



Form and functionality of starch

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ABSTRACT

Starch is a macro-constituent of many foods and its properties and interactions with other constituents, particularly water and lipids, are of interest to the food industry and for human nutrition. Starch varies greatly in form and functionality between and within botanical species, which provides starches of diverse properties but can also cause problems in processing due to inconsistency of raw materials. Being able to predict functionality from knowledge of the structure, and explain how starch interacts with other major food constituents remain significant challenges in food science, nutrition, and for the starch industry generally. This paper describes our current understanding of starch structure that is relevant to its functionality in foods and nutrition. Amylose influences the packing of amylopectin into crystallites and the organization of the crystalline lamellae within granules, which is important for properties related to water uptake. Thermal properties and gel formation appear to be influenced by both amylose content and amylopectin architecture. While amylose content is likely to have an important bearing on the functional properties of starch, subtle structural variations in the molecular architecture of amylopectin introduces uncertainty into the prediction of functional properties from amylose content alone. Our ability to relate starch granule structure to suitability for a particular food manufacturing process or its nutritional qualities depends not only on knowledge of the genetic and environmental factors that control starch biosynthesis, and in turn granule morphology, but also on how the material is processed.

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1. Introduction

Ensuring food security and delivering foods that provide health benefits are major global challenges. Increased demand for dietary animal protein in Asia, continuing population growth, a worldwide increase in diet-related illnesses, and competition for arable land and water from alternative crops such as biofuels are pressures that are driving the need to increase the efficiency and quality of food production. Improving processes and products through ensuring fitness-for-purpose and better use of raw materials will be critical in achieving these objectives. This requires increasing our understanding of the relationship between form and functional properties of food constituents.

Most foods are multi-component, multi-phase systems that contain complex mixtures of water, polysaccharides, proteins, lipids and numerous minor constituents. Starch is present as a macro-constituent in many foods and its properties and interactions with other constituents, particularly water and lipids, are of interest to the food industry and for human nutrition. Starch contributes 50–70% of the energy in the human diet, providing a direct source of glucose, which is an essential substrate in brain

and red blood cells for generating metabolic energy. Indeed, the availability of a reliable source of starch from agriculture is considered to have been an important factor in human development (Perry et al., 2007), although it now seems that the glycemic response to excessive consumption of rapidly digesting starch may be a factor in some diet-related illnesses. Starch is also an important industrial material. Approximately, 60 million tonnes are extracted annually worldwide from various cereal, tuber and root crops, of which roughly 60% is used in foods (for example, bakery products, sauces, soups, confectionery, sugar syrups, ice cream, snack foods, meat products, baby foods, fat replacers, coffee whitener, beer, soft drinks) and 40% in pharmaceuticals and non-edible purposes, such as fertilisers, seed coatings, paper, cardboard, packing material, adhesives, textiles, fabrics, diapers, bioplastics, building materials, cement, and oil drilling (Burrell, 2003). Starches with a wide range of functional properties are needed to ensure fitness-for-purpose for such a diverse range of end uses.

Starch varies greatly in form and functionality between and within botanical species, and even from the same plant cultivar grown under different conditions. This variability provides starches of diverse properties, but it can also cause problems in processing due to inconsistency of raw materials. As a result, chemically modified starches are used extensively to overcome the variability of native starches and their lack of versatility over a wide range of processing conditions. However, consumer interest in “more

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natural foods” is increasing, and hence there is a need for greater understanding of how processing and nutritional performance are related to starch morphology.

Starch has been the subject of intensive research over many decades, resulting in a vast body of published literature on preparative and analytical methods, molecular structure, physical, chemical and biochemical properties, functionality and uses. Yet being able to predict functionality from knowledge of the structure, and explain how starch interacts with other major food constituents remain significant challenges in food science, nutrition, and for the starch industry generally. It is not intended in this article to review the extensive literature on starch. Rather, the aim is to provide the reader with a reasonably concise discussion of our current knowledge of starch structure that is relevant to its functionality in foods and nutrition. The reference articles cited are intended to be illustrative rather than comprehensive. Clearly, many relevant references that could have been included have been omitted to achieve brevity. For comprehensive treatises on starch structure, function and applications, the reader is referred to the compendia edited by Eliasson (2004) and by Yuryev and Tomasik (2007).

2. The form of starch

Starch is the main storage carbohydrate of plants. It is deposited as insoluble, semi-crystalline granules in storage tissues (grains, tubers, roots) and it also occurs to a lesser extent in most vegetative tissues of plants. Starch is made up of two polymers of D-glucose: amylose, an essentially unbranched $\alpha[1 \rightarrow 4]$ linked glucan, and amylopectin, which has chains of $\alpha[1 \rightarrow 4]$ linked glucoses arranged in a highly branched structure with $\alpha[1 \rightarrow 6]$ branching links. The moisture content of native starch granules is usually about 10%. Amylose and amylopectin make up 98–99% of the dry weight of native granules, with the remainder comprising small amounts of lipids, minerals, and phosphorus in the form of phosphates esterified to glucose hydroxyls. Starch granules range in size (from 1 to 100 μm diameter) and shape (polygonal, spherical, lenticular), and can vary greatly with regard to content, structure and organization of the amylose and amylopectin molecules, the branching architecture of amylopectin, and the degree of crystallinity (Lindeboom, Chang, & Tyler, 2004). Granules may occur individually or clustered as compound granules, and in wheat, barley, rye and triticale they occur in bimodal size distributions. This diversity in the form of starch granules and their molecular constituents influences starch functionality.

Although a minor component by weight, lipids can have a significant role in determining the properties of starch. The lipid content and composition of starch granules varies among plant species. Lipids associated with isolated cereal starch granules occur on the surface as well as inside the granule. Surface lipids are mainly triglycerides, and to a lesser extent free fatty acids, glycolipids and phospholipids, which can be extracted with diethylether. Internal lipids of cereal starches are predominantly monoacyl lipids that are usually extracted with hot aqueous alcohol. Both surface and internal lipids may be present in the free state, linked through ionic or hydrogen bonds to hydroxyl groups, or bound in the form of amylose inclusion complexes (Morrison, 1988; Morrison, 1995; Vasanthan & Hoover, 1992). The lipid content of native starches is highly correlated with amylose content: the higher the amylose content the more lipid is present.

The structure of amylose and amylopectin have been studied extensively and have been the subject of numerous reviews, as summarized in the following section (for example: Blanshard, 1987; Buléon, Colonna, Planchot, & Ball, 1998; Hoover, 2001; Srichuwong & Jane, 2007; Tester, Karkalas, & Qi, 2004; Zobel, 1988). Amylose has a molecular weight range of approximately 10^5 – 10^6 ,

corresponding to a degree of polymerization (DP) of 1000–10,000 glucose units. Less than 0.5% of the glucoses in amylose are in $\alpha[1 \rightarrow 6]$ linkages, resulting in a low degree of branching, and a structure with 3–11 chains of approximately 200–700 glucose residues per molecule. Because of the low degree of branching, dissolved amylose has a tendency to form insoluble semi-crystalline aggregates, depending on the placement of the branches in the structure.

Amylopectin is a much larger polymer, with molecular weight about 10^8 and a DP that may exceed one million. Most starches contain 60–90% amylopectin, although high-amylose starches, with as little as 30% amylopectin, and waxy starches with essentially 100% amylopectin are well known. Amylopectin has about 5% of its glucoses in $\alpha[1 \rightarrow 6]$ linkages, giving it a highly branched, tree-like structure and a complex molecular architecture that can vary substantially between different starches with regard to placement and length of branches. The amylopectin branches may be classified according to their pattern of substitution: A-chains are defined as unsubstituted, B-chains are substituted by other chains, and there is a single C-chain that carries the reducing glucose. Glycogen, a storage polysaccharide of animals, has the same chemical composition as amylopectin but it has a higher degree of branching giving it a more compact globular shape. More glucose can be packed into the open ended, tree-like structure of amylopectin than in the more closed, globular configuration of glycogen.

The natural variability in amylose and amylopectin molecules is due to the complexity of starch biosynthesis. Again, the reader is referred to several excellent in-depth reviews of this topic (Buléon et al., 1998; Morell & Myers, 2005; Smith, Denyer, & Martin, 1997; Tetlow, Morell, & Emes, 2004). The biosynthetic pathway involves several types of enzymes: ADP pyrophosphorylases, which form the glucosyl donor ADP-glucose from precursor hexose-phosphates; soluble and granule bound starch synthases, which catalyse the formation of $\alpha[1 \rightarrow 4]$ linkages; starch branching enzymes, which catalyse the formation of $\alpha[1 \rightarrow 4]$ branching linkages; and starch debranching enzymes, which are considered to have a role trimming newly synthesized amylopectin branches to enable them to pack into crystalline structures. These enzymes occur in multiple forms, and their activities may be subject to temporal and spatial differences in expression, environmental influences at both the genetic and enzyme level, and differences in substrate specificities of multiple forms. The end products of the biosynthetic pathway reflect the genetic diversity among the enzymes involved, and environmental influences acting on their expression and activity. The biosynthesis of amylose and the assembly of amylopectin and amylose into the granules are not well understood.

3. Starch granules

The extent of crystallinity of native starch granules ranges from about 15% for high-amylose starches to about 45–50% for waxy starches. The granules have a hierarchical structure that can be observed readily by light and electron microscopy. Multiple concentric layers of so-called growth rings of increasing diameter extend from the hilum (the centre of growth) towards the surface of granules. The growth rings are typically 120–400 nm in thickness, and are considered to represent diurnal fluctuations in the deposition of starch in storage tissues (Donald, Kato, Perry, & Waigh, 2001; Gallant, Bouchet, & Baldwin, 1997; Ridout, Gunning, Parker, Wilson, & Morris, 2002; Sevenou, Hill, Farhat, & Mitchell, 2002). The concentric growth rings, in turn, contain alternating crystalline and amorphous regions of higher and lower density, respectively. The higher density regions have a lamellar structure of alternating crystalline and amorphous layers with a repeat distance of 9–11 nm (Donald, 2004; Donald et al., 2001; Yuryev et al., 2004). Within these lamellae, the crystalline layers are considered to be formed

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