Food & Function

ROYAL SOCIETY OF CHEMISTRY

REVIEW

View Article Online
View Journal | View Issue

Cite this: *Food Funct.*, 2025, **16**, 4202

The interaction between starch and phenolic acids: effects on starch physicochemical properties, digestibility and phenolic acids stability

Faying Zheng,[a] Feiyue Ren,[a] Xuchun Zhu,[a] Zhaowei Han,[a] Yuanqiang Jia,[a] Xiaoyong Liu,[b] Bingyu Chen*[a] and Hongzhi Liu*[a]

Starch and phenolic acids, two common plant-based food components, can interact to form complexes during food processing, thus improving the functional properties of both starch and phenolic acids. This review provides a comprehensive summary of the effects of the interaction of the two components on the multi-scale structure, and key physicochemical and functional properties of starch, as well as the stability of phenolic acids. The main conclusions are as follows: (i) factors such as starch conformation, specific properties of phenolic acids and experimental conditions influence the extent of starch–phenolic acid interactions; (ii) the formation of the complexes significantly alters the microstructure, crystalline structure and thermal stability of starch; (iii) phenolic acids compete with starch for available free water, thereby altering starch gelatinization. This competition reduces the self-interaction of starch chains and retards the starch retrogradation; (iv) combined phenolic acids alter the structural properties of starch, while free phenolic acids inhibit the activity of digestive enzymes, collectively resulting in decreased starch digestibility; and (v) the thermal stability and biological activity of phenolic acids are closely related to the stability of the structure of starch–phenolic acid complexes. Finally, the review highlights current challenges and future research directions in the study of starch–phenolic acid interactions, aiming to advance the development of starch and phenolic acids in food and industrial applications.

Received 18th February 2025,
Accepted 11th April 2025

DOI: 10.1039/d5fo00855g

rsc.li/food-function

1 Introduction

Starch, a plant polysaccharide, has processing and functional properties that significantly influence food quality and nutrition. For example, gelatinization, retrogradation, and rheology are critical processing properties that determine the quality of starch-based foods.[1] Digestibility is the primary physiological characteristic of starch, and reducing its digestibility helps mitigate sharp fluctuations in blood glucose levels.[2,3] Low glycemic index (GI) starch-based foods are beneficial in preventing overweight,[4] hyperglycemia,[5] cardiovascular diseases,[6] and other chronic conditions.[7] However, native starch exhibits certain limitations in its processing characteristics, including low solubility, high susceptibility to degradation, elevated pasting temperatures, poor emulsification capacity, and high digestibility.[8–10] To address these limitations, various modifications have been used to change the structure of starch and functional properties of starch, including physical (moist heat, annealing, autoclaving and non-thermal modification, *etc.*),[11–13] chemical (oxidation, cross-linking, esterification and acid hydrolysis, *etc.*)[14] and enzymatic (α-amylase, glucoamylase, debranching enzyme and isoamylase, *etc.*) methods.[15] Recently, safe, eco-friendly, and low-cost modification methods have attracted significant attention. Phenolic acids, a group of natural organic compounds, have shown potential in modifying the structure of starch through interactions with its amylose and amylopectin chains.[16] Such interactions can enhance or impart new processing characteristics on native starch and slow its hydrolysis rate, thereby expanding the potential applications of native starch.

Phenolic acids are dietary antioxidants with biological activities, and they are widely distributed in grains, fruits, and vegetables.[17,18] They are primarily categorized into two major types: hydroxybenzoic acid derivatives and hydroxycinnamic acid derivatives.[19] Phenolic acids exhibit anti-inflammatory, antimicrobial, antiviral, and immune-modulating properties, and many other potential health benefits.[20–22] In recent years, with intensive research into the bioactivities of phenolic acids, studies on the interactions between phenolic acids and starch have become increasingly prominent. Phenolic acids can

[a]*Key Laboratory of Geriatric Nutrition and Health, Ministry of Education, School of Food and Health, Beijing Technology & Business University (BTBU), Beijing 100048, China. E-mail: liuhz0700@btbu.edu.cn, bychen313@gmail.com*
[b]*College of Food Science and Technology, Henan Agricultural University, Zhengzhou 450002, China*

improve the gelatinization properties,[23] long-term or short-term retrogradation,[24,25] and viscoelasticity[26] of starch, as well as significantly reduce its digestibility by forming complexes with starch.[27–29] Specifically, the effects of the processing and functional properties of rice starch are influenced by the structure of the substituent group in the selected phenolic acid, the number of hydroxyl groups, spatial site resistance, and molecular weight, among other factors.[30] Yu *et al.* emphasized that variations in the number of hydroxyl groups and the presence of a methoxyl group influence the interaction between corn starch and cinnamic acid-based phenolic acids.[31] On the other hand, the interaction between starch and phenolic acids can preserve the bioactivity of phenolic acids, primarily by forming single-helix complexes that regulate their release and enhance their thermal stability.[32–34] Due to the safety and diverse applications of phenolic acids, their effect on the multi-scale structure of starch leads to changes in processing and functional properties, suggesting their potential as a green modification tool. Meanwhile, natural polymers serve as wall materials that play a positive role in encapsulating bioactive phenolic acids, which can be used to enhance their stability and bioavailability.[35,36]

At the molecular level, interactions between starch and phenolic acids can form complexes, which alter the properties of both starch and phenolic acids. The modification of the starch structure, physicochemical properties, and functionality by natural phenolic acids is considered an eco-friendly modification method. At the same time, starch–phenolic acid complexes show great potential to protect the bioactivity of phenolic acids. This review discusses the mechanisms and subsequent effects of starch and phenolic acid interactions based on recent conclusions and evidence. At least two reasons can explain the necessity for this study: (i) starch and phenolic acid interactions are important for the development of novel modified starch for precision and green modification; and (ii) the instability and low bioavailability of phenolic acids are yet to be resolved. Additionally, polyphenol-modified starch, the structure of starch–polyphenol complexes, the complexation of starch–polyphenol compounds during food processing, and green methods used in starch–polyphenol interaction have been systematically reviewed.[16,37–39] However, limited research has addressed the interactions between starch and phenolic acids. Therefore, this study reviewed the recent advances in the mechanisms of starch–phenolic acid interaction. It also explores the effects of these interactions on the physicochemical and digestive properties of starch, the stability of phenolic acids, and their potential applications, thereby providing a theoretical reference for their joint use in improving food product quality.

2 Overview of starch

Starch serves as the primary form of energy storage in plants and a crucial source of energy in the human diet. As a raw material, starch showed distinct physicochemical properties closely related to its fine structure.[40] Currently, the relationship between the multi-scale supramolecular structure of starch and its physicochemical properties has been systematically investigated.[41–43] The multi-scale structure of starch, as illustrated in Fig. 1, includes a granular structure, growth rings, block structure, lamellar structure (amorphous lamellar and crystalline lamellar), crystalline structure, and molecular chain structure. Starch primarily exists in the form of granules, which commonly exhibit shapes such as oval, polygonal, and spherical, with a particle size distribution ranging from 1 to 100 μm.[44] Just below the granule structural level, the unique lamellar structure of starch, known as growth rings (with a size of 100–500 nm), can be observed using microscopy techniques. This feature results from the extension of multiple concentric shells of increasing diameter, radiating from the interior of the granule to its surface. Block structures are subunits of the

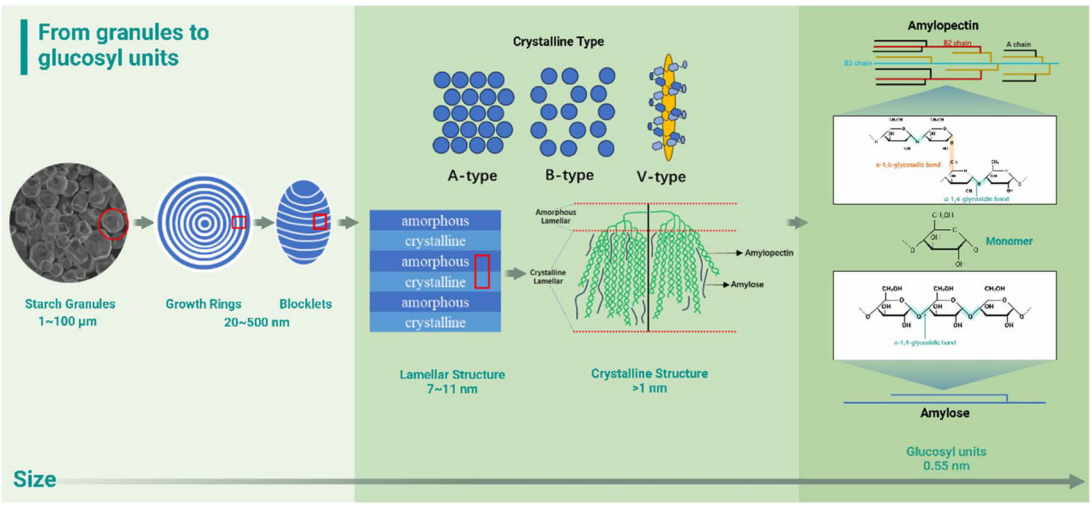

Fig. 1 The schematic representation of the multi-scale structure of starch.

growth rings, primarily found in the semi-crystalline regions and amorphous regions.[45] A periodic semi-crystalline layered structure (7–11 nm) within starch can be detected using X-ray diffraction (XRD) and small-angle X-ray (SAXS) scattering techniques. The crystalline structure (>1 nm) is composed of a double-helix arrangement of ordered amylopectin, whereas the amorphous structure primarily consists of the branching points of amylopectin and starch chains located outside the crystalline region.[46] In addition, amylopectin with an appropriate degree of polymerization can self-assemble to form a double-helix structure. These double-helix structures accumulate within the starch granules, leading to the formation of A-, B-, and C-type crystals. A-type crystals contain tightly packed helical structures, while B-type crystals are arranged in a hexagonal pattern and have a lower density than A-type. In general, grain starch exhibits typical A-type crystals, while tuber starch exhibits B-type crystals. C-type crystals are a mixture of type A and type B crystals, primarily found in bean starch.[47] In contrast, the single-helical structures are usually contained with guest small molecules through hydrophobic interactions to form V-type crystals.[43] Additionally, amylose and amylopectin constitute the starch polymer. Amylose is a linear polymer primarily composed of α-1,4-glycosidic linkages, showing a minimal amount of branching. By contrast, amylopectin is a clustered polymer characterized by a significant number of branches, with the branch points formed through α-1,6-glycosidic bonds.[12] From the structural point of view, the branched structure seems to create an obstacle to interactions with other small molecules such as iodine, lipids, and polyphenolic compounds.

The structure of starch assembled at multiple scales determines its physicochemical and functional properties, such as gelatinization, retrogradation, rheology, and digestion. These properties vary among different types of starch, influencing their suitability for diverse food applications. However, native starch often exhibits limitations in processing properties, prompting researchers worldwide to develop diverse modification techniques to broaden its applicability. Modified starches are now utilized in numerous food processing applications, such as pasta products (to enhance rehydration and shelf life), dairy products (to improve consistency and mouthfeel), meat products (as a gelling agent that enhances texture), and bakery products (to provide optimal volume and structural integrity).

3 Overview of phenolic acids

Phenolic acids are an important class of secondary metabolites derived from polyphenolic compounds. Structurally, phenolic acids are generated by the substitution of hydrogen atoms on the aromatic ring with a carboxylic acid group and at least one hydroxyl group. Plant phenolic acids are primarily biosynthesized *via* the shikimate and phenylpropane metabolic pathways.[48] The structural diversity of phenolic acids is shown in Fig. 2. Hydroxybenzoic acid and hydroxycinnamic acid are the

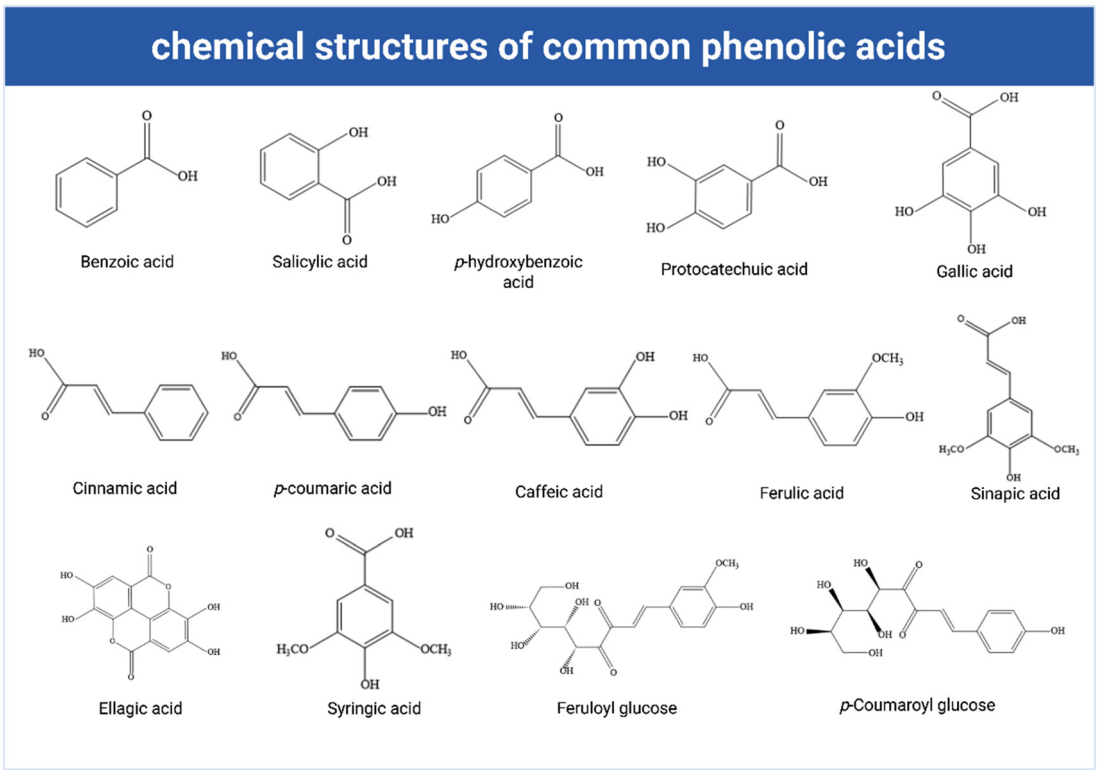

Fig. 2 Chemical structures of common phenolic acids.

two major classes of phenolic acids, distinguished by C6–C1 and C6–C3 structures, respectively. Common hydroxybenzoic acid derivatives include benzoic acid, salicylic acid, *p*-hydroxybenzoic acid, protocatechuic acid, and gallic acid, while cinnamic acid, *p*-coumaric acid, caffeic acid, ferulic acid, and sinapic acid are classified as hydroxycinnamic acid derivatives. Additionally, phenolic acid compounds exhibit bioactive functions, including anti-inflammatory, antiviral, anticancer, and antioxidant effects. Phenolic acids can bind to specific proteins, inhibiting their activity, and can also bind directly to viruses, thereby inhibiting their proliferation in cells.[49] Furthermore, phenolic acid compounds exhibit strong antioxidant activity, mainly by scavenging free radicals and inhibiting oxidative reactions, thus mitigating or preventing the damaging effects of free radicals on cells.[50] Moreover, the various groups within the structure of phenolic acids provide a structural basis for their interactions with other macromolecules. As a guest small molecule, phenolic acid can interact with both amylose and amylopectin to varying degrees. Hydroxyl groups in phenolic acids can form hydrogen bonds with hydroxyl groups in starch molecules, facilitating the tight binding of phenolic acids to starch through these non-covalent interactions.[51] The number and position of the hydroxyl groups are correlated with the strength of the interaction between starch and phenolic acids.[25] Additionally, the aromatic rings in the phenolic acid structure exhibit hydrophobic interactions in solution. When phenolic acid and starch coexist, the aromatic ring may interact with the hydrophobic region of the starch. Thus, the differences and structures of these substituent groups provide potential sites for interaction with starch. The mode and strength of the interaction between starch and phenolic acids can be partially attributed to the polar and nonpolar nature of the phenolic acid substituent groups, as well as their number and positions on the benzene ring.

4 Mechanism of starch–phenolic acid interaction

4.1 Starch–phenolic acid complexes

Research has confirmed that the interactions between starch and phenolic acids are mainly driven by non-covalent bonds, including hydrogen bonding, hydrophobic forces, electrostatic interactions, and van der Waals forces.[25,31,32,52,53] Therefore, non-covalent bonds are the main drivers of starch–phenolic acid interaction. From the molecular scale, the complexes formed between starch and phenolic acids can be classified into two categories: (i) inclusion complexes, where the phenolic acids are partially or fully encapsulated in the hydrophobic helical cavities of amylose, and (ii) non-inclusion complexes, where the phenolic acid molecules are not in the helical cavities but instead form molecular polymers with the starch (Fig. 3).

As shown in Table 1, coprecipitation is a common method to prepare starch–phenolic acid complexes, and the steps are shown in Fig. 4. In general, starch and/or phenolic acid are mixed for a period of time in solvents such as DMSO, alcohol solutions, and high-temperature water. This process aims to increase the mobility of the starch chains and promote their interaction with free phenolic acids. Then, the hydrophobic portion of the phenolic acid more readily enters either partially or fully into the helical cavities of the amylose to form the starch–phenolic acid complexes. In order to achieve precise

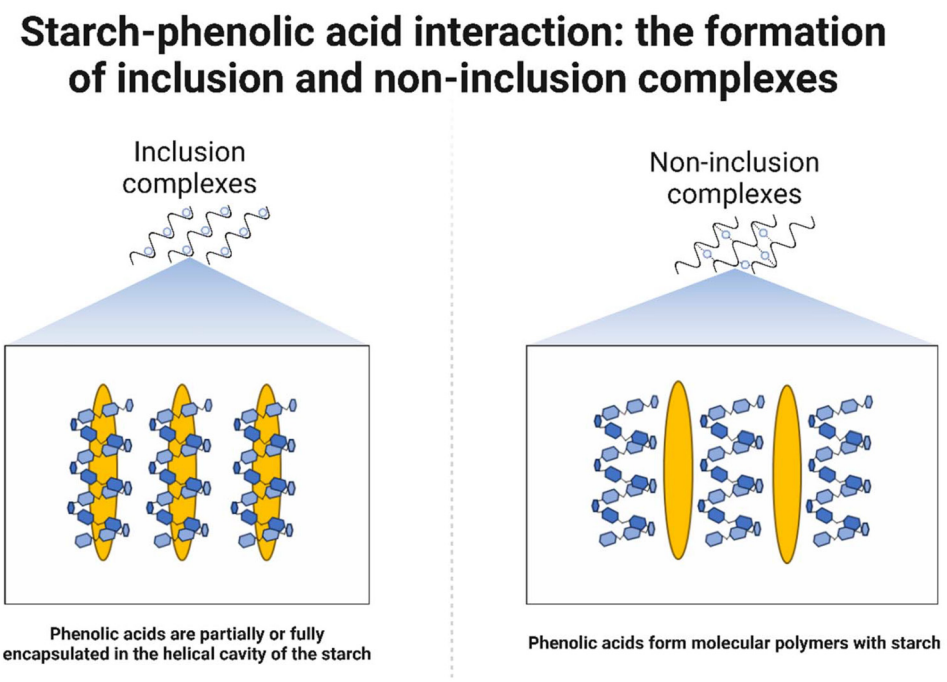

Fig. 3 Types of starch–phenolic acid complex.

Table 1 The types and preparation of starch–phenolic acid complexes

Starch	Phenolic acid type	Preparation method	Complex type	Ref.
Potato starch	Protocatechuic acid, ferulic acid and gallic acid	Coprecipitation (high-temperature water method)	Non-inclusive complexes	25
Rice starch	Caffeic acid	Coprecipitation (high-temperature water method)	Non-inclusive complexes	28
Corn starch	Cinnamic acid, caffeic acid, and ferulic acid	Coprecipitation (high-temperature water method)	Non-inclusive complexes	31
Rice starch	Ferulic acid	Coprecipitation (high-temperature water method)	Non-inclusive complexes	52
Euryale ferox kernel starch	Ferulic acid	Coprecipitation (high-temperature water method)	Non-inclusive complexes	56
Rice starch	Gallic acid, and sinapic acid	Coprecipitation (plasma-activated water, high-temperature water method)	Inclusion complexes	57
Black rice starch	Gallic acid	Coprecipitation (high-temperature water method)	Non-inclusive complexes	58
Rice starch	*p*-Coumarinic acid and chlorogenic acid	Coprecipitation (alcohol method)	Inclusion complexes	30
Maize starch	Caffeic acid	Coprecipitation (high-temperature water method)	Inclusion complexes	59
High amylose corn starch	Protocatechuic acid, ferulic acid and caffeic acid	Coprecipitation (DMSO method)	Inclusion complexes	34
Rice starch	Gallic acid	Heating and high pressure homogenization	Inclusion complexes	60
High amylose corn starch	Ferulic acid	Ball milling pretreated and heating	Inclusion complexes	61
Wheat starch	Caffeic acid	Hot-extrusion 3D printing	Inclusion complexes	62

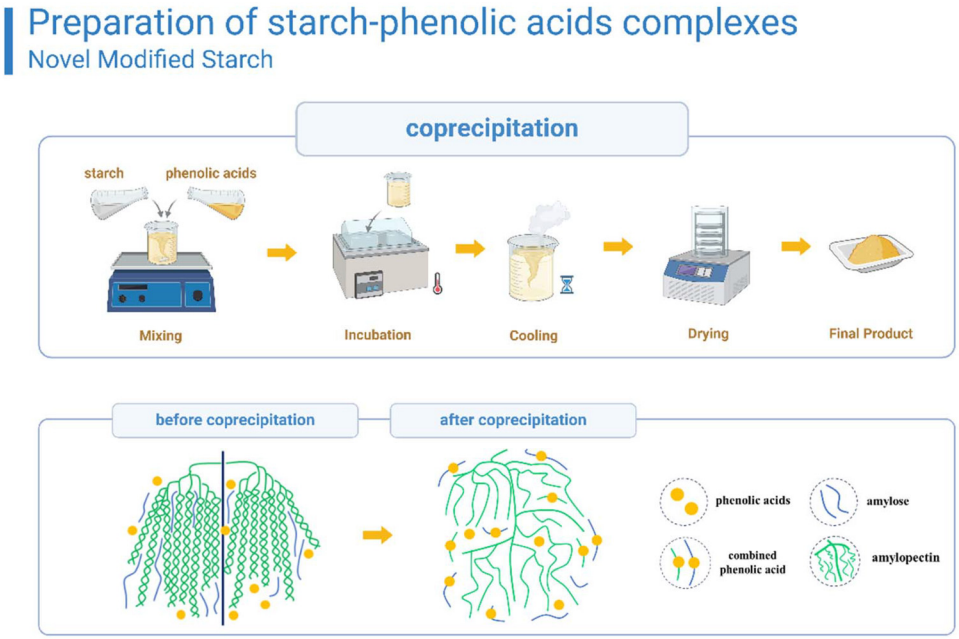

Fig. 4 Preparation of starch–phenolic acid complexes *via* coprecipitation and the associated structural modifications.

modification of starch, the modification conditions can be adjusted appropriately to increase the interaction between the starch and phenolic acids. For instance, pea starch and gallic acid, when dispersed in distilled water, are recommended to be complexed at elevated temperatures.[54] Additionally, higher amylose content or debranching of native starch is recommend before mixing with phenolic acid to increase the possibility of their physical contact.[28,55]

4.2 Factors affecting the starch–phenolic acid interaction

4.2.1 Starch conformation. The ratio of amylose to amylopectin is a key factor in the interactions between starch and phenolic acids, influencing the structure and function of the starch–phenolic acid complexes, including long-/short-range ordering, the number of single/double-helix structures, enthalpy, and digestibility.[34,63,64] Amylose exhibits a higher binding capacity for phenolic acids than amylopectin. Li *et al.* observed that caffeic, ferulic, and gallic acids can form single-helix structures by interacting with the side chains of amylopectin and amylose under acidic conditions.[26] High-amylose corn starch can encapsulate more caffeic acid than waxy or normal corn starch due to its large number of linear chains, increasing the opportunity for interaction between phenolic acid ligands and starch chains.[55] Consequently, the high-amylose and phenolic acid complexes showed the highest resistant starch content (31.71–42.33%) and dramatically

reduced hydrolysis rates compared with waxy corn starch (18.65–25.79%) and normal maize starch (12.04–28.98%). Another study showed that samples with a higher amylose content could form more complexes with caffeic acid, leading to a significant increase in the number of single-helical structures, short-range order, and relative crystallinity in the complexes.[65] Reducing the degree of branching in amylopectin and increasing the apparent amylose content are commonly used methods to enhance the interaction between starch and phenolic acids. This may be attributed to the difficulty in complexing with phenolic acids caused by the large spatial hindrance imposed by the multi-branched structure of amylopectin. It has been reported that the length of the amylose chain is related to the number of bound guest molecules.[66,67] Very short linear chains are difficult to complex with phenolic acids because these helices are too short to fully encapsulate small molecules.[54] It can be speculated that phenolic acids can form stable complexes with linear chains of a specific length. However, few studies have been published on the effects of the fine structure of amylose and amylopectin on the interaction between starch and phenolic acids.

4.2.2 Phenolic acid properties. The molecular size, substituent groups and concentration of phenolic acids play an important role in the interaction between starch and phenolic acids.[34,52,64] Specifically, these structural differences can alter both the strength and mode of starch–phenolic acid interactions. At pH < 7, the complexation rate of gallic acid–pea starch complexes was significantly higher than that of ferulic acid–pea starch complexes. The authors emphasized that gallic acid was more easily complexed with starch compared with ferulic acid due to its smaller spatial hindrance and higher number of phenolic hydroxyl groups.[68] In addition, the number of phenolic hydroxyl groups also influences the mode of interaction with starch. Yu *et al.* showed that if there are two or more hydroxyl groups in the phenolic acid structure they tend to interact with starch through hydrogen bonding, while the presence of methoxy groups (*e.g.*, in ferulic acid) converts this interaction into a hydrophobic force.[31] Moreover, the interaction with starch can be enhanced or weakened by adjusting the concentration of phenolic acids. Chi *et al.* concluded that low concentrations of phenolic acids contributed to the improvement of the ordered structure of starch gels, whereas excess phenolic acids weakened the molecular order of starch gels. On the one hand, higher concentrations of phenolic acid molecules increase spatial hindrance. On the other hand, the interaction of these small molecules with starch also induces a decrease in the rearrangement of starch chains.[69] As biologically active small molecules, the substituent groups of phenolic acid ligands, such as hydroxyl, carboxyl, and methoxy groups, are potential binding sites for interaction with starch. Therefore, the molecular size, number, and distribution of these small molecule ligands are associated with the entanglement and aggregation properties of starch.

4.2.3 Experimental conditions. Experimental conditions are another key factor influencing the interaction between starch and phenolic acids. For example, under high mechanical forces, cavitation effects, and elevated temperatures, swelling and collapse of the starch structure, disruption of the crystal structure, stretching of the double-helix structure, release of starch chains, and degradation of branched starch side chains occur, leading to an increased number of linear chains.[61,62,70–72] This, in turn, increases the chances of physical contact between starch chains and free phenolic acids (Fig. 5).

The pH of the processing conditions is also critical for the interaction between starch and phenolic acids. For example, Luo *et al.* found that the complexation of pea starch with two phenolic acids (gallic and ferulic) was lowest under alkaline

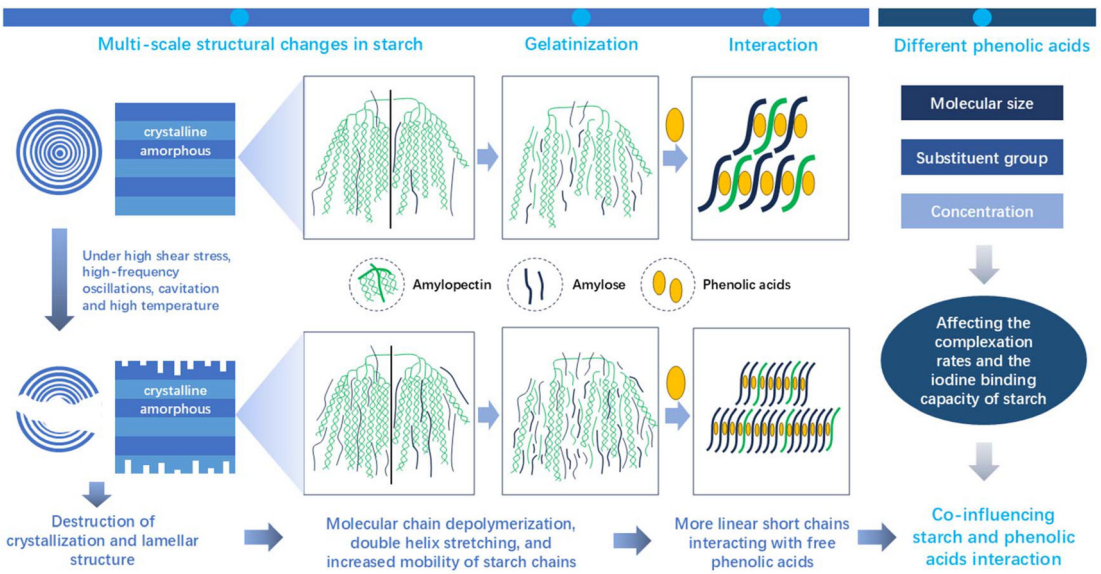

Fig. 5 Factors affecting starch–phenolic acid interactions.

followed by neutral conditions, with acidic conditions yielding the highest complexation.[68]

In other words, acidic conditions confer clear advantages in the formation of stable complexes. This may be attributed to (1) the change in the ionization state of the phenolic hydroxyl groups at higher pH, and the increased sensitivity of phenolic acids to oxidative decomposition, which weakens the complexation between starch and phenolic acids; and (2) the positively charged nature of certain phenolic acids under acidic conditions, which favors electrostatic interactions with the negatively charged starch in the system.

4.3 Interaction studies

Earlier studies have confirmed that amylose and amylopectin can form complexes with small guest molecules through hydrogen bonding, van der Waals forces, hydrophobic interactions, and electrostatic forces.[73,74] As a powerful analytical technique, isothermal titration calorimetry (ITC) can probe the interaction patterns between ligands and receptors, providing insights into the energy changes during ligand–receptor interactions. For example, Wei *et al.* investigated the interactions of gallic acid, epigallocatechin gallate, and tannic acid with amylose using ITC techniques. They found that these interactions were spontaneous and primarily driven by hydrogen bonding ($\Delta H < 0$ and Gibbs free energy < 0). Additionally, these interactions reduced the number of binding sites available on the amylose, which affected the interaction strength between the polyphenols and starch.[63] Yu *et al.* demonstrated that the adsorption processes between caffeic, cinnamic, and ferulic acids and corn starch were also spontaneous (Gibbs free energy < 0). They concluded that the multiple phenolic hydroxyl groups preferentially interacted with starch *via* hydrogen bonding, while methoxy groups shifted the driving force toward hydrophobic interactions.[55] From a structural perspective, different functional groups in phenolic acids induce distinct interactions with starch, influencing its physicochemical and functional properties. The variations in interactions resulting from chemical group differences warrant further investigation.

As an advanced research method, molecular dynamics (MD) simulation provides valuable insights into the interactions between biological macromolecules and small molecules.[75,76] This technique is widely used to study the complexation mechanisms between starch and phenolic acids. It can provide detailed information on binding sites, interaction strength, stability, and modes of interaction, which can be validated against experimental results. For example, MD simulations revealed that starch helices without phenolic acids transformed from a single-helix structure to a loose, disordered conformation. Short-chain glucose (SGS) is a commonly used biomolecule receptor model because of its relatively simple structure, which allows an efficient prediction of binding sites for interactions with small-molecule ligands. These simulations showed that weak binding between the phenolic hydroxyl groups of protocatechuic acid and SGS altered the starch's spatial conformation.[77] The interaction between amylose and gallic acid was found to be a spontaneous, low-energy process driven by non-covalent interactions, leading to amylose aggregation.[63] Fan *et al.* used MD simulations to study the interactions between amylose and various phenolic acids. The results showed that protocatechuic acid and ferulic acid were located at the center of the single-helix structure. For 3,5-dihydroxybenzoic acid and caffeic acid, their phenolic rings were trapped in amylose's hydrophobic cavity, while their carboxyl and phenolic hydroxyl groups remained outside.[34] Another study indicated that interactions between starch and ferulic acid were driven by hydrophobic forces, hydrogen bonding, van der Waals forces, and spatial site resistance effects. Key interaction sites in phenolic acids included hydroxyl and carboxyl groups, which formed single-helix complexes with starch, inducing changes in lamellar and crystalline structures.[61] These findings highlight molecular dynamics simulations as an essential tool for studying starch–phenolic acid interactions. However, due to the complexity of amylopectin's multi-branched structure, there is limited information on the dynamic simulation of amylopectin–phenolic acid interactions.

5 Interaction between starch and phenolic acids: characterization techniques and multi-scale structural changes

Researchers have used a variety of techniques to observe alterations in starch microstructure, short-range ordered structure, helical structure, lamellar structure, and crystal structure resulting from the interaction between starch and phenolic acids. Table 2 summarizes the effects of the interaction between starch and different phenolic acids on the multi-scale structure of the starch.

5.1 Microstructure

SEM and CLSM can visually identify the surface morphology and physical structure of samples. In reported studies, complexes formed by starch–phenolic acid interactions exhibited the following characteristics: irregular and compact structures, and semi-composite agglomerates.[56,63,78] Starch–polyphenol interactions are reported to involve specific regions of starch molecules.[83,84] Maibam *et al.* found that ferulic acid may act as a plasticizer, rearranging the crystalline and amorphous regions of starch, as evidenced by the formation of relatively smooth granule surfaces.[56] Due to the weak interaction between gallic acid and amylose chains, the complexes were relatively dispersed fragments, unlike network structures.[63] Yang *et al.* observed that adding 10% gallic acid under hydrothermal conditions at 90 °C significantly inhibited the starch recrystallization process.[32] Similar results were observed in the study of Zheng *et al.*[85] Moreover, phenolic acids with polyhydroxy structures demonstrated strong water retention properties. Consequently, their presence in the complexes may

Table 2 Changes in the multi-scale structure of starch induced by the interaction between starch and phenolic acids

Starch type	Phenolic acid type	Microstructure	Thermal stability	Short-range ordered structure	Long-range ordered structure	Helical structure	Lamellar structure	Ref.
Rice starch	Gallic acid and sinapic acid	SEM (agglomerate formed)	TGA (onset temperatures↓)	FT-IR (new absorption peak appeared)	XRD (diffraction peak 2θ = 7.58°, 12.86° and 19.88° with strong reflection)	—	—	57
Black rice starch	Gallic acid	SEM (aggregate formed)	TGA (mass loss↓)	FT-IR (absorption peak of the related hydroxyl group was broadened) Raman (lower content of free amylose single helices)	XRD (crystallinity↑↓)	—	—	58
Rice starch	Ferulic acid	SEM (looser microstructure)	DSC (T_0, T_p and T_c↓)	FT-IR (decreased intensity of the associated hydroxyl absorption peak, 995/1022 ratio↓)	XRD (a weak broad peak at 2θ = 20° was observed)	—	—	52
Euryale ferox kernel starch	Ferulic acid	SEM (compact microstructure)	DSC (thermal peak is shifted)	FTIR (absorption peak of the related hydroxyl group was broadened)	XRD (relative crystallinity↑)	—	—	56
Arrowhead starch	Ferulic acid and gallic acid	SEM (agglomerate formed and partial fusion, particle size↑)	DSC (ΔH↓)	FT-IR (absorption peak of the related hydroxyl group was broadened, 995/1022 ratio↓) Raman (FWHM: molecular order↑)	—	—	—	78
Rice starch	Gallic acid	—	—	ATR-FTIR (at lower amount: 1047/1022 ratio↓, at higher amount: 1047/1022 ratio↑)	—	—	SAXS (formation of ordered starch aggregates (suitable phenolic acid concentration))	69
Corn starch	Cinnamic acid, caffeic acid, and ferulic acid	—	DSC (ΔH_r↓)	Raman (FWHM: molecular order↓)	XRD (relative crystallinity↓)	—	SAXS (thinner semi-crystalline lamellae)	31
Purple sweet potato starch	Ferulic, isoferulic, 4-hydroxybenzoic and caffeic acids	SEM (looser matrix)	DSC (ΔH↑)	FT-IR (no new characteristic absorption peak appeared)	XRD (new peak at 2θ = 20° was observed)	—	—	79
Potato starch	Vanillic acid	—	DSC(ΔH↑↓)	FT-IR (1045/1015 cm^{-1} ratio↓)	XRD (no new diffraction peak appeared)	—	—	53
Cassava starch	Ferulic acid	SEM (broken sheet)	TGA (mass loss↓)	FT-IR (absorption peak of the related hydroxyl group was broadened)	XRD (diffraction peak was diffuse)	—	—	80
High-amylose corn starch	Ferulic acid	SEM (irregularly shaped)	—	FT-IR (1047/1022 cm^{-1} ratios↑) Raman (FWHM: short-range ordering↑)	XRD (new diffraction peak appeared at 2θ = 13°, 17° and 20°)	^{13}C CP/MAS NMR (single helix and double helix content↑)	—	61
Pea starch	Gallic acid and ferulic acid	SEM (spherulite appeared)	DSC (ΔH↑)	FT-IR (1047/1022 cm^{-1} and 995/1022 cm^{-1} ratios↑)	XRD (new diffraction peak appeared at 2θ = 17.21°, 19.72°, 22.20° and 24.01°, relative crystallinity↑)	—	—	68
Rice starch	Gallic acid	—	—	FT-IR (1047/1022 cm^{-1} ratios increased from phenolic acid concentration 15 to 30%)	XRD (new diffraction peak appeared at 2θ = 13.0° and 19.8°, increased proportion of V-type)	^{13}C (single helix content ↑, double helix content ↓)	—	60

Table 2 *(Contd.)*

Starch type	Phenolic acid type	Microstructure	Thermal stability	Short-range ordered structure	Long-range ordered structure	Helical structure	Lamellar structure	Ref.
Yam starch	Gallic acid	SEM (rough and irregular)	DSC (ΔH↓)	FT-IR (1047/1022 cm^{-1} ratios↓)	XRD (new diffraction peak appeared at 2θ = 20.05°)	—	—	71
Corn starch	Ferulic acid	SEM (depressions and pits)	DSC (ΔH↓)	FT-IR (1056/1022 and 995/1022 cm^{-1} ratios↓)	XRD (new peak at 2θ = 19.8°, relative crystallinity↓)	^{13}C (amorphous content↑)	—	81
Maize starch (except for waxy maize starch)	Caffeic acid	—	TGA (decomposition temperature↓)	FT-IR (1045/1022 cm^{-1} ratios↓)	XRD (crystallinity↑)	^{13}C CP/MAS (single helix contents↑)	—	65
Maize starch	Protocatechuic acid	CLSM (diameter↑)	DSC (T_0, T_p, T_c and ΔH↓)	FT-IR (1047/1022 cm^{-1} ratios↑)	WAXD (crystallinity↑)	—	—	77
Maize starch	Gallic acid	—	—	FT-IR (1047/1035 cm cm^{-1} ratios↑↓) Raman (FWHM: short-range ordering↑↓)	XRD (crystalline structure integrity)	—	SAXS (thicker crystalline lamellae)	82

—: not performed; SEM: scanning electron microscopy; CLSM: confocal laser scanning microscopy; TGA: thermogravimetric analysis; DSC: differential scanning calorimetry; FT-IR: Fourier transform infrared spectroscopy; XRD: X-ray diffraction; WAXD: wide-angle X-ray diffraction; SAXS: small-angle X-ray diffraction; FWHM: full width at half maximum; ΔH: gelatinization enthalpy; ΔH_r: retrogradation enthalpy; T_0: onset temperature; T_p: peak temperature; T_c: conclusion temperature; ^{13}C: nuclear magnetic resonance spectroscopy.

reduce water evaporation and maintain microstructural integrity.[52] Variations in the structure of phenolic acids may result in different forms and strengths of interaction with starch.[86]

5.2 Thermal stability

The thermal properties and stability of starch–phenolic acid complexes can be analyzed using DSC and TGA techniques. TGA monitors weight changes in samples as temperature increases, while DSC measures the thermal effects of substances during temperature changes. The addition of protocatechuic, ferulic, and caffeic acids raised the onset temperature (T_0), peak temperature (T_p), and conclusion temperature (T_c) of high-amylose corn starch, thereby enhancing its thermal stability. This is mainly due to the ordered structure of the inclusion complex, which prevents heat and mass transfer, leading to elevated thermal stability.[34] Wang *et al.* also observed improved thermal stability in black rice starch complexed with gallic acid, attributed to enhanced intermolecular binding between the starch and phenolic acids.[58] However, changes in the thermal properties of starch were reported when varying amounts of caffeic acid were added to the rice starch–water system prior to heating.[24] The presence of gallic acid lowered the gelatinization enthalpy of rice starch, thereby reducing its thermal stability.[52] Furthermore, the addition of ferulic acid decreased the onset (T_0), peak (T_p), and conclusion (T_c) temperatures of rice starch.[87] With increasing doses of phenolic acids, protocatechuic acid promoted the gelatinization of maize starch,[77] and similar trends were observed in fucoidan starch–ferulic acid and maize starch–ferulic acid complexes.[23,88] In fact, the bonding strength of the starch chain is high, and if phenolic hydroxyl groups occupy the hydrogen bonding sites of the starch chains, they may weaken the interactions among the starch chains, thus reducing the gelatinization enthalpy. If the interaction between starch and phenolic acids forms an ordered structure, it could improve thermal stability. Conversely, if their incorporation disrupts the crystalline structure of the starch, it may decrease thermal stability. There is currently no consensus on the effects of phenolic compound–starch interactions on the thermal properties of starch.[34,89–91] Factors such as starch source, phenolic acid structure, preparation conditions, and thermodynamic parameters likely contribute to the variability in observed effects.

5.3 Short-range ordered structure

FT-IR is highly sensitive to molecular structural changes and is widely used to analyze chemical structures following molecular interactions. No new peaks were observed in the FT-IR spectra of maize starch interacting with ferulic acid. The binding of phenolic acids and starch is likely due to physical changes.[85] Additionally, the hydroxyl group stretching vibration peak shifted from 3280 cm^{-1} to 3282 cm^{-1} with the addition of gallic acid, indicating that non-covalent interactions, particularly hydrogen bonding, occurred between the phenolic acids and starch.[63] Similar results were observed in wheat starch, black rice starch, high-amylose maize starch, normal maize starch, waxy maize starch, rice starch, potato starch and

cassava starch.[30,58,59,80,88,92] The FT-IR bands at 1047 cm^{-1}, 1022 cm^{-1} and 995 cm^{-1} are associated with the short-range ordered and double-helix structure of starch.[12] For instance, adding vanillic acid into potato starch reduced the 1045/1015 cm^{-1} peak area ratio, indicating a lower degree of order in the starch.[53] Similarly, a significant decrease in the absorbance ratios of the maize starch–phenolic acid complexes at 1047/1022 cm^{-1} and 1022/995 cm^{-1} was observed.[85] Phenolic acids may disrupt starch chain interactions, hindering the formation of double-helix structures and interfering with amylose helix association. This may explain the loss of the short-range ordered structure.[53,93]

In addition to the FT-IR technique, Raman spectroscopy is also an important method for investigating the ordered structures in starch–phenolic acid complexes. The full width at half maximum (FWHM) of the band at 480 cm^{-1} correlates with the short-range order of the starch. Yu *et al.* found that the presence of ferulic, cinnamic, and caffeic acids significantly increased the FWHM values of maize starch after co-gelatinization and 14 days of storage, suggesting that the phenolic acids may weaken the short-range molecular order of the starch during retrogradation.[31] Similar results were observed in black rice starch–gallic acid complexes. High ultrasonic power (>300 W) was found to induce the formation of V-type inclusion complexes, accompanied by a significant reduction in FWHM values.[58] These results indicate that appropriate treatments can enhance the interaction between starch and phenolic acids and effectively induce the formation of V-type crystalline structures.

5.4 Long-range ordered structure

The X-ray diffraction (XRD) technique is frequently used to verify interactions between starch and phenolic acids. Starch–phenolic acid inclusion complexes exhibit typical V-type crystallization characteristics, with strong diffraction peaks at 2θ = 19.8° and 20.1° in XRD patterns. In contrast, non-inclusion starch–phenolic acid complexes do not produce these characteristic peaks. For instance, new diffraction peaks were observed in black rice starch–gallic acid complexes and arrowhead starch–gallic acid complexes at 2θ = 13° and 20°,[58,78] as well as in rice starch–ferulic acid complexes at 2θ = 13°,[52] demonstrating that the selected phenolic acids and starch indeed form the inclusion complexes. The increase in crystallinity of maize starch with ferulic acid addition indicates that the ferulic acid may preserve the internal structure of the starch.[85] Additionally, ferulic, protocatechuic, and caffeic acids may increase the relative crystallinity of high-amylose corn starch, and *p*-coumarinic acid, ellagic acid and *p*-hydroxybenzoic acid could also increase the crystallinity of debranched rice starch.[30,34] For potato starch, Mao *et al.* found that ferulic, protocatechuic, and gallic acids may not affect its long-range ordered structure.[25] However, the disruption of hydrogen bonding within the starch granules may lead to disturbed and diffused starch crystals. For example, vanillic acid formed non-inclusion complexes with potato starch, resulting in a loss of crystalline order.[53] The phenolic hydroxyl groups and starch chains may interact *via* hydrogen bonding, while the exposed benzene rings may disrupt the crystalline structure of the starch through hydrophobic interactions, potentially explaining the reduced crystallinity observed in some complexes.

5.5 Helical structure

The ^{13}C NMR technique provides insights into changes in the helical structure of starch, as different carbons in the glucose unit generate distinct signals depending on their chemical environments.[94] In the spectra, the changes in the C1 (93–105 ppm), C2,3,5 (68–78 ppm), and C4 (77–86 ppm) positions reflect changes in the aggregation states of starch.[95] The absorption peaks at the C1 and C4 positions correspond to the ordered and disordered states of starch molecules, respectively. Additionally, the spectra can be analyzed to determine the proportions of single-helix, double-helix, and amorphous regions in starch. For instance, ball-milling pretreatment facilitated the incorporation of ferulic acid into the hydrophobic regions of amylose or the long side chains of amylopectin, slightly increasing the single-helix content without significantly altering the typical signals of C1, C2, C3, and C5.[61] Liu *et al.* found that starch–gallic acid complexes with single-helix structures tended to form tighter structural domains, reducing the proportion of amorphous regions in starch.[60] The results of ^{13}C CP/MAS NMR showed that peaks centered at 99 ppm at C1 were found for corn starch. However, these peaks transformed into broad peaks centered at 103 ppm after the interaction between corn starch and ferulic acid under high hydrostatic pressure.[81] signals. Moreover, coprecipitation of starch and caffeic acid in high-temperature water reduced the proportion of double-helix structures while increasing the single-helix content compared with the control.[65]

5.6 Lamellar structure

The changes in the lamellar structure of starch are usually studied using SAXS.[96] After co-gelatinization with phenolic acids (cinnamic, caffeic, and ferulic) in high-temperature water, the scattering peak corresponding to the semi-crystalline structure of corn starch at q = 0.67 nm^{-1} disappeared, and a "shoulder-like" peak appeared ($q \approx 0.40$ nm^{-1}). The formation of the shoulder peak was related to the formation of ordered aggregates during retrogradation, as confirmed by the scattering power law equation ($I \sim q^{-\alpha}$).[31] In addition, the Lorentz variation ($I^{*}q^{2} \sim q$) could better identify the location of these scattering peaks. According to the literature, the position and intensity of the scattering peaks in the low-q region in SAXS are related to the electron cloud density in the amorphous and ordered regions of starch.[97] As the concentration of gallic acid increased to 20%, it was observed that the intensity of the rice starch–gallic acid complex was higher than that of rice starch in the low-q region. This indicated that the addition of gallic acid increased the molecular aggregation within the ordered region of the starch and induced a compact network structure. However, higher concentrations did not promote tighter molecular aggregation, and a significant decrease in the small-angle region was observed in rice starch containing

50% gallic acid.[69] Chi *et al.* also observed an increased scattering intensity of phenolic acids in the low-q region in a concentration-dependent manner.[82] Thus, it can be seen that phenolic acids affect the state of molecular aggregation in the crystalline or amorphous regions of starch, thereby altering the lamellar structure of starch.

6 Interaction between starch and phenolic acids: effects on starch physicochemical and digestive properties

This review systematically discusses the effects of starch–phenolic acid interactions on the key physicochemical and functional properties of starch. The latest data are summarized in Table 3, providing insight into how these interactions influence the gelatinization, retrogradation, rheological properties, and digestive properties of starch, along with their possible mechanisms.

6.1 Starch gelatinization

The effects of phenolic acids on starch gelatinization are summarized in Table 3. The complexation of ferulic acid with *Euryale ferox* kernel starch may increase intermolecular hydrogen bonding and impede heat transfer, thereby delaying starch gelatinization. The pasting temperature of corn starch decreased with increasing doses of protocatechuic acid, attributed to starch–phenolic acid interactions through intermolecular hydrogen bonding, which may impair the crystalline structure of starch and promote gelatinization.[77] P.E. Igoumenidis *et al.* noted that ΔH decreased with increasing additions of caffeic acid to a rice starch–caffeic acid mixture, attributed to the dilution effect of phenolic acid interfering with the starch–water matrix during the gelatinization process.[24] However, high percentages of caffeic acid (undiluted) did not lead to significant changes during starch gelatinization.[100] In contrast, slightly higher ΔH values were observed for ultrasound-treated arrowhead starch–ferulic acid and arrowhead starch–gallic acid complexes.[78] This might be mainly due to the cavitation effect of ultrasound resulting in distortion of the amorphous regions of starch or different arrangements of hydrogen bonding linkages.[101] Therefore, the hydroxyl groups of phenolic acids may promote the transfer of water from the amorphous region to the crystalline region, allowing starch to hydrate more readily. The interaction between starch and phenolic acids has been shown to influence not only the structure of starch chains but also the chain interactions in the crystalline and amorphous regions. This may restrict amylopectin hydration and alter the enthalpy and gelatinization temperature.[26]

On the other hand, phenolic compounds may affect water distribution during starch gelatinization.[102] For instance, Su *et al.* showed that changes in the pasting properties of purple sweet potato starch were attributed to reduced water availability, caused by interactions between the hydroxyl groups of phenolic acids and water molecules.[79] Similarly, the addition of ferulic and gallic acids was shown to limit water availability and hinder rice starch gelatinization.[52] Caffeic acid may interact with rice starch through van der Waals forces, limiting water mobility and reducing the degree of gelatinization.[24] The hydroxyl groups of phenolic acids may compete with the hydroxyl groups of potato starch for water molecules, reducing granule swelling and delaying starch gelatinization.[25] Therefore, the possible effects of phenolic acids on starch gelatinization may include two mechanisms: (1) alteration of the crystalline structure by changing the intermolecular hydrogen bonding through complexation, and (2) competition between the hydroxyl groups in phenolic acids and starch for water molecules.

6.2 Starch retrogradation

Retrogradation is the reverse process of gelatinization. When starch paste cools over a period of time, the leached or dissolved starch chains recombine through hydrogen bonding and hydrophobic forces.[103] The reorganized structure of starch after retrogradation can be influenced by phenolic acid–starch interactions, which may alter the nutritional quality, shelf life, and consumer acceptability of starch-based foods (Table 3).

The long-term retrogradation trend of gelatinized starch was evaluated based on the ratio of retrogradation enthalpy (ΔH_r) to ΔH (R-value = $\Delta H_r/\Delta H$). Starch retrogradation was completely inhibited when the mass ratio of caffeic acid exceeded 6% (w/w) of rice starch.[24] When the ferulic acid concentration reached 15%, the R-value decreased by 50% (0.03), indicating that ferulic acid effectively retards corn starch long-term retrogradation.[104] Similarly, cinnamic, caffeic, and ferulic acids reduced the ΔH_r of maize starch in a dose-dependent manner (2%, 5%, and 10%).[31] The interaction of phenolic acids with starch affects the arrangement and orientation of starch chains during retrogradation, thereby affecting the retrogradation process.[105]

The short-term retrogradation trend of gelatinized starch was determined by the difference between the final viscosity (FV) and trough viscosity (TV) measured *via* RVA (setback = FV – TV). Phenolic acids could reduce the short-term retrogradation of starch to varying degrees. For instance, the setback (SB) decreased by 56.28% (851 cP) for debranched rice starch (DRS)–ferulic acid complexes, 55.26% (836 cP) for DRS–gallic acid complexes, 45.50% (688 cP) for DRS–caffeic acid complexes, 44.64% (675 cP) for DRS–syringic acid complexes, 40.34% (610 cP) for DRS–protocatechuic acid complexes, and 38.76% (586 cP) for DRS–*p*-coumaric acid complexes, indicating that most hydroxybenzoic and hydroxycinnamic acids significantly retard the short-term retrogradation of starch.[30] Compared with potato starch without phenolic acid, the SB values of the starch system decreased by 11%, 21%, and 30% when the additions of ferulic, gallic, and protocatechuic acids were increased from 3% to 6%, respectively.[25] This may be because phenolic acids interact with amylose through hydrogen bonding, reducing the opportunity for starch chains to

Table 3 Effect of phenolic acids on the physicochemical and digestive properties of starch

Property	Phenolic acid type	Main findings	Possible mechanisms	Ref.
Gelatinization	Ferulic acid, gallic acid	SB↓	Polyphenols interact with amylose in the hydrophobic region and bind to amylopectin through van der Waals forces and hydrogen bonding	52
	Dihydroxybenzoic acid, homoprotocatechuic acid and high vanillic acid	PV↑ BD↑ SB↓	Phenolic acid may increase the viscosity of the complex, and starch granules may be more easily deformed by higher shear forces	30
	Ferulic acid, protocatechuic acid, and gallic acid	SB↓	The hydroxyl groups of phenolic acid interact with starch chains or water molecules, hindering the retrogradation of starch	25
Retrogradation	Ferulic acid	Retrogradation rate↓	Soluble ferulic acid interacts with starch chains through hydrogen bonding, occupying sites, which reduces the availability of interactions between starch chains	88
	Caffeic acid	Retrogradation is inhibited	Caffeic acid interferes with the starch–water matrix and may prevent the binding of starch chains in rearrangement	24
Rheological	Ferulic acid	Viscosity↓	Ferulic acid interferes with the coupling between the microcrystalline and amorphous regions, and the starch granules interact more readily with water to form a stable gel network with increased elasticity	88
	Ferulic acid, protocatechuic acid, and gallic acid	G' and G' ↓	Hydroxyl groups in phenolic acids may prevent the production of amylose double helix	25
	Gallic acid	Gel strength↑ (at lower amount) Gel strength↓ (at higher amount)	Suitable amounts of phenolic acids may act as molecular chaperones for starch, assisting the rearrangement of starch chains	69
Digestibility	Ferulic, isoferulic, 4-hydroxybenzoic and caffeic acids	RDS↓ RS↑	Inhibition of digestive enzymes and/or starch by phenolic acids	79
	Naringin, tannic acid and protocatechuic acid	Starch hydrolysis rate↓ (protocatechuic acid)	Interaction of free phenolic acids and phenolic acids released from complexes with digestive enzymes	89
	Gallic acid, sinapic acid, and *Glochidion wallichianum* Muell Arg extract	RDS↓ RS↑	The hydrophobic cavity of amylose may have a low affinity due to the embedment of phenolic acids, limiting the interaction between starch and phenolic acids	57
	Gallic acid, ferulic acid, caffeic acid, genistein, quercetin, and naringin	Complexes show enzyme resistance	Polyphenols released from the complex inhibited the activities of α-amylase and amyloglucosidase and retarded the subsequent digestion of starch	28
	Caffeic and ferulic acid	Reduce glycemic response in Wistar rat	RS and SDS formation by starch complexed with ferulic acid	33
	Benzoic, protocatechuic, vanillic and veratric acid	Phenolics show anti-hyperglycemic effect	Remarkable inhibition effect of α-amylase by phenolic compounds with more than one hydroxyl group	98
	Ferulic acid	RDS↓ SDS↑ RS↑ eGI↓	Phenolic acid acts as a plasticizer, inducing a more ordered molecular structure, and the highly crystalline complex is resistant to enzymatic digestion	56
	16 structurally different phenolic acids	RS↑	Acidification and methoxylation by phenolic acids synergistically reduce starch digestibility	30
	Gallic acid	RDS↓ SDS↑ RS↑	Phenolic acid acts as a starch protector by occupying the spatial site of starch digestion	58
	Ferulic acid, protocatechuic acid and gallic acid	RDS↓ RS↑	Phenolic acid improved the structural characteristics of starch, possibly by inhibiting starch swelling and maintaining its integrity	25
	Caffeic acid, gallic acid and ferulic acid	Digestibility is lower for complexes than for physical mixtures	Phenolic acid may alter the amylose and amylopectin stacking arrangements in the amorphous region	26
	Gallic acid	eGI↓	Synergistic effects of a reorganized ordered structure and inhibition of digestive enzymes by phenolic acids	69
	Ferulic acid, sinapic acid, and *p*-coumaric acid	Digestibility↓	Larger granules and greater steric hindrance of phenolic acid starch esters	99

SB: setback viscosity; PV: peak viscosity; BD: breakdown viscosity; G': storage modulus; G'': loss modulus; RDS: rapidly digestible starch; SDS: slowly digestible starch; RS: resistant starch; eGI: estimated glycemic index.

interact and rearrange, thereby inhibiting starch retrogradation.[106] Meanwhile, the presence of some insoluble phenolic acids could dilute the starch matrix. Additionally, this dilution effect may reduce the entanglement and formation of starch double-helix linkage regions, ultimately reducing the frequency of starch interactions.[104] These factors may explain the delay in starch retrogradation.

6.3 Starch rheology

In addition to gelatinization and retrogradation, rheological properties play an important role in starch-based food applications. Phenolic acids may act as molecular chaperones to maintain partially disintegrated starch granules by filling the gaps between gelatinized starch, thereby altering the starch gel network structure.[69] However, the impact of these small guest molecules on the rheological properties of starch is complex and subject to various factors, such as chemical structure, substituent groups, concentration, and preparation methods. Therefore, contradictory results have appeared in the reported literature, with phenolic acids either enhancing or disturbing the viscoelasticity of starch (Table 3). For example, Li *et al.* reported that the peak viscosities of potato starch and phenolic acid (caffeic acid, ferulic acid and gallic acid) complexes (204–281 cP) was more than 19 times lower than those of potato starch–phenolic acid mixtures (5910–7040 cP).[26] Another study showed that the viscoelasticity of rice starch improved by producing strong cross-linking properties through sinapic acid and gallic acid.[57] Conversely, a significant increase in storage modulus (G') and loss modulus (G'') was observed after the complexation of gallic acid with rice starch[57,69] and black rice starch.[58] The addition of phenolic acids may alter starch gel strength to varying degrees. For instance, researchers reported that phenolic acids decreased the G' and G'' values of potato starch in a dose-dependent manner. The order of modulus reduction in potato starch–phenolic acid complexes was ferulic acid < protocatechuic acid < gallic acid, suggesting that the number of hydroxyl groups in phenolic acids may be one of the possible reasons for inhibiting the formation of gel structures in potato starch.[25] The hydroxyl groups in phenolic acids may interfere with the formation of double-helix regions in the starch gel system, leading to weaker tangled network junctions and consequently a decrease in the modulus.

Moreover, due to its low spatial site resistance and simple molecular structure, protocatechuic acid may not restrict the movement of starch chains and therefore exhibits stronger gel-like liquid behavior.[77] In another study, ferulic acid enhanced the elasticity of rice starch and increased resistance to the flow of starch gel. This effect is primarily due to the formation of a rigid structure by ferulic acid between the starch chains through non-covalent bonds.[87] Additionally, three-dimensional gel networks are formed by the aggregation of amylose after leaching from starch granules. Appropriate amounts of phenolic acids may act as molecular chaperones, helping swell starch to create a composite network, thus increasing the strength of starch gels.[69]

6.4 Starch digestion

It was found that phenolic acids significantly affected starch digestibility.[30,32,63,85,89] For different sources of starch, phenolic acids were shown to differentially inhibit starch digestibility. For instance, gallic acid could inhibit the digestion of rice starch; however, complexes prepared in acidic, neutral, and alkaline environments exhibited varying levels of enzyme resistance. These differences arise from the ability of gallic acid to form complexes and the structural characteristics of the resulting complexes.[32] The complexation of phenolic acids with maize amylopectin and potato starch could reduce the estimated glycemic index and hydrodynamic radii of the starch.[107] Mao *et al.* found that the addition of ferulic acid, protocatechuic acid, and gallic acid limited the expansion of potato starch, and the integrity of the starch may be related to its reduced digestibility.[25] The *Euryale ferox* kernel starch containing ferulic acid was found to exhibit resistance to enzymatic digestion, which may be attributed to its increased molecular order.[56] Moreover, the gradual release of phenolic acid molecules from starch–phenolic acid complexes may inhibit the activity of starch digestive enzymes, thereby reducing the rate of starch hydrolysis.[28] Therefore, the reduction in the rate of starch hydrolysis by phenolic acids can be explained from two perspectives: (1) the alteration of starch structural characteristics and (2) the inhibition of digestive enzyme activity (Fig. 6).

6.4.1 Alteration of the starch structural characteristics by phenolic acids. The process of starch digestion involves the migration of enzymes onto starch granules, followed by the hydrolysis of glycosidic bonds.[108] Consequently, the structural characteristics of starch can directly influence the accessibility of enzymes, thereby affecting the starch hydrolysis rate.[12] The portion of phenolic acids combined with starch may reduce enzyme accessibility by altering the structural characteristics of starch (Fig. 6). Phenolic acids may attenuate starch digestion by altering the structure of amylose and the stacking arrangements of amylose–amylopectin and amylose–amylose in the amorphous region. For example, the combination of ferulic acid with *Euryale ferox* kernel starch increased its long-range crystallinity, resulting in the formation of a denser network structure that slowed the hydrolysis rate.[56] Similarly, the incorporation of ferulic acid and protocatechuic acid into potato starch induced the formation of an ordered structure, which inhibited starch swelling and maintained its structural integrity.[25] The hierarchical structure of starch plays a major role in the initial phase of digestion.[69] It was confirmed that the content of single helixes and the ordered arrangement of single helixes in starch–polyphenol complexes were related to the resistance of the complexes to enzymes.[28] The relatively ordered structure may prevent the dispersion of starch molecules in the microcrystals.[109] Therefore, complexes with higher crystallinity or short-range ordering exhibit stronger enzyme resistance compared with those with lower crystallinity or short-range ordering.

Additionally, phenolic acids may induce a larger steric hindrance effect on starch molecules through non-covalent inter-

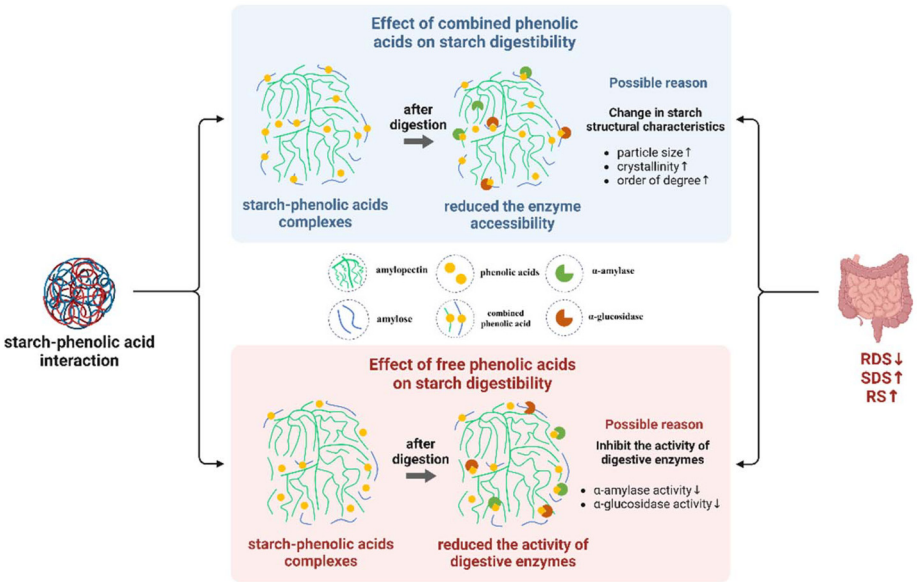

Fig. 6 The mechanism of starch–phenolic acid interaction regulating starch digestion.

actions, thus reducing the starch hydrolysis rate. These phenolic acids may increase the inter- or intra-molecular interactions of starch, while esterified starch might self-assemble into larger micellar bundles.[92,110] One study evaluated the enzyme–starch interactions of phenolic acids by molecular docking. The results showed that ferulic and sinapic acids exhibited greater steric hindrance in ring 1 and ring 2 substitutions. This increased steric hindrance was linked to reduced digestibility of starch esters. Additionally, the structural basis for the reduced digestibility may be due to the increased particle size resulting from the hydrophobic interaction between the starch ester molecules. Phenolic acids bound to starch may also directly shield starch molecules from enzymatic attack through steric effects.[26] Furthermore, the reduced flexibility of the starch structure may elevate the energy requirements for enzymatic hydrolysis, thereby further inhibiting digestion.[111] Overall, the complexation of phenolic acids may reduce enzyme accessibility by forming protective shells that alter the structural characteristics of starch.

6.4.2 Inhibition of starch digestive enzyme activity by phenolic acids. The digestion of starch is mainly associated with α-amylase and α-glucosidase. In the small intestine, pancreatic amylase and pancreatic maltase degrade starch into α-limit dextrins (consisting of 3 to 10 glucose units), maltose, and maltotriose. These intermediate products are subsequently hydrolyzed into glucose by enzymes such as α-glucosidase, maltase, and isomaltase, leading to an increase in blood glucose levels. Additionally, free phenolic acids can bind to the active sites of α-amylase, α-glucosidase, or other digestive enzymes, thereby reducing the rate of starch hydrolysis (Fig. 6).

It was found that phenolic acids may inhibit the activity of α-amylase and α-glucosidase by binding to specific amino acid residues.[28,69,79,98] Zheng *et al.* reported that the gradual release of ferulic acid during digestion could further inhibit enzyme activity.[85] The inhibition of amylase activity by phenolic acids can be further categorized as competitive, non-competitive, anti-competitive, and mixed competitive. For example, Han *et al.* showed a dose-dependent inhibition of amylase activity by phenolic acids. Specifically, when the concentration of caffeic acid was increased about 60 times, the rate of inhibition increased by about 80%. The inhibition mechanism of α-glucosidase by caffeic acid was identified as anti-competitive reversible, while that of α-amylase was irreversible.[59] Zheng *et al.* investigated the interactions between phenolic acids and α-glucosidase/α-amylase using FT-IR spectroscopy and molecular docking. The results showed that the inhibition mechanisms of α-glucosidase and α-amylase by ferulic acid were mixed and non-competitive, respectively. Moreover, ferulic acid may alter the secondary structure of α-glucosidase and α-amylase, modulating the microenvironment of amino acid residues.[29]

Similarly, under simulated physiological conditions, gallic acid was shown to induce static quenching of the intrinsic fluorescence of α-amylase, altering its molecular conformation and reducing its activity.[112] Oboh *et al.* reported the effective inhibition of α-amylase by phenolic acids.[113] However, Nyambe-Silavwe *et al.* noted that cinnamic acid-based phenolic acids were weak inhibitors of α-amylase.[114] These different results may be influenced by several factors, such as the source (saliva and porcine pancreas) and concentration of α-amylase, the concentration of phenolic acids, the type of starch, and the experimental conditions.[115]

In addition, the number of phenolic hydroxyl groups may also be related to the inhibition of enzyme activity. A study showed that a higher number of hydroxyl groups may occupy more action sites of the enzyme, thereby decreasing the attack

of the enzyme on the starch to reduce the digestion of the starch.[116] The digestibility of potato–phenolic acid complexes was observed to follow this order: ferulic acid (1 hydroxyl group) > protocatechuic acid (2 hydroxyl groups) > gallic acid (3 hydroxyl groups). Similarly, Aleixandre and Rosell pointed out that higher inhibition of α-amylase was observed for protocatechuic acid with multiple hydroxyl groups compared with benzoic acid.[98]

Overall, the reduced digestibility of starch–phenolic acid complexes may result from changes in the structural characteristics of starch and the inhibitory effects of phenolic acids on digestive enzymes. Furthermore, these two mechanisms do not conflict but instead work synergistically. The above results indicate that it seems reasonable to use phenolic acids as an ingredient to develop low-GI starch foods with desired properties.

7 Interaction between starch and phenolic acids: effects on phenolic acid stability

In general, phenolic acids are extremely unstable under different pH level, thermal processing, and storage conditions. Their stability can be significantly enhanced using various embedding techniques. Starch, as a low-cost, renewable material, shows excellent potential in phenolic acid delivery systems. For instance, compared with native starch, phenolic acid-esterified starch exhibited increased DPPH radical scavenging capacity (DPPH-RSC) in a substitution-dependent manner.[99] It was found that the DPPH-RSC of ferulic acid and high-amylose corn starch complexes decreased by only 5.99% after baking.[34] In addition, the thermal degradation of phenolic acids is regulated by the degree of complexation with starch. Compared with caffeic acid, dihydroxybenzoic acid, and protocatechuic acid, starch–ferulic acid complexes exhibited the highest encapsulation and loading efficiency, along with superior thermal stability and crystallinity. This enhanced stability may be attributed to the methoxyl group in phenolic acid structures, which facilitates hydrophobic interactions with starch, forming compact and stable complexes. In addition, phenolic acids with hydrophobic structures and smaller molecular sizes may be more likely to interact with starch, and such complexes exhibit higher thermal stability.[34] A study further revealed that starch (maize amylopectin or potato starch) and phenolic acid (caffeic and ferulic acid) complexes significantly altered the bioaccessibility of phenolic acids due to complexation-induced encapsulation.[33] Starch may act as a trapping matrix for phenolic compounds, improving their stability and antioxidant properties.[57,117] However, Yang *et al.* found that gallic acid was almost completely released from gallic acid–starch complexes during simulated digestion, suggesting that starch needs to be under specific conditions to effectively protect phenolic acids.[32]

Under suitable conditions, starch-coated phenolic acids are protected against the acid environment. The improved stability of phenolic acids after complexation with starch provides more options to enhance their bioavailability. However, for the industrial application of starch–phenolic acid complexes, more studies are needed to explain the mechanism of phenolic acid release, as well as the stability and safety of such complexes in food transportation and storage.

8 Interaction between starch and phenolic acids: applications

The properties of starch–phenolic acid interactions in food applications are depicted in Fig. 7 and Table 4.

8.1 Novel resistant starch

For instance, protocatechuic acid alters the properties of cold maize cake, reducing its digestibility while enhancing its antioxidant capacity.[77] Similar effects are observed in extruded buckwheat noodles.[119] Research shows that cereal germination increases the phenolic acid content, particularly ferulic acid, *p*-coumaric acid, and caffeic acid.[128] The addition of sprouted flour to bread enhances antioxidant activity, which may help prevent lipid oxidation during storage.[129] Moreover, phenolic acids promote the formation of resistant starch by increasing SDS fractions, likely through enhanced hydrogen bonding and steric hindrance. This effect is primarily due to enzyme resistance and the entrapment of phenolic acids within the starch matrix, which inhibits enzymatic hydrolysis. As a result, glucose production rates and insulin demand are reduced, potentially helping to prevent insulin resistance.[16,77,130] Therefore, the interaction between starch and phenolic acids, which forms starch–phenolic complexes, may offer a promising dietary strategy for managing diabetes.

8.2 Quality modifiers

Phenolic acids serve as quality modifiers in food processing, improving the functional properties of starch through the formation of complexes with it. For example, caffeic acid significantly reduces the cooking loss rate of extruded buckwheat noodles by tightening the gel structure of starch.[119] The addition of moderate amounts of protocatechuic acid to cold maize cake improves the texture of the final product and results in a desirable color.[77] In addition, the well-known antioxidant capacity of phenolic acids may prolong the shelf-life of these products, thereby providing a promising application in food processing.[131,132] However, more research is needed to explore the interaction between starch and phenolic acids in practical food applications, as current studies mainly focus on laboratory-scale experiments.

8.3 Packaging material

Starch is an important substrate for biomolecular materials because of its abundant availability, affordability, eco-friendliness, and biodegradability. However, starch-based materials must overcome certain undesirable properties in practical applications, such as low mechanical strength, poor compat-

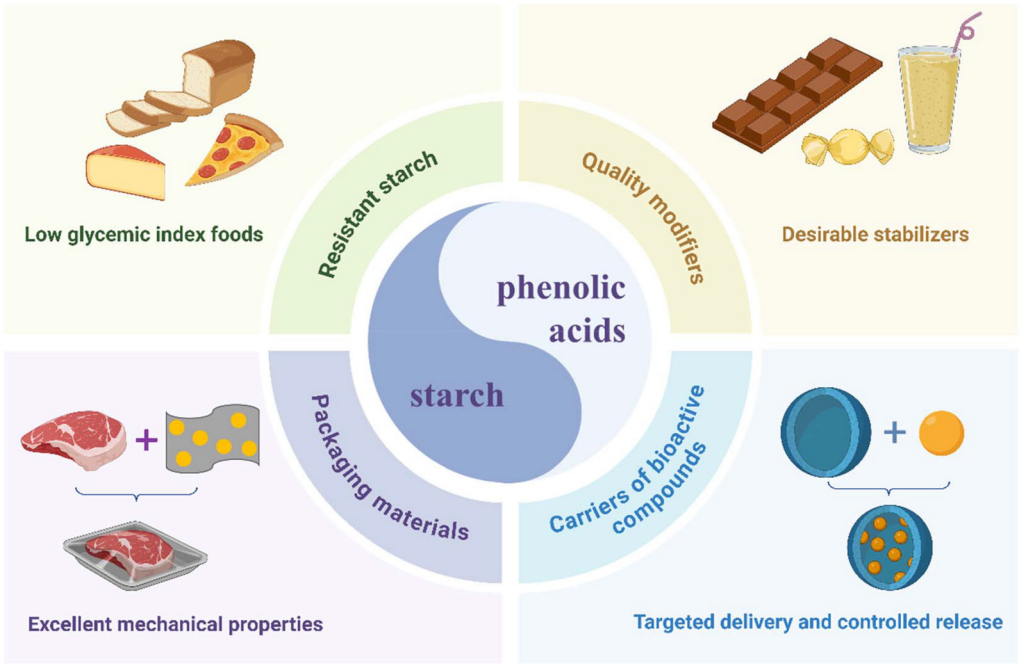

Fig. 7 Application of starch and phenolic acid interactions.

ibility, and lack of specific functions.[133] Phenolic acids, widely found in natural plants, exhibit high biosafety along with valuable antioxidant and antimicrobial properties. The application of phenolic acids in starch-based packaging materials in recent years is summarized in Table 4. The addition of different phenolic acids may improve the physical properties of starch-based films, enabling enhanced mechanical strength.[122,124,126]

For example, active edible films were produced using benzoic acid, chitosan, and corn starch. The results showed that benzoic acid was present as submicron particles within the film matrix. When the concentration of benzoic acid was increased from 0% to 2%, the tensile strength of the films increased from 17.2 MPa to 25.2 MPa.[125] Chen *et al.* found that a low dose of protocatechuic acid (2.5% of the total mixture weight) significantly reduced the tensile strength and elongation at break of maize starch-based films compared with high-dose samples. The binding affinity of phenolic acids to starch varies and is influenced by the amount and concentration of phenolic hydroxyl groups in the acids. The V-type inclusion complexes formed by starch and protocatechuic acid may enhance the resistance of the film matrix to external forces.[121,134] It has been shown that an appropriate increase in the number of phenolic hydroxyl groups can enhance the binding power between starch and phenolic acids, limiting intermolecular displacement and improving the mechanical properties of film materials.[121]

For the preservation of fruits, vegetables, and meat, the use of polymer films to cover surfaces can avoid microbial contamination and reduce moisture diffusion, thereby extending the shelf life of food products. Films incorporating benzoic acid and chitosan exhibited a reduced rate of preservative release, which extended food shelf life.[125] Similarly, the incorporation of phenolic acids improved the barrier capacity and antioxidant properties of starch–polyester bilayer films. A bioactive film prepared using gallic acid, chitosan, and cassava starch successfully extended the shelf life of ham.[135] Ferulic acid incorporated into edible coating material effectively prolonged the shelf life of pork and beef.[136,137] Ordoñez *et al.* prepared cinnamic acid-based cassava starch films and investigated their antimicrobial effectiveness on chicken breasts and fresh-cut melons. Their study revealed that the presence of cinnamic acid significantly inhibited the growth of *E. coli* and *L. innocua*.[127] Similarly, the addition of phenolic acids enhanced the antioxidant activity of starch–polyester bilayer films and inhibited the growth of microorganisms in pork. The study noted that the inhibition occurred gradually as phenolic acids were slowly released from the polymer matrix.[123]

Researchers continue to seek ideal materials for food packaging. Co-blending phenolic acids and starch using solvent casting, extrusion molding, or electrospinning has demonstrated the potential to produce food packaging films with antioxidant, antimicrobial, and improved mechanical properties.[138,139] Notably, starch-based materials with added phenolic acids are sustainable and allow degradation by soil microorganisms, making them an eco-friendly alternative. However, further studies are needed to explore the effects of starch films containing phenolic acids on microbial flora in the presence of microorganisms. Additionally, the impact of these materials on food during storage remains a key concern.

Table 4 Applications related to the interaction between starch and phenolic acids

Type of phenolic acid	Starch type	Specific applications	Properties after addition of phenolic acids	Possible mechanisms	Ref.
Ferulic acid, procyanidins and gallic acid	Wheat flour	Steamed bread	eGI↓	Phenolic acids bind to the active site of α-amylase *via* the non-covalent bond, resulting in a conformational change of α-amylase The formation of V-shaped inclusion complexes	118
Caffeic acid	Buckwheat flour	Extruded buckwheat noodles	eGI↓, hardness↓	Caffeic acid reduced the accessibility of digestive enzymes	119
Protocatechuic acid	Maize starch	Cold maize cake	Hardness, chewiness and cohesiveness↓	Phenolic acid affects the internal structure of starch in a dose-dependent manner and alters the pore distribution of gels	77
Gallic acid	Pea starch	Starch donut-shaped microparticles	No loss of antioxidant activity	Interaction of phenolic acids with starch through hydrogen bonding rather than formation of inclusion complexes	120
Protocatechuic acid	Maize starch	Starch-based film	Antioxidant activity↑ Thickness↑ (at higher concentration) Tensile strength↑ (at lower concentration) Elongation at break↑ (at lower concentration) Water vapor permeability↑ (at lower concentration)	Stronger, denser and more continuous intermolecular hydrogen bonding	121
Gallic acid	Chinese yam starch and chitosan	Starch biodegradable film and pork preservation	Tensile strength↑	Gallic acid may affect the ionization of the –OH group	122
Ferulic, *p*-coumaric or protocatechuic acid	Cassava starch	Starch–polyester bilayer film and pork meat preservation	Water vapor↑ Oxygen barrier capacity↑ Antioxidant and antimicrobial capacity↑ Microbial growth was inhibited Meat weight loss↓ Lipid oxidation↓	The interaction of phenolic acids and polyester chains restricted the mass transfer process of the film	123
Protocatechuic acid	Maize starch	Alginate-based hydrogel bead	Hardness↑ Young's modulus↑	Non-covalent interactions of phenolic hydroxyl groups with starch may result in the formation of a more uniform and complete gel network structure	124
Benzoic acid	Corn starch and chitosan	Active edible films	Tensile strength↑ Film strength↑ Antifungal activity (*A. niger*)↑	Films containing benzoic acid and chitosan showed lower preservative release rates	125
Ellagic acid	Apple starch	Active films	Tensile strength↑ Antioxidant capacity↑ Blocking UV light	Possible formation of ester and hydrogen bonds between ellagic acid and starch during gelatinization	126
Cinnamic acid	Cassava starch	Active films and their antibacterial effect on chicken breasts and fresh cut melons	Water soluble↓ Thermal stability↑ Antibacterial activity (*E. coli* and *L. innocua*)	The interaction between the carboxyl group of cinnamic acid and the hydroxyl group of starch restricted the formation of more hydrogen bonds and reduced the hydrophilicity of starch	127

8.4 Delivery materials for bioactive compounds

Natural phenolic acids with antioxidant properties offer numerous health benefits, including anti-inflammatory and anti-bacterial effects, improvement of behavioral disorders and inhibition of thrombosis.[140,141] However, these compounds exhibit instability under varying pH levels, temperatures, and light conditions due to their multiple phenolic groups. Native starch can encapsulate phenolic acids to enable efficient delivery and sustained release of these compounds, making it a suitable delivery system for biologically active compounds.[124] Yang *et al.* emphasized that the controlled release of gallic acid could be adjusted by modulating the efficiency of its complexation with rice starch. Additionally, interactions between

native starch (maize amylopectin or potato starch) and phenolic acids (caffeic acid and ferulic acid) significantly altered phenolic acid bioaccessibility and cellular uptake;[33] furthermore, phenolic acids, including protocatechuic acid, *p*-hydroxybenzoic acid, *p*-coumaric acid, ferulic acid, and caffeic acid, encapsulated in starch *via* electrospinning, exhibited remarkable stability in simulated gastric and intestinal environments.[142] Recent studies have demonstrated the potential for encapsulating therapeutic phenolic acids in both natural and synthetic materials (*e.g.*, chitosan, polylactic acid, and gelatin) for medicinal applications.[143] Starch, as an easily accessible and cost-effective material, provides additional opportunities for phenolic acids in drug delivery.

9 Conclusions and future trends

9.1 Conclusions

The effects of interactions between starch and phenolic acids on starch properties and phenolic acid stability were reviewed. The modification of starch properties and functions by phenolic acids is attributed to the formation of starch–phenolic acid complexes. Factors such as amylose content, phenolic acid properties, and experimental conditions directly influence the complexation efficiency of these complexes. Phenolic acids interact with starch and affect its properties in the following ways: (i) competing with starch for free water and altering starch gelatinization; (ii) reducing the interaction between starch chains and retarding starch retrogradation; (iii) altering the structural characteristics of starch and inhibiting digestive enzyme activities to reduce starch digestibility; and (iv) the bioavailability and thermal stability of phenolic acids are significantly improved when tightly encapsulated in starch. In the food and pharmaceutical fields, starch–phenolic acid complex interactions are utilized as resistant starch, quality modifiers, packaging materials, and delivery carriers for bioactive components. This review highlights the importance of starch–phenolic acid interactions in understanding the processing and functional properties of starch as well as the stability regulation of phenolic acids.

9.2 Future work

Regarding starch–phenolic acid interactions, most researchers have proposed complexation mechanisms by studying the physicochemical and functional properties of starch–phenolic acid complexes. However, further studies are needed to fully understand the mechanisms of these interactions. For example:

(i) To study the effects of different types of starch, as well as varying degrees of polymerization and chain lengths of starch chains, on starch–phenolic acid interactions

(ii) To compare the effects of different substituent groups within the same phenolic acid structure on the structure, physicochemical properties, and digestibility of starch

(iii) To investigate possible conformational changes during the dynamic process of starch–phenolic acid interactions and the specific morphology of the complexes formed

(iv) To elucidate the anti-digestive mechanism of phenolic acid-modified starch *in vivo* and its effect on intestinal flora

(v) To conduct systematic studies on the mechanism of the slow release of phenolic acids. It should be emphasized that very high doses of phenolic acids can be harmful to humans, and the safe doses range of phenolic acids and their effects must be rigorously evaluated.

Data availability

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

Conflicts of 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.

Acknowledgements

This research was funded by Henan Province Key Research Development Project (241111110600), Beijing High-level Talent Project (19008024075) and National Key Research and Development Plan (2024YFF1105602).

References

1 J. Qiao, Z. Zhang, B. Xing, Y. Liang, M. Jia, J. Yun, J. Niu, H. Li, G. Ren and P. Qin, Starch chain-length distributions affect the processing and digestion characteristics of proso millet starch, *Food Chem.*, 2024, 140104.
2 D. Chang, X. Hu and Z. Ma, Pea-Resistant starch with different multi-scale structural features attenuates the obesity-related physiological changes in high-fat diet mice, *J. Agric. Food Chem.*, 2022, **70**, 11377–11390.
3 M. K. Lal, B. Singh, S. Sharma, M. P. Singh and A. Kumar, Glycemic index of starchy crops and factors affecting its digestibility: A review, *Trends Food Sci. Technol.*, 2021, **111**, 741–755.
4 M. Zafar, K. Mills, J. Zheng, M. Peng, X. Ye and L. Chen, Low glycaemic index diets as an intervention for obesity: a systematic review and meta–analysis, *Obes. Rev.*, 2019, **20**, 290–315.
5 S. M. Grant, T. M. Wolever, D. L. O'Connor, R. Nisenbaum and R. G. Josse, Effect of a low glycaemic index diet on blood glucose in women with gestational hyperglycaemia, *Diabetes Res. Clin. Pract.*, 2011, **91**, 15–22.
6 M. Hanefeld, B. M. Frier and F. Pistrosch, Hypoglycemia and cardiovascular risk: is there a major link?, *Diabetes Care*, 2016, **39**, S205–S209.

7 A. Reynolds, J. Mann, J. Cummings, N. Winter, E. Mete and L. Te Morenga, Carbohydrate quality and human health: a series of systematic reviews and meta-analyses, *Lancet*, 2019, **393**, 434–445.
8 P. A. Magallanes-Cruz, L. F. Duque-Buitrago and N. del Rocío Martínez-Ruiz, Native and modified starches from underutilized seeds: Characteristics, functional properties and potential applications, *Food Res. Int.*, 2023, **169**, 112875.
9 G. C. Milanezzi and E. K. Silva, Pulsed electric field-induced starch modification for food industry applications: A review of native to modified starches, *Carbohydr. Polym.*, 2024, 122793.
10 F. Zheng, F. Nie, Y. Qiu, Y. Xing, Q. Xu, J. Chen, P. Zhang and H. Liu, Changes in Functional Properties and In Vitro Digestibility of Black Tartary Buckwheat Starch by Autoclaving Combination with Pullulanase Treatment, *Foods*, 2024, **13**, 4114.
11 C. E. Chávez-Murillo, J. I. Veyna-Torres, L. M. Cavazos-Tamez, J. de la Rosa-Millán and S. O. Serna-Saldívar, Physicochemical characteristics, ATR-FTIR molecular interactions and in vitro starch and protein digestion of thermally-treated whole pulse flours, *Food Res. Int.*, 2018, **105**, 371–383.
12 F. Zheng, Q. Xu, S. Zeng, Z. Zhao, Y. Xing, J. Chen and P. Zhang, Multi-scale structural characteristics of black Tartary buckwheat resistant starch by autoclaving combined with debranching modification, *Int. J. Biol. Macromol.*, 2023, **249**, 126102.
13 Z. Wu, D. Qiao, S. Zhao, Q. Lin, B. Zhang and F. Xie, Nonthermal physical modification of starch: An overview of recent research into structure and property alterations, *Int. J. Biol. Macromol.*, 2022, **203**, 153–175.
14 N. Masina, Y. E. Choonara, P. Kumar, L. C. du Toit, M. Govender, S. Indermun and V. Pillay, A review of the chemical modification techniques of starch, *Carbohydr. Polym.*, 2017, **157**, 1226–1236.
15 S. P. Bangar, A. O. Ashogbon, A. Singh, V. Chaudhary and W. S. Whiteside, Enzymatic modification of starch: A green approach for starch applications, *Carbohydr. Polym.*, 2022, **287**, 119265.
16 N. Deng, Z. Deng, C. Tang, C. Liu, S. Luo, T. Chen and X. Hu, Formation, structure and properties of the starch-polyphenol inclusion complex: A review, *Trends Food Sci. Technol.*, 2021, **112**, 667–675.
17 M. M. G. Karasawa and C. Mohan, Fruits as prospective reserves of bioactive compounds: a review, *Nat. Prod. Bioprospect.*, 2018, **8**, 335–346.
18 J. Perez-Jimenez, V. Neveu, F. Vos and A. Scalbert, Systematic analysis of the content of 502 polyphenols in 452 foods and beverages: an application of the phenol-explorer database, *J. Agric. Food Chem.*, 2010, **58**, 4959–4969.
19 H. B. Rashmi and P. S. Negi, Phenolic acids from vegetables: A review on processing stability and health benefits, *Food Res. Int.*, 2020, **136**, 109298.
20 N. Kumar and N. Goel, Phenolic acids: Natural versatile molecules with promising therapeutic applications, *Biotechnol. Rep.*, 2019, **24**, e00370.
21 B. Badhani, N. Sharma and R. Kakkar, Gallic acid: A versatile antioxidant with promising therapeutic and industrial applications, *RSC Adv.*, 2015, **5**, 27540–27557.
22 P. G. Anantharaju, P. C. Gowda, M. G. Vimalambike and S. V. Madhunapantula, An overview on the role of dietary phenolics for the treatment of cancers, *Nutr. J.*, 2016, **15**, 1–16.
23 R. Karunaratne and F. Zhu, Physicochemical interactions of maize starch with ferulic acid, *Food Chem.*, 2016, **199**, 372–379.
24 P. E. Igoumenidis, P. Zoumpoulakis and V. T. Karathanos, Physicochemical interactions between rice starch and caffeic acid during boiling, *Food Res. Int.*, 2018, **109**, 589–595.
25 S. Mao, Y. Ren, X. Ye, X. Kong and J. Tian, Regulating the physicochemical, structural characteristics and digestibility of potato starch by complexing with different phenolic acids, *Int. J. Biol. Macromol.*, 2023, **253**, 127474.
26 M. Li, C. Pernell and M. G. Ferruzzi, Complexation with phenolic acids affect rheological properties and digestibility of potato starch and maize amylopectin, *Food Hydrocolloids*, 2018, **77**, 843–852.
27 B. R. Tonsic, V. G. Correa, J. A. A. Garcia-Manieri, A. Bracht and R. M. Peralta, An in vivo approach to the reported effects of phenolic acids and flavonoids on the pancreatic α-amylase activity, *Food Biosci.*, 2023, **51**, 102357.
28 N. Deng, X. Bian, S. Luo, C. Liu and X. Hu, The starch-polyphenol inclusion complex: Preparation, characterization and digestion, *Food Biosci.*, 2023, **53**, 102655.
29 Y. Zheng, J. Tian, W. Yang, S. Chen, D. Liu, H. Fang, H. Zhang and X. Ye, Inhibition mechanism of ferulic acid against α-amylase and α-glucosidase, *Food Chem.*, 2020, **317**, 126346.
30 L. Chen, X. Li, W. Li, X. Hao, S. Wu, M. Zhang, F. Zheng and N. Zhang, Structural, physicochemical, and digestive properties of enzymatic debranched rice starch modified by phenolic compounds with varying structures, *Int. J. Biol. Macromol.*, 2024, 133262.
31 M. Yu, S. Zhu, F. Zhong, S. Zhang, C. Du and Y. Li, Insight into the multi-scale structure changes and mechanism of corn starch modulated by different structural phenolic acids during retrogradation, *Food Hydrocolloids*, 2022, **128**, 107581.
32 J. Yang, M. Dong, F. Fang, Y. Li and C. Li, Effects of varied preparation processes on polyphenol-rice starch complexes, in vitro starch digestion, and polyphenols release, *Food Chem.*, 2024, **450**, 139330.
33 M. Li, L. E. Griffin, S. Corbin, A. P. Neilson and M. G. Ferruzzi, Modulating phenolic bioaccessibility and glycemic response of starch-based foods in wistar rats by physical complexation between starch and phenolic acid, *J. Agric. Food Chem.*, 2020, **68**, 13257–13266.

34 H. Fan, X. Yao, Z. Chen, R. Ma, Y. Wen, H. Li, J. Wang and B. Sun, Interaction of high amylose corn starch with polyphenols: Modulating the stability of polyphenols with different structure against thermal processing, *Food Chem.*, 2024, **437**, 137708.
35 E. Tavassoli-Kafrani, S. A. H. Goli and M. Fathi, Fabrication and characterization of electrospun gelatin nanofibers crosslinked with oxidized phenolic compounds, *Int. J. Biol. Macromol.*, 2017, **103**, 1062–1068.
36 B. Poornima and P. S. Korrapati, Fabrication of chitosan-polycaprolactone composite nanofibrous scaffold for simultaneous delivery of ferulic acid and resveratrol, *Carbohydr. Polym.*, 2017, **157**, 1741–1749.
37 R. Wang, M. Li, M. A. Brennan, S. Dhital, D. Kulasiri, C. S. Brennan and B. Guo, Complexation of starch and phenolic compounds during food processing and impacts on the release of phenolic compounds, *Compr. Rev. Food Sci. Food Saf.*, 2023, **22**, 3185–3211.
38 H. Raza, H. Xu, Q. Zhou, J. He, B. Zhu, S. Li and M. Wang, A review of green methods used in starch–polyphenol interactions: Physicochemical and digestion aspects, *Food Funct.*, 2023, **14**, 8071–8100.
39 T. Xu, X. Li, S. Ji, Y. Zhong, J. Simal-Gandara, E. Capanoglu, J. Xiao and B. Lu, Starch modification with phenolics: Methods, physicochemical property alteration, and mechanisms of glycaemic control, *Trends Food Sci. Technol.*, 2021, **111**, 12–26.
40 Y. Zhang, Y. Zhang, F. Xu, G. Wu and L. Tan, Molecular structure of starch isolated from jackfruit and its relationship with physicochemical properties, *Sci. Rep.*, 2017, **7**, 13423.
41 S. Wang, C. Li, L. Copeland, Q. Niu and S. Wang, Starch retrogradation: A comprehensive review, *Compr. Rev. Food Sci. Food Saf.*, 2015, **14**, 568–585.
42 I. J. Tetlow and E. Bertoft, A review of starch biosynthesis in relation to the building block-backbone model, *Int. J. Mol. Sci.*, 2020, **21**, 7011.
43 T. J. Gutiérrez and J. Tovar, Update of the concept of type 5 resistant starch (RS5): Self-assembled starch V-type complexes, *Trends Food Sci. Technol.*, 2021, **109**, 711–724.
44 J. Zhu, L. Han, M. Wang, J. Yang, Y. Fang, Q. Zheng, X. Zhang, J. Cao and B. Hu, Formation, influencing factors, and applications of internal channels in starch: A review, *Food Chem.: X*, 2024, 101196.
45 A. Raguin and O. Ebenhöh, Design starch: stochastic modeling of starch granule biogenesis, *Biochem. Soc. Trans.*, 2017, **45**, 885–893.
46 C. G. Biliaderis, Structural transitions and related physical properties of starch, in *Starch*, Academic Press, 2009, pp. 293–372.
47 J. F. Robyt, Starch: structure, properties, chemistry, and enzymology, *Glycoscience*, 2008, 1437.
48 S. Schefer, M. Oest and S. Rohn, Interactions between phenolic acids, proteins, and carbohydrates—Influence on dough and bread properties, *Foods*, 2021, **10**, 2798.
49 S. W. Park, M. J. Kwon, J. Y. Yoo, H.-J. Choi and Y.-J. Ahn, Antiviral activity and possible mode of action of ellagic acid identified in Lagerstroemia speciosa leaves toward human rhinoviruses, *BMC Complementary Altern. Med.*, 2014, **14**, 1–8.
50 A. Galano, G. Mazzone, R. Alvarez-Diduk, T. Marino, J. R. Alvarez-Idaboy and N. Russo, Food antioxidants: chemical insights at the molecular level, *Annu. Rev. Food Sci. Technol.*, 2016, **7**, 335–352.
51 M. Cai, J. Feng, J. Wang, P. Chen, Z. Ge, W. Liu, P. Sun, L. Wu and J. Wu, Characterization of Various Noncovalent Polyphenol–Starch Complexes and Their Prebiotic Activities during In Vitro Digestion and Fermentation, *J. Agric. Food Chem.*, 2024, **72**, 2250–2262.
52 X. Han, M. Zhang, R. Zhang, L. Huang, X. Jia, F. Huang and L. Liu, Physicochemical interactions between rice starch and different polyphenols and structural characterization of their complexes, *LWT–Food Sci. Technol.*, 2020, **125**, 109227.
53 J. H. Dupuis, R. Tsao, R. Y. Yada and Q. Liu, Physicochemical properties and in vitro digestibility of potato starch after inclusion with vanillic acid, *LWT–Food Sci. Technol.*, 2017, **85**, 218–224.
54 D. Luo, Z. Sang, Q. Xie, C. Chen, Z. Wang, C. Li and W. Xue, Complexation temperature regulated the structure and digestibility of pea starch–gallic acid complexes during high pressure homogenization, *Food Res. Int.*, 2024, **178**, 113943.
55 M. Yu, B. Liu, F. Zhong, Q. Wan, S. Zhu, D. Huang and Y. Li, Interactions between caffeic acid and corn starch with varying amylose content and their effects on starch digestion, *Food Hydrocolloids*, 2021, **114**, 106544.
56 B. D. Maibam, C. Nickhil and S. C. Deka, Preparation, physicochemical characterization, and in vitro starch digestibility on complex of Euryale ferox kernel starch with ferulic acid and quercetin, *Int. J. Biol. Macromol.*, 2023, **250**, 126178.
57 P. Chumsri, W. Panpipat, L.-Z. Cheong, M. Nisoa and M. Chaijan, Comparative evaluation of hydrothermally produced rice starch–phenolic complexes: Contributions of phenolic type, plasma-activated water, and ultrasonication, *Foods*, 2022, **11**, 3826.
58 Y. Wang, S. Han, Z. Hao, Z. Gu, C. Li, Z. Wu, Z. Zhao, Y. Xiao, Y. Liu and K. Liu, Preparation of the black rice starch-gallic acid complexes by ultrasound treatment: Physicochemical properties, multiscale structure, and in vitro digestibility, *Int. J. Biol. Macromol.*, 2024, **263**, 130331.
59 M. Han, W. Bao, Y. Wu and J. Ouyang, Insights into the effects of caffeic acid and amylose on in vitro digestibility of maize starch-caffeic acid complex, *Int. J. Biol. Macromol.*, 2020, **162**, 922–930.
60 Y. Liu, L. Chen, H. Xu, Y. Liang and B. Zheng, Understanding the digestibility of rice starch-gallic acid complexes formed by high pressure homogenization, *Int. J. Biol. Macromol.*, 2019, **134**, 856–863.
61 Z. Hao, S. Han, Z. Zhao, Z. Wu, H. Xu, C. Li, M. Zheng, Y. Zhou, Y. Du and Z. Yu, Investigation of physicochemical

properties and structure of ball milling pretreated modified starch-ferulic acid complexes, *Food Chem.: X*, 2024, **24**, 101919.
62 X.-R. Cui, Y.-S. Wang, Y. Chen, H.-Y. Mu and H.-H. Chen, Understanding the digestibility of wheat starch-caffeic acid complexes prepared by hot-extrusion 3D printing technology, *Food Hydrocolloids*, 2023, **141**, 108692.
63 X. Wei, H. Xie, Z. Hu, X. Zeng, H. Dong, X. Liu and W. Bai, Multiscale structure changes and mechanism of polyphenol-amylose complexes modulated by polyphenolic structures, *Int. J. Biol. Macromol.*, 2024, **262**, 130086.
64 D. B. Amoako and J. M. Awika, Resistant starch formation through intrahelical V-complexes between polymeric proanthocyanidins and amylose, *Food Chem.*, 2019, **285**, 326–333.
65 B. Liu, F. Zhong, W. Yokoyama, D. Huang, S. Zhu and Y. Li, Interactions in starch co-gelatinized with phenolic compound systems: Effect of complexity of phenolic compounds and amylose content of starch, *Carbohydr. Polym.*, 2020, **247**, 116667.
66 X. Liu, S. Huang, C. Chao, J. Yu, L. Copeland and S. Wang, Changes of starch during thermal processing of foods: Current status and future directions, *Trends Food Sci. Technol.*, 2022, **119**, 320–337.
67 J. Putseys, L. Lamberts and J.A. Delcour, Amylose-inclusion complexes: Formation, identity and physicochemical properties, *J. Cereal Sci.*, 2010, **51**, 238–247.
68 D. Luo, J. Fan, M. Jin, X. Zhang, J. Wang, H. Rao and W. Xue, The influence mechanism of pH and polyphenol structures on the formation, structure, and digestibility of pea starch-polyphenol complexes via high-pressure homogenization, *Food Res. Int.*, 2024, **194**, 114913.
69 C. Chi, X. Li, Y. Zhang, L. Chen, F. Xie, L. Li and G. Bai, Modulating the in vitro digestibility and predicted glycemic index of rice starch gels by complexation with gallic acid, *Food Hydrocolloids*, 2019, **89**, 821–828.
70 X. Zhou, T. Huang, S. Deng, H. Liu and W. Yu, Variations in the effects of extrusion treatments and ferulic acid addition on starch digestibility with different botanical backgrounds, *Carbohydr. Polym.*, 2024, **329**, 121768.
71 M. Shi, X. Dong, X. Jiao, H. Wang, S. Chen, X. Ji and Y. Yan, Effect of extrusion on the formation, structure and properties of yam starch-gallic acid complexes, *Int. J. Biol. Macromol.*, 2024, **264**, 130461.
72 D. Luo, Q. Xie, C. Chen, K. Mu, Z. Wang, S. Gu and W. Xue, Increasing the pressure during high pressure homogenization regulates the starch digestion of the resulting pea starch-gallic acid complexes, *Int. J. Biol. Macromol.*, 2023, **235**, 123820.
73 L. Shi, H. Hopfer, G. R. Ziegler and L. Kong, Starch-menthol inclusion complex: Structure and release kinetics, *Food Hydrocolloids*, 2019, **97**, 105183.
74 N. Bordenave, B. R. Hamaker and M. G. Ferruzzi, Nature and consequences of non-covalent interactions between flavonoids and macronutrients in foods, *Food Funct.*, 2014, **5**, 18–34.
75 D. B. Roche, D. A. Brackenridge and L. J. McGuffin, Proteins and their interacting partners: An introduction to protein–ligand binding site prediction methods, *Int. J. Mol. Sci.*, 2015, **16**, 29829–29842.
76 X. Tao, Y. Huang, C. Wang, F. Chen, L. Yang, L. Ling, Z. Che and X. Chen, Recent developments in molecular docking technology applied in food science: a review, *Int. J. Food Sci. Technol.*, 2020, **55**, 33–45.
77 N. Chen, Z.-J. Feng, H.-X. Gao, Q. He and W.-C. Zeng, Elucidating the influence and mechanism of different phenols on the properties, food quality and function of maize starch, *Food Chem.*, 2024, **449**, 139191.
78 H. Raza, K. Ameer, X. Ren, Y. Liu, L. Kang, Q. Liang, T. Guo, H. Ma and M. Wang, Synergistic impact of heat-ultrasound treatment on the properties and digestibility of Sagittaria sagittifolia L. starch-phenolic acid complexes, *Int. J. Biol. Macromol.*, 2023, **245**, 125457.
79 J. Su, C. Tan, Y. Gao and Y. Feng, Four phenolic acids from purple sweet potato and their effects on physicochemical, digestive and structural characteristics of starch, *Int. J. Food Sci. Technol.*, 2021, **56**, 1896–1904.
80 K. Fang, W. He, Y. Jiang, K. Li and J. Li, Preparation, characterization and physicochemical properties of cassava starch-ferulic acid complexes by mechanical activation, *Int. J. Biol. Macromol.*, 2020, **160**, 482–488.
81 B. Song, Q. Zheng, J. Xing, Z. Miao, M. Zheng, C. Zhao, Y. Wu, X. Xu and J. Liu, Understanding the multiscale structure and in vitro digestibility changes of corn starch-ferulic acid complexes induced by high hydrostatic pressure, *Int. J. Biol. Macromol.*, 2024, **279**, 135215.
82 C. Chi, X. Li, Y. Zhang, L. Chen, L. Li and Z. Wang, Digestibility and supramolecular structural changes of maize starch by non-covalent interactions with gallic acid, *Food Funct.*, 2017, **8**, 720–730.
83 M. Wang, Q. Shen, L. Hu, Y. Hu, X. Ye, D. Liu and J. Chen, Physicochemical properties, structure and in vitro digestibility on complex of starch with lotus (Nelumbo nucifera Gaertn.) leaf flavonoids, *Food Hydrocolloids*, 2018, **81**, 191–199.
84 D. B. Amoako and J. M. Awika, Polymeric tannins significantly alter properties and in vitro digestibility of partially gelatinized intact starch granule, *Food Chem.*, 2016, **208**, 10–17.
85 Y. Zheng, S. Chen, Y. Hu, X. Ye, S. Wang and J. Tian, The cooperation of maize starch and ferulic acid under different treatments and its effect on postprandial blood glucose level, *Food Hydrocolloids*, 2024, 110361.
86 N. Chen, H.-X. Gao, Q. He, Z.-L. Yu and W.-C. Zeng, Interaction and action mechanism of starch with different phenolic compounds, *Int. J. Food Sci. Nutr.*, 2020, **71**, 726–737.
87 N. Xu, Y. Zhang, G. Zhang and B. Tan, Effects of insoluble dietary fiber and ferulic acid on rheological and thermal properties of rice starch, *Int. J. Biol. Macromol.*, 2021, **193**, 2260–2270.
88 N. Meng, Z. Kang, P. Jiang, Y. Liu, M. Liu and Q. Li, Effects of fucoidan and ferulic acid on potato starch:

Pasting, rheological and retrogradation properties and their interactions, *Food Hydrocolloids*, 2024, **150**, 109635.
89 N. Chen, H. X. Gao, Q. He and W. C. Zeng, Insight into property, function, and digestion of potato starch modified by phenolic compounds with varying structures, *J. Food Sci.*, 2023, **88**, 962–976.
90 H. Xiao, Q. Lin, G.-Q. Liu and F. Yu, Evaluation of black tea polyphenol extract against the retrogradation of starches from various plant sources, *Molecules*, 2012, **17**, 8147–8158.
91 H. Xiao, Q. Lin, G.-Q. Liu, Y. Wu, W. Wu and X. Fu, Inhibitory effects of green tea polyphenols on the retrogradation of starches from different botanical sources, *Food Bioprocess Technol.*, 2013, **6**, 2177–2181.
92 N. Chen, H.-X. Gao, Q. He, Z.-L. Yu and W.-C. Zeng, Interaction and action mechanism of starch with different phenolic compounds, *Int. J. Food Sci. Technol.*, 2020, **71**, 726–737.
93 H. Lu, X. He, Y. Qin, N. Ji, L. Dai, L. Xiong, R. Shi, T. Wang and Q. Sun, Preparation and characterization of V-type starch nanoparticles by an oil-water interface method, *Food Hydrocolloids*, 2023, **138**, 108455.
94 B. M. Flanagan, M. J. Gidley and F. J. Warren, Rapid quantification of starch molecular order through multivariate modelling of 13 C CP/MAS NMR spectra, *Chem. Commun.*, 2015, **51**, 14856–14858.
95 M. J. Gidley and S. M. Bociek, Carbon-13 CP/MAS NMR studies of amylose inclusion complexes, cyclodextrins, and the amorphous phase of starch granules: Relationships between glycosidic linkage conformation and solid-state carbon-13 chemical shifts, *J. Am. Chem. Soc.*, 1988, **110**, 3820–3829.
96 F. Daming, W. Liyun, C. Wei, M. Shenyan, M. Wenrui, L. Xiaoming, Z. Jianxin and Z. Han, Effect of microwave on lamellar parameters of rice starch through small-angle X-ray scattering, *Food Hydrocolloids*, 2013, **35**, 620–626.
97 T. Suzuki, A. Chiba and T. Yarno, Interpretation of small angle X-ray scattering from starch on the basis of fractals, *Carbohydr. Polym.*, 1997, **34**, 357–363.
98 A. Aleixandre and C. M. Rosell, Starch gels enriched with phenolics: Effects on paste properties, structure and digestibility, *LWT–Food Sci. Technol.*, 2022, **161**, 113350.
99 X. Tao, Z. Yongheng, C. Qi, W. Lipeng, J. Shengyang, Y. Bowen, Z. Yongzhu, S. Jianfu and L. Baiyi, Modulating the digestibility of cassava starch by esterification with phenolic acids, *Food Hydrocolloids*, 2021, **127**, 107432.
100 F. Zhu and Y.-J. Wang, Rheological and thermal properties of rice starch and rutin mixtures, *Food Res. Int.*, 2012, **49**, 757–762.
101 A. J. Vela, M. Villanueva, Á. G. Solaesa and F. Ronda, Impact of high-intensity ultrasound waves on structural, functional, thermal and rheological properties of rice flour and its biopolymers structural features, *Food Hydrocolloids*, 2021, **113**, 106480.
102 M. Xu, J. Du, G. G. Hou and X. Du, Effect of tea extract on starch gelatinisation, gluten aggregation and quality characteristics of dry yellow alkaline noodle, *Int. J. Food Sci. Technol.*, 2023, **58**, 1263–1274.
103 Q. Chang, B. Zheng, Y. Zhang and H. Zeng, A comprehensive review of the factors influencing the formation of retrograded starch, *Int. J. Biol. Macromol.*, 2021, **186**, 163–173.
104 R. Karunaratne and Z. Fan, Physicochemical interactions of maize starch with ferulic acid, *Food Chem.*, 2016, **199**, 372–379.
105 G. Giuberti, G. Rocchetti and L. Lucini, Interactions between phenolic compounds, amylolytic enzymes and starch: An updated overview, *Curr. Opin. Food Sci.*, 2020, **31**, 102–113.
106 É. A. Moraes, R. da Silva Marineli, S. A. Lenquiste, C. J. Steel, C. B. de Menezes, V. A. V. Queiroz and M. R. M. Júnior, Sorghum flour fractions: Correlations among polysaccharides, phenolic compounds, antioxidant activity and glycemic index, *Food Chem.*, 2015, **180**, 116–123.
107 M. Li, C. Ndiaye, S. Corbin, E. A. Foegeding and M. G. Ferruzzi, Starch-phenolic complexes are built on physical CH-π interactions and can persist after hydrothermal treatments altering hydrodynamic radius and digestibility of model starch-based foods, *Food Chem.*, 2020, **308**, 125577.
108 D. Qiao, W. Tu, B. Zhang, R. Wang, N. Li, K. Nishinari, S. Riffat and F. Jiang, Understanding the multi-scale structure and digestion rate of water chestnut starch, *Food Hydrocolloids*, 2019, **91**, 311–318.
109 S. Luo, Z. Zeng, Y. Mei, K. Huang, J. Wu, C. Liu and X. Hu, Improving ordered arrangement of the short-chain amylose-lipid complex by narrowing molecular weight distribution of short-chain amylose, *Carbohydr. Polym.*, 2020, **240**, 116359.
110 B. Ju, D. Yan and S. Zhang, Micelles self-assembled from thermoresponsive 2-hydroxy-3-butoxypropyl starches for drug delivery, *Carbohydr. Polym.*, 2012, **87**, 1404–1409.
111 H.-J. Chung, Q. Liu and R. Hoover, 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, *Carbohydr. Polym.*, 2009, **75**, 436–447.
112 Q. Lu, C. Chen, S. Zhao, F. Ge and D. Liu, Investigation of the interaction between gallic Acid and α-amylase by spectroscopy, *Int. J. Food Prop.*, 2016, **19**, 2481–2494.
113 G. Oboh, O. M. Agunloye, S. A. Adefegha, A. J. Akinyemi and A. O. Ademiluyi, Caffeic and chlorogenic acids inhibit key enzymes linked to type 2 diabetes (in vitro): a comparative study, *J. Basic Clin. Physiol. Pharmacol.*, 2015, **26**, 165–170.
114 H. Nyambe-Silavwe and G. Williamson, Chlorogenic and phenolic acids are only very weak inhibitors of human salivary α-amylase and rat intestinal maltase activities, *Food Res. Int.*, 2018, **113**, 452–455.
115 M. Miao, B. Jiang, H. Jiang, T. Zhang and X. Li, Interaction mechanism between green tea extract and

human α-amylase for reducing starch digestion, *Food Chem.*, 2015, **186**, 20–25.
116 A. K. Oladele, K. G. Duodu and N. M. Emmambux, Hydrolysis and antioxidant activity of starch modified with phenolic extracts from grape pomace and sorghum bran under alkaline conditions, *Carbohydr. Polym.*, 2020, **240**, 116291.
117 M. Chaijan and W. Panpipat, in *Natural Antioxidants*, Apple Academic Press, 2017, pp. 21–58.
118 S. Liu, H. Sun, M. Ma and T. Mu, Effects of dietary fibres, polyphenols and proteins on the estimated glycaemic index, physicochemical, textural and microstructural properties of steamed bread, *Int. J. Food Sci. Technol.*, 2024, **59**, 4041–4052.
119 P. Tang, S. Zhang, L. Meng, Z. Wang, Y. Yang, X. Shen and X. Tang, Effects of different content of EGCG or caffeic acid addition on the structure, cooking, antioxidant characteristics and in vitro starch digestibility of extruded buckwheat noodles, *Int. J. Biol. Macromol.*, 2023, **252**, 126426.
120 C. Sabando, R. Bouza, S. Rodríguez-Llamazares, N. Pettinelli, W. Ide, L. Barral, A. Linares, R. Quiroga, J. Castaño and N. Müller, Donut-shaped microparticles prepared from different C-type starch sources: characterization and encapsulation of gallic acid, *ACS Food Sci. Technol.*, 2022, **2**, 862–871.
121 N. Chen, H.-X. Gao, Q. He and W.-C. Zeng, Potential application of phenolic compounds with different structural complexity in maize starch-based film, *Food Struct.*, 2023, **36**, 100318.
122 L. Rong, X. Ji, M. Shen, X. Chen, X. Qi, Y. Li and J. Xie, Characterization of gallic acid-Chinese yam starch biodegradable film incorporated with chitosan for potential use in pork preservation, *Food Res. Int.*, 2023, **164**, 112331.
123 E. Hernández-García, M. Vargas and A. Chiralt, Starch-polyester bilayer films with phenolic acids for pork meat preservation, *Food Chem.*, 2022, **385**, 132650.
124 N. Chen, Z.-J. Feng, H.-X. Gao, Q. He and W.-C. Zeng, Core-shell structured alginate-based hydrogel beads modified by starch and protocatechuic acid: Preparation, characterization, phenolic slow release and stable antioxidant potential, *Food Chem.*, 2024, **459**, 140389.
125 I. Lipatova, A. Yusova and L. Makarova, Functional films based on mechanoactivated starch with prolonged release of preservative, *Food Biosci.*, 2022, **47**, 101694.
126 J. M. Tirado-Gallegos, P. B. Zamudio-Flores, J. D. J. Ornelas-Paz, C. Rios-Velasco, G. I. Olivas Orozco, M. Espino-Díaz, R. Baeza-Jiménez, J. J. Buenrostro-Figueroa, M. A. Aguilar-González and D. Lardizábal-Gutiérrez, Elaboration and characterization of active apple starch films incorporated with ellagic acid, *Coatings*, 2018, **8**, 384.
127 R. Ordoñez, L. Atarés and A. Chiralt, Physicochemical and antimicrobial properties of cassava starch films with ferulic or cinnamic acid, *LWT–Food Sci. Technol.*, 2021, **144**, 111242.
128 C. Tian, Y. Wang, T. Yang, Q. Sun, M. Ma and M. Li, Evolution of Physicochemical Properties, Phenolic Acid Accumulation, and Dough-Making Quality of Whole Wheat Flour During Germination Under UV-B Radiation, *Front. Nutr.*, 2022, **9**, 877324.
129 U. Gawlik-Dziki, D. Dziki, W. Pietrzak and R. Nowak, Phenolic acids prolife and antioxidant properties of bread enriched with sprouted wheat flour, *J. Food Biochem.*, 2017, **41**, e12386.
130 H. Zhang, G. Kai, Y. Xia, G. Wang and L. Ai, Antioxidant and in vitro digestion property of black rice (Oryza sativa L.): a comparison study between whole grain and rice bran, *Int. J. Food Eng.*, 2020, **16**, 20190260.
131 S. P. Bangar, W. Scott Whiteside, S. Suri, S. Barua and Y. Phimolsiripol, Native and modified biodegradable starch–based packaging for shelf–life extension and safety of fruits/vegetables, *Int. J. Food Sci. Technol.*, 2023, **58**, 862–870.
132 Y. Ma, H. Zhao, Q. Ma, D. Cheng, Y. Zhang, W. Wang, J. Wang and J. Sun, Development of chitosan/potato peel polyphenols nanoparticles driven extended-release antioxidant films based on potato starch, *Food Packag. Shelf Life*, 2022, **31**, 100793.
133 X. Hou, H. Wang, Y. Shi and Z. Yue, Recent advances of antibacterial starch-based materials, *Carbohydr. Polym.*, 2023, **302**, 120392.
134 P. Liu, X. Kang, B. Cui, R. Wang and Z. Wu, Effects of glycerides with different molecular structures on the properties of maize starch and its film forming capacity, *Ind. Crops Prod.*, 2019, **129**, 512–517.
135 Y. Zhao, J. S. Teixeira, M. M. Gänzle and M. D. Saldaña, Development of antimicrobial films based on cassava starch, chitosan and gallic acid using subcritical water technology, *J. Supercrit. Fluids*, 2018, **137**, 101–110.
136 G. Wang, Y. Liu, H. Yong, S. Zong, C. Jin and J. Liu, Effect of ferulic acid-grafted-chitosan coating on the quality of pork during refrigerated storage, *Foods*, 2021, **10**, 1374.
137 A. El-Refai, A. Hassan, K. Nagy and M. Rabie, Antimicrobial effect for both of carboxy methyl cellulose and chitosan treated with ferulic acid or nanosilver particles as edible coatings used for some refrigerated beef samples, *J. Food Dairy Sci.*, 2017, **8**, 87–91.
138 W. Zhu, D. Zhang, X. Liu, T. Ma, J. He, Q. Dong, Z.-U. Din, J. Zhou, L. Chen and Z. Hu, Improving the hydrophobicity and mechanical properties of starch nanofibrous films by electrospinning and cross-linking for food packaging applications, *LWT–Food Sci. Technol.*, 2022, **169**, 114005.
139 B. Kaczmarek-Szczepańska, S. Grabska-Zielińska and M. Michalska-Sionkowska, The Application of Phenolic Acids in The Obtainment of Packaging Materials Based on Polymers—A Review, *Foods*, 2023, **12**, 1343.
140 M. Shi, F. Huang, C. Deng, Y. Wang and G. Kai, Bioactivities, biosynthesis and biotechnological production of phenolic acids in Salvia miltiorrhiza, *Crit. Rev. Food Sci. Nutr.*, 2019, **59**, 953–964.

141 J. Xiang, M. Zhang, F. B. Apea-Bah and T. Beta, Hydroxycinnamic acid amide (HCAA) derivatives, flavonoid C-glycosides, phenolic acids and antioxidant properties of foxtail millet, *Food Chem.*, 2019, **295**, 214–223.
142 H. Fan, X. Yao, Z. Chen, R. Ma, Y. Bi, Y. Wen, H. Li, J. Wang and B. Sun, Study on the improvement of complexation efficiency and anti-digestibility of phenolic acids based on electrospun starch fibers, *Food Res. Int.*, 2024, **177**, 113921.
143 Z. Chen, M. A. Farag, Z. Zhong, C. Zhang, Y. Yang, S. Wang and Y. Wang, Multifaceted role of phyto-derived polyphenols in nanodrug delivery systems, *Adv. Drug Delivery Rev.*, 2021, **176**, 113870.