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Resistant Starch- Chemistry and Nutritional properties

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Abstract
The concept of resistant starch (RS) has evoked new interest in the bioavailability of starch and its use as a source of dietary fiber (Sharma *et al*., 2008). Resistant starch has received much attention for both its potential health benefit (similar to soluble fibre) and functional properties (Sajilata, *et al*, 2006). Resistant starch positively influences the functioning of the digestive tract, microbial flora, blood cholesterol level, glycemic index and assists in the control of diabetes (Nugent, 2005). Apart from the potential health benefits of resistant starch, another positive advantage is its lower impact on the sensory properties of food compared with traditional sources of fibre, as whole grains, fruits or bran (Buttriss & Stokes, 2008). Among its desirable physicochemical properties are its swelling capacity, viscosity, gel formation and water-binding capacity, which make it useful in a variety of foods (Tharanathan and Mahadevamma 2003).

Keywords: resistant starch, dietary fibre, functionality, digestibility, physiological effects

Introduction

From the early years of emergence of nutritional science, it has been recognized that the ingested nutrients in the diet are not completely utilized in the body. An increasing volume of evidence suggests that with very few exceptions, only a proportion of the total ingested nutrients in a diet or food is available, and the term “availability” has come into use for this proportion (Southgate 1989) [17]. During food processing, derivatization of nutrients and formation of cross linkages occur, thereby making the food inaccessible for digestion or/and metabolism. Such parts of nutrients are also “unavailable” (Erbersdobler 1989) [17].
Starch, which is the major dietary source of carbohydrates, is the most abundant storage polysaccharide in plants, and occurs as granules in the chloroplast of green leaves and the amyloplast of seeds, pulses, and tubers (Ellis and others 1998) [16]. The relatively recent recognition of incomplete digestion and absorption of starch in the small intestine as a normal phenomenon has raised interest in nondigestible starch fractions (Cummings and Englyst 1991; Englyst and others 1992) [14]. These are called “resistant starches,” and extensive studies have shown them to have physiological functions similar to those of dietary fiber (Fuentes Zaragoza *et al*., 2010; Nugent, 2005) [35]. The diversity of the modern food industry and the enormous variety of food products it produces require starches that can tolerate a wide range of processing techniques and preparation conditions. These demands are met by modifying native starches with chemical, physical, and enzymatic methods (woo and others 1999) [53], which may lead to the formation of indigestible residues. The availability of such starches therefore deserves consideration.

Starch and its classification

Chemically, starches are polysaccharides, composed of a number of monosaccharides or sugar (glucose) molecules linked together with _-D-(1-4) and/or _-D-(1-6) linkages. The starch consists of 2 main structural components, the amylose, which is essentially a linear polymer in which glucose residues are _-D-(1-4) linked typically constituting 15% to 20% of starch, and amylopectin, which is a larger branched molecule with _-D-(1-4) and _-D-(1-6) linkages and is a major component of starch (BNF 1990). Amylose is linear or slightly branched, has a degree of polymerization up to DP 6000, and has a molecular mass of 105 to 106 g/mol. The chains can easily form single or double helices (Takeda and Takeda 1989) [50].
On the basis of X-ray diffraction studies on oriented amylase fibers, the presence of type A and type B amyloe is indicated (Figure 1, Galliard 1987) [22]. The structural elements of type B are double helices, which are packed in an antiparallel, hexagonal mode. The central channel surrounded by 6 double helices is filled with water (36 H2O/unit cell). Type A is very similar to type B, except that the central channel is occupied by another double helix, making the packing closer. In this type, only 8 molecules of water per unit cell are inserted between the double helices. Amylopectin (107 to 109 g/mol) is highly branched and has an average DP of 2 million, making it one of the largest molecules in nature. Chain lengths of 20 to 25 glucose units between branch points are typical. Its structure is often described by a cluster model (Figure 2). The cluster model gained greater credence when Hizukuri postulated that amylopectin chains are either located within a single cluster or serve to connect 2 or more clusters (Hizukuri 1986; Thompson 2000). Short chains (A) of DP 12-16 that can form double helices are arranged in clusters. The clusters comprise 80% to 90% of the chains and are linked by longer chains (B) that form the other 10% to 20% of the chains. Most B-chains extend into 2 (DP about 40) or 3 clusters (DP about

70), but some extend into more clusters (DP about 110) (Figure 2 and 3) (www.lsbu.ac.uk). On the basis of X-ray diffraction experiments, starch granules are said to have a semicrystalline character, which indicates a high degree of orientation of the glucan molecules. About 70% of the mass of starch granule is regarded as amorphous and about 30% as crystalline. The amorphous regions contain the main amount of amylose but also a considerable part of th amylopectin. The crystalline region consists primarily of the amylopectin.

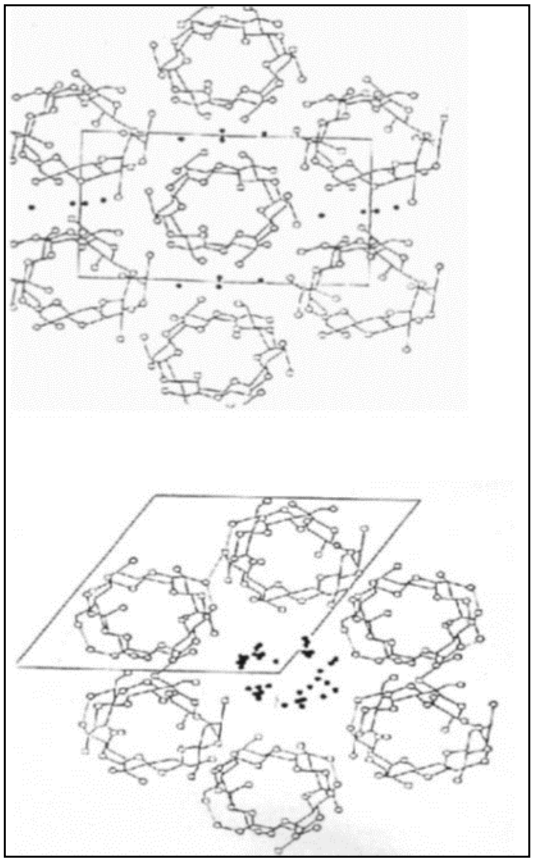


Figure 1–Unit cells and arrangement of double helices (cross section) in A-amylose (top) and B-amylose (bottom) (Galliard 1987)

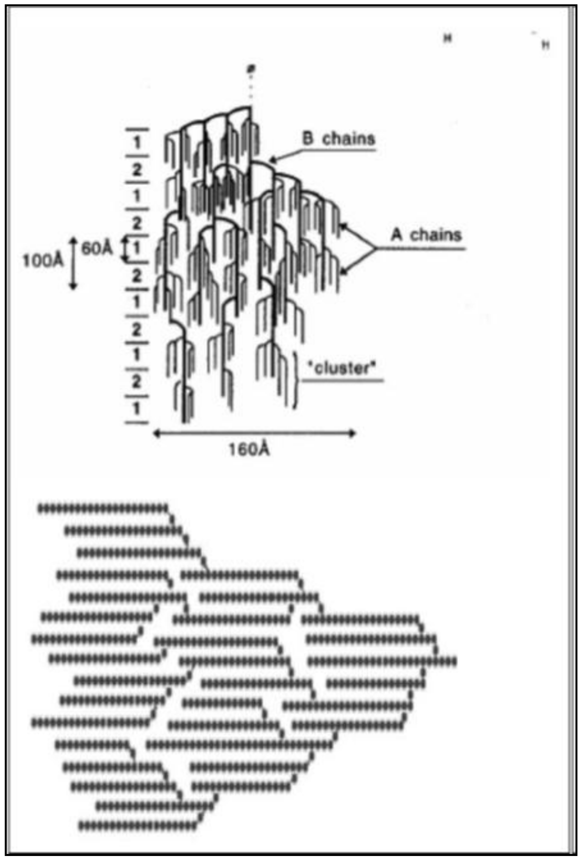


Figure 2–Cluster model of amylopectin

Three types of starches, designated as type A, type B, and type C, have been identified based on X-ray diffraction patterns. These depend partly on the chain lengths making up the amylopectin lattice, the density of packing within the granules, and the presence of water (Gillard., 1987). Although type A and type B are real crystalline modifications, type C is a mixed form. The important features of the types of starches are as follows.

Type A

The type A structure has amylopectin of chain lengths of 23 to 29 glucose units. The hydrogen bonding between the hydroxyl groups of the chains of amylopectin molecules results in the formation of outer double helical structure. In between these micelles, linear chains of amylose moieties are packed by forming hydrogen bonds with outer linear chains of amylopectin. This pattern is very common in cereals.

Type B

The type B structure consists of amylopectin of chain lengths of 30 to 44 glucose molecules with water inter-spread. This is the usual pattern of starches in raw potato and banana.

Type C

The type C structure is made up of amylopectin of chain lengths of 26 to 29 glucose molecules, a combination of type A and type B, which is typical of peas and beans. An additional form, called type V, occurs in swollen granules.

Based on the action of enzymes

According to Berry (1986), starches can be classified according to their behavior when incubated with enzymes without prior exposure to dispersing agents as follows.

Rapidly digestible starch (RDS)

RDS consists mainly of amorphous and dispersed starch and is found in high amounts in starchy foods cooked by moist heat, such as bread and potatoes. It is measured chemically as the starch, which is converted to the constituent glucose molecules in 20 min of enzyme digestion.

Slowly digestible starch (SDS)

Like RDS, SDS is expected to be completely digested in the small intestine, but for 1 reason or another, it is digested more slowly. This category consists of physically inaccessible amorphous starch and raw starch with a type A and type C crystalline structure, such as cereals and type B starch, either in granule form or retrograded form in cooked foods. It is measured chemically as starch converted to glucose after a further 100 min of enzyme digestion.

Resistant starch (RS)

The term "resistant starch" was first coined by Englyst and others (1982) to describe a small fraction of starch that was resistant to hydrolysis by exhaustive _-amylase and pullulanase treatment in vitro. RS is the starch not hydrolyzed after 120 min of incubation (Englyst and others 1992). However, because starch reaching the large intestine may be more or less fermented by the gut microflora, RS is now defined as that fraction of dietary starch, which escapes digestion in the small intestine. It is measured chemically as the difference between total Starch (TS) obtained from homogenized and chemically treated sample and the sum of RDS and SDS, generated from non-homogenized food samples by enzyme digestion.

$$RS = TS – (RDS + SDS)$$

Resistant starch may not be digested for four reasons

1. This compact molecular structure limits the accessibility of digestive enzymes, various amylases, and explains the resistant nature of raw starch granules (Haralampu, 2000). The starch may not be physically bioaccessible to the digestive enzymes such as in grains, seeds or tubers.
2. The starch granules themselves are structured in a way which prevents the digestive enzymes from breaking them down (e.g. raw potatoes, unripe bananas and high-amylose maize starch) (Nugent, 2005) [35].
3. Starch granules are disrupted by heating in an excess of water in a process commonly known as gelatinization, which renders the molecules fully accessible to digestive enzymes. Some sort of hydrated cooking operation is typical in the preparation of starchy foods for consumption, rendering the starch rapidly digestible (Haralampu, 2000). However, if these starch gels are then cooled, they form starch crystals that are resistant to enzymes digestion. This form of 'retrograded' starch is found in small quantities (approximately 5%) in foods such as ''corn-flakes" or cooked and cooled potatoes, as used in a potato salad.
4. Selected starches that have been chemically modified by etherisation, esterisation or cross-bonding, cannot be broken down by digestive enzymes (Lunn & Buttriss, 2007) [30].

Types of resistant starch

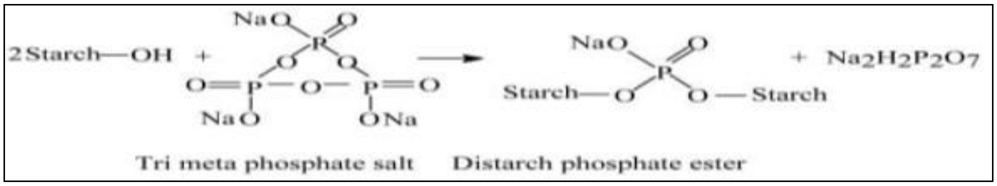
Resistant starch has been classified into four general subtypes called RS1–RS4.

The four distinct classes of RS in foods are: (1) RS1 – physically inaccessible starch, which is entrapped within whole or partly milled grains or seeds; (2) RS2 – some types of raw starch granules (such as banana and potato) and high-amylose (high-amylose corn) starches; (3) RS3 – retrograded starch (either processed from unmodified starch or resulting from food processing applications); (4) RS4 – starches that are chemically modified to obtain resistance to enzymatic digestion (such as some starch ethers, starch esters, and cross-linked starches) (Ratnayake & Jackson, 2008; Sanz, Salvador, Baixauli, & Fiszman, 2009).

RS1 and RS2 represent residues of starch forms, which are digested very slowly and incompletely in the small intestine. RS1 is the term given to RS where the starch is physically inaccessible to digestion, e.g. due to the presence of intact cell walls in grains, seeds or tubers (Hernández, Emaldi, & Tovar, 2008). RS1 is heat stable in most normal cooking operations, which enables its use as an ingredient in a wide variety of conventional foods (Sajilata, Singhal, & Kulkarni, 2006). RS2 are native, uncooked granules of starch, such as raw potato or banana starches, whose crystallinity makes them poorly susceptible to hydrolysis (Hernández *et al*., 2008). RS2 describes native starch granules that are protected from digestion by the conformation or structure of the starch granule. This compact structure limits the accessibility of digestive enzymes, various amylases, and accounts for the resistant nature of RS2 such as, ungelatinized starch. In the diet, raw starch is consumed in foods like banana (Sajilata *et al*., 2006). A particular type of RS2 is unique as it retains its structure and resistance even during the processing and preparation of many foods; this RS2 is called high-amylose maize starch (Wepner, Berghofer, Miesenberger, & Tiefenbacher, 1999, Efenbacher, 1999).

RS3 refers to non-granular starch-derived materials that resist digestion. RS3 forms are generally formed during the retrogradation of starch granules (Wepner *et al*., 1999). RS3 are retrograded starches, which may be formed in cooked foods that are kept at low or room temperature (Hernández *et al*., 2008). Most moistheated foods therefore contain some RS3 (Sajilata *et al*., 2006). RS3 is of particular interest, because of its thermal stability. This allows it to be stable in most normal cooking operations, and enables its use as an ingredient in a wide variety of conventional foods (Haralampu, 2000). Food processing, which involve heat and moisture, in most cases destroys RS1 and RS2 but may form RS3 (Faraj, Vasanthan, & Hoover, 2004). RS3 has shown a higher water-holding capacity than granular starch (Sanz *et al*., 2008a). Some examples of RS3 are cooked and cooled potatoes and ''corn-flakes" (Wepner *et al*., 1999). In addition to the three main types of RS, chemically-modified starch has been defined as RS type 4, similar to resistant oligosaccharides and polydextrose (Wepner *et al*., 1999). RS4 describes a group of starches that have been chemically modified and include starches which have been etherised, esterified or cross-bonded with chemicals in such a manner as to decrease their digestibility. RS4 may be further subdivided into four subcategories according to their solubility in water and the experimental methods by which they can be analyzed (Nugent, 2005) [35].

Figure 6.



RS4 can be produced by chemical modifications, such as conversion, substitution, or cross-linking, which can prevent its digestion by blocking enzyme access and forming atypical linkages such as a (1?4) and a(1?6) linkages (Kim *et al*., 2008; Sajilata *et al*., 2006).

Different sources of RS2 and RS3 of different origins and with different percentages of RS are available as commercial ingredients in the European market to be included in food. As RS4 is made up of chemically-modified starches, with a far higher number of modifications than the usual chemically-modified starches authorized in Europe, it is a novel food not yet approved by the European Union. However, RS4 is authorized in Japan (Sanz *et al*., 2008b; Lunn & Buttriss, 2007) [30].

In addition to the structural factors mentioned above whereby the chemical structure of starch can influence the amount of RS present, other factors intrinsic to starchy foods can affect a-amylase activity and therefore starch breakdown. These include the formation of amylose–lipid complexes, the presence of native a-amylase inhibitors and also non-starch polysaccharides, all of which can directly affect a-amylase activity. Extrinsic additives, e.g. phosphorus, may also bind to starch, making it more or less susceptible to degradation. In addition, physiological factors can affect the amount of RS in a food. Increased chewing decreases particle size (smaller particles being more easily digested in the gut), while intra-individual variations in transit time and biological factors (e.g. menstrual cycle) also affect the digestibility of starch. At present, it is not known how RS4 is affected by digestion in vivo (Nugent, 2005) [35].

Table 1: Classification of RS, food sources and factors effecting their resistance to digestion Bird *et al*. (2008), Sharma *et al*. (2008) [45], Rajman *et al*. (2007), Lunn and Buttriss (2007) [30], Sajilata *et al*. (2006), and Nugent, 2005 [35].

Type of RS	Description	Food sources	Resistance reduced by
RS 1	Physically inaccessible	Whole/partly milled grains, seeds, legumes	Milling, chewing
RS 2	Ungelatinized resistant granules	Raw potatoes, green banana, high amylose maize	Food processing, cooking
RS 3	Retrograted starch	Cooked and cooled potatoes, bread, cornflakes, cook/cool moist heat treatment	Processing conditions
RS 4 (PO4)	Chemically modified starches —cross-bonded	Fiber-drinks, foods with modified starches	Less susceptible to digestion *in vitro*

Food sources of resistant starch

Resistant starch is naturally found in cereal grains, seeds and in heated starch or starch-containing foods (Charalampopoulos *et al*., 2002).

Factors that determine whether starch is resistant to digestion include the physical form of grains or seeds in which starch is located, particularly if these are whole or partially disrupted, size and type of starch granules, associations between starch and other dietary components, and cooking and food processing, especially cooking and cooling (Slavin, 2004). The digestibility of starch in rice and wheat is increased by milling to flour (Sajilata *et al*., 2006).

Unripe banana is considered the RS-richest non-processed food. Several studies have suggested that consumption of unripe bananas confers beneficial effects for human health, a fact often associated with its high resistant starch (RS) content, which ranges between 47% and 57%. Recently, the preparation of unripe banana flour was described, with 73.4% total starch content, 17.5% RS content and a dietary fibre level of 14.5%. Although banana represents an alternative source of indigestible carbohydrates, mainly RS and dietary fibre, it is important to keep in mind that, when the unripe fruit is cooked, its native RS is rendered digestible (Rodríguez, Islas, Agama, Tovar, & Bello, 2008).

As a percentage of total starch, potato starch has the highest RS concentration and corn starch has the lowest. Raw potato starch contain 75% RS as a percentage of Total Starch (TS). Starches from tubers such as potatoes tend to exhibit B-type crystallinity patterns are highly resistant to digestion. Amylomaize contains mostly amylose, which has been shown to lower not only digestibility but also blood insulin and glucose values in humans (Bednar *et al*., 2001).

Whole grains are rich sources of fermentable carbohydrates including dietary fibre, resistant starch and oligosaccharides (Slavin, 2004). Fibre provided by the whole grain includes a substantial resistant starch component, as well as varying amounts of soluble and fermentable fibres, depending on the whole grain source (Lunn & Buttriss, 2007) [30].

RS concentrations are low for the flour group as a whole. Cereal flours display an A-type crystalline pattern, which is more readily hydrolyzed than raw cereals that are not as highly processed as flours. Therefore, cereal flours contain more RDS and SDS than RS.

Legumes are known for their high content of both soluble and insoluble dietary fibre. Pulse grains are high in RS and retain their functionality even after cooking (Rochfort & Panozzo, 2007). Legume starches have higher amylose levels than cereal and pseudocereal starches (Mikulíková *et al*., 2008). Legumes has high TDF and RS concentrations (mean 36.5% and 24.7%, respectively). RS concentrations generally constituted the highest proportion of the starch fractions of legumes. Leguminous starches display a C-type pattern of crystallinity. This type of starch is more resistant to hydrolysis than that with an A-type crystallinity pattern and helps explain why legumes have high amounts of RS. Another possible reason for the higher RS concentrations in legumes could be the relationship between starch and protein. When red kidney beans are preincubated with pepsin, there is an increase in their susceptibility to amylolytic attack (Bednar *et al*., 2001).

Cooked legumes are prone to retrograde more quickly, thereby lowering the process of digestion. Processed legumes contain significant amount of RS3. The digestibility of legume starch is much lower than that of cereal starch. The higher content of amylose in legumes, which probably leads to a higher RS content, may account for their low digestibility. High-amylose cereal starch has been shown to be digested at a significantly lower rate (Tharanathan & Mahadevamma, 2003).

There is a very high diversity of the content of resistant starch in seeds of leguminous plants (from 80% to only a few percent). Nevertheless, is very important influence processing on part resistant starch. Hydrothermal processing can cause an increase or reduction in the fraction of resistant starch (depending on the parameters of processing and varieties of legumes) (Giczewska & Borowska, 2003).

Table 2: Food sources of resistant starch (Nugent, 2005) [35]

low content 1-2.5%	medium content 2.5-5%	high content 5-15%	Very high (>15%)
•Breakfast cereals •Biscuits •Bread •Pasta •Boiled potato (cool) •Boiled rice (cool)	•Breakfast cereals (Corn Flakes, Rice Crispies) •Fried potatoes •Extruded legumes	•Cooked legumes (lentils, chick peas, beans) •Peas •Raw rice •Autoclaved and cooled starches (wheat, potato, maize) •Cooked and frozen starchy foods	•Raw potatoes •Raw legumes •Amylo-maize •Unripe banana •Retrograded amylose

As a food ingredient, RS has a lower calorific (8 kJ/g) value compared with fully digestible starch (15 kJ/g); however, it can be incorporated into a wide range of mainstream food products such as baked products without affecting the processing properties or the overall appearance and taste of the product (Rochfort & Panozzo, 2007).

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Prepared grain products contain moderate levels of RS (mean 9.6% as a percentage of TS). Starch in foods like spaghetti is more slowly digested because of the densely packed starch in the food (Bednar *et al*., 2001).

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constituted the highest proportion of the starch fractions of legumes. Leguminous starches display a C-type pattern of crystallinity. This type of starch is more resistant to hydrolysis than that with an A-type crystallinity pattern and helps explain why legumes have high amounts of RS. Another possible reason for the higher RS concentrations in legumes could be the relationship between starch and protein. When red kidney beans are preincubated with pepsin, there is an increase in their susceptibility to amylolytic attack (Bednar *et al*., 2001).
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There is a very high diversity of the content of resistant starch in seeds of leguminous plants (from 80% to only a few percent). Nevertheless, is very important influence processing on part resistant starch. Hydrothermal processing can cause an increase or reduction in the fraction of resistant starch (depending on the parameters of processing and varieties of legumes) (Giczewska & Borowska, 2003).

Factors Influencing the Formation of RS
Several factors influence the formation of RS.

Inherent Properties of Starch
Crystallinity of starch. One of the causes of resistance to enzymes is the crystallinity of native type B starch granules as observed in the case of amylomaize starch and also the encapsulation of starch within plant cell or tissue structures. X-ray diffraction and differential scanning calorimetry studies on crystalline residues from amylomaize starch samples have suggested that chain fragments packed in a type B crystalline structure with a slightly enlarged crystal lattice contribute to formation of RS from amylomaize starch. Any treatment that eliminates starch crystallinity (that is, gelatinization) or the integrity of the plant cell or tissue structure (that is, milling) increases enzyme availability and reduces the content of RS, whereas recrystallization and chemical mod0difications tend to increase the RS.

Granular Structure
A large variability in susceptibility to amylases shown by raw starch granules also influences RS formation. Potato starch and high amylose maize starch are known to be very resistant in vitro and incompletely absorbed in vivo, whereas most cereal starches are slowly but virtually completely digested and absorbed in vivo (Holm and others 1987). The smaller surface- to-volume ratio of the large potato granules is probably important. The nature of the granule surface also needs to be considered; an adsorbed layer of non-starch material would effectively impede the action of the enzyme (Ring and others 1988). Raw tepary starch is found to be more resistant to hydrolysis than maize starch, perhaps due to differences in granule structure and amylose content (Abbas and others 1987).

Amylose: Amylopectin Ratio
A higher content of amylose lowers the digestibility of starch due to positive correlation between amylase content and formation of RS (Berry 1986; Sievert and Pomeranz 1989b). The importance of the amylose: amylopectin ratio in the postprandial glycaemic and insulinaemic responses to corn was studied in commonly consumed corn products (Granfeldt and others 1995). The meals containing high amylose (70%) corn flour had an RS of 20 g/100 g DM than that containing ordinary corn flour (25% amylose) that had RS of 3g /100 g DM.

Retrogradation of Amylose
When heated to about 50 °C, in the presence of water, the amylose in the granule swells; the crystalline structure of the amylopectin disintegrates and the granule ruptures. The polysaccharide chains take up a random configuration, causing swelling of the starch and thickening of the surrounding matrix such as, gelatinization—a process that renders the starch easily digestible. On cooling/drying, recrystallization (retrogradation) occurs. This takes place very fast for the amylase moiety as the linear structure facilitates cross linkages by means of hydrogen bonds. Figure 10 shows the formation of gel and micelle on cooling of a concentrated solution of amylase (Belitz and Grosch 1999). The branched nature of amylopectin inhibits its recrystallization to some extent and it takes place over several days.
The rate and extent to which a starch may retrograde after gelatinization essentially depends on the amount of amylose present. Repeated autoclaving of wheat starch may generate up to 10% RS. The level obtained appeared to be strongly related to the amylase content, and the retrogradation of amylose was identified as the main mechanism for the formation of RS that can be generated in larger amounts by repeated autoclaving (Berry 1986; Bjorck and others 1990). During storage, the dispersed polymers of gelatinized starch are said to undergo retrogradation to semicrystalline forms that resist digestion by pancreatic _amylase. It forms a major portion of RS in wheat bread and corn flakes (Englyst and Cummings 1985), whereas only 25% of the RS in cooked, cooled potatoes can be accounted for as retrograded amylose. The digestibility of legume starch is much lower than that of cereal starch, which is attributable to higher content of amylose in the former. The digestibility of high amylose cereal starch is reported to be significantly lower (Tharanathan and Mahadevamma 2003).

Influence of Amylose Chain Length
Influence of amylose chain length on enzyme RS formation was studied by Eerlingen and others (1993b) by hydrolyzing potato starch amylose to varying degrees by incubationn with barley_amylase for different periods, and monitored by measuring the number of average chain lengths or degree of polymerization (DPn). The DPn of RS varied between 19 and 26 and was independent of the chain length of the amylose (DPn 40 to 610) from which it was formed. Results suggested that RS might be formed by aggregation of amylose helices in a crystalline type structure over a particular region of the chain (about 24 glucose units).

Heat and Moisture

Water content is an important factor that affects formation of RS. Repeated heat/moisture treatment is associated with a decrease in the hydrolysis limit of pancreatic _-amylase and increased formation of RS. Maximum RS yield was obtained at a starch:water ratio of 1: 3.5 (w/w) (Sievert and Pomeranz 1989b) and a heat treatment at 18% moisture gave increased levels of the degree of crystallinity of normal and waxy starches and thus reduced enzyme susceptibility. However, at 27% moisture, starch degradation to some extent made areas of starch more accessible to enzyme attack. Thus, proper heat treatment could be used as a method of preparation of RS (Franco and others 1995). In addition, higher temperature and less water results in type A configuration, whereas lower temperature and high water content results in type B configuration.

Interaction of Starch with Other Components

Interactions of starch with different components present in the food system are known to influence the formation of RS as follows.

Protein

Starch-protein interaction has been believed to reduce RS contents as observed in case of potato starch and added albumin when autoclaved and subsequently cooled at –20 °C (Escarpa and others1997).

Dietary Fiber

Insoluble dietary fiber constituents such as cellulose and lignin have been shown to have minimal effects on RS yields compared with other constituents such as potassium and calcium ions and catechin (Escarpa and others 1997).

Enzyme Inhibitors

Polyphenols, phytic acid, and lectins present mainly in leguminous seeds, have been reported to inhibit in vitro starch hydrolysis and to lower the glycemic index (Thompson and Yoon 1984). Tannic acid significantly inhibits both amylases and intestinal maltase activity (Bjorck and Nyman 1987). Indigestible residues from black beans (Phaseolus vulgaris cv. Tacari gua), green beans (P. vulgaris), carrots (Daucus carota), and rice bran (Oryza sativa) are all reported to inhibit pancreatic _- amylase in vitro (Moron and others 1989). Since amylolysis is inhibited by phytic acid, a decrease in phytate content increases starch digestibility (Thompson and Yoon 1984). Contradictory information exists in the literature on this aspect. The autoclaving and subsequent cooling of potato starch and catechin was found to significantly reduce the yields of RS, whereas the addition of phytic acid to potato starch reduced the RS contents to a minor extent (Escarpa and others 1997) compared with the RS formed from potato starch with no added constituent. The reasons for the same are still not clear.

Ions

The yields of RS in potato starch gels decrease in the presence of calcium and potassium ions compared with those with no added constituent (Escarpa and others 1997), presumably due to the prevention of formation of hydrogen bonds between amylase and amylopectin chains caused by adsorption of these ions.

Sugars

The addition of soluble sugars such as glucose, maltose, sucrose, and ribose has been found to reduce the level of crystallization and subsequently reduce the yields of RS (Buch and Walker 1988; I'Anson and others 1990; Kohyama and Nishinari 1991). The mechanism of retrogradation inhibition was considered as the interaction between sugar molecules and the starch molecular chains, which change the matrix of gelatinized starch (the sugars act as anti-plasticizers and increase the glass transition temperature).

Lipids

Lipids are most important non starch components associated with starch granule. These are Complexed with amylose chains making them less acessible to active sites of amylase and are found on the surface of granule-reducing contact between enzyme and substrate.

Processing Conditions

Processing techniques may affect both the gelatinization and retrogradation processes, influencing RS formation. This fact is of great importance for the food industry since it offers the possibility of increasing the RS content of processed foods and foodstuffs. Baking, pasta production, extrusion cooking, autoclaving, and so forth are known to influence the yield of RS in foods (Siljestrom and Asp 1985; Bjorck and Nyman 1987; Siljestrom and others 1989; Muir and O'Dea 1992; Rabe and Sievert 1992).

Thermal Processing

Cooking

Cooking under condition of high moisture and temperature can significantly lower RS content by disrupting crystalline structur (Gelencser,2009;Sajilata *et al.*, 2006)Some RS starches show lower sensitivity to heat than others(Gelencser,2009;Htoon *et al*.,2009)

Autoclaving

Autoclaving results in increase in RS. Autoclaved wheat starch has 9% RS compared with less than 1% in uncooked wheat starch (Siljestrom and Asp 1985). Autoclaved wheat starch contained 6.2% RS (of dm); this increased to 7.8% after 3 further reboiling/cooling cycles (Bjorck and others 1987).

The number of cycles exerted the most pronounced effect on RS; increasing the number of cycles to 20 raised RS level to >40%. Furthermore, the thermoanalytical data suggested that amylose-lipid complexes were not involved in the formation of RS. Yields in excess of 20% RS can be obtained from autoclaved amylomaize starch containing 70% amylose. They can be raised to levels of 40% by increasing the number of autoclaving-cooling cycles up to 20 (Eerlingen and Delcour 1995).

Parboiling

Parboiling increases RS production. In studies on 5 rice varieties, differing in amylose content, the in vitro and in vivo RS levels were low and positively correlated with amylose content (Eggum and others 1993). Higher RS starch levels were found in cooked and parboiled-cooked rice than in raw rice; waxy rice had very low values. Higher contents of RS have been reported in parboiled rice than raw white rice, which also increased by cooling or freezing (Marsono and Topping 1999)

Baking

Baking increases RS content. A low-temperature, long-time baked product contained significantly higher amounts of RS than bread baked under ordinary conditions (Liljeberg and others 1996).

Extrusion Cooking

The RS content of the native flours, in general, decreased by extrusion cooking, but not significantly. Storage of extruded flour samples at 4 °C for 24 h before oven drying slightly increased RS3 content (Faraj and others 2004). When tested in an expanded, corn-based breakfast cereal formula, RS3 was shown to have no detrimentaleffect on the structure**.**

Storage Conditions

Generally, RS increases on storage, especially low-temperature storage. Cold storage seems to support an increase in RS content. Whole corn bread and corn bread crumb, when stored at different temperatures (20 °C, 4 °C, or 20 °C) for 7 d showed RS contents to reach a maximum between 2 and 4 d at all storage temperatures, after which they decreased (Niba 2003). Lowest RS levels in whole corn bread were found after storage at –20 °C (2.18 g/100 g) for 7 d.

Preparation of RS

RS can be prepared by using heat treatment, combined heat treatment and enzyme treatment, and chemical treatment.

Heat Treatment

Heat treatment of starch to various extents leads to formation of RS. RS can be obtained by cooking the starch above the gelatinization temperature and simultaneously drying on heated rolls like drum driers or even extruders. The gelatinization of starch granules by heat processing strongly influences their susceptibility to enzymatic hydrolysis. In a high-moisture environment, amylase leaches from the granules, increasing the solubility of starch and thereby its susceptibility (Holm and others 1988).

An enzyme-RS type III, which has a melting point or endothermic peak of at least about 140 °C, as determined by differential scanning calorimetry (DSC) can be produced in yields of at least 25% by weight, based on the weight of the original starch ingredient (Haynes and others 2000). A gelatinization stage, nucleation/propagation stage, and preferably a heat-treatment stage are required to produce reduced calorie starch-based compositions that contain the enzyme-resistant starch. It is produced using crystal nucleation and propagation temperatures, which avoid substantial production of lower melting amylopectin crystals, lower melting amylose crystals, and lower melting amylose-lipid complexes. The nucleating temperature used is above the melting point of the amylopectin crystals. The propagating temperature used is above the melting point of any amylose-lipid complexes but below the melting point of the enzyme RS. The high melting point of the enzyme RS permits its use in baked good formulations.

Partial acid hydrolysis (PAH) of a high-amylose corn starch enhances the effects of hydrothermal treatments used to produce granular RS, which is stable to further heat treatment at atmospheric pressure (Brumovsky and Thompson, 2001).

Selective heat treatment of high amylose starch in the presence of agents inhibiting the swelling of starch like alkali and alkaline earth metal salts of halides, sulfates, and phosphates yield granular RS with high dietary fiber. Recently, pyrodextrinization has been recognized as a way of producing a RS that is water-soluble and has non-starch linkages (Laurentin and Edwards 2004).

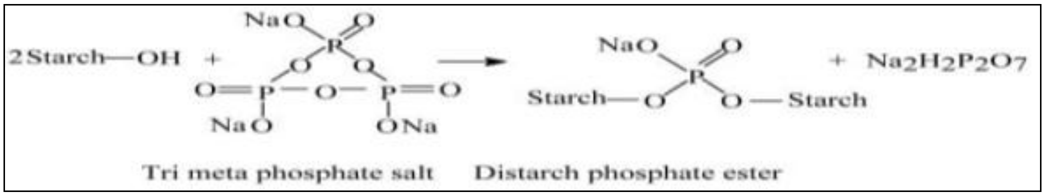
Pyroconversion refers strictly to the modification of dry starch through heat treatments, with or without addition of acids. Acids used include hydrochloric acid at 0.15% (based on starch dry weight) and orthophosphoric or sulfuric acids at 0.17% (Wurzburg 1995). Commercial pyrodextrins are generally produced by heating dry, acidified starch in a reactor with agitation. Acid may be sprayed on the starch to facilitate hydrolysis and transglycosidation. Depending on reaction conditions, pyroconversion produces a range of products that vary in digestibility, available starch, viscosity, cold-water solubility, swelling power, color, and stability (Ohkuma and Wakabayashi 2001).

Heat and Enzyme Treatment

RS is Prepared, by retrogradation of starch followed by enzymatic or chemical hydrolysis to reduce or remove the amorphous regions of retrograded starch (Iyengar 1991). RS can be prepared from high amylase starch by gelatinization followed by treating the slurry with debranching enzymes like pullulanase and isolating the starch product by drying/extrusion. Controlled heat treatment of starch so as to achieve swelling and at the same time retain its granular structure followed by enzymatic debranching (Haralampu and Gross 1998) and annealing at suitable temperature followed by drying produces RS.

Chemical Treatment

In type IV RS, the enzyme resistance is introduced by modifying the starch by crosslinking with chemical agents (Haynes and others 2000). Crosslinked starches are obtained by the reaction of starch with bi- or polyfunctional reagents like sodium trimetaphosphate, phosphorus oxychloride, or mixed anhydrides of acetic acid and dicarboxylic acids like adipic acid. Cross-linking carried out by sulphonate and phosphate groups between various starch molecules involves their hydroxyl group thus bringing resistance to amylolytic attack on the starch molecule.



Beneficial Physiological Effects of RS

A number of physiological effects have been ascribed to RS (Nugent 2005) [35], which have been proved to be beneficial for health.

Table 3: physiological effects of RS (Nugent 2005) [35].

Potential physiological effects	Conditions where there may be protective effect
Control of glycaemic and insulinaemic responses	Diabetes, impaired glucose and insulin responses, metabolic syndrome
Improved bowel health	Colorectal cancer, ulcerative colitis, inflammatory bowel disease, constipation
Improved blood lipid profile	Cardiovascular disease, lipid metabolism, metabolic syndrome
Prebiotic	Colonic health
Improved satiety and reduced energy intake	Obesity
Increased micronutrient absorption	Enhanced mineral absorption, osteoporosis
Thermogenesis	Obesity, diabetes

RS as a Component of Dietry Fiber (DF)

RS appears to be highly resistant to mammalian enzyme and may be classified as a component of fiber on the basis of the recent definitions of dietary fiber given by AACC (2000) and NAS (2002). While part of the RS may consist of low-molecular-weight dextrins, the bulk consists of polymers, of which retrograded amylase often forms the major fraction (Ranhotra and others 1991a). Although not a cell wall component, RS is obviously nutritionally more similar to NSP than to digestible starch. There is ample justification that RS behaves physiologically like fiber. RS assays as insoluble fiber, but has the physiological benefits of soluble fiber. Additionally, RS exhibits a level of slow digestibility and can be used as a vehicle for the slow release of glucose. Also, like soluble fiber, it has a positive impact on colonic health by increasing the crypt cell production rate, or decreasing the colonic epithelial atrophy in comparison with no-fiber diets. There is indication that RS like guar, a soluble fiber, influences tumorigenesis, and reduces serum cholesterol and triglycerides. Overall, since RS behaves physiologically as a fiber, it should be retained in the TDF assay (Haralampu 2000).

Prevention of Colonic Cancer

Starch unabsorbed in the small intestine is fermented by the microflora of the large intestine. Generally, starch is not present in the feces of humans or experimental animals, indicating more or less complete fermentation. In vitro experiments with human fecal inocula have shown that the butyrate yield from starch is high. As butyrate is a main energy substrate for large intestinal epithelial cells and inhibits the malignant transformation of such cells in vitro; this makes easily fermentable RS fractions especially interesting in preventing colonic cancer (Asp and Bjorck 1992).

Significant changes in fecal pH and bulking as well as greater production of SCFA in the cecum of rats fed RS preparations have been reported (Ferguson and others, 2000), which have been suggested to resemble the effects of soluble dietary fiber. However, when RS was combined with an insoluble dietary fiber like wheat bran, much higher SCFA levels, in particular butyrate was observed in the feces (Leu and others 2002). In rats, when RS was combined with psyllium, the site of RS fermentation was pushed more distally. As the distal colon is the site where most tumors arise it may be of additional benefit for cancer protection if fermentation is further enhanced within the distal colon (Morita and others 1999).

Hypoglycaemic Effects

Foods containing RS moderate the rate of digestion. The slow digestion of RS has implications for its use in controlled glucose release applications. The metabolism of RS occurs 5 to 7 h after consumption, in contrast to normally cooked starch, which is digested almost immediately. Digestion over a 5- to 7-h period reduces postprandial glycemia and insulinemia and has the potential for increasing the period of satiety (Raben and others 1994;
Reader and others 1997).

A study using 10 healthy normal-weight males fed test meals containing either 50 g starch free of RS (0% RS), or 50 g starch containing a high level of RS (54% RS) proved the ability of high RS meals to significantly lower the postprandial concentration of blood glucose, insulin, and epinephrine (Raben and others 1994). Similarly, from a human study (Reader and others 1997), using a commercial RS3 ingredient (CrystaLean®), the maximum blood glucose level was found to be significantly lower than that of other carbohydrates (simple sugars, oligosaccharides, and common starch). The RS3-containing bar decreased postprandial blood glucose and may play a role in providing improved metabolic control in type II diabetes (non-insulin dependent).

As a Prebiotic

RS has been suggested for use in probiotic compositions to promote the growth of such beneficial microorganisms as Bifidobacterium (Brown and others 1996). Since RS almost entirely passes the small intestine, it can behave as a substrate for growth of the probiotic microorganisms.

Reduction of Gall Stone Formation

The digestibility of starch in rice and wheat is increased by milling to flour (Heaton 1988). Digestible starch contributes gall stone formation via a greater secretion of insulin and insulin in turn leads to the stimulation of cholesterol synthesis. RS is found to reduce the incidence of gallstones (Malhotra 1968). Gallstones are less in South India where, whole grains are consumed rather than as flour in Northern India. Notably, dietary intake of RS is 2- to 4- fold lower in the United States, Europe, and Australia, compared with populations consuming high-starch diets, such as India and China, which may reflect in the difference in the number of gallstone cases in these countries (Birkett and others 2000).

Hypocholesterolaemic Effects

Hypocholesterolemic effects of RS have been amply proved. In rats, RS diets (25% raw potato) markedly raised the cecal size and the cecal pool of short-chain fatty acids (SCFA), as well as SCFA absorption and lowered plasma cholesterol and triglycerides. Also, there was a lower concentration of cholesterol in all lipoprotein fractions, especially the HDL1 and a decreased concentration of triglycerides in the triglyceride-rich lipoprotein fraction (Han and others 2003).

Inhibition of Fat Accumulation

Replacement of 5.4% of total dietary carbohydrates with RS in a meal could significantly increase postprandial lipid oxidation suggesting reduction in fat accumulation in the long term (Higgins and others 2004).

Absorption of Minerals

A study to compare the intestinal apparent absorption of calcium, phosphorus, iron, and zinc in the presence of either resistant or digestible starch brought out that a meal containing 16.4% RS resulted in a greater apparent absorption of calcium and iron compared with a completely digestible starch (Morais and others 1996). Thus RS could have a positive effect on intestinal calcium and iron absorption.

Food Applications of Resistant Starch

Resistant starch has a great interest to product developers and nutritionists for two reasons, the first being the above-mentioned potential physiological benefits and the second the unique functional properties, yielding high quality products not attainable otherwise with traditional insoluble fibres (Yue & Waring, 1998; Baixauli *et al*., 2008).

Historically, fibre-containing foods have been coarser, denser and sometimes less palatable than refined, processed foods. The use of resistant starches as food ingredients typically does not change the taste or significantly change the texture, but may improve sensory properties compared with many of the traditionally used fibres, such as brans and gums (Sajilata *et al*., 2006).

RS has desirable physicochemical properties (Fausto, Kacchi, & Mehta, 1997) such as swelling, viscosity increase, gel formation and water-binding capacity, making it useful in a variety of foods. RS has a small particle size, white appearance, bland flavor and also provides good handling in processing and crispness, expansion, and improved texture in the final product (Sajilata *et al*., 2006). Its low water-holding capacity, make it a functional ingredient that provides good handling and provides and improves texture in the final product (Yue & Waring, 1998).

RS shows improved crispness and expansion in certain products and better mouthfeel, color, and flavor than can be obtained with some traditional, insoluble fibres (Sajilata *et al*., 2006). This greatly increases the likelihood that consumers will accept these foods and hence increase their dietary fibre intake (Buttriss & Stokes, 2008). These properties make it possible to use most resistant starches to replace flour on a 1-for-1 basis without significantly affecting dough handling or rheology. RS not only fortifies fibre but also imparts special characteristics not otherwise attainable in high-fibre foods (Tharanathan & Mahadevamma, 2003). Some of the functional properties and advantages of commercial sources of RS2 and RS3 (Nugent, 2005) [35] are shown in Table 4.

They may also be used to provide fibre in some commercially available low-carbohydrate foods marketed for those following low-carbohydrate dieting regimens (Nugent, 2005) [35]. There are alsome potential uses in fermented foods, such as dry-cured sausages. The processing conditions can affect the resistant content of starch by influencing its gelatinisation and retrogradation (Thompson, 2000). Augustin, Sanguansri, and Htoon (2008) describe that it is possible to make a physically functional RS ingredient by the application of physical processes to starch suspension. Technically, it is possible to increase the RS content in foods by modifying the processing conditions such as pH, heating temperature and time, number of heating and cooling cycles, freezing, and drying (Sajilata *et al*., 2006). The substitution of 3% milk solids in yoghurts (12% total solids) with heated, sheared and microfluidised starch suspensions increased the viscosity and decreased syneresis of yoghurts but the incorporation of starch that had only been heated and sheared without microfluidisation did not.

Unlike natural sources of RS (e.g. legumes, potatoes, bananas), commercially manufactured resistant starches are not affected by processing and storage conditions. For example, the amount of RS2 in green bananas decreases with increasing ripeness, while a commercial form of RS2, Hi-maize, does not present these difficulties (Nugent, 2005) [35].

The food manufacture may be thought of as enhancement of the proportion of the starch that test as RS. The reason for including an ingredient high in RS is to combine physical functionality, processing stability and nutritional functionality. The physical functionality of RS is required for the physical characteristics of the food, such as texture, water-holding capacity. The processing stability of RS is important in order to preserve the nutritional functionality of the RS-containing ingredients. The nutritional functionality of the RS-containing ingredients can involve both resistance to digestion in the small intestine and resistance to fermentation in the colon. Eventually, we should be able to produce starch materials with the desired rate and extent of digestion (in terms of mean population responses) and (for any RS that might be present) a desired rate of hydrolysis and fermentation in the colon.

The industrial applications of RS mainly involve the preparation of moisture-free food products (Yue & Waring, 1998). Bakery products such as bread, muffins, and breakfast cereals can be prepared by using RS as a source of fibre. The amount of RS used to replace flour depends on the particular starch being used, the application the desired fibre level, and, in some cases, the desired structure– function claims.

Table 4: Functional properties and advantages of commercial sources of RS2 and RS3. Sources: Sharma *et al*. (2008) [45], Augustin, Sanguansri, and Htoon (2008), Sajilata *et al*. (2006), and Nugent (2005) [35].

Natural sources	Increase coating crispness of products
Bland in flavor	Increase bowl life of breakfast cereals
White in color	Functional food ingredients
High gelatinization temperature	Lowering the calorific value of foods
Fine particle size (which causes less interference with texture)	Lower water properties than traditional fibre products
Useful in products for coeliacs as bulk laxatives and in products for oral rehydration therapy	Good extrusion and film-forming qualities
Allow the formation of low-bulk high-fibre products with improved texture, appearance, and mouth feel (such as better organoleptic qualities) compared with traditional high-fibre products	

The incorporation of RS in baked products, pasta products and beverages imparts improved textural properties and health benefits (Premavalli, Roopa, & Bawa, 2006). A panel rated 40% TDF RS loaf cakes as best for flavor, grittiness moisture perception, and tenderness 24 h after baking. Based on an evaluation by a trained sensory panel of toasted waffles for initial crispness, crispness after 3 min, moistness and overall texture, RS waffle showed greater crispness than control or traditional fibre. RS can improve expansion in extruded cereals and snacks. RS may also be used in thickened, opaque health beverages in which insoluble fibre is desired. Insoluble fibres generally require suspension and add opacity to beverages. Compared with insoluble fibres, RS imparts a less gritty mouth feel and masks flavors less (Sajilata *et al*., 2006).
0% TDF RS had greater loaf volume and better cell structure compared with traditional fibres tested (Baghurst, Baghurst, & Record, 1996).
Hydrolyzed starches (those which retain their granular structure and essentially behave like unmodified starches in undergoing gelatinization on heating), which are also referred to as thin boiling starches, are also a form of RS. The advantage of this starch is the high concentration, which can be used as a paste of low viscosity, and its ability to set as a firm gel (Seib & Kyungsoo, 1999). Crosslinked starches of RS4 type, based on maize, tapioca and potato, have been useful in formulations needing pulpy texture, smoothness, flowability, low pH storage, and high temperature storage (Sajilata & Singhal, 2005).

New Sources of Production

There is considerable opportunity for future developments, especially for tailor-made starch derivatives with multiple modifications, although the problem of obtaining legislative approval for the use of novel starch derivatives in processed food formulations is still under debate. Nevertheless, it can be predicted that new ventures in starch modifications and their diverse applications will continue to be of great interest in applied research (Rudrapatnam & Tharanathan, 2005).
More recent innovation has seen the development of insoluble, resistant maltodextrins with a functionality similar to that of resistant starches (Buttriss & Stokes, 2008).
Chemically-modified starch derivatives, for example, phosphorylated starches, which are also non-digestible, have been categorized as RS, similar to polydextrose or resistant oligosaccharides (Rudrapatnam & Tharanathan, 2005).
Esterification of native starch using citric acid resulted in chemically-modified starch with an RS content that depended on the degree of esterification. The production of this modified starch is relatively simple, and good results regarding the RS content can be achieved independent of the source of starch so that a range of RS-products can be produced,
suitable for various foods. The results show that the RS content in toast bread could be increased by approximately 3%, when 7.5% citrate starch is added, compared to non-fortified bread (Wepner *et al*., 1999). The use of citric acid for esterification seems to be evident as it rated as nutritionally harmless compared to other substances used for starch derivatisation (Jyothi, Moorthy, Sreekumar, & Rajasekharan, 2007).
Powdered preparations enriched in resistant starch (RS) have been obtained from native and lintnerized (prolonged acid treatment) banana starches by consecutive autoclaving/cooling treatments. The autoclaved samples had a higher RS content than their parental counterparts, but the chemical modification (lintnerization process) allowed development of higher RS proportions
(19%, dry matter basis). These RS-enriched products appear suitable for the formulation of functional foods (Aparicio-Saguilán *et al*., 2005).
Bello-Pérez, González-Soto, Sánchez-Rivero, Gutiérrez-Meraza, Vargas-Torres (2006) reported that extrusion can be used to elaborate products with a higher RS content that their native counterparts. The native starches of unripe banana and mango had a purity higher than 90%, with a 37% amylose content in banana starch and 27.5% in mango starch. No effect was observed in RS formation, which was 5.7% for banana starch (with more amylose) and 9.7% for mango starch. Reaction conditions were optimized to increase the content of resistant starch in adlay starch using esterification with glutaric acid, and the physicochemical properties of the prepared glutarate starches were investigated. Glutarate starches with lower crystallinity than raw starch had a similar RS content before and after heating with excess water. This glutarate starch could be used to enhance the textural properties and health benefits of low-moisture products, such as crackers and cookies, due to its low solubility and digestibility and heat stability (Kim *et al*., 2008).
Wheat bran starch isolated from commercial wheat brans using a wet-milling process was shown to have unique

properties compared to commercial wheat endosperm starch. Starch recovery was 90% and the starch fraction contained a low level of protein (0.15%). The more resistant starch content and lower retrogradation rate are properties that present an opportunity to make wheat bran starch a new functional ingredient for the food industry (Xie, Cui, Li, & Tsao, 2008).

Energy Value, and RDA of RS.

In human subjects, replacement of 27 g of digestible starch by RS (raw potato starch) in a single meal lowered diet-induced thermogenesis by an average of 90 KJ/5 h (Heijnen and others 1995). A study was designed to compare the metabolizable energy of 2 starch sources, standard cornstarch and high amylose cornstarch (Behall and Howe 1996). Based on energy intake and fecal excretion from all subjects, the partial digestible energy value for the RS averaged 11.7 KJ/g RS, which was 67.3% of the energy of standard cornstarch. Control and hyperinsulinemic subjects differed in their ability to digest RS, averaging 81.8% and 53.2%, respectively. RS averaged 2.8 kcal/g for all subjects but only 2.2 kcal/g in the hyperinsulinemic subjects. This enables the use of RS in reducing the energy value of foods.

Approximately 20 g/d is recommended to obtain the beneficial health benefits of RS. However, worldwide, dietary intakes of RS are believed to vary considerably. It is estimated that intakes of RS in developing countries with high starch consumption rates range from approximately 30 to 40 g/d (Baghurst and others 2001). Dietary intakes in India and China were recently estimated at 10 and 18 g/d (Platel and Shurpalekar 1994; Muir and others 1998). Intakes in the EU are believed to lie between 3 and 6 g/d (Dyssler and Hoffmann 1994). Dietary intakes of RS in the U.K. are estimated at 2.76 g/d (Tomlin and Read 1990) and are believed to range from 5 to 7 g/d in Australia (Baghurst and others 2001).

Commercial Sources of RS

In the commercial development of RS, it is advantageous to start with a native starch high in amylose. Nearly all patented processes are based on the propensity of high-amylose starch to retrograde, or form highly crystalline regions, which are resistant to enzymatic hydrolysis (Crosby 2001). High-amylose maize starches have high gelatinization temperatures, requiring temperatures that are often not reached in conventional cooking practices (154 °C to 171 °C) before the granules are completely disrupted. These starches offer an opportunity to manipulate the amount of RS present in food products.

The first commercial RS was introduced as Hi-maize in Australia in 1993 by Starch Australasia, now part of Natl. Starch and Chemical Co. This product is a natural granular form of starch produced from a corn hybrid containing more than 80% amylose. Hi-maize analyses as 42% RS and has gained widespread use in Australia in breads and other baked goods.

Commercial sources of RS (Ranhotra and others 1996), such as CrystaLean® (Opta Food Ingredients, Inc., Bedford, Mass., U.S.A.), Novelose® (Natl. Starch and Chemical Co., Bridgewater, N.J., U.S.A.) and Amylomaize VII (Cerestar Inc., Hammond, Ind., U.S.A.) are now available to increase the DF content in foods and provide other functional properties. CrystaLean ® is a commercial, highly retrograded RS3 based on the ae–VII hybrid. It is produced by first fully hydrating and disrupting the starch granules, followed by an enzymatic debranching of the amylopectin to yield a low DE maltodextrin mixture, which is almost entirely a straight chain. Then, the mixture is treated through thermal cycles to achieve a high level of retrogradation before drying. CrystaLean ® containing 41% RS is digested slowly, at approximately half the rate of maltodextrin. The ingredient was introduced in the early 1990s and is now used in products for diabetics.

Shortly after the launch of CrystaLean, Natl. Starch introduced a very similar product named Novelose 330. More recently, Natl. Starch Chemical Co. has developed processes for manufacturing granular forms of concentrated RS containing 47% to 60% RS by heating and cooling high-amylose corn starch under conditions of carefully controlled moisture and temperature. These products are marketed as Novelose 240 and 260. Novelose ® 240 is a thermally modified RS2 based on ae-VII hybrid of corn (Shi and Trzasko 1997). The modification renders the native granule more stable by holding the starch at elevated temperature (60 °C to 160 °C) in the presence of limited water (10% to 80%). Novelose 260 contains 60% TDF, the highest level available in a RS. It can be formulated into a broad range of foods such as pasta, cereals, and snack foods that can carry a rich-in-fiber labeling. Novelose 240 (RS2), 260 (RS2), and 330 (RS3) have melting temperatures of 99.7 °C, 114.4 °C, and 121.5 °C, respectively. These products offer medium/high, high, and very high process tolerance and are therefore suitable for use in a variety of processed foods. Another player is Cerestar (a Cargill company), which has launched Ac tistar containing 58% RS, made by crystallizing hydrolyzed tapioca starch (maltodextrins).

High-amylose corn (amylomaize) is the generic name for corn that has an amylose content higher than 50%. The endosperm mutant amylose-extender (ae) increases the amylose content of the endosperm to about 60% in many dent backgrounds. Modifying factors alter the amylose contents as well as desirable agronomic characteristics of the grain. The amylose-extender gone expression is characterized by a tarnished, translucent, sometimes semi-full kernel appearance. U.S. production of high-amylose corn is forecasted at 50000 acres for 2001. 100% of this product is grown under contract in Indiana for Cerestar and Pioneer. Highamylose corn yields vary, depending upon location, but average only 65% to 75% of that of ordinary dents. Three types are produced commercially: Class V (50% to 60% amylose) and Class VII (70% to 80% amylose), and Class IX (90% amylose).

C*ActiStar (Cerestar Food and Pharma Specialties) is made from native, partially hydrolyzed starch by generating microscopic structures that are not hydrolyzed by digestive enzymes in the small intestine (58% RS). The specific structure of C*ActiStar favors its fermentation to butyrate and helps to reach the lower parts of the large bowel, which is the most relevant segment of the colon for the gut health maintenance. It can be used in a variety of foodstuffs such as bread, cereal bars, biscuits/cookies, muesli, low-fat fermented milk, UHT flavored milk drinks, and ready-to-use powdered mixes such as instant soups and instant chocolate. With C*ActiStar, each serving can provide a significant amount of RS, which will contribute to an increase in the pre-existing daily intake of RS. MGP Ingredients, Inc. (Atchison, Kans.) and Cargill have announced a business alliance for the production and marketing of a new RS product called FibersymTM HA that is derived from high-amylose corn and ideal for use in a wide array of lower net carbohydrate food products. Delivering more than 70% dietary fiber, it greatly reduces net carbohydrate levels in foods. Applications cover a wide variety of products, including breads, tortillas, pizza crust, cookies, muffins, waffles, breakfast cereals, snack products, and nutritional bars. Fibersym TM HA joins MGPI's other resistant starches, which include a wheat-based RS, FibersymTM 70 and a potato-based variety, Fibersym TM 80 ST.

Roquette (Roquette, Freres, France) recently developed Nutriose FB, a new dextrin that offers all the benefits of RS and, in addition, is a soluble fiber. Because it is only slightly digested in the small intestine and then slowly fermented in the colon, it fits the functional pattern of RS with a low glycemic response. Fibersol-2, offered through a joint venture of ADM and Matsutani, is a digestion-resistant maltodextrin. Resistant starches that test high in TDF such as Roquette's Nutriose FB 06 at 85% fiber content or ADM/Matsutani's Fibersol-2 at 90% make it possible to enrich products with fiber to optimum recommended levels and to support label claims.

Conclusion

RS has received much attention for both its potential health benefits and functional properties. As a functional fiber, its fine particles and bland taste make possible the formulation of a number of food products with better consumer acceptability and greater palatability than those made with traditional fibers. RS shows improved crispness and expansion in certain products and better mouthfeel, color, and flavor over products produced with some traditional, insoluble fibers. It is ideal for use in RTE cereals, snacks, pasta/ noodles, baked goods, and fried foods and permits for easy labeling as simply starch, conferring additional nutraceutical benefits. Being nondigestible, RS can be used in reduced-fat and sugar formulations. RS has properties similar to fiber and shows promising physiological benefits in humans, which may result in disease prevention. Foods containing high levels of RS yield fewer calories and lower glycaemic loads—important formulation considerations for diabetics as well as the weight-conscious. It is classified as a fiber component with partial or low fermentation. Technically, it is possible to increase the RS content in foods by modifying the processing conditions such as pH, heating temperature and time, number of heating and cooling cycles, freezing, and drying. A number of commercially available RS preparations would make it possible for a wide range of applications with nutraceutical implications.

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