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Designing food structure to slow down digestion in starch-rich products

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The category of starch-rich foods is on the spot for its role in the development of obesity and related diseases. Therefore, the production of food having a low glycemic index should be a priority of modern food industry. In this paper three different food design strategies that can be used to modulate the release of glucose during the gastrointestinal process of starch-rich foods, are illustrated. The structure of the starch granules can be modified by controlling processing parameters (i.e. moisture, temperature and shear) thus influencing the gelatinization and retrogradation behavior. The intactness of plant cell walls hindering the access of amylases to the starch granules and the formation of a stiffed food matrix using the crosslinking between proteins and the melanoidins generated by Maillard reaction are also very effective approaches.

Following these food design strategies several practical approaches can be pursued by food designers to find reliable solutions combining the consumers request of palatable and rewarding foods with the public health demand of having food products with better nutritional profile.

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Introduction

The bad nutritional quality of industry products is at the very center of the societal debate, and the correlation between their excessive consumption and the obesity pandemic has been put forward by several authors [1]. One of the main concerns is about industrial foods formulations: in many cases, pillar foods lack of some specific nutrients while others are too abundant. To tackle this point, reformulation strategies have been implemented in the last 10 years to reduce the presence of free sugars, fats, salt and to increase the amount of proteins, vitamins, dietary fiber, and phytochemicals. A second, subtler, concern is related to the degree of processing: the notation of 'ultraprocessed' foods was introduced to indicate the excessive use of refined ingredients and the extensive thermal treatments causing micronutrients loss and favoring fast nutrients uptake [1]. Although a better digestibility was considered a plus of the food processing until some years ago, in the present obesogenic context, the fast calorie uptake, especially from starch-rich foods, turned to be one of the main disadvantages of the Western diets [2].

Despite the fact that human metabolism is based on glucose hydrolysis, the wide availability of starch-rich food came relatively late in human evolution: the discovery of agriculture and the cultivation of cereals can be dated only 10–20 thousand years ago. Before that time, the hunter gathered-man collected some starchy tubers and cooked them on fire [3]. In some cases, these tubers provided a significant contribution to the total caloric intake, however the degree of processing was always very limited. After grain domestication (wheat, corn, rice or millet in the different part of the world), grain refining has been always very limited and the adoption of 'white bread' was traditionally limited to a restricted number of wealthy people [4]. After the Second World War, the abrupt switch toward a modern food production system brought a wide availability of industrial foods rich in refined flours and fully gelatinized starch. White bread, tortillas, maize porridge and other cereal-based products became the major contributors to the calorie intake of what we call 'Western diet', which is considered a hallmark for an unhealthy diet. In most of these foods, starch hydrolysis during the gastro-intestinal digestion is particularly fast and in some products the starch becomes metabolically similar to free sugar with well-known negative consequences on consumer health.

The fast starch digestion in the small intestine, its immediate absorption and the consequent peak of blood glucose, and in turn the fast release of insulin, together constitute one of the main causes of weight gain and type 2 diabetes insurgence. Moreover, in industrial foods design, starch is often used as matrix to incorporate fats and free sugars resulting in high-calorie dense foods [5].

Unfortunately, for most people it is extremely difficult to resist the temptation of eating too much of these starch-rich foods always available at a very affordable price. All these factors together contribute to establish the so called 'obesogenic environment' of the modern societies, which clearly explains the overwhelming spread of obesity pandemic.

Different strategies are currently pursued to face the issue: consumer education, enforcement of restrictive policies and food reformulations are the most obvious [6]. Unfortunately, all together they produced only limited results thus far.

This review will deal with a food technology approach aiming at designing starch-rich foods having reduced/delayed starch digestibility. The goal is to obtain products that are similar to the conventional ones without substantially changing consumers' sensory experience. This allows to target those consumers who are not sensitive to education campaigns and not willing to change their food choices or dietary habits. This type of consumers is very attracted by the sensory cues of energy-dense starch-rich foods such as the cooked flavors and appealing textures. They strongly prefer foods that are soft and palatable, or crunchy and airy, having the common denominator to be easily masticated and rapidly swallowed. Most of the starch-rich foods having these features have a high speed of calories ingestion preventing satiety stimuli and inevitably leading to the intake of an excessive amount of food [7].

In this framework, food designers' goal should be to develop structures that can delay starch digestion without compromising the desired sensory characteristics and the characteristic features of the food expected by the consumers.

In this paper, three strategies to achieve this goal are discussed illustrating the existing findings and suggesting possible future developments.

Modulate starch structure in starch-rich food

It is well known that native starch is assembled into relatively ordered granular structures. Upon heating in the presence of water, starch granules undergo an irreversible structural change, named gelatinization, that results in an amorphous macromolecular assembly. Starch gelatinization has very important implications on food texture as it is associated to the formation of a viscous gel where starch molecules have a dis-ordered conformation and a relatively high molecular mobility [8]. The open and flexible molecular conformation of gelatinized starch makes it accessible to amylases with the consequent glucose release.

From a nutritional perspective, the ability to control starch digestion is extremely important to design food with desired characteristics: the key to control such process is to modulate the accessibility of enzyme to its substrate.

Food formulation, processing and storage variables must all be considered in their relevance to favor/hinder starch hydrolysis. To slow down starch digestion all strategies that limit attainment of a flexible, continuous, and mobile gel and favor the formation of rigid, aggregated, low mobility, and not accessible structures should be considered.

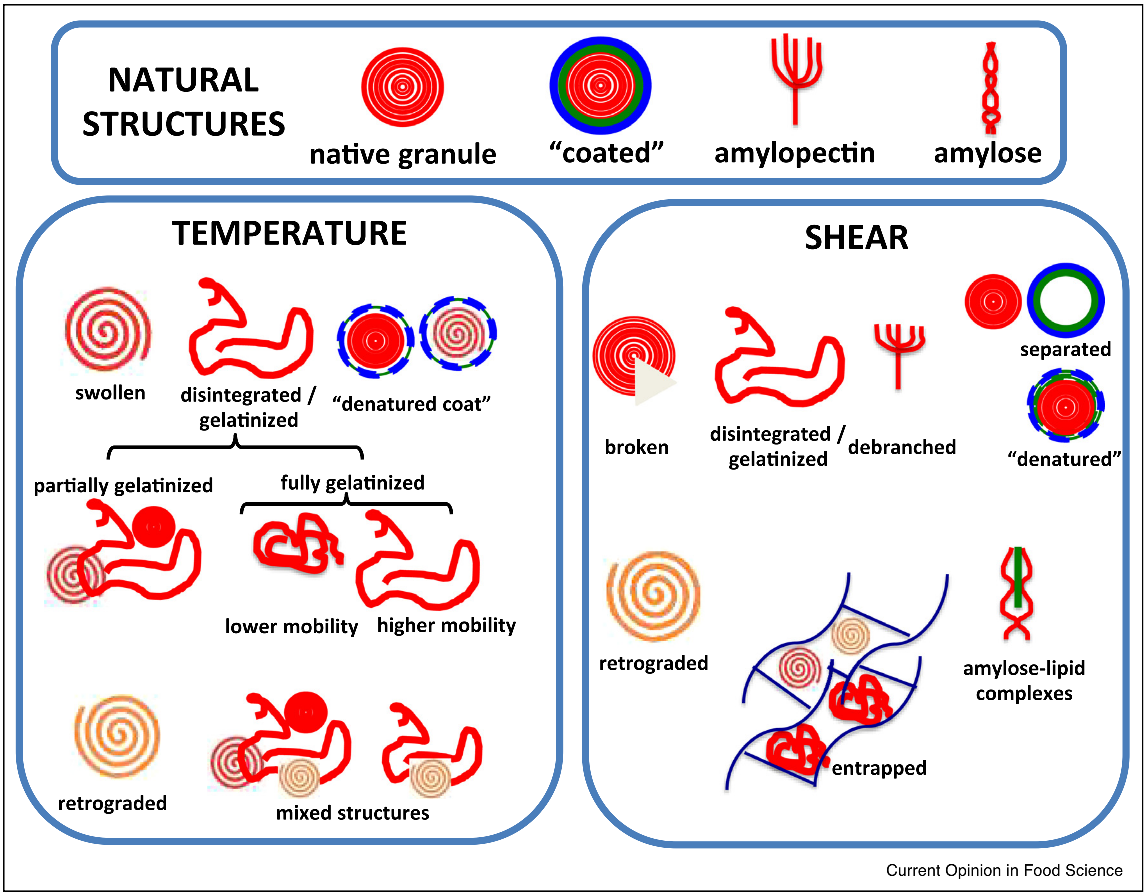
Ingredients selection should move toward vegetables having starch with large, non-porous granules. A high amylose content (smaller surface area per molecule than amylopectin limits amylolytic attack), long branches, and type B crystalline conformations are other features delaying amylases action [9–12,13•,14,15].

Also the concentration of water present in the food before thermal treatment should be carefully considered, as water content is a critical factor determining the degree of starch granule swelling, gel formation and structural/molecular mobility [10]. More complex food formulations may be preferred as protein and lipids may interact with starch by means of weak and steric interactions (e.g. gluten network formation and amylose–lipid complexes) forming complexes that diminish starch digestibility [9,10,13•,16,17]. The presence of hydrocolloids, dietary fiber, and thickening agents has also an important role in limiting starch hydrolysis by a dual mechanism: limiting gelatinization by subtracting available water and increasing gel viscosity [18–22]. However, not all types of fiber have the same efficacy in reducing the starch digestibility [18,20].

Food processing variables having a paramount effect on starch structure are temperature and shearing conditions, as schematically summarized in Figure 1. Temperature increase is necessary to induce starch gelatinization, a process that begins with swelling of starch granules and, eventually, ends with their destruction and the formation of a continuous and flexible gel. In the presence of fully gelatinized starch, molecular and structural mobility, free volume, and flexibility of the gel determine the easiness of the enzyme to reach its substrate. Homogeneous and continuous gels guarantee a high accessibility, while limiting heat transfer and reducing availability of water can restrict starch gelatinization and preserve partial structural integrity while providing desired textural modifications [9,10]. A gel containing starch only partially gelatinized (e.g. containing native and swollen starch granules in a gelatinized matrix) is less digestible than a fully gelatinized starch without necessarily impact on the sensory characteristics.

Cooling and storage temperature have also an important effect on the fraction of gelatinized starch molecules that

Figure 1



Schematic representation of the effect of processing on native starch structures (not to scale). The figure highlights the effect of temperature and shear on major structural components of native starch and the multiple starch structures that may be found in the final product.
Coated starch is covered by a lipid or a protein layer. Entrapped starch refers to the granules surrounded by cell wall or by an artificial protein network created during processing, as it happens in dry pasta.

retrogrades re-associating in ordered/crystalline forms. It is well documented that amylose retrogrades more easily and faster (minutes) than amylopectin (hours, days) [17]. Moreover, amylose tends to retrograde as resistant starch while amylopectin as slowly digestible starch. To maximize starch retrogradation, starch should be heated and hold at temperatures between the glass transition and gelatinization onset temperatures (annealing) or be stored at refrigerated temperatures [13•,16,23,24].

Processing techniques operating at low temperatures (below gelatinization temperature) can be very useful in producing foods with non-gelatinized starch. Techniques such as sprouting, germination, malting, and soaking cause a de-structuring of natural assemblies, but the increase of starch digestibility is lower than the one obtained with gelatinization [9,25•]. Moreover, if coupled with an acidifying technological step (i.e. sourdough fermentation), these techniques may promote interaction between starch and proteins (gluten) and reduce starch bioavailability [25•,26]. High hydrostatic pressure processing is a very promising technique for the designing low digestible starch products.: it operates at relatively low temperatures and causes partial gelatinization and preservation of starch granule integrity, favors spontaneous retrogradation (resistant starch formation), and amylose–lipids complexation [16,27,28]. Finally, even when processing techniques operating at high temperatures are used (i.e. boiling, pressure cooking, frying, puffing, flaking, popping), the formation of less digestible structures may be favored by limiting water availability (i.e. baking of cookies), promoting amylose–lipid complexes formation (i.e. frying), or enabling fast heating and cooling cycles (i.e. microwave heating) [9,25•].

Shear has also a detrimental effect on starch structural elements and can be modulated to influence them at different levels. Low share (i.e. gentle mixing) may cause structural modifications of proteins–lipids present in the grains but has little effect on intact starch granules which preserve their structure. On one hand, the formation of a coherent and continuous amorphous matrix (e.g. gluten network) around starch granules may act as barrier to enzymatic attach (e.g. pasta) [29]. On the other hand, the removal of proteins/lipids on the starch granule surface may have an effect in exposing starch pores and making them accessible to amylases. High shear (i.e. milling, extrusion) may have very different effects on starch properties depending on processing variables such as water content, energy, temperature and duration. In an effort to minimize starch digestion, milling should be modulated to minimize starch granules breakage, separation of proteins and lipids from granule surface, and to control the degree of de-branching of starch molecules to favor crystallization [25•,30]. Extrusion processing most commonly combines the effect of high shear and high temperature thus favoring starch granule breakage, destruction and consequent gelatinization with the production of highly amorphous and accessible starch assemblies [9,31,32]. However, the extrusion process might be optimized to favor incorporation of lipids into swollen amylose (amylose–lipid complexes), formation of starch–protein interactions, de-branching of amylopectin molecules producing straight chains that are more likely to retrograde [24,25•,33•]. All these phenomena favor the formation of non-accessible structures and delay the speed of starch degradation.

Summarizing, in order to reduce starch digestibility, processing conditions should be carefully optimized to:

1) Preserve as much as possible granular/crystalline structures and/or favor the formation of retrograded-crystalline structures
2) Limit mobility of gelatinized-amorphous matrix
3) Preserve/build barriers to surround gelatinized starch

Preserving the native structure of plant tissue in starch-rich foods

In starchy foods, the presence of intact cell walls prevents the complete swelling of starch granules during gelatinization and restricts their interaction with digestive enzymes. Besides the cell wall, starch granules are embedded in a tightly packed cytoplasmic matrix, also hindering enzymes' diffusion, and restricting complete starch granule swelling during gelatinization due to steric hindrance and other limiting effects (i.e. restricted water availability) [34].

To leverage on the effectiveness of native structure with the goal to prevent/delay starch digestion, mechanical processes, and especially milling, must be carefully designed. Milling of grains into flour disrupts cell walls and hence increases accessibility of starch by amylolytic enzymes, especially when the flour is processed in food using conditions favoring starch gelatinization. It is known that glycaemic responses of wholemeal and white bread are comparable because both flours have undergone structural disintegration during milling. Conversely, the glycaemic responses decreased linearly with increasing proportion of whole and intact grains present in wheat or barley bread [35]. The presence of higher portions of intact cells in coarse flour (average particle size: 705 μm) reduced the *in vitro* starch digestion rate as compared to fine flour and flour (average particle size: 85 and 330 μm, respectively) with lower or negligible content of intact cells [36•]. However, when cell wall structure was degraded by xylanase, the rate of digestion increased also in coarse flour, confirming that intact wheat endosperm cell walls pose a physical barrier to amylase diffusion into the cells [36•].

In evaluating starch digestibility, the botanical origin of starchy foods is also an important feature to be considered. When *in vitro* amylolysis of hydrothermally processed chickpea and durum wheat with different particle sizes was studied, durum wheat cell walls are less effective as enzyme barriers than chickpea cell walls [37]. Moreover, a different gelatinization behavior was reported for these two plant species: the extent of gelatinization was inversely related to particle size and strongly correlated to starch digestibility in chickpea but it was not in durum wheat [38]. Thick and mechanically resistant nature of the cotyledon cell walls in legumes may restrict the access of digestive enzymes and also prevent the complete swelling of starch granules during gelatinization. The thin cell walls of cereals endosperm are less efficient in limiting starch digestion. However, the porosity and permeability of the walls play also a pivotal role in the extent to which digestive enzymes enter and hydrolyzed products diffuse out of cells. Li *et al.* [39] showed red kidney beans have a less porous structure compared to potato cells, suggesting that this feature could also explain the low starch digestibility in beans.

Depending upon the processing conditions that plant foods undergo and their tissue characteristics (e.g. cell–cell adhesion strength), cells can either separate along the middle lamella or rupture across cell walls [40]. High pressure processing of legume cotyledons fractures cell walls and liberates nutrients enclosed within cells [41]. When domestic cooking is applied, cell walls appear intact and retain their morphology even in rice where most of the starch granules are disrupted and digested [42]. However, thermal processing modifies cell wall architecture (e.g. swelling, increase solubility and porosity, etc.). The effectiveness of cell walls in limiting starch digestion changes as processing conditions are modified. Pallares *et al.* [43] found that the cotyledon cells isolated from common beans had similar microstructural properties and starch gelatinization degree and retained their cellular integrity when where processed at 95°C at different times (between 30 and 180 min). However, a higher diffusion of fluorescently labelled pancreatic α-amylase inside the cells was shown with increasing processing time. Solubilization of pectin and other polymers, probably from the pectin, cellulose and hemicellulose network, could have led to different degrees of cell wall permeability to α-amylase. However, crosslinking between matrix polymers in the cell wall may impart wall strength that resists solubilization. Potato varieties with a high amount of rhamnogalacturonan galactans, which interact strongly with cellulose, in cell wall have lower pectin solubilization during cooking and an *in vitro* starch digestibility than common potatoes [44].

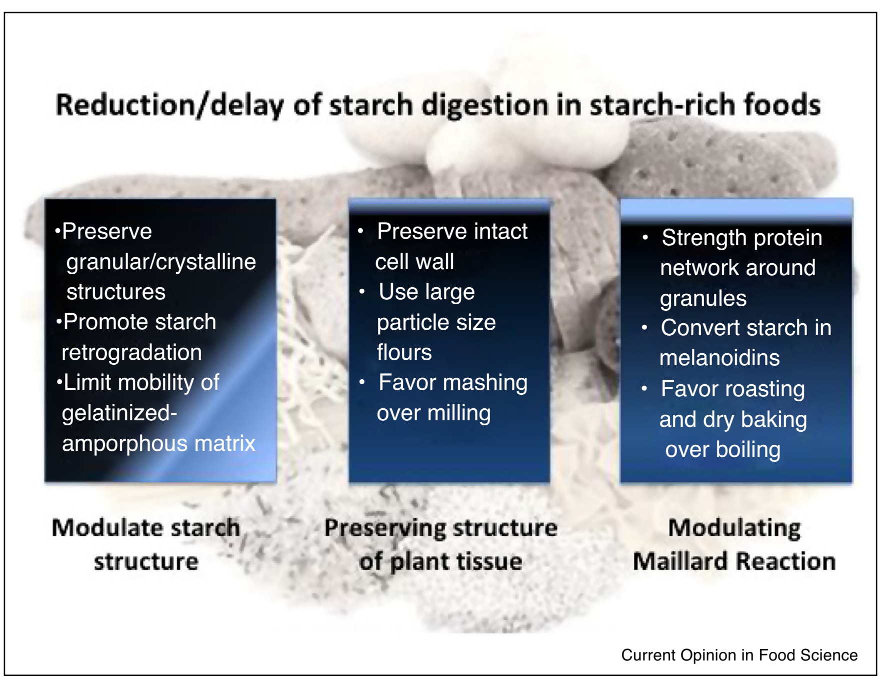
Different combinations of processing variables could generate different microstructures with different starch digestibility. Pallares *et al.* [45•] generated different microstructure applying a traditional thermal treatment (95°C, 0.1 MPa) and two alternative treatments including high hydrostatic pressure at room temperature (25°C, 600 MPa) and at high temperature (95°C, 600 MPa) to common beans. In both treatments involving high temperature, the lowest starch digestibility was observed in samples mostly characterized by the presence of cell clusters compared to samples obtained by the same processing technique but exhibiting a different microstructure (individual cells). In high hydrostatic pressure-treated samples at room temperature, starch gelatinization happened to a low extent due to the absence of high temperature. Therefore, although starch granules were not hindered by physical barriers, their hydrolysis was reduced due to the preservation of native organization.

To sum up, foods produced by using milled grains with large particle size would represent a useful strategy to reduce their starch digestibility. 'Mild' milling can produce large clusters of intact cells in which the diffusion of digestive enzymes to the core of the particles is slower compared to small particles [46]. Short time processing, which affects less the permeability of cell walls and produces large cell clusters, is also desired to limit the starch digestibility. Finally, the design of biomimetic food systems, for example, starch-entrapped microspheres fabricated by entrapment of starch granules in calcium-induced gel network of pectin and alginate, could be the near future in the design of slowly digestible starch foods [40].

Modulating Maillard reaction in starch-rich foods

The Maillard Reaction (MR) typically occurs when starchy foods are roasted, baked or fried. At a first glance, because of the extensive thermal treatments, MR development can be associated with starch gelatinization, and so with food having a high starch digestibility. However, this is not completely correct: MR develops faster in food processed at low water activity, a condition that also favors limited starch gelatinization and formation of slow digestible starch [47]. In other words, two opposite effects related to low water activity take place in food: MR

Figure 2



Summary of the food design strategies proposed in this paper to reduce or delay the degradation of starch into glucose.

development and inhibition of starch gelatinization. The most straightforward example to observe this phenomenon is a bread loaf: in the crumb, the abundance of water promotes starch gelatinization with minimal MR development. In the crust, the formation of the brown MR polymers, the melanoidins, is accompanied by a reduced starch digestibility. This is due to the reaction of starch with the amino group available on protein leading to the formation of a brown heterogeneous polymer known as melanoidins [48]. There are few papers dealing with starch-containing cereal melanoidins: these molecules are difficult to extract, poorly digestible and a good substrate for human microbiota [49]. The possibility to use a range of baking conditions modulating time, temperature and moisture provides many opportunities to design bread having reduced starch digestibility [50]. In general formulation with different ingredients can be used to modify the properties of the food matrix surrounding the starch granules to modulate their degradation

In the same vein, also pasta drying conditions can be modulated to change starch digestibility: when a low temperature is used for drying (common in artisanal processing) no MR products are formed, and the protein matrix is quite open: when cooked the starch granules can easily gelatinize and becoming fully digestible. However, when more severe drying conditions are used as it happens in industrial drying of pasta, the high temperature at low water activity promotes the formation of a strong protein network reinforced by MR products covalently bound to different gluten protein chains (crosslinking) [51]. Starch granules are stiffed within the matrix and do not completely gelatinize even during cooking in excess boiling water [52]. A similar approach can also be pursued in extruded products like breakfast cereals: Singh *et al.* reported that severe thermal treatment and presence of reducing sugar reduces the nutritional quality of the final products by preventing starch digestion [53]. Now looking from the opposite standpoint of reducing the calorie uptake from the starch-rich foods, we can make a good use of the extrusion process to prevent the starch gelatinization and to trap the starch granules in a matrix rich in indigestible MR products.

Conclusion

Fighting obesity is a challenge that food designers must tackle in a pragmatic way using all the possibilities offered by new ingredients and advanced processing techniques. We must look at the product from the consumers' perspectives considering psychological and hedonistic aspect taking in mind that long-term dietary behaviors are in most of the cases driven by liking before than healthy, convenience and sustainability considerations. This is particularly true for low educated and low-income consumers who find in starch-rich foods the best solution to fulfill their eating preference at affordable prize.

Starch digestion provides our body with a large moiety of the daily calorie intake: targeting this physiological process has the potential to impact on the negative metabolic consequences that an excessive occurrence of glucose load has on human health. Recently a great interest was devoted to the use of amylase inhibitors especially polyphenols which act in multiple ways delaying digestive enzyme activity (see for review Lijun *et al.* [54]). Details of this approach are not described in this paper but it is relevant to mention that polyphenols interaction with amylase can be also modulated by processing and formulation adding another element of variability to the whole picture.

Dogmatic classifications of food into good and bad categories, such as those proposed by NOVA, YUKA and SIGA and also the NUTRISCORE system, do not serve the purpose of reducing the obesity of vulnerable consumers and impairing the innovation at food industries including the design of healthier foods [55•,56].

The different food design approaches highlighted in this paper and the main recommendation are summarized in Figure 2. The final message is that a combination of formulation and processing strategies can be very effective in achieving the objective of designing starchy foods having reduced/delayed digestibility. The future challenge is to obtain this goal matching consumers' sensory expectation with the public health needs.

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Conflict of interest statement

Nothing declared.

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