%)	Maximum RS (%) after modification (The effective condition)	Reference
DHT	MC < 10%; Temp: 110, 130, and 150 °C; Time: 1, 2 and 4 h	high amylose rice	42.0	52.1[*] (110 °C, 2 h)	(Oh et al., 2018)
	MC < 10%; Temp: 140 °C; Time: 4 and 8 h	chestnut	57.59	61.77[*] (8 h)	(Liu et al., 2022)
RDHT and CDHT	RDHT: MC < 10%; one cycle: Temp: 140 °C; Time: 4 h; individually repeat the cycle from 2 to 5 times CDHT: MC < 10% Temp: 140 °C; Time: 4, 12, 16, and 20 h	quinoa	21.6	26.0[*] (RDHT at 2 cycles)	(Zhou et al., 2021)
Autoclaving	Sample: 20% (w/v) starch in sodium acetate buffer (0.02 M, pH 5.0); Pre-gelatinization: 30 min; Autoclave: 121 °C for 1 h and RT for 1 h	rice	1.1	8.9[*]	(Li et al., 2020)
	Sample: 35% (*w/v*) starch in water; Autoclave: 120 °C for 30 h; Pressure: 1:1 bar; Temp: RT for 1 h and	Sweet potato	1.44	9.15[*]	(Sun et al., 2022)
HMT	MC:10, 20, 30%; Temp: 110 °C; Time: 4 h	rice	2.6	14.5[*] (MC 30%)	(Wang et al., 2018)
	MC:15, 20, 25, 30%; Temp: 110 °C; Time: 4 h	adlay	6.7	20.6[*] (MC 30%)	(Wang et al., 2020)
	MC:20%; Temp: 100 °C; Time: 2, 5, 12 h	cowpea	60.6	67.2[*] (5 h)	(Acevedo et al., 2022)
ANN	Starch 25% w/v; Temp: 50 °C; Time: 24 h	normal maize potato common buckwheat	5.44 5.68 46	7.15[*] 7.71[*] 49[ns]	(Chi et al., 2019) (Liu et al., 2015)
	Starch 50% w/v; Temp: 50 °C; Time: 24 h	foxtail millet	18.20	42.32[*]	(Babu et al., 2019)
	(1) One step 24: Starch 50% w/v, Temp: 50 °C; Time: 24 h (2) One step 48: Starch 50% w/v, Temp: 50 °C; Time: 48 h (3) Two steps: Starch 50% w/v, Temp: 50 °C for 24 h and Temp: 55 °C for another 24 h and	*Castanopsis sclerophylla* fruit	6.5	8.8[ns] (Two steps)	(Shi et al., 2021)
US	Starch slurries at 20% *w/w*; Ultrasonic power 660 W; Temp: 30 °C; Time: 30 min	potato	20.28	67.37[*]	(Cao et al., 2020)
HUT	All treatments used starch slurries at 5% w/v. (1) 200 W, 30 min (2) 400 W, 30 min (3) 600 W, 30 min (4) 600 W, 100 min (5) 600 W, 20 min (6) 600 W, 30 min	kiwi	57.69	72.73[*] (200 W, 30 min)	(Wang et al., 2022)
PMT	MC: 25%; Pressure: 350, 450, 550 MPa; Time: 10 min; Temp: RT	corn, potato, rice, tapioca	corn: 2.1, potato: 2.1, rice: 2.5, tapioca: 4.3	corn: 10.1[*] (550 MPa), potato: 6.3[*] (550 MPa), rice: 10.3[*] (550 MPa), tapioca: 10.2[*] (550 MPa)	(Kim et al., 2023)
CP	CP: 40 V; Time: 1, 3, 5 min	proso millet	51.84	52.89[*] (1 min)	(Sun et al., 2022)
EBI	EBI dose: 0, 1, 2, 4, and 8 kGy EBI dose: 0, 4, and 8 kGy	quinoa naked barley	15.2 7.11	38.8[*] (2 kGy) 9.39[*] (4 kGy)	(Du et al., 2020) (Ge et al., 2023)

Abbreviations: ANN, annealing; CP, cold plasma; DHT, dry heat treatment; EBI, electron beam irradiation; RDHT, repeat dry heat treatment; CDHT, continue dry heat treatment; dw, dry basis; HMT, heat moisture treatment; HUT, high-power ultrasound treatment; MC, moisture content; PMT, pressure moisture treatment; RT, room temperature; Temp, temperature; US, ultrasonication treatment.

[*] indicates that the highest RS content of the modified starch was significantly different from that of native starch.

[ns] indicates the lack of a significant difference observed for modified starch compared to that of native starch.

2009; Fonseca et al., 2021). During ANN, water functions as a plasticizer that assists mobility and induces swelling in amorphous regions, promoting the reconstruction of the starch structure (Shi et al., 2021). The formation of RS after ANN is a result of an increases in amylose-amylose and amylose-amylopectin interactions, which contribute to the reconformation of the ordered structures (Babu, Mohan, & Parimalavalli, 2019). In addition, the results of ANN modifications on Table 1 can assume that the increased RS levels after ANN are independent of the crystalline pattern.

2.3. *Non-thermal treatment*

2.3.1. *Ultrasound*

Ultrasonication is a powerful technology that is widely applied in food science and adapted for starch modification (Bonto, Tiozon, Sreenivasulu, & Camacho, 2021). During the treatment, ultrasound introduces acoustic cavitation, which promotes the collapse of bubbles in aqueous media. The collapse of these microbubbles creates microjets, shear energy, and heat (Bonto et al., 2021). Cao and Gao (2020) reported that ultrasonic treatment (US) can increase the RS content in potato starch, resulting from the interactions of starch chains.

High-power ultrasound treatment (HUT) is an ultrasonic treatment with a density rate >5 W/cm^2 (Bonto et al., 2021). HUT (200–600 W) has a substantial effect on increasing the enzymatic resistance of kiwi starch (Wang et al., 2022). However, among the HUT-treated samples, increases in ultrasonic power and time had an insignificant impact on the digestion process and starch composition, suggesting that there was partial degradation during treatment, causing a slight change in the structure of the HUT-treated starch (Wang et al., 2022).

2.3.2. *Pressure moisture treatment (PMT)*

PMT is a new physical modification method (Kim et al., 2023; Kim &

Baik, 2022). It is performed under HHP conditions (100–600 Mpa, ≤ 30 min, 20–30 °C) with <30% moisture (wet basis) (Kim & Baik, 2022). The degree of in vitro digestibility is significantly influenced by the pressure levels (Kim et al., 2023). As PMT is performed under limited moisture conditions, starch gelatinization is inhibited, blocking the access of digestive enzymes to the undamaged starch granules at the interior of the starch (Kim et al., 2023). In addition, PMT changes the physicochemical properties of native starch, regardless of its crystalline structure, by decreasing the intermolecular distance, enforcing amylose-amylose and amylose-amylopectin interactions, and suppressing granule swelling (Kim et al., 2023). These phenomena occur owing to high amylose leaching, resulting in decrease the starch solubility and activate an internal rearrangement of starch granules (Kim et al., 2023). Therefore, PMT plays a crucial role in improving RS (Kim et al., 2023).

2.3.3. *Cold plasma (CP) technology*

CP is an environmental-friendly method that has attracted increasing attention for starch modification (Han, Shi, & Sun, 2020; Sun, Fan, et al., 2022; Yan, Feng, Shi, Cui, & Liu, 2020). During CP treatment, gas ionization generates a large number of free radicals, which either chemically or physically react with starch, resulting in crosslinking or depolymerization (Ge et al., 2021). In addition, Sun, Saleh, et al. (2022) found that short-term treatment of proso millet with CP (1 min) promoted interactions among glucan chains, homogeneity of the ordered structure, and rearrangement of starch molecules, leading to high RS content.

2.3.4. *Electron beam irradiation (EBI)*

EBI is a powerful sterilization technology that has been widely applied at doses of 1–10 kGy to prevent microbial contamination (Lung et al., 2015). EBI damages starch, eliminates hydrogen bonds in the starch structure, and disrupts the crystalline structure, resulting in changes to the starch structure (Du et al., 2020). An increase in RS content was observed with an increase in the irradiation dose (Du et al., 2020; Ge et al., 2023). In addition, the higher carboxyl groups generated by the radiation treatment can affect enzymatic access and increase RS content (Pan, Xing, Zhang, Luo, & Chen, 2020).

3. Thermomechanical methods for starch-fatty acid inclusion complex (RS5 preparation) and RS improvement

3.1. *Simple stirring*

It is apparent that the presence of fatty acids in the starch structure potentially reduces digestive enzyme accessibility to starch molecules (Królikowska, Pietrzyk, Pustkowiak, & Wolak, 2022; Zhuang et al., 2023). Cassava and wheat starches were complexed with oleic acid (OA), stearic acid (SA), and palmitic acid (PA) by adding 10 g starch (dry weight) in 1.5 mmol of fatty acid dissolved in ethanol, followed by stirring in a fume hood until evaporation (approximately 2 h) (Królikowska et al., 2022). SA and PA significantly increased the RS content of cassava starch-fatty acid complexes, whereas OA and SA gradually increased the RS content of wheat starch-fatty acid complexes (Królikowska et al., 2022).

3.2. *Pre-gelatinization prior to forming the complexes*

Amylose has ability to form helical structures or inclusion complexes with the hydrophobic molecules owing to the position of hydroxyl groups of glucosyl residues on the outer surface of the helix whereas the internal cavity is a hydrophobic (Panyoo & Emmambux, 2017). To increase the complexing ability of polymers with fatty acids, native starch is firstly performed the gelatinization or debranching process (Królikowska et al., 2022).

Sun et al. (2021) and Sun et al. (2023) used pregelatinized starch to form complexes with seven fatty acids. The starch suspension (5% *w*/w of dry basis) was heated at 95 °C for 30 min under constant stirring (Sun et al., 2021). The starch paste was then mixed with fatty acids (10% w/w of starch dry basis, dissolved in 50% ethanol), followed by incubation at 75 °C for 90 min with constant stirring. The mixture was immediately cooled, freeze-dried, ground into a fine powder, and stored at 4 °C until property analysis (Sun et al., 2021). All starch complexes with the seven fatty acids showed an increase in RS content in the following order: myristic acid (C14:0) > lauric acid (C12:0) > palmitic acid (C16:0) > linoleic acid (C18:2) > oleic acid (C18:1) > decanoic acid (C10:0) > stearic acid (C18:0) (Maziarz et al., 2017; Sun et al., 2021).

Sun et al. (2023) found that the resistance to seven starches to amylase hydrolysis, including maize starch, waxy maize starch, high-amylose maize starch, rice starch, cassava starch, and potato starch, improved after complexation with myristic acid. Moreover, the complexes of high-amylose maize starch and maize starch with myristic acid had stronger digestion resistance, showing high RS contents of 31.05 and 24.08%, respectively, compared to those of other complexes (Sun et al., 2023).

3.3. *Hydrothermal treatment*

Hydrothermal treatment has been applied to prepare starch-fatty acid inclusion complexes, as reported previously (Exarhopoulos & Raphaelides, 2012; Lu, Shi, Zhu, Li, & Huang, 2019). Chang, He, Fu, and Huang (2014) introduced heating systems of (1) heating starch prior to the addition of fatty acids (HM), and (2) adding fatty acids prior to heating the starch (MH) to form a complex between normal corn starch and lauric acid under conditions of different moisture contents (10–50%). The HM method dries the starch at 105 °C for 3 h, and then adjusted the moisture content to 10, 20, 30, 40, and 50%, followed by heating at 80 °C for 2 h. Subsequently, lauric acid (15% *w*/w of starch dry basis, dissolved in ethanol) is added to the hydrothermally treated starch and heated at 80 °C for 2 h. In MH, lauric acid (15% w/w of starch dry basis, dissolved in ethanol) is firstly added to the starch and then heated at 80 °C for 2 h. The treated samples are subsequently adjusted to 10, 20, 30, 40, and 50% moisture and heated at 80 °C for 2 h (Chang et al., 2014). Chang et al. (2014) found that the products of the MH method were more resistant to enzymatic hydrolysis than those of HM. Moreover, with increasing moisture content, the RS values of the complexes obtained using both methods gradually increased, resulting from more ordered crystallites and limited swelling of the starch granules (Chang et al., 2014).

3.4. *Extrusion*

Extrusion processing is a physical modification that is performed using high levels of moisture content, pressure, and temperature for the production of starch-lipid complexes through the shearing force along the barrel surface (Li, Liu, Zhang, Xue, & Luo, 2021). Liu et al. (2023) studied the extrusion of potato, corn, and pea starches mixed with lauric acid (1, 2, and 4% w/w of starch dry basis) at a mixing rate of 35 rpm for 15 min. The mixture samples were then extruded at a feed rate of 6 kg/h, extrusion moisture of 50 wt%, and screw speed of 150 rpm, with temperature profiles of 40, 60, 80, 100, and 120 °C (Liu et al., 2023). The authors found that the extrusion processing played a crucial role in the complexation of starch-fatty acids with a reduction in starch digestibility, and also reported that the RS content of all complexes was closely related to the content of amylose and lauric acid (Liu et al., 2023).

3.5. *Dynamic high pressure microfluidization (DHPM)*

DHPM is a common homogenization technology widely used in the chemical, pharmaceutical, and food industries (Chen et al., 2018; Hu, Xiong, Xiong, Chen, & Zhang, 2021). In a DHPM system, a suspension containing solid particles is subjected to ultrahigh shear pressure (200

MPa) for a short duration, typically <3 s at ambient temperature in a microchannel chamber, which activates rearrangement and decreases the molecular weight of macromolecules (Liu et al., 2009).

Chen et al. (2018) performed DHPM using six saturated fatty acids (5% w/w of starch dry basis, dissolved in 50% ethanol) mixed with lotus seed starch slurry (4% *w*/w) under DHPM at 200 MPa (eight cycles), followed by freeze-drying. Compared to the native lotus seed starch, all complexes with fatty acids showed a noticeable increase in RS content with a decrease in chain length as follows: octanoic acid (C8) > decanoic acid (C10) > lauric acid (C12) > myristic acid (C14) > palmitic acid (C16) > stearic acid (C18). Moreover, the authors found that lotus seed starch with a C8 complex showed a heat-stable V_6-type structure, indicating a more compact lamellar morphology for the accessibility of digestive enzymes (Chen et al., 2018).

3.6. Ultrasonication

Recently, ultrasonication has been used to promote the production of starch-fatty acid inclusion complexes (Chumsri, Panpipat, Cheong, & Chaijan, 2022; Kang et al., 2020). Ultrasonication produces a mechanical force, cavitation effect, and strong shock waves that can disintegrate swollen starch granules, release linear amylose chains, and assist in the dispersion of fatty acids in gelatinized starch, thereby contributing to the complexation of starch with fatty acids (Monroy, Rivero, & García, 2018). Chumsri et al. (2022) reported that the productive synthesis condition based on the ultrasonication method for complexing brown rice starch and butyric acid was 7.5% butyric acid with 20% amplitude for 30 min, providing the highest RS content (80.78%), followed by other complexes with linoleic acid (69.12%), lauric acid (51.62%), and stearic acid (48.93%).

4. Dual treatment of physical modification for RS3 and RS5 improvement

4.1. Potential of dual physical modification

4.1.1. Effects CP treatment on dry heated starch

Red adzuki bean starch was treated with DHT at 130 °C for 1, 3 and 9 h, followed by the dielectric barrier discharge (DBD) plasma or CP at 40 V and 1 A for 1, 5, and 10 min (Ge et al., 2021). Compared to non-modified starch (12.90%), the RS content significantly increased, up to 13.23%, in the treatments of DH 1 h coupled with CP 1 min and DH 1 h coupled with CP 10 min (Ge et al., 2021).

4.1.2. Synergistic of DHT and ANN treatment

Chi et al. (2019) firstly performed DHT on normal maize and potato starches with a moisture content <10%, followed by heating at 130 °C for 2 h. After that, the treated slurry (25% *w/v*) was placed in polyethylene bags and subjected to ANN in a water bath at 50 °C for 24 h, centrifuged at 4000 rpm for 10 min, and air dried at 40 °C for 24 h. The authors found that dual modification based on DHT and ANN had a crucial synergistic effect on starch digestibility by elevating SDS to a peak at 9.98% and boosting RS to a maximum value of 10.72% in modified maize and potato starches, respectively (Chi et al., 2019). In this particular case, synergistic methods play a significant role in reducing starch digestibility, with a broader magnitude than that of a single modification (Chi et al., 2019).

4.1.3. Ultrasonication prior to ANN

The starch slurry (50% w/v) of foxtail millet was placed in an ultrasound bath at a frequency of 33 kHz and 50 °C for 30 min, followed by cooling at 4 °C for 24 h and drying at 40 °C for 24 h (Babu et al., 2019). The ultrasonicated starch was then subjected to ANN at 50% w/v starch slurry and 50 °C for 30 min (Babu et al., 2019). This ordered method increased the RS content to a maximum of 45.59% compared to that of the ultrasonic treatment alone (20.14%) and to native starch (18.20%). The authors suggested that ultrasonication prior to ANN generated high-pressure intensity and transformed it into shear forces, damaging the starch granules and long chains of starch (Babu et al., 2019).

4.1.4. High voltage electric field (HVEF) prior to ultrasonication

Potato starch slurry (20% *w*/w) was treated with HVEF at 30 kV for 30 min and oven-dried prior to ultrasonic treatment at 660 W for 30 min (Cao & Gao, 2020). The resulting dual modification resulted in the highest RS content (79.98%) because of the induced interactions between the starch chains and the formation of hydrogen bonds in the inner structures. In contrast, ultrasonication prior to HVEF resulted in a relatively low RS content (10.56%), indicating that this particular method caused a partial disruption of the ordered chains that prompted starch hydrolysis (Cao & Gao, 2020).

4.2. Impacts of ultrasound-pretreated (UTP) on starch-lauric acid complex

Pea starch (NS) was subjected to UTP at 0, 20, and 40 °C for 20 min (20 kHz, 300 W) (Xiao, Yu, Yang, Wei, & Han, 2023). After drying and sieving, the resulting samples were complexed with lauric acid (LA) by using a rapid viscosity analyzer (RVA) at 50 °C for 1 min, 95 °C for 2.5 min, followed by 50 °C for 2 min (Xiao et al., 2023). UTP did not affected the RS content of native NS, but caused a significant increase in RS levels on starch forming starch-lipid complexes, especially in the treatment of UTP at 40 °C, which was attributed the highest complexing index (Xiao et al., 2023).

5. Semi-green technologies for RS3 improvement

Semi-green technologies by means of dual modification through chemical modification coupled with physical method are sometimes preferable technique for RS3 improvement due to higher efficiency, time and cost savings, and ease of access (Masina et al., 2017; Zhang & Bao, 2021).

5.1. Acetylation and HMT

Chen, Fu, Zhang, Ma, and Kan (2023) modified wheat starch by adding maleic anhydride (MA) and the reaction was performed at 30 and 65 °C to obtain acetylated wheat starch (AWS). The moisture content of the AWS was adjusted to 18% (*w*/w), and the AWS was subjected to 115 °C for 3 h. The highest RS content was 7.7%, observed in AWS (65 °C) with HMT, whereas that of native wheat starch was 2.8% (Chen et al., 2023). MA modification may produce various short chains that enhance the mobility and rearrangement of starch molecules during HMT, increasing RS content (Chen et al., 2023).

5.2. Acetylation and EBI treatment

EBI plays a crucial role in the depolymerization of the starch structure, which is suitable for molecular rearrangement, and increases the capability of subsequent modification by acetylation (Ge et al., 2023). Naked barley starch was treated with EBI using an accelerator at 10 MeV/20 kW at doses of 4 and 8 kGy, followed by acetylation based on the application of 4 and 6% acetic anhydride, neutralization, and washing (Ge et al., 2023). After dual treatment with EBI and acetylation, the results showed that the highest RS (11.62%) was observed at an irradiation dose of 8 kGy with 6% acetylation (Ge et al., 2023).

Acetylation is an esterification process that replaces the free hydroxyl groups of starch molecules with acetyl groups in the aqueous phase of an alkaline catalyst (Tupa, Altuna, Herrera, & Foresti, 2020). The resulting acetylation has a significant impact on the starch structure by increasing the steric hindrance of starch chains and slowing the hydrolysis reaction (Khurshida, Das, Deka, & Sit, 2021).

5.3. *Organic acid and HMT*

Before performing HMT Van-Hung, Huong, Phi, and Tien (2017) changed the moisture content of cassava and potato starches by dispersing them in distilled water containing citric acid (0.2 M), and lactic acid (0.2 M) to achieve a moisture content of 30% in each sample. HMT was then performed by heating the starches at 110 °C for 8 h, followed by neutralization with 1 M sodium hydroxide. Citric acid and HMT were found to double the RS content of native cassava and potato starches (Van-Hung et al., 2017). The improved RS content was a result of the crystallite formation of various short chains produced after acid and HMT modifications (Hung, My, & Phi, 2014; Van-Hung et al., 2017).

6. Factors limiting RS improvement regarding physical modification methods

6.1. *Physical characteristics of starch granule after treatment*

Gao et al. (2019) reported more fissures and holes on DBD plasma-treated starch granules of tartary buckwheat (TBS) and sorghum (SS), which increased enzyme accessibility and decreased RS levels by 7.38% and 12.23% in TBS and SS, respectively, compared to native starch. Zhou et al. (2021) applied DHT to quinoa starch and found that the disrupted and rearranged structures of the treated samples were more susceptible to enzyme access, resulting from the increase in amylose content and reduction of crystalline regions after DHT treatment.

6.2. *Complexation process*

Complexation between starch and lipids decreases susceptibility to enzymatic hydrolysis (Ai & Hasjim, 2013; Wang & Copeland, 2013) and plays an important role in determining the digestibility properties of starch (Królikowska et al., 2022). The complexing index (CI) represents the percentage of complexation between starch and lipids (Wang et al., 2018). There are two primary factors contributing to CI: (1) the higher flexibility of carbon atoms next to the double bond(s) in unsaturated fatty acids, especially in the *cis* conformation, facilitating the formation of a starch complex similar to that of saturated fatty acids (Karkalas, Ma, Morrison, & Pethrick, 1995; Królikowska et al., 2022), and (2) the healthier hydrophobic interactions between the long chains of lipids and the interior of the helix contributing to the formation of complexes (Arik Kibar, Gönenç, & Us, 2014). In addition, Kawai, Takato, Sasaki, and Kajiwara (2012) suggested that the digestive properties of starch-fatty acid complexes are only dependent on CI. Chumsri et al. (2022) reported that the RS content was strongly correlated with CI values, which decreased with an increase in the length of the saturated fatty acid chain.

6.3. *Chain length, degree of unsaturation and concentration of fatty acids*

Sun et al. (2021) found that with an increase in the chain length of fatty acids from 10 (decanoic acid) to 14 (myristic acid) carbons, a remarkable increase in the RS content of maize-fatty acid inclusion complexes was observed, followed by a dramatic decrease upon increasing the chain length to 18 carbons (stearic acid). Among the 18-carbon fatty acids, the RS content of the resulting complexes steadily increases with the number of double bonds within the fatty acid chain (Sun et al., 2021). In addition, fatty acid concentration plays a significant role in determining the RS content. Based on ultrasonication, Chumsri et al. (2022) studied the effects of butyric acid concentrations varying at 1–10% and the results showed that RS content followed the order: 7.5% > 10% > 2.5% > 5% > 1%.

6.4. *Miscellaneous factors affecting RS content*

Abundant end products of starch depolymerization play an important role in RS improvement, and plasma treatment induces the release of large amounts of maltose, maltotriose, and maltotetrose, leading to increased starch hydrolysis after treatment (Lii, Liao, Stobinski & Tomasik, 2002).

Typically, fatty acids form inclusion complexes with amylose components via hydrophobic interactions (Chao et al., 2020; Oyeyinka, Singh, & Amonsou, 2021). Sun et al. (2023) confirmed that high-amylose maize starch complexed with myristic acid showed the highest RS content (31.05%), resulting from the highest amylose content compared with other treated starches.

In addition, Sun et al. (2023) noted that different varieties of maize starch, rice starch, cassava starch, and potato starch with amylose contents of 23.21, 16.83, 20.32, and 16.92%, respectively, showed significant differences in RS content after complexation with myristic acid, which were 24.08, 12.90, 16.27, and 18.34%, respectively. Therefore, starch sources are important factors that regulate the complex state and structural order, contributing to different RS contents (Sun et al., 2023).

Moreover, Zhou et al. (2021) found that a short period of DHT (4 h) caused a reduction in the RS content owing to weak associations of the starch chain and partial disruption of the ordered chain structures. However, Sun et al. (2022) reported that long-time CP treatments (3–5 min) caused a lower RS content by damaging the interior structure of starch granules, reducing crystallinity, promoting the binding sites of digestive enzymes, and improving the sensitivity of starch to enzymatic digestion. This phenomenon is consistent with a previous report of various starches treated with DBD (Gao et al., 2019).

In summary, there are four factors that enable the reduction of RS content and increase starch hydrolysis during starch modification: (1) high-end products of starch depolymerization, (2) starch with lower amylose content for starch-lipid complexation, (3) native starch sources, and (4) time period of treatment.

7. Conclusion and future prospects

RS preparation has been developed over several decades, based on physical, chemical, and enzymatic modifications. With growing interest in eliminating environmental pollution and sustainable healthcare, methods for RS preparation using eco-friendly technologies have been the subject of extensive research. Recent studies have addressed RS3 formation based on thermal, hydrothermal, and non-thermal methods using heating, shear forces, and physical stress on starch granules. The resulting treatments trigger the rearrangement and associations of glucan chains, disturb amorphous regions, degrade long chains, activate recrystallization and depolymerization of starch, eliminate hydrogen bonding, and promote the shield-like structure against the access of digestive enzymes. RS5 is mainly formed by the complexation between starch and fatty acids. Compared with single modifications, dual treatments usually provide a higher RS content because of synergistic effects. In addition, the RS3 and RS5 contents were mainly affected by the preparation conditions and starch type.

With the increasing number of breakthroughs in the physical modification and complexation of starch and fatty acids, meta-analyses will be helpful in summarizing data and grouping knowledge across many published studies for RS improvement and applications. Genetic engineering coupled with advanced omics is an effective green technique for developing sustainable starch sources rich in RS. In addition, dual treatment is a promising choice for boosting RS, owing to its synergistic effects. The information in this review updates the existing methods for RS3 and RS5 preparation with the conditions to increase the RS content, which will be applied in the food industry and beneficial to further studies regarding RS improvement.

CRediT authorship contribution statement

Piengtawan Tappiban: Writing – review & editing, Writing – original draft, Visualization, Investigation. **Supajit Sraphet:** Writing – review & editing. **Nattaya Srisawad:** Writing – review & editing.

Sulaiman Ahmed: Writing – review & editing. **Jinsong Bao:** Writing – review & editing. **Kanokporn Triwitayakorn:** Writing – review & editing, Writing – original draft, Visualization, Conceptualization.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

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References

Acevedo, B. A., Villanueva, M., Chaves, M. G., Avanza, M. V., & Ronda, F. (2022). Modification of structural and physicochemical properties of cowpea (*Vigna unguiculata*) starch by hydrothermal and ultrasound treatments. *Food Hydrocolloids, 124*, Article 107266. https://doi.org/10.1016/j.foodhyd.2021.107266

Ai, Y., Hasjim, J., & Jane, J.-L. (2013). Effects of lipids on enzymatic hydrolysis and physical properties of starch. *Carbohydrate Polymers, 92*(1), 120–127. https://doi.org/10.1016/j.carbpol.2012.08.092

Arik Kibar, E. A., Gönenç, İ., & Us, F. (2014). Effects of fatty acid addition on the physicochemical properties of corn starch. *International Journal of Food Properties, 17*(1), 204–218. https://doi.org/10.1080/10942912.2011.619289

Ashkani, S., Rafii, M. Y., Shabanimofrad, M., Miah, G., Sahebi, M., Azizi, P., & Nasehi, A. (2015). Molecular breeding strategy and challenges towards improvement of blast disease resistance in Rice crop. *Frontiers. Plant Science, 6*. https://www.frontiersin.org/articles/10.3389/fpls.2015.00886.

Ashwar, B. A., Gani, A., Shah, A., Wani, I. A., & Masoodi, F. A. (2016). Preparation, health benefits and applications of resistant starch—A review. *Starch - Stärke, 68*(3–4), 287–301. https://doi.org/10.1002/star.201500064

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. https://doi.org/10.1016/j.foodchem.2018.07.197

Birt, D. F., Boylston, T., Hendrich, S., Jane, J.-L., Hollis, J., Li, L., & Whitley, E. M. (2013). Resistant starch: Promise for improving human health. *Advances in Nutrition, 4*(6), 587–601. https://doi.org/10.3945/an.113.004325

Blennow, A., Skryhan, K., Tanackovic, V., Krunic, S. L., Shaik, S. S., Andersen, M. S., & Nielsen, K. L. (2020). Non-GMO potato lines, synthesizing increased amylose and resistant starch, are mainly deficient in isoamylase debranching enzyme. *Plant Biotechnology Journal, 18*(10), 2096–2108. https://doi.org/10.1111/pbi.13367

Bonto, A. P., Tiozon, R. N., Sreenivasulu, N., & Camacho, D. H. (2021). Impact of ultrasonic treatment on rice starch and grain functional properties: A review. *Ultrasonics Sonochemistry, 71*, Article 105383. https://doi.org/10.1016/j.ultsonch.2020.105383

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

Chang, F., He, X., Fu, X., Huang, Q., & Jane, J.-L. (2014). Effects of heat treatment and moisture contents on interactions between Lauric acid and starch granules. *Journal of Agricultural and Food Chemistry, 62*(31), 7862–7868. https://doi.org/10.1021/jf501606w

Chao, C., Huang, S., Yu, J., Copeland, L., Wang, S., & Wang, S. (2020). Molecular mechanisms underlying the formation of starch-lipid complexes during simulated food processing: A dynamic structural analysis. *Carbohydrate Polymers, 244*, Article 116464. https://doi.org/10.1016/j.carbpol.2020.116464

Chen, B., Guo, Z., Miao, S., Zeng, S., Jia, X., Zhang, Y., & Zheng, B. (2018). Preparation and characterization of lotus seed starch-fatty acid complexes formed by microfluidization. *Journal of Food Engineering, 237*, 52–59. https://doi.org/10.1016/j.jfoodeng.2018.05.020

Chen, H., Fu, M., Zhang, Y., Ma, C., & Kan, J. (2023). Effect of temperature during acetylation and heat moisture treatment on the structural and physicochemical properties and application of wheat starch. *Food Hydrocolloids, 144*, Article 109036. https://doi.org/10.1016/j.foodhyd.2023.109036

Chi, C., Li, X., Lu, P., Miao, S., Zhang, Y., & Chen, L. (2019). Dry heating and annealing treatment synergistically modulate starch structure and digestibility. *International Journal of Biological Macromolecules, 137*, 554–561. https://doi.org/10.1016/j.ijbiomac.2019.06.137

Chumsri, P., Panpipat, W., Cheong, L.-Z., & Chaijan, M. (2022). Formation of intermediate amylose Rice starch-lipid complex assisted by Ultrasonication. *Foods, 11*.

Chung, H.-J., Liu, Q., & Hoover, R. (2009). Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil starches. *Carbohydrate Polymers, 75*(3), 436–447. https://doi.org/10.1016/j.carbpol.2008.08.006

Damaiyanti, S., Faridah, D. N., Indrasti, D., Jayanegara, A., & Afandi, F. A. (2023). A Meta-analysis study: The impact of amylose content on resistant starch levels in carbohydrate sources with heat moisture treatment. *Starch - Stärke, 75*(3–4), 2200131. https://doi.org/10.1002/star.202200131

Du, Z., Li, Y., Luo, X., Xing, J., Zhang, Q., Wang, R., & Chen, Z. (2020). Effects of Electron beam irradiation on the physicochemical properties of quinoa and starch microstructure. *Starch - Stärke, 72*(11−12), 1900178. https://doi.org/10.1002/star.201900178

Dupuis, J. H., Liu, Q., & Yada, R. Y. (2014). Methodologies for increasing the resistant starch content of food starches: A review. *Comprehensive Reviews in Food Science and Food Safety, 13*(6), 1219–1234. https://doi.org/10.1111/1541-4337.12104

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. http://europepmc.org/abstract/MED/1330528.

Exarhopoulos, S., & Raphaelides, S. N. (2012). Morphological and structural studies of thermally treated starch-fatty acid systems. *Journal of Cereal Science, 55*(2), 139–152. https://doi.org/10.1016/j.jcs.2011.10.011

Fang, G., Liu, K., & Gao, Q. (2023). Effects of heat-moisture treatment on the digestibility and physicochemical properties of waxy and Normal potato starches. *Foods, 12*.

Faridah, D. N., Silitonga, R. F., Indrasti, D., Afandi, F. A., Jayanegara, A., & Anugerah, M. P. (2022). Verification of autoclaving-cooling treatment to increase the resistant starch contents in food starches based on meta-analysis result. *Frontiers. Nutrition, 9*. https://www.frontiersin.org/articles/10.3389/fnut.2022.904700.

Fonseca, L. M., Halal, S. L. M. E., Dias, A. R. G., Zavareze, E., & d. R.. (2021). Physical modification of starch by heat-moisture treatment and annealing and their applications: A review. *Carbohydrate Polymers, 274*, Article 118665. https://doi.org/10.1016/j.carbpol.2021.118665

Gao, S., Liu, H., Sun, L., Liu, N., Wang, J., Huang, Y., & Wang, M. (2019). The effects of dielectric barrier discharge plasma on physicochemical and digestion properties of starch. *International Journal of Biological Macromolecules, 138*, 819–830. https://doi.org/10.1016/j.ijbiomac.2019.07.147

Ge, X., Hu, Y., Shen, H., Liang, W., Sun, Z., Zhang, X., & Li, W. (2023). Electron beam irradiation application for improving the multiscale structure and enhancing physicochemical and digestive properties of acetylated naked barley. *Food Chemistry, 404*, Article 134674. https://doi.org/10.1016/j.foodchem.2022.134674

Ge, X., Shen, H., Su, C., Zhang, B., Zhang, Q., Jiang, H., & Li, W. (2021). The improving effects of cold plasma on multi-scale structure, physicochemical and digestive properties of dry heated red adzuki bean starch. *Food Chemistry, 349*, Article 129159. https://doi.org/10.1016/j.foodchem.2021.129159

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

Hu, C., Xiong, Z., Xiong, H., Chen, L., & Zhang, Z. (2021). Effects of dynamic high-pressure microfluidization treatment on the functional and structural properties of potato protein isolate and its complex with chitosan. *Food Research International, 140*, Article 109868. https://doi.org/10.1016/j.foodres.2020.109868

Huang, L., Xiao, Y., Zhao, W., Rao, Y., Shen, H., Gu, Z., & Liu, Q. (2023). Creating high-resistant starch rice by simultaneous editing of *SS3a* and *SS3b*. *Plant Biotechnology Journal.*. https://doi.org/10.1111/pbi.14053

Hung, P. V., 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

Jiang, F., Du, C., Jiang, W., Wang, L., & Du, S.-K. (2020). The preparation, formation, fermentability, and applications of resistant starch. *International Journal of Biological Macromolecules, 150*, 1155–1161. https://doi.org/10.1016/j.ijbiomac.2019.10.124

Kang, X., Liu, P., Gao, W., Wu, Z., Yu, B., Wang, R., & Sun, C. (2020). Preparation of starch-lipid complex by ultrasonication and its film forming capacity. *Food Hydrocolloids, 99*, Article 105340. https://doi.org/10.1016/j.foodhyd.2019.105340

Karkalas, J., Ma, S., Morrison, W. R., & Pethrick, R. A. (1995). Some factors determining the thermal properties of amylose inclusion complexes with fatty acids. *Carbohydrate Research, 268*(2), 233–247. https://doi.org/10.1016/0008-6215(94)00336-E

Kawai, K., Takato, S., Sasaki, T., & Kajiwara, K. (2012). Complex formation, thermal properties, and *in-vitro* digestibility of gelatinized potato starch–fatty acid mixtures. *Food Hydrocolloids, 27*(1), 228–234. https://doi.org/10.1016/j.foodhyd.2011.07.003

Keenan, M. J., Zhou, J., Hegsted, M., Pelkman, C., Durham, H. A., Coulon, D. B., & Martin, R. J. (2015). Role of resistant starch in improving gut health, adiposity, and insulin resistance. *Advances in Nutrition, 6*(2), 198–205. https://doi.org/10.3945/an.114.007419

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, H.-Y., & Baik, M.-Y. (2022). Pressure moisture treatment and hydro-thermal treatment of starch. *Food Science and Biotechnology, 31*(3), 261–274. https://doi.org/10.1007/s10068-021-01016-5

Kim, H.-Y., Ye, S.-J., & Baik, M.-Y. (2023). Pressure moisture treatment (PMT) of starch, a new physical modification method. *Food Hydrocolloids, 134*, Article 108051. https://doi.org/10.1016/j.foodhyd.2022.108051

Królikowska, K., Pietrzyk, S., Pustkowiak, H., & Wolak, K. (2022). The effect of cassava and wheat starches complexation with selected fatty acids on their functional properties. *Journal of Food Science and Technology, 59*(4), 1440–1449. https://doi.org/10.1007/s13197-021-05153-x

Lan, H., Hoover, R., Jayakody, L., Liu, Q., Donner, E., Baga, M., & Chibbar, R. N. (2008). Impact of annealing on the molecular structure and physicochemical properties of normal, waxy and high amylose bread wheat starches. *Food Chemistry, 111*(3), 663–675. https://doi.org/10.1016/j.foodchem.2008.04.055

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., Liu, Z., Zhang, W., Xue, B., & Luo, Z. (2021). Production and applications of amylose-lipid complexes as resistant starch: Recent approaches. *Starch - Stärke, 73* (5–6), 2000249. https://doi.org/10.1002/star.202000249

Liu, H., Guo, X., Li, W., Wang, X., & lv, M., Peng, Q., & Wang, M.. (2015). Changes in physicochemical properties and *in vitro* digestibility of common buckwheat starch by heat-moisture treatment and annealing. *Carbohydrate Polymers, 132*, 237–244. https://doi.org/10.1016/j.carbpol.2015.06.071

Liu, Q., Wang, Y., Yang, Y., Yu, X., Xu, L., Jiao, A., & Jin, Z. (2023). Structure, physicochemical properties and in vitro digestibility of extruded starch-lauric acid complexes with different amylose contents. *Food Hydrocolloids, 136*, Article 108239. https://doi.org/10.1016/j.foodhyd.2022.108239

Liu, W., Liu, J., Xie, M., Liu, C., Liu, W., & Wan, J. (2009). Characterization and high-pressure microfluidization-induced activation of Polyphenoloxidase from Chinese pear (*Pyrus pyrifolia* Nakai). *Journal of Agricultural and Food Chemistry, 57*(12), 5376–5380. https://doi.org/10.1021/jf9006642

Liu, W., Zhang, Y., Wang, R., Li, J., Pan, W., Zhang, X., & Xie, J. (2022). Chestnut starch modification with dry heat treatment and addition of xanthan gum: Gelatinization, structural and functional properties. *Food Hydrocolloids, 124*, Article 107205. https://doi.org/10.1016/j.foodhyd.2021.107205

Liu, X., Wang, Y., Yu, L., Tong, Z., Chen, L., Liu, H., & Li, X. (2013). Thermal degradation and stability of starch under different processing conditions. *Starch - Stärke, 65*(1–2), 48–60. https://doi.org/10.1002/star.201200198

Lu, X., Shi, C., Zhu, J., Li, Y., & Huang, Q. (2019). Structure of starch-fatty acid complexes produced via hydrothermal treatment. *Food Hydrocolloids, 88*, 58–67. https://doi.org/10.1016/j.foodhyd.2018.09.034

Lung, H.-M., Cheng, Y.-C., Chang, Y.-H., Huang, H.-W., Yang, B. B., & Wang, C.-Y. (2015). Microbial decontamination of food by electron beam irradiation. *Trends in Food Science & Technology, 44*(1), 66–78. https://doi.org/10.1016/j.tifs.2015.03.005

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

Maziarz, M. P., Preisendanz, S., Juma, S., Imrhan, V., Prasad, C., & Vijayagopal, P. (2017). Resistant starch lowers postprandial glucose and leptin in overweight adults consuming a moderate-to-high-fat diet: A randomized-controlled trial. *Nutrition Journal, 16*(1), 14. https://doi.org/10.1186/s12937-017-0235-8

Monroy, Y., Rivero, S., & García, M. A. (2018). Microstructural and techno-functional properties of cassava starch modified by ultrasound. *Ultrasonics Sonochemistry, 42*, 795–804. https://doi.org/10.1016/j.ultsonch.2017.12.048

Nugent, A. P. (2005). Health properties of resistant starch. *Nutrition Bulletin, 30*(1), 27–54. https://doi.org/10.1111/j.1467-3010.2005.00481.x

Oh, I. K., Bae, I. Y., & Lee, H. G. (2018). Effect of dry heat treatment on physical property and *in vitro* starch digestibility of high amylose rice starch. *International Journal of Biological Macromolecules, 108*, 568–575. https://doi.org/10.1016/j.ijbiomac.2017.11.180

Oyeyinka, S. A., Singh, S., & Amonsou, E. O. (2021). A review on structural, digestibility and physicochemical properties of legume starch-lipid complexes. *Food Chemistry, 349*, Article 129165. https://doi.org/10.1016/j.foodchem.2021.129165

Pan, L., Xing, J., Zhang, H., Luo, X., & Chen, Z. (2020). Electron beam irradiation as a tool for rice grain storage and its effects on the physicochemical properties of rice starch. *International Journal of Biological Macromolecules, 164*, 2915–2921. https://doi.org/10.1016/j.ijbiomac.2020.07.211

Panyoo, A. E., & Emmambux, M. N. (2017). Amylose–lipid complex production and potential health benefits: A mini-review. *Starch - Stärke, 69*(7–8), 1600203. https://doi.org/10.1002/star.201600203

Piecyk, M., & Domian, K. (2021). Effects of heat–moisture treatment conditions on the physicochemical properties and digestibility of field bean starch (*Vicia faba* var. minor). *International Journal of Biological Macromolecules, 182*, 425–433. https://doi.org/10.1016/j.ijbiomac.2021.04.015

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

Raben, A., Tagliabue, A., Christensen, N. J., Madsen, J., Holst, J. J., & Astrup, A. (1994). Resistant starch: The effect on postprandial glycemia, hormonal response, and satiety. *The American Journal of Clinical Nutrition, 60*(4), 544–551. https://doi.org/10.1093/ajcn/60.4.544

Raghunathan, R., Pandiselvam, R., Kothakota, A., & Mousavi-Khaneghah, A. (2021). The application of emerging non-thermal technologies for the modification of cereal starches. *LWT, 138*, Article 110795. https://doi.org/10.1016/j.lwt.2020.110795

Raigond, P., Dutt, S., & Singh, B. (2018). Resistant starch in food. In J.-M. Mérillon, & K. G. Ramawat (Eds.), *Bioactive molecules in food* (pp. 1–33). Cham: Springer International Publishing.

Shang, W., Si, X., Strappe, P., Zhou, Z., & Blanchard, C. (2017). Resistant starch attenuates impaired lipid biosynthesis induced by dietary oxidized oil via activation of insulin signaling pathways. *RSC Advances, 7*(80), 50772–50780. https://doi.org/10.1039/C7RA08855H

Shen, L., Li, J., & Li, Y. (2022). Resistant starch formation in rice: Genetic regulation and beyond. *Plant Communications, 3*(3), Article 100329. https://doi.org/10.1016/j.xplc.2022.100329

Shi, X., Ding, Y., Wan, J., Liu, C., Prakash, S., & Xia, X. (2021). Effect of annealing on structural, physicochemical, and in vitro digestive properties of starch from Castanopsis sclerophylla. *Starch - Stärke, 73*(7–8), 2100005. https://doi.org/10.1002/star.202100005

Silva, Y. P., Bernardi, A., & Frozza, R. L. (2020). The role of short-chain fatty acids from gut microbiota in gut-brain communication. *Frontiers in Endocrinology, 11*. https://www.frontiersin.org/articles/10.3389/fendo.2020.00025.

Slavin, J. L. (2013). Carbohydrates, dietary Fiber, and resistant starch in white vegetables: Links to health outcomes. *Advances in Nutrition, 4*(3), 351S–355S. https://doi.org/10.3945/an.112.003491

Lii, C.-Y., Liao, C.-D., Stobinski, L., & Tomasik, P. (2002). Effects of hydrogen, oxygen, and ammonia low-pressure glow plasma on granular starches. *Carbohydrate Polymers, 49*(4), 449–456. https://doi.org/10.1016/S0144-8617(01)00351-4

Sui, Z., Yao, T., Zhao, Y., Ye, X., Kong, X., & Ai, L. (2015). Effects of heat–moisture treatment reaction conditions on the physicochemical and structural properties of maize starch: Moisture and length of heating. *Food Chemistry, 173*, 1125–1132. https://doi.org/10.1016/j.foodchem.2014.11.021

Sun, H., Fan, J., Tian, Z., Ma, L., Meng, Y., Yang, Z., & Nan, X. (2022). Effects of treatment methods on the formation of resistant starch in purple sweet potato. *Food Chemistry, 367*, Article 130580. https://doi.org/10.1016/j.foodchem.2021.130580

Sun, S., Hong, Y., Gu, Z., Cheng, L., Ban, X., Li, Z., & Li, C. (2023). Different starch varieties influence the complexing state and digestibility of the resulting starch-lipid complexes. *Food Hydrocolloids, 141*, Article 108679. https://doi.org/10.1016/j.foodhyd.2023.108679

Sun, S., Jin, Y., Hong, Y., Gu, Z., Cheng, L., Li, Z., & Li, C. (2021). Effects of fatty acids with various chain lengths and degrees of unsaturation on the structure, physicochemical properties and digestibility of maize starch-fatty acid complexes. *Food Hydrocolloids, 110*, Article 106224. https://doi.org/10.1016/j.foodhyd.2020.106224

Sun, X., Saleh, A. S. M., Lu, Y., Sun, Z., Zhang, X., Ge, X., & Li, W. (2022). Effects of ultra-high pressure combined with cold plasma on structural, physicochemical, and digestive properties of proso millet starch. *International Journal of Biological Macromolecules, 212*, 146–154. https://doi.org/10.1016/j.ijbiomac.2022.05.128

Tupa, M. V., Altuna, L., Herrera, M. L., & Foresti, M. L. (2020). Preparation and characterization of modified starches obtained in acetic anhydride/tartaric acid medium. *Starch - Stärke, 72*(5–6), 1900300. https://doi.org/10.1002/star.201900300

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

Walsh, S. K., Lucey, A., Walter, J., Zannini, E., & Arendt, E. K. (2022). Resistant starch—An accessible fiber ingredient acceptable to the Western palate. *Comprehensive Reviews in Food Science and Food Safety, 21*(3), 2930–2955. https://doi.org/10.1111/1541-4337.12955

Wang, H., Ding, J., Xiao, N., Liu, X., Zhang, Y., & Zhang, H. (2020). Insights into the hierarchical structure and digestibility of starch in heat-moisture treated adlay seeds. *Food Chemistry, 318*, Article 126489. https://doi.org/10.1016/j.foodchem.2020.126489

Wang, H., Liu, Y., Chen, L., Li, X., Wang, J., & Xie, F. (2018). Insights into the multi-scale structure and digestibility of heat-moisture treated rice starch. *Food Chemistry, 242*, 323–329. https://doi.org/10.1016/j.foodchem.2017.09.014

Wang, J., Lv, X., Lan, T., Lei, Y., Suo, J., Zhao, Q., & Ma, T. (2022). Modification in structural, physicochemical, functional, and in vitro digestive properties of kiwi starch by high-power ultrasound treatment. *Ultrasonics Sonochemistry, 86*, Article 106004. https://doi.org/10.1016/j.ultsonch.2022.106004

Wang, L., Wang, W., Wang, Y., Xiong, G., Mei, X., Wu, W., & Liao, L. (2018). Effects of fatty acid chain length on properties of potato starch–fatty acid complexes under partially gelatinization. *International Journal of Food Properties, 21*(1), 2121–2134. https://doi.org/10.1080/10942912.2018.1489842

Wang, S., Chao, C., Cai, J., Niu, B., Copeland, L., & Wang, S. (2020). Starch–lipid and starch–lipid–protein complexes: A comprehensive review. *Comprehensive Reviews in Food Science and Food Safety, 19*(3), 1056–1079. https://doi.org/10.1111/1541-4337.12550

Wang, S., & Copeland, L. (2013). Molecular disassembly of starch granules during gelatinization and its effect on starch digestibility: A review. *Food & Function, 4*(11), 1564–1580. https://doi.org/10.1039/C3FO60258C

Wang, Y., Chen, J., Song, Y.-H., Zhao, R., Xia, L., Chen, Y., & Wu, X.-T. (2019). Effects of the resistant starch on glucose, insulin, insulin resistance, and lipid parameters in overweight or obese adults: A systematic review and meta-analysis. *Nutrition & Diabetes, 9*(1), 19. https://doi.org/10.1038/s41387-019-0086-9

Xiao, L., Yu, Y., Yang, X., Wei, Z., & Han, L. (2023). Physicochemical properties of ultrasound-pretreated pea starch and its inclusion complexes with lauric acid. *Food Chemistry: X, 20*, Article 100879. https://doi.org/10.1016/j.fochx.2023.100879

Yan, Y., Feng, L., Shi, M., Cui, C., & Liu, Y. (2020). Effect of plasma-activated water on the structure and *in vitro* digestibility of waxy and normal maize starches during heat-moisture treatment. *Food Chemistry, 306*, Article 125589. https://doi.org/10.1016/j.foodchem.2019.125589

Zhang, Z., & Bao, J. (2021). Recent advances in modification approaches, health benefits, and food applications of resistant starch. *Starch - Stärke, 2100141*, 2100141. https://doi.org/10.1002/star.202100141

Zhou, Y.-L., Cui, L.-H., You, X.-Y., Jiang, Z.-H., Qu, W.-H., Liu, P.-D., & Cui, Y.-Y. (2021). Effects of repeated and continuous dry heat treatments on the physicochemical and structural properties of quinoa starch. *Food Hydrocolloids, 113*, Article 106532. https://doi.org/10.1016/j.foodhyd.2020.106532

Zhou, Z., Wang, F., Ren, X., Wang, Y., & Blanchard, C. (2015). Resistant starch manipulated hyperglycemia/hyperlipidemia and related genes expression in diabetic rats. *International Journal of Biological Macromolecules, 75*, 316–321. https://doi.org/10.1016/j.ijbiomac.2015.01.052

Zhuang, J., Liu, H., You, L., Xu, F., Zeng, H., & Zeng, S. (2023). Influence of ultrasonic-microwave power on the structure and *in vitro* digestibility of lotus seed starch-glycerin monostearin complexes after retrogradation. *International Journal of Biological Macromolecules, 228*, 59–67. https://doi.org/10.1016/j.ijbiomac.2022.12.188