

HIGH AMYLOSE STARCHES - NEW DEVELOPMENTS IN HUMAN NUTRITION

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Summary

Scientific research has indicated the importance of starch, and that portion which is resistant to digestion and absorption in the small intestine, in our diets. Resistant starch exists in the foods that we eat and is composed of native starches and crystallites of retrograded starch formed during food processing. One native starch obtained from high amylose maize maintains an ability to resist digestion in the small intestine in foods consumed after normal food processing. An Australian developed high amylose maize starch, Hi-Maize™, has been commercially released to allow the level of resistant starch in processed foods to be increased. The physiological effects of Hi-Maize™ will be discussed. The opportunity now exists to increase the level of resistant starch in foods without significantly changing their organoleptic properties.

I. INTRODUCTION

Starch is the main storage carbohydrate in the higher plants such as wheat, maize, potato, tapioca and rice. The starch granule provides an economical means of storing carbohydrate in an insoluble and densely packed manner (Imberly et al. 1991). Because of its abundant availability, multiple functionality and relative low cost, starch, modified starches and starch derivatives are widely used in the preparation of food. Starch is quantitatively the most important dietary carbohydrate contributing between 20 and 40 percent of the energy intake in Western diets (Asp et al. 1986).

The fate of dietary starch did not for many years receive the same level of attention as did dietary fibre. It was assumed that all starch was readily digested. This view was suggested by the definition of dietary fibre proposed by Trowell and his colleagues in 1976 as "the remnants of plant cells which are resistant to hydrolysis by the alimentary enzymes of man and include indigestible polysaccharides (cellulose, hemicellulose, oligosaccharides, pectins, gums, waxes) and lignin".

However, as knowledge on the composition and function of dietary fibre has increased, the definition has continued to be revised. Kritchevsky stated that dietary fibre was "plant material that resists digestion by alimentary enzymes. It includes substances of unique chemical structure, characteristic physical properties and individual physiological effects. Except for lignin, all are carbohydrates in nature. They are broken down by the enzymes of gastro-intestinal bacteria to give, by fermentation, H₂, CH₄, CO₂ and short-chained fatty acids" (Kritchevsky 1988).

A number of researchers have noted differences in the relative levels of digestibility for different types of starch and starch-derived products (Asp et al. 1986; Wolf et al. 1977; Englyst and Cummings 1985). A number of factors, such as the degree of gelatinisation, biological origin of the starch, particle size, amylose/amylopectin ratio, entrapment by plant cell walls, starch-protein interactions, protein encapsulation of starch, amylose-lipid complexes, the percentage of retrograded starch (Holm et al. 1987) and the presence of amylase inhibitors (Asp and Bjorck 1992) have been shown to affect starch digestion.

Now that it is recognised that starch may not be fully digested in the small intestine, the implications for human nutrition and health of this material entering the large bowel are being assessed.

The starch escaping digestion in the small intestine has been called resistant starch. EURESTA (European Concerted Action on Resistant Starch) has defined resistant starch as "the sum of starch and products of starch degradation not absorbed in the small intestine of healthy individuals" (EURESTA 1991).

Englyst and Cummings (1987) have proposed three categories for the *in vitro* digestion of starch. Starch when gelatinised, for instance by cooking, is rapidly digested (rapidly digested starch) while the native starch granules from many cereals are only slowly, though completely, digested (slowly digested starch). Finally there are starches which are completely resistant to digestion *in vitro* (resistant starch).

Resistant starch (RS) has been subdivided into three categories. The first is based on the physical inaccessibility of the starch granules (RS1). This includes starch granules, such as those trapped in the food matrix, which are prevented from complete swelling and dispersion (Worsch et al. 1986). This effect occurs in whole or partially milled grains of, for example, wheat, maize, oats, legumes and other starch-containing materials where the size or composition of the food particles prevent or delay the action of the digestive enzymes. Englyst and Cummings (1987) observed that after the consumption of a meal containing sweetcorn, peas and beans "up to 20% of faecal solids may be starch contained in recognisable, undigested food". The physical structure of foods such as parboiled rice (Wolever et al. 1986) and spaghetti (Hermansen et al. 1986) can also inhibit digestion.

The second category refers to resistant starch granules (RS2). The amount of resistant starch in native starches is dependent on the crystalline structure of the granule. X-ray diffraction crystallography has identified three possible arrangements of the crystalline structure (Katz 1934; French 1984).

In each case the starch α -glucan-chains exist as left-handed, parallel-stranded double helices. The so-called A pattern has the centre of the hexagonal array occupied by an additional helix and is found in wheat and corn. These starches are digestible when measured *in vitro* (Imberty et al. 1988). When the centre of the array is occupied by water, the B-pattern is observed. Potato, banana and high-amylose maize starches have the B pattern. Starch granules from these species have demonstrated resistance to digestion (Imberty and Perez 1988). C patterns, found commonly in legume starches, are considered to be a combination of the A and B arrangements and have also demonstrated resistance to enzyme degradation. These patterns are influenced by the chain length of the amylopectin fraction of the starch (Hizukuri 1985).

Another factor influencing the resistance of native starch granules is their susceptibility to gelatinisation. In an aqueous medium starch granules undergo a series of irreversible structural changes involving the disruption of the hydrogen bonds which stabilise the internal crystalline structure of the granule when the gelatinisation temperature is reached. For potato and banana starches, the gelatinisation temperature is less than 70°C (Snyder 1984; Lii C-Y et al. 1982). However, complete gelatinisation of high amylose maize starch does not occur until the temperature is in the range 154-171°C (Doublier and Choplin 1989). This temperature range exceeds those normally encountered in food processing. The disruption or gelatinisation of the starch granules renders the starch accessible to enzymatic hydrolysis. Once gelatinised, the starch is no longer resistant to digestion and ceases to be of importance in this aspect of nutrition.

The final category reflects the formation of retrograded starch during processing (RS3). Starch is composed of two major components, amylose and amylopectin, which can be dispersed in water by heating above the granule gelatinisation temperature. Upon cooling, the dispersed molecules of amylose and amylopectin spontaneously reassociate and can form crystallites that resist enzymatic hydrolysis (Sievert and Pomeranz 1989).

Gelatinisation of starch in aqueous solution causes the disruption of the hydrogen bonds stabilising the helical structure (Leach 1964). The x-ray pattern of the retrograded starch can be

manipulated by the conditions used to cool the gel. The formation of B type crystalline material is favoured by conditions involving solutions with low dispersed solids and low crystallisation temperatures. These conditions are found in the preparation of many types of food (Wu and Sarko 1978; Crawford 1987). The application of repeated heating and cooling cycles has been used (Sievert and Pomeranz 1989; Sievert and Wursch 1993) to increase the amount of resistant starch that can be isolated from potato amylose and maize starch.

Retrogradation is favoured by the presence of linear polymer chains. High amylose content, the presence of amylopectin treated with a debranching pullulanase (Berry 1986), or acid hydrolysed amylopectin (Zhang and Jackson 1992) can increase the opportunity for inter- and intra-helical hydrogen-bonding in the retrograded starch and the formation of resistant starch. In bread for example, Siljestrom and Asp (1985) have shown that under the limited moisture conditions which prevail in bread manufacture, resistant starch is formed by the retrogradation of amylose.

The *in vivo* digestibility of the starch in the small intestine is thought to reflect the divisions suggested by *in vitro* analytical techniques (Englyst et al. 1992). Analysts continue to refine testing procedures that seek to predict the digestion of starch *in vivo*.

The classification system for RS distinguishes between the readily digestible starch found in freshly cooked foods (Lee et al. 1985), the partially resistant native starches, such as raw potato, green banana and high amylose maize (Asp and Bjorck 1992), and resistant starch formed as a result of food preparation (Sievert and Pomeranz 1989).

Table 1. Resistant starch and dietary fibre content of processed foods.

Product	Resistant Starch (%) dsb	Dietary Fibre (%) dsb
Bread		
White, crust	0.92	3.19
White, crumb	0.83	4.71
Brown	1.52	7.69
Wholemeal	1.34	11.17
Flour confectionery		
Crumpets	1.62	5.66
Sponge cake	0.21	1.69
Biscuits		
Wafers	0.13	3.23
Oat cakes	0.27	7.74
Whole rye crispbread	1.24	14.33
Breakfast cereals		
Cornflakes, traditional	2.03	3.17
Cornflakes, extruded	0.20	1.51
All-Bran	0.39	23.22
Shredded Wheat	1.12	11.94
Rice Krispies	0.12	1.14

Crawford (1987) dsb - dry solids basis

Many common foods contain detectable levels of resistant starch (Crawford 1987), however the amount can be variable and unpredictable "depending on the degree of processing or cooking, and the length of time and conditions of storage to which the starch is subjected" (Dreher 1987). This variability has led analysts to try and separate resistant starch from the

more analytically reproducible non-starch polysaccharides (Englyst et al. 1987a). Accepted methods for determining dietary fibre, such as the AOAC enzymatic-gravimetric method, include some resistant starch in the result (Prosky et al. 1984). This inclusion can be significant in starch containing foods such as white bread where the dietary fibre content of the finished product can be up to 50% higher than the flour used to make the bread (Dreher 1987). Siljestrom and Asp (1985) demonstrated an increase of about 0.8% (dry solids basis) in the resistant starch content of bread baked above an internal temperature of 48°C. This increase is due to some of the starch being rendered resistant to enzyme digestion *in vitro*.

The analysis of a wide range of foods for the presence of resistant starch was conducted by Crawford (1987). Resistant starch was found in many prepared foods such as white and brown bread, crumpets, pastry, crispbread, crackers, breakfast cereals including cornflakes and shredded wheats, pasta, pizza base and chapattis.

The importance of establishing the physiological role of resistant starch in the diet has been highlighted by a number of researchers. These effects include its contribution to anaerobic bacterial fermentation (Asp and Bjorck 1992), the production of volatile fatty acids including propionate (Topping 1994) and butyrate (Englyst et al. 1987b; Muir et al. 1993), lowering the glucose response and the development of insulin resistance (Goddard et al. 1984; Byrnes et al. 1993), the increase in faecal output due to increased bacterial cell mass (Bingham 1988), the lowering of plasma cholesterol (Berry 1987) and the promotion of bowel health (Rickard et al. 1993).

Table 2. Australian research on the physiological properties of high amylose maize starch (Hi-Maize™).

Mild dose dependent laxative	Young 1994
Lowers glucose response and the development of insulin resistance	Byrnes et al. 1993
Some escapes digestion in the small intestine	Muir et al. 1993 Topping 1994
Increase levels of short chain fatty acids in the large bowel - butyrate and propionate	Muir et al. 1993 Topping 1994
Promotes bowel health	Rickard et al. 1993
Acts like a dietary fibre	Young 1993 Topping 1994
Increases the length of the large bowel	Topping 1994

High amylose starches, particularly from maize due to the high gelatinisation temperature, provide an opportunity to increase the apparent dietary fibre content of foods without greatly changing their organoleptic properties (Annison and Topping 1994). The physiologically important role that resistant starch appears to play in the diet, may be important for groups in the community who are reluctant to change their food preferences in response to nutritional information.

In 1993 Starch Australasia Limited commercially released Hi-Maize™, a high amylose maize starch, that contains a significant amount of resistant starch. It had been observed that the amount of resistant starch in high amylose maize increased as the quantity of apparent amylose in the starch increased (Brown 1993). Selection and evaluation of Australian developed maize varieties resulted in the identification of the hybrid from which Hi-Maize™ was obtained. The nutritional and functional properties of this very high amylose maize starch have been found to be significantly different from existing maize starches with lower amylose contents.

White bread is favoured by many sections of the population, particularly the young, even though wholemeal bread has been promoted as being better nutritionally. The addition of many fibres to white bread tend to change the appearance and structure of the bread rendering it less acceptable to consumers.

When Hi-Maize™ was used to replace 10% of the flour in the mix, the dietary fibre content of the loaf was more than doubled (Brown 1993). The loaves of bread containing the HiMaize™ were acceptable, as indicated by the loaf score. The bread was white and there was no discolouration as normally found with the inclusion of other fibre sources.

Table 3. Baking trials including Hi-Maize™

		Control	Regular Maize Starch		Hi-Maize™	
Rate of Flour Replacement	(%)	0	5	10	5	10
Total loaf score	(max. 100)	76	79	71	75	73
Dietary Fibre	(%) dsb	4.2	4.0	-	6.9	8.7

(Brown 1993)

In pasta, such as spaghetti, Hi-Maize™ can also be used to significantly increase the amount of apparent dietary fibre present.

Table 4. Spaghetti prepared with Hi-Maize™

Rate of semolina replacement with Hi-Maize™	(%)	0	12	24
Dietary fibre	(%) dsb	3.3	5.6	7.9

(McNaught et al. 1992)

Depending on the processing conditions used, some of the high amylose maize starch can interact with the other components of the food to provide a range of functional properties.

These functionalities assist in the preparation of snack foods and breakfast cereals. Extruded breakfast cereals can benefit from an increase in the apparent dietary fibre by the inclusion of Hi-Maize™ and also from the improved extrudability, better crunch and longer flake-bowl-life.

Table 5. Functional properties of high amylose maize starch.

Good film formation
 Decreases oil absorption
 Increase moisture retention
 Reduce soggy interfacing
 Improve coating crispness

Table 6. Hi-Maize™ in breakfast cereals

Extruded Flake Formulation		Control	Containing Hi-Maize™
Maize polenta	(%)	45.0	45.0
Hi-Maize™	(%)	-	42.0
Regular maize	(%)	42.0	-
Sugar	(%)	8.7	8.7
Salt	(%)	1.9	1.9
Malt	(%)	2.9	2.5
		100	100
Dietary fibre content	(%) dsb	3.5	12.0

(McNaught et al. 1992)

High amylose maize starches and more particularly Hi-Maize™, can be used to increase the level of resistant starch in conventional staple foods. This provides nutritionists with the opportunity of increasing the level of resistant starch in food without adversely affecting its appearance, taste or texture. The challenge is now "to define more precisely the links between the physiological actions of resistant starches on the one hand and their chemical and physical properties on the other" (Annison and Topping 1994).

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