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# Physical and Chemical Modifications in Starch Structure and Reactivity

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## Abstract

Starch is a naturally occurring glucose homo-polysaccharide of nutritional, pharmaceutical, and industrial importance. The complex polymeric structure and poor solubility of native starch in water limits their importance at pharmaceutical and industrial level. The structure, reactivity, and functionality of the native starch can be modified by physical, chemical, enzymatic, and biotechnological methods. Various physical modifications techniques, including the thermal, radio-thermal, freezing and thawing, annealing, high-pressure, ultrasonic, and pulsed electric field treatment, and chemical modifications, including oxidation, etherification, esterification, cationization, cross-linking, and graft polymerization, have been found to change the surface properties, polarity and linearity of the molecular chains, the degree of substitution, the polymeric, granular, and crystalline structure, amylose to amylopectin ratio, solubility, viscosity, pasting, gelatinization, swelling, water absorption, and emulsifying properties of starch. The structural changes have resulted in the improvement of thermal and freeze-thaw stability, viscosity, solubility, water binding capacity, swelling power, gelling ability, and enzymatic digestibility of starch. The exposure of reactive functional groups after physical or chemical modification modifies the reactivity of starch toward water, oil, acids, enzymes, and other chemical species. These modification techniques have led to some revolutionary changes in reactivity, functionality, and application of starch in various fields.

**Keywords:** starch structure, starch reactivity, functional properties, chemical modifications, physical modification

## 1. Introduction

Starch is the most important polysaccharide as well as storage polymer of plants abundantly found in leaves, stem, fruit, seed, tubers, and roots of various plants. Starch is produced in chloroplast and amyloplast of plant cells by photosynthesis, stored as a source of food and energy. It is stored in plant cell during tubers sprouting, germination of seeds and fruit maturation [1, 2]. Major sources of starch included cereals grains such as wheat, barley, rice and corn, the seeds of the legumes such as beans, garden peas, chickpeas, and pulses, the

tubers such as potato, sweet potato, ginger, turmeric and groundnut and immature fruits and vegetables [3–5].

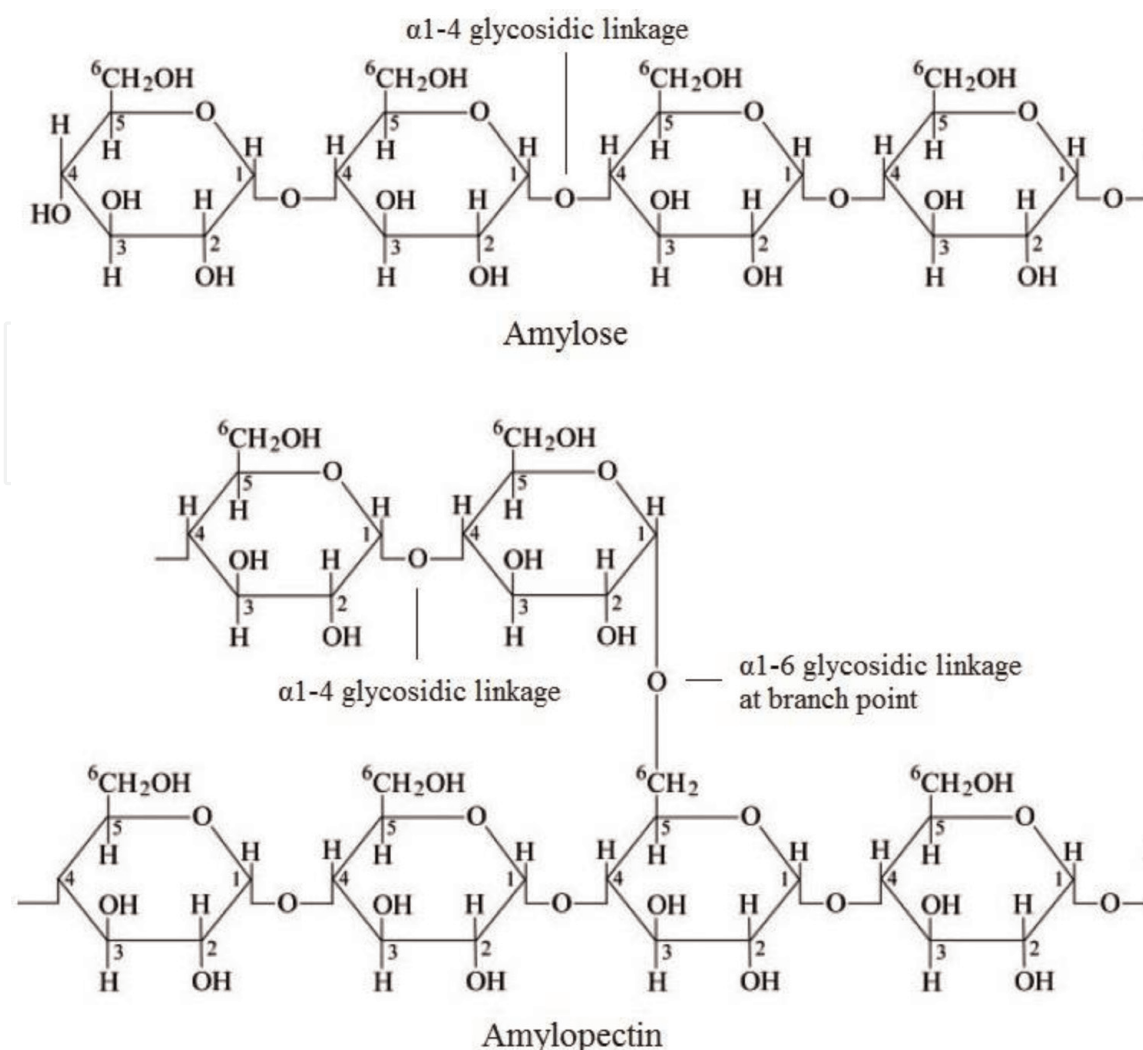
Starch has great nutritional, pharmaceutical and industrial significance due to its unique physical, chemical and functional and nutritional properties. Starch is a good source of nutrition as it is hydrolyzed into glucose on digestion by  $\alpha$ -amylase. The metabolic oxidation of glucose provides instant energy which is utilized in various metabolic and other cellular activities [6–8]. Due to the higher concentration of amylose, starch is used as an excipient to activate drugs and act as an encapsulating agent facilitating the deliver the drug to its target organ [9–11]. As a natural polymer, starch is used to replace plastic in the coating of food materials and production edible films in the food industry. It is usually mixed with food components to protect them from mechanical damage, to extend their half-life and to improve their appearance. It is also used as a recyclable component for molds production in the food industry. It is added as a bulking agent in food and pharmaceutical formulations to enhance handling and stability as well as preservation of components texture and to enhance their viscosity [12–14]. Moreover, due to water-resistant nature of amylose, it can form excellent films due to which it has great importance at industrial level [15].

### **1.1 Starch structure and composition**

Chemically starch is a homopolymer of  $\alpha$ -Glucopyranose units with the chemical formula  $(C_6H_{10}O_5)_n$ . Starch is composed of two types of polymer chains known as amylose and amylopectin. Amylose possesses a linear structure with  $\alpha$ 1–4 glycosidic linkage while amylopectin possesses a branched structure with  $\alpha$ 1–4 as well as  $\alpha$ 1–6 glycosidic linkages (**Figure 1**) [16, 17]. Normally, starch consists of relatively lower amount of amylose (20–30%) than that of amylopectin (70–80%). The ratio of amylose and amylopectin affects the starch structure in terms of crystallinity, size of the granules and chemical nature and arrangement of polymers within the granule. The studies have shown that the fine structure of amylopectin plays an important role in the functionality of starch. It is the relative concentration of amylose and amylopectin which determines the physical and functional properties of starch. The starches containing low amylopectin have been found to show the quick onset of gelation as compared to low amylose starches. The starches containing relatively high amylose content have been found to form comparatively hard and rigid gels and strong films while high amylopectin starches are dispersed easily in water and form soft gels and weak films [15, 18–21]. The amylose to amylopectin ratio also influences the nutritional quality of starch that is assessed by its rate of digestion and glycemic index (GI) as an indicator to check the quality of carbohydrates [22].

### **1.2 Functional properties of starch**

Based on its compact structure, starch possesses diverse functional properties and applications in biomedical and industrial fields. Due to polymeric and branching nature starch shows relatively less solubility in water and possesses relatively lower ability to absorb water and oil. Starch shows good iodine-binding ability. It also possesses a relatively high viscosity and good swelling power and gelatinization abilities. It also shows good pasting properties with consistency, smoothness, and clarity and can form thin films. Starch shows freeze–thaw and cold storage stabilities which make it a favorable candidate for various food and industrial formulations. Starch is resistant to moderate temperature and pressure but



**Figure 1.**  
 Structure of amylose and amylopectin in starch.

susceptible to acid and enzyme-catalyzed hydrolysis. However, the native starches show relatively lower values of enzymatic digestibility [18, 23–26]. To increase its nutritional, biomedical and industrial importance, the functional properties of starch can be improved under the influence of various physical and chemical factors.

### 1.3 Factors affecting the structure and properties of starch

The native starches possess a complex granular and crystalline structures which differ in size in various plants [2, 16]. Several factors have been reported which affect the structural, physical, chemical, and functional properties of starch. Starch is sensitive to very high and very low pH, high temperature, high pressure, and osmotic pressure, light, radiation, mechanical stress, and ultrasound waves. Heating treatment of starch in aqueous medium has been found to cause transition of amorphous form to crystalline starch resulting in gelatinization of starch. The treatment with microwave radiation has been found to affect the crystalline structure and functional properties of starch which is linked with the loss of birefringence and crystallinity due to deformation during modification [27–36]. Interaction of starch with water and oil also affects the properties of starch. The absorption of water results in the breakdown of amylose-amylopectin linkages, loss of

crystallinity and swelling of starch granules. The swelling of starch granules is reversible at the initial stage but irreversible after a certain period [37]. Freezing at low temperature after gelatinization results in recrystallization of starch granules and increases the resistance and hardness of starch [38].

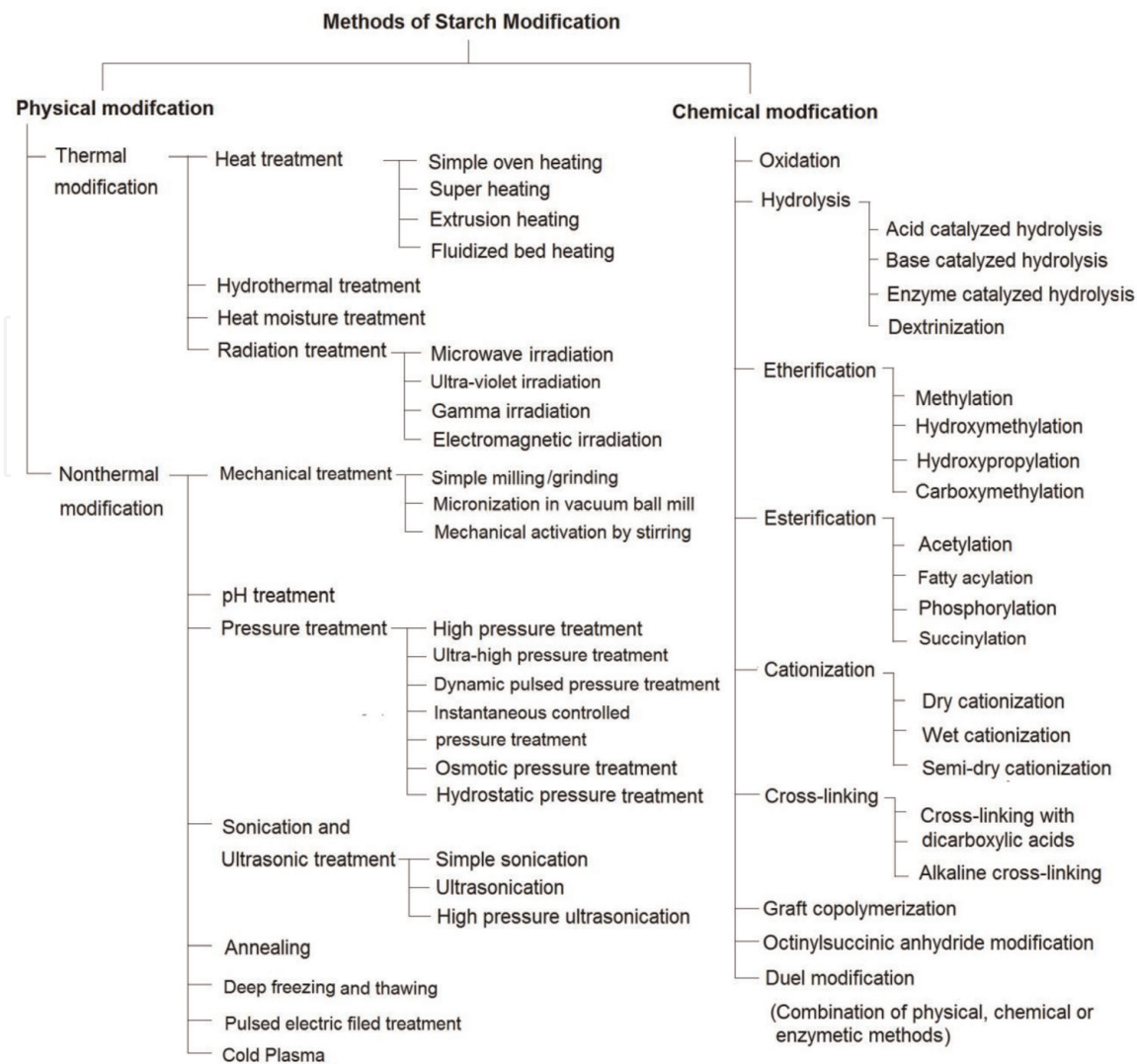
Along with these physical factors, some chemical factors have been also reported to affect the structure and functions of starch. Various oxidizing agents, hydroxy or carboxy derivatives of hydrocarbons, some carboxylic acids, phosphates, different acid, and base cross-linkers and synthetic polymers, and some cationic molecules are the major chemical factors which have been reported to modify the structure and properties of native starches [39–46]. Starch is also susceptible to acids and enzymatic hydrolysis which results in degradation of amylose and amylopectin and alter the morphology and surface properties of granules leading to the change in functional value of starch [47–49]. These physical and chemical factors have helped improve the functional quality of starch to obtain better results while used in various food and industrial formulations.

## **2. Starch modification**

Any changes in the structure of starch molecule caused by various environmental, operational and processing factors are termed as modifications. These modifications may exert either positive or negative effects on the structure and functionality of starch molecules. The native starches obtained from various plants are diverse in their structure and functions. To enhance the structural and functional quality of these starches and achieve better results in various formulations, the researchers suggest some modification in their structure. Several studies have been reported on the improvement of functional quality of starch by physical, chemical or mechanical modifications [23, 43, 45, 48, 50–58]. However, some environmental and processing factors may reduce the functional quality of starch by various modifications during storage and processing [57]. The physical modifications are comparatively safe and preferable over chemical modifications as the later involve the changes in the chemical structure of the molecule which limit its use in most of the formulations.

### **2.1 Physical modification of starch**

Physical modifications involve the changes in the morphology and three-dimensional structure of starch under the influence of some physical factors such as milling, moisture, temperature, pressure, pH, radiation, pulse-electric field, ultrasonic waves, etc. Physical modifications result in the variation in particle size, surface properties, solubility index and functional properties such as water absorption, swelling capacity, pasting and gelation ability of starch. These modifications directly influence the functional quality and selectivity and suitability of the modified starch for various nutritional, pharmaceutical and industrial formulations. Several studies have been reported on the physical modification of starch using different techniques. The commonly used methods of physical modification include superheating of starch, thermal inhibition treatment, UV and gamma irradiation, microwave treatment, high pressure, osmotic pressure and instantaneous controlled pressure treatment, mechanical activation by stirring ball mill, treatment by pulsed electric field, micronization in vacuum ball mill, annealing and freeze-thaw treatment [28, 29, 31, 33, 51, 53, 55, 56, 59–68]. The most frequently used and the most effective methods of physical modification are presented in **Figure 2** and their effects on the structure and properties of various starches are summarized in **Table 1**.



**Figure 2.**  
 Methods of physical and chemical modifications of starch.

## 2.2 Chemical modification of starch

The chemical modification involves the alteration of physiochemical properties of starch by introducing new chemical or functional groups in starch without any physical alteration in the shape and size of the molecule. Each of the glucose units in amylose and amylopectin has three reactive hydroxyl groups which are the major sites for chemical modification in starch. The chemical modification alters the physical behavior of starch including retrogradation, salting, and gelatinization that work by stabilizing the intermolecular and intramolecular bonding of starch granules. The commonly used methods of chemical modification of starch include oxidation by different oxidizing agents, etherification by addition of some hydroxyethyl, hydroxypropyl or carboxymethyl moieties on hydroxyl groups of starch, esterification by condensation of some fatty acids, other carboxylic acids and phosphates with active hydroxyl groups of starch, cationization by introducing some cationic molecules, cross-linking by addition of various cross-linkers and graft-polymerization of starch with synthetic polymers [40–43, 46, 68–72]. Cationic modifications involve the reaction of starch molecules that contain tertiary and secondary ammonium, imino, amino, sulfuric and phosphate groups which react with hydroxyl groups of starch. It improves the dielectric constant of starch granules. It has great importance in the textile industry as an additive, in paper and cosmetic industry due to low cost, rapid degradation and bioavailability [73].

| Modification method         | Treatment                                                                                                                                                                         | Change in starch structure                                                                                                                                                                                                                                                                                                                                               | Change in starch properties                                                                                                                                                                                                                                                                                             | References          |
|-----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|
| <b>Thermal modification</b> |                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                         |                     |
| <i>Heating treatments</i>   |                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                         |                     |
| Gentle heating              | Heating starch at low temperature (45–65°C)                                                                                                                                       | It causes slight changes in starch structure and amylopectin to amylose ratio.                                                                                                                                                                                                                                                                                           | It shows no significant effect on the physicommechanical properties of starch.                                                                                                                                                                                                                                          | [35]                |
| Superheating                | Heating starch at relatively high temperature (180–220° C)                                                                                                                        | It results in the formation of spreadable gel particles with a creamy texture on cooling.                                                                                                                                                                                                                                                                                | It improves the gelatinization and pasting properties of starch.                                                                                                                                                                                                                                                        | [76]                |
| Extrusion heating           | Application of mechanical force in low-temperature environment                                                                                                                    | It causes the degradation of amylose and amylopectin of the starch polymer by random chain-splitting. It also causes a high degree of granule disruption with complete loss of crystallinity                                                                                                                                                                             | It lowers the swelling power and viscosity and improves the water solubility and digestibility of starch.                                                                                                                                                                                                               | [51, 77]            |
| Hydrothermal treatment      | Heating of starch in an aqueous medium.                                                                                                                                           | It causes physical reorganization of starch granules                                                                                                                                                                                                                                                                                                                     | It improves the granule size, mobility, and stability which make it able to be digested easily by amylase. It also improves the gelatinization properties of starch.                                                                                                                                                    | [30, 67, 78]        |
| Heat-moisture treatment     | Heat application in the presence of limited moisture levels: 22–27% and high temperature above the glass-transition temperature: 100–120°C for a specified length of time: 1–24 h | It results in a change in size, shape and granular and crystalline structure of starch. It causes a partial or complete conversion of the B-type crystalline starch to A-type. It also causes disruption of helical structures within the amorphous regions of starch granules. It induces the molecular degradation of starch and increases the degree of polarization. | It decreases the amylose leaching, peak viscosity, and swelling capacity and enhances the solubility, thermal stability, gelatinization temperatures, pasting temperature, pasting time, interaction properties and susceptibility of starch to chemical and enzymatic attack ( $\alpha$ -amylase and acid hydrolysis). | [28, 50, 59, 79–82] |
| <i>Radiation treatment</i>  |                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                         |                     |
| Microwave irradiation       | Application of microwave radiation at different ranges of moisture and temperature to influence the dielectric constant of starch.                                                | It improves the granular crystallinity and surface morphology.                                                                                                                                                                                                                                                                                                           | Microwave treatment Improves the water and oil holding capacity, emulsifying activity, swelling capacity, solubility, and gelling ability. It also increases the pasting temperature and paste viscosity. It decreases the peak viscosity and gelatinization, and the degree of relative crystallinity.                 | [27, 31, 53, 83]    |

| Modification method               | Treatment                                                                    | Change in starch structure                                                                                                                                                                                                                                    | Change in starch properties                                                                                                                                                                                                                                                                                                      | References       |
|-----------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|
| Ultraviolet (UV) irradiation      | Starch granules exposed to UV light.                                         | It causes free radical-induced cross-linking and depolymerization, oxidative photodegradation, and dextrinization in starch.                                                                                                                                  | UV treatment Influences the physical, chemical and functional properties of starch.                                                                                                                                                                                                                                              | [61, 84, 85]     |
| Gamma irradiation                 | Exposure of starch granules to various doses of high energy gamma radiation. | Gamma irradiation causes the breakage of the amylopectin chains at the amorphous regions and decreases the amylopectin to amylose ratio. It also causes the radiolysis and radio-depolymerization of starch                                                   | The exposure to gamma radiation decreases the pasting viscosity, and enthalpy change of starch and molecular weight and gyration radius of amylopectin. It increases the susceptibility of starch towards amylase. It also improved the rheological properties such as gelatinization viscosity, swelling power, and solubility. | [54, 86–88]      |
| <b>Non-thermal modification</b>   |                                                                              |                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                  |                  |
| pH treatment                      | Addition of some acid or base to change the pH of the medium.                | A high pH results in partial degradation of starch granules with a decrease in molar size and radius of gyration. A low pH results in hydrolysis of starch particularly in the amorphous region of granules and decreases the molecular weight of the starch. | Increase in pH improves the solubility, swelling power, and compression properties. Low pH treatment improves the gelation properties of starch.                                                                                                                                                                                 | [35, 48, 49, 89] |
| Moisture treatment                |                                                                              | Moisture acts as plasticizer and anti-plasticizer for starch films for different properties                                                                                                                                                                   | It causes a plasticizing effect on calorimetric glass transition temperature, linear expansion, tensile modulus, and water vapor permeability while an anti-plasticizing effect on mechanical properties i.e. tensile strength and toughness.                                                                                    | [90]             |
| <b>Mechanical treatment</b>       |                                                                              |                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                  |                  |
| Simple milling/ grinding          | It involves the grinding of starch by physical forces.                       | It decreased the crystalline/amorphous ratio, crystallinity, content of double helix of starch. It also results in a rapid increase and then a gradual decrease in surface parameters.                                                                        | It reduces the viscosity and increases the susceptibility of physical and chemical factors to starch. It increases water-binding capacity, adsorptive capacity, and reactivity of starch.                                                                                                                                        | [91, 92]         |
| Micronization in vacuum ball mill |                                                                              | It damages the B-type starch granules, results in loss of the granular order and double-helix content and reductions in crystallinity. It also                                                                                                                | Changes the rheological properties of starch. It increases the water adsorption, iodine binding capacity, granule swelling, solubility and                                                                                                                                                                                       | [59, 93, 94]     |

| Modification method                         | Treatment                                                                                                               | Change in starch structure                                                                                                                                     | Change in starch properties                                                                                                                                                                                                       | References   |
|---------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
|                                             |                                                                                                                         | causes depolymerization of starch polymer molecules.                                                                                                           | susceptibility of starch to amylase. It decreases the viscosity, and elasticity of paste.                                                                                                                                         |              |
| Mechanical activation by stirring           | Application of mechanical force on starch by stirring ball mill.                                                        | The treatment results in the degradation of the crystal structure to amorphous particles and formation of an agglomerate of the resulting amorphous particles. | It reduces the gelatinization temperature and enthalpy, shear-thinning, and apparent viscosity of starch resulting in enhancement of cold-water solubility of the starch.                                                         | [29]         |
| <i>Pressure treatment</i>                   |                                                                                                                         |                                                                                                                                                                |                                                                                                                                                                                                                                   |              |
| High-pressure treatment                     | Treatment of starch under pressure < 400 MPa.                                                                           | It exerts a pressure and time-dependent effect on the microstructure of starch. It causes melting of amylopectin crystals and loss of birefringence.           | The pressure treatment causes changes in rheological properties of starch. It increases the hardness and chewiness and improves the freeze-thaw stability of the starch gels.                                                     | [33, 95]     |
| Ultra-high pressure treatment               | Treatment of starch under pressure > 400 MPa.                                                                           | It distorts in the crystalline region and transits A-type crystalline starch to B-type.                                                                        | It increases the swelling of starch granules and restricts the amylose leaching. It lowers the gelatinization temperature.                                                                                                        | [33, 59, 65] |
| Instantaneous controlled pressure treatment |                                                                                                                         | The treatment increases the median volume diameter in cold water.                                                                                              | It decreases the gelatinization enthalpy and birefringence under polarized light.                                                                                                                                                 | [30]         |
| Osmotic pressure treatment                  | Heating of starch in a hypertonic (saturated) solution of sodium sulfate at 100–120°C across the semipermeable membrane | It causes distortion in the shapes of starch granules and changes the B-type crystalline starch to A-type.                                                     | This modification increases the gelatinization temperature.                                                                                                                                                                       | [32, 80, 96] |
| Hydrostatic pressure treatment              | Application of high pressure ranging from 400 to 900 MPa.                                                               | It causes the disintegration and retrogradation of starch granules.                                                                                            | It retards the swelling of granules or reduces viscosity with preserving the taste and nutrient of starch                                                                                                                         | [56]         |
| <i>Ultrasound treatment</i>                 |                                                                                                                         |                                                                                                                                                                |                                                                                                                                                                                                                                   |              |
| Ultra-sonication                            | Treatment of starch with ultrasonic waves.                                                                              | It distorts the starch granules.                                                                                                                               | It increases the solubility, viscosity and swelling capacity of granules and reduces the pasting ability and digestibility of starch. It also increases the gelatinization temperature and enthalpy and decreases the solubility. | [36, 53, 63] |
| High-pressure ultra-sonication              | The treatment of ultrasound waves to native starch granules.                                                            | It distorts in the crystalline region of the starch granules.                                                                                                  | It decreases the enthalpy of gelatinization, consistency coefficient,                                                                                                                                                             | [63, 97]     |

| Modification method                   | Treatment                                                                                                                                                                               | Change in starch structure                                                                                                                                                                                                                                                                                                                              | Change in starch properties                                                                                                                                                               | References         |
|---------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|
|                                       | at 24KHz to 360KHz frequency                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                         | crystallinity and molecular weight of starch granules.                                                                                                                                    |                    |
| Annealing                             | Modification of starch in the presence of intermediate water contents (40–50% w/w) or excess water more than 65% w/w at temperatures lower than the onset temperature of gelatinization | It increases interaction between the amylose–amylopectin and amylose-amylose chains and the crystalline perfection. It enhances the mobility of double-helical chain segments within granules, allows subsequent recrystallization, restructuring, or both of starch chains, enhances molecular order and provides more homogeneity among crystallites. | Decreases the amylose leaching and swelling of granules and increases thermal stability gelatinization temperatures, and susceptibility towards $\alpha$ -amylase.                        | [59, 80]           |
| Thermal inhibition                    | Dehydration of starch at a high temperature until it becomes anhydrous (<1% moisture                                                                                                    | It results in a decrease in granular size.                                                                                                                                                                                                                                                                                                              | It increases the cohesive-texture and stabilizes the viscosity of starch.                                                                                                                 | [52, 98]           |
| Cold plasma                           | Treatment of starch with low-temperature plasma or glow-discharge plasma.                                                                                                               | It causes free radical-induced cross-linking of starch and increases the amylose leaching. It reduces the relative crystallinity due to active plasma species-induced depolymerization.                                                                                                                                                                 | It influences the physical and functional properties of starch. It increases the pasting and viscosity but decreases the retrogradation tendency.                                         | [99–101]           |
| Pulsed electric field (PEF) treatment | Processing of starch-water suspension in electric field strength of 50 kV/cm.                                                                                                           |                                                                                                                                                                                                                                                                                                                                                         | It reduces enthalpy, gelatinization temperature, enthalpy, viscosity and crystallinity of granules. The granule diameters increase with increase in the field strength.                   | [62, 64, 102, 103] |
| Freezing                              | Freezing the starch at very low temperature (sub-zero levels)                                                                                                                           | Reversible structural disorder on starch granules,                                                                                                                                                                                                                                                                                                      | It causes the change in the texture and gelatinization properties and increase in retrogradation.                                                                                         | [80]               |
| Freeze–Thaw treatment                 | Heating of starch at high temperature (59–79°C) flowed by freezing and defrosting.                                                                                                      | An increase in the number of Free–Thaw cycles changes the complex modulus and phase angle of the starch.                                                                                                                                                                                                                                                | Affects the rheological properties of starch. Increases the swelling power, viscosity, and thermal stability of starch. It also influences the surface properties of the starch granules. | [60]<br>[38, 51]   |
| Dual modification                     | Treatment of starch with a combination of different physical factors.                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                           |                    |

| Modification method                           | Treatment                                        | Change in starch structure                                                                                                                                                                                   | Change in starch properties         | References |
|-----------------------------------------------|--------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|------------|
| Heat-moisture treatment-annealing             | Heat-moisture treatment followed by annealing.   | No significant damage of individual treatment on the structure of starch granules has been observed.<br>Heat-moisture-annealing treatment resulted in disruption of crystalline structure.                   | Increase in enthalpy.               | [58, 72]   |
| Annealing-sonication and Sonication-annealing | Annealing followed by sonication and vice versa. | Both treatments promote a synergic behavior on crystallite collapse and result in a decrease in relative crystallinity. The later also results in irregular surface morphologies and granule disintegration. | Both increase the pasting viscosity |            |

**Table 1.**  
*Methods of physical modification of starch and changes in starch structure and properties.*

| Modification method                    | Treatment                                                                                  | Change in structure                                                                                                                                                              | Change in properties                                                                                                                                                                                                                          | References    |
|----------------------------------------|--------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| Oxidation                              | Addition of carboxyl and carbonyl group to native starch by the use of an oxidizing agent. | It causes depolymerization of starch resulting in retardation in recrystallization due to the incorporation of carbonyl and carboxyl groups.                                     | It increases the stability, clarity and biding properties but reduces the dispersion viscosity of starch.                                                                                                                                     | [23, 44, 104] |
| Stabilization by addition of a polymer | Copolymerization with synthetic polymers                                                   | It provides the structural stability to starch and reduces the retrogradation.                                                                                                   | It improves the freeze–thaw stability and shelf life of starch-based food products.                                                                                                                                                           | [23]          |
| Etherification                         |                                                                                            |                                                                                                                                                                                  |                                                                                                                                                                                                                                               |               |
| Hydroxyethylation                      | Introduction of hydroxyethyl group to the starch.                                          | Changes in the granular structure.                                                                                                                                               | Improves the drug binding ability for some anticancer and other drugs.                                                                                                                                                                        | [71]          |
| Hydroxypropylation                     | Addition of hydroxypropyl group on the starch.                                             | It disrupts the inter- and intra-molecular hydrogen bonds and weakens the granular structure of starch. It increases the motional freedom of starch chains in amorphous regions. | It increases the peak viscosity, water binding capacity, swelling power, solubility and enzymatic digestibility of starch. It also improves the paste clarity and freeze–thaw stability. However, it decreases the gelatinization parameters, | [26, 68, 105] |

| Modification method | Treatment                                                               | Change in structure                                                                                                                                          | Change in properties                                                                                                                                                                                                         | References             |
|---------------------|-------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
|                     |                                                                         |                                                                                                                                                              | enthalpy of gelatinization, and transition temperatures. It also decreases the hardness and adhesiveness of the gels.                                                                                                        |                        |
| Carboxymethylation  | Carboxymethyl substitution of hydroxyl groups in starch                 | It adds the hydrophobic groups on the starch molecule.                                                                                                       | It increases the stability of starch in aqueous media, reduces the recrystallizing ability and prevents the damage from heat and microorganisms.                                                                             | [51]                   |
| Esterification      |                                                                         |                                                                                                                                                              |                                                                                                                                                                                                                              |                        |
| Acetylation         | Reaction of an acetyl group with the hydroxyl group of polymeric starch | It retards the crystallization or retrogradation in starch granules.                                                                                         | It inhibits the formation of intramolecular hydrogen bonds and enhances the viscosity and swelling capacity of granules. It reduces the pasting temperature and solubility.                                                  | [39, 99]               |
| Fatty acylation     | Reaction of fatty acids with starch                                     | It results in the formation of amylose-fatty acyl complexes.                                                                                                 | It changes the optical activity and thermal behavior of starch                                                                                                                                                               | [106]                  |
| Phosphorylation     | Addition of phosphate group on hydroxyl groups of starch                | It results in the formation of either monophosphate or diphosphate starch. It increases the steric hindrance and prevents the linearity of molecular chains. | It improves the viscosity, textural properties, paste clarity and Freeze-Thaw stability of starch. It also increases resistance to low pH, high temperature, and high shear. It decreases the temperature of gelatinization. | [68]<br>[45]           |
| Succinylation       | Treatment of starch with Octinyl succinic anhydride                     | It results in the derivatization of starch with alkenyl succinic anhydrides.                                                                                 | The modification increases the swelling volume, peak viscosity, hot paste viscosity, and cool paste viscosity but decreases the gelatinization temperature and gel hardness. It also increases the                           | [107]<br>[108]<br>[51] |

| Modification method                                           | Treatment                                                                                                                                                                                                                                          | Change in structure                                                                                                                                                                                                                                                                                                  | Change in properties                                                                                                                                                                                                                                                                                                                                                                                                                                 | References                 |
|---------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|
|                                                               |                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                                                      | production of slow-digesting and resistant starch.                                                                                                                                                                                                                                                                                                                                                                                                   |                            |
| Cationization                                                 | Treatment of starch with various cationic molecules.                                                                                                                                                                                               | Introduction of amino, ammonium, imino, phosphonium or sulfonium groups to give a positive ionic charge to starch.                                                                                                                                                                                                   | Increases the solubility, stability, dispersibility, and clarity of the starch.                                                                                                                                                                                                                                                                                                                                                                      | [43]                       |
| Dry cationization                                             | Dry heating of citric acid to anhydride. The cationic molecules are sprayed in the absence of liquid phase on dried starch during extrusion.                                                                                                       | It results in the formation of cross-linked starch citrate.                                                                                                                                                                                                                                                          | It alters the granular structure of starch and improves its adsorption properties.                                                                                                                                                                                                                                                                                                                                                                   | [70, 80]                   |
| Wet cationization                                             | Homogenous and heterogenous reactions of starch with cationic molecules in the presence of a liquid medium.                                                                                                                                        | It also results in the formation of cross-linked starch.                                                                                                                                                                                                                                                             | It increases the viscosity and decreases the paste temperature.                                                                                                                                                                                                                                                                                                                                                                                      | [70]                       |
| Semi-dry cationization                                        | Mixing of starch with cationic molecules followed by a thermal reaction.                                                                                                                                                                           | Results in cationic cross-linking of starch.                                                                                                                                                                                                                                                                         | It produces a high degree of substitution in starch granules.                                                                                                                                                                                                                                                                                                                                                                                        | [70]                       |
| Cross-linking (Formation of inter and intramolecular bridges) | Etherification and esterification of granules with cross-linking polymers by reacting with a mixture (99:1) of sodium trimetaphosphate and sodium tripolyphosphate or other cross-linkers in an aqueous alkaline slurry containing sodium sulfate. | It reduces the mobility of amorphous chains in the starch granule. It introduces the inter- and intra-molecular bonds with multifunctional small molecules with hydroxyl groups on starch to strengthen the granules against various factors. It increases the ordering of internal granule structure and stability. | It decreases the solubility of starch in water which reduces its association with lipids, moisture, and proteins. It also causes decreases in viscosity, swelling capacity, digestibility, retrogradation rate, the peak temperature of relaxation endotherm and enthalpy of starch. It increases the gelatinization temperature, glass transition temperature, melting enthalpy, free volume of starch chains, relaxation enthalpy and stability of | [23, 42, 45, 46, 109, 110] |

| Modification method                                                                               | Treatment                                                                                                                                                              | Change in structure                                                     | Change in properties                                                                                                                      | References |
|---------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|------------|
|                                                                                                   |                                                                                                                                                                        |                                                                         | starch to high temperature.                                                                                                               |            |
| Acid cross-linking                                                                                | The reaction of starch with acids                                                                                                                                      |                                                                         | It increases the gelatinization temperature and the breadth of the gelatinization endotherm.                                              | [48]       |
| Graft copolymerization                                                                            | Copolymerization of starch with synthetic polymers such as poly (ethylene terephthalate), polyethylene, polypropylene, polyvinyl chloride, and polystyrene.            | It changes the structure of starch from a homopolymer to heteropolymer. | It results in changes in physical properties and reactivity of starch.                                                                    | [41]       |
| Duel modification (Modification using the combination of different physical and chemical methods) | Modification with a combination of microwave and ultrasound irradiation and esterification of carboxymethyl cold-water-soluble starch with octenyl succinic anhydride. |                                                                         | It reduces the esterification time and produces the starch with better emulsifying and surfactant properties, good freeze-thaw stability. | [42, 69]   |
|                                                                                                   | Cross-linking in combination with hydroxypropylation or acetylation.                                                                                                   |                                                                         | It increases the production of slow-digesting and resistant starch.                                                                       | [108]      |

**Table 2.**  
*Methods of chemical modification and changes in the structure and properties of modified starches.*

Cross-linking is the mechanism of covalent interaction between starch molecules. The reagents used to form copolymer in starch are sodium trimetaphosphate, sodium tripyrophosphate, epichlorohydrin and phosphoryl chloride. It has been reported to modify the starch to form frozen products in the food industry and also used to make plastics due to resistant properties [42, 45, 46]. The mechanism of addition of anhydrous acetyl group or vinyl acetate in the presence of sodium hydroxide and potassium hydroxide to native starch granules is called esterification. Acetylated starch has great importance at the industrial level as a thickener, stabilizer, adherent and encapsulator [39, 74, 75]. The commonly used effective methods of chemical modification of starch are presented in **Figure 2** and their effects on the structure and properties of various starches are summarized in **Table 2**.

### 3. Effect of modification on the reactivity of starch

Both the physical and chemical modifications have been found to result in a change in the granular and molecular structure of starch which leads to the change in its reactivity and functionality. The mechanical, thermal radiolytic, and acid-catalyzed hydrolytic degradation of starch granules result in an increase in its

reactivity due to the exposure of reactive functional groups after the breakdown of amylose and amylopectin chains. Oxidation, acetylation, phosphorylation, carboxymethylation, cationization, and copolymerization also introduce some new functional groups on starch resulting in a change in reactivity of starch towards the water, oil, acids, enzymes, and other chemical species. Cross-linking by the addition of cross-linker molecules also results in the formation of inter and intramolecular bridges among the components of starch which alters its reactivity and specificity for use in industrial and biomedical fields.

#### **4. Conclusion**

The physical and chemical modifications have been found to improve the functional quality of starch for its use in certain formulations while such modifications may also limit its use for other purposes. The choice of modification type and treatment method depends on what types of changes in functionality and reactivity of starch are required for a specific application. The modification of starch by various physical methods have been found to affect its structural parameters and physical and functional properties including crystallinity, surface properties, solubility, viscosity, swelling ability, pasting and gelatinization properties, and thermal and freeze-thaw stability. The modifications of starch by the chemical method have been also found to affect the molecular structure and reactivity of starch by addition of new functional groups, degradation of the polymeric structure, oxidation by free radical or cross linking of starch molecules. The change in the polarity due to exposure of reactive functional groups and the increase in the degree of substitution and intermolecular cross-linking results in a change in the reactivity of starch towards water, oil, acids, enzymes, and other chemical species. These modification techniques may lead to some revolutionary changes in reactivity, functionality starch and application of starch in the nutritional, pharmaceutical, biomedical and industrial field. However, the selection of a suitable modification method is much more important for the researchers to make the desired and targeted improvement in the functional quality of starch.

#### **Conflict of interest**

I confirm that there are no conflicts of interest.

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