



## VARIOUS TECHNIQUES FOR THE MODIFICATION OF STARCH AND THE APPLICATIONS OF ITS DERIVATIVES

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### ABSTRACT

Starch is a major carbohydrate easily extractable from various native sources, like potato, maize, corn, wheat, etc, which finds wide application in various food and non food industries. Since time immemorable various attempts are being made in order to modify this highly flexible polymer with an aim to enhance the positive attributes and eliminate the short comings of the native starches. Modifications are generally made by physical methods like osmotic-pressure treatment, deep-freezing and thrashing; chemical methods that primarily include derivatizations such as etherification, esterification and crosslinking, oxidation, cationization and grafting of starch; enzymatic degradation techniques and genetical modifications which involves the transgenic techniques targeting the various enzymes involved in starch biogenesis. All these techniques tends to produce a variety of derivatives with altered physicochemical properties and modified structural attributes of high technological value for instance carboxymethylated starch used as a binding and disintegrating agent. This review summarizes the various methods of starch modification that can be employed to produce a novel molecule with substantial applications in various industries including a large number of advances in pharmaceutical industry along with the future prospectives.

**KEYWORDS:** Osmotic-pressure treatment, Enzymatic degradation, Transgenic techniques

### INTRODUCTION

Starch is a naturally occurring, biodegradable, inexpensive and abundantly available polysaccharide molecule. It is widely distributed in the form of tiny granules as the major reserve carbohydrate in stems, roots, grains, and fruits of all forms of green leafed plants. Cereal grains, such as corn, wheat, sorghum, and tubers, and roots, such as potato, tapioca, arrowroot, etc., are some of the commercial sources of starch for industrial exploitation. It consists of glucose units ( $C_6H_{10}O_5$ )<sub>n</sub> with n ranging from 300 to 1000. Starch is composed of a mixture of two polymers called amylose and amylopectin. Amylose is a linear polymer with molecular weight of less than 0.5 million Dalton (degree of polymerization of  $15 \times 10^2 - 6 \times 10^3$ ) depending on its botanical source. Amylose macromolecules consist of  $\alpha$ -D-glucopyranose units joined by  $\alpha$ -1,4 acetal linkages. Amylopectin molecules are much larger and highly branched with molecular weight of 50–100 million Dalton and degree of polymerization of about  $3 \times 10^5 - 3 \times 10^6$ . The molecules contain  $\alpha$ -1,4 linear bounds, and is branched through  $\alpha$ -1,6 linkages<sup>1-2</sup>.

In addition to being a major food item, it is currently used industrially as coatings and sizing in paper, textiles and carpets, as binders and adhesives, as absorbants<sup>3</sup>, and as encapsulants<sup>4</sup> bone replacement implants<sup>5</sup>, bone cements<sup>6</sup>, drug delivery systems, and tissue engineering scaffolds<sup>7</sup>. However, in native state it exhibits limited applications due to low shear stress resistance and thermal decomposition, high retrogradation and syneresis, in addition to poor processability and solubility in common organic solvents.

Therefore, to meet the demanding technological needs of today, the properties of starch are modified by a variety of modification methods. Starch modification is aimed at correcting one or some of the abovementioned shortcomings, which will enhance its versatility and satisfy consumer demand.

The techniques for starch modification have been broadly classified into four categories; physical, chemical, enzymatic and genetical modifications, that aim to produce various novel derivatives with improvised physicochemical properties

along with useful structural attributes. There is a huge market for the many new functional and added value properties resulting from these modifications. A number of review articles<sup>8-10</sup> on the subject of starch modification are available. However in the last few years there has been intense research by various pharmaceutical professional to quest for an appropriate modification method that can yield a suitable candidate to be used as pharmaceutical excipient in improvised drug delivery systems. This review covers the various techniques that yield modified starches for pharmaceutical as well as other industrial applications.

### Physical methods

Physical modification of starch is mainly applied to change the granular structure and convert native starch into cold water-soluble starch or small-crystallite starch. These set of techniques are generally given more preference as these do not involve any chemical treatment that can be harmful for human use. A large no of physical methods are available today that include:

#### 1. Heat-moisture treatment

Heat-moisture treatment (HMT) of pulse starches at restricted moisture levels (22–27%) and high temperature (100–120°C) for 16 h has been shown to alter the structure and physicochemical properties of smooth pea, wrinkled pea, navy bean, lentil and pigeon pea starches<sup>11-15</sup>. HMT of pulse starches has been shown by the above authors to decrease amylose leaching, granular swelling and peak viscosity, and to increase thermal stability, gelatinization temperatures and susceptibility towards  $\alpha$ -amylase and acid hydrolysis. These changes were attributed to an interplay of factors such as: (1) amylose content, (2) interactions between starch chains, (3) arrangement of amylose chains within the amorphous domains and (4) lipid-amylose complexes.

#### 2. Annealing

Annealing refers to treatment of starch in excess water (<65% w/w) or at intermediate water contents (40–50% w/w) at temperatures below the onset temperature of gelatinization. The physical aim of annealing is to approach the glass transition temperature, which enhances molecular mobility without triggering gelatinization. Annealing of lentil, smooth

pea and wrinkled pea starch<sup>11-12,16-17</sup> has also been shown to decrease granular swelling and amylose leaching and to increase gelatinization temperatures, thermal stability, and susceptibility towards  $\alpha$ -amylase. These changes were attributed by the above authors to an increase in crystalline perfection and increased interaction between amylose-amylose and amylose-amylopectin chains.

### 3. Retrogradation

The retrogradation process is defined as the linking of starch chains into ordered crystalline structures<sup>18</sup>. The linear fraction of starch is particularly susceptible to retrogradation. Amylose crystals are characterized by high thermostability (dissolution in water at 120-150° C) and resistance to the activity of amylase. Amylopectin, being the branched fraction of starch is, however, slowly retrogradable; whilst crystalline forms appearing only on the outside of the globule are characterized by a significantly lower temperature (40-70° C) of re-pasting and an increased susceptibility to amylases activity than the retrograded amylose<sup>19</sup>. The productivity and properties of the retrograded starch obtained have been reported to be largely affected by: origin of starch<sup>20-21</sup>, amylose content<sup>22-23</sup>, length of the amylopectin end chains<sup>24-25</sup>, density of the paste<sup>26-27</sup>, physical<sup>28-29</sup> or chemical<sup>30-31</sup> modifications, the presence of other compounds<sup>29,32-34</sup> as well as by paste storage conditions<sup>35</sup>. Recrystallization of starch occurs most easily at a temperature approximating 0° C, but also at temperatures over 100° C, yet then it applies to amylase only. The retrogradation is intensified by the application of repeated freezing and defrosting of the starch paste<sup>27</sup>. The resulting starch thus produced is known as resistant starch that demonstrates resistance to digestibility by amylase enzymes and thus can be as an alternative nutrient aid for diabetic patients and as a rate controlling polymer coat in controlled drug delivery systems.

### 4. Freezing

Freezing is a physical treatment widely applied for preservation, drying and lyophilisation of starchy food<sup>36-37</sup>. It is also used for sample preparation in granule structural investigations by means of many physical methods, for instance in scanning electron microscopy (SEM) or transmission electron microscopy (TEM)<sup>38-41</sup>. It was reported that freezing influenced textural and gelatinization characteristics of starch<sup>42-43</sup>. It was also considered to cause some changes in the nutritional properties of starch<sup>44</sup>. Freezing of starch sols resulted in their coacervation and increasing retrogradation, while pregelatinised starch became less sensitive to retrogradation and stayed smooth after the process<sup>43,45</sup> as well as Perry and Donald (2001)<sup>46</sup> reported that some reversible structural disorder of starch granules occurred at sub-zero temperatures. Freezing water inside or outside of the starch granule seems to be a particularly effective way for modification for potato starch. This is because the starch B granules contain a significant amount of structural water, which determines the granular inner structure.

### 5. Ultra High Pressure Treatment

UHP treatment of the starch-water suspension reversibly hydrates amorphous regions within granules, leading to the granule swelling and crystalline region distortion, and thus, the crystalline regions become more accessible to water<sup>47-50</sup>. Finally, starch granules are non-thermally gelatinized over a critical pressure level which varied depending on botanical sources and crystal packing arrangements of starch<sup>47,50-52</sup>.

Further, UHP-treated starch that is little or partially gelatinized maintains its granular structure<sup>51-53</sup>, and restricts amylose leaching from granules and granule swelling capacity<sup>52-54</sup>. Moreover, UHP treatment has been shown to transit A-type crystallite pattern to B-type crystallite pattern<sup>54-55</sup>. These noted physical and structural characteristics of UHP-treated starch granules are anticipated to impact its reactivity in starch chemical modification and modified starch property.

### 6. Glow Discharge Plasma Treatment

A glow discharge plasma is used which can produce high energy electrons and other highly active species at room temperature. This approach has been extensively used in material modification<sup>56</sup>. When applied to starch, the highly active species can excite chemical groups in starch, inducing modification process without the assistance of other chemicals. Thermal degradation is minimized. Starch is highly cross linked by glow discharge plasma, without the assistance of conventional chemical agents, thus avoiding any environmental concerns<sup>57</sup>.

### 7. Osmotic-Pressure Treatment

“Osmotic-pressure treatment” (OPT) was carried out in the presence of high salt solutions<sup>58</sup>. Starch solution was suspended in sodium sulphate to obtain a uniform starch suspension and heat distribution. The potato-starch treated changed from a B to an A type after treatment with the gelatinization temperatures increasing significantly. A uniform heat distribution is provided for using this method as compared to heat-moisture treatment and modified starch is able to be produced in a large scale.

### 8. Thermal Inhibition

Thermal inhibition of starch is done by dehydrating starch until it is anhydrous (<1% moisture) and treating it to a temperature of 100° C or greater for a period of time enough to inhibit starch. An alkaline condition enhanced the effect of heating. Pastes formed from these starches had increased resistance to viscosity breakdown and a non-cohesive texture<sup>59</sup>. Thermal inhibition with ionic gums had sodium alginate, CMC and xanthan behaving as crosslinking agents and were able to form graft copolymers through ester formation<sup>60</sup>.

### 9. Gelatinization

The process of gelatinization causes substantial changes in both the chemical and the physical nature of granular starch due to the rearrangement of intra- and intermolecular hydrogen bonding between the water and starch molecules resulting in the collapse or disruption of molecular orders within the starch granule<sup>61</sup>. This results in irreversible changes in the starch properties<sup>62</sup>. Evidence of the loss of an organized structure includes irreversible granule swelling, loss of birefringence and crystallinity<sup>63,64</sup>.

### Chemical Modifications

Chemical modification involves the introduction of functional groups into the starch molecule, resulting in markedly altered physico-chemical properties. Such modification of native granular starches profoundly alters their gelatinization, pasting and retrogradation behavior. The chemical and functional properties achieved when modifying starch by chemical substitution depend, inter alia, on starch source, reaction conditions (reactant concentration, reaction time, pH and the presence of catalyst), type of substituent, extent of substitution (degree of substitution, DS1; or molar substitution, MS2), and the distribution of the substituents in

the starch molecule<sup>65-69</sup>. Modification is generally achieved through derivatization such as etherification, esterification, cross-linking and grafting of starch; decomposition (acid or enzymatic hydrolysis and oxidization of starch). These techniques are however limited due to issues concerning costumers and the environment. These techniques include:

#### 1. Etherification & Esterification

This method primarily includes substitution of hydrophilic hydroxyl groups of starch by various hydrophobic functional groups resulting into hydroxypropylation, carboxymethylation, acetylation, succinylation, etc.

The carboxymethyl substitution of starch hydroxyl groups gives rise to derivatives that are cold water-soluble. To prevent starch gelatinization, the reaction has to be carried out in an organic medium. Carboxymethyl starch, under the name sodium starch glycolate, is used in the pharmaceutical industry as a disintegrant and as a sizing and printing agent in the textile industry. Highly substituted derivatives are possible.

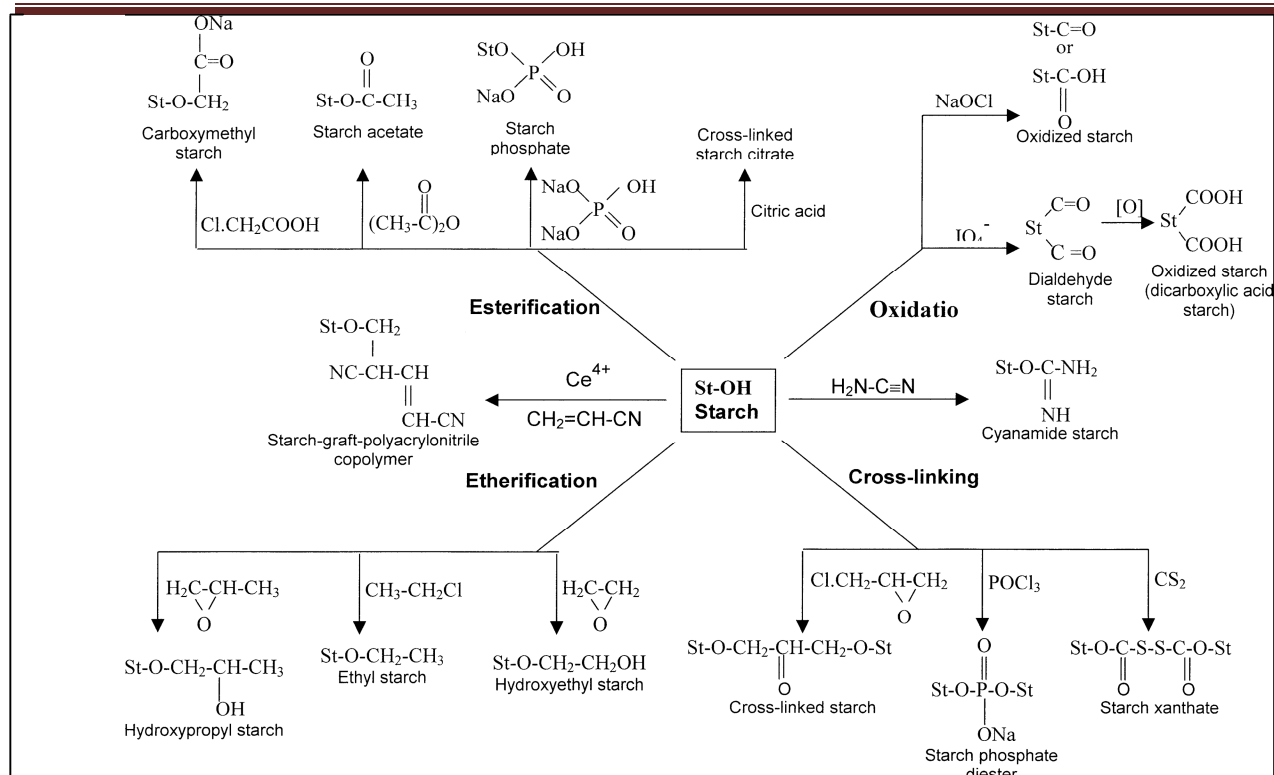
In acetylation, hydrophilic hydroxyl groups are substituted with hydrophobic acetyl groups. Acetylation makes starch more hydrophobic and prevents the formation of hydrogen bonding between hydroxyl groups and water molecules. Since the tendency of an aqueous starch dispersion to increase in viscosity on cooling and finally to gel is related to the association of amylose molecules, a treatment such as acetylation which retards or eliminates this crystallization or retrogradation will effect stabilization of the starch sol. Acetylation also prevents or minimizes association of amylopectin outer branches. This is of practical value in many industrial and food applications because such associations can cause cloudiness and syneresis in aqueous dispersions of starches<sup>70</sup>.

Hydroxypropylated starches are generally prepared by etherification of native starch with propylene oxide in the presence of an alkaline catalyst. The hydroxypropyl groups introduced into the starch chains are capable of disrupting the inter- and intra-molecular hydrogen bonds, thereby weakening the granular structure of starch, leading to an increase in motional freedom of starch chains in amorphous regions. Hydroxyethyl starch, prepared by reaction with ethylene oxide, was of considerable biomedical interest as a blood plasma expander and also as a cryoprotective agent for erythrocytes<sup>71</sup>.

Starch phosphorylation is the earliest method of starch modification<sup>72</sup>. The reaction gives rise to either monostarch phosphate or distarch phosphate (cross-linked derivative), depending upon the reactants and subsequent reaction conditions. Monoesters, rather than diesters, are produced with a higher level of phosphate substitution on starch. The introduction of phosphate substitution on amylose or outer branches of amylopectin prevents linearity of molecular chains due to steric hindrance. Thus, a situation is achieved where individual chain segments can no longer approach each other closely enough to establish intermolecular or intramolecular association; they, therefore, lead to a better paste clarity. The phosphate diester starches have the phosphate esterified with two hydroxyl groups, very often from two neighboring starch molecules<sup>73</sup>. This leads to the formation of a covalent bridge or cross-linking. Phosphate cross-linked starches show resistance to high temperature, low pH, high shear, and leads to increased stability of the swollen starch granule. They improve viscosity and textural properties of the starch. As a thickener and stabilizer, starch phosphate diesters are superior to unmodified starches. They also provide resistance to gelling and retrogradation, and do not synerese on storage.

Derivatization of starch with an ionic substituent group such as succinate at low degree of substitution (DS) converts it into a polyelectrolyte, which makes it acquire typical properties of a polyelectrolyte like increased hydrophilic character and increased solution viscosity<sup>74</sup>. This modification is also known to weaken the internal bonding that holds the granules together. In addition starch succinate offers very desirable properties such as low-temperature stability, high-thickening power, and low-gelatinization temperature, clarity of cooked food, good film-forming properties and reduced tendency to retrograde.

High cationic properties have been observed for starch citrates. The reaction is facilitated thermochemically by the dry heating (~120° C for 24 h) of citric acid to an anhydride, which reacts with starch to form an adduct, followed by further reaction to yield cross-linked starch citrate. The reaction can be controlled to maximize reaction efficiency, minimize cross-linking, and maximize carboxyl content. They are used to remove toxic, heavy metal ions in water purification (industrial waste water) as biodegradable ion-exchange materials against the petrochemically derived ion-exchange resins.



## 2. Cross-Linking

Cross-linking reinforces the hydrogen bonds in the granule with chemical bonds that act as a bridge between the starch molecules. Important factors in the cross-linking reaction include chemical composition of reagent, reagent concentration, pH, reaction time and temperature. Because the degree of cross-linking for food starch is very low, the extent of reaction and yield of cross-linked starch are difficult to measure chemically; hence there is a need for physical property measurement. When phosphorus oxy chloride (phosphoryl chloride,  $\text{POCl}_3$ , MW153.3) is added to starch slurry under alkaline conditions (pH 8–12), the hydrophilic phosphorus group immediately reacts with the starch hydroxyls, forming a distarch phosphate<sup>65</sup>.

Cross-linking alters, not only the physical properties, but also the thermal transition characteristics of starch, although the effect of cross-linking depends on the botanical source of the starch and the cross-linking agent. Decrease in retrogradation rate and increase in gelatinization temperature has been observed with cross-linked starch, and these phenomena are related to the reduced mobility of amorphous chains in the starch granule as a result of intermolecular bridges<sup>75</sup>. However, Jyothi et al.<sup>76</sup> showed that cross-linked starch has more pronounced syneresis than has native starch because of ordered structure in the starch paste, thus resulting in a higher degree of retrogradation.

## 3. Acid Treatment

In acid modification, the hydroxonium ion attacks the glycosidic oxygen atom and hydrolyses the glycosidic linkage. An acid acts on the surface of the starch granule first before it gradually enters the inner region. Acid modification changes the physicochemical properties of starch without destroying its granule structure and the properties of acid-thinned starches differ according to their origin<sup>70</sup>. The gelatinization temperature and the breadth of the gelatinization endotherm have also been shown to increase on acid hydrolysis. The retrogradation rate of acid thinned starch

increased as hydrolysis proceeded. The method for the manufacture of acid thinned starch entails treating concentrated starch slurry with mineral acid at temperatures below gelatinization temperature for specific period depending on the desired viscosity or degree of conversion. Effect of different acids ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ ) under similar conditions of treatment on molecular weight, alkali fluidity number, iodine binding capacity and intrinsic viscosity of various starches has also been studied<sup>77</sup>.

## 4. Oxidation

Oxidized starch is produced by reacting starch with a specified amount of oxidizing reagent under controlled temperature and pH<sup>78</sup>. Oxidation causes depolymerisation, which results in a lower dispersion viscosity and introduces carbonyl and carboxyl groups, which retard Recrystallization<sup>79</sup>.

## 5. Dual Modification

These include methods that involve the chemical reaction in the presence of a specific physical environment or an enzymatic treatment that make serve to enhance the rate of derivatization or can enhance the degree of substitution in some instances. Microwave-assisted esterification to produce starch maleate using the dry method had a reaction efficiency of up to 98% and a reaction time of less than 5 min. This is thought to be an efficient method in esterifying starch<sup>80</sup>. The high efficiency in producing succinylated cassava starch with microwave assistance was also observed by Jyothi et al, (2005)<sup>81</sup>. This is a good method to decrease the use of chemicals to enhance production.

Microwave and ultrasound irradiation was used for the Esterification of carboxymethyl cold-water-soluble potato starch with octenyl succinic anhydride. They were positively able to shorten the esterification time from a few hours to a few minutes. The derivatives displayed excellent emulsifying and surfactant performance properties<sup>82</sup>. A combined method of modification using crosslinking and phosphorylation on

rice starch provided modified rice starch with good freeze-thaw stability.

Modified corn and mung bean starch was prepared by treating native starch with a mixture of fungal  $\alpha$ -amylase and glucoamylase followed by hydroxypropylation with propylene oxide. This partial enzymatic hydrolysis produces modified starch that possesses significantly different functional properties to that of hydroxypropyl starch prepared under normal conditions<sup>83</sup>.

Rajan et al., 2007 have also demonstrated that the use of fungal lipase to enhance the Esterification of cassava starch using recovered coconut oil gives thermoplastic starch which has got wide use in plastic industry, pharmaceutical industries, and in biomedical applications such as materials for bone fixation and replacements, carriers for controlled release of drugs and other bioactive agents. Unlike chemical esterification, enzymatic esterification is ecofriendly and avoids the use of nasty solvents.

### Enzymatic Modifications

This involves the exposure of starch suspensions to a no of enzymes primarily including hydrolyzing enzymes that tend to produce highly functional derivatives. Origin of this technique can be dated back to the times when glucose syrup or high fructose corn syrup was produced.

The enzymes amyloamylases ( $\alpha$ -1,4- $\alpha$ -1,4 glucosyl transferases) found in eukarya, bacteria and archa representatives, breaks an  $\alpha$ -1,4 bond between two glucose units to subsequently make a novel  $\alpha$ -1,4 bond producing a modified starch that can be used in foodstuffs, cosmetics, pharmaceuticals, detergents, adhesives and drilling fluids. It is also a good source of plant-derived substitute for gelatin except that it forms a turbid gel whereas gelatin gels are transparent<sup>84</sup>. In the study by Hansen, Blennow, Pedersen, Nørgaard, and Engelsen (2008)<sup>85</sup> on gel texture formed in the modification of potato, high-amylose potato, maize and pea starch with amyloamylase (AM) isolated from the hyperthermophilic bacterium *Thermus thermophilus*, there was an improvement in gel texture compared to the parent starch. All the modified starches showed broadened amylopectin chain length profiles.

Cyclomaltodextrinase (CDase; EC 3.2.1.54), isolated from alkalophilic *Bacillus* sp. I-5 (CDase I-5) was used to modify rice starch to produce low-amylose starch products. The amylose content was found to have decreased significantly from 28.5 to 9% while there was no significant change in the side chain length distribution of the amylopectin. Storage of the modified rice starch at 4°C for 7 days, showed that the retrogradation rate had significantly retarded compared to the control sample<sup>86</sup>.

Treatment of maize starch with  $\beta$ -amylase,  $\beta$ -amylase and transglucosidase, maltogenic  $\alpha$ -amylase, and maltogenic  $\alpha$ -amylase and transglucosidase, resulted into significant reduction in digestion rate by 14.5%, 29.0%, 19.8%, and 31.0%, respectively producing resistant starch with reduced glycemic index that can be used in diabetes, prediabetes, cardiovascular disease and obesity. An increase in the starch branch density and crystalline structure in the modified starches was thought to contribute to the slow digestion<sup>87</sup>.

Kim & Robyt, 2000 worked with Cyclomaltodextrin Glucanoyltransferase (CGTase, EC 2.4.1.19) in the presence of isoamylase to produce cyclodextrins (CDs) with a maximum yield of 3.4 and 100% retention inside waxy maize

starch granules. Cyclomaltodextrins are also formed in situ, with the retention of CDs in the granule and this leads to the production of a new material that has properties of starch granules and Cyclomaltodextrins. Formation of complexes of organic molecules with Cyclomaltodextrins provides stabilization of light, heat and oxygen-sensitive materials in the starch granules and also a mechanism for their slow release besides providing special tastes, odors and flavors to the starch granules.

### Genetic Modification

These set of techniques involve transgenic technology that targets the enzymes involved in starch biosynthesis thus avails the advantage over environmentally hazardous post harvest chemical or enzymatic modifications. Genetic modification can be carried out by the traditional plant-breeding techniques or through biotechnology<sup>88</sup>.

#### 1. Amylose-Free Starch

Amylose-free waxy starch was produced by the simultaneous antisense downregulation of three starch synthase genes (Granular Bound Starch Synthetase, Starch Synthetase II and Starch Synthetase III), that resulted in waxy starch with small amylopectin chains. Generally mutant maize is grown on commercial scale, through modified corn, wheat, sorghum, amaranth are also available. Waxy starch thus produced is generally used in food industry as it gelatinizes easily, yielding clear pastes that will not gel.

#### 2. High-Amylose Starch

High-amylose starch in cereals is produced by a mutation in the gene that encodes starch-branching enzyme (SBE) IIB, which is also known as 'amylose extender (ae)'. In potato, discovery of the corresponding gene and the downregulation of its expression in tubers using antisense techniques enabled the production of starches that have slightly increased amylose levels<sup>89</sup>. However, both SBEI and SBEII had to be inhibited to create starches with amylose levels of more than 60%<sup>90</sup>. Recently, a more efficient method of inhibiting gene function using single domain antibodies against SBEII was used to produce starches that had even higher amylose levels<sup>91</sup>.

The derivative thus produced serves as an important precursor for the development of coating polymers that are resistant to enzymatic degradation and can be used in colon-targeted drug delivery systems. High-amylose starches can also be processed into 'resistant starch', which has nutritional benefits<sup>92</sup>.

#### 3. Altered amylopectin structure

Amylopectin synthesis is governed by a no of enzymes including starch Synthetase, branching enzymes and debranching enzymes each of which also has an isoforms. Therefore the downregulation of any one enzyme fails to produce an entirely new amylopectin features. However the inhibition of SS II and SS III isoforms in a few rice species demonstrates functional derivatives with low gelatinization temperature (below 50°C).

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