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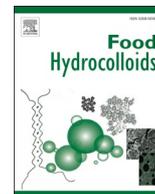
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# Review of the ethanol-induced V-type starch (EVS) with different types, including its preparation, characterization, and possible application in food field

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## ABSTRACT

Ethanol can induce the formation of a class of V-type starch under different conditions, which is later evaporated during subsequent drying process, and this ethanol-induced V-type starch (EVS) has two distinctive features. On the one hand, most of EVS can quickly swell into paste or dissolve in cold water, which could be expressed in terms of increased solubility, swelling power, viscosity, water absorption, or water retention capacity in cold water; on the other hand, the evaporation of ethanol leaves a V-type single helix cavity structure, which has the potential to rapidly encapsulate a variety of guest molecules under mild conditions and has attracted more and more attention of researchers. Different preparation methods result in EVS of different types: granular EVS, non-granular EVS and nanoscale EVS depending on the size and the structural scale of the native starch that is preserved during the preparation process. Different types of EVS have different performances in terms of paste properties and encapsulation characteristics. Among the three EVS, the granular and non-granular EVS have much higher cold-water viscosity, and the EVS at nanoscale has a higher proportion of V-type single helical cavity structure with a higher encapsulation potential. This paper summarizes the variety of preparation methods of EVS, discusses the mechanism underlying its formation, analyses the relationship between structure and function properties, presents the prospects of development and the existing challenges in perfecting the structure of EVS, and further proposes the possible applications of granular, non-granular and nanoscale EVS in food field.

## 1. Introduction

Starch, a macromolecular substance with a multi-scale structure (BeMiller, 2018). During centuries of exploration of the structure of starch, most researchers believe that the multi-scale structure of native starch can be divided into several layers, such as molecular structure (1–10 Å), crystalline structure (1–5 nm), lamellae structure (9–10 nm), “blocklets” structure (20–500 nm), growth ring structure (100–400 nm), granular structure (1–200 μm) and so on (Le Corre, Bras, & Dufresne, 2010; Gallant, Bouchet, & Baldwin, 1997). Starch is composed of two

α-D glucose polymers, amylose (AM) and amylopectin (AMP). The molecular structure of starch refers to the fine structure based on the content and distribution of AM and AMP (Junejo, Flanagan, Zhang, & Dhital, 2022; Zhu, Bai, & Gilbert, 2023). The linear structure, molecular weight, and degree of polymerization of AM and AMP vary to some extent, which exhibit unique conformation and aggregation patterns in starch granules (Li et al., 2023; Oates, 1998). For native starch, the AM is often distributed in the amorphous region of starch or intertwined with AMP (Bertoft, 2017), the short side chains of AMP intertwine with each other to form a double helix, which forms the crystalline region, and the

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difference in arrangement of double helix structure results in different crystal types (Gilbert et al., 2013; Junejo et al., 2022; Li, Powell, & Gilbert, 2017; Wang et al., 2021). Based on the X-ray diffraction patterns, three types of starch can be identified, namely A-, B-, and C-types, which varies with the plant origin. Generally, grain starches such as wheat starch and corn starch show A-type crystalline structure, and their X-ray diffraction patterns have strong diffraction peaks near 15°, 17°, 18° and 23°, the double helix of A-type crystalline structure are arranged in the form of monoclinic crystals, which are closely arranged; tubers and other starches with high content of amylose, such as potato starch and high amylose maize starch show B-type crystalline structure, and their diffraction peaks are found at 15°, 17°, 20°, 22° and 24°, the double helix of B-type crystalline structure are arranged parallel and aggregated in the form of a hexagonal shape; the C-type crystalline structure is a mixed system of A-type and B-type (Chi et al., 2021; Dominguez-Ayala, Ayala-Ayala, Velazquez, Espinosa-Arbelaez, & Mendez-Montelvo, 2023; Guo, Zhang, Bian, Cao, & Wei, 2020). The “blocklets” structure is formed by crystalline and amorphous lamellae through a certain spiral arrangement, and it is considered as the basic constituent unit of granule and shell structure. The further stacking of “blocklets” results in the formation of growth ring structure and granular structure of native starch (Le Corre et al., 2010; Han, Shi, & Sun, 2020; Huang, Wei, Li, Liu, & Yang, 2014).

Except for the native crystalline structure, there is a V-type crystalline structure, which is formed by the AM and some suitable guest molecules, such as iodine, linear alcohols, lipids, aroma compound, gas molecules, polyphenols, etc. (Deng et al., 2021; Gao, Zhang, Qiu, Fu, & Huang, 2020). Amylose in native starch can form part of V-type complex with endogenous lipids, but the content of natural V-type complex is small. V-type complex can also be prepared under some conditions such as thermal gelatinization or alkali gelatinization with the existence of guest molecules. In the absence of guest molecules, AM is usually in a randomly coiled state or aggregated with each other through hydrogen bonding to form a double helix structure (Sang et al., 2019). Under certain conditions, the presence of suitable molecular guests in the system can induce AM to form a V-type single helical structure (Putseys, Lamberts, & Delcour, 2010; Shi, Zhou, Guo, Gladden, & Kong, 2021). According to the size of molecules in the helical cavity of AM, V<sub>6</sub>-, V<sub>7</sub>- and V<sub>8</sub>-type single-helical structures with 6, 7, and 8 glucose units in the helical cycle can be formed respectively (Le et al., 2022; Putaux et al., 2011). V-type starch refers to one kind of starch whose crystalline structure is mostly dominated by a V-type single helix structure, which is accompanied by part of a double helix structure and an amorphous structure.

When the guest is a volatile small-molecule guest molecule, such as ethanol, the formed V-type complex is different from the common V-type AM-lipid/iodine complex. The ethanol that formed V-type complex can be evaporated during drying process, leaving a V-type single helical cavity structure (Chen & Jane, 1994; Li, Zhou, & Jin, 2021). Modified starch containing a large amount of this ethanol-induced V-type single helix structure can be collectively referred to as ethanol-induced V-type starch (EVS). For EVS, the crystalline region is mainly caused by the V-type single helical cavity structure, and partial double helix structure and amorphous structure may also exist in EVS due to the different combinations of reaction conditions. The V-type single helical cavity structure was formed by AM (Chen & Jane, 1994; Dries, Gomand, Delcour, & Goderis, 2016; Li, Zhou, & Jin, 2021), and the unwound AMP is distributed in the amorphous region, the crystalline structure and amorphous region of EVS are interchanged compared with the native starch, which causes the different properties (Li, Zhou, & Jin, 2021).

Compared with the native starch, on the one hand, the EVS has the capacity of cold-water swelling or has much higher cold-water solubility, which may make it a suitable food additive for improving the texture of foods (Bello-Pérez, Romero-Manilla, Acapulco, Paredes-López, & Irapuato, 2000; Chen & Jane, 1994; Eastman & Moore, 1984; Jane, 1992; Majzoobi, Kaveh, Blanchard, & Farahnaky, 2015); on the other

hand, the V-type single helical cavity structure of EVS has the potential to form complex and deliver active substance under mild conditions (Dries, Knaepen, Goderis, & Delcour, 2017; Kong & Ziegler, 2014). Both remarkable features are related to the formation of V-type single helical cavity structure induced by ethanol. This V-type single helical cavity structure can exist in starch under different structural scales, such as granular starch, non-granular starch and nano-starch depending on the preservation degree of original size and granular morphology structure of native starch during the preparation process. Therefore, the EVS can be classified in three types, according to the different structural scales, namely, ethanol-induced V-type granular starch (EVGS) (Dries, Gomand, Goderis, & Delcour, 2014; Zhang, Dhital, Haque, & Gidley, 2012), ethanol-induced V-type non-granular starch (EVNGS) (Kong & Ziegler, 2014; Zhou, Xing, et al., 2021), and ethanol-induced V-type nanoparticles starch (EVNPS) respectively (Qin et al., 2019; Qin, Liu, Jiang, Xiong, & Sun, 2016). The granular and non-granular here refers to whether the granular morphology of native starch is retained or not. Each kind of EVS requires specific and distinct preparation methods and has different formation mechanism and different properties.

Despite the growing interest in EVS at different scales, EVS has not been systematically classified and summarized according to their common structural feature: V-type single helical cavity structure induced by ethanol, which is the main reason why they have some common properties. Furthermore, there are still several aspects of EVS are not investigated adequately, such as the perfection of EVS's multi-scale structure, the relationship between EVS structure and functional properties, etc. Consequently, here we reviewed the most research progresses on the preparation methods of the different EVS, understanding of their formation mechanism, characterization of their properties, and their application in food products. In addition, the strengths, weaknesses, and challenges faced by the application of different EVS in food products are also discussed.

## 2. Preparation of EVS at different structural scales

### 2.1. Ethanol-induced V-type granular starch (EVGS)

EVGS is one kind of EVS that maintains the granular structure of native starch when its crystalline structure changes from native A-, B-, or C-type to V-type (Dries, Gomand, & Delcour, 2016; Zhang et al., 2012). One of the most remarkable properties of EVGS is the improvement of native starch's virtually unswelling and insoluble properties in cold water. It can swell into paste immediately when it contacts cold water. EVGS belongs to the granular cold-water swelling starch (GCWSS), which is one kind of cold-water swelling starch (CWSS) (Table 1). The traditional preparation technology of pre-gelatinized starch (PGS) can destroy the granular morphology of native starch (Hedayati, Shahidi, Koocheki, Farahnaky, & Majzoobi, 2016b; Majzoobi et al., 2015), and the GCWSS has a relatively intact granular morphology that is similar to the native starch, and it is considered that the properties of the cold-water paste obtained from GCWSS are more similar to the native starch paste after thermal gelatinization (Jane, 1992; Li, Zhou, & Jin, 2021). Compared with EVGS, the crystalline structure of PGS and GCWSS with A-, B-, or C-type crystal types are double helix structures formed by incomplete pre-gelatinization or partial recrystallization during the modification process (Sun et al., 2021; Xi et al., 2024; Zhang et al., 2023). Another remarkable property of EVGS is the potential to form the complex with guest molecules rapidly under mild conditions (Dries, Gomand, et al., 2017; Li, Zhou, & Jin, 2022a; Shi, Hopfer, Ziegler, & Kong, 2019). Several methods are available to prepare EVGS, the most common three being: ethanol-aqueous heat treatment (EAHT) (Dries et al., 2014, 2016; Eastman & Moore, 1984; Li, Zhou, & Jin, 2021; Sarifudin, Soontaranon, Rugmai, & Tongta, 2019; Zhang et al., 2012), alcoholic-alkaline treatment (AAT) (Chen & Jane, 1994; Hedayati, Shahidi, Koocheki, Farahnaky, & Majzoobi, 2020; Jivan, Yarmand, & Madadlou, 2014; Kaur, Fazilah, & Karim, 2011; Shi et al., 2022; Yu

**Table 1**

Classification of CWSS: cold-water swelling starch; PGS: pre-gelatinized starch; GCWSS: granular cold-water swelling starch.

Starch modification	Classification basis (① and ②)		② Crystalline structure			
			Amorphous		Crystalline	
Native starch (Unswelling and insoluble in cold water) ↓ Cold-water swelling starch (CWSS) (Improved cold-water solubility + viscosity)	① Granular morphology	Destroyed	Pre-granular starch (PGS)	PGS-amorphous (dos Santos et al., 2018; He et al., 2020; Nakorn, Tongdang, & Sirivongpaisal, 2009)	PGS-crystalline	Partially retained native crystalline structure or recrystallized crystalline structure (Sun et al., 2021; Zhang et al., 2023)
		Retained	Granular cold-water swelling starch (GCWSS)	GCWSS-amorphous (Liu, Ma, Yu, Shi, & Xue, 2011; Pitchon, Rourke, & Joseph, 1981; Song, Choi, Kim, Kim, & Baik, 2015)	GCWSS-crystalline	V-type (ethanol-induced V-type non-granular starch, EVNGS) (Zhou, Xing, et al. (2021)) Partially retained native crystalline structure or recrystallized crystalline structure (A-/B-type) (dos Santos et al., 2018; Fang et al., 2021; Kaul, Kaur, Kaur, Mehta, & Kennedy, 2023) V-type (ethanol-induced V-type granular starch, EVGS) (Dries et al., 2016; Shi, Zhang, Li, Fu, & Huang, 2019; Zhang et al., 2012)

et al., 2018), and atmospheric-pressure polyhydric-alcohol heat treatment (APHT) (Rajagopalan & Seib, 1992a; 1992b). The cold-water solubility/viscosity, crystalline structure, granular morphology, and other properties of the products are quite different with different preparation methods.

#### 2.1.1. Ethanol-aqueous heat treatment (EAHT) and the mechanism of starch modification

It is generally believed that the EAHT induces the formation of EVGS by balancing the thermal gelatinization on starch and the inhibitory effect of ethanol on starch swelling (Li, Zhou, & Jin, 2021; Zhang et al., 2012). A certain proportion of starch-ethanol-water mixture is heated in an airtight container that could withstand high temperature and pressure. After holding preservation, cooling, ethanol washing and high temperature drying process to obtain EVGS (Dries et al., 2014; Eastman & Moore, 1984; Li, Zhou, & Jin, 2021). The EVGS has much higher cold-water solubility and cold-water viscosity (Table 2) (Eastman & Moore, 1984; Li, Zhou, & Jin, 2021; Li, Zhou, & Jin, 2022b), which is related to the formation of V-type crystalline cavity structure induced by ethanol (Chen & Jane, 1994; Li, Zhou, & Jin, 2021; Li, Qi, Li, Chen, & Xu, 2022). AM and ethanol can form V-type complex during the heat treatment, and the V-type crystalline cavity structure is left after the ethanol in the V-type complex is evaporated during the drying process (Jane, Craig, Seib, & Hosene, 1986), and it is thought to be more soluble than A- or B-type starch (Eastman & Moore, 1984; Li et al., 2022; Sarko & Wu, 1978).

From the perspective of the cold-water properties of EVGS prepared by EAHT, the cold-water solubility and viscosity of EVGS are thought to be related to the different combinations of reaction temperatures and ethanol concentrations (Dries et al., 2014; Li et al., 2022b; Zhang et al., 2012), the recent studies about the cold-water properties of EVGS are shown in Table 2. Based on retaining the granular morphology, the higher the reaction temperature, the more completely the double helical structure is destroyed, the higher the V-type relative crystallinity (RC) (Dries et al., 2014; Li, Zhou, & Jin, 2021; Zhang et al., 2012), and the higher the cold-water viscosity, which is thought to be associated with the exposed hydrophilic hydroxyl groups caused by a large number of hydrogen bond breaks (Li, Zhou, & Jin, 2021). In addition, a decrease in the molecular weight of EVGS could be observed at even high temperatures, which have contributed to the decrease in cold-water viscosity of EVGS formed at higher temperature (Chen & Jane, 1994; Li, Zhou, & Jin, 2021). To retain the granular morphology of starch at high temperatures, a higher ethanol concentration was also required, which means the higher the ethanol concentration, the higher the temperature required for the EVGS formation (Dries et al., 2014; Li et al., 2022b).

Some research tried to regulate the water activity by controlling the water content of the water-ethanol system and found the granule size, swelling power (25 °C), solubility (25 °C) and initial viscosity of treated starch increased as the increased of water content (Kurakake, Noguchi, Fujioka, & Komaki, 1997). In another study, it was found the cold-water viscosity of EVGS was positively correlated with the V-type RC, which could be controlled by the different combinations of temperatures and ethanol concentrations (Li, Zhou, & Jin, 2021; Zhou, He, & Jin, 2024; Zhou, Xing, et al., 2021). It was also found there were some non-rigid and slit-shaped pores on the surface of EVGS, and these pores were related to the better water adsorption capacity of EVGS due to the water molecules could more likely enter into the starch granules (Li et al., 2022b; Sarifudin, Keeratiburana, Soontaranon, Tangsathitkulchai, & Tongta, 2020; Zhang, Cai, Shan, Zhang, & Dong, 2014). When EVGS contacts the water, a large number of hydrophilic hydroxyl groups absorb water rapidly, and EVGS granules swell quickly (Li, Zhou, & Jin, 2021; 2022b), which increases the friction between starch granules, manifesting as high cold-water viscosity. However, for the EAHT, because the ethanol and high temperature involved, the confined pressure-resistant environment required for the EAHT is harder to achieve safely in industry.

From the perspective of the formation of EVGS through EAHT. During the preparation process, the heat treatment could melt the crystalline structure of native starch, ethanol can form a V-type complex with AM, but the interaction between ethanol and AM is relatively weak due to the strong hydrophilic and volatile properties of ethanol, the ethanol could be evaporated in the subsequent drying process, leaving a V-type single helical cavity structure, which is a metastable structure with relatively higher solubility than A- or B- type natural starch structure (Chen & Jane, 1994; Sarko & Wu, 1978). In the whole reaction system, ethanol plays a role in protecting the granular morphology of native starch (Zhang et al., 2012), water as a plasticizer can affect the hydrogen bonding between the molecular chains of starch and lead to the rearrangement of the molecular chains, the higher the concentration of ethanol, the lower the water content, the more energy required to destroy the double helix structure of native starch, so that the molecules can be rearranged, which is manifested by a gradual increase in the gelatinization temperature (Kurakaka et al., 1997; Li, Zhou, & Jin, 2021). Based on the retention of granular morphology of native starch, the optimal EVGS under 50%, 60% and 70% ethanol concentrations and different temperatures could be prepared by taking the cold-water viscosity as the index (Li et al., 2022b). For its V-type single helical cavity structure, most of the studies think that is formed by ethanol and AM. But there are some different opinions (Dries et al., 2014; Li, Zhou, & Jin, 2021; Zhang et al., 2012). It was proposed the AMP might be involved in

**Table 2**

Preparation parameters and characterization of ethanol-induced V-type granular starch (EVGS) prepared by ethanol-aqueous heat treatment (EAHT) and alcoholic-alkaline treatment (AAT).

EVGS	Types of starch	Reaction conditions Temperature/Starch concentration/Ethanol concentration	Morphology/Size	Crystal type (RC)	Solubility/Swelling power/Viscosity/ Absorption capacity	AM content (NS→EVGS)	Reference
EVGS prepared by EAHT	Normal corn starch (A-type)	T: 149–182 °C S: 10–25%, w/w E: 80–95%, w/v	ND	ND	Solubility: 50.0–91.1%	ND	<a href="#">Eastman and Moore (1984)</a>
	Normal corn/wheat starch (A-type)	T: 149–182 °C S: 10–25%, w/w E: 80–95%, w/v	Intact granule with a little distortion	V-type (ND)	Solubility (25 °C): 93.7% (corn); 80.3% (wheat) Viscosity (25 °C): 6%, dry-starch basis 300–490 B-U.	32.1%→27.3% 31.9%→30.2%	<a href="#">Jane, Craig, and Seib (1986)</a>
	Maize starch (A-type)	T: 70 °C for 10 min →120 °C for 20 min S: 20%, w/v E: 30–100%, w/w	Slightly shrunken granular morphology 10–45 µm	ND	Swelling power: 8–14 g/g (25 °C); 17–24 g/g (97 °C) Solubility (25 °C): 0.5–9%	ND	<a href="#">Kurakake et al. (1997)</a>
	Maize starch (A-type)	T: 70 °C for 10 min →120 °C for 20 min S: 20%, w/v E: 50–100%, w/w	Slightly shrunken granular morphology 14.2–32.2 µm	ND	Viscosity: Around 75–225 RVU	Leaching of AM: 3–17%	<a href="#">Kurakake, Noguchi, Fujioka, and Komaki (2008)</a>
	Normal maize/waxy maize/ high amylose maize potato and tapioca starch (A, B-type)	T: 95 °C S: 10%, w/w E: 33.33–88.89%, v/v	Similar to raw starch but with wrinkled surfaces	V-type (ND)	ND	ND	<a href="#">Zhang et al. (2012)</a>
	Corn starch (A-type)	T: 70–92 °C S: 20%, w/v E: 40%, v/v	Similar to native starch, wrinkling, deformation, and agglomeration increased with the increase in temperature	V-type (2.1–10.0%)	Swelling power: 2.62–16.97%	ND	<a href="#">Zhang et al. (2014)</a>
	Normal/waxy maize starch (A-type)	T: 80–95 °C S: 10%, w/v E: 48–68%, v/v	Granules showed a homogenous weaker birefringence	V-type (2–22%)	Swelling power: 2.8–10.4%	23.7%→22.2%	<a href="#">Dries et al. (2014)</a>
	Maize/cassava/potato/rice and pea starch (A-, B- and C-type)	T: 95 °C S: 10%, w/v E: 48–68%, v/v	Maltese cross pattern gradually disappeared, varied with the botanical origin	V-type (2–18%)	ND	Almost no AM leached out	<a href="#">Dries et al. (2016)</a>
	Normal maize/potato starch (A-, B-type)	T: 40–90 °C S: 50%, w/v E: 50%, v/v	Maltese cross of the granules gradually distorted to disappear	V-type (ND)	ND	ND	<a href="#">Sarifudin et al. (2019)</a>
	Normal maize/potato/rice/ cassava starch (A-, B-type)	T: 80, 90, 100 °C S: 10%, w/v E: 50%, v/v	Granular structure of cassava and rice starch was more easily destroyed than that of maize and potato starch	V-type (0–14%)	Water absorption: 140–869%	ND	<a href="#">Sarifudin, Keeratiburana, Soontaranon, Tangsathitkulchai, and Tongta (2020)</a>
	Normal maize starch (A-type)	T: 80–160 °C S: 20%, w/w E: 70%, v/v	Similar to the native starch, slight aggregation could be observed at higher temperatures	V-type (15.16–25.78%)	Viscosity (26 °C): 17.00–1932.00 cP	ND	<a href="#">Li, Zhou, and Jin (2021)</a>
	Normal maize starch (A-type)	T: 110–150 °C S: 10–40%, w/w E: 60–90%, v/v Enzymatic hydrolysis: 16 h, 45 °C	Granular surface showed an irregular sponge-like structure	V-type (10.31–26.13%)	Water adsorption: 450.00–805.59% Oil adsorption: 125.00–241.70%	ND	<a href="#">Zhou, Chang, et al. (2021)</a>
	Normal maize starch (A-type)	T: 70–160 °C S: 10%–50%, w/w E: 50–70%, v/v	Granular morphology of EVGS formed at higher ethanol concentrations was more similar to native starch D50 (dry): 20.70–38.13 µm	V-type (14.91–28.79%)	Viscosity (26 °C): 391.00–2793.00 cP Water adsorption: 836.19–880.94% Oil adsorption: 150.36–218.32%	16.24%→ 13.06–16.20%	<a href="#">Li et al. (2022b)</a>

(continued on next page)

Table 2 (continued)

EVGS	Types of starch	Reaction conditions Temperature/Starch concentration/Ethanol concentration	Morphology/Size	Crystal type (RC)	Solubility/Swelling power/Viscosity/ Absorption capacity	AM content (NS→EVGS)	Reference
	Native oat starch (A-type)	T: 75–150 °C S: 10%, w/v E: 38–78%, v/v	Individual particles with a distorted shape, some honeycomb was formed on the surface 12 µm	V-type (ND)	Swelling power (25 °C): 6.73%→25.79% Solubility (25 °C): 1.26%→54.55%	26.18%→ 31.68%	<a href="#">Li et al. (2022)</a>
EVGS	Types of starch	Component ratio/ Temperature/Alkaline concentration Ethanol concentration	Morphology/Size	Crystal type (RC)	Solubility/Swelling power/Viscosity/ Absorption capacity	AM content (NS→EVGS)	Reference
EVGS prepared by AAT	Waxy corn starch Normal corn starch High-amylose corn starch (A-, B- type)	Starch: alkali: absolute ethanol: water = 1: 0.2–0.8: 1–10: 2–7 (mass ratio) Temperature: 20–40 °C Alkaline: 2.5–3 M NaOH Ethanol: 100%	ND	V-type (ND)	Solubility (25 °C): 50–94% Viscosity (25 °C): WMS: 375 BU NMS: 405 BU HAMS: 10.0–11.0 cps	ND	<a href="#">Chen and Jane (1994)</a>
	Banana starch (C-type)	Starch: alkali solution: ethanol solution = 1: 2.2–5: 4–7 (m: m) Temperature: 25 or 35 °C Alkali: NaOH, 3 M Ethanol: 40% or 60%	ND	ND	Solubility (25 °C): 15.2–54.3%	ND	<a href="#">Bello-Pérez et al. (2000)</a>
	Sago starch Normal corn starch (A-, C-type)	Starch: alkali solution: ethanol solution = 1: 0.6–1.5: 4 (m: m) Temperature: 35 °C Alkali: NaOH, 3 M Ethanol: 100%	Shriveled and agglomerated granules; loss of Maltose-cross Size: 55.7–137.6 µm	V-type (ND)	Solubility (25 °C): 15.4%–63.8% Viscosity (30 °C): 231.1–271.1 RVU	30.3%→32.6%	<a href="#">Kaur et al. (2011)</a>
	Buckwheat starch (A-type)	Starch: alkali solution: ethanol solution = 1: 4: 20 (m: v: v) Temperature: 70 °C Alkali: NaOH, 15.75 M Ethanol: 80%, v/v	Shrinkage and grouping in clusters, retained the granular structure	V-type (6.25%)	Solubility (50–90 °C): 93.33%–97.77% Swelling power (50–90 °C): 5.38%–39.28% Paste Temp: 4.87 min	ND	<a href="#">Li et al. (2014)</a>
	Potato starch (B-type)	Starch: alkali solution: ethanol solution = 1: 1: 8–10 (m: m: m) Temperature: room temperature Alkali: NaOH, 3 M Ethanol: 60%, v/v	Slightly larger intact granular shape with a dimple	V-type (ND)	Solubility (25 °C): 81.01% Viscosity: Much lower viscosity, which is close to 0	ND	<a href="#">Choi, Baik, and Kim (2017)</a>
	Native tapioca and corn starch (A-, B-type)	Starch: alkali solution: ethanol solution = 1: 2–3: 7–10 (m: m: m) Temperature: 25, 35 °C Alkali: NaOH, 2.5 M Ethanol: 40%, v/v	Irregular wrinkled granular shapes	ND	Water absorption (25 °C): 3.63%–18.81% Solubility (25 °C): 2.36%–20.89%	ND	<a href="#">Kaveh, Azadmard-Damirchi, Yousefi, &amp; Hosseini, 2021)</a>
	Native rice starch (A-type)	Starch: alkali solution: ethanol solution = 1: 4: 10 (m: m: v) Temperature: RT	Larger in size, with irregular shape and porous surface marked by indentation	V-type (7.95%)	Solubility (30 °C): 15% Swelling capacity (30 °C):	ND	<a href="#">Limpongsa and Jaipakdee (2020)</a>

(continued on next page)

Table 2 (continued)

EVGS	Types of starch	Reaction conditions Temperature/Starch concentration/Ethanol concentration	Morphology/Size	Crystal type (RC)	Solubility/Swelling power/Viscosity/ Absorption capacity	AM content (NS→EVGS)	Reference
	Native maize starch (Combined with ultrasound treatment, UT) (A-type)	Alkali: NaOH, 3 M Ethanol: 30%, v/v Starch: alkali solution: ethanol solution = 6: 20: 100 (m: v: v) Temperature: 25 °C Alkali: NaOH, 3–5 M Ethanol: 70–90%, v/v	Indented appearance and larger size than native maize starch; more holes and damages could be found on EVGS combined UT	V-type (ND)	700%/Viscosity (90–25 °C): 75 mPa s Solubility (25 °C): 69.24–75.05%	ND	<a href="#">Yu et al. (2018)</a>
	Sorghum starch and corn starch (Pre-modified by citric acid) (A-type)	Starch: alkali solution: ethanol solution = 1: 5: 12 (m: v: v) Temperature: 25 °C Alkali: NaOH, 3 M Ethanol: 40%, v/v	The loss of smoothness and wrinkling on the surface of EVGS was observed	ND	Water retention capacity (25 °C): 8.88–9.41% Swelling power (25 °C): 9.23–11.41%	ND	<a href="#">Zehra, Ali, and Hasnain (2020)</a>
	Sorghum starch and corn starch (Pre-hydroxypropylation) (A-type)	Starch: alkali solution: ethanol solution = 1: 5: 12 (m: v: v) Temperature: 25 °C Alkali: NaOH, 3 M Ethanol: 40%, v/v	Retained the granular structure was disintegrated after hydroxypropylation	ND	Water retention capacity: 6.45%–10.74% Swelling power: 7.74–12.56 g/g	ND	<a href="#">Zehra, Ali, and Hasnain (2021)</a>
	Normal maize/potato starch; High-amylose maize starch (A-, B-type) (Combined with annealing treatment)	Starch: alkali solution: ethanol solution = 1: 12: 7 (m: m: m) Temperature: 35 °C Alkali: NaOH, 3 M Ethanol: 40%, v/v	Remained intact granules with a slightly wrinkled surface	V-type (13.2–28.4%)	ND	ND	<a href="#">Shi et al., 2022</a> ; <a href="#">Shi, Zhang, et al., 2019</a>
	Rice starch (A-type) (Combined with dielectric barrier discharge cold plasma)	Starch: alkali solution: ethanol solution = 1: 2: 10 (m: v: v) Temperature: 25 °C Alkali: NaOH, 4 M Ethanol: 80%, v/v	Uneven surface structure, broken edges, and agglomerated layered structure; the depression on the surface and adjacent starch granules aggregation is more severe after cold plasma treatment	V-type (20.69–27.54%)	Solubility (25 °C): 29.38%–51.57%	22.46%→ 18.47%	<a href="#">Ge et al. (2022)</a>

ND: not determined; RC: relative crystallinity; NC: native starch; EVGS: ethanol-induced V-type granular starch; AM: amylose.

the formation of V-type crystalline structure of EVGS (Chen & Jane, 1994; Jane, Craig, & Seib, 1986; Sarifudin et al., 2019), and some studies thought the AM was mainly responsible for the formation of V-type crystalline structure, and the AMP could not form the EVGS (Dries et al., 2014; Zhang et al., 2012). The higher the AM content, the more beneficial to maintain the integrity of starch granules and the formation of V-type crystalline structure (Zhou et al., 2024). It was also proposed that the exposure of hydrophilic hydroxyl groups caused by a large number of hydrogen bond breaks in AMP was an important reason for the cold-water swelling properties of EVGS (Li, Zhou, & Jin, 2021; 2022b). Therefore, there is still no precise explanation for the role of AMP in the formation of EVGS (Li, Zhou, & Jin, 2021). And for the formation process of V-type crystalline structure, the process of EAHT on a milligram scale was simulated through differential scanning calorimetry (DSC) measurement, the change of heat flow caused by crystal melting was monitored. It could be found the gelatinization temperature and melting enthalpy of starch in ethanol-aqueous solutions increased and decreased with the increase of ethanol concentration, respectively, and some research observed no melting peak, it could be explained by the formation of V-type single helical structure and the destruction of the native double helical structure occurred simultaneously, the endothermic and exothermic process might have balance out (Dries et al., 2014; Li, Zhou, & Jin, 2021). The V-type RC increased first and then decreased with the increase of temperature, which might be attributed to the different mobility of starch molecular chains within granules (Zhang et al., 2014). The transformation of the crystalline structure of EVGS was explored through in situ wide- and small-angle X-ray scattering, and a model to elucidate the transformations at three structural levels was proposed. It was thought that the crystalline lamellae were rearranged into a more perfect register before being disrupted (Sarifudin et al., 2019). Most of the researchers agreed with the formation mechanism of EVGS prepared by EAHT in Fig. 1.

From the perspective of the transformation of different crystalline starch to EVGS. The recent studies on EVGS preparation with different crystal types are also summarized in Table 2. EVGS from starch with different botanical origins and AM contents could be prepared (Dries et al., 2016; Zhang et al., 2012), all normal maize starch (A-type), high amylose starch (B-type) (Li et al., 2022,2022b; Zhang et al., 2012), potato starch (B-type) (Sarifudin et al., 2019, 2020), and pea starch (C-type) could be modified to EVGS (Dries et al., 2016), but not for waxy maize starch (A-type) (Dries et al., 2014; Zhang et al., 2012). When the ratio of native starch to water was less than 1:3, no melting peak could

be observed in DSC after EAHT, which meant the EVGS could absorb heat and swell at room temperature (Li et al., 2022a; Zhang et al., 2012). The influence of crystal types and DP (degree of polymerization) of AM on the formation of EVGS was also explored, it could be found that the thermal stability of B-type starch in ethanol-aqueous system was lower than that of A-type. At the same time, it was also proposed that the V-type single helical structure was formed during the heating and heat preservation process for starch with low-DP AM, and formed during the heat preservation and cooling process for the starch with medium- and high-DP AM (Dries et al., 2016).

### 2.1.2. Alcoholic-alkaline treatment (AAT) and the mechanism of starch modification

AAT can be carried out under atmospheric pressure and room temperature. Therefore, it is considered to be one of the most commonly used methods to prepare EVGS. AAT is to prepare EVGS by balancing the gelatinization effect of alkali on starch and the inhibition effect of ethanol on the swelling of starch (Chen & Jane, 1994; Li et al., 2014). The different combinations of alkali amounts, temperatures and ethanol concentrations can give EVGS different properties (Bello-Pérez et al., 2000; Kaur et al., 2011; Zabar, Azadmard-Damirchi, Yousefi, & Hosseini, 2020; Zhu, Liu, & Gao, 2017). The studies about the preparation of EVGS by AAT and the detailed experimental parameters are summarized in Table 2. The starch is weighed in ethanol-aqueous solution at certain temperature, the alkali solution is added gradually, the mixture is stirring for several mins, and the sediment is washed by ethanol solution, neutralized by acid-alcohol solution, washed by ethanol solution again for 1–3 times, dehydrated by absolute ethanol and air dried at 80 °C for 3 h to obtain the EVGS (Chen & Jane, 1994). To be specific, starch is thought to be a weak ion exchanger, there are many hydroxyl groups on the glucose molecules in starch, which would carry negative charges in alkaline environment. The higher the concentration of alkali, the more negative charges formed in starch molecules, which creates stronger repulsion between the molecules. When the repulsion force is strong enough, starch granules swell slightly, the hydrogen bond in starch molecules gradually breaks (Chen, Xie, Liu, & Chen, 2019), the double-helical structure unwinds due to the electric repulsion, and the crystalline structure is destroyed gradually, which is presented in Fig. 1. The granule morphology of starch is maintained by the inhibition of ethanol and the cross-linked network structure formed by AM and AMP, and there is less AM leaching out consequently. After the neutralization reaction, ethanol not only restricts the swelling of starch granules by

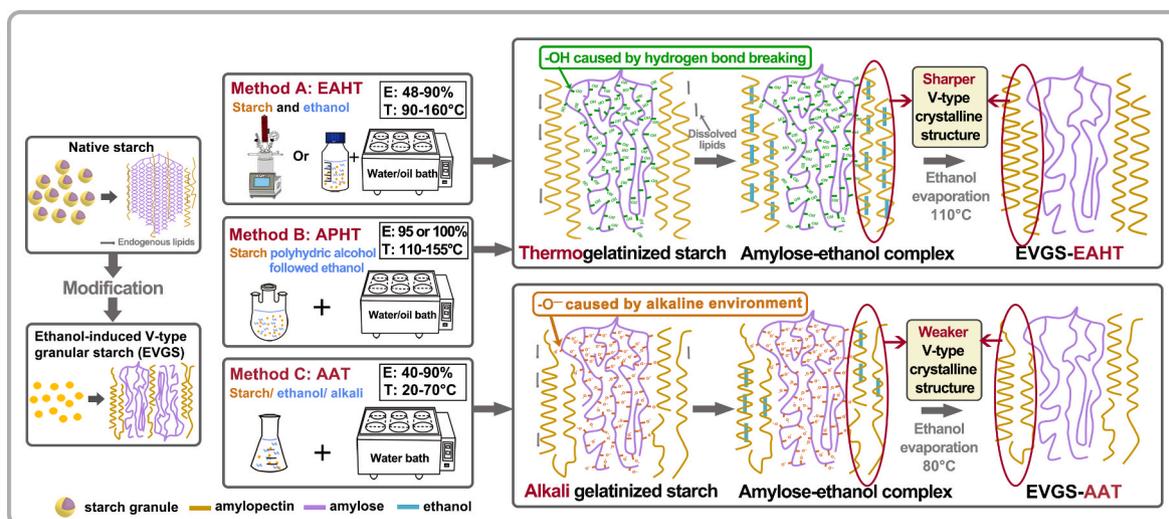


Fig. 1. Schematic visual representation of starch modification induced by different preparation methods of ethanol-induced V-type granular starch (EVGS). EAHT stands for the Ethanol-aqueous heat treatment, APHT stands for the Atmospheric-pressure polyhydric-alcohol heat treatment, AAT stands for the Alcoholic-alkaline treatment.

decreasing the amount of effective water, but also forms a V-type complex with AM as a complexing agent, which stabilizes the dissociated starch (Kaur et al., 2011; Li et al., 2014). During the drying process, ethanol is steamed out at a high temperature, leaving a V-type metastable cavity structure (Chen & Jane, 1994; Shi et al., 2022). Nevertheless, the environmental problems generated by the large amount of acid and alkali involved in the AAT are what affect its continuous industrial production (Li et al., 2022).

For the cold-water properties of EVGS prepared by AAT, the cold-water solubility is usually taken as the main index. At present, it is generally recognized that the reasons for EVGS having much higher cold-water solubility are mainly that the alkali solution could destroy the hydrogen bond in starch molecules, and the RC of native starch decreased significantly due to the destruction of crystalline structure after unwinding of double helical structure (Chen & Jane, 1994; Limpongsa & Jaipakdee, 2020; Zabar et al., 2020). In addition, there is no change of molecular weight of EVGS prepared by AAT (Chen & Jane, 1994). In general, the proper combinations of alkali concentrations, ethanol concentrations, and reaction temperatures are important to improve the cold-water solubility of EVGS prepared by AAT (Bello-Pérez et al., 2000; Kaur et al., 2011; Zabar et al., 2020; Zhu, Liu, & Gao, 2017). Some studies proposed the improvement of water absorption capacity, solubility, and rheological properties in cold water was positively related to the alkali amount and reaction temperature, and negatively related to the ethanol concentration (Zabar et al., 2020), but other researchers found the increased of ethanol concentration would lead to the increase of cold-water solubility when the NaOH concentration was 4 M (Yu et al., 2018), the opposite conclusion might be related to the different crystalline types and sources of starch studied (Bello-Pérez et al., 2000). In addition, different drying methods also had a significant influence on the cold-water properties, freeze-dried EVGS had much higher cold-water solubility and more intact granular morphology than oven dried EVGS. This might be related to the surface of freeze-dried EVGS was swollen and dented, which made it easier for water molecules enter the granules, resulting in improved cold-water solubility (Zhu, Cao, Liu, & Gao, 2018; Zhu, Wu, Liu, & Gao, 2017).

For the formation of EVGS prepared by AAT, the V-type crystalline is thought to be formed by ethanol and AM, and the V-type single helical cavity structure is obtained after the evaporation of ethanol during the drying process, which is similar to the EAHT (Chen & Jane, 1994; Limpongsa & Jaipakdee, 2020; Zabar et al., 2020). Different from the EAHT, the strength of V-type crystalline characteristic peak of EVGS prepared by AAT is much weaker than that of V-type crystalline structure formed by EAHT, which could be manifested by RC in Table 2. This might be related to different gelatinization methods, but there is no accurate explanation at present. The AAT can modify native starch with different AM contents into EVGS except for the waxy starch, the V-type RC and sharpness of characteristic peaks of V-type crystalline structure increases with the increase of AM content (Chen, Chen, et al., 2019; Chen & Jane, 1994). Waxy starch modified through AAT could retain the granular morphology of native starch, but shows an amorphous crystalline structure, which is also different from the EAHT (Chen, Chen, et al., 2019). Besides the ethanol, the EVGS could be prepared with methanol, n-propanol, isopropanol, t-butanol, etc., through AAT, and the obtained V-type structures of EVGS have different single-helical dimensions (Shi, Zhong, Zhang, Fu, & Huang, 2020).

For the modification of native starch from diverse biological sources, the transformation by AAT is quite different, which might be related to the multi-scale structure of different starch, such as, it is found that potato starch (B-type) is more susceptible to the AAT than corn starch (A-type), and this might due to the larger granules of potato starch are easier to be affected by the AAT than the smaller granules of corn starch, and further related to the different crystalline structure, the smaller starch granules is thought relatively resistant to the swelling during the AAT process and the A-type structure are comparatively more stable and resistant to the AAT (Singh & Singh, 2003). Several studies have

performed AAT treatments on different starch, such as banana starch (Bello-Pérez et al., 2000), buckwheat starch (Li et al., 2014), sago starch, sorghum starch (Zehra et al., 2021), etc. However, they mostly focused on the characterization of paste properties and did not analyze the crystalline structure in detail.

Some studies combine AAT with other modification methods for compound modification of starch. For example, it was shown that AAT followed by ultrasonic treatment could effectively further enhance the cold-water solubility of EVGS (Yu et al., 2018; Zhu, Liu, & Gao, 2017), the hydroxypropylation on sorghum and corn starch before AAT could improve the shear and thermal resistance of EVGS, but the granular disruption was more prominent (Zehra et al., 2021), the citric acid modification before AAT could give the EVGS stronger gels (Butt, Ali, & Hasnain, 2019; Zehra et al., 2020), EVGS with different RC and granular morphology could be obtained by annealing treatment at different ethanol concentrations and temperatures after AAT (Shi, Zhang, et al., 2019).

### 2.1.3. Atmospheric-pressure polyhydric-alcohol heat treatment (APHT)

The EVGS also could be prepared by the other methods, such as atmospheric-pressure polyhydric-alcohol heat treatment (APHT) (Rajagopalan & Seib, 1992a). The modification mechanism of APHT is similar to the EAHT (Fig. 1), the polyhydric alcohols (PHA) is used to replace monohydric alcohols in EAHT to increase the boiling temperature of the liquid phase during the heating process (Rajagopalan & Seib, 1992a; 1992b). Despite the whole preparation process could be carried out in atmospheric pressure environment, but the crystalline structure of starch after heating in the aqueous-PHA solutions showed a relatively weak V-type pattern or amorphous pattern (Rajagopalan & Seib, 1992a; Xu et al., 2020), which need the intervention of ethanol. The whole preparation has cumbersome operation, and the recycling of PHA and ethanol used requires fractional distillation (Li et al., 2022). Therefore, there are few studies on this method in recent years.

The EVGS obtained by the three methods have a similar multi-scale structure and the characteristics of rapid swelling and high solubility in cold water (Chen & Jane, 1994; Jane, 1992), but there are still certain differences in structure, such as V-type RC, granular morphology and so on, which results in differences in their cold-water properties (Dries et al., 2014; Rajagopalan & Seib, 1992b; Shi, Zhang, et al., 2019).

Although there have been some studies on EVGS, there is still a lot of unknown information about such a V-type intact granular starch, such as whether the shell layer and “blocklets” structure still exist, further characterization and simulation of V-type single helical cavity structure, ethanol residue problem and so on. Furthermore, the complete granular morphology of EVGS is favorable for further modification on its basis, but there are few studies about its development, which needs more research. Such as V-type granular porous starch under ethanol-phase from EVGS was prepared, it was found the EVGS was easier to enzymatic hydrolyze compared with native starch, and the obtained porous starch had much higher water/oil adsorption capacity (Zhou, Chang, et al., 2021).

### 2.2. Ethanol-induced V-type non-granular starch (EVNGS)

EVNGS is  $\mu\text{m}$ -scale non-granular EVS, which means the granular morphology of native starch is destroyed during the modification process, the morphology of EVNGS is reformed through the grinding and sieving process. Similar to the EVGS, EVNGS also has the cold-water swelling capacity and the potential to form complex with guest molecules under relatively mild conditions. However, without the effective inhibitory effect of organic solvent (such as ethanol, acetone, etc.) on swelling of starch granules, the granular structure and natural crystalline structure of starch are both destroyed at high temperatures (Gao et al., 2022; Shi et al., 2022; Zhou, Xing, et al., 2021). The crystalline structure is transformed to V-type form the native A-, B- and C-type, and the  $\mu\text{m}$ -scale particle structure is re-formed at the stage of

post-modification grinding. The recent studies about the EVNGS are shown in Table 3, and the modification mechanism is shown in Fig. 2.

The DMSO-ethanol method is an important method for the preparation of EVNGS. The double helical structure of native starch is destroyed by the high temperature, and the AM is partially leached out from the network structure formed by AM and AMP, and retains a randomly coiled state (Gao et al., 2022; Zhou, Xing, et al., 2021). A large amount of ethanol and AM can form V<sub>6</sub>-type complex. The ethanol is gradually evaporated during the drying process, leaving a V<sub>6</sub>-type single helical cavity structure (Kong & Ziegler, 2014; Shi et al., 2022; Shi, Hopfer, et al., 2019). It was also found that the RC of the EVNGS increased significantly, and the V<sub>6</sub>-type starch could be transformed into V<sub>7</sub>- and V<sub>8</sub>- type starch after annealing treatment in ethanol solution at certain temperature and ethanol concentration with the involvement of the tert-butanol and salicylic acid (Guo, Ziegler, & Kong, 2022; Shi et al., 2022; Shi, Hopfer, et al., 2019), which further affected the complexation ability. The EVNGS prepared by the DMSO-ethanol method was often used as a carrier for some molecules such as methanol (Shi, Hopfer, et al., 2019), ascorbyl palmitate, palmitic acid, and so on. The

complexation happened under relatively mild conditions (70 °C, 40% ethanol concentration) (Guo & Kong, 2022). Nevertheless, most studies about this kind of EVNGS focused on the properties of complexation with some guest, and few studies explored the properties of EVNGS itself, further analyzed and modified it, which is conducive to better use of EVNGS.

Another kind of EVNGS can be prepared by the ethanolic-extrusion method, the ethanolic-extrusion method takes advantage of the effect of high temperature, high pressure, and high shear of the extruder, and uses a certain proportion of starch and ethanol solution as raw materials to obtain the new EVNGS (Zhou, Xing, et al., 2021). The ratio of starch to ethanol was 1:0.3 for the ethanolic-extrusion method, of which the starch concentration is much higher than other preparation methods, which results in higher production efficiency. The original granular structure of native starch is totally disrupted by high starch concentration and the high shear of the extruder, the double helix structure of native starch is unwound by the high temperature and the involvement of water molecules. The single helix V-type complex is formed by the inducing of ethanol under this situation (Zhou, Xing, et al., 2021). The

**Table 3**

Preparation parameters and characterization of ethanol-induced V-type non-granular starch (EVNGS) and ethanol-induced V-type nanoparticles starch (EVNPS).

EVS	Starch type	Modification method	Crystal type (RC)	Changes of properties	Reference	
EVNGS	High amylose starch/Potato amylose (B-type)	DMSO-ethanol method	V-type (ND)	Encapsulation for ascorbyl palmitate at 20–70 °C	Kong and Ziegler (2014)	
	High amylose starch (B-type)	DMSO-ethanol method combined different annealing treatment	V-type with different helix sizes	Encapsulation for methanol and ethylene	(Shi et al., 2022; Shi, Hopfer, et al., 2019)	
	Normal maize starch (A-type)	Ethanolic-extraction method	V-type (3.08–12.90%)	Viscosity (25 °C): distilled water: sample = 25: 4.4 (v/m) 750-3500 cP	Zhou, Xing, et al. (2021)	
	High amylose starch (B-type)	High-temperature-gelatinization-ethanol method	V + B-type (V: 23.89–35.78% B: 1.32–4.37%)	Encapsulation for thymol	Gao et al. (2022)	
	Native maize starch (A-type)	NaOH/urea gelatinization-ethanol method	V-type (ND)	Solubility (25 °C) 3.16%→2.82–90.57% Water absorption (25 °C) 16%→26%	Chen, Xie, Liu, and Chen (2019)	
	Lotus starch (A-type)	Ultrasonication-mediated high-temperature-ethanol method	B + V-type (V: 11.8–20.1% B: 2.0–3.0%)	Encapsulation for butyric acid	Liu, Yao, Zhang, Zheng, and Zeng (2023)	
	Normal maize starch (A-type)	Debranching and anti-solvent precipitation	V or A + V-type (29.8–45.1%)	Encapsulation for ethylene	Liu, Junejo, Zhang, Fu, and Huang (2022)	
EVS	Starch type	Modification method	Crystal type (RC)	Size of EVNPS	Reference	
EVNPS	Corn starch (A-type)	Gelatinization-ethanol precipitation method	V-type (ND)	50–100 nm	Ma, Jian, Chang, and Yu (2008)	
	Native potato starch (B-type)	Ultrasonic treatment combined gelatinization ethanol precipitation	V-type (ND, weak)	77.0–221.6 nm	Chang et al. (2017)	
	Native maize starch (A-type)	NaOH-gelatinization ethanol precipitation method	V-type (ND)	132–396 nm	Hebeish, El-Rafie, El-Sheikh, and El-Naggar (2013)	
	Potato starch (B-type)	DMSO-heat gelatinization combined with ethanol precipitation	V-type (30.2–45.6% for AM)	10–20 nm width and 200–500 nm length for AMP	Qiu, Qin, Zhang, Xiong, and Sun (2016)	
	High amylose/normal/waxy corn starch, potato starch, sweet potato starch, tapioca starch, pea starch (A-, B-, and C-type)	Ethanol was added dropwise to the cooled-gelatinized starch solution, and the EVNPS was obtained from the supernatants after centrifugation	8.8–9.2% for AMP) V-type (7.1–39.8%)	20–50 nm for AM 20–80 nm (HASNP) 30–150 nm (PESNP) 50–225 nm (PSNP), 15–80 nm (CSNP), 40–100 nm (SPSNP), 30–110 nm (TSNP) 20–200 nm (WXNP).	20–100 nm	Qin et al. (2016)
	Waxy corn starch (A-type)	Debranching and ethanol precipitation	V-type (43.2–49.5%)	20–50 nm and 146.0–343.5 nm	Qiu, Yang, et al. (2016)	
	Amylose with purity of 99.5%	β-amylase enzymatic hydrolysis combined DMSO-ethanol precipitation	V-type (ND)	40–200 nm	Chang, Yang, Ren, and Zhou (2018)	
	Waxy maize starch (A-type)	Ethanol was added dropwise to different temperatures debranching starch solution	V or A + V-type (11.1–71.6%)	176.5–308.4 nm	Qin et al. (2019)	
	Amylose starch (B-type)	Acid hydrolysis combined ethanol precipitation on amylose pastes at 90 °C	V-type (28.38–60.72%)		Yan, Wei, Kou, Ren, and Zhou (2021)	

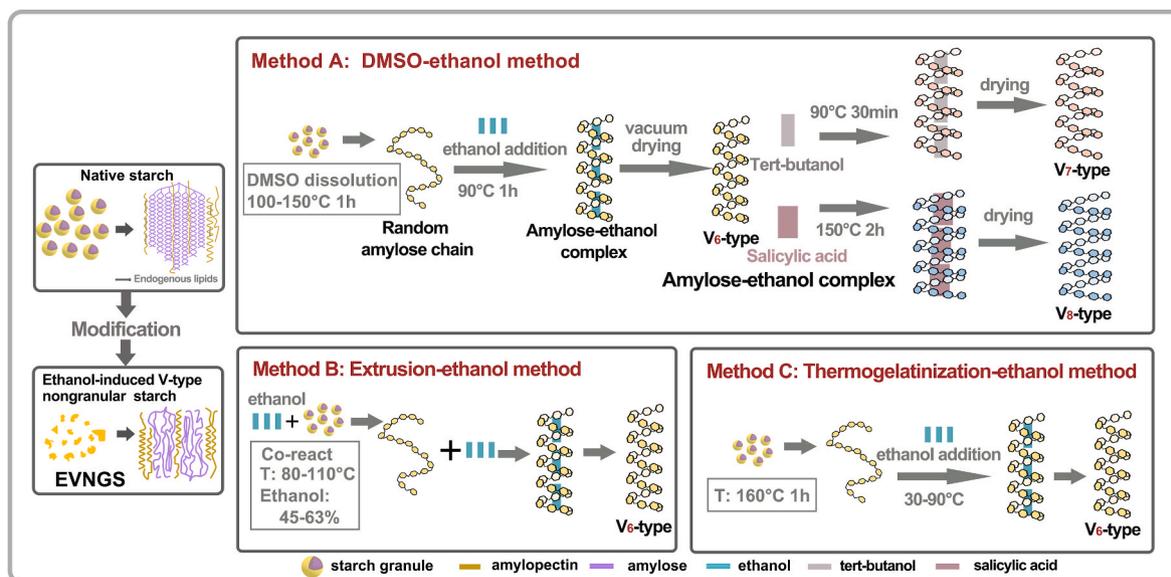


Fig. 2. Schematic visual representation of starch modification induced by different preparation methods of ethanol-induced V-type non-granular starch (EVNGS).

ethanol is evaporated during drying process, and the obtained EVNGS can quickly swell into a paste in cold water and maintain a high cold-water viscosity (Table 3). However, the other properties of EVNGS prepared by the ethanolic-extrusion method, such as encapsulation, have not been explored. For industrial production, although continuous production has been further advanced, the safety and recycling of ethanol in the whole preparation process have not been solved.

There are several other methods to prepare EVNGS, such as the high-temperature-gelatinization-ethanol method (Gao et al., 2022), NaOH/urea gelatinization-ethanol method (Chen, Chen, et al., 2019), the ultrasonication-mediated high-temperature-ethanol method (Liu, Shao, et al., 2023), and the debranching and anti-solvent precipitation (Liu et al., 2022). The formation of V-type single helical cavity structures all involves the inducing of ethanol, the detailed information are summarized in Table 2.

### 2.3. Ethanol-induced V-type nanoparticles starch (EVNPS)

EVNPS is nanoscale EVS. The size of the EVNPS is reduced to nano-level during the modification process and exhibits V-type single helical cavity structure (Qin et al., 2016; Yan et al., 2021). Nano-starch (NS) can be divided into two types according to whether it contains amorphous crystal structure: starch nanoparticles (SNP) and starch nanocrystals (SNC), respectively, and the NS has large specific surface areas and total surface energy, with a high reactive surface containing a large number of active hydroxyl groups (Bajer, 2023; Li et al., 2023; Wang & Zhang, 2021). Therefore, NC has been widely used in food packaging, drug carriers, granule stabilizers purifiers, etc. (Bajer, 2023). NC could be prepared by two main methods, including the “top-down method” and “bottom-up method” (Kim, Park, & Lim, 2015; Wang & Zhang, 2021; Yu et al., 2020). The “top-down method” refers to these treatments that can destroy the amorphous regions of starch to obtain modified starch with high crystallinity, while the “bottom-up method” refers to the self-assembly of NC by starch recrystallization and anti-solvent precipitation (Chang et al., 2018; Wang & Zhang, 2021; Yan et al., 2021). Same to the different crystalline native starches, NC also have different crystalline types (Apostolidis & Mandala, 2020; Jeong & Shin, 2018; Qiu, Yang, et al., 2016; Yu et al., 2020), among which EVNPS is expected to be more beneficial for delivery with certain drugs or active substances than other crystalline NC. It is related to the fact that in addition to the high encapsulation capacity of NS conferred by the large specific surface area (Marta, Wijaya, Sukri, Cahyana, & Mohammad, 2022), EVNPS can

form complex with guest molecules through its V-type single helical cavity structure (Qiu, Qin, Zhang, Xiong, & Sun, 2016). Compared with EVGS and EVNGS, the cold-water properties of EVNPS are still unknown, which still need to be further explored. The recent studies about the EVNPS are shown in Table 3.

The most common preparation method for EVNPS is the “bottom-up method” (Fig. 3), EVNPS could be prepared by adding the ethanol dropwise into the gelatinized starch, and the V-type crystalline structure could originate from a single-helical structure made up of AM and ethanol (Ma et al., 2008), which is more conducive for further modification with citric acid. Some studies also added ethanol dropwise into the cooled-gelatinized starch solution and gelatinized AM to obtain the EVNPS from the supernatants after centrifugation (Qin et al., 2016; Qiu, Qin, et al., 2016). With further development, the EVNPS could be prepared by adding ethanol into the debranched short-linear starch chain (Qin et al., 2019; Qiu, Yang, et al., 2016). In addition, the EVNPS could also be prepared by  $\beta$ -amylase enzymatic hydrolysis combined DMSO-ethanol precipitation (Chang et al., 2018), and acid hydrolysis combined ethanol precipitation on amylose paste at 90 °C (Yan et al., 2021).

The above methods of preparing EVNPS from debranched starch have greatly improved the purity of V-type single helical cavity structure, but the current methods are relatively cumbersome and still far from the industrial continuous development, the preservation method of V-type single helical cavity structure still needs to be further improved. In addition, most of the existing studies focus on the analysis of particle size, crystalline structure, and complexation properties, further exploration is still needed, such as whether the EVNPS have the characteristics of  $\mu$ m-sized EVS (EVGS and EVNGS) in cold water, the stability of EVNPS, and the emulsification as nanocrystals, etc.

## 3. Characterization of EVS

### 3.1. Particle morphology

The particle morphology of EVS varies in different scales, and even the morphology of EVS prepared by different methods in the same scale is quite different, which is shown in Fig. 4. Diverse particle morphology can affect the properties of EVS in various aspects. The investigation of the relationship between particle morphology and starch properties is conducive to better modifying starch, so that different EVS could be applied to a certain aspect more specifically. For example, in the case of

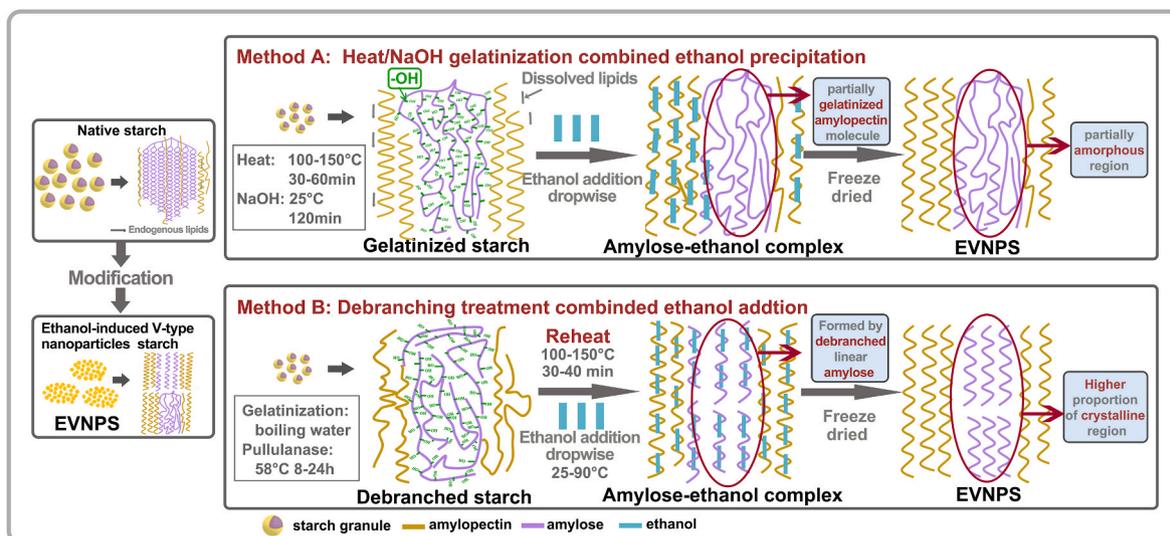


Fig. 3. Schematic visual representation of starch modification induced by different preparation methods of ethanol-induced V-type nanoparticles starch (EVNPS).

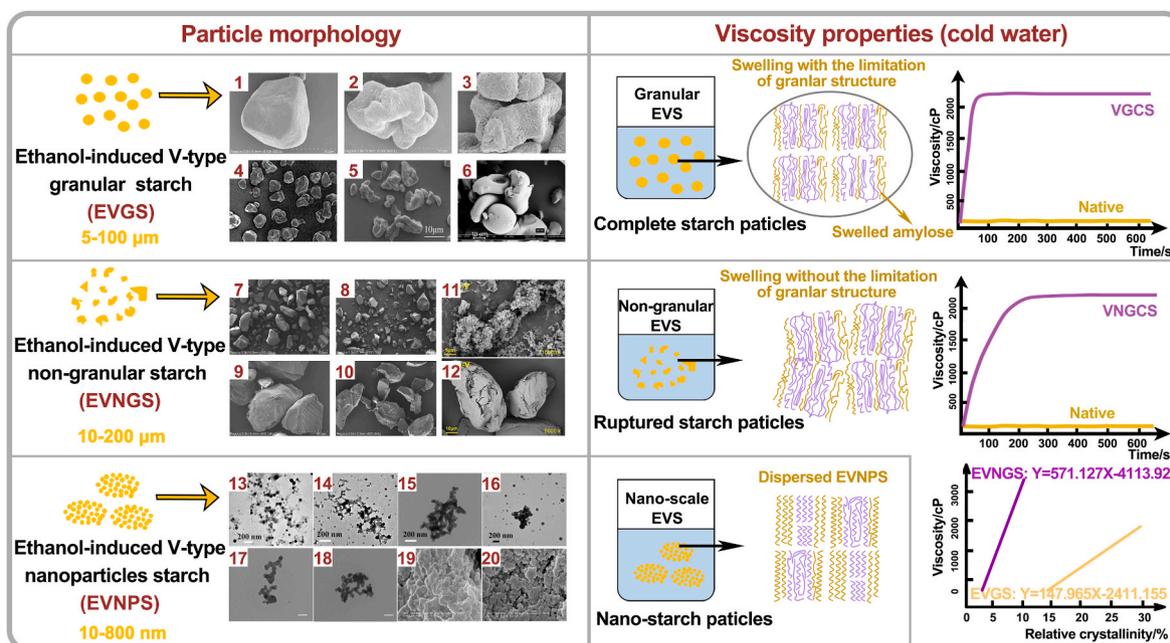


Fig. 4. The particle morphology and viscosity properties of ethanol-induced V-type starch (EVS) under different scales. SEM or TEM pictures: 1-3 (Li et al., 2022b); 4 (Rajagopalan & Seib, 1992a); 5 (Shi, Fu, Huang, & Zhang, 2017); 6 (Kaur et al., 2011); 7-10 (Zhou, Xing, et al., 2021); 11-12(Gao et al., 2022); 13-16 (Qin et al., 2019); 17-18 (Qiu, Qin, et al., 2016); 19-20 (Chang et al., 2018).

EVGS, the more complete the granular form and the less agglomeration between the granules, the more rapidly the starch swells into a paste in cold water (Li et al., 2022b; Rajagopalan & Seib, 1992a). Therefore, it is necessary to summarize and analyze the particle morphology of different EVS.

For EVGS, the retention of granular morphology is related to the V-type complex formed by AM and ethanol on the one hand, and on the other hand, the limited water content in the preparation system retards the swelling of the crystal-melted starch granules. Comparing the three preparation methods of EVGS, the granular morphology of EVGS obtained by EAHT at high ethanol concentration is the most complete, and the higher the ethanol concentration, the more complete the EVGS granule morphology will be obtained (Li et al., 2022b; Zhang et al., 2012), and the granules of EVGS prepared at low ethanol concentration have more cracks distributed on the surface, while the wrinkling and

agglomeration of EVGS granules prepared by AAT are more obvious regardless of the ethanol concentration, but the surface of granule is smoother (Shi, Fu, Huang, & Zhang, 2017; Shi, Fu, Tan, Huang, & Zhang, 2017). EVGS prepared by APHT is fractured internally but contained an intact shell at the surface (Rajagopalan & Seib, 1992b). Furthermore, the granular morphology would change with the environment EVGS is exposed to, which in turn affects its physicochemical properties. Such as, when EVGS is exposed to solution with a higher sugar concentration, the EVGS with wrinkled surface would become smooth (Hedayati, Shahidi, Koocheki, Farahnaky, & Majzoobi, 2016a). It was also found EVGS was more stable in alkaline pH environment compared to acidic pH, such as the granular integrity could be shrieved in acidic pH (Majzoobi et al., 2015), and the morphology of EVGS became smoother at alkaline pH (Hedayati et al., 2016b; Majzoobi et al., 2015).

For  $\mu\text{m}$ -scale EVNGS, the granular structure of native starch is totally destroyed, for the DMSO-ethanol method, the recrystallized particles shows irregular shapes with the porous surface, so as the NaOH/urea gelatinization-ethanol method (Chen, Chen, et al., 2019; Shi et al., 2022). But for the ethanolic-extrusion methods, the obtained EVNGS shows irregular rock-like morphology, which is caused by high pressure and high shearing force from the extruding machine (Zhou, Xing, et al., 2021). For the high-temperature-gelatinization-ethanol method, the different reaction temperatures give EVNGS different morphology, lower temperatures give the EVNGS a larger and blocky shape, and higher temperatures give the EVNGS larger spherulites morphology that aggregated from small particle sphere (Gao et al., 2022).

For the EVNPS, the EVNPS prepared by different methods shows similar morphology, which is mainly of spherical and elliptical shape with some aggregation, but differs in the particle sizes (Qiu, Yang, et al., 2016). The particle size of EVNPS prepared by adding ethanol dropwise into cold-gelatinized starch with different AM contents are range from 20 to 200 nm (Table 3), and the particle size distribution is inhomogeneous, it was concluded that the medium content of AM content was more suitable for preparation of EVNPS (Qin et al., 2016). The EVNPS prepared from AM displays uniform spherical shapes with a smooth and compact surface, and the EVNPS prepared from AMP displays worm-like or chain-like structures (Qiu, Qin, et al., 2016). For the EVNPS formed by different DP short linear starch chains, the debranched starch with an average of 20 is more favorable to form small and well-distributed EVNPS (Qin et al., 2019).

### 3.2. Crystalline structure

During the preparation process of EVS, the volatile ethanol molecule that forms the complex with the AM is evaporated during the subsequent drying process, leaving a metastable V-type single helical cavity structure. As with the conventional V-type complex with guests, they can still be classified into  $V_6$ ,  $V_7$ , and  $V_8$ -type according to the number of glucose residues per helix. The different V-type structures can also be transformed by annealing and drying treatment, and there are significant differences between the V-type RC (Fig. 2 and Tables 2 and 3) (Guo et al., 2022), the strength of the characteristic peaks and the types of V-type crystalline structure of the EVS at different scales prepared by different methods is different, which may affect the subsequent application of EVS.

Under granular scale, EVGS obtained by EATH and APHT have relatively sharper V-type crystalline characteristic peaks and higher V-type RC than EVGS obtained by AAT (Dries et al., 2014, 2016). The V-type crystalline structure of EVGS prepared by AAT could also be converted to sharper V-type crystalline structure by annealing treatment in ethanol solution at different temperatures (Table 2) (Shi, Hopfer, et al., 2019). EVS with high V-type RC has a more ordered crystalline structure and a greater proportion of single-helical cavity structures, which will have greater potential for encapsulation (Li et al., 2022b).

Under  $\mu\text{m}$  non-granular-scale, the characteristic peaks of V-type crystalline structure from EVNGS are similar to the V-type crystalline structure in EVGS prepared by the EATH and APHT. The three distinct characteristic peaks around  $7^\circ$ ,  $13^\circ$ , and  $21^\circ$  could be observed ( $V_6$ -type), such as the EVNGS prepared by the DMSO-ethanol method, ethanolic extraction method, and high-temperature-gelatinization-ethanol method. The EVNGS prepared by the DMSO-ethanol method could form V-type crystalline with different single-helix sizes combined with some hydration, or thermal treatments with the existing of some guest molecules (Guo et al., 2022; Shi et al., 2022; Shi, Hopfer, et al., 2019). According to the results of NMR carbon spectra, the RC and number of single helices of  $V_{6a}$ -type structure are the highest (Shi et al., 2022).

For the EVNPS, the crystalline structure prepared by different methods shows significant differences. The EVNPS formed by adding ethanol into gelatinized starch showed relatively sharper V-type

crystalline characteristic peaks and higher V-type RC, the formation of this V-type structure is induced by ethanol. Meanwhile, the V-type RC exhibits no relations to the crystalline type of native starch, and higher positive relations to the AM content (Qin et al., 2016), which is different from the EVGS prepared from different plant sources starch, the EVNPS from AMP shows weaker V-type crystalline structure (Qiu, Qin, et al., 2016). Compared with the other methods, the enhancement of V-type crystalline characteristics and the increasing of V-type RC in EVNPS prepared by ethanol precipitation combined debranching treatment could be observed (Qiu, Yang, et al., 2016). However, the typical A + V-type crystalline structure was observed by the same method (Qin et al., 2019). The appearance of A-type structure is due to the quick retrogradation of the refined debranched short starch chain. The difference in the crystalline structure might be caused by the differences in the speed and temperature at which ethanol is added (Qin et al., 2019).

### 3.3. Thermodynamic properties

EVS is considered to be a metastable structure starch because its hollow single helical structure, and its structural transformation causes changes in the thermodynamic properties, and the thermodynamic properties of EVS vary with the different structural scales. For EVGS, the thermodynamic property was explored by DSC, when native crystalline structure was totally changed to V-type structure, the endothermic peak of crystalline structure melting disappeared with the disappearance of the Maltese cross (Chen & Jane, 1994; Li, Zhou, & Jin, 2021; Zhang et al., 2012). That indicated the endothermic melting of V-type crystalline structure in EVGS was completed at room temperature without the intervention of extra heat, which was the reason that its cold-water swelling properties are different from the traditional V-type complex (Li et al., 2022, 2022a). The several EVGS melting peaks observed in some studies might be due to the incomplete transformation from native crystalline to V-type crystalline structure during the modification process (Dries et al., 2014; Li et al., 2022; Zhang et al., 2012). Some studies have observed the weak peak of the formation and melting of V-type complex during the heating and cooling process, it might be related to the lipid content of the native starch used, as AM also could form the V-type complex with lipid (Dries et al., 2014, 2016).

For the  $\mu\text{m}$ -scale EVNGS, the EVNGS prepared by the ethanolic-extrusion method only exhibited the melting peak of V-type complex formed by AM and native lipid, there is still no peak about the melting of V-type single helical cavity structure. However, the EVNGS formed by the high-temperature gelatinization-ethanol method exhibited an endothermic peak (Gao et al., 2022). There are no relevant studies that can accurately explain this opposite phenomenon, which needs to be further investigated.

For EVNPS, the thermodynamic property was also explored by DSC and thermogravimetric analysis (TGA) measurement, EVNPS prepared by debranching and ethanol precipitation method showed significantly higher melting temperature than native starch, which might be related to the melting of V-type crystalline structure that accounts for most of the crystalline structure, and there is also a small amount of the A-type crystalline structure formed, which might also be related to the melting peaks of EVNPS (Qin, Yang, et al., 2016). However, EVNPS prepared by ethanol precipitation on gelatinized starch with native starch as material showed significantly lower melting temperature, with isolated AM and AMP as material showed higher and lower melting temperature (Qiu, Qin, et al., 2016). It is also interesting to find that the melting of some EVNPS appears highly reversible (Qin, Yang, et al., 2016), which also differs from the EVGS and EVNGS. The TGA analysis showed the degradation temperature of EVNPS prepared by debranching and ethanol precipitation method, and ethanol precipitation on gelatinized starch decreased significantly, which showed the reduced thermal stability, as with the other crystal types of SNP (Qin et al., 2016; Qiu, Yang, et al., 2016).

### 3.4. Paste properties

#### 3.4.1. Cold-water solubility and viscosity

The EVS was first prepared to improve the cold-water solubility of native starch, the formed V-type single helical structure is thought to be more soluble than the native A-, B-, or C-type crystalline structure (Sarko & Wu, 1978), which could be expressed in terms of increased solubility, swelling power, viscosity, water absorption, or water retention capacity in cold water, as shown in Table 2. EVGS and EVNGS shows much higher cold-water viscosity (Chen & Jane, 1994; Kaur et al., 2011; Li et al., 2022b; Limpongsa & Jaipakdee, 2020), but the cold-water solubility fluctuates over a wide range (Chen & Jane, 1994; Eastman & Moore, 1984; Jane, Craig, & Seib, 1986; Li et al., 2014, 2022; Yu et al., 2018). There is still no clear explanation for why EVGS and EVNGS exhibit such high cold-water solubility without a large decrease in molecular weight, although EVGS prepared by AAT shows much weakened crystalline structure and EVGS prepared by EAHT shows small reductions in molecular weight (Choi et al., 2017; Jane, Craig, & Seib, 1986; Li, Zhou, & Jin, 2021), but it is still not reasonable and sufficient, which needs to be further explored.

For the cold-water viscosity, the related curves of viscosity are shown in Fig. 4. EVGS and EVNGS could swell quickly in cold water, the cold-water viscosity is significantly higher than native starch and pre-gelatinized starch (Zhou, Xing, et al., 2021). During the swelling process, the particles swell due to the hydrophilic hydroxyl group absorbs a large amount of water and then the friction between the particles increases, which is exhibited as the increase of cold-water viscosity. It could be found that there is a significant relationship between the integrity of the particle morphology and the properties of the paste. Such as the pasting speed of EVGS is faster than EVNGS according to the RVA curves, which could be observed from the fact that the slope of the RVA curve of EVGS is greater than that of EVNGS (Fig. 4), and the cold-water viscosity of EVGS reaches its peak value faster than that of EVNGS (Li, Zhou, & Jin, 2021; Zhou, Xing, et al., 2021). This might be related to the EVGS has smaller granule size than EVNPS, which means the EVGS has bigger specific surface area. Furthermore, the cold-water viscosity of both EVGS and EVNGS was found to be positive with the V-type RC (Li, Zhou, & Jin, 2021; Zhou, Xing, et al., 2021). During the hydration process of EVS, AM is gradually leaching out and the V-type crystalline structure is gradually destroyed, which might be related to the V-type single helical cavity structure is metastable in water (Li et al., 2022a; Zhou, Xing, et al., 2021).

Another interesting phenomenon worthy of attention is the relationship between cold-water solubility and cold-water viscosity in EVS. Some studies found that EVS with high cold-water solubility also had high cold-water viscosity (Chen & Jane, 1994; Jane, Craig, & Seib, 1986; Kaur et al., 2011), while others found that EVS with high cold-water solubility had poor cold-water viscosity (Choi et al., 2017; Qian et al., 2019), which still need further exploration.

For EVNPS, there is no related research about the paste properties, such as cold-water solubility and cold-water swelling property of EVNPS, but reduction of molecular weight and size caused by nanometer technology should improve its cold-water solubility, which also need to be further developed.

#### 3.4.2. Rheological properties

The rheological properties of cold-water paste from EVGS were explored to see the cold-water paste properties. All apparent viscosity of EVGS paste prepared by AAT was found to be decreased with the increase of shear rate, showing the “shear-thinning” behavior, belonging to non-newtonian pseudoplastic fluid (Bello-Pérez et al., 2000). Also, the cold-gelation matrix of EVGS after pasting in cold water was also explored. The storage modulus ( $G'$ ), loss modulus ( $G''$ ), and dynamic viscosity ( $\eta'$ ) increased and the loss factor ( $\tan \delta$ ) decreased with the increase in temperature. During the frequency sweep testing, the potato EVGS showed higher  $G'$ ,  $G''$ ,  $\eta'$  and lower  $\tan \delta$  than corn EVGS (Singh &

Singh, 2003), which still need to be further explored, such as the rheological properties can also be used to characterize the retrogradation properties of EVS after the formation of cold water paste.

#### 3.4.3. Freeze-thaw stability and transmittance of paste

The freeze-thaw stability of the starch gel formed by the EVS after swelling into a paste in cold water was explored to see its possible applications in starch-based frozen foods. The EVGS prepared by AAT has significantly improved freeze-thaw stability, which could be attributed to the integrity of the swelled granules that are not completely dispersed (Chen & Jane, 1994), which might slow the retrogradation rate of starch.

The freeze-thaw stability also varies with the environment that EVGS is exposed to, the freeze-thaw stability reduces when there is acetic acid in the EVGS solutions, which is more pronounced after the first freeze-thaw cycle, and the changes would enhance with the increase of the acetic acid concentration (Majzoobi et al., 2015). However, the freeze-thaw stability would enhance in the high pH environment due to the alkaline solution could increase the interaction between starch molecules and water, the trapped water in the starch network cannot be easily separated from the paste (Hedayati et al., 2016b), the freeze-thaw stability would also enhance with the increase of the sugar concentration in paste, which might be related to the hydrophilic nature of the sugars that reduces the amount of mobile water (Hedayati et al., 2016a).

The transmittance of EVGS paste is different from the native starch, the transmittance of EVGS prepared by AAT is lower than native starch, but the decrease of transmittance with the storage time is less pronounced than native starch (Singh & Singh, 2003). This phenomenon is considered to be related to the retrogradation rate of starch, which depends on the amounts of leached AM and dissociated AMP (Zabar et al., 2020). The retrogradation rate of EVGS paste prepared by EAHT was found to be faster than that of native thermal-gelatinized starch paste (Li et al., 2022b), which is different from the EVGS prepared by AAT. This may be related to the granule integrity and the distribution state of hydrogen bonds, and the differences in paste properties of these two different EVGS need to be further explored.

In addition, some research reported the addition of some hydrocolloids, such as xanthan gum and  $\beta$ -lactoglobulin/xanthan gum electrostatic coupled gel, could improve the physical and mucoadhesive properties of EVGS, including viscosity, consistency, pseudo-plasticity and so on (Kaveh, Azadmard-Damirchi, Yousefi, & Hashem Hosseini, 2021). The cold plasma treatment can be used as a pretreatment method for the preparation of EVGS or as a secondary modification of starch for EVGS, and the dual-modified starch shows better solubility, moisture absorption, swelling power, and flowing capacity (Ge et al., 2022; Sudheesh et al., 2023). However, most research about the paste property of EVS focuses on the EVGS, very little on EVNGS and EVNPS, let alone the differences in the property among the three EVS, which deserves further investigation for their precise application.

### 3.5. Amphiphilicity of EVS

In addition to the hydrophilicity described in part “3.4.1 Cold-water solubility and viscosity”, EVS is also thought to have the ability to absorb oil, the oil absorption capacity of EVGS and EVNGS is also significantly improved compared with native starch, which is related to the porous and cracked structure on the surface and can be regulated by controlling different reaction conditions (Feng et al., 2022; Li et al., 2022b; Zhou, Chang, et al., 2021). Meanwhile, the V-type porous granular starch (VPGS) can be prepared by EAHT combined ethanol-phase amylase enzymatic modification, and the oil absorption rate was further improved with a little decrease in water absorption rate (Zhou, Chang, et al., 2021). But the amphiphilicity of EVNPS is still unclear and needs to be further explored.

### 3.6. Digestibility of EVS

The rate and the extent of starch digestion have important consequences on human health. The rate of starch digestion affects the postprandial rise in blood glucose and the consequent insulinemic response, which are associated with several chronic diseases such as obesity, type 2 diabetes mellitus, and cardiovascular disease (Blaak et al., 2012). Resistant starch (RS) has a beneficial effect on health through regulating the balance of gut microbiota and promoting the production of short-chain fatty acids (Bindels et al., 2017; Johnston, Thomas, Bell, Frost, & Robertson, 2009; Maki et al., 2012; Robertson, Bickerton, Dennis, Vidal, & Frayn, 2005). The RS content of EVNPS is increased compared to waxy maize starch and normal maize starch (Qin et al., 2019), but the EVGS prepared by EAHT is more susceptible to  $\alpha$ -amylase compared with native starch, which suggests the EVGS may be more digestible than native starch (Zhou, Chang, et al., 2021). Beside the digestibility of pure EVS, it has been suggested that the complexation of guest molecules in its cavity can affect, mostly reducing, starch digestibility. This is long known for free fatty acids which complex with AM is now classified as V-type resistant starch (Cai, Tian, Sun, & Jin, 2022). It has been suggested that incorporation of phenolics and salicylic acid in EVS produced a similar decreasing effect on starch digestibility (Deng et al., 2021; Guo, Shi, & Kong, 2023; Qin et al., 2019), and different helical sizes of EVS (V<sub>6</sub>, V<sub>7</sub>, and V<sub>8</sub>) also showed different anti-digestion effect (Guo et al., 2023). In general, EVS at different scales may exhibit different potential digestive properties, but there is paucity of studies investigating digestibility of EVS as well as investigating the relationship between structural properties (at different structural scales)

and digestibility of EVS. More importantly, the effect of thermal treatments on digestibility of EVS also needs to be further explored (Guo et al., 2023), which has a major practical significance for the application of EVS in food systems that are subjected to thermal treatments during industrial or domestic processing.

The impact of the starch modification on its susceptibility to colonic fermentation by gut microbiota is also relevant from a health perspective and it is largely unknown and still needs to be explored. EVS that are partly indigestible in the small intestine (either because of structural modification of the starch molecules or complexation of guest molecules) can be fermented by the gut microbiota. Noteworthy, the fermentation profile in the large intestine depends on starch molecular features, hence structural differences in EVS may also result in differences in EVS fermentability (Liu, Deng, et al., 2023; Luo et al., 2023).

Regarding the behavior of different type of EVS and their inclusion complexes in the human gastrointestinal tract, further work is needed to characterize, including the digestibility and fermentation of EVS, and the kinetics of release of the guest molecules encapsulated by EVS in the human gastrointestinal tract as well as its digestibility and its interaction with the gut microbiota.

### 4. Possible applications of ethanol-induced V-type starch (EVS)

The structure of EVS gives it two remarkable properties, which endow EVS with different application possibilities, as shown in Fig. 5. One is the ability to encapsulate guest molecules under relatively mild conditions rapidly (Dries, Gomand, et al., 2017; Sarifudin, Soontaranon, et al., 2020; Shi, Zhang, et al., 2019; Zhou, Guo, Gladden, Contreras, &

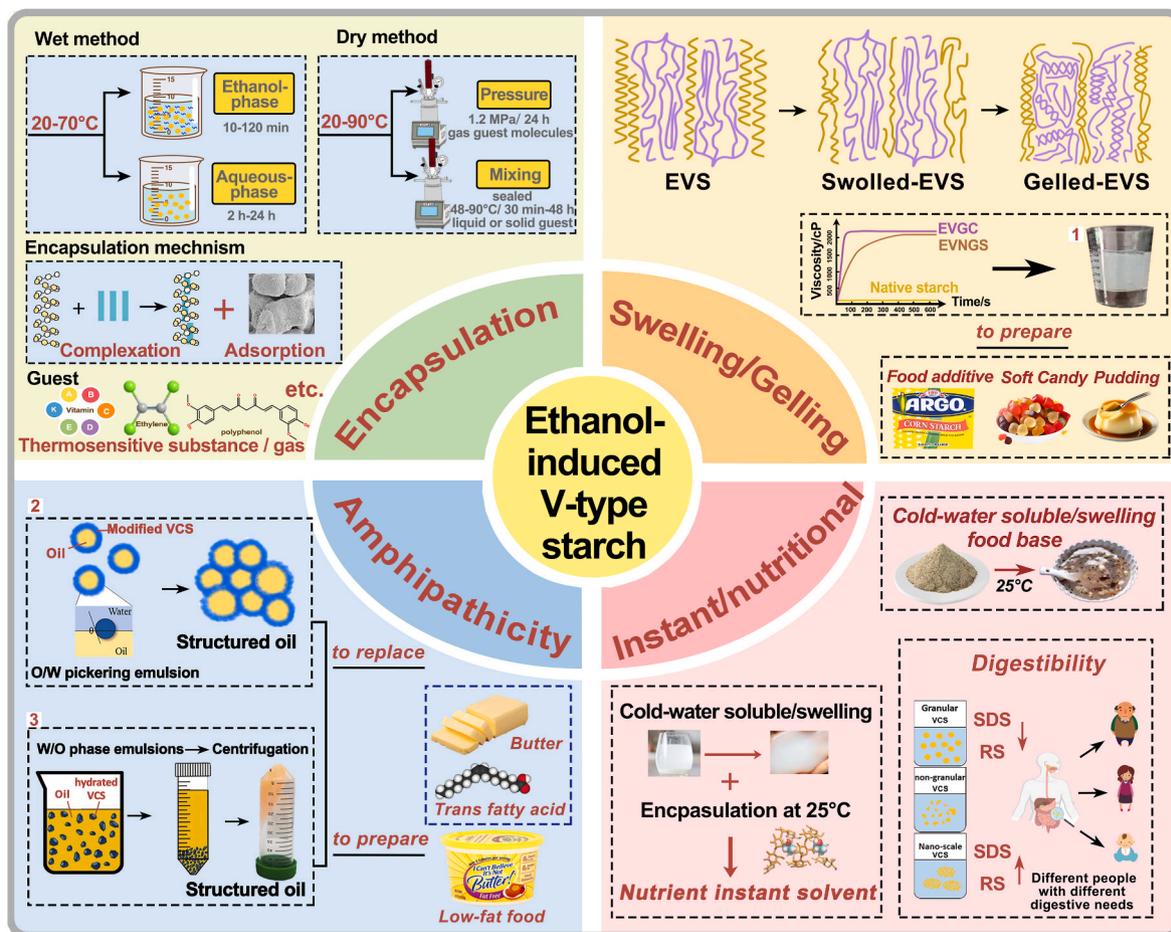


Fig. 5. The main application of ethanol-induced V-type starch (EVS), 1 (Majzoobi & Farahnaky, 2021); 2 (Champrasert, Sagis, & Suwannaporn, 2023); and 3 (Li, Zhou, & Jin, 2021).

Kong, 2022), which is given by the formation of ethanol-induced V-type single helical cavity structure. That makes it suitable for the encapsulation and delivery of drugs and bioactive molecules (Kong & Ziegler, 2014; Qin et al., 2019; Qiu, Qin, et al., 2016). The second is the EVS can swell in cold water, the cold-water viscosity of EVS is much improved (Chen & Jane, 1994; Li et al., 2022b; Zhou, Xing, et al., 2021), which makes it a suitable food additive to improve the texture of foods. For the third one, the oil absorption of EVS is also greatly improved, allows it to be used as the oil structurant in the preparation of low-fat food due to its amphiphilicity (Li, Kierulf, & Abbaspourrad, 2021; Majzooobi et al., 2015). In addition, the starchy instant and functional nutritional products may be developed based on the properties of the EVS.

#### 4.1. Ability to encapsulate compounds in a relatively mild condition

Traditional preparation methods of V-type complex often happen in a relatively harsh environment, such as high temperature, strong pH, high concentration of DMSO, etc., the unwound single helical structure of AM can form complex with the guest molecules through hydrophobic interactions (Putseys et al., 2010). The obtained V-type complex has improved thermal stability (Cheng et al., 2018), of which the dissociation temperature is generally between 95 and 120 °C and the melting enthalpy increases with the increase of the RC of the complex (Cervantes-Ramirez et al., 2020). However, the harsh complexation conditions may affect the properties of guest molecules and limit the application of V-type starch (Kong & Ziegler, 2014). Therefore, some researchers have divided the preparation of V-type complexes into two steps. First, the preparation of a V-type single helical cavity structure, that is the EVS, and then the insertion of the guest, the latter can happen under relatively mild conditions, such as relatively lower temperature (Feng et al., 2022; Li et al., 2022a; Zhou & Kong, 2023b). The traditional V-type complexes have been prepared and summarized in many places (Chi et al., 2021; Putseys et al., 2010). Therefore, this paper only discusses the V-type complex formed by V-type single helical cavity structure of EVS and guests. Cyclodextrin, a commonly used polysaccharide encapsulation material, also has a cavity structure. It is generally believed that cyclodextrins have a relatively fixed cavity structure and are less effective in the encapsulation of big molecules and has risk to cause intestinal burden such as diarrhea at high doses (Matencio, Navarro-Orcajada, García-Carmona, & López-Nicolás, 2020), the V-type single helical cavity structure of EVS can form different sizes according to different sizes of guest molecules (Ma, Wang, Lu, & Tian, 2022). For the complexation of EVS, there are two main complexation methods including wet method and dry method. The wet method refers to the guest molecule could be complexed by EVS in the solution with different ethanol concentrations and the dry method refers to the guest molecules could be complexed by EVS through the physical mixing in certain temperatures and pressures.

For the wet method, the V-type single helical cavity structure can be stable during the dry state, but when EVS is dispersed in water, the AM will leach out with the swelling of EVS, and the V-type single helical cavity structure would be destroyed gradually due to its metastable property in water, which may affect the complexation of EVS (Li et al., 2022a; Zhou, Xing, et al., 2021). However, when a certain concentration of ethanol solution is chosen for the encapsulation system or a certain concentration of guest molecules that can form complex with AM is exist in the system, the V-type single helical cavity structure will be preserved (Li et al., 2022a). The ethanol can limit the swelling of the EVS and the further leaching of AM, which allows the cavity structure to be used for complexation, and the formed guest-AM complex can further inhibit the swelling of EVS. But the ethanol concentration should be valued and chosen according to different guests (Dries, Gomand, et al., 2017; Guo & Kong, 2022; Kong & Ziegler, 2014; Sarifudin, Keeratiburana, et al., 2020; Zhou et al., 2022).

EVGS has been used for the rapid encapsulation of ascorbyl palmitate and monoglyceride at room temperatures. The obtained complex shows

obvious V-type crystalline structure, it could be melted between 110 and 130 °C, which shows better thermal stability compared with the traditional V-type complex (Dries, Knaepen, et al., 2017; Li et al., 2022a; Putseys et al., 2010). The effect of different encapsulation conditions (ethanol concentration, temperature, time) was explored (Dries, Gomand, et al., 2017; Li et al., 2022a). In addition, it was also proposed that the encapsulation mechanism: EVGS could encapsulate guests through physical adsorption on surface and formation of V-type complexes (Chen & Jane, 1995; Li et al., 2022a).

The EVNGS prepared by the DMSO-ethanol method has been used to encapsulate ascorbyl palmitate and C18 fatty acids at relatively lower temperatures (20–70 °C) with different ethanol concentrations (Kong & Ziegler, 2014; Zhou et al., 2022), and the EVNGS prepared by the ultrasonication-mediated high-temperature-ethanol method can encapsulate the butyric acid in aqueous system (Liu, Shao, et al., 2023), but the DMSO residues involved in these two methods limit its applicability in food systems (Dries, Gomand, et al., 2017). When EVS is applied in food field, the preparation methods of EVS that does not involve DMSO are more practical.

For EVNPS, phenolic compounds can also be encapsulated by simple mixing at room temperature in aqueous phase, but there is no further research has been conducted to show the preference of EVS for phenolic substances of which structure, and the encapsulation mechanism have not been clarified, which still need further investigation (Qin et al., 2019; Qiu, Qin, et al., 2016).

For the dry method, which is also named solid encapsulation. The encapsulation can be completed by mixing the EVS and guest molecules in a moderate temperature environment, under atmospheric or pressurized environment, but the encapsulation effect of solid encapsulation is much less effective than encapsulation in solution (Gao et al., 2023). For the gas molecules, the encapsulation is performed in pressure vessel chamber with a certain pressure requirement, such as CO<sub>2</sub> and ethylene and so on (Li et al., 2019; Shi et al., 2022; Shi, Fu, Huang, & Zhang, 2017; Shi, Fu, Tan, et al., 2017; Shi, Zhang, et al., 2019; Shi et al., 2020), which can be used in the ripening of banana (Liu, Shao, et al., 2023), and deodorizing aquatic products (Shi et al., 2024). For the solid or liquid guest molecules, the encapsulation can be performed by physical mixing at 48–90 °C, such as menthol (EVNGS, 70 °C) (Shi, Hopfer, et al., 2019), lauric acid (EVNGS, 48–90 °C) (Huang et al., 2021), cinnamaldehyde (EVNGS, 60–90 °C) (Gao et al., 2023), guest aroma compounds (EVNGS, 70 °C) (Zhou & Kong, 2023a), D-limonene (EVNGS, 25 °C) (Sun et al., 2023), and thymol (EVNGS, 70 °C) (Zhou & Kong, 2023b). The melting peaks of V-type complexes could be observed between 110 and 135 °C, indicating higher thermal stability (Shi, Hopfer, et al., 2019; Zhou & Kong, 2023a).

In general, the complexation reaction between the V-type single helical cavity structure in EVS and the guest molecule is considered to be completed in wet or dry methods rapidly at lower temperatures. Therefore, the EVS is considered to be a potential material that can encapsulate guest molecules with unstable properties, such as heat-sensitive compounds, like vitamins, flavor compounds, and polyphenols (Li et al., 2022a). However, there is still a lot of unknown information about EVS as an encapsulation material, such as, what structural properties of molecules are better suitable for EVS have not been specifically explored, the encapsulation mechanism has not been fully elucidated, and the digestion and release of guest molecules in gastrointestinal tract also need to be studied.

#### 4.2. Improvement of the texture

Both EVGS and EVNGS have cold-water swelling capacity. Compared with the PGS, the fluidity, shear resistance, glossiness, and cold-water viscosity of EVGS and EVNGS are more similar to the paste of native starch after thermal gelatinization. That is related to the formation of V-type single helical cavity structure, which gives EVGS and EVNGS a more compact structure, limits the flow and dispersion of unwinding

starch molecules, and improves the water-holding capacity of starch molecules. Meanwhile, some preparation methods of EVGS and EVNGS does not involve chemical modification. On the one hand, the EVGS and EVNGS can be used as food additives, such as thickeners and hydrocolloids, to improve the texture of food due to high hydrophilicity. On the other hand, the EVGS and EVNGS may rapidly swell into paste and set to a gel without cooking and cooling procedure, which might be used in the development of foods systems, such as pie, fillings, jellies, desserts, and pudding, to improve the viscoelasticity and stability (Bello-Pérez et al., 2000; Eastman & Moore, 1984; Majzoobi et al., 2015). Such as the puddings made from EVGS are thought to be smooth, continuous, homogeneous, and non-grainy, and have a high sheen and desirable mouth-feel and viscosity characteristics, the EVGS is expected to be an effective substitute for some crosslinking agents (Jane, 1992). However, the current application in this field is based on the assumption about the property of EVGS and EVNGS, there are particularly few published studies on the above application directions, which deserves further exploration.

Ethanol is the common reagent during the different preparation methods of EVS, which is mainly responsible for the formation of V-type single helical cavity structure. For the problem of residual ethanol, when EVNGS contacts the water, the ethanol could be detected in EVNGS by GC-fame ionization detector (GC-FID) in pervious study (Zhou, King, et al., 2021), it could be found most of the ethanol was evaporated during the drying process, and the residual ethanol was easily leached out from EVS when contact with water. The residual ethanol content might be related to the different drying method, and when EVS is applied into the food field, the exact residual ethanol content should be detected and controlled according to prescribed standards for different types of food (Meng et al., 2019).

#### 4.3. Application in low-fat food

Solid fats often contain a higher content of trans fatty acids, although they can bring better taste to food, the higher content of trans fatty acids may increase the incidence of some chronic diseases. Liquid oil intake is thought to be greatly improve the situation, but it requires some treatments to bring liquid oil to the same physical properties and texture as solid fats, which means the solidifying of liquid oil. Oleogelation, a semi-solid material composed of liquid oil esters (generally vegetable oils) and a small amount of gelator, can be used as a type of healthy fat to replace the traditional solid fats due to its characteristics of containing zero trans fats and low saturated fat content, as well as similar strength and plasticity properties to those of solid fats (Champrasert et al., 2023). The liquid oil could be converted into a solid-like gel. The EVGS has been reported to be amphiphilic, the porous structure on the surface of EVGS gives it a certain ability to absorb oil except for its cold-water swelling properties (Feng et al., 2022; Li et al., 2022b; Zhou, Chang, et al., 2021). The granular morphology endows EVGS the potential to undergo substantial flattening upon adsorption at the oil-water interface (Champrasert et al., 2023). Some study found the low-fat oil-in-water emulsions prepared with EVGS as a stabilizer showed higher stability compared to PGS as a stabilizer, which might be used as a suitable fat replacer for the production of reduced-fat food (Hedayati et al., 2020). In addition, the EVGS could also be used to structure oil via the water-in-oil high internal phase emulsion method, the rheological properties were similar to the butter spreads and oleogels, which suggested a high potential for reducing solid fats in the daily diet (Li, Kierulf, & Abbaspourrad, 2021). The advantage of starch-based EVS is that it is more in line with today's clean and green development needs than common gelators that are chemically synthesized (ethyl cellulose) or that are not the main food components (wax) (Li, Kierulf, & Abbaspourrad, 2021). For the EVNGS and EVNPS, no published studies have been conducted in this area.

#### 4.4. Potential application of EVS in starchy instant and functional nutritional products

Preparation methods of EVGS and EVNGS may be further applied to the development of cereals product, such as improving the cooking characteristics of cereals to prepare cereal instant food. For now, only the ethanolic-extrusion method has been used to prepare the instant whole wheat powder, the product has good pasting properties in cold water, fast dispersion, and low caking rate (Meng et al., 2019), which is related to the starch in the wheat being modified into EVS. But the effect of the presence of other components (e.g., proteins) or the physical accessibility to starch in cereal flour has not been studied systematically, which may affect the modification process and still needs further investigation.

Combination of encapsulation and cold-water swelling properties is also expected to make a contribution in the application of instant nutrient food, such as nutrient instant solvent (Dries, Knaepen, et al., 2017; Sarifudin, Keeratiburana, et al., 2020). In addition, the different digestibility of EVS at different scales also might be used to prepare food products for people with different digestive needs.

### 5. Conclusion and future challenges

In this paper, the preparation methods, formation mechanisms, properties, and applications in the food field of different EVS are summarized. EVS is one kind of modified starch with the V-type single helical cavity structure induced by ethanol, which can exist at different structural scales. There are several methods to prepare EVS at different scales, and their formation mechanisms and product properties are different. The functional properties also vary with the structural scales. Both  $\mu\text{m}$ -scale EVGS and EVNGS have higher cold-water viscosity and better gelling properties, while their V-type single helical cavity structure can be used as an encapsulation carrier of bioactive compounds. Although the properties of nanoscale EVNPS in cold water are still unknown, it also can be used as an encapsulation carrier.

In terms of application in the food field, EVS has four main potential application directions, the single helical cavity structure can be used for encapsulation and delivery of drugs or bioactive compounds. The excellent cold water swelling and gelling properties make EVS promising for use as a food additive to improve the texture of food. EVS is promising as a potential material for structuring oil, which may be used in the low-fat food. It is also expected to prepare the instant and functional nutritional products based on EVS.

However, there are still unknown properties of EVS that needed to be explored, such as the digestion behavior of different type of EVS in the human gastrointestinal tract, the interaction between the EVS and the gut microbiota, kinetics of release of the guest molecules in the human gastrointestinal tract, and the further implementation and development of the potential applications of EVS. In addition, compared with the native starch, a large number of exposed hydrophilic hydroxyl groups and metastable V-type single helical cavity structure endows EVS with improved reactivity and is worthy of further diversified modification.

#### CRediT authorship contribution statement

**Jiaxin Li:** Writing – review & editing, Writing – original draft, Visualization, Investigation. **Aixia Wang:** Writing – review & editing. **Mengzi Nie:** Writing – review & editing. **Lili Wang:** Writing – review & editing. **Liya Liu:** Writing – review & editing. **Fengzhong Wang:** Writing – review & editing. **Edoardo Capuano:** Writing – review & editing, Supervision. **Li-Tao Tong:** Writing – review & editing, Supervision, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

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

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## References

- Apostolidis, E., & Mandala, I. (2020). Modification of resistant starch nanoparticles using high-pressure homogenization treatment. *Food Hydrocolloids*, *103*, Article 105677.
- Bajer, D. (2023). Nano-starch for food applications obtained by hydrolysis and ultrasonication methods. *Food Chemistry*, *402*, Article 134489.
- Bello-Pérez, L. A., Romero-Manilla, R., Acapulco, Paredes-López, O., & Irapuato. (2000). Preparation and properties of physically modified banana starch prepared by alcoholic-alkaline treatment. *Starch Stärke*, *52*, 154–159.
- BeMiller, J. N. (2018). *Carbohydrate chemistry for food scientists*.
- Bertoft, E. (2017). Understanding starch structure: Recent progress. *Agronomy*, *7*(3).
- Bindels, L. B., Segura Munoz, R. R., Gomes-Neto, J. C., Mutemberezi, V., Martínez, I., Salazar, N., et al. (2017). Resistant starch can improve insulin sensitivity independently of the gut microbiota. *Microbiome*, *5*(1), 12.
- Blaak, E. E., Antoine, J. M., Benton, D., Björck, I., Bozzetto, L., Brouns, F., ... Vinoy, S. (2012). Impact of postprandial glycaemia on health and prevention of disease. *Obesity Reviews*, *13*(10), 923–984.
- Butt, N. A., Ali, T. M., & Hasnain, A. (2019). Rheological characterization of cold water soluble rice (*Oryza sativa*) starch lactates and citrates prepared via alcoholic-alkaline method. *International Journal of Biological Macromolecules*, *123*, 558–568.
- Cai, C., Tian, Y., Sun, C., & Jin, Z. (2022). Resistant structure of extruded starch: Effects of fatty acids with different chain lengths and degree of unsaturation. *Food Chemistry*, *374*, Article 131510.
- Cervantes-Ramirez, J. E., Cabrera-Ramirez, A. H., Morales-Sanchez, E., Rodriguez-Garcia, M. E., Reyes-Vega, M. L., Ramirez-Jimenez, A. K., et al. (2020). Amylose-lipid complex formation from extruded maize starch mixed with fatty acids. *Carbohydrate Polymers*, *246*, Article 116555.
- Champrasert, O., Sagis, L. M. C., & Suwannaporn, P. (2023). Emulsion-based oleogelation using octenyl succinic anhydride modified granular cold-water swelling starch. *Food Hydrocolloids*, *135*, Article 108186.
- Chang, Y., Yan, X., Wang, Q., Ren, L., Tong, J., & Zhou, J. (2017). High efficiency and low cost preparation of size controlled starch nanoparticles through ultrasonic treatment and precipitation. *Food Chemistry*, *227*, 369–375.
- Chang, Y., Yang, J., Ren, L., & Zhou, J. (2018). Characterization of amylose nanoparticles prepared via nanoprecipitation: Influence of chain length distribution. *Carbohydrate Polymers*, *194*, 154–160.
- Chen, H., Chen, L., Dang, X., Shan, Z., Dai, R., & Wang, Y. (2019). The structure and properties of granular cold water soluble starch by a NaOH urea aqueous solution. *International Journal of Biological Macromolecules*, *141*, 732–737.
- Chen, J., & Jane, J. (1994). Properties of granular cold-water soluble starches prepared by alcoholic-alkaline treatments. *Cereal Chemistry*, *71*(6), 623–626.
- Chen, J., & Jane, J. (1995). Effectiveness of granular cold-water-soluble starch as a controlled-release matrix. *Cereal Chemistry*, *72*(3), 265–268.
- Chen, F., Xie, F., Liu, P., & Chen, P. (2019). Structure, thermal stability and suspension rheological properties of alcohol-alkali-treated waxy rice starch. *International Journal of Biological Macromolecules*, *134*, 397–404.
- Cheng, L., Feng, T., Zhang, B., Zhu, X., Hamaker, B., Zhang, H., et al. (2018). A molecular dynamics simulation study on the conformational stability of amylose-linoleic acid complex in water. *Carbohydrate Polymers*, *196*, 56–65.
- Chi, C., Li, X., Huang, S., Chen, L., Zhang, Y., Li, L., et al. (2021). Basic principles in starch multi-scale structuration to mitigate digestibility: A review. *Trends in Food Science & Technology*, *109*, 154–168.
- Choi, Y.-J., Baik, M.-Y., & Kim, B.-Y. (2017). Characteristics of granular cold-water-soluble potato starch treated with alcohol and alkali. *Food Science and Biotechnology*, *26*(5), 1263–1270.
- Deng, N., Deng, Z., Tang, C., Liu, C., Luo, S., Chen, T., et al. (2021). Formation, structure and properties of the starch-polyphenol inclusion complex: A review. *Trends in Food Science & Technology*, *112*, 667–675.
- Dominguez-Ayala, J. E., Ayala-Ayala, M. T., Velazquez, G., Espinosa-Arbelaiz, D. G., & Mendez-Montealvo, G. (2023). Crystal structure changes of native and retrograded starches modified by high hydrostatic pressure: Physical dual modification. *Food Hydrocolloids*, *140*, Article 108630.
- dos Santos, T. P. R., Franco, C. M. L., Demiate, I. M., Li, X.-H., Garcia, E. L., Jane, J.-I., et al. (2018). Spray-drying and extrusion processes: Effects on morphology and physicochemical characteristics of starches isolated from Peruvian carrot and cassava. *International Journal of Biological Macromolecules*, *118*, 1346–1353.
- Dries, D. M., Gomand, S. V., & Delcour, J. A. (2016). V-type crystal formation in starch by aqueous ethanol treatment: The effect of amylose degree of polymerization. *Food Hydrocolloids*, *61*, 649–661.
- Dries, D. M., Gomand, S. V., Goderis, B., & Delcour, J. A. (2014). Structural and thermal transitions during the conversion from native to granular cold-water swelling maize starch. *Carbohydrate Polymers*, *114*, 196–205.
- Dries, D. M., Gomand, S. V., Pycarelle, S. C., Smet, M., Goderis, B., & Delcour, J. A. (2017). Development of an infusion method for encapsulating ascorbyl palmitate in V-type granular cold-water swelling starch. *Carbohydrate Polymers*, *165*, 229–237.
- Dries, D. M., Knaepen, L., Goderis, B., & Delcour, J. A. (2017). Encapsulation of the antioxidant ascorbyl palmitate in V-type granular cold-water swelling starch affects the properties of both. *Carbohydrate Polymers*, *165*, 402–409.
- Eastman, J. E., & Moore, C. O. (1984). *Cold-water-soluble granular starch for gelled food compositions*. U.S. Patent 4465702.
- Fang, C., Huang, J., Pu, H., Yang, Q., Chen, Z., & Zhu, Z. (2021). Cold-water solubility, oil-adsorption and enzymolysis properties of amorphous granular starches. *Food Hydrocolloids*, *117*, Article 106669.
- Feng, Y., Wu, C., Junejo, S. A., Zhang, B., Fu, X., Tan, C. P., et al. (2022). Effect of V-type crystallinity and starch particle structure on the oil loading capacity and anti-oxidation. *Carbohydrate Polymers*, *297*, Article 120015.
- Gallant, D. J., Bouchet, B., & Baldwin, P. M. (1997). Microscopy of starch: Evidence of a new level of granule organization. *Carbohydrate Polymers*, *32*(3–4), 177–191.
- Gao, Q., Sun, Y., He, R., Zheng, J., Zhang, B., Tan, C. P., ... Huang, Q. (2023). Molecular encapsulation of cinnamaldehyde in V-type starch: The role of solvent and temperature. *Food Hydrocolloids*, *136*, Article 108285.
- Gao, Q., Zhang, B., Qiu, L., Fu, X., & Huang, Q. (2020). Ordered structure of starch inclusion complex with C10 aroma molecules. *Food Hydrocolloids*, *108*, Article 105969.
- Gao, Q., Zheng, J., Meeren, P. V. d., Xia, J., Zhang, B., Fu, X., et al. (2022). Complexation temperature regulation of the ordered structure of “empty” V-type starch. *Carbohydrate Polymers*, *298*, Article 120086.
- Ge, X., Shen, H., Sun, X., Liang, W., Zhang, X., Sun, Z., ... Li, W. (2022). Insight into the improving effect on multi-scale structure, physicochemical and rheology properties of granular cold water soluble rice starch by dielectric barrier discharge cold plasma processing. *Food Hydrocolloids*, *130*, Article 107723.
- Gilbert, R. G., Wu, A. C., Sullivan, M. A., Sumarriva, G. E., Ersch, N., & Hasjim, J. (2013). Improving human health through understanding the complex structure of glucose polymers. *Analytical and Bioanalytical Chemistry*, *405*(28), 8969–8980.
- Guo, J., & Kong, L. (2022). Enhancement of enzymatic resistance in V-type starch inclusion complexes by hydrothermal treatments. *Food Hydrocolloids*, *127*, Article 107533.
- Guo, J., Shi, L., & Kong, L. (2023). Structure-digestibility relationship of starch inclusion complex with salicylic acid. *Carbohydrate Polymers*, *299*, Article 120147.
- Guo, K., Zhang, L., Bian, X., Cao, Q., & Wei, C. (2020). A-, B- and C-type starch granules coexist in root tuber of sweet potato. *Food Hydrocolloids*, *98*, Article 105279.
- Guo, J., Ziegler, G. R., & Kong, L. (2022). Polymorphic transitions of V-type amylose upon hydration and dehydration. *Food Hydrocolloids*, *125*, Article 107372.
- Han, Z., Shi, R., & Sun, D.-W. (2020). Effects of novel physical processing techniques on the multi-structures of starch. *Trends in Food Science & Technology*, *97*, 126–135.
- He, X., Xia, W., Chen, R., Dai, T., Luo, S., Chen, J., et al. (2020). A new pre-gelatinized starch preparing by gelatinization and spray drying of rice starch with hydrocolloids. *Carbohydrate Polymers*, *229*, Article 115485.
- Hebeish, A., El-Rafie, M. H., El-Sheikh, M. A., & El-Naggar, M. E. (2013). Ultra-fine characteristics of starch nanoparticles prepared using native starch with and without surfactant. *Journal of Inorganic and Organometallic Polymers and Materials*, *24*(3), 515–524.
- Hedayati, S., Shahidi, F., Koocheki, A., Farahnaky, A., & Majzoobi, M. (2016a). Functional properties of granular cold-water swelling maize starch: Effect of sucrose and glucose. *International Journal of Food Science and Technology*, *51*(11), 2416–2423.
- Hedayati, S., Shahidi, F., Koocheki, A., Farahnaky, A., & Majzoobi, M. (2016b). Physical properties of pregelatinized and granular cold water swelling maize starch at different pH values. *International Journal of Biological Macromolecules*, *91*, 730–735.
- Hedayati, S., Shahidi, F., Koocheki, A., Farahnaky, A., & Majzoobi, M. (2020). Influence of pregelatinized and granular cold water swelling maize starches on stability and physicochemical properties of low fat oil-in-water emulsions. *Food Hydrocolloids*, *102*, Article 105620.
- Huang, L., Li, S., Tan, C. P., Feng, Y., Zhang, B., Fu, X., et al. (2021). Solid encapsulation of lauric acid into “empty” V-type starch: Structural characteristics and emulsifying properties. *Carbohydrate Polymers*, *267*, Article 118181.
- Huang, J., Wei, N., Li, H., Liu, S., & Yang, D. (2014). Outer shell, inner blocklets, and granule architecture of potato starch. *Carbohydrate Polymers*, *103*, 355–358.
- Jane, J. L. (1992). Preparation and food applications of physically modified starches. *Trends in Food Science & Technology*, *3*, 145–148.
- Jane, J. L., Craig, S. A. S., & Seib, P. A. (1986). Characterization of granular cold water-soluble starch. *Starch Stärke*, *38*, 258–263.
- Jane, J. L., Craig, S. A. S., Seib, P. A., & Hoseney, R. C. (1986). A granular cold water-soluble starch gives a V-type X-ray diffraction pattern. *Carbohydrate Research*, *150*, C5–C6.
- Jeong, O., & Shin, M. (2018). Preparation and stability of resistant starch nanoparticles, using acid hydrolysis and cross-linking of waxy rice starch. *Food Chemistry*, *256*, 77–84.

- Jivan, M. J., Yarmand, M., & Madadlou, A. (2014). Preparation of cold water-soluble potato starch and its characterization. *Journal of Food Science and Technology*, 51(3), 601–605.
- Johnston, K. L., Thomas, E. L., Bell, J. D., Frost, G. S., & Robertson, M. D. (2009). Resistant starch improves insulin sensitivity in metabolic syndrome. *Diabetic Medicine*, 27(4), 391–397.
- Junejo, S. A., Flanagan, B. M., Zhang, B., & Dhital, S. (2022). Starch structure and nutritional functionality – past revelations and future prospects. *Carbohydrate Polymers*, 277, Article 118837.
- Kaul, S., Kaur, K., Kaur, J., Mehta, N., & Kennedy, J. F. (2023). Properties of potato starch as influenced by microwave, ultrasonication, alcoholic-alkali and pre-gelatinization treatments. *International Journal of Biological Macromolecules*, 226, 1341–1351.
- Kaur, B., Fazilah, A., & Karim, A. A. (2011). Alcoholic-alkaline treatment of sago starch and its effect on physicochemical properties. *Food and Bioprocess Processing*, 89, 463–471.
- Kaveh, Z., Azadmard-Damirchi, S., Yousefi, G., & Hashem Hosseini, S. M. (2021). A new approach in improving granular cold water swelling starch properties using xanthan gum and  $\beta$ -lactoglobulin/xanthan gum electrostatic coupled gel. *Food Hydrocolloids*, 113, Article 106438.
- Kim, H.-Y., Park, S. S., & Lim, S.-T. (2015). Preparation, characterization and utilization of starch nanoparticles. *Colloids and Surfaces B: Biointerfaces*, 126, 607–620.
- Kong, L., & Ziegler, G. R. (2014). Molecular encapsulation of ascorbyl palmitate in preformed V-type starch and amylose. *Carbohydrate Polymers*, 111, 256–263.
- Kurakake, M., Noguchi, M., Fujioka, K., & Komaki, T. (1997). Effects on maize starch properties of heat-treatment with water-ethanol mixtures. *Journal of Cereal Science*, 25, 253–260.
- Kurakake, M., Noguchi, M., Fujioka, K., & Komaki, T. (2008). Pasting characteristics of maize starch heat-treated with different water-ethanol mixtures. *Cereal Chemistry*, 85(4), 566–570.
- Le Corre, D., Bras, J., & Dufresne, A. (2010). Starch nanoparticles: A review. *Biomacromolecules*, 11(5), 1139–1153.
- Le, C. A. K., Ogawa, Y., Grimaud, F., Nishiyama, Y., Morfin, I., Potocki-Veronese, G., et al. (2022). Helical inclusion complexes of amylose with aromatic compounds: Crystallographic evidence for new V-type allomorphs. *Crystal Growth & Design*, 22(12), 7079–7089.
- Li, W., Cao, F., Fan, J., Quyang, S., Luo, Q., Zhen, J., et al. (2014). Physically modified common buckwheat starch and their physicochemical and structural properties. *Food Hydrocolloids*, 40, 237–244.
- Li, C., Guo, Y., Chen, M., Wang, S., Gong, H., Zuo, J., ... Dai, L. (2023). Recent preparation, modification and application progress of starch nanocrystals: A review. *International Journal of Biological Macromolecules*, 250, Article 126122.
- Li, P., Kierulf, A., & Abbaspourad, A. (2021). Application of granular cold-water-swelling starch as a clean-label oil structurant. *Food Hydrocolloids*, 112, Article 106311.
- Li, C., Powell, P. O., & Gilbert, R. G. (2017). Recent progress toward understanding the role of starch biosynthetic enzymes in the cereal endosperm. *Amylase*, 1, 59–74.
- Li, Y., Qi, Y., Li, H., Chen, Z., & Xu, B. (2022). Improving the cold water swelling properties of oat starch by subcritical ethanol-water treatment. *International Journal of Biological Macromolecules*, 194, 594–601.
- Li, H., Zhang, B., Li, C., Fu, X., Wang, Z., & Huang, Q. (2019). CO<sub>2</sub> inclusion complexes of Granular V-type crystalline starch: Structure and release kinetics. *Food Chemistry*, 289, 145–151.
- Li, J., Zhou, X., & Jin, Z. (2021). Effect of high-temperatures and aqueous ethanol treatment on the formation process and properties of V-type Granular Starch (VGS). *Carbohydrate Polymers*, 258, Article 117713.
- Li, J., Zhou, X., & Jin, Z. (2022a). Encapsulation of monoglycerides in V-type granular starch prepared under different ethanol concentrations. *Food Hydrocolloids*, 133, Article 107935.
- Li, J., Zhou, X., & Jin, Z. (2022b). V-type granular starch prepared using aqueous-ethanol heat treatment at different ethanol concentrations. *Food Hydrocolloids*, 123, Article 107176.
- Limpongka, E., & Jaipakdee, N. (2020). Physical modification of Thai rice starch and its application as orodispersible film former. *Carbohydrate Polymers*, 239, Article 116206.
- Liu, Z., Deng, N., Luo, S., Liu, C., & Hu, X. (2023). Fermentation of resistant starch from the starch-ferulic acid inclusion complex compared with high-amylose corn starch. *International Journal of Biological Macromolecules*, 246, Article 125647.
- Liu, Z., Junejo, S. A., Zhang, B., Fu, X., & Huang, Q. (2022). Characteristics and ethylene encapsulation properties of V-type linear dextrin with different degrees of polymerisation. *Carbohydrate Polymers*, 277, Article 118814.
- Liu, T. Y., Ma, Y., Yu, S. F., Shi, J., & Xue, S. (2011). The effect of ball milling treatment on structure and porosity of maize starch granule. *Innovative Food Science & Emerging Technologies*, 12(4), 586–593.
- Liu, Z., Shao, M., Junejo, S. A., Zhang, B., Jiang, H., Fu, X., et al. (2023). Controlled ethylene-releasing from V-type starch coated with sodium alginate for banana ripening via changing the humidity of environment. *Postharvest Biology and Technology*, 202, Article 112377.
- Liu, H., Yao, Y., Zhang, Y., Zheng, B., & Zeng, H. (2023). Ultrasonication-mediated formation of V-type lotus seed starch for subsequent complexation with butyric acid. *International Journal of Biological Macromolecules*, 236, Article 124000.
- Luo, X., Huang, Q., Fu, X., Kraithong, S., Hu, Y., Yuan, Y., ... Zhang, B. (2023). In vitro fecal fermentation characteristics of mutant rice starch depend more on amylose content than crystalline structure. *Carbohydrate Polymers*, 307, Article 120606.
- Ma, X., Jian, R., Chang, P. R., & Yu, J. (2008). Fabrication and characterization of citric acid-modified starch nanoparticles plasticized-starch composites. *Biomacromolecules*, 9, 3314–3320.
- Ma, R., Wang, X., Lu, H., & Tian, Y. (2022). Debranched starch: Preparation and hydrophobic cavity characterization using carbon nanotubes. *LWT-Food Science & Technology*, 153, Article 112548.
- Majzoobi, M., & Farahnaky, A. (2021). Granular cold-water swelling starch; properties, preparation and applications, a review. *Food Hydrocolloids*, 111, Article 106393.
- Majzoobi, M., Kaveh, Z., Blanchard, C. L., & Farahnaky, A. (2015). Physical properties of pregelatinized and granular cold water swelling maize starches in presence of acetic acid. *Food Hydrocolloids*, 51, 375–382.
- Maki, K. C., Pelkman, C. L., Finocchiaro, E. T., Kelley, K. M., Lawless, A. L., Schild, A. L., et al. (2012). Resistant starch from high-amylose maize increases insulin sensitivity in overweight and obese men. *The Journal of Nutrition*, 142(4), 717–723.
- Marta, H., Wijaya, C., Sukri, N., Cahyana, Y., & Mohammad, M. (2022). A comprehensive study on starch nanoparticle potential as a reinforcing material in bioplastic. *Polymers*, 14(22).
- Matencio, A., Navarro-Orcajada, S., García-Carmona, F., & López-Nicolás, J. M. (2020). Applications of cyclodextrins in food science: A review. *Trends in Food Science & Technology*, 104, 132–143.
- Meng, T., Zhou, X., Li, J., Chang, Q., Zhao, J., & Jin, Z. (2019). Study on preparation of instant whole wheat powder by extruding with alcohol and water. Sciencepaper Online <http://www.paper.edu.cn/releasepaper/content/201912-4>.
- Nakorn, K. N., Tongdang, T., & Sirivongpaisal, P. (2009). Crystallinity and rheological properties of pregelatinized rice starches differing in amylose content. *Starch Staerke*, 61(2), 101–108.
- Oates, C. G. (1998). Towards an understanding of starch granule structure and hydrolysis. *Trends in Food Science & Technology*, 8(11), 375–382.
- Pitcher, E., Rourke, J. D. O., & Joseph, T. H. (1981). *Process for cooking or gelatinizing materials*. U.S. Patent, Article 4280851.
- Putaux, J. L., Nishiyama, Y., Mazeau, K., Morin, M., Cardoso, M. B., & Chanzy, H. (2011). Helical conformation in crystalline inclusion complexes of V-amylose: A historical perspective. *Macromolecular Symposia*, 303(1), 1–9.
- Putseys, J. A., Lamberts, L., & Delcour, J. A. (2010). Amylose-inclusion complexes: Formation, identity and physico-chemical properties. *Journal of Cereal Science*, 51(3), 238–247.
- Qian, S.-Y., Tang, M.-Q., Gao, Q., Wang, X.-W., Zhang, J.-W., Tanokura, M., et al. (2019). Effects of different modification methods on the physicochemical and rheological properties of Chinese yam (*Dioscorea opposita* Thunb.) starch. *LWT - Food Science and Technology*, 116, Article 108513.
- Qin, Y., Liu, C., Jiang, S., Xiong, L., & Sun, Q. (2016). Characterization of starch nanoparticles prepared by nanoprecipitation: Influence of amylose content and starch type. *Industrial Crops and Products*, 87, 182–190.
- Qin, Y., Wang, J., Qiu, C., Hu, Y., Xu, X., & Jin, Z. (2019). Effects of degree of polymerization on size, crystal structure, and digestibility of debranched starch nanoparticles and their enhanced antioxidant and antibacterial activities of curcumin. *ACS Sustainable Chemistry & Engineering*, 7(9), 8499–8511.
- Qiu, C., Qin, Y., Zhang, S., Xiong, L., & Sun, Q. (2016). A comparative study of size-controlled worm-like amylopectin nanoparticles and spherical amylose nanoparticles, their characteristics and the adsorption properties of polyphenols. *Food Chemistry*, 213, 579–587.
- Qiu, C., Yang, J., Ge, S., Chang, R., Xiong, L., & Sun, Q. (2016). Preparation and characterization of size-controlled starch nanoparticles based on short linear chains from debranched waxy corn starch. *LWT-Food Science & Technology*, 74, 303–310.
- Rajagopalan, S., & Seib, P. A. (1992a). Granular cold-water-soluble starches prepared at atmospheric pressure. *Journal of Cereal Science*, 16, 13–28.
- Rajagopalan, S., & Seib, P. A. (1992b). Properties of granular cold-water-soluble starches prepared at atmospheric pressure. *Journal of Cereal Science*, 16, 29–40.
- Robertson, M. D., Bickerton, A. S., Dennis, A. L., Vidal, H., & Frayn, K. N. (2005). Insulin-sensitizing effects of dietary resistant starch and effects on skeletal muscle and adipose tissue metabolism. *American Journal of Clinical Nutrition*, 82, 559–567.
- Sang, S., Chen, Y., Zhu, X., Narsimhan, G., Hu, Q., Jin, Z., et al. (2019). Effect of egg yolk lipids on structure and properties of wheat starch in steamed bread. *Journal of Cereal Science*, 86, 77–85.
- Sarifudin, A., Keeratiburana, T., Soontaranon, S., Tangsathitkulchai, C., & Tongta, S. (2020). Pore characteristics and structural properties of ethanol-treated starch in relation to water absorption capacity. *LWT - Food Science and Technology*, 129, Article 109555.
- Sarifudin, A., Soontaranon, S., Peerapattana, J., & Tongta, S. (2020). Mechanical strength, structural and hydration properties of ethanol-treated starch tablets and their impact on the release of active ingredients. *International Journal of Biological Macromolecules*, 149, 541–551.
- Sarifudin, A., Soontaranon, S., Rugmai, S., & Tongta, S. (2019). Structural transformations at different organizational levels of ethanol-treated starch during heating. *International Journal of Biological Macromolecules*, 132, 1131–1139.
- Sarko, A., & Wu, H.-C. H. (1978). The crystal structures of A-, B- and C-polymorphs of amylose and starch. *Starch Staerke*, 30, 73–78.
- Shi, L., Fu, X., Huang, Q., & Zhang, B. (2017). Single helix in V-type starch carrier determines the encapsulation capacity of ethylene. *Carbohydrate Polymers*, 174, 798–803.
- Shi, L., Fu, X., Tan, C. P., Huang, Q., & Zhang, B. (2017). Encapsulation of ethylene gas into granular cold-water-soluble starch: Structure and release kinetics. *Journal of Agricultural and Food Chemistry*, 65(10), 2189–2197.
- Shi, L., Hopfer, H., Ziegler, G. R., & Kong, L. (2019). Starch-menthol inclusion complex: Structure and release kinetics. *Food Hydrocolloids*, 97, Article 105183.
- Shi, L., Li, Z., Guo, J., Kong, L., Ren, Z., & Weng, W. (2022). Encapsulation and release kinetics of ethylene into “pre-formed” V-type starch and granular cold-water soluble starch. *Carbohydrate Polymers*, 287, Article 119360.

- Shi, L., Li, Z., Yang, Z., Ren, Z., Zhang, Y., & Weng, W. (2024). Adsorption characteristics of V-type starch for off-odors of sea cucumber intestinal peptides in solid-phase environment. *Food Chemistry*, 433, Article 137171.
- Shi, L., Zhang, B., Li, C., Fu, X., & Huang, Q. (2019). Annealing improves the concentration and controlled release of encapsulated ethylene in V-type starch. *International Journal of Biological Macromolecules*, 141, 947–954.
- Shi, L., Zhong, L., Zhang, B., Fu, X., & Huang, Q. (2020). Encapsulation and release characteristics of ethylene gas from V6- and V7-type crystalline starches. *International Journal of Biological Macromolecules*, 156, 10–17.
- Shi, L., Zhou, J., Guo, J., Gladden, I., & Kong, L. (2021). Starch inclusion complex for the encapsulation and controlled release of bioactive guest compounds. *Carbohydrate Polymers*, 274, Article 118596.
- Singh, J., & Singh, N. (2003). Studies on the morphological and rheological properties of granular cold water soluble corn and potato starch. *Food Hydrocolloids*, 17, 63–72.
- Song, M. R., Choi, S. H., Kim, H. S., Kim, B. Y., & Baik, M. Y. (2015). Efficiency of high hydrostatic pressure in preparing amorphous granular starches. *Starch Staerke*, 67 (9–10), 790–801.
- Sudheesh, C., Sunooj, K. V., Navaf, M., Akhila, P. P., Aaliya, B., Mounir, S., et al. (2023). An efficient approach for improving granular cold water soluble starch properties using energetic neutral atoms treatment and NaOH/urea solution. *Food Hydrocolloids*, 141, Article 108723.
- Sun, Y., Jia, X., Tan, C. P., Zhang, B., Fu, X., & Huang, Q. (2023). High hydrostatic pressure (HHP) reinforces solid encapsulation of d-limonene into V-type starch and its application in strawberry storage. *International Journal of Biological Macromolecules*, 235, Article 123886.
- Sun, Y., Li, F., Luan, Y., Li, P., Dong, X., Chen, M., et al. (2021). Gelatinization, pasting, and rheological properties of pea starch in alcohol solution. *Food Hydrocolloids*, 112, Article 106331.
- Wang, Y., Chen, L., Yang, T., Ma, Y., McClements, D. J., Ren, F., ... Jin, Z. (2021). A review of structural transformations and properties changes in starch during thermal processing of foods. *Food Hydrocolloids*, 113, Article 106543.
- Wang, Y., & Zhang, G. (2021). The preparation of modified nano-starch and its application in food industry. *Food Research International*, 140, Article 110009.
- Xi, W., Liu, P., Ling, J., Xian, D., Wu, L., Yuan, Y., et al. (2024). Pre-gelatinized high-amylose starch enables easy preparation of flexible and antimicrobial composite films for fresh fruit preservation. *International Journal of Biological Macromolecules*, 254.
- Xu, Y., Chen, X., Xu, X., Wang, B., Du, X., & Chen, P. (2020). Investigation on morphological structure and crystal transition of maize starch gelatinized in pure glycerol. *Journal of Cereal Science*, 92, Article 102924.
- Yan, X., Wei, H., Kou, L., Ren, L., & Zhou, J. (2021). Acid hydrolysis of amylose granules and effect of molecular weight on properties of ethanol precipitated amylose nanoparticles. *Carbohydrate Polymers*, 252, Article 117243.
- Yu, M., Ji, N., Wang, Y., Dai, L., Chengzhen, L., & Sun, Q. (2020). Starch-based nanoparticles Stimuli responsiveness, toxicity, and interactions with food components. *Comprehensive Reviews in Food Science and Food Safety*, 20(1), 1075–1100.
- Yu, Y., Wang, Y., Wang, Y., Lin, D., Li, X., & Liu, J. (2018). Preparation and properties of granular cold-water-soluble maize starch by ultrasonic-assisted alcoholic-alkaline treatment. *Starch Staerke*, 70(11–12), Article 1700354.
- Zabar, S., Azadmard-Damirchi, S., Yousefi, G., & Hosseini, S. M. H. (2020). Effect of different alcoholic-alkaline treatments on physical and mucoadhesive properties of tapioca starch. *International Journal of Biological Macromolecules*, 153, 1005–1015.
- Zehra, N., Ali, T. M., & Hasnain, A. (2020). Comparative study on citric acid modified instant starches (alcoholic treated) isolated from white sorghum and corn grains. *International Journal of Biological Macromolecules*, 150, 1331–1341.
- Zehra, N., Ali, T. M., & Hasnain, A. (2021). Combined effects of hydroxypropylation and alcoholic alkaline treatment on structural, functional and rheological characteristics of sorghum and corn starch. *International Journal of Biological Macromolecules*, 174, 22–31.
- Zhang, L., Cai, W., Shan, J., Zhang, S., & Dong, F. (2014). Physical properties and loading capacity of gelatinized granular starches. *Industrial Crops and Products*, 53, 323–329.
- Zhang, B., Dhital, S., Haque, E., & Gidley, M. J. (2012). Preparation and characterization of gelatinized granular starches from aqueous ethanol treatments. *Carbohydrate Polymers*, 90(4), 1587–1594.
- Zhang, S., Zhao, K., Xu, F., Chen, X., Zhu, K., Zhang, Y., et al. (2023). Study of unripe and inferior banana flours pre-gelatinized by four different physical methods. *Frontiers in Nutrition*, 10.
- Zhou, X., Chang, Q., Li, J., Jiang, L., Xing, Y., & Jin, Z. (2021). Preparation of V-type porous starch by amylase hydrolysis of V-type granular starch in aqueous ethanol solution. *International Journal of Biological Macromolecules*, 183, 890–897.
- Zhou, J., Guo, J., Gladden, I., Contreras, A., & Kong, L. (2022). Complexation ability and physicochemical properties of starch inclusion complexes with C18 fatty acids. *Food Hydrocolloids*, 123, Article 107175.
- Zhou, X., He, S., & Jin, Z. (2024). Impact of amylose content on the formation of V-type granular starch. *Food Hydrocolloids*, 146, Article 109257.
- Zhou, J., & Kong, L. (2023a). Complexation with pre-formed "empty" V-type starch for encapsulation of aroma compounds. *Food Science and Human Wellness*, 12, 488–493.
- Zhou, J., & Kong, L. (2023b). Encapsulation and retention profile of thymol in the preformed "empty" V-type starch inclusion complex. *Food Frontiers*, 4(2), 902–910.
- Zhou, X., Xing, Y., Meng, T., Li, J., Chang, Q., Zhao, J., et al. (2021). Preparation of V-type cold water-swelling starch by ethanolic extrusion. *Carbohydrate Polymers*, 271, Article 118400.
- Zhu, J., Bai, Y., & Gilbert, R. G. (2023). Effects of the molecular structure of starch in foods on human health. *Foods*, 12(11).
- Zhu, B., Cao, X., Liu, J., & Gao, W. (2018). Effects of different drying methods on physicochemical and sizing properties of granular cold water swelling starch. *Textile Research Journal*, 89(5), 762–770.
- Zhu, B., Liu, J., & Gao, W. (2017). Process optimization of ultrasound-assisted alcoholic-alkaline treatment for granular cold water swelling starches. *Ultrasonics Sonochemistry*, 38, 579–584.
- Zhu, B., Wu, S., Liu, J., & Gao, W. (2017). Optimization of an alcoholic-alkaline freeze-drying treatment for granular cold-water swelling starches. *Starch Staerke*, 69(5–6).