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REVIEW ARTICLE

An Insight into the Gelatinization Properties Influencing the Modified Starches Used in Food Industry: A review

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Abstract

Native starch is subjected to various forms of modification to improve its structural, mechanical, and thermal properties for wider applications in the food industry. Physical, chemical, and dual modifications have a substantial effect on the gelatinization properties of starch. Consequently, this review explores and compares the different methods of starch modification applicable in the food industry and their effect on the gelatinization properties such as onset temperature (T_o), peak gelatinization temperature (T_p), end set temperature (T_c), and gelatinization enthalpy (ΔH), studied using differential scanning calorimetry (DSC). Chemical modifications including acetylation and acid hydrolysis decrease the gelatinization temperature of starch whereas cross-linking and oxidation result in increased gelatinization temperatures. Common physical modifications such as heat moisture treatment and annealing also increase the gelatinization temperature. The gelatinization properties of modified starch can be applied for the improvement of food products such as ready-to-eat, easily heated or frozen food, or food products with longer shelf life.

Keywords Starch · Modified starch · Differential scanning calorimetry · Gelatinization

Introduction

Starch is a widely available, biodegradable natural, and hydrophilic polymeric carbohydrate derived from plants. Major sources of starch include cereals, roots, tubers, and legumes, which contain nearly 70% of starch by dry weight (Alcázar-Alay & Meireles, 2015; Wang et al., 2020). Starch has two polysaccharide components — amylose (15–30%) and amylopectin (70–85%) (Wang et al., 2020). The ratio of amylose and amylopectin in starch differs based on their botanical source. Amylose is a linear chain of α-D-glucose linked by α (1–4) glycosidic linkage whereas, in amylopectin, glucose units are linked linearly with α (1–4) glycosidic linkage, but branching occurs by α (1–6) glycosidic linkage frequently at 24 to 30 glucose units. Internally, starch granules are composed of alternating semi-crystalline (amylopectin) and amorphous (amylose) rings, which are referred to as growth rings. These rings are about 100–400 nm thick. Starch has several applications in various industries including the textile, pharmaceutical, and food industries. In the food industry, starch is either used in unprocessed native form (extracted from the plant) or in processed/modified form (Mathobo et al., 2021; Ulbrich & Flöter, 2019; Wang et al., 2019a, b, c). Unprocessed or raw native starches are not widely used in advanced food industries. This is because they possess low thermal and shear resistance, and higher retrogradation tendency which is the main reason behind the staling of food products (Wang et al., 2019a, b, c). To overcome these liabilities, starch modification is an obligation to alter its physicochemical properties based on the requirement. Starch modifications may be of different types like chemical, physical, or dual modifications (Dai et al., 2020). The chemical modification alters the physiochemical properties of starch by introducing new chemical or functional groups in starch without altering the shape and

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size of starch granules. Physical modifications change the morphology and structure of starch influenced by physical factors such as moisture, temperature, pressure, pH change, radiation treatment, and ultrasonic treatment. Dual modification is when starch is modified using two different methods. Compared with physical modifications, chemical methods provide more options for the functionalization of starch and therefore broaden the application field significantly. However, those treatments can be harmful to the environment (Fan & Picchioni, 2020). Modified starch is widely used in the food industry as a fat replacer, thickener, stabilizer, or textural modifier. Starch is modified by hydrolysis to form a fat replacer such as maltodextrin. It is widely used in low-fat spread, mayonnaise, and ice cream (Chen et al., 2020). Modified starch is also used as a water-soluble gelling agent to stabilize high-shear emulsions such as mayonnaise and salad dressings (Depree & Savage, 2001). Several studies have also been conducted on the use of modified starch to improve the textures of food products. Bread crumbs prepared with phosphorylated cross-linked tapioca starch exhibit a dry texture compared to bread produced from flour substituted with native hydroxypropylated and acetylated tapioca starches (Abbas et al., 2010). The limits of starch modification, use, and labeling are distinctly specified by the US Code of Federal Regulation and its consumption does not usually exhibit any side effects (Abbas et al., 2010). However, a rare case study had reported that acetylated distarch phosphate starch, a modified starch used in some baby foods, leads to diarrhea. In the experiment, 20 normal infants and 21 toddlers aged 8–24 months were fed with formulae that contained 8% native or 8% acetylated distarch phosphate waxy maize starch. The study concluded that acetylated distarch phosphate starch consumption contributed to increased breath hydrogen and loose stools (Lebenthal-Bendor et al., 2001).

Modifications, whether physical, chemical, or dual, end up affecting the gelatinization parameters of starch making it suitable for several purposes that the native starch may be unable to fulfill. When starch is heated with water, intermolecular bonds within the starch molecule are broken, and this phenomenon is known as gelatinization. The process of gelatinization is exceedingly influenced by starch modifications (Shi et al., 2020). Gelatinization is an important phenomenon when it comes to the cooking properties, texture, and palatability of starch-based food products. Starch gelatinization disrupts the molecular orderliness within the granule and results in granular swelling, crystallite melting, loss of birefringence, increase in viscosity, and solubilization. Figure 1A depicts the mechanism of starch gelatinization from various sources in the presence of water and heat. This review elaborates on the applications of various modified starch in food industries and their gelatinization properties studied using differential scanning calorimetry (DSC). Finally, the purpose of this review will contribute to develop specialized modified starch-based food products with specific applications of modification methods including improved texture, better freeze–thaw stability, and reduced syneresis.

Factors Affecting Gelitinization of Starch

The gelatinization property of starches is a very crucial factor in the food industry. The differential scanning calorimetry (DSC) is a very powerful technique to study the effect of modifications on the thermal behavior, gelatinization, and structural organization of starch granules. During gelatinization, DSC measures the degree of disruption of hydrogen bonds within the starch granules and quantifies the heat energy that is represented by enthalpy (Liu et al., 2019). A DSC instrument may be of two types, namely, heat flux DSC and power compensation DSC. In a heat flux DSC, the difference in temperature between the reference and the given sample is measured as a function of temperature. On the other hand, power compensation DSC directly measures the change in enthalpy of the sample as a function of time (Menczel & Kohl, 2020). Figure 1B depicts a commonly used typical heat flux DSC instrument with a gelatinization curve of starch.

Gelatinization is a semi-cooperative or cooperative process in which the starch breaks down in presence of water and heat; first, the amorphous region (amylose) hydrates and swells, straining and tearing away crystalline regions (amylopectin). Gelatinization begins in the amorphous regions since the hydrogen bonds are weaker in this domain. This process is initiated at the hilum of the starch granule and slowly spreads to the periphery. The gelatinization properties depend on the molecular structure of amylopectin and the ratio of amylopectin to amylose (Abbas et al., 2010). Therefore, starch gelatinization is an "order-to-disorder transition" that results in loss of birefringence, increased swelling power, and solubility (Palanisamy et al., 2020). This action of gelatinization stresses the crystallites so that they cooperatively melt at a lower temperature. Structural relationships between the amorphous and crystalline domains of the starch granule are accountable for the peak temperature of gelatinization, and the sharpness of the gelatinization endotherm. Starch gelatinization is obtained as an endotherm as starch granules consume heat energy resulting in disruption of their molecular order. However, the peaks of the endotherm may be up or down, due to the instrument program, depending on the manufacturer. Onset (T_o) and end set/ceasing (T_c) refer to the temperature of onset and ceasing of gelatinization process. The peak temperature of gelatinization (T_p) is defined as the temperature at the peak apex of the gelatinization endotherm of starch. Gelatinization enthalpy (ΔH) shows the loss of molecular organization in the granule

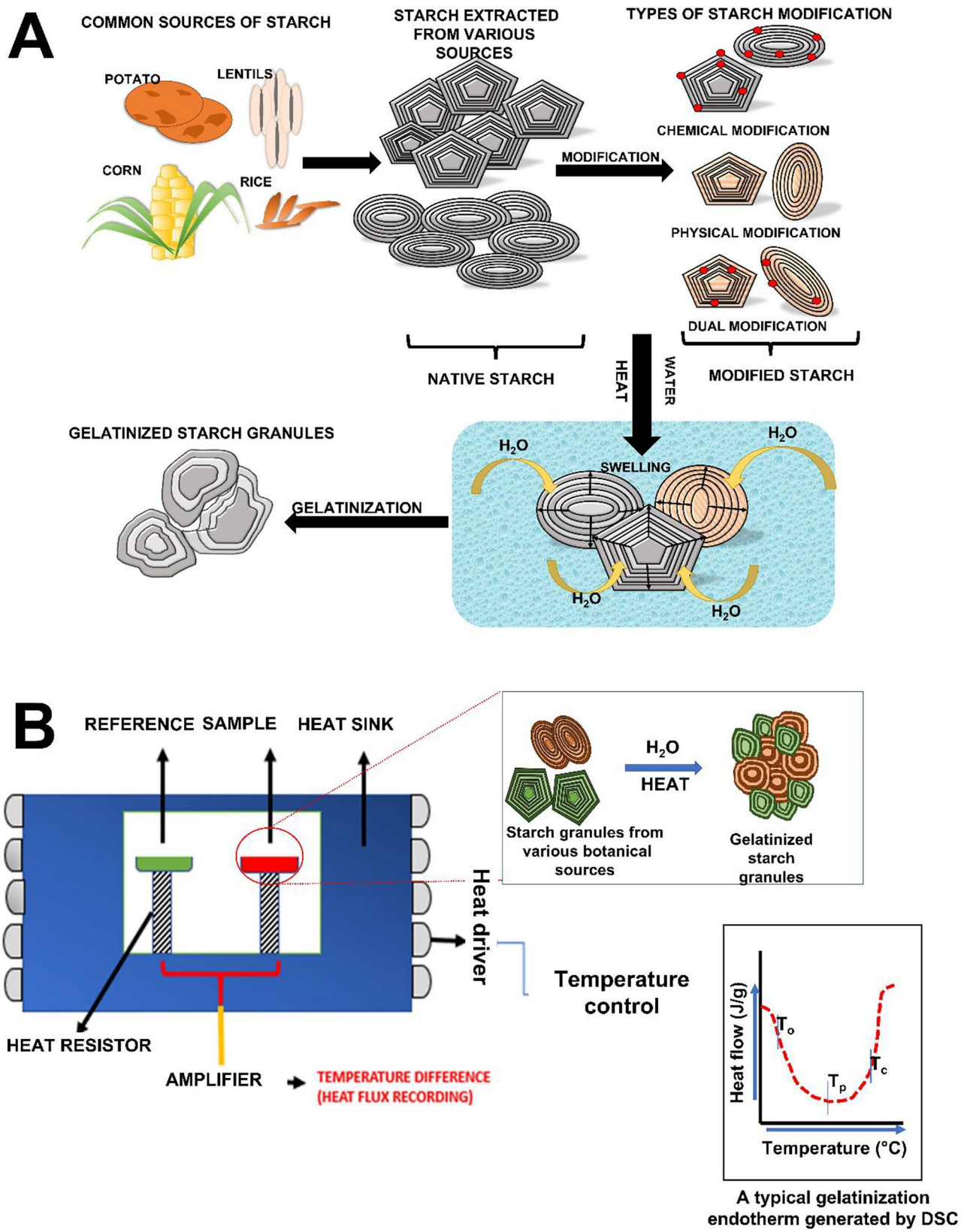

Fig. 1 (**A**) Gelatinization of native and modified starch from various sources in presence of water and heat. (**B**) Working mechanism of a heat flux DSC instrument with typical gelatinization curve of starch

(Alvani et al., 2011). The palatability, structure, and texture of starch-based food are mostly affected by functional properties including starch swelling and gelatinization behavior. Interpreting the mechanisms affecting the gelatinization of the starch is essential for developing food formulations with enhanced nutritional composition, such as sugar reduction and fiber enrichment (Renzetti et al., 2021). The phenomenon of starch gelatinization depends on various factors are discussed in the following.

Variety and Origin of Starch

The gelatinization properties of starch largely depend on various factors such as their botanical origin, amylose–amylopectin ratio, granular shape and size, relative crystallinity, and moisture content (Govindaraju et al., 2020). The most common sources of starch are corn, wheat, rice, sorghum, potato, and barley (Hu et al., 2020). A previous study has reported that changes in gelatinization properties of starch occur primarily based on particle size where smaller starch granules result in decreased thermal stability (Hong et al., 2020). Another study has reported that large granules are gelatinized first at higher temperatures followed by smaller granules at lower temperatures and a broader gelatinization range (Vermeylen et al., 2005). In a recent study, ten indigenous rice varieties from Northeast India were subjected to gelatinization study using DSC. All ten varieties exhibited variations in T_o, T_p, T_c, and ΔH values. These variations were accredited to factors mentioned above including the architecture of the starch granules, amylose–amylopectin content, and crystallinity (Govindaraju et al., 2021). According to Zhu and Liu (2020), the internal molecular structure of amylopectin plays an important role in starch gelatinization and concluded that a more ordered structure of amylopectin in starch results in higher thermal stability and melting enthalpy changes of the starches.

Moisture and Temperature

Moisture content also affects the gelatinization of native starch. In excess water, as temperature rises, the starch crystals melt cooperatively as a single peak at higher gelatinization temperature (T_{p1}). In limited water, starch crystals melt partly, and the remaining crystals produce a second peak at higher temperatures (T_{p2}). A study reported that rice and maize starches displayed gelatinization temperatures ranging between 58.9 and 72.4 °C (rice) and 64.3 and 77.2 °C (maize). Further, starch that has been pre-treated with heat–water will have an increased gelatinization temperature. It was reported that the degree and temperature of gelatinization of 5% (w/w) tapioca, corn, potato, and wheat starch suspensions increased with an increase in treatment temperature in the range between 25 °C (Bauer & Knorr, 2005). Corn starch was treated at specific temperatures ranging between 35 and 90 °C for 30 min. An increase in T_p and ΔH was observed with the increasing temperature of treatment (Jackson & Ratnayake, 2006). Another study revealed that a high-temperature exposure during the rice grain filling stage led to an increase in gelatinization temperatures of rice starch, irrespective of rice genotypes. Studies have reported that the increase in gelatinization temperatures is usually accredited cooperative melting of starch crystallites mediated by water (Liu et al., 2017).

Concentration of Sugar and Salt

Sugar is known to increase the temperature of starch gelatinization (Zhang et al., 2020), (Table 1) since it limits the availability of water to starch. When sugar is placed in water, it binds some of the water and lowers the free water in the system. Research suggests that the chemical nature and concentration of salts can cause either an increase or a decrease in gelatinization temperature and enthalpy of starch. A study reported that the increasing concentrations of NaCl to native potato starch exhibited a rise in gelatinization temperature and a decrease in ΔH (Shi et al., 2019).

Lipid and Protein Content

Starch, lipids, and proteins are three macronutrients in the human diet that provide the body with energy. Lipids and protein content influence starch gelatinization properties. In a study, three rice varieties, namely, high-lipid rice (GZ1), a low apparent amylose content (GZ93), and parent rice (R7954), were employed for thermal characterization using DSC. It was noted that the ΔH value of GZ1 with high lipid content was lower than those of R7954 and GZ93. However, the removal of lipids significantly increased the ΔH value (Zhang et al., 2019a, b, c). Starch and lipids form inclusion complexes or starch–lipid complexes either naturally or during repeated heating and cooling, commonly occurring during food processing. The formation of starch–lipid complexes with the amylose component of starch alters the gelatinization properties of starch. On the other hand, proteins bind to starch molecules, preventing the escape of exudates through the granule surface. The interaction between protein and starch is mainly electrostatic, between the anionic groups of the starch and the positively charged groups of the protein. The protein–starch interactions in bulk solutions and at interfaces have an important influence on the stability properties of food dispersions. This protein–starch interaction results in increased gelatinization temperature of starch. A recent study revealed the effect of starch–protein interactions on the thermal properties of starch using DSC. Obtained results showed that corn starch–whey protein isolate (WPI) blends exhibited delayed gelatinization as the swelling process was restricted. This was accredited to

Table 1 Table comparing the gelatinization properties of native starch to their chemically and physically modified versions from common and conventional botanical sources along with common applications in the food industry

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)	
Chemical modifications							
Corn	Native	Acquired in Colombo/PR-Brazil	66.63	71.74	78.84	9.53	de Siqueira et al. (2017)
	Acid thinning	Modified by HCl (0.1 mol/ L solution)	65.69	71.23	77.46	7.38	
		Modified by HCl (0.5 mol/L solution)	67.37	71.61	77.49	6.66	
Corn	Native	Commercial grade granular corn starch (Maizena) Unilever Bestfoods, Mogi Guaçu, SP, Brazil	66.33	72.44	ND	19.92	Beninca et al. (2008)
	Acid thinning	Hydrochloric acid solution 0.15 mol L^{-1}, 8 h at 30 °C	65.23	69.60	ND	13.41	
Sorghum	Native	Extracted from grains of red sorghum (*Sorghum bicolor*) provided by the company Embrapa Clima Temperado of Pelotas, Rio Grande do Sul, Brazil	66.06	69.68	74.38	8.12	Biduski et al. (2017)
	Acid thinning	Modified by lactic acid (3 g/100 g starch)	67.93	70.58	75.08	9.42	
White sorghum	Native	Extracted from white sorghum grains from a single cultivar Johar (Type I, non-tannin variety) was obtained from Pakistan Agriculture Research Council, Karachi, Pakistan	69.8	73.5	83.2	14.1	Mehboob et al. (2015)
	Acid thinning	Modified by HCl (0.1 M solution)	70.5	73.6	79.8	9.1	
		Modified by HCl (0.5 M solution)	68.9	72.6	78.8	9.3	
		Modified by HCl (1.0 M solution)	70.5	73.9	81.2	9.6	
Porso millet	Native	Extracted from Porso millet flour was purchased from Bob's Red mill (Milwaukie, OR, USA) using alkaline steeping method	72.93	78.61	94.55	3.83	Singh and Adedeji (2017)
	Acid thinning	Modified by HCl (0.14 mol/L solution)	69.71	77.26	96.27	3.97	
African bread fruit kernel	Native	Extracted from unprocessed African breadfruit bought from Afigwe Main Market, Anambra State, Nigeria	79.3	84.7	89.4	14.1	Oderinde et al. (2020)
	Acid thinning	Modified by 0.5 L of HCl (0.15 M solution)	73.7	80.2	87.6	15.7	
Taro (Colocasia esculenta)	Native	Extracted from Taro (Colocasia esculenta) in immature physiological state, harvested in March of 2016 in Tuxtepec, Oaxaca, Mexico	73.33	77.31	84.18	11.07	Rincon-Aguirre et al. (2018)
	Acetylation	Modified by acetic anhydride (2.5 g)	74.60	79.19	84.19	10.37	
Tapioca	Native	Purchased from Zhengde Food 113 Co., Ltd (Shandong, China)	59.8	65.6	74.0	ND	Ren and Wang (2019)
	Acetylation	Purchased from Zhengde Food 113 Co., Ltd. (Shandong, China)	58.3	60.9	67.2	ND	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Chestnut	Native	Extracted from chestnut fruits (Tsukuba cultivar) were purchased from local markets in Hadong, Gyeongsangnam, Korea using alkaline steeping method	59.9	64.7	71.0	12.1	Oh et al. (2019)
	Acetylation	Modified by acetic anhydride (12%)	50.3	57.5	65.6	9.5	
Mung bean	Native	Obtained from mung bean starch was obtained at Hengshuifu Bridge Starch Co., Ltd. (Hengshui, China)	57.37	65.67	72.60	8.61	Zhang et al. (2019a, b, c)
	Acetylation	Modified by 1.00 g acetic anhydride for 48 h	56.13	64.33	72.77	5.60	
African bread fruit kernel	Native	Extracted from unprocessed African breadfruit bought from Afigwe Main Market, Anambra State, Nigeria	79.3	84.7	89.4	14.1	Oderinde et al. (2020)
	Acetylation	Modified by 10.3 g acetic anhydride	76.5	81.9	85.6	11.8	
High amylose corn starch	Native	High-amylose corn starch (amylose content = 69%) purchased from Shandong Huanong Special Corn Development Co. Ltd. (China)	73.6	127.5	194.6	265.7	Min et al. (2017)
	Acetylation	Modified by acetic anhydride	71.1	121.7	186.0	298.1	
Corn	Native	Procured from Xuejing Starch Ltd., Gansu (China)	64.3	72.8	81.8	1.97	Han et al. (2012)
	Acetylation	Modified by acetic anhydride with resulting degree of substitution (DS) 0.133)	54.7	63.3	72.6	1.25	
Pearl millet	Native	Extracted from pearl millet grains (WCA-78), obtained from PARC (Pakistan Agriculture Research Council)	69.6	73.7	87.23	9.86	Shaikh et al. (2017)
	Acetylation	Modified by acetic anhydride (6%, db of starch)	68.7	71.4	75.2	2.5	
Yellow sorghum	Native	Extracted from Yellow sorghum grains from Institute of Agricultural Research Samaru, Zaria, Nigeria, using wet milling procedure	69.69	73.41	79.78	1.69	Olayinka et al. (2015)
	Acetylation	Modified by 10.2 g acetic anhydride	69.63	73.32	76.56	1.60	
Rice	Native	Extracted from Rice flour was purchased from Nongshim Co., Ltd. (Seoul, Korea) using alkaline steeping method	59.56	64.89	71.53	1.59	Kim et al. (2017)
	Cross-linking	Modified by 1% citric acid	58.26	63.10	69.05	1.31	
		Modified by 10% citric acid	ND	ND	ND	ND	
		Modified by 30% citric acid	ND	ND	ND	ND	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Lotus seed	Native	Extracted from Dried lotus seeds were collected from Imphal Market, Manipur, India	44.51	71.56	81.43	7.31	Ali et al. (2020)
	Cross-linking	Modified by 0.2 M citric acid	52.37	87.51	95.23	10.88	
Acha	Native	Extracted from Acha purchased from a local market in Kano, Nigeria using alkaline steeping method	41.56	98.31	128.00	17.22	Alimi and Workneh (2018)
	Cross-linking	Modified by citric acid (15% of weight of dry starch)	52.23	88.85	128.00	9.60	
Iburu	Native	Extracted from Iburu purchased from a local market in Kano, Nigeria, using alkaline steeping method	56.34	84.38	104.46	17.79	
	Cross-linking	Modified by citric acid (15% of weight of dry starch)	49.72	90.10	130.02	12.70	
Chestnut	Native	Extracted from Chestnut fruits (Tsukuba cultivar) were purchased from local markets in Hadong, Gyeongsangnam, Korea using alkaline steeping method	59.9	64.7	71.0	12.1	Oh et al. (2019)
	Cross-linking	Modified by sodium trimetaphosphate (STMP), and sodium tripolyphosphate (STPP)	58.5	63.6	69.5	12.5	
Corn	Native	Obtained from Dacheng Corn Development Co. Ltd (Changchun, Jilin, China)	52.30	82.06	103.29	400.01	Zuo et al. (2017)
	Oxidation	2.94 g of sodium periodate in distilled water	56.81	86.45	96.56	317.04	
Corn	Native	Produced by Roquette (Lestrem, France)	64.6	71.1	77.8	9.86	Pietrzyk et al. (2012)
	Oxidation	Modified by NaClO in amounts equivalent to 10 g Cl per kg of starch	63.8	70.8	77.2	8.26	
		Modified by NaClO in amounts equivalent to 20 g Cl per kg of starch	63.2	70.8	78.4	6.39	
		Modified by NaClO in amounts equivalent to 30 g Cl per kg of starch	62.8	70.2	77.5	8.05	
Sorghum	Native	Extracted from grains of red sorghum (Sorghum bicolor) provided by the company Embrapa Clima Temperado of Pelotas, Rio Grande do Sul, Brazil	66.06	69.68	74.38	8.12	Biduski et al. (2017)
	Oxidation	Modified by sodium hypochlorite (1.5 g active chlorine/100 g starch)	67.93	71.03	75.50	9.47	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
African bread fruit kernel	Native	Extracted from unprocessed African breadfruit bought from Afigwe Main Market, Anambra State, Nigeria	79.3	84.7	89.4	14.1	Oderinde et al. (2020)
	Oxidization	Modified by 8% w/ v NaOH. NaOCl (10 g, 4% w/w active chlorine)	74.3	82.4	83.8	12.9	
Potato	Native	Potato starch "Superior" produced by PEPEES S.A. (Łomza, Poland)	61.1	66.1	75.7	17.0	Pietrzyk et al. (2012)
	Oxidization	Modified in an acid environment, by hydrogen peroxide alone and with the addition of Cu(II) ions (as CuSO4 5H2O) at 0.1 g/100 g d.m. starch	64.3	68.7	75.5	14.6	
		Modified in an acid environment, by hydrogen peroxide alone and with the addition of Cu(II) ions (as CuSO4 5H2O) at 0.2 g/100 g d.m. starch	63.8	67.5	76.7	17.6	
		Modified in an acid environment, by hydrogen peroxide alone and with the addition of Cu(II) ions (as CuSO4 5H2O) at 0.3 g/100 g d.m. starch	63.0	67.2	73.4	15.5	
Pearl millet	Native	Extracted from pearl millet grains (WCA-78), obtained from PARC (Pakistan Agriculture Research Council)	69.6	73.7	87.23	9.86	Shaikh et al. (2017)
	Oxidization	Modified by 10 g of NaOCl for 30 min	67.5	71.8	77.4	7.8	
Physical modifications							
Breadfruit	Native	Extracted from breadfruit was purchased from a local market in Owerri, Imo State, Nigeria	59.86	142.81	150.67	1332.18	Okunlola and Adewusi (2019)
	Pre/partially gelatinized	Modified by heating starch suspension at 100 °C with constant stirring for 45 min followed by drying at 50 °C for 48 h	61.60	144.77	152.58	1686.12	
Porso millet	Native	Extracted from Porso millet flour was purchased from Bob's Red mill (Milwaukie, OR, USA) using alkaline steeping method	72.93	78.61	94.55	3.83	Singh and Adedeji (2017)
	HMT	Heated for 3 h at 110 °C, at 30% moisture content	79.13	87.17	99.35	1.95	
Lotus seed	Native	Extracted from Dried lotus seeds were collected from Imphal Market, Manipur, India	44.51	71.56	81.43	7.31	Ali et al. (2020)
	HMT	Heated for 8 h, at 110 °C, at 30% moisture content	57.5	87.26	108.25	16.22	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Acha	Native	Extracted from Acha purchased from a local market in Kano, Nigeria, using alkaline steeping method	41.56	98.31	128.00	17.22	Alimi and Workneh (2018)
	HMT	Heated in hot air circulation oven at 110 °C for 16 h, at 25% moisture	48.32	92.83	129.00	8.81	
Iburu	Native	Extracted from Iburu purchased from a local market in Kano, Nigeria using alkaline steeping method	56.34	84.38	104.46	17.79	
	HMT	Heated in hot air circulation oven at 110 °C for 16 h, at 25% moisture	49.12	92.32	128.2	13.86	
Rice	Native	Extracted from Grains of paddy rice cultivar IRGA-424 from the firm Cooplantio, Pelotas RS Brazil	56.43	62.38	68.42	9.13	Arns et al. (2015)
	HMT	Heated for 120 °C for 10 min, at 13% moisture content	57.68	63.55	69.86	6.10	
		Heated for 120 °C for 30 min, at 13% moisture content	56.55	65.99	71.37	7.11	
		Heated for 120 °C for 60 min, at 13% moisture content	56.40	68.26	72.37	6.47	
Sweet potato	Native	Provided by Hunan Xiang Feng Potato Industry, China	69.10	79.04	86.87	10.34	Liao et al. (2019)
	Hear moisture treatment (HMT)	Heated in a dry oven at 105 °C for 1 h at 26% moisture content	72.41	81.50	88.86	11.37	
		Heated in a dry oven at 10 5 °C for 1 h at 30% moisture content	74.06	84.97	90.27	10.74	
		Heated in a dry oven at 105 °C for 1 h at 34% moisture content	74.78	86.27	90.53	10.44	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Potato	Native	Purchased from Dongsheng Starch Co., Ltd., Lin Zhao, Gansu province, China, with 28.59% of amylose	61.49	65.53	75.05	16.70	Xu et al. (2018)
	Annealing	Modified by repeated annealing with a gap of 30 min at room temperature after each annealing cycle of 12 h, for 24 h at 55 °C	68.02	70.73	79.67	17.29	
		Modified by repeated annealing with a gap of 30 min at room temperature after each annealing cycle of 12 h, for 48 h at 55 °C	69.79	72.28	80.27	17.80	
		Modified by repeated annealing with a gap of 30 min at room temperature after each annealing cycle of 12 h, for 72 h at 55 °C	70.99	73.43	82.78	18.06	
		Modified by repeated annealing with a gap of 30 min at room temperature after each annealing cycles of 12 h, for 96 h at 55 °C	71.38	73.92	84.70	18.4	
		Modified by continuous annealing at 55 °C for 24 h	68.64	71.36	80.93	17.77	
		Modified by continuous annealing at 55 °C for 48 h	69.44	71.85	80.19	18.06	
		Modified by continuous annealing at 55 °C for 72 h	70.42	72.99	82.14	18.06	
		Modified by continuous annealing at 55 °C for 96 h	71.14	73.18	82.37	18.45	
Pea	Native	Obtained from Emsland-Starke Group—Food Division, Germany, with 33% of amylose	53.61	58.79	62.78	3.75	Leite et al. (2017)
	High hydrostatic pressure (HHP) treatment	600 MPa/15 min/25 °C	53.73	58.34	62.08	2.57	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Waxy wheat	Native	Obtained from Yangzhou Academy of Agricultural Sciences, China	61.17	64.87	71.19	13.48	Hu et al. (2017)
	High hydrostatic pressure (HHP) treatment	Modified with HHP of 300 MPa at 20 °C for 30 min, followed by retrogradation at 4 °C for 4 days	60.86	64.50	74.03	13.17	
		Modified with HHP of 400 MPa at 20 °C for 30 min, followed by retrogradation at 4 °C for 4 days	61.36	65.27	72.73	11.37	
		Modified with HHP of 500 MPa at 20 °C for 30 min, followed by retrogradation at 4 °C for 4 days	45.51	55.47	65.46	19.96	
		Modified with HHP of 600 MPa at 20 °C for 30 min, followed by retrogradation at 4 °C for 4 days	45.34	53.70	62.57	2.81	
Waxy rice	Native	Purchased from Jiangsu Baobao Group (Nantong, China)	70.2	75.0	82.0	12.4	Zeng et al. (2018)
	High hydrostatic pressure (HHP) treatment	Modified with HHP of 100 MPa at room temperature (25 °C) for 20 min	71.8	75.5	81.3	12.3	
		Modified with HHP of 200 MPa at room temperature (25 °C) for 20 min	72.5	76.3	81.8	10.6	
		Modified with HHP of 300 MPa at room temperature (25 °C) for 20 min	75.6	79.3	83.2	9.3	
		Modified with HHP of 400 MPa at room temperature (25 °C) for 20 min	77.7	81.5	85.6	6.4	
		Modified with HHP of 500 MPa at room temperature (25 °C) for 20 min	75.3	79.2	82.9	5.2	
		Modified with HHP of 600 MPa at room temperature (25 °C) for 20 min	ND	ND	ND	ND	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Rice	Native	Purchased from Sigma Co. (St. Louis, MO, USA)	64.19	71.82	ND	11.79	Du et al. (2019)
	High hydrostatic pressure (HHP) treatment	Modified in an excess water using 10% (w/w) starch–water suspensions with 0% tea polyphenol (based on the starch weight) 200 MPa at room temperature for 30 min	63.54	71.08	ND	11.23	
		Modified in an excess water using 10% (w/w) starch–water suspensions with 5% tea polyphenol (based on the starch weight) 200 MPa at room temperature for 30 min	60.76	70.33	ND	10.17	
		Modified in an excess water using 10% (w/w) starch–water suspensions with 10% tea polyphenol (based on the starch weight) 200 MPa at room temperature for 30 min	57.11	64.89	ND	5.93	
		Modified in an excess water using 10% (w/w) starch–water suspensions with 30% tea polyphenol (based on the starch weight) 200 MPa at room temperature for 30 min	53.67	64.93	ND	4.94	
		Modified in an excess water using 10% (w/w) starch–water suspensions with 0% tea polyphenol (based on the starch weight) 600 MPa at room temperature for 30 min	ND	ND	ND	ND	
		Modified in an excess water using 10% (w/w) starch–water suspensions with 5% tea polyphenol (based on the starch weight) 600 MPa at room temperature for 30 min	ND	ND	ND	ND	
		Modified in an excess water using 10% (w/w) starch–water suspensions with 10% tea polyphenol (based on the starch weight) 600 MPa at room temperature for 30 min	ND	ND	ND	ND	
		Modified in an excess water using 10% (w/w) starch–water suspensions with 30% tea polyphenol (based on the starch weight) 600 MPa at room temperature for 30 min	ND	ND	ND	ND	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Cassava	Native	Commercial grade (Yoki – lot. MT-55)	58.77	64.57	69.56	10.88	Colman et al. (2014)
	Microwave treated	Heated in a conventional microwave oven at 150 °C for 5 min	55.78	64.63	66.98	11.45	
		Heated in a conventional microwave oven at 150 °C for 10 min	52.20	62.26	66.67	13.25	
		Heated in a conventional microwave oven at 150 °C for 15 min	51.36	59.45	64.46	9.14	
Cassava	Native	Purchased from Guangxi Mingyang biochemical technology co., Ltd., China	64.8	70.5	79.1	12.9	Zhang et al. (2020)
	Microwave treated	2 g of cassava starch (dry base) treated at 300 W microwave oven for 1.5 min	65.2	69.5	77.3	10.7	
		2 g of cassava starch (dry base) and 2 g (1 equ.) of sucrose mixed treated at 300 W microwave oven for 1.5 min	78.1	82.2	88.3	10.9	
		2 g of cassava starch (dry base) and 2 g (1 equ.) of glucose mixed treated at 300 W microwave oven for 1.5 min	74.0	78.5	85.1	10.1	
		2 g of cassava starch (dry base) and 2 g (1 equ.) of trehalose mixed treated at 300 W microwave oven for 1.5 min	77.2	80.2	83.7	9.0	
Maize	Native	Maize flour was procured from Adpan Europe S.L. (Asturias, Spain)	66.6	74.0	77.3	−2.819	Román et al. (2015)
	Microwave treated	400 W (intermediate continuous power) for 4 min	69.6	75.2	80.4	−5.645	
Millet	Native	Extracted from Millet grain (Long Gu 25) was obtained from the Liaoning Academy of Agricultural Sciences (Liaoning, China)	71.25	78.26	82.44	8.48	Li et al. (2019)
	Microwave treated	Heated by microwave for 30 s, at 30% moisture content	76.32	79.96	85.95	1.93	
		Heated by microwave for 60 s, at 30% moisture content	ND	ND	ND	ND	
		Heated by microwave for 90 s, at 30% moisture content	ND	ND	ND	ND	
		Heated by microwave for 120 s, at 30% moisture content	ND	ND	ND	ND	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Corn	Native	Purchased from Aoboxing Biotechnology Co., Ltd. (Beijing, China)	51.6	61.3	65.2	14.8	Wang et al. (2019a, b, c)
	Microwave treated	Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 8 h	ND	ND	ND	ND	
		Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 24 h	43.1	52.9	55.8	6.2	
		Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 72 h	45.3	55.8	57.3	8.7	
Potato	Native	Purchased from Aoboxing Biotechnology Co., Ltd. (Beijing, China)	61.1	65.0	69.0	3.5	
	Microwave treated	Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 8 h	ND	ND	ND	ND	
		Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 24 h	52.2	56.2	58.5	1.2	
		Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 72 h	53.6	58.2	61.3	1.6	
Chestnut	Native	Purchased from Aoboxing Biotechnology Co., Ltd. (Beijing, China)	56.5	60.9	66.8	4.1	
	Microwave treated	Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 8 h	ND	ND	ND	ND	
		Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 24 h	48.6	53.1	56.1	1.5	
		Heated in microwave oven at 2450 MHz and 120 mA for 90 s and stored at 4 °C for 72 h	49.5	54.3	56.5	2.1	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Rice	Native	Purchased from Sigma–Aldrich Chemical Co. (Milwaukee, WI, USA)	62.94	69.82	78.69	8.70	Yang et al. (2019a, b)
	Ultrasonification	Starch slurries were ultrasonicated using an ultrasonic probe processor with a 10-mm ultrasonic horn (single frequency factor at 22 kHz) 20 min in a pulsed mode at 150 W	62.95	69.74	78.25	7.60	
		Starch slurries were ultrasonicated using an ultrasonic probe processor with a 10-mm ultrasonic horn (single frequency factor at 22 kHz) 20 min in a pulsed mode at 300 W	62.91	69.86	76.56	7.21	
		Starch slurries were ultrasonicated using an ultrasonic probe processor with a 10-mm ultrasonic horn (single frequency factor at 22 kHz) 20 min in a pulsed mode at 450 W	63.11	69.19	75.57	7.30	
		Starch slurries were ultrasonicated using an ultrasonic probe processor with a 10-mm ultrasonic horn (single frequency factor at 22 kHz) 20 min in a pulsed mode at 600 W	62.62	69.26	77.15	9.58	
Millet	Native	Extracted from Millet grain (Long Gu 25) was obtained from the Liaoning Academy of Agricultural Sciences (Liaoning, China)	71.25	78.26	82.44	8.48	Li et al. (2019)
	Ultrasonification	Modified in an ultrasonic sink for 15 min at 30% moisture content	71.34	77.41	83.98	10.01	
		Modified in an ultrasonic sink for 30 min 30% moisture content	70.84	77.24	84.82	9.12	
		Modified in an ultrasonic sink for 45 min 30% moisture content	70.81	76.24	83.24	9.02	
		Modified in an ultrasonic sink for 60 min 30% moisture content	70.1	77.69 ±	83.52	8.84	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Corn	Native	Purchased from Sigma-Aldrich (St. Louis, MO, USA)	64.21	65.67	70.67	7.70	Flores-Silva et al. (2017)
	Ultrasonification	Modified with ultrasound (24 kHz) for various times 1 min at 20 °C	64.91	65.64	70.50	7.94	
		Modified with ultrasound (24 kHz) for various times 2 min at 20 °C	64.86	65.91	70.98	8.53	
		Modified with ultrasound (24 kHz) for various times 4 min at 20 °C	65.34	65.52	70.43	8.75	
		Modified with ultrasound (24 kHz) for 8 min at 20 °C	65.26	65.45	70.46	8.64	
		Modified with ultrasound (24 kHz) for 16 min at 20 °C	65.56	65.72	70.48	8.72	
Cassava	Native	Provided by the Cooperativa Agrícola Mixta de Montecarlo (Misiones, Argentina), containing 17% amylose	57.5	65.2	78.8	14.44	Monroy et al. (2018)
	Ultrasonification	Modified with ultrasound at a power of 750 W and 40% amplitude for 5 min	56.9	65.0	76.9	13.58	
		Modified with ultrasound at a power of 750 W and 40% amplitude for 10 min	56.9	65.1	79.5	13.47	
		Modified with ultrasound at a power of 750 W and 40% amplitude for 20 min	58.3	64.5	77.3	13.30	
Quinoa	Native	Flour extracted from quinoa seeds of Peruvian origin purchased from Ceres Organics (Auckland, New Zealand) with 58.4% starch content	67.1	73.2	79.7	10.9	Zhu and Li (2019)
	Ultrasonification	Modified with ultrasound at frequency of 20 kHz, power of 250 W, and pause of 80% for 1.2 h	66.7	72.4	78.9	9.5	
		Modified with ultrasound at frequency of 20 kHz, power of 250 W, and pause of 80% for 2.4 h	66.6	72.3	78.6	10.2	
		Modified with ultrasound at frequency of 20 kHz, power of 250 W, and pause of 80% for 4.8 h	65.6	72.6	79.6	8.9	
		Modified with ultrasound at frequency of 20 kHz, power of 250 W, and pause of 80% for 9.6 h	64.1	71.0	78.9	7.9	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Tapioca	Native	Purchased from Fars Glucosine, Shiraz, Iran, with 18.78% amylose content	61.1	61.9	63.10	14.3	Abedi et al. (2019)
	Ultrasonification	Modified in ultrasonic generator with 20 mm diameter probe (400 W, 24 kHz), maintained at the desired temperature (35–65 °C) by a circulating water bath for 5–15 min	62.6	63.8	66.10	12.22	
		Modified in ultrasonic generator with 10 mm diameter probe (400 W, 24 kHz), maintained at the desired temperature (35–65 °C) by a circulating water bath for 5–15 min	65.9	67.0	71.7	7.8	
Wheat	Native	Purchased from Fars Glucosine, Shiraz, Iran, with 25.3% amylose content	57.6	58.1	60.2	12.1	
	Ultrasonification	Modified in ultrasonic generator with 20 mm diameter probe (400 W, 24 kHz), maintained at the desired temperature (35–65 °C) by a circulating water bath for 5–15 min	58.8	59.4	64.4	9.8	
		Modified in ultrasonic generator with 10 mm diameter probe (400 W, 24 kHz), maintained at the desired temperature (35–65 °C) by a circulating water bath for 5–15 min	64.8	66.4	73.4	5.2	
Dual modifications							
Corn	Native	Obtained from Nacalai Tesque, Inc. (Kyoto, Japan)	66.8	73.5	81.7	7.9	Ariyantoro et al. (2018)
	Heterogeneous (succinylation and annealing)	*Succinylation:* modified by 1 g of sodium carbonate and succinic anhydride for 24 h at room temperature Annealing: 62.5 g starch heated with 125 mL of distilled water at 55 ◦C for 24 h	67.6	74.1	82.6	9.7	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Corn	Native	Purchased from the industrial corn company (IMSA, S.A. de C.V., Mexico)	76.69	80.45	85.46	10.94	Basilio-Cortés et al. (2019)
	Homogenous (acid thinning and succinylation)	*Acid Thinning:* modified by HCl at 5% (300 mL) for approximately 5 h at room temperature Succinylation: modified by succinic anhydride (3% w/w based on the dry weight of starches) for 6 h	60.52	67.09	73.99	9.14	
Waxy maize	Native	Extracted from grains of waxy maize cultivar, Mi-beak 2, were grown at Hongcheon-gun a	66.3	71.4	86.9	14.81	Park et al. (2018)
	Heterogeneous (HMT and cross-linking)	*Cross-linking of heat-moisture treated starch-* HMT waxy maize starch (120 °C for 3 h) was reacted with a 99:1 mixture of STMP/STPP (10%, w/w, sb) and sodium sulfate (10%, w/w, sb)	68.4	72.5	90.2	7.68	
		Heat-moisture treatment of cross-linking starch- 99:1 mixture of STMP/STPP (10%, w/w, sb), cross-linked waxy maize starch was subjected to HMT at 120 °C for 3 h	68.5	72.5	90.8	7.66	
Maize	Native	Purchased from Sigma-Aldrich (St. Louis, MO, USA) with 25.3% amylose content	68.70	73.12	82.20	11.40	Flores-Silva et al. (2018)
	Homogeneous (ultrasonification and HMT)	*Ultrasonification followed by HMT-* *Ultrasonification:* Modified by ultrasound (50 kHz) for various times for 16 min at 20 °C using a titanium Sonotrode H7, type 7 (7-mm-tip diameter), with a maximum width of 175 µm and density acoustic power of 300 W/cm^2 and power 80% *HMT:* Starch with 30% moisture modified by heating at 20 °C for 2 h	65.33	71.96	84.64	7.57	
		HMT followed by ultrasonification- *HMT:* starch with 30% moisture modified by heating at 20 °C for 2 h *Ultrasonification:* Modified by ultrasound (50 kHz) for various times for 16 min at 20 °C using a titanium Sonotrode H7, type 7 (7 mm tip diameter), with a maximum width of 175 µm and density acoustic power of 300 W/cm^2 and power 80%	65.48	73.26	85.21	16.63	

Table 1 (continued)

Botanical origin of starch	Type of modification	Experimental conditions	Gelatinization properties				Reference
			To (°C)	**Tp (°C)**	**Tc (°C)**	**ΔH (J/g)**	
Tapioca	Native	Purchased from SIM Supply Company Sdn. Bhd. (Pulau Penang, Malaysia) with 21% amylose content	63.26	75.39	82.16	14.40	Javadian et al. (2021)
	Homogenous (acid thinning and hydroxypropylation	Acid thinning: modified by 0.14 N HCl at 50 °C for 24 h	53.17	66.61	75.26	8.75	
		Hydroxypropylation: modified by 20% w/v sodium sulfate and 30% propylene oxide for etherification					
Potato	Native	Extracted from unknown cultivar of potatoes purchased from a local market with 32.94% amylose	61.90	66.41	76.65	16.10	Colussi et al. (2020)
	Homogenous (HMT and HHP)	HMT: Modified by heating starch in an oven at 110 °C for 16 h with 25% moisture	64.98	69.11	78.32	3.15	
		HHP: Modified at 600 MPa for 6 cycles of 10 min at 21 °C					

the interference of starch–water interactions during gelatinization due to the presence of protein, therefore showing a significant increase in gelatinization temperature and drop in ΔH (Yang et al., 2019a, b). Starch and protein from cereals, meat, and other sources play key roles in providing the appropriate textural and rheological characteristics in food items (Jamilah et al., 2009).

Starch Modification

To procure appropriate for use in food industries, native starches undergo chemical, physical, or dual modification to get the desired properties such as adhesion, texture, heat tolerance, and solubility. These chemical and physical modifications also affect the gelatinization properties of starch which are discussed in detail in the following section.

Chemical Modification

Chemical modification includes introducing a new functional group into the already existing native starch molecule that results in distinctive changes in its physicochemical properties. Chemical modifications affect characteristics like proximate composition, gelatinization temperature, retrogradation, and pasting characteristics of native starch granules. Major types of chemical modifications used in the food industries include the following.

Acid-Hydrolyzed (Thinned) Starches

Acid-hydrolyzed (thinned) starches are obtained by treatment of starch with mineral acids such as hydrochloric or sulfuric acids resulting in depolymerization of the starch polymer. (de Siqueira et al., 2017). Acid modification is performed to improve the physicochemical properties of starch and eliminate fatty substances associated with native starches. Acid-treated starches exhibit many desired properties such as increased ΔH, reduced tendency to be retrograded and swelling power, and broadened range of gelatinization temperature as well as loss in pasting viscosities (Pratiwi et al., 2018). The acid treatment initially affects the amorphous domain of the starch granule which is more susceptible followed by slowly moving towards the crystalline domain of the starch granule. Acid hydrolysis leads to an increase in short amylose chains and favors the retrogradation of starch that leads to resistant starch formation. Acid affects hydrolysis amorphous domains followed by slow degradation of crystalline regions leading to an increase in the peak gelatinization temperature (T_p). In a recent study, native and hydrochloric acid-modified (0.1 and 0.5 mol L^{-1}) pine seed starch was studied using DSC

and it was concluded that higher acid concentrations promoted crystallinity reduction and loss in the internal structure of the starch granule. However, the gelatinization behavior varied between different genetic varieties (de Siqueira et al., 2019). Another study reported that there is an approximately three-fold reduction in the ΔH of granules, indicating a weakening of granules post-acid hydrolysis modification (Mehfooz et al., 2019). Figure 2A depicts the DSC endotherm of acid-hydrolyzed tapioca starch. Acid-thinned starches are widely used in the manufacture of gelled sweets like gum candies and baked goods. Acid hydrolysis also reduces the tolerance of starches to refrigeration, storage (5 °C), and freeze–thaw cycles (Thys et al., 2013; Ulbrich & Flöter, 2019). To summarize, acid thinning lowers the peak gelatinization temperature of starch and increases the solubility. This is also accompanied by loss of swelling capacity and viscosity.

Acetylation of Starch

During acetylation, the acetyl group replaces the –OH groups of glucose molecules using acetic anhydride and catalysts such as sodium hydroxide**.** During the acetylation process, the hydroxyl groups (–OH) of glucose monomers are converted into CH_3COO (acetyl) groups. Hence, acetylation can be considered as esterification of hydroxyl groups that present an anhydroglucose monomer of the starch molecule (Fitch-Vargas et al., 2019). Acetylated starches serve different purposes depending upon the degree of substitution (Colussi et al., 2017). Acetylation increases the solubility of starch in acetone and chloroform in which native starch is sparingly soluble (Abba et al., 2014). Acetylation introduces hydrophilic acetyl groups in the amorphous domain of the starch granules resulting in a decrease of the onset temperature (T_o), suggesting initial disruption of the order in the starch granules with a temperature rise. This decrease indicates the fact

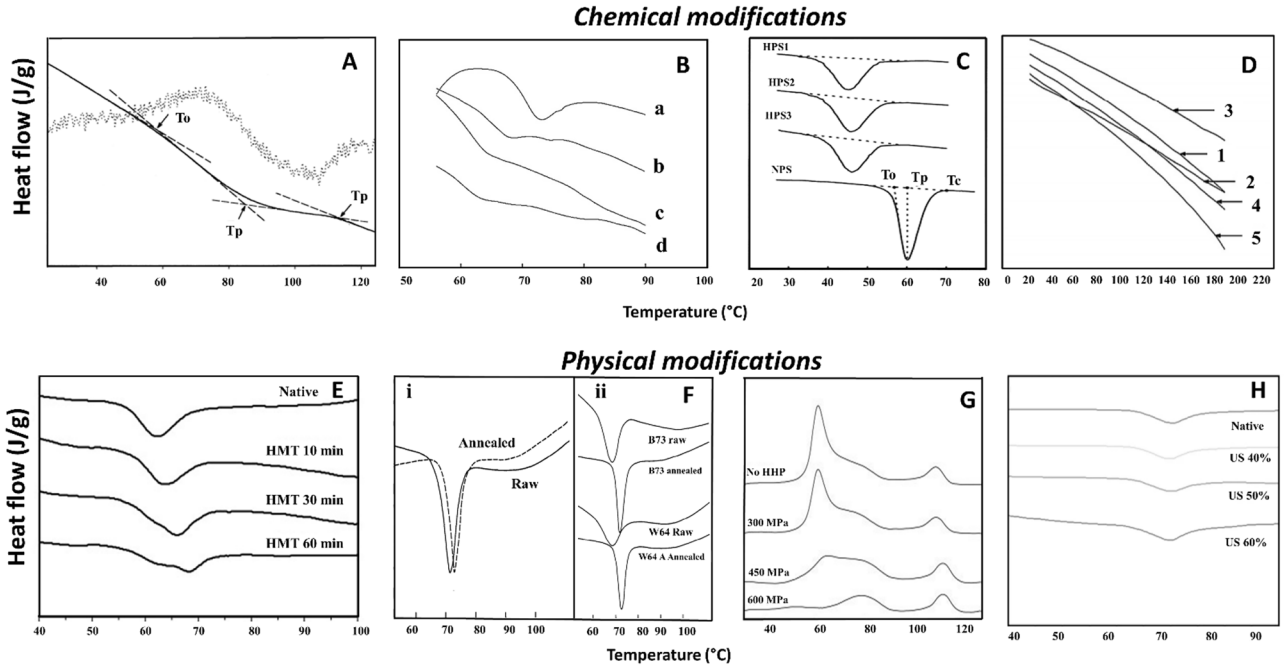

Fig. 2 (**A**) DSC curve of acid-modified tapioca starch and its derivative for measuring temperature. Figure reproduced from Atichokudomchai et al. (2002) with kind permission from John Wiley and Sons. (**B**) The DSC curves of native corn starch (a), acetylated corn starches with a degree of substitution (DS) of 0.071 (b), with a DS of 0.105 (c), with a DS of 0.133 (d). Figure reproduced from Han et al. (2012) with kind permission from Elsevier. (**C**) The heating DSC curves of native and hydroxypropylated phosphate cross-linked potato starch with different degrees of hydroxypropyl substitution and phosphate cross-linking. Figure reproduced from Morikawa et al. (2000) with kind permission from Elsevier. (**D**) DSC curves of the native starch and the oxidized starches with different degrees of oxidation (1) native starch, (2) oxidized starch 5.9%, (3) oxidized starch 19.5%, (4) oxidized starch 40.5%, and (5) oxidized starch 56.3%. The figure is reproduced from Zhang et al. (2012) with kind permission from Elsevier. (**E**) Effect of heat moisture treatment on DSC curves of rice starch for different periods. Figure reproduced from Arns et al. (2015) with kind permission from Elsevier. (**F**) The DSC spectra (i) exhibit typical endothermic thermogram of commercial starch: raw and annealed, (ii) comparison of raw and annealed starches from two varieties of maize, namely, B73 and W64A starches. Annealing conditions were 50 °C for 48 h. The figure was reproduced from Krueger et al. (1987) with kind permission from Wiley. (**G**) DSC thermograms for wheat starch after HHP treatment in 0.1 M NaCl (1:1, w/w) for 15 min at 257 °C. The image was reproduced from Kweon et al. (2008) with kind permission from Wiley. (**H**) DSC curves of native and ultrasonically modified (US) purple taro starch. The figure has been reproduced from Martins et al. (2020) with kind permission from Springer

that the gelatinization of starch is controlled in part by the molecular structure of amylopectin that is affected by any form of chemical modification (Olayinka et al., 2015). While studying the thermal properties of yellow sorghum starch, a similar reduction in ΔH was observed from 1.7 to 1.61 J/g in acetylated starch. The T_o, T_p, and T_c values also decrease with an increasing degree of acetylation (Beninca et al., 2008). In another recent study, the effect of acetylation of hulless barley starch on its thermal properties was studied. They have found a declined T_p with the increased acetylation. The hydrophilic acetyl groups make the starch more susceptible to water leading to early gelatinization (Chang & Lv, 2017). A similar trend was also observed while studying the thermal properties of microwave pre-treated acetylated corn starch with different degrees of substitution. With the increasing degree of acetylation, a downward trend in T_p and ΔH was observed. According to the authors, this decrease of T_p and ΔH in microwave-pre-treated acetylated starch was accredited to the destruction of the amorphous regions in starch molecules, hindering the spatial association of starch molecules, thus promoting improved hydration and easy gelatinization compared to native starch (Lin et al., 2019). Figure 2B depicts the decrease in peak areas with an increasing degree of acetylation. The onset temperature (T_o), peak temperature (T_p), and ceasing temperature (T_c) value also decrease with increasing degree of acetylation. In the food industry, they may act as adhesion, thickening, texturizing, film-forming, stabilizing, and binding agents; plentiful applications in are found in the food industry in baked, frozen, and baby foods (Zia-ud-Din et al., 2017). Acetylated starch is stable at low temperatures and resists retrogradation. It also affects the swelling power and freeze–thaw stability of starches (Abba et al., 2014).

Cross-linking of Starch

Cross-linked starch is obtained by treating native starches using different cross-linking agents like sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin (ECH), and phosphoryl chloride ($POCl_3$). Cross-linking of carboxymethylated starch (CMS) produces hydrogels which can be used in the removal of metal ions from water, as a pharmaceutical gelling agent and emulsion stabilizer, as a tablet disintegrant, or for drug delivery systems (Haq et al., 2019; Wilpiszewska et al., 2019). (Shah et al., 2016). Cross-linking increases resistance to high temperature, high shear, and low pH and further improves the viscosity and texture of starch. It also restricts the swelling of starch granules under cooking conditions and prevents gelatinization (Ayoub & Rizvi, 2009). Cross-linking is often used in the food industry to decrease the retrogradation and gelation of amylose in starch. Cross-linking affects other bonds like hydrogen bonds resulting in resistance to higher temperatures, lower pH, and higher shear compared to native starch. Cross-linked starches exhibit biphasic endotherms with a relatively narrow endotherm compared to native samples. Gelatinization temperatures were found to be significantly increased with increasing degrees of cross-linking. The introduction of cross-linking agents such as phosphate groups strengthens the molecular organization of the starch molecules, thus inhibiting gelatinization and increasing T_p. In a study, the thermal characteristics of glutaraldehyde-cross-linked corn starch were studied using DSC in both acidic and alkaline mediums. T_p of cross-linked starches in the acidic medium increased while ΔH decreased substantially. However, in alkaline medium, both T_p and ΔH decreased compared to the native starch (Gonenc & Us, 2019). In another study conducted on faba bean and field pea, and corn starch was cross-linked using three methods: phosphoryl chloride ($POCl_3$-aqueous), sodium trimetaphosphate/sodium tripolyphosphate (STMP/STPP) (STMP-semidry), and STMP/STPP (STMP-aqueous). Corn starch exhibited the highest T_o, T_p, and T_c compared to faba bean and field pea starch, owing to its characteristic compact crystal arrangement of A-type crystalline cereal starch, compared to C-type crystalline pulse starches. The unique C-type starch crystal structure consists of both A- and B-type polymorphs (Guo et al., 2017). Gelatinization in C type starch granules initiates from B-type polymorphs at the central hilum at a lower temperature due to loose packing and then moves to A-type polymorphs. The lower T_o, T_p, and T_c for native starches indicate low amylopectin contents. Cross-linking increased T_o, T_p, T_c, and ΔH, but the extent of increase in T_o, T_p, and T_c varied with the technique of cross-linking and type of starch. The influence of STMP-semidry on thermal stability was more pronounced in faba bean and field pea starch, while the T_p of corn starch was more influenced more by the $POCl_3$-aqueous method (Dong & Vasanthan, 2020). A study reported that the gelatinization properties of different hydroxy propylated phosphate cross-linked potato starch (HPS) by heating and classified as HSP1, HSP2, and HSP3 based on the degree of hydroxypropyl substitution and phosphate cross-linking. It was observed that the T_p of HPS1, 2, and 3 were about 15 °C lower than that of the native potato starch, but the ΔH did not differ between the three HPS samples. This decrease was due to an increasing degree of hydroxypropylation as the phosphate cross-linking content was almost equal in all three cases (Morikawa & Nishinari, 2000). This is depicted in Fig. 2C. Cross-linked starches are extensively used in the food industry as thickeners and stabilizers and to improve food textures as well as freeze–thaw stability of starch.

Oxidization of Starches

Oxidized starches are obtained by treating them with oxidizing agents such as sodium hypochlorite or hydrogen peroxide, or potassium permanganate. The hydroxyl groups of starch can be subjected to a wide number of reactions for modification like oxidation. The oxidizing agents react with the free hydroxyl group in the monomer (glucose) which results in a carbonyl or carboxyl group. Oxidation of starch results also in the depolymerization of starch molecules by breaking the glycosidic linkages (Moreno et al., 2017). The use of oxidized starch as food additives is increasing in the food industry due to its low viscosity, high stability, and binding properties (Zhang et al., 2012). Oxidation of starch also leads to increased relative crystallinity compared to its native counterpart and shows an increase in gelatinization temperature. It was reported that oxidized white sorghum starch substantially increased the T_o, T_p, and T_c (Mehfooz et al., 2019). In another recent study, the thermal properties of vacuum-assisted oxidized corn, cassava, and canna starches were studied. The ΔH of native starches were the highest followed by oxidized and vacuum-oxidized starches, respectively. This indicated that oxidation partially degrades the crystalline region of the starch granule, and therefore, less energy was required for gelatinization. Vacuum-oxidized corn and canna starches exhibited lower T_o, T_p, and T_c compared to their native counterparts. This reduction was explained by the weakening of starch granules, resulting in the destruction of amylopectin in the crystalline region. However, vacuum-oxidized cassava starch revealed an opposite trend with an increase in T_o, T_p, and T_c compared to its native form. This was explained by depolymerization in the amorphous region of the starch granule and subsequently in the destruction of their destabilizing effect on the crystalline regions, thus resulting in a rise of T_o, T_p, and T_c (Zhang et al., 2018). Figure 2D depicts DSC thermograms of oxidized starches. The oxidized starch is used in the food industry for its exceptional functional properties such as low viscosity, high stability, clarity, film-forming, and binding properties. Oxidized starch is often used for coating, sealing, batter binding, emulsification, and dough conditioning in baking (Matsuguma et al., 2009).

Physical Modification

Physical modification of starch includes alcoholic–alkaline and drum drying methods. These are novel methods for the physical modification of starch. Physically modified starch alters the starch properties including morphology, and functional properties like swelling capacity, water absorption, pasting, and gelatinization, influenced by factors such as temperature, moisture, and pressure. Pre-gelatinization, heat moisture treatment (HMT), and annealing (ANN) are common methods that have found wide applications in the food industry (Lv et al., 2018; Yan & Zhengbiao, 2010). Commonly used physical modifications techniques are-

Pre/Partially Gelatinized Starches

They are pre-cooked starches that are dried using a drum (drum drying) to form a stable suspension that can be dispersed in cold water. Drum drying is an extensively popular method to modify the starch to obtain improved textures and porous structures for better functional properties in different types of industry. For example, partially gelatinized corn starch exhibited peak gelatinization between 64–72 °C which is higher compared to the native starch. According to a study conducted by Li et al. (2020), the addition of pre-gelatinized starch increased the viscosity and improved the texture of a gluten-free dough (Li et al., 2020).

However, a decrease in ΔH was observed when compared to native starch (from 12.97 ± 0.28 to 0.51 ± 0.08 J/g) (Fu et al., 2012). A study was conducted to reveal the effect of partial gelatinization on the physicochemical properties of corn, waxy corn, and wheat starch. The partially gelatinized starches exhibit less ΔH compared to their native counterparts. For native corn, wheat, and waxy corn starch, the T_o increase from 65.5 to 80.3 °C, from 58.1 to 77.9 °C, and from 64.3 to 77.4 °C, respectively. Further, the T_o is also found to increase from 70.6 to 83.9 °C, from 62.4 to 81.6 °C, and from 69.9 to 81.6 °C, respectively, for corn, wheat, and waxy corn starch. The rise in gelatinization temperature indicates the degree of reorganization during partial gelatinization (Hickman et al., 2009). These are widely used in the food industry, as a thickening agent. Pregelatinized starch is used extensively in products such as instant food items for infants, confectionaries, and soups. Pre-gelatinized starch swells rapidly in cold water and resulting in improved viscosity and texture of starch-based food products (Vanier et al., 2019).

Hydrothermal Modification of Starch

Heat–moisture treatment (HMT) and annealing are types of physical modifications involving the heating of starch above glass transition temperatures along with water. Annealing differs from HMT in terms of water content used. Annealing occurs with excess water, whereas the heat–moisture treatment requires less than 35% water. Hydrothermal treatments affect the functional properties of starch which results in better application in starch-based food products (Kaur & Singh, 2019; Schafranski et al., 2021). The hydrothermal

treatment during the gelatinization process especially in the food processing industries is known to cause disorientation of the starch granular organization (Wang et al., 2016). HMT results in a decrease in onset temperature and an increase in T_p due to the strengthening of intramolecular bonds promoted by the HMT indicating better thermal stability (Singh et al., 2005). High temperature during HMT increases the mobility of double helixes that form the crystal structure, leading to breakage of hydrogen bonds decreasing in the ΔH of hydrothermally treated starches when compared to that of native starches (Arns et al., 2015). Figure 2E depicts the effect of HMT on the thermal properties of rice starch. Annealing like HMT increases the onset and peak gelatinization temperature and decreases the ΔH as well as the gelatinization temperature range of starch. Figure 2F exhibits gelatinization endotherms of annealed starch. These changes during annealing are accredited to the structural transformation of the crystalline domain into amorphous domains, providing increased thermodynamic stability and increased peak gelatinization temperature. The decrease in enthalpy with annealing or HMT of starch implies that the molecular order of the treated starch granules had increased. Annealing of starch thus increases granule structure stability and structural transformations of crystalline domains into amorphous domains. Recent studies were conducted on a new source of starch obtained from Kithul palm (*Caryota urens*) and observed that the gelatinization parameters (T_o, T_p, and T_c) of Kithul starch are higher than that of sago and corn. The Kithul starch was subjected to dual chemical modification (oxidation and acetylation), and physical modification like annealing. DSC analysis showed that modified forms of Kithul starch exhibited an increase in gelatinization temperatures compared to native starch (Sudheesh et al., 2019a, b). This change depends on crystalline perfection, and the interaction between new functional groups presenting hydroxyl groups in starch granules. An increase in T_o, T_p, and T_c was observed in annealed starch. This rise is credited to an escalation in the interaction between amylose–amylose, and amylose–amylopectin chains. HMT starch exhibits greater thermal stability and shear resistance and is hence used in food products like confectionaries, sauces, soups noodles, and pasta. Recent studies have explored the use of HMT starch in food items like pasta and noodles to obtain desirable qualities like good expansion, minimum cooking time, and good tensile strength (Chandla et al., 2017; Kaur & Singh, 2019; Liao et al., 2019; Schafranski et al., 2021). Annealing is a lucrative and simple technique used to modify the functional properties of starch to develop several food products. Annealed starches are used majorly as viscosity modifiers, glazing agents, fat replacers, emulsion agents, encapsulation material, and bulking agents (Schmiele et al., 2018).

Non-Thermal Physical Modification of Starch

Food items are preserved by exposing them to high temperatures for a short period. These treatments result in the loss of essential nutrients, and flavors. These problems can be solved by non-thermal technology. Non-thermal treatments preserve the important characteristics of food including texture, color, nutrients, and taste as compared to the traditional thermal processes (Zhang et al., 2019a, b, c). Some of the non-thermal methods use ultrasound effects, high hydrostatic pressure, and microwave treatments for the modification of starches. Some established applications of ultrasound in food processing consist of homogenization, defoaming, filtration, extraction, emulsification, crystallization, and extrusion (Jambrak et al., 2010). High hydrostatic pressure has been effectively used to prolong the shelf life of food products with the least impact on their taste, nutrition, and aroma (Huang et al., 2017). Effects of high hydrostatic pressure (100, 300, and 500 MPa for 15 and 30 min at 25 °C) on thermal properties of maize, potato, and sweet potato starches (20%, w/w) were investigated by Rahman et al. (2020). It was observed that the effect of high hydrostatic pressure on starch is a function of molecular structure. Sweet potato starch with a complex molecular structure is not affected by high hydrostatic pressure compared to maize and potato starch which show an increase in gelatinization temperature (Rahman et al., 2020). Figure 2G exhibits DSC parameters of high hydrostatic pressure treated starch.

Microwaves are electromagnetic radiations in the frequency range of 300 MHz–300 GHz. The microwaves generate heat inside the starch granules due to alternating electromagnetic fields at high frequencies. Other advantages of microwave treatment involve faster and selective heating, energy efficiency, and control of the treatment process (Colman et al., 2014). A study conducted by Colman et al. (2014) showed that starch exposed to microwave exhibits an increase in gelatinization temperature. Ultrasonic treatment requires a shorter time and provides better yield compared to traditional food processing techniques. According to Jambrak et al. (2010), ultrasonicated corn starch did not show a statistical increase in the gelatinization temperature compared to native corn starch (74.99 °C). Lower T_p and less ΔH (8.733 kJ/kg) for corn starch suspensions were sonicated for 15 min and was observed compared to the untreated corn starch (Jambrak et al., 2010). Ultrasonicated starch is shown to increase the pore size of starch granules, easing the release of flavoring agents and spices (Sujka, 2017). Figure 2H shows the gelatinization parameters of ultrasonicated starch. A study was conducted to investigate rice starch modified by a combined ultrasonic-microwave technique. The treatment exhibited substantial changes in important functional properties including gel firmness, degree of hydrolysis, and retrogradation of starch (Brasoveanu & Nemtanu, 2014).

Dual Modification

Dual modification of starch combines two methods—either chemical and physical modifications or chemical and enzymatic methods. A combination of two chemical modifications is the most common. There are two classes of dual modification, namely, homogeneous and heterogeneous dual modifications. The homogeneous dual modification consists of either physical/physical or chemical/chemical dual modification. Heterogeneous dual modifications include a combination of physical and chemical dual modifications (Ashogbon, 2021). Frequently applied dual chemical modifications include acetylation/oxidation or cross-linking/acetylation (Zia-ud-Din et al., 2017). Heterogeneous dual modification of starch (succinylation–annealing) increases swelling power, water binding capacity, gelatinization temperature, and enthalpy gelatinization. This is highly desirable for food products like sauces, pasta, and noodles that require starch to be heated and shear-stress resistant during processing (Lin et al., 2019). A previous study has suggested that DSC analysis exhibited improved thermal stability and peak gelatinization temperature after dual modification. (Ashogbon, 2021). For example, the Kithul starch was subjected to dual chemical modification (oxidation and acetylation), and physical modification like annealing. DSC analysis showed that modified forms of Kithul starch exhibited an increase in gelatinization temperatures compared to native starch. This change depends on crystalline perfection, and the interaction between new functional groups presenting hydroxyl groups in starch granules (Sudheesh et al., 2019a, b). In another recent study, taro starch was subjected to dual modification by HMT and ultrasonication. The dual-modified samples exhibited reduced ΔH and increased T_p. This was accredited to the fact that HMT causes reorganization of starch chains in a more ordered structure which was disturbed by the application of ultrasound. This resulted in easy penetration of water and resulted in less energy for gelatinization (Thomaz et al., 2020). In yet another study conducted, the effect of the dual modification, acid thinning, and succinylation is studied, for possible applications in the food industry. It was observed that there was no extensive difference in the thermal properties of native and modified starch since the treatments only affected the amorphous regions of the starch granules. The T_p of native starch was 66.51 °C whereas the dual modified starch exhibited T_p at 65.87 °C. ΔH for native starch was 13.67 J/g whereas modified starch had ΔH of 13.80 J/g (Cabrera-Canales et al., 2021). A corn starch was exposed to hydrothermal treatments in various orders. The native acorn starch exhibited T_o, T_p, T_c, and ΔH at 59.9, 71.3, 80.6 °C, and 14.9 mJ/mg, respectively. The T_o of HMT-annealed and HMT starches were comparable but higher than that of annealed starch. It shows that HMT had a greater effect on the crystalline region of starch compared to annealing. However, the T_o of annealed-HMT starch and the T_p and T_c of both dual modified starches were lower than HMT starch but higher than annealed starch. This revealed that the second treatment in each case counteracts the effects of the first treatment (Molavi et al., 2018). In the baking industry, cross-linked starch decreased the crumb firmness of bread. This undesirable property was improved by subjecting the starch to dual modification (cross-linking and acetylation) leading to an increase in bread volume and crumb structure (Lakshmi, 2005). Table 1 compares the gelatinization properties of native and modified starch from recent studies.

Other Techniques for Physicochemical Characterization

The thermal gelatinization properties of starches may vary depending on various factors including botanical source, amylose to amylopectin ratio, type crystallinity, and conditions of chemical, physical, or dual modification (Table 1). Although DSC is an indispensable tool in understanding the thermal characteristics, it alone cannot represent the overall thermal properties of starch. Often other techniques like thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are inevitable and critical in predicting the overall thermal events of any material including starch. Further, DSC shows other drawbacks including its destructive nature and the dynamic nature of the technique. In addition, it is hard to differentiate the individual changes in gelatinization properties of starch which has undergone overlapping dual modification. Since the pursuit of producing better, cheaper, and healthier starch-based food products never stops, further research and multidisciplinary approaches using various techniques including viscometry, microscopy, spectroscopy, X-ray diffraction, and other methods of thermal analysis are used to investigate the altered physicochemical properties of modified starch used in the food industry which can extend more efficient services to the consumers. Microscopy techniques such as scanning electron microscopy are used to investigate the morphology of modified starch granules. X-ray diffraction measurements are used to analyze if the modifications alter the crystalline structure of starch. Fourier transform infrared spectroscopy is the most widely used technique to study characteristic functional groups. Further, Raman spectroscopy is also applied extensively to study the chemical and structural characteristics of modified starch (Pineda-Gomez et al., 2021). To select modified starch for a particular application, especially the food industry, properties such as structure, chemical composition, organoleptic characteristics, viscosity, shelf stability, and resistance to heat, and low pH must be considered. Therefore, detailed characterization of modified starch using the techniques is necessary.

Conclusion

Since starch forms a major part of our daily diet, gelatinization properties have become an important parameter to be considered while processing or cooking food. Modified starch can be used in all sectors of the food industry including the beverage, canned food, baby food, and sweet industries. Starch modification influences the functional quality, selectivity, and suitability of the modified starch for various nutritional, pharmaceutical, and food industrial formulations. Further, starch modification alters the gelatinization properties to improve and tailor its functional characteristics to specific food applications. DSC analysis is important for elucidating the complicated gelatinization characteristics of starch subjected to various types of modifications used in food industries. Thus, it is important to choose the correct form of modification based on gelatinization properties for the processing of starch in the food industry.

This review suggests that generally physically modified starches including partial/pre-gelatinization, HMT, annealing, and high hydrostatic pressure treatment are widely used in pre-cooked/ready-to-eat meals like soups and sauces since they provide high gelatinization temperatures and better solubility of starch. Similarly, cross-linked and oxidized starches also require a short duration and higher temperature to gelatinize and improve the texture as well as the shelf life of starch-based food products. Other modification methods including acid hydrolysis, acetylation, and ultrasonication reduce the gelatinization temperature of starch, making them appropriate for the manufacture of gelled sweets, sauces, and soups owing to lowered T_p. However, these modifications also exhibit some disadvantages including lowering firmness of starch gels, reduction in swelling capacity, or viscosity. These disadvantages can be overcome by dual modification. A combination of cross-linked and acetylated starch is useful for the packaged and frozen food industry. While cross-linking increases the gelatinization temperature, cross-linked starch improves the texture and resistance of starch to extremely cold and high temperatures. A wide array of modified starch is yet to be tested for increased thermal stability.

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Declarations

Ethics Approval Not applicable.

Conflict of Interest The authors declare no competing interests.

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