Slowing starch digestibility in foods

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CHAPTER 3

Effect of hydrocolloids on lowering blood glucose

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ABSTRACT

There is growing interest in lowering the post-prandial blood glucose response (PPG) to carbohydrate-rich meals, to help reduce risks of chronic cardiometabolic diseases. Starch digestibility is mainly determined by the intrinsic starch characteristics such as amylose/amylopectin ratio and the botanical source. Processing factors such as cooking, baking and cooling also determine the glycaemic effects. Much effort has been dedicated to transforming rapidly digestible starch (RDS) into slowly digestible starch (SDS) by changing the properties of the starch, but this is complicated by the simultaneous formation of resistant starch (RS), which in large amounts can lead to gastrointestinal complaints. Hydrocolloids contain colloid particles, either digestible such as starch or indigestible such as gums (viscous/gelling fibres), dispersed in water. SDS content can be increased by adding hydrocolloids which are viscous (such as guar gum) or gel-forming (alginates, pectins) under gastrointestinal conditions, and these can lower PPG. Both the viscosifying and gelating potential of these hydrocolloids are related to their concentration and intrinsic properties e.g., the hydrodynamic properties, molecular weight, and solubility. In addition, the hydrodynamic properties of the gums depend on the solvent nature and environment i.e. food matrix and composition of gastrointestinal fluid and mechanical forces exerted by the body. Lastly, *in vitro* methods are an inexpensive tool to evaluate the properties of hydrocolloids under gastrointestinal conditions, to screen and prioritize hydrocolloid-containing materials for clinical testing of their PPG-lowering efficacy, and clarify their mechanism of action, which can be used to further optimise effects.

1 INTRODUCTION

There is growing interest in lowering the post-prandial blood glucose response (PPG) to carbohydrate-rich meals. Higher PPG has been implicated in the development of chronic diseases particularly type 2 diabetes mellitus and cardiovascular diseass.[1] In addition the European Food Safety Authority (EFSA) recognizes that lowering of PPG may be a physiologically beneficial effect, thus allowing products to carry claims (where substantiated) for this effect.[2] Hydrocolloids are a heterogeneous group of long chain polymers (polysaccharides and proteins) characterized by their property of forming viscous dispersions and/or gels when dispersed in water. [3] The focus of this chapter is on starch, which is digestible, and hydrocolloid gums such as galactomannans (guar gum, tara gum and fenugreek gum) and beta-glucans, which are indigestible.

2 DIGESTIBILITY OF STARCH

Starch is the predominant carbohydrate in grain-based foods and contributes a substantial proportion of calories in modern human diets. [4] Starch is first digested by salivary amylase in the oral cavity; however, hydrolysis by salivary amylase is reduced as the food bolus is mixed with gastric acid in the stomach. In the intestine pancreatic alpha-amylase hydrolyzes starch to soluble glucose oligomers with linear and branched structures.[4] These are converted to glucose in the small intestine by the combined action of mucosal maltase-glucoamylase (MGAM) and sucrose-isomaltase (SI) (see **figure 1**). Both MGAM and SI can hydrolyze alpha-1,4 and alpha-1,6 linkages from non-reducing ends of linear chains of glucose oligomers and polymers to release free glucose as the final step in small intestinal digestion.[5] SI displays more hydrolytic activity on branched alpha-1,6 linkages than MGAM. MGAM substrate specificity somewhat overlaps with that of SI. [6]

The main factors which determine starch digestibility are the intrinsic starch characteristics such as the amylose/amylopectin ratio and the botanical source.[7] In addition, processing factors such as cooking, baking and cooling determine the blood glucose response via intermediate processes such as gelatinization and retrogradation. Starch can be classified into rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) based on *in vitro* digestion by Englyst method.[8] The *in vitro* estimates of starch digestibility by the Englyst method has been shown to predict post-prandial blood glucose concentrations. [9]

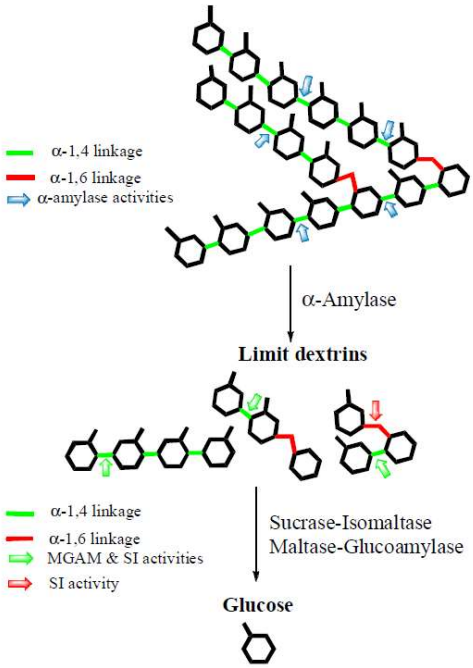

Figure 1: Starch digestion by the action of pancreatic and salivary alpha-amylase and small intestinal alpha-glucosidases (Eskandari, PhD thesis, 2012, Simon Fraser University, Burnaby, Canada; [10] with permission from author)

2.1 Intrinsic starch characteristics

Starch is composed of two different polymers, amylose and amylopectin, usually present at about 15-30% and 70-85% by weight, respectively. [11] Exceptions to this are waxy and high-amylose plant varieties, having 0% to 5% amylose and 50% to 90% amylose, respectively. Amylose is defined as a linear molecule of (1→4) linked alpha-D-glucopyranosyl units, but it is now well-established that some molecules are slightly branched by (1→6)-alpha-linkages.[12] Amylopectin is highly branched; 5% of its links are alpha (1→6).

Native starches naturally exist in the form of starch granules which are composed of semi-crystalline regions, alternating with amorphous regions as ring-like structures. Amylopectin is the more important of the two starch fractions for granule structure, because on its own it is sufficient to generate granules, as occurs in waxy starches that are devoid of amylose. The first level of granule structures is the 'cluster arrangement' of the amylopectin branches. This arrangement describes a structure characterized by alternating regions of ordered, tightly packed, parallel glucan chains and less-ordered regions that are predominantly composed of branched-points.[13]

Crystallinity occurs within the ordered arrays of amylopectin and is created by the intertwining of chains with a linear length of >10 glucose units to form double helices, which associate in pairs to give either the 'A', 'B' or 'C' crystal structures as classified by X-ray diffraction.[13] Cereal starches generally display the A-form, whereas potatoes and some tropical tubers give the B-form. Most legume starches have the C-pattern. Some A-type starches (maize, sorghum, millets and large granules of wheat, rye and barley at the equatorial groove) have surface pores connected to interior cavities through channels.[14] There are no such surface pores in B-type starch granules and this is the reason that B-type granules are more slowly and less completely hydrolysed when exposed to amylases than A-type. C-type starches have an intermediate digestibility, between A- and B-type starches. Native A-type wheat starch granules from both soft and hard wheat flour showed much higher resistant starch content after 2 hour *in vitro* incubation compared with B-type wheat starch granules. Next to A- or B-type starch, higher apparent amylose content, larger granular size, and lower protein content of A-type wheat starch granules play significant roles in starch digestibility.[15]

The ratio of amylose/amylopectin influences starch digestibility, as amylose tends to form secondary structures that are hard to disperse, both in the native starch granules and after food processing.[16] Therefore starches with a higher amount of amylose are more resistant to digestion.[17] Higher amylose rice and maize starches show lower levels of RDS and higher levels of RS than normal rice and maize starches.[18]

The botanical source of starch also plays a determining role in digestibility, by influencing aspects such as the amylose content and location in the granule, the amylopectin fine structure, and the size and shape of the starch granules. The location of amylose with respect to the amorphous and/or crystalline regions is dependent on the botanical source of the starch. In wheat starch, amylose is mainly found in the amorphous region, but in potato starch it may be co-crystallised with amylopectin. Large amylose molecules that are present in the granule core are able to participate in double helices with amylopectin and contribute to crystallinity, whereas smaller amylose molecules, present at the granule periphery, are able to leach from the granule, and thus are more rapidly digested.[13] The amylopectin fine structure is determined by the unit chain length, which is correlated to the digestibility: the proportions of amylopectin unit chain length with a degree of polymerization (DP) 8-2 and DP 16-26 were positively and negatively correlated with hydrolysis, respectively.[19] Smaller barley and wheat starch granules hydrolyse faster than large granules.[20]

2.2 Processing factors

Cooking and cooling processes can influence the starch digestibility by the degree of gelatinization and retrogradation of starch. Gelatinization is the collapse (disruption) of molecular order (breaking of H-bonds) within the starch granule manifested in irreversible changes in properties such as granular swelling, native crystallite melting, loss of birefringence and starch solubilisation during hydrothermal treatment.[21] This leads to dissociation of the crystalline regions and (in cereal starches) amylose-lipid complexes. The associated hydration and swelling of the starch granules increases the accessibility of starch molecules for enzymatic digestion, leading to a higher digestion rate relative to native starch (see **fig 2**). [21, 23]

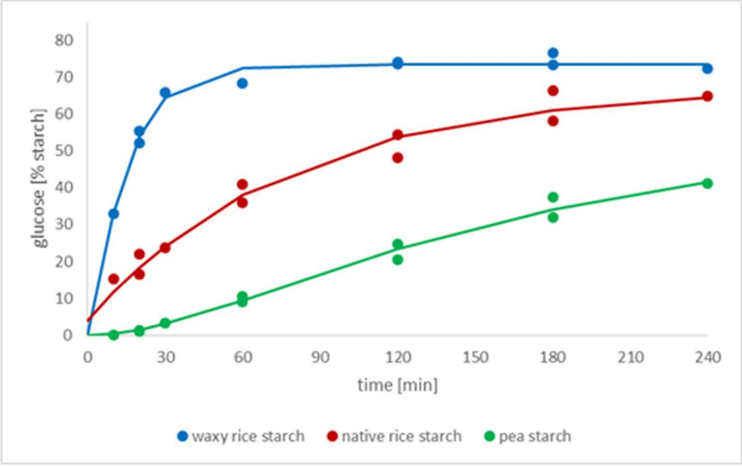

Fig 2: In vitro digestibility of different (native) starches by Englyst method (unpublished work; native rice starch has an intermediate amylose content)

Retrogradation is the recrystallization of the amorphous phases created by gelatinization into double helical crystalline structures [24] and results in the case of amylose in formation of type 3 resistant starch (RS3).[25] Amylose aggregation and crystallization in cooked starch pastes have been reported to be complete within the first few hours, while amylopectin aggregation and crystallization occur at later stages during refrigerated storage.[26] Retrograded amylopectin is thought to melt upon reheating, due to the low melting point (46-65 ^{0}C) of these crystallites and is therefore digestibility increases again upon (re-)cooking.

The amylose content of retrograded starch is an important factor for decreasing the glycaemic response to starch-rich products. The PPG response was shown to be significantly lower after cooked rice with a high amount of amylose (25% w/w of carbohydrates) compared to low amylose rice.[27] The amylose contents vary

substantially among starch sources of different botanical sources.[28] In addition, the amylose fine structures are of importance for digestibility in cooked rice grains.[29, 30] The *in vitro* digestion rate tends to increase with longer amylose branches and smaller ratios of long amylose branches to short amylopectin branches. [29, 30] In addition, amylose presents a helical conformation and can form inclusion complexes with small hydrophobic molecules such as fatty acids which results in retrogradation and resistance towards the action of digestive enzymes. [31]

The gelatinization and retrogradation processes are dependent on the water content and conditions of processing and storage.[32] Miao et al (2010) [33] and Chung et al (2006)[34] studied the effect of controlled gelatinization in excess water on digestibility of waxy maize and waxy rice starches. With increasing temperature, the RDS content increased, and SDS and RS content decreased gradually. [33, 34] However, most of our food products are processed under limited water conditions, in which starch is partially gelatinized and thus somewhat less accessible to digestible enzymes (examples of these are breakfast cereal flakes and some baked products such as Scottish shortbread).[23] Extrusion cooking particularly increases the *in vitro* digestibility of starches. [35] The rate and extent of retrogradation is also dependent on the water content and the time and temperature conditions of storage. [32] The effect of water content on starch retrogradation, displayed a parabolic shape across a range of water contents, with maximum retrogradation occurring in the starch gels at 35-45% water content. [36] Temperature cycling during storage can greatly decrease the enzyme susceptibility of retrograded starch and some conditions can lead to high formation of SDS. [37]

2.3 Formation of slowly-digestible starch

Much effort has been put in shifting transforming RDS to SDS by changing the properties of the starch. However, transforming RDS to SDS is complicated by the simultaneous formation of RS, which in large amounts can lead to gastrointestinal complaints (e.g. bloating and flatulence).

Processing conditions

Hydrothermal treatment is commonly used to modify the physical properties of starch granules while maintaining granular structure.[38] Three parameters are varied in the hydrothermal treatment of starch granules: temperature, moisture and time.[39] The treatment can be divided into two general areas: annealing and heat-moisture treatment. Annealing is usually performed in conditions of excess (>66%) or intermediate water content (40-55% w/w), while heat-moisture treatment is defined for low-moisture conditions (<35% w/w). Hydrothermal treatment can be used as a way of increasing the SDS nature of native starch granules.[38] The hydrothermal treatment of sweet potato converted its C-type structure to A-type, and the SDS of the treated granule increased 200% compared with native starch granules.[40] However, the

opposite effect can also be observed after hydrothermal treatment.[41] Compared with raw flour, the SDS levels of several flours were increased by autoclaving and parboiling, but were significantly reduced by microwaving. [41]

Starch structure modification

As noted, starches are dominated by the highly branched and very large amylopectin molecules consisting of alpha-1,4, linked d-glucopyranosyl polymeric units joined through alpha 1,6-linked branches. The alpha-1,4 linkages are easier to digest than the alpha-1,6-linked branches. Starch structural modification (to increase branching) can also be viewed as a strategy to achieve SDS from RDS.[39]

Enzyme modification

Enzyme modification is an alternative way of changing the structure of starch molecules to achieve appropriate digestion or glycaemic properties.[39] Partially debranching waxy starch with pullulanase has been used to make SDS from RS.[42] We have shown that a medium-chain pullulan has slow-release properties, while a long-chain pullulan is resistant to digestion.[43] In another publication [44], a combination of beta-amylase or alpha-amylase, and transglucosidase treatment of normal corn starch was used to form starch with an increased proportion of SDS at the expense of RDS. This was related to an increase in the amount of alpha-1,6-linkages and a decrease of alpha-1,4-linkages. Both the increase in the starch branch density and the crystalline structure in the treated starches likely contribute to the slow digestion properties.[44]

Chemical modification

Most chemical modifications eventually result in the formation of RS.[45] However, Han and Bemiller demonstrated high SDS amounts in 2-octen-1-ylsuccinic anhydride esterified waxy starch, and relatively high SDS and RS amounts in cross-linked hydroxypropylated and acetylated waxy starches. [46]

Introduction of other food components

The introduction of proteins (pasta), lipids, organic acids and gums (see paragraph 3) could also interact with starch during gelatinization and result in lower blood glucose and insulin response. Pasta is a good example of a low glycaemic response food due to the protein network surrounding starch. [47, 48] In addition, lipid addition during partial gelatinization of large barley starch granules prevented the swelling of starch completely. As a result the starch was less susceptible to amylase.[49] Inclusion of lactic acid in bread reduced the rate of starch digestion by creating interactions between the gluten and the starch, which makes the bread structure very firm and less porous.[50,51] The presence of lactic acid during starch gelatinization appeared to be a prerequisite for a reduced starch bioavailability. [51]

3. INFLUENCE OF GUMS ON DIGESTIBILITY OF STARCH

Another technique to increase the SDS is by adding other gums. Particularly gums which are viscous (such as guar gum) or gel-forming (alginates, pectins) under gastrointestinal conditions can lower PPG.[52,,53] Substantial amounts of viscous fibres are needed, with doses 5g or higher for high MW guar gum [54,55] to give a reasonable effect on PPG (~30% decrease in positive incremental area under the curve(+iAUC)). Lower doses of beta-glucans (from ~3 gram) have been shown to reduce the +iAUC for glucose by 12 to 18%.[56] Jenkins et al.[57] showed that the glycaemic index decreased by 4 units for each gram of beta-glucan. For gel-forming gums (high-guluronate alginate) 1.5-3.75g has been found to give a relatively large effect.[53,58]

3.1 Nature of and variation in viscosity of gums

The dose as well as specification of gums is important for the viscosifying effect under gastrointestinal conditions. These specifications, even within the same type of gum, can vary enormously (e.g. due to difference in MW, solubility) resulting in a huge variation in viscosity and PPG-lowering efficacy. Viscosity is a function of the concentration of dissolved gum and of its MW[59] and lowering the MW results in lower viscosity resulting in a decreased effect on PPG. Native guar gum can be hydrolysed into partially hydrolysed guar gums (PHGG) with a reduction in chain length and a lower average MW, Some studies have shown an effect of PHGG on plasma glucose in type 2 DM,[60, 61] but other studies do not confirm this beneficial effect [62, 63], probably due to the PHGGs differing in chemical characterization, which could influence viscosity. In a recent study, Thondre et al. [64] showed that the MW of barley beta-glucan in soup had an effect on glycaemic response and gastric emptying: A high MW barley beta-glucan delayed gastric emptying due to increased viscosity, resulting in a decreased glycaemic response compared to a low MW barley beta-glucan. [64] The MW of beta-glucans is determined by endogenous beta-glucanases which can depolymerize beta-glucans in oat flour and seeds.[65] Inactivation of these enzymes by processing (such as IR heating, steaming or boiling in aqueous ethanol) is essential to obtain high MW beta-glucan extracts from the oat-grain flours and seeds.[66]

Because of the large potential variation in the types and size of effects observed for different gums in different food matrices, it is not appropriate to make generic claims for benefits on the basis of “fibre”, or even “gum” content alone without further specification and substantiation. In the EU, PPG claims have been approved for SDS and particular gums such as beta-glucans and pectins. [67]

3.2 Relationship of viscosity to physiological effect

Viscosity under gastrointestinal conditions seems likely to play a dominant role in the PPG-lowering effects of viscosifying fibres. Viscosity is determined by the physico-chemical properties of the gums, which directly influences intermediate physiological

processes such as e.g. gastric emptying. An increased viscosity[68] or gel formation[57] delays gastric emptying resulting in a lower blood glucose response.[69] In addition, lower in the gastrointestinal tract, higher viscosity can inhibit the propulsive and mixing effects of intestinal contractions. [70, 71] Slower digestion in the small intestine can possibly lead to a stimulation of release of incretins (GLP-1 and GIP). Incretins are intestinal hormones which affect insulin production and hepatic glucose production.[72] In addition, GLP-1 also delays gastric emptying which influences PPG response. [73] It is important to measure the viscosity (or gel) characteristics *in vitro* under conditions similar to those in the gastrointestinal tract [74] where the composition of gastrointestinal fluid (e.g. dilution) and mechanical forces (shear rate) play an important role and hydrocolloid behaviour may differ substantially from the product environment. [75] Methods used for this are briefly discussed in Section 4 below.

3.3 Factors which determine variance in viscosity and PPG

Wood et al. [76] and Tappy et al. [77] showed that there is an inverse linear relationship between viscosity of beta-glucan and the change in the peak of plasma glucose. The viscosifying and gelling potential of gums under gastrointestinal conditions are related to intrinsic properties of the gums e,g,, their hydrodynamic properties, molecular weight, concentration and solubility.[75] In particular there are many studies with the viscous fibres, beta-glucan and guar gum, which focus on the topic on physico-chemical characteristics in relation to its blood-glucose effect. [75, 78].

Next to MW and concentration, solubility should be taken into account. The relative solubility of the gum also has an impact on blood glucose, because insoluble gums do not contribute to solution viscosity or the PPG lowering effect.[79] The solubility is determined by the source of the gum[80], processing condition[81, 82] and storage (especially under frozen conditions). [79, 83]

Kwong et al.[84] tested the effect of the viscosity *per se* or beta-glucan solution viscosity by altering solution volume at a fixed amount of beta-glucan of differing MWs in a beverage. The effects of beta-glucan on peak blood glucose rise (PBGR) were altered by changes in beverage viscosity achieved through changes in MW but not in volume. [84] The beta-glucan /starch ratio is also of importance, because beta-glucan was significantly more active in reducing the PBGR and iAUC when the beta-glucan/starch ratio was 1.6:10 rather than 1.1:10 in wheat and oat granolas.[85] In addition, the hydrodynamic properties of the gums depend on the solvent quality i.e. food matrix and composition of gastrointestinal fluid (dilution) and mechanical forces (shear rate) exerted by the body. [75]

3.4 Factors other than viscosity on PPG

The acute glucose lowering effect of guar gum may not solely be explained by viscosity under gastrointestinal conditions, but also by direct inhibitory effects on digestive

enzymes by complexation. [86] In addition, Brennan et al.[87], showed that guar gum can also coat the starch granules resulting in a decrease in swelling and gelation of starch and the formation of a physical barrier to alpha-amylase.

3.5 Sensory issues

The viscosity or gel formation which plays an important role in blood glucose response can, however, have a negative impact on product oro-sensory attributes.[88] A number of approaches have been described to try to achieve desired 'in body' effects of viscous and gelling fibres whilst minimizing their adverse impacts on product quality. There are examples reported of low viscosity formulations where gelling is triggered by exposure to pH or temperature changes in the body, sufficient to generate significant physiological effects, [89,90] Another proposed approach is to compress viscous fibres into granules, by which viscosity formation is delayed.[91]

4. METHODS TO EVALUATE MECHANISM OF ACTION (MAO) OF GUMS UNDER GASTROINTESTINAL CONDITIONS

There are different methods to evaluate the MAO of gums under *in vivo* gastrointestinal conditions. The standard method to measure gastric emptying is scintigraphy, which involves using a physiological test meal labelled with radioactive chemicals (e.g. ^{51}Cr as $CrCl_3$ in hydrochloric acid) [58] and imaging their transit and dispersion in the gastrointestinal tract.[92] Other methods to measure gastric emptying include stable isotope breath testing, ultrasonography, the use of wireless motility capsules, and Magnetic Resonance Imaging (MRI). [93] With the latter method (i.e. MRI) the behaviour of gums (e.g. viscosity) under *in vivo* gastrointestinal conditions can be observed.[94] Blood glucose concentration or glycaemic index is suggested in many studies to be a reflection of the rate of food digestion and absorption.[95] However, this is not really correct, because the total plasma glucose concentration is not only determined by the glucose coming from the food, but also by the glucose produced from the liver and the disposal of glucose in the tissues.[96] The only validated method to actually measure the rate of food digestion requires the use of stable isotopes in which saccharides or starch in the food are labelled with ^{13}C in order to follow the ^{13}C glucose in the blood. [96]

Lastly, *in vitro* methods can be used as an inexpensive tool to evaluate the properties of gums under gastrointestinal conditions [65], to screen and prioritize for clinical testing of PPG-lowering efficacy and characterise the mechanism of action, and to use these to further optimise effects.

There are three different types of models for gastric processing: 1) biochemical models, introducing low pH and gastric enzymes,[97] 2) mechanical models, mimicking (in addition to the biochemistry) physical forces in the stomach (e.g., the dynamic

gastric model of Wickham et al) [91] and 3) computational fluid dynamics models. [98] Of course, not all features of the gastric environment can be reproduced *in vitro*. For example, in addition to the absence of systemic feedback mechanisms, shear rate is related to the degree of mixing of fluid (digesta) caused by peristalsis and this is not always known for different regions in the gut. [75] The intestinal digestive models can roughly be divided into static (e.g. Englyst model)[7] and dynamic models. The Englyst method is based on an *in vitro* enzymatic method to determine the response of food carbohydrates to enzymatic digestion.[7] An example of a dynamic model, which includes both chemical and physical breakdown in the stomach as well as the intestine, is the TIM-Carbo model as described by Bellman et al.[99] Dynamic mechanical models of digestion have an advantage over static models, as they allow for examination of both physical and chemical breakdown of food products. However, these models are more complex in design and fabrication and always require validation with human clinical data.[95]

5. CONCLUSIONS AND RECOMMENDATIONS

- Starch digestion is a very complex process and mainly determined by intrinsic starch characteristics (e.g. amylose, cultivar) and industrial and consumer processing which determine gelatinization and retrogradation.
- Viscosity or gelling of specific hydrocolloids under gastrointestinal conditions seems to be the dominant contributor to their effects on blood glucose control. However, these may also act by direct enzyme inhibition and coating of the starch granules which inhibits enzyme access.
- Viscosity is determined by the hydrodynamic properties, the molecular weight, dose and the solubility of the viscous hydrocolloids under gastrointestinal conditions.
- Generic claims cannot be made for hydrocolloids (e.g. dietary fibres) in general and may even need to be qualified for specific hydrocolloid types. For substantiation of efficacy and claims, these need to be tested in the actual processed product format in human trials.

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