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A Review

Starch : Modification techniques and resistant starch on human wellness

NOUSHEEN NOORUL IYN.I, P. BANUMATHI, S. KANCHANA, S.P. SUNDARAM, S.M. IBRAHIM, M. ILAMARAN **AND** J.SELVI

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See end of the paper for authors' affiliations

Correspondence to **:**
NOUSHEEN NOORUL IYN. I.
Department of of Food Science and Nutrition, Home Science College and Research Institute, T.N.A.U., MADURAI (T.N.) INDIA
Email:noush_f 007@yahoo.com

ABSTRACT : Starch modifications such as physical, chemical and enzymatic treatments are done to disrupt the granule structure and to induce the required functional properties of native starches. Resistant starch, a non-digestible polysaccharide and highly retrograded starch fraction used as a functional food ingredient which is formed upon modification of starch and food processing is a useful starch derivative. Resistant starch had evoked a considerable position in human society due to its reputed and positive impacts on health analogous to dietary fibre.The present review focuses on the starch modification techniques to improve the functional properties and resistant starch content in foods.

KEY WORDS : Starch modification, Starch derivative, Resistant Starch, Food ingredient, human health

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In modern societies, great emphasis is frequently placed on the relationship between health, lifestyle and diet. A focus has shifted from reactive cure to proactive prevention for major diseases like coronary heart disease, diabetes, obesity and certain cancers (e.g. of the colon and rectum). Given the nutritional connotation that "you are what you eat", there is much debate surrounding food fortification with fibre. Resistant starch (RS) in its natural or commercial has a role to play with regard to the nutritional benefits of fibre fortification (Murphy, 2005). RS goes under many definitions but, in essence, it is the starch or products of starch degradation that escapes digestion in the human small intestine of healthy individuals and may be completely or partially fermented in the large intestine as a substrate for the colonic microflora. The consumption of resistant starches may improve glucose and lipid metabolism and can reduce the risk of the chronic disorders (Hodsagi, 2001).

Starch is a naturally occurring biodegradable, inexpensive and abundantly available polysaccharide. Resistant starch is an important starch derivative obtained by modification of starches. Pure isolated starch (native starch) is white in colour, amorphous, relatively tasteless solid which possess no odour and insoluble in cold water. Starches find major applications as texture stabilisers and regulators in food systems, but limitations like low shear stress resistance, low thermal resistance, susceptibility to thermal decomposition hinder their use in food applications (Kaur *et al.*, 2007). In general, native starches produce weak-bodied, cohesive, rubbery pastes when heated and undesirable gels when the pastes are cooled (Adzahan, 2002) . So in the unmodified form, starches have limited use in the food industry. That is why, the food manufacturers generally prefer starches with better behavioural characteristics than those provided by native starches. The properties of starches can be improved by various modifications. Modified starches have been developed for a very long time and its applications in food industry and in human health are really significant nowadays.The manufacturing of resistant starch (indigestible residues) could be done by physical modifications, chemical modifications and enzymatic modifications. The physical modifications is safe, easy and cheaper than chemical modifications (Chinfu, 2010) but chemically modified starches such as esterified, etherified and/or cross-linked starches have been widely used for various prepared foods such as snack foods, breads and cakes to improve their quality (Miyazaki *et al.*, 2006). Modified starches serve as thickeners, texture agents, fat replacers and emulsifiers with excellent process and useful functional properties of food. Resistant starch exhibit lower impact on the sensory properties of food compared with traditional aspects due to its swelling capacity, viscosity, gel formation and water-binding capacity which make it useful in a variety of foods (Abbas *et al.*, 2010). By this resistant starch has drawn considerable attention over the last two decades.

Starch :

Among food carbohydrates, starch or amylum occupies a unique position and is considered as the main foundation of carbohydrate in the diet of human (Ratnayake and Jackson, 2008). It is one of the naturally occurring major reserve polysaccharides and the most abundant renewable resources available to man. No other single food ingredient compares with starch in terms of sheer versatility of application in the food industry. Second only to cellulose in natural abundance, this polymeric carbohydrate was designed by nature as a plant energy reserve. Starch molecules are hydrogen bonded and aligned radially in the granules that have semi crystalline characteristics. This a-glucan is a composite polysaccharide of homo-glucan amylose, a minor component usually 20-30 per cent and amylopectin usually 70-80 per cent of the total glucan (Roder *et al*., 2005).Amylose has a linear structure with 1, 4 glycosidic bonds, whereas in amylopectin the structure is highly branched with a-1, 4 and a-1, 6 glycosidic bonds. The molar masses amount to about 150.000 to 750.000 for amylose, whereas it amounts up to 10 million for amylopectin. Amylose may be found in various crystalline polymorphous with right-handed double helices and left-handed single helices (Trevor *et al*., 1998). Amylopectin is a branched polydisperse polymer with an amylose type 1-4 a linked backbone that bears clusters of 1-6 a linked glucopyranosyl branched with average length of 20-30 residues (Subarica *et al.*, 2012). 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 (Rooney and Pfugfelder, 1986) Table 1.

Modified starches-definition :

Modified starches are those which have one or more of their original characteristics altered by treatments in accordance with good manufacturing practices (Light, 1990). Starch modifications are a means of altering the structure and affecting the hydrogen bonding in a controllable manner to enhance and extend their application. The alterations take place at the molecular level, with little or no change taking place in the superficial appearance of the granule (Aberoumand, 2011). Modified starch is produced when the morphological or physico - chemical structure of native starch is disrupted in some way, such as during food preparation. Since it is more susceptible to organic decay than native starch granules, ancient modified starch is only to be preserved in particular conditions, such as in arid or otherwise unusually protected situations (Samuel, 2006).

Why modification :

To achieve much (new) functionality during processing and make starch suitable for many foods, industrial and in human health applications. Due to increase in economic development and market demand, the research on production of modified starches is developing very rapidly. Starch modification is done to improve the functional properties like conferring rheology (flow ability, elastic/viscous properties, texturizing) and stabilizing, viscosity control, long shelf-life stability and to increase shear stability, process tolerance and for the improvement of pH-stability, acidic stability of the native starch. The improvement of paste stability are such as retrogradation (resistant starch), gelling, amylose crystallisation, freeze-thaw-stability and the film forming properties (elasticity, cohesion) and adhesiveness, to improve flocculation, water binding and the starch for sensoric properties (Kozich and Wastyn, 2012).

Resistant starch and its classification :

The term "resistant starch" (RS) was adopted by Englyst, a British physiologist, in the early 1980s. Resistant starch (RS) is a starch that escapes digestion in human's small intestine and may be digested in the large intestine where it is fermented by colonic microflora (Chou and Lin, 2007; Kim *et al.*, 2006; Mun and Shin, 2006). Resistant starch may be used in the management of diabetes, and diet high in resistant starch has been related to reduce post-prandial glycemic and

Table 1 : Properties of Starch components (Rooney and Pfugfelder, 1986)

Starch properties	Component	
	Amylose	Amylopectin
General structure	Linear	Branched
Branch points	Name [a]	1 per 20 to 25 glucose units
Degree of polymerisation (DP)[b]	˜ 1,000	˜ 10,000 to 100,000
Iodine complex colour	Intense blue	Reddish - brown
Solution stability	Low	High

[a] Branched amylose may have 1 or 2α-1,3 branches per molecule, [b] Number of glucose residues per molecule

insulinemic responses (Alanso *et al.*, 1999). Therefore, products containing high level of RS might be qualified as functional foods (Englyst and Hudson,1997) Table 2.

Methods of modification :

Starch modifications - mean that numerous highly functional derivatives have enabled the evolution of new processing technologies and market trends. Starch modification can be broadly grouped as namely: physical, chemical and enzymatic modifications. Among these modification methods, chemical means is the most frequently used process (Daramola and Osanyinlusi, 2006).

Physical modifications :

Physical modification of starch mainly applied to change the granular structure and convert native starch into cold water soluble starch or into 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. There are numerous physical treatments leading to novel functional properties of starch that are due to the modification of the crystalline structure of starch granule while its integrity is preserved. Among them, the most investigated processes are pregelatinization, annealing and heat-moisture treatments (HMT) which are using a great variety of operating conditions. Recently, the effects of high pressure and gamma irradiation applied in a hydrostatic or dynamic ways were also explored.

Pregelatinization :

Pregelatinized starch (called pregels or instant starches) is starch cooked and then dried in the starch factory on a drum dryer or in an extruder, making the starch cold water soluble. A spray dryer is used to obtain high quality pregelatinized starch powder. These dispersions show less thickening and gelling power than the corresponding, freshly cooked pastes prior to drying. There is an industrial need for instant products that disperse readily, giving various types of texture: smooth, pulpy or grainy. Physical treatments of starch can be classified according to the preservation of the granular structure of starch. Drum drying or extrusion cooking are common processes to produce pregelatinized starches; such treatments are accompanied by the loss of the integrity of the starch granules together with a partial depolymerisation of starch components.

Pregelatinization methods discussed here include drum drying, spray cooking, solvent based processing and extrusion.

Drum drying (starch suspensions or starch pastes) - very widely used :

Pregelatinized starches are produced commercially by applying starch-water slurries to a heated surface (rolls or drums) in order to destroy the hydrated starch granules and produce a cooked starch (Colona *et al*., 1987). Drum - drying is the most widely used technique at industrial scale in producing pre-gels. The overall pregelatinization process occurs in one or two steps. For the one-step process, the starch slurry (up to 45% dry matter) is fed onto the drums that are used to gelatinize and to dehydrate starch paste at the same time. For the two-step process, the starch slurry is primarily cooked in a heat exchanger or a high-temperature jet cooker and dehydrated by drum drying (Loisel *et al.*, 2004). The process is simple and straight forward in theory, but becomes unpredictable and elusive to control in actual practice, which explains the difficulty of obtaining reproducible products by this process (Powel, 1967). The roll or drum drying involves spreading a hot starch paste between rolls or drums to produce a dried flake product. The food material can vary from slurry of raw starch to a thoroughly cooked starch paste. The end product, which depends upon the parameters of rolls and drums, can be roughly cube shaped, or flat and flaky, the former giving high bulk densities and slow rehydration rates and the latter, low bulk densities with high rehydration rates. The results of a study in a wheat starch (Majzoobi *et al.*, 2011) indicated that drum drying destroyed native starch granules, degraded molecular structure and reduced the degree of crystallinity of starch. Pre-gelatinized starch (PGS) showed cold water viscosity at 25ºC, while native wheat starch was not able to increase the viscosity under this condition.

Spray cooking (starch suspensions) - increasing in use:

Pregels can be made by first cooking starch slurry in a high-pressure, high-shear jet-cooker and then pumping it through a spray dryer. As the cooked starch passes through the nozzle of the dryer, it is atomized and dried. However, this method is not generally used commercially because of its high costs. An alternative spray-cooking process omits the jet-cooking step and instead uses steam injection at the spray dryer nozzle to cook out the starch as it is being atomized.

Table 2 : Nutritional classification of resistant starches (RS) (Englyst and Hudson, 1997)

Type of RS	Examples of occurrence
RS1 - Physically inaccessible	Whole or partly milled grains and seeds
RS2 - Resistant granules	Raw potato, unripe banana, some legumes and high amylose starch
RS3 - Retrograded	Cooked and cooled potato, bread and corn flakes
RS4 – Chemically modified	Etherised, esterified or cross bonded starches (used in processed foods)

Starch produced by this method is uniformly cooked or gelatinized with a minimum amount of shear and heat damage. Because the pregelatinized granules remain essentially intact, upon rehydration they have the smooth texture and viscosity of a cook-up starch. These types of pregels are considered high-performance cold water soluble products.

Extrusion cooking (semi - dry starch) - rarely used:

Extrusion cooking was first applied in the pasta industry in the mid-1930s to allow continuous production and versatility. Pasta products are generally obtained by extrusion cooking of flour (semolina) dough through a die to produce a required shape. Pasta extrusion cooking is characterized by low shear and low heat (30-40°C), insufficient to cook the material. The development of synthetic polymers has created a demand for a technology of shaping by extrusion cooking or moulding and this process was transferred to the food industry in the 1960s, initially for the production of ready-to-eat (RTE) breakfast cereals. In extrusion cooking, the pressure, generated behind the discharge die, forces the material through the aperture; at the die exit, the product expands due to the pressure drop. The temperatures attained by food materials during extrusion-cooking can be high (~ 200°C) although the residence time in the extruder is normally very short (30-45 s); hence, the extrusion process is often called a high-temperature short-time treatment (HTST) Table 3.

Solvent - based processing :

A process for preparing pregelatinized starch by using aqueous alcohol was reported in 1971 and put into commercial use during the mid-1980s. The process generally involves heating about 20 per cent starch in an alcohol such as ethanol containing 20-30 per cent water at approximately 160-175°C (320-350°F) for 2-5 min. The resulting product is generally referred to as a CWS granular starch. The granular integrity is maintained (unlike drum-dried or extruded starch products), but its birefringence is lost. The use of alkali in the process has been reported; however, it has not yet been adopted commercially (Haghayegh and Schoenlechner, 2011).

Heat - moisture treatment :

Heat-moisture treatment of starch is a physical treatment in which starches are treated at varying moisture levels (<35%) for a certain period of time at a temperature above the glass transition temperature but below the gelatinization temperature. However, the temperature is often chosen without considering the gelatinization temperature.

HMT of pulse starches at restricted moisture levels (22-27%) and high temperature (100-120^{0}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 (Chung *et al*., 2010).

The difference of physical modifications, treatment time and storage time on the resistant starch content (RSC) of high amylose maize starch (HAMS) were compared to establish the optimal conditions of physical modifications for resistant starch manufacturing. The effects of different physical modifications (hot plate, water bath, high pressure autoclave) and storage time (storage at 7°C for 7 and 14 days) on the resistant starch content was experimented (Chou *et al*., 2010). The results of storage indicated that the RSC of most sample would be significant increased by storage. Thus, the HAMS treated by water bath for 60 min, subsequent storage at 7°C for 7 days exhibited the highest RSC. In addition, the RSC of water bath and high pressure autoclave treatment were higher than that of hotplate treatment after storage.

Resistant starch type 3 (RS3) is the retrograded amylose formed after heat-moisture treatment, which occurs in cooked and cooled potatoes and also in ready-to-eat breakfast cereals. Commercially developed RS3 starches such as NOVELOSE by National Starch and Chemical Company are derived from heat-moisture treated high amylose corn starch and are ready for the market as a functional food ingredient.

Annealing :

Annealing of starch is a physical treatment whereby the starch is incubated in excess water (>60% w/w) or intermediate water content (40 to 55% w/w) at a temperature between the glass transition temperature and the gelatinization temperature for a certain period of time. Annealing increases starch gelatinization temperature and sharpens the gelatinization range. However, there are few commercial processes to be used to generate starches with higher gelatinization temperatures. Often annealing is applied unintentionally, such as the steeping step used in the maize wet-milling process.

Starch obtained from red sorghum grains can be modified physically by two common modifications such as annealing and HMT. Temperature (60-90^{0}C) exerted a change on the swelling capacity and solubility of the starch, and also the starches behaved differently towards acidic and alkaline regions. Both annealing and HMT increased the surface hardness of red sorghum starch gels and the hardness was

Table 3: Comparison of drum drying and extrusion cooking on the properties of wheat starch (Haghayegh and Schoenlechner, 2011)

Drum drying	Extrusion cooking
Reduced degradation leading to low water solubility	Pronounced degradation leading to high water solubility
High swelling power (10-20 g water/g dry sediment)	Low swelling power (3-10 g water/g dry sediment)
Water-soluble fractions enriched with amylose	Water-soluble fractions with the same amylose/amylopectin ratio as in native starch

inversely proportional to the swelling power. Therefore, physical modifications would enhance gel formation, which is good for the food industries (Kayode *et al.*, 2005).

The hydrothermal treatments such as annealing and heat-moisture treatment for the germinated brown rice increased pasting viscosity and reduced starch digestibility (Chung *et al.*, 2012).

Impact of annealing (ANN) and heat-moisture treatment (HMT) on rapidly digestible starch (RDS), slowly digestible starch (SDS), resistant starch (RS) and expected glycemic index (EGI) of corn, pea, and lentil starches in their native and gelatinized states were determined (Chung *et al.*, 2009). ANN was done for 24 h at 70 per cent moisture at temperatures 10^0Cand 15^0C below the onset (T_0) temperature of gelatinization, while HMT was done at 30 per cent moisture at 100 and 120^0C for 2 h. The gelatinization temperature range decreased on ANN but increased on HMT. ANN and HMT increased RDS, RS and expected glycemic index levels and decreased SDS levels in granular starches. HMT had a greater impact than ANN on RDS, RS and SDS levels.

Gamma irradiation :

Modern, non-conventional methods of starch modification is Gamma irradiation which are fast, low cost and environmentally friendly because they do not use pollutant agents, do not allow the penetration of some toxic substances in the treated products and do not generate undesirable residual products, do not require catalysts and laborious preparation of sample. There are reported several studies related to starch treatment with ionizing radiation, especially with gamma radiation (Mac Arthur *et al.*, 1984, Sokhey *et al.*, 1993; Kang *et al.*, 1999; Wu *et al.*, 2002 and Ezhekiel, 2007). Recently, information regarding starch treatment with electron beam (e-beam) in different irradiation dose range, either at low or relative high doses (0 - 25 kGy (DeKerf *et al.*, 2001; Pimpa *et al.*, 2001) or at very high doses (> 50 kGy) (Kamat *et al.*, 2007; Shishonok, 2007) were reported. The studies concerning the effects of ionizing radiation were performed on starches extracted from various vegetable sources such as corn (Kang *et al.*, 1999; DeKerf *et al.*, 2001; Adail *et al.*, 2001) wheat (MacArthur *et al.*, 1984; Kaksel *et al.*, 2008), potato (Shishonk *et al.*, 2007; Ezhekiel *et al.*, 2007) barley endosperms, rice (Wu *et al.*, 2002; Bao *et al.*, 2005) or sago (Pimpa *et al.*, 2001). The reported data showed that ionizing radiation treatment generates free radicals on starch molecules that can alter their size and structure (Raffi *et al.*, 1980;Ceisla and Eliasson, 2002; Sabularse *et al.*, 1991; Sokhey *et al.*, 1993). Therefore, hydrolyze of the chemical bonds occurs by cleavage of starch macromolecule into lower fragments of dextrin, which can be either electrically charged or uncharged as free radicals (Kamg *et al.*, 1999). This type of treatment may change the functional and physicochemical properties of starch leading to the increase of solubility (Bao and Carke, 2002) the reduction of swelling power (Mc Arthur *et al.*, 1984) as well as the reduction of relative viscosity of starch paste (Adeil *et al.*, 2001) as a function of the irradiation dose.

High hydrostatic pressure in modifying functional properties of starches :

High hydrostatic pressure can be applied to starch to induce gelatinisation at room temperature (20-25^0C), at a pressure ranging from 400 MPa (for wheat starch) to 900 MPa (for potato starch). It is also possible to use the combined effect of pressure and temperature to achieve gelatinisation. The properties of heat gelatinised starches are different from the ones of pressure gelatinised starches. The results of many papers indicate a limited swelling power of pressure gelatinised wheat starch compared to the heat gelatinised one. Similar results were found for standard maize, whereas waxy maize starch and tapioca starch exhibited a higher swelling power after pressure treatment (Stute *et al.*, 1996).

The effects of hydrostatic pressure on the structural and functional properties of starch can be summarized as follows:

- Transition from A to B-type X-ray pattern, the B-type starch remains unchanged (Guraya and James, 2002).
- Preservation of the granular structure and restricted amylose leaching during gelatinisation (Marutha *et al.*, 1994).
- No change in the molecular weight distribution of starch components.
- Modification of the paste viscosity and gel formation due to restricted swelling power of the starch granules and low solubility of amylose. The retrogradation of pressure-induced gels is supposed to occur within starch granules; this would make starch gels less sensitive to ageing. As a possible application pressurized starch could be used as fat substitute; the starch granules might simulate fat droplets as they can be considered as micro particles of well - defined size distribution (Loisel *et al.*, 2004).

In general, HHP restricts the swelling power of starch granules, so their viscosity is lower in comparison with the samples processed by heating. On the other hand, it provides the possibility of starch gelatinization at room temperature or even below 0°C. A number of starches when pressurized at concentrations higher than 15 per cent produce paste with creamy texture which can be used in dietary foods instead of oil. Furthermore, HHP treatment prevents the harmful effect of starches in some tissues due to reduced size of starch granules. In addition, HHP treatment produces resistant starches, which are valuable in the treatment of diabetes and some cancers. In all, since the degree of similarity of changes is achievable in different situation, that it has great importance in food industry, because of the optimum pressure condition is determined, based on the main objectives a like deactivation of microorganisms and enzymes, transferring, mixing, pumping, maintaining quality, aroma, texture, etc (Nasehi and Javahari, 2012).

Chemical modifications :

The starch modification is the treatment of native starch with small amounts of approved chemical reagents reactions under proper agitation, temperature, and pH associated with the hydroxyl groups of the starch polymer. When the reaction is complete, the starch is brought to the desired pH by a neutralizing agent and then purified by washing with water and recovered as a dry powder for a functional food ingredient and pharmaceutical application. In most cases, the derivatization efficiency is about 70 per cent or more. Modification is generally achieved through substitution, degradation and cross linking .In general; the chemical modification of starch is usually performed in an aqueous medium. The extent of chemical modification is generally expressed as the *degree of substitution* (*DS*) when the substituent group (e.g., acetate or phosphate) reacts with the hydroxyl groups of the D-glucopyranosyl unit. Molar substitution (MS) is used when the substituent group can further react with the reagent itself to form a polymeric substituent.

Substitution :

Chemical modification of starch resulting in the addition of a chemical blocking group between starch polymers and involving derivatization with a monofunctional reagent through ester or ether formation (Thomas and Williams, 1999).

Multiple treatments with acetic anhydride under alkaline conditions (acetylation) on corn starches caused no significant changes in shape, size or external appearance of the starch granules.Acetylation has caused an increase in swelling power, solubility, paste clarity, and freeze-thaw stability of corn starch (Ayucitra, 2012).

The properties of resistant starch are also observed in monostarch phosphate, however in this case the resistance degree increases along with a degree of substitution with phosphoric acid (Sitohy and Ramadan, 2012). A product of monostarchphosphate heating with glycine is characterised by substantially higher resistance to the activity of amylolytic enzymes than the monostarch phosphate itself (Maslyk *et al.*, 2003). Heating of soluble starch saturated with iron (III) ions also decreases its susceptibility to the enzymatic activity (Leszczynski *et al.*, 2000). Acetylated starch of papilionaceous plants is characterized by a relatively high degree of resistance to the activity of amylolytic enzymes. Similar properties are displayed by starch of papilionaceous plants modified by hydroxypropylation. Resistance of the above - mentioned starch preparations increases with an increasing degree of substitution (Hoover and Zhou, 2003). Hydroxypropyl distarch phosphate exhibits twofold lower susceptibility to the activity of amylases compared to native starch.

Cross-linking :

Cross-linking is a type of chemical modification to improve granule stability with new covalent bonds, thus providing desired functional properties. Cross-linked starches offer acid, heat and shear stability over their parent native starches. The common crosslinking reagents are sodium trimetaphosphate (STMP), epichlorohydrin (ECH) and phosphoryl chloride ($POCl_3$). Crosslinking of starch with STMP and ECH precedes slowly and therefore STMP and ECH could penetrate into the inner of the starch granules. The reaction with ECH forms mono or di-starch glycerols depending on the conditions, such as starch concentration, temperature, and starch state.The cross-linking treatment prevents granule rupture under acidic conditions using STMP and ECH reagent. ECH produced higher cross linked in banana starch (Marin *et al.*, 2011).

The present study shows the effect of diets supplemented by different kinds of chemically-modified potato starch on small mammals (rats). Partial substitution of rats diets by the experimental starches (chemically-modified potato starches subjected to oxidation, esterification, cross-linking and dual modification) caused a significant increase in body weight gain compared with the control animals. A statistically significant increase of the total SCFA (especially butyric acid) in the caecal digesta was found. The significant lowering of luminal ammonia concentration, pH of caecal or colonic content, triacylglycerols, total cholesterol and activity of β-glucuronidase in caecum content were noticed compared to the control rats. The results indicate that the chemically-modified potato starch preparations are a good substrate for the intestinal micro ecosystem and may promote the beneficial status of the gastrointestinal tract of rats (Wronkowska *et al.*, 2011).

Degradation :

Degradation is a collective term for a range of chain-cleavage reactions of starch.

Pyroconversion (dextrinization) :

In pyroconversion, starch products are prepared by dry roasting acidified starch. These products are referred to as dextrins or more accurately as pyrodextrins. Depending upon the reaction conditions (e.g., pH, moisture, temperature, and length of treatment). Pyrodextrins are typically classified as white dextrins, yellow dextrins, and British gums, depending upon processing conditions and their resultant properties.Commercial pyrodextrins are generally produced by heating dry, acidified starch in a reactor with good agitation.

Acid may be sprayed onto the starch to facilitate glycosidic hydrolysis. The chemistry of acid-catalyzed pyrolysis is complex. Depending upon the conditions of dextrinization, both hydrolysis and repolymerization can occur Pyroconversion generally creates new glycosidic bonds in addition to the existing α-1,4 and α-1,6 linkages (Table 4).

Dextrins obtained under specified conditions demonstrate the properties of resistant starch (Ohkuma *et al*., 1990). The resistance of the resultant dextrins to the activity of amylolytic enzymes increases with a proceeding degree of dextrinization and elongated time of the process (Wang *et al*., 2001).

Nutritional aspects :

Dextrins are also seen as similar to intermediates in normal digestion and as analogous to products formed in the baking and toasting of bread; for this reason too, they may be considered as normal food constituents, useful as binders, and for their ability to retain flavour and colour (Sharma, 1996). However, pyrodextrinization alters nutritional features. Modern emphasis on the importance in the diet of resistant fiber has prompted many investigations into the status of dextrinized starches as modifiers of nutritional properties. A large increase in indigestible starch results from heating at 140^0C for 3 h in the presence of catalytic HCl (Roberts *et al*., 1988) and other effects of processing have been shown. (Be Mille, 1998) Starch-derived dietary fiber may be manufactured (Staub, 1965). Thermochemical modification may also lead to a product suitable as a "fat replacer"(Markowitz and Lange, 1965).

Enzymatic modifications :

This involves the exposure of starch suspensions to a number of enzymes primarily including hydrolyzing enzymes that tend to produce highly functional derivatives. The most common enzymes for starch modification include:

α-Amylase (1, 4-α-D-Glucan Glucanohydrolase)
β-Amylase (1, 4-α-D-Glucan Maltohydrolase)
Glucoamylase(Amyloglucosidase)(1,4-α-D-Glucan Glucohydrolase)
Pullulanase (Pullulan 6-Glucanohydrolase)
Isoamylase (Glycogen 6-D-Glucanohydrolase)
Cyαclomaltodextrin D-Glucotransferase (1,4-α-D-Glucan 4 α-D-
[1, 4-α-D-Glucano]-Transferase [Cyclizing]

These enzymes have been isolated from fungi, yeasts, bacteria and plant kingdom (Sherry *et al.*, 2005). Starch hydrolysis involves liquefaction and saccharification of starch. Heat treatment subjected with enzymes results in the increase of resistant starch content.

An appropriate amount of 0.5 U/g of thermostable α-amylase was good for resistant starch formation on corn starch. The optimal condition for pullulanase hydrolysis was carried out with 0.8 PUN/g (dry starch) pullulanase in pH 5.5 starch gel at 60^0C for 12 h. The highest yield of resistant starch could be obtained as 19.02 per cent (Gao *et al.*, 2011).

High resistant starch content product was prepared by hydrolyzing maize starch with pullulanase. The optimal hydrolyzing conditions were time, 32 h; pH, 5.0; temperature, 46^0C; amount of pullulanase, 12 ASPU/g (Acid Stable Pullulanase Unit). The product of resistant starch was obtained by pressure-cooking the resulting hydrolysate in an autoclave at 121^0C for 1 h, cooling at room temperature, storing at 4 ^{0}C overnight, autoclaving/cooling for 2 repetition cycle, drying an oven (105^0C) and finally grounding into fine particles (<150_m). The content of resistant starch in the product was 44.7% (w/w) (Zhang and Jin, 2011).

A study on gel structure formed in the modification of potato,high amylose potato,maize and pea starch with amylomaltase(AM) isolated from the hyperthermophillic bacterium *Thermus thermophilus*,there was an improvement in the gel texture when compared to the parent starch. All the modified starches showed broadened amylopectin chain length profiles (Harsen *et al.*, 2008).

Treatment of maize starch with β- amylase, β- amylase and transglucosidase, maltogenic α-amylase and transglucosidase resulted into significant reduction in digestion rate by 14.5 per cent, 29.0 per cent,19.8 per cent and 31.0 per cent, respectively producing resistant starch with reduced glycemic index that can be used in diabetes,pre diabetes,cadivascular 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 (Ao *et al.*, 2007).

Table 4 : Reaction conditions and properties of white dextrin, yellow dextrin and British Gum (Thomas and Williams, 1999)

Condition	White dextrin	Yellow dextrin	British Gum
Roasting temperature (º C)	110 - 130	135 – 160	150 – 180
Roasting time (hr)	3-7	8 - 14	10 – 24
Amount of catalyst	High	Medium	Low
Solubility	Low to high	High	Low to high
Viscosity	Low to high	Low	Low to high
colour	White to cream	Buff to dark tan	Light to dark tan
Type of reaction	Mainly hydrolysis	Hydrolysis and repolymerization	Mainly repolymerization

The banana starch after debranching (incubated with pullulanase (20 U/g starch, Sigma-Aldrich Co.) with constant stirring for 24 h at 50^{o}C and retrogradation) had the B-type structure with significantly improved resistant starch content. The native banana starch analyzed as 11.2 per cent of resistant starch, whereas the debranched starch had significantly higher amounts of resistant starch (31.8-48.1%). As a result, the debranched banana starch can be used as a functional food with high amount of resistant starch (Hung *et al.*, 2013) Fig. 1.

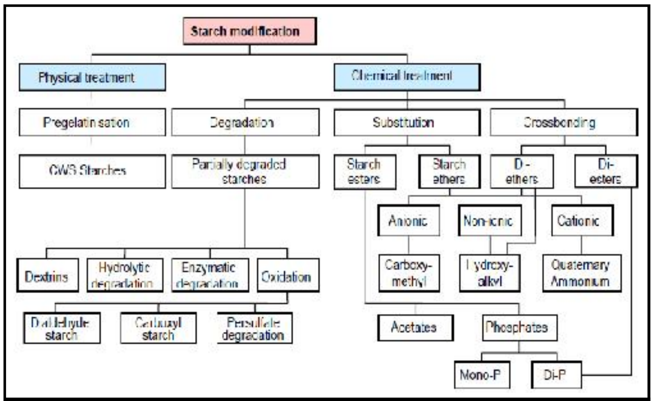

Fig. 1 : **Classification of starch modification techniques (Kozich and Wastyn, 2012)**

Measurement of resistant starch (RS) :

The main step of any method to measure the content of RS in foods must first remove all of the digestible starch from the product using thermostable α- mylases (Mcleary and Rossitter, 2004). At present, the method of McCleary and Monaghan (2002) and AOAC method (2002.02) is considered the most reproducible and repeatable measurement of RS in starch and plant materials, but it has not been shown to analyse all RS as defined (Champ *et al.*,2003) It is based on the principle of enzymatic digestion and measures the portions of starch resistant to digestion at 37 ^{0}C that are typically not quantitated due to the gelatinisation at 100^{0} C followed by digestion at 60^{0} C. A commercial test kit is available and further details of the method are available at http://*www.megazyme.com*/booklets/KRSTAR.pdf (Nugen, 2005).

Significance of resistant starch on health :

Resistant starch can reduce the risk of the development of type 2 diabetes mellitus, obesity, coronary disease, inflammatory bowel diseases and gastrointestinal disorders. Resistant starch doses of 20-30 g/day are needed to observe physiological effects. RS2 resistant starch actually delivers fewer calories than flour and is a valuable part of diets designed for maintaining healthy weight. The energy value has been estimated to be between 2 and 3 calories (8-12 kilojoules), depending on each individual's metabolism. By comparison, digestible starch - like flour delivers 4 calories (16 kilojoules). A number of physiological effects have been ascribed to RS, (Nugen, 2005) which have been proved to be beneficial for health (Table 5).

The characteristics of RS are similar to those of insoluble fibres and soluble fibres, and as insoluble fibres it acts as it does not affect postprandial insulin, glucose and free fatty acid response after a glucose load (Ranganathan, 1994) and once in the colon, it moderately increases stool weight (Cummings *et al.*, 1996). However, like soluble fibre, RS is a substrate for microbial fermentation, giving origin to end products, mainly short-chain fatty acids and influencing lipid and N metabolism in human and animal studies. (Cummings and Macfarlane, 1991; De Deckere *et al.*, 1995; Morand *et al.*, 1994; Phillips *et al.*, 1995). A particularity of RS is that its fermentation generates high levels of butyric acid compared with other fermentable carbohydrates(Englyst and Macfarlane, 1986; Scheppach *et al.*, 1988).

Conclusion:

Modified starches really offer tremendous number of functional benefits to variety of foods such as bakeries, ready to eat products, snacks and beverages as well as nutritional foods. Other related benefits of modified starches include such as stabilizer, emulsifier, thickening agent, dusting agent,

Table 5 : Physiological effects of resistant starch (Brown, 2004 and Champ, 2004)

Potential physiological effects	Conditions where there may be a protective effect
Improve glycaemic and insulinaemic responses	Diabetes , impaired glucose and insulin responses , the metabolic syndrome
Improved bowel health	Colorectal cancer, ulcerative colitis, inflammatory bowel disease, diverticulitis, constipation
Improved blood lipid profile	Cardiovascular disease, lipid metabolism, the metabolic syndrome
Prebiotic and culture protagonist	Colonic health
Increased satiety and reduced energy intake	obesity
Increase micronutrient absorption	Enhanced mineral absorption, osteoporosis
Adjunct to oral rehydration therapies	Treatment of cholera, chronic diarrhoea
Synergistic interactions with other dietary components e.g. dietary fibres, proteins, lipids	Improved metabolic control and enhanced bowel health
Thermogenesis	Obesity, diabetes

drying aids, binder, clouding agent, suspending agent and for freeze-thaw stability. Technically, it is possible to increase the resistant starch content in foods with nutraceutical implications by modifying the processing conditions such as pH, heating temperature and time, number of heating and cooling cycles, freezing, and drying by combining one or more modifying techniques (dual modifications) of starch. Thus, resistant starch offers a much amazing attention for both its potential health benefits and functional properties as an ingredient.

Authors' affiliations:

P. BANUMATHI, S. KANCHANA, M. ILAMARAN AND J. SELVI, Home Science College and Research Institute, T.N.A.U., MADURAI (T.N.) INDIA

S.P. SUNDARAM, Agricultural College and Research Institute, Tamil Nadu Agricultural University, MADURAI (T.N.) INDIA

S.M. IBRAHIM, Department of Plant Breeding and Genetics, Agricultural College and Research Institute, Tamil Nadu Agricultural University, MADURAI (T.N.) INDIA

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