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Studies on Methods of Starch Modification and its Uses in Food and Non-Food Industries Products

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Abstract: Starch modification is a process whereas the alteration of starch structure is by affecting the hydrogen bond in a controllable manner. Starch - it's what holds our favorite foods together. Often utilized as a thickening and binding agent, starch is an integral ingredient in an assortment of foods. Modified starches provide enhanced properties to meet a variety of processing requirements and functionalities in the food industry. They serve as thickeners, texture agents, fat replacers and emulsifiers with excellent process and storage stability in products such as salad dressings, sauces, yogurt and frozen foods. Starch has numerous useful functional properties for food and nonfood applications. These include thickening, coating, gelling, adhesion and encapsulation. Modified starches are now a well established polymer which is used other than contemporary food based industries like textile, paper, petrochemicals etc.

Key words: Modified Starches · Starch Functionality · Applications · Modification Methods

INTRODUCTION

Starch is one of the most important, but flexible food ingredients possessing attributes for innumerable industrial applications [1]. 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. Starch contributes significantly to the texture and sensory properties of processed foods [2]. It exhibits a wide range of functional properties and it is probably the most commonly used hydrocolloid. One third of total starch produced is utilized for a variety of industrial applications that take advantage of its unique properties. Presently, the modern life is more and more dependent upon processed and convenience foods; it is almost impossible to live without them today. Starch is a carbohydrate of high natural abundance next to cellulose and chitin. It is the most common constituent of human diet, whereas it accounts for the major share of energy required for the sustenance of life. Starch granule differences amongst various plant species are accounted for, not only by the ratio of constituent molecules, but also by their location and interaction. Their interactions with other minor components, such as lipids and proteins, also influence the properties and the molecular architecture of the granules. A method using enzyme-gold cytochemical markers has been developed for the localization of amylose and amylopectin in starch granule. The shape of the granule appears to be modulated by the amylose content, especially in the appearance of concentric alternating layers Starch, the adsorptive material in corn grits, is used as a natural desiccant in several industries. The porosity and other surface properties of starch can be suitably modified by a preliminary α-amylase treatment. The resulting material has better surface properties [2].

Starch modification is a process whereas the alteration of starch structure is by affecting the hydrogen bond in a controllable manner. Usually, starch degradation can be done by several methods such as chemical degradation, physical alteration, genetic modification or enzymatic transformation. Chemically modified starches are of significant importance in many industrial applications. It can be used to improve functional properties of food products and used in the production of glue, coatings, chemicals and building materials [3]. Some chemical methods were used to produce simple carbohydrates through hydrolysis, cross linking or oxidation. Acid hydrolysis has been used to

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modify starch for over 150 years. This process involves suspending starch in an aqueous solution of hydrochloric acid or sulfuric acid at certain temperatures. In the presence of a strong acid and heat, the glycosidic bond between monosaccharides in a polysaccharide is cleaved. Modification of several starch bases such as potato, wheat, rice, maize and tapioca with acid-alcohol treatment has been studied. Ma and Robyt successfully prepared soluble starch from potato and waxy-maize starches by acid hydrolysis in different alcohols. All of the modified starches were readily soluble in hot water and their molecular weights progressively decreased from methanol modified starches to 1-butanol modified starch. The modified starches showed uniform granular appearance. Tharanathan *et al.* [4] continued their study on starches and investigated how acid concentration influences the hydrolysis inside the granule. Their results confirm that the mechanism of hydrolysis of starch granules suspended in alcohol involves the hydrolysis of glycosidic bonds with the water inside the granules. Meanwhile, the molecular and granular characteristics of corn starches [5] and physicochemical properties of maize and potato starches [6] modified by acid-alcohol treatments have been investigated. In the present study, we investigated the effect of acid hydrolysis in alcohol on some physical properties and degree of polymerization of sago starch (*Metroxylon sagu*).

Amylose Physicochemical Properties: The abundance of hydroxyl groups along the amylose molecules imparts hydrophilic properties to the polymer, giving it an affinity for moisture. Because of their linear nature, mobility and the presence of many hydroxyl groups along the polymer chains, amylose molecules have a tendency to orient themselves in a parallel fashion and approach each other closely enough to permit hydrogen bonding between adjacent chains. As a result, the affinity of the polymer for water is reduced and the solution becomes opaque [7].

Amylopectin Physicochemical Properties: The large size and the branched nature of amylopectin reduce its mobility in solution and eliminate the possibility of significant levels of interchain hydrogen bonding. On average, amylopectin has one branch point every 20 to 25 residues. The branch points are not randomly located. The amylopectin chains can be classified into three types according to their length and branching points. The shortest A chains carry no branch points. The B chains are branched by A chain or other B chains (e.g., B1, B2 and B3) The C chain carries B chains but contains the sole reducing terminal residue. It is now widely accepted that linear branched chains with DP~15 in amylopectin are the crystalline regions present in the granules [8]. These short chains form double helical ordered structure; part of the double helices can pack together in organized arrays in cluster form. This concept is compatible with cluster models of amylopectin, which during the last 20 years have received general acceptance. Modifications have been proposed since the model was introduced [9-12].

Starch-Value Addition by Modification: 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 above mentioned shortcomings, which will enhance its versatility and satisfy consumer demand [13]. Thus, the various chemically or otherwise modified starch derivatives offer significant value addition and give scope to develop a variety of fabricated food products having varied texture and mouthfeel [14]. These modifications are aimed at introducing desirable alterations in the starch structure so that its behavior is predictable and controllable. Therefore, the modified starch derivatives are the products of either glucosidic bond cleavage (acid modification to dextrins or forming new functional groups (carbonyl group formation during oxidation), or substitution of free available hydroxyl groups (by etherification or esterification), or bridging of molecular chains by cross-linking reactions. Functional property modification is better exemplified by ionic hydrophilic substitution than by non ionic hydrophobic substitution. In such functionalizations, the distribution of the introduced chemical substituents and of the remaining free hydroxyl groups within the anhydroglucose residue and along the polymer chain can exert a strong influence on the product properties. Some of the newly developed starch derivatives have been designed for nonfood uses because of escalating costs for safety studies necessary to clear them for food use. The various modifications employed are physical modification, non-destructive and degradative chemical (and enzymatic) modifications. Hydrothermal treatments, such as extrusion cooking (processing and drying), radiation, sonication and pressure treatments, are the physical modification methods used; starch is (partially) gelatinized, resulting in decreased hydrogen bonding. Such starches are cold water dispersible and are generally used in cold water dispersible foods, such as ice creams, infant foods, dry baking premixes, etc. Annealing of starch is another hydrothermal modification, where the granular starch is heated in excess water at a temperature above the Tg but below GT. Although no total gelatinization of starch takes place, annealing brings in significant changes in some of its properties [15]. Pre-gelatinization is the simplest of all starch modifications. It is effected by the cooking of aqueous starch slurry and subsequent drum drying. These starches are very useful in the preparation of ready-to-eat convenience foods, they give a palatable texture and help to hold other components in a uniform suspension. The market for such starches is steadily expanding. They are also useful as wall paper adhesives.

The different thermal processing treatments employed routinely in traditional cooking practices affect wheat starch properties to a considerable extent [16]. The processing conditions vary considerably between the treatments, especially with regard to water content, pressure, temperature and shear forces. Starch undergoes degradation during popping and extrusion cooking. The processed starch shows lower hot paste viscosity and higher water solubility. Gel permeation chromatography of such processed starch shows extensive macromolecular degradation. Pyrodextrins are starch derivatives obtained by either dry heating or heating of the aqueous starch slurry with or without pH change. They are commercially very useful products for various applications. The extent of dextrinization reaction can be controlled to get well-defined, tailor-made products [17]. Depending upon the experimental conditions, different products, such as white dextrins, yellow dextrins and British gums, are obtained. The three major reactions taking place during dextrinization are glycosidic bond cleavage (by hydrolysis), glycosidic bond formation (transglycosidation) and repolymerization. Increased branching was apparent upon dextrinization as evidenced by altered β-amylase digestion data, which indicates that the primary 6-OH groups are more reactive towards the formation of acetal linkages than secondary hydroxyl groups. Nevertheless, hydrolysis is the predominant reaction. Photooxidation of starch in the presence of atmospheric oxygen gives rise to gluconic and glucuronic acids. The former further degrades to yield D-arabinose. The reaction is of free radical type involving glycosidic bond cleavage, as well as the cleavage of C-5 and C-1 bond of glucose residues [12]. The baking expansion characteristics of sour cassava starch have been attributed to photooxidation during sun drying, especially at 254 nm [18]. The extent of depolymerization was also dependent on the botanical origin of the starch source. For example, corn starch was refractory to such an oxidation. Staining with Schiff's reagent revealed aldehydic groups in photodegraded starch and this reaction mechanism was akin to starch oxidation by periodate ions that results in the scission of C-2-C-3 bond, giving rise to dialdehyde groups. The HP-SEC profile sowed random depolymerization products, essentially induced by free radicals. The micronization (a physical damage induced by McCrone micronizing mill) of barley starch showed amylopectin of low molecular weight being preferentially solubilized in cold water [19]. Depending upon the conditions, more amylose was extracted into cold water. Some studies have been made on the degradation of starch by polarized light. Moonlight is assumed to be a source of polarized light [20]. Preliminary exposure to polarized light did not affect the crystalline structure of starch, although some changes in melting temperature and transition enthalpy were seen. Prolonging the exposure led to some degree of cross-linking, as shown by increased molecular weight. This has been attributed to activation of enzymes adhering to starch granule surface. Sensitivity of amylopectin to illumination exceeds that of amylose. In the case of UV light induced starch degradation, the radiation is first absorbed by acetal chromophore at C-1 of glucose unit followed by further photoreaction [21]. Formation of peroxide ion at C-1 leads to gradual chain scission and reduced molecular weight, paste clarity/viscosity and melting enthalpy. Prolonged irradiation leads to cross-linking with increase in molecular weight. The surface derivatization of starch granules is another approach for bringing in desirable property changes. The complexing of amylose by lipid molecules influences both thermal and rheological properties of wheat starch, whereby the leaching of amylose molecules from the granules to the water is restricted. Light microscopic studies show the presence of regions without birefringence, indicating lipid complexation. Such a surface modification with lipids would also affect starch gelatinization properties. For example, treatment with stearoylchloride in $CCl4$ and triethylamine (as catalyst) gives a starch derivative a fatty feel to the fingers [22]. It creates a carbohydrate water network that can mimic the texture of fat. They are of use as fat replacers in frozen desserts. Recently, a lot of concern has been shown by health conscious people on reducing the dietary calorie intake to avoid complications of obesity. Some of the starch derivatives are, indeed, being increasingly used as fat replacers or fat substitutes [23]. They provide the mouth-feel of high fat emulsions in low fat or fat free products, lend a glossy, fat-like appearance, allow less fat pickup in some fried products and are of use in the formulation of dietetic foods. They are either partially or totally undigested, thus contributing zero calories to the food on consumption. A lower rate of starch uptake also promotes a longer duration of satiety. The high water-holding capacity of some of the modified starches, which controls batter viscosity to aid in gas retention and starch and protein gelation, helps stimulating the moist mouth-feel of a high fat product. A number of fat mimetics, such as Maltrin, Oatrim, Amalean, Rice-Trim, Steller, etc., have been successfully commercialized in the west. Starch based fat replacers provide a slippery mouth feel when hydrated and depending upon the modification type, the sensory perception varies. They work well in high moisture systems, such as salad dressings, meat emulsions and some bakery products. They are not generally recommended for use in low moisture products [24].

High cationic properties have been observed for starch citrates. The reaction is facilitated thermo chemically by the dry heating (120?C for 24 hr.) 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 petro chemically derived ion-exchange resins. Recently, citrate starch has been used in food formulations as a source of RS.48 Depending upon the degree of esterification, the RS content of derivatized starch can be altered [25].

Controlled Acid /Enzymatic Degradation: This is one of the earliest methods of starch modification and the derived degradation products have a vast application potential. In its simplest methodology, the native granular starches are subject for treatment with acids, either at room temperature (for a period of several days) or at elevated temperature (for several hours). The extent of degradation is measured by the release of reducing sugar (called dextrose equivalent). Our understanding of starch granule structure and its hydrolysis pattern are still far from complete. Many new processing operations of starch hydrolysis have been described that would be useful in food technological applications [26]. Care should be taken to avoid transglycosylation reaction (acid reversion) that occurs during acid hydrolysis. Products such as gentiobiose, maltose, cellobiose, trehalose, etc., have been identified during acid reversion step. The partial decomposition of glucose may lead to the formation of hydroxylmethylfurfural, which is relatively a very reactive compound. This is subsequently broken down to formic and laevulinic acids [27]. Nageli dextrins, Lintner starch, etc., are some of the acid modified starch derivatives. The degree of polymerization of amylopectin or acid modified corn starch drops from 1450 to 625, while that of amylose drops from 525 to 480.59 A random attack at the branch point would create new linear chain segments that could appear as ‘apparent’ amylose and account for its observed increase [28]. Owing to problems encountered with acid hydrolysis, such as random attack, high yield of glucose, removal of acid later on, etc., the method is replaced by enzymatic hydrolysis. The production of starch syrups (high fructose corn syrups, HFCS) by enzymatic method is amongst the most advanced food technologies. It is probably the most successful enzyme technology of the food industry that is characterized by higher yields, wide range of products, higher products [29].

Methods have been standardized to use granular starches as such instead of gelatinized starch suspensions. Saccharification and liquification (thinning, decrease in viscosity) are the two major events taking place during starch amylolysis. The derived sugar syrups generally contain 71% solids, of which fructose is 42%, glucose is 52% and the rest are oligosaccharides. Syrups with higher fructose content (>90%) are also available, but they are expensive. These fructose-rich sugar syrups are highly valued in the food industry because of reduced calorie content and good tolerance by diabetics. They can be effectively used as fat mimetics and calorie reducers in flour-based dry mixes, baking systems, fillings, etc. Some of the corn starch derived chemicals, namely D-glucose and its O-methyl glycoside, are convertible to polymerizable derivatives, such as allyl ethers, acrylates and methacrylates, which can further be copolymerized to improve the properties [30]. Some of the multifunctional monomers produced by them are extremely useful in thermoset applications, such as fiberglass insulation binders and plywood adhesive resins. Especially regarding the latter, methyl glucosides showremarkable formaldehyde scavenging properties in high formaldehyde resins. They are also useful as textile finishing resins. A host of highly useful non-food applications are envisaged for such chemicals derived from corn starch. During the particleboard formation, the incorporation of starch hydrolyzates into urea-formaldehyde resins improves moisture stabilization of the resin and prevents oozing of formaldehyde in the hot press. Such resins also show improved burning behavior [31]. Recently, maltodextrins have been used as a biodegradable substitute for organic carrier liquids in ceramic molding [32]. Cross-linking helps preventing formation of cracks during thermal treatment. Glyoxal and glutaraldehyde are shown to be effective cross-linking agents for maltodextrins via acetalation- type reaction involving hemiacetal followed by acetal formation. Cyclodextrins are another well known cyclic maltooligosaccharides having 6, 7, or 8 glucose residues linked by α 1,4- bonds and are called α-, β- and γ cyclodextrins, respectively. They are produced by enzymatic conversion of liquefied starch by cyclodextringlucosyl transferases from *B. circulans* and *B. macerans*. Having a polar-hydrophilic exterior and an apolarhydrophobic interior, cyclodextrins form inclusion complexes with hydrophobic molecules of suitable dimension and configuration. This property is made use of in the food, pharmaceutical and agrochemical industries.

Oxidation: Oxidation is an useful modification method for bringing in changes in physicochemical properties of starch. Oxidative agents modify starch by forming new functional groups in the molecule. Oxidations with hypochlorite or more rarely with potassium permanganate are old methods but still used [33]. It involves conversion of primary hydroxyl group to carboxyl group. Because oxidation is an exothermic reaction, care must be taken to control the reaction temperature, lest an additional polymer chain degradation takes place [34]. The rate of oxidation is higher when carried out on gelatinized starch dispersion compared to granular suspensions. It is most rapid at neutral pH and the reaction is controlled by lowering the pH and destroying the liberated chlorine. A low amount of carbonyl groups introduced during oxidation is beneficial for imparting stability to starch dispersions. A-type crystal structure of cereal starches, being morestable, is less reactive than B-type crystal structure of potato starch. The iodine binding power of oxidized potato starch decreases with increase in oxidation, probably due to Am being preferentially oxidized/degraded. Periodate oxidation of starch leads to the session of C-2 and C-3 hydroxyl groups with the formation of dialdehyde or dicarboxylic acid derivative of starch. The reactive free aldehyde groups are capable of reacting with free amino- or imino groups to form rigid structures, a property made use of in hardening of paper and leather tanning. Acidic or neutral pH favors oxidation and at high pH carboxyl groups are formed. The latter leads to increased hydrophilicity, provides steric bulk, interrupts linearity of the molecule, impart anionic charge and minimizes retrogradation. Dialdehyde starch that mixes with proteins (zein or soy protein) at high temperature and pressure cross-links by reacting with hydroxyls to form hemiacetals/acetals, or it can react with amino groups to form Schiff bases; it may also react with sulfhydryl groups. Bioplastics made out of such composites show increased tensile strength and percentage of elongation. Darkening of color, due to decomposition during film molding by extrusion or thermopress method, can be eliminated by the incorporation of antioxidants. Dialdehyde starch is also used in medical applications as a chemical scavenger for urea and ammonia. Dialdehyde or dicarboxyl starches could also be subjected to hydrolytic cleavage giving rise to D-erythrose and glyoxal or cleavage followed by hydrogenation yielding mesoerythritol and ethyleneglycol [35]. All these products have considerable industrial potential, although new approaches for such glycol cleavage are needed. The process of the disordering of amylose and amylopectin chains through the melting of crystallites taking place during heating of starch with limited amounts of water is called ‘destructurized starch[31].The latter is useful in the development of extrusion-blown films from starch and poly (ethylene co-acrylic acid) graft copolymers. As much as 50% of the weight of starch can be incorporated into such composites, yet still retain acceptable properties. Bio-Pac packages consist of potato starch, maize starch, wheat starch and other similar raw materials that in the presence of water are finally baked and conditioned. To overcome the formation of homopolymerization of synthetic monomers during grafting to a considerable extent, intermediate formation of diazonium compounds from starch esters, such as anthranilates, has been developed, which creates primary free radicals directly on the starch molecule and favors enhanced graft copolymerization [36]. By variation in their ratio and mix-up, products are prepared that absorb more than 1000 g water. Such super absorbents are very useful in hygienic and sanitary product manufacture. Polymer grafted sago starch has been further modified by reacting with hydroxylamine to obtain derivatives having the property of high water absorption (192 g water/g material at31%starch in the absorbent [33]. Such products are useful in feminine napkins, disposable diapers, water blocking tapes, medicine and agriculture, where water absorbency or water retention is important.

Biotechnological Applications: Starch and its partially hydrolyzed products (dextrins, maltose and glucose) are an excellent fermentation base for the bulk production of a wide variety of biotechnological products, such as organic acids, antibiotics, vitamins, hormones, etc. As a sole carbon source providing energy for maintaining biological functions, starch derived carbohydrates are of very high commercial value. The oxidation of glucose by bacterial fermentation using *Aspergillus niger* or *Acetobacter suboxidans* yields gluconic acid (>97% yield) [37]. Sodium gluconate is the most useful salt, used as a chelating agent to produce deltagluconolactone, which is useful as an acidulant in food processing. Microbial fermentation of glucose using *Xanthomonas campestris* yields xanthan gum, a very useful commercial hydrocolloid. Osmophilic yeast *Moniliella tomentosa* utilizes glucose to convert into erythritol, which is an interesting, useful C-4 polyol with a functionality of 2-primary and 2-secondary hydroxyl groups. It is used in the manufacture of polyurethanes, alkyl resins, etc. Starch derived glucose can be fermented to produce lactic acid, which can either be polymerized or graft-co-polymerized to poly(lactic acid) polymer or composites having use as biodegradable films or bioplastics [38]. Potato starchwaste is used as a feed stock in such fermentative reactions. High molecular weight copolymers, which are spliced through using suitable coupling agents, have excellent mechanical properties. The dehydrated dimer, the lactide, upon ring opening polymerization, gives high molecular weight polylactide polymers that are of use in a number of biomedical applications, such as resorbable sutures, prosthetic devices, drug delivery systems, etc. [39]. Several polyhydroxyalkanoates are prepared using a variety of starch based feed-stocks.

Starch Functionality: Starch has numerous useful functional properties for food and nonfood applications. These include thickening, coating, gelling, adhesion and encapsulation. Some of these functionalities are unique to the polymer due to the structure of amylose and amylopectin and their organization. Gelatinization, retrogradation and pasting, which underlie starch functionality, are the three most important phenomena in starch applications. In this section, the mechanism, analytical techniques and factors influencing starch gelatinization, retrogradation and pasting will be discussed. The study of starch gelatinization and retrogradation will help us to understand the relationship between the structure and properties of starch [40-41].

Role of Starches in Foods: As a natural component, starch contributes to the characteristic properties of food products made from wheat, rice, maize, potato and legume seed. It is also widely used as a functional ingredient in many food products such as sauces, puddings, confectionery, comminuted meat, fish products and low fat dairy products. In order to meet the requirement of some food products, starch is chemically and/or biotechnologically modified as an ingredient. The role of starch in some foods is well known. In a food system, the roles of starch are to stabilize the structure and interact with other components to deliver or maintain nutrient and flavor. For example, starch can serve as thickening agents for sauces, cream soups and pie fillings; colloidal stabilizers for salad dressing; moisture retention for cake toppings; gel-forming agents for gum confections; binders for wafers and ice cream cones; and coating and glazing agents for nut meats and candies. An increased understanding of starch functionality and how it is affected by other ingredients and methods could lead to improvements in the quality of food products. The properties of foods are not governed simply by the starch and its molecular structure. Processing conditions and the amount of water available are crucial determinants of the final characteristics of the product. Starch molecules differ from other carbohydrate hydrocolloids because they are made functionally useful only by altering the granule package. When starch is heated in the presence of water or other components during processing, swelling of the granule, loss of crystallinity and a largely irreversible uptake of water are the results. In general, gelatinized starch begins to change (retrograde) when the system is cooled. Thus, starch retrogradation must be considered as a potential destabilizing influence on the physicochemical properties generated by starch gelatinization for the development of starch related food products. Based on the requirement of food products such as clarity and storage stability, starch from different sources with different physicochemical properties can be selected to meet specific needs. For example, maize starch retrogrades and becomes increasingly opaque much more rapidly at low temperature (e.g., 4°C) than potato starch. In this case, potato starch would provide greater clarity to the food product.

Thickening and stabilization are important functional properties of food starches. Although waxy cereal starches are more tolerant to cold storage than non waxy cereal and root and tuber starches [42], the granules are readily ruptured during cooking, resulting in low paste viscosity and pastes with a "long" cohesive nature. Native starches are also sensitive to shear, high temperature and acid treatment when cooked in water. Therefore starches used in food industry are often modified to improve their functionality and cross linking is the most widely used technology for this purpose. Cross-linked waxy cereal starches generally show a "short" spoonable texture, higher paste stability and resistance to cooking shear, temperature and low pH as compared to native starches [43]. However, cross linking reduces paste clarity and stability to cold storage. These undesirable characteristics can be improved by further modifications such as esterification or etherification.Although waxy corn is used as the major modified food starch in North America, [44, 45] reported that hydroxypropylated distarch phosphate from waxy barley showed higher freeze-thaw stability when compared to commercial samples of similarly modified waxy corn and tapioca starches. Lichtenthaler, *et al.* [30] reported lines of waxy hull-less barley (HB) that were completely devoid of amylose. The zero-amylose HB starch showed higher paste clarity and freeze thaw stability than waxy HB, corn and potato starches [46]. The zero-amylose HB starch may be modified by crosslinking to improve its paste properties while maintaining clarity and freeze-thaw stability.

Resistant Starch: As mentioned earlier, resistant starch is impervious to the effects of digestive enzymes, is not digested in the small intestine and undergoes some degree of fermentation in the large intestine, which allows it to function likes dietary fiber. Resistant starch has been categorized into four main types: type I is physically entrapped starch within whole plant cells and food material (e.g., in partly milled grains and seeds). The presence of intact cell walls contributes to the resistant starch content of legumes. More extensive milling and chewing can make these starches more accessible and less resistant. Type II resistant starch includes those granules from certain plant sources (e.g., the native crystalline starch granules in raw potatoes, green bananas and high amylase corns). Type III resistant starch comprises retrograded starch. Type IV resistant starch includes chemically modified starches that are used by food manufacturers to improve the functional characteristics of the starch. Although these resistant starches are found very widely in processed foods, their physiological effects may not be the same [47-50].

Characteristics: Resistant starch has a low calorie profile and can be used as a bulking agent in reduced sugar or reduced fat food formulations. It holds significantly less water than traditional dietary fiber. Resistant starch does not compete for the water needed by other ingredients and allows for easier processing because it does not contribute to stickiness. This may be advantageous in the production of low moisture products such as cookies and crackers. Products ranging from bread, crackers to muffins have better taste, mouth feel and appearance when resistant starch is used to replace traditional fiber sources. In most applications, it does not alter the taste, texture, or appearance of the food [51].

Application in Non-Food Industry: Modified starches are now a well established polymer which is used other than contemporary food based industries like textile, paper, petrochemicals etc. Paper Industry Starch is used as a flocculants and retention aid, as a bonding agent, as a surface size, as a binder for coatings and as an adhesive in paper industry [52]. Current consumption of industrial corn starch for paper and paperboard production in the US exceeds 2.5 billion pounds (1.1 million metric tons) of which 40% is chemically modified starch.

Textile Industry: Textile industry is another major user of modified starches in different ways. It is specifically used for warp sizing preparatory to weaving, for sizing or finishing the cloth after it is woven and in printing certain types of fabrics. Modified starches are also used in large quantities in laundering, both in commercial establishment and in home [53].

Plastic Industry: Starch offers several prospective advantages as a raw material for plastics applications because it is renewable, biodegradable and obtained from a variety of plant sources and is a low-cost material. Addition of polyvinyl produces thermoplastic starch and addition of polystyrene produces biodegradable. Granular starch can be used as a filler to enhance biodegradation of commodity plastics, such as conventional and linear low density polyethylene and high density polyethylene, polypropylene and polystyrene [54].

Petroleum Industry: The petroleum industry has found that modified starch imparts desirable characteristics to the mud used in drilling oil wells and thousands of wells have been drilled using such mixtures (sand, water and pregelatinized starch). Numerous modified starches have been prepared and their suitability studied for various oilfield applications such as filtrate-loss control, mud-rheology modification, shale stabilization, enhanced oil recovery (EOR), drag reduction and water shutoff and some of these starches have been widely used in this area [55].

CONCLUSIONS

In conclusion, it seems obvious that the technological potential and industrial utility of starch gets multiplied by several folds by suitable modification, as exemplified in this article and other contemporary literature. Although legislative approval for the use of novel starch derivatives in processed food formulations is still under debate, many tailor-made starch derivatives with multiple modifications are being prepared and characterized. In the area of thermoplastic bio-packaging, the usefulness of starch is much more significant and rewarding. Synthetic polymers are gradually being replaced by biodegradable polymers. It may be predicted that eventually biodegradable packaging will find larger and more receptive markets in future. Surely, tomorrow's packaging needs will be dictated by such biodegradable materials/ composites. By the specific functionalization of starch, new products are continuously being developed that find increasing use in a wide variety of industrial applications, leading to a significant value addition. With the explosion of interests and the availability of a very wide variety of such bio-packaging materials in recent years, it is only natural that there can be no boundaries-only possibilities.

Value addition in native starch produces derivatives remains very attractive area due to high margins and abundant food and industrial applications. This is a critical review on industrial prospects of modified starch products that are utilized in different food and non-food.

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