

## 1 INTRODUCTION

In plants starch is stored as easily accessible energy resource but to use it for humans, either as structuring compound in foods or for technical applications, it does not provide all the desired properties. As early as in the beginning of the 19<sup>th</sup> century researchers studied the modification of starch [1]. The first patent on modified starch was filed 1897 by Bellman [2] and extensive research has been carried out ever since.

### 1.1 Starch

Starch is one of the most abundant storage polysaccharides in plants and at the same time the most important energy source in human and animal nutrition [3]. The worldwide estimated production is in the range of 170 to 180 billion tons annually from which only 5 % are actually used [4]. Highly starch-containing plants are roots and tubers (potato, cassava, canna), legumes (peas, beans), and cereals (corn, wheat, barley, rye). In Europe, wheat and potato starch are the most produced varieties and are mainly used for industrial application such as starch modification for technical uses. The cereal starches have their biggest field of use in food production, e.g. in bread and pasta. The world's starch production for the year 2000 was an estimated 48.5 million tons from which 50 % were produced in the USA. Annual starch production in the European Community is about 8.4 million tons. An overview of the different sources is presented in Figure 1-1 [5].

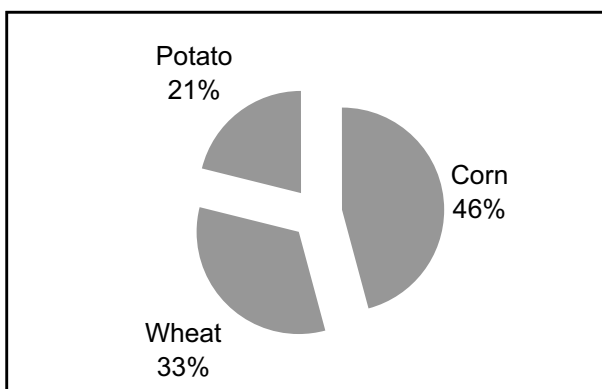


Figure 1-1: Starch production in the European Community, year 2000/2001

### 1.1.1 The granular and molecular structure of starch

Starch is accumulated in granules that are responsible for its unique characteristics. Granule size varies between 2 and 150  $\mu\text{m}$  depending on the botanical origin [6]. There is also a variation in shape and size distribution. Potato starch consists of only one type of large granules whereas cereal starches occur in smaller B-type granules and large disc-shaped A-type granules. The starch granules are accumulated mainly in storage tissues of plants, e.g. seeds or roots. The polymeric nature of the saccharide enables the plants to store large amounts of easily accessible sugar (glucose) without working against an osmotic pressure [7].

The two starch polysaccharides are amylose and amylopectin, both of them consisting of  $\alpha$ -D-glucopyranosyl units. The amylose content is normally in the range of 15 to 30 % but can vary with the genotype. There are amylose-rich starches (high amylose starch) and also amylopectin-rich starches (waxy starch). A classification of the crystal type of the amylopectin double helices in starch can be made by their X-ray diffraction patterns: A-type starches, which are mainly cereal starches, B-type starches (potato) and C-type starches (legumes) that are not fully elucidated in their structure [3, 8].

Upon heating in aqueous systems starch is gelatinizing, amylose leaks out of the granule and dissolves, crystalline amylopectin molecules melt and a viscous gel is formed. This characteristic is of great importance for the application of starches especially as a major food compound or additive since it determines the structure, texture and storage stability [6, 9, 10].

Common feature of amylose and amylopectin is their monomer unit  $\alpha$ -D-glucopyranosyl units, which is connected by 1  $\rightarrow$  4 linkages to form long chain polysaccharides.

*Amylose* is a linear molecule having a helical conformation and an average degree of polymerization (DP) of 500 to 6,000 and an average molecular weight ( $M_w$ ) of 200,000 to 1 million. Only 0.3 to 0.5 % of the glucose units in amylose are branched [11].

*Amylopectin* in contrast is a much higher branched macromolecule (5 % branching points) and its DP is in the range of 6,000 to 600,000, which means a  $M_w$  of 50 to 100 million. The branching regions within an amylopectin molecule were found to

occur accumulated [12]. Amylopectin chains often exhibit a double helical, crystalline structure. The structure of amylose and amylopectin is schematically shown in Figure 1-2.

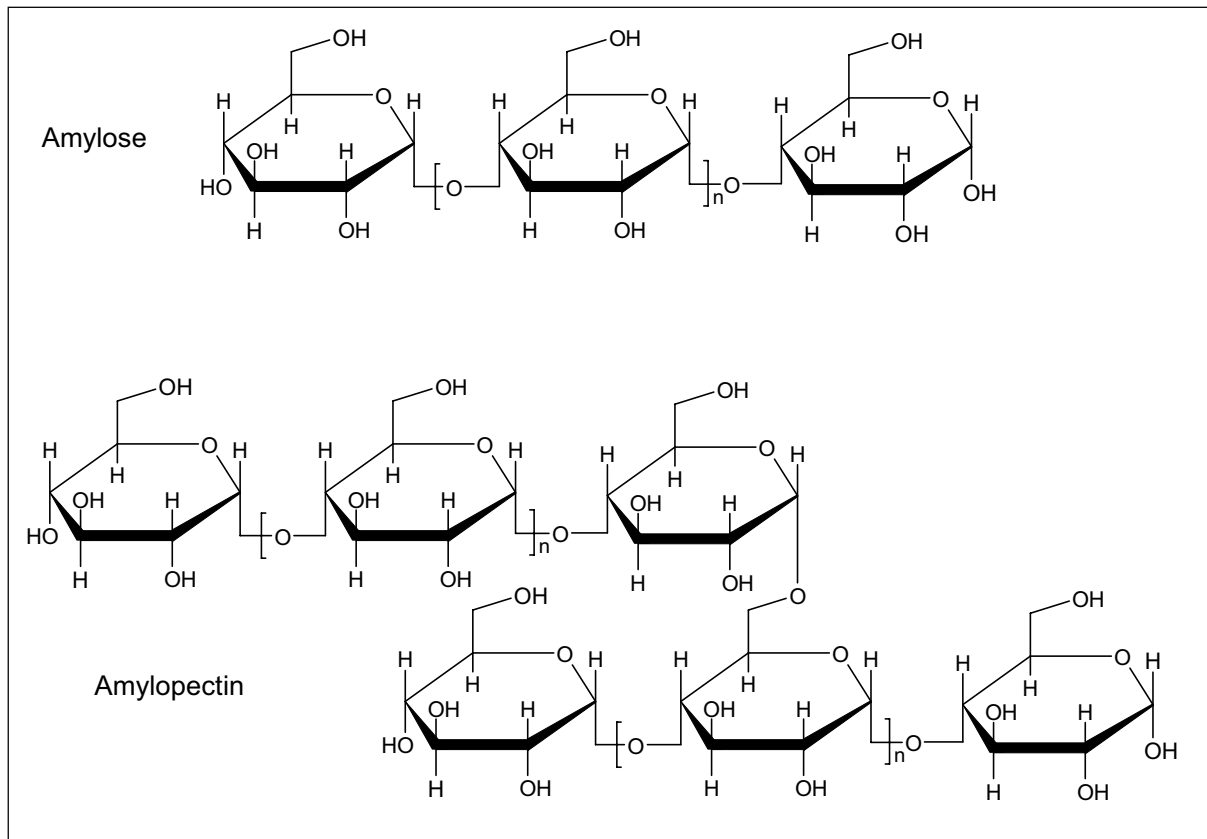


Figure 1-2: Structure of amylose and amylopectin,  $[n]$  is different for amylose, the amylopectin main chain, and the short amylopectin side chains

The polymer chains are synthesized from inside the granule (hilum) outwards [13]. Concentric rings are caused by alternating crystalline and amorphous layers with a thickness of 1,200 to 4,000 Å [14].

An overview on the structure of a starch granule is given in Figure 1-3. The alternating crystalline (hard) and amorphous (soft) shells, which present the lowest level of granule organization, are shown in the upper left part of Figure 1-3. Due to the increasing surface area that is added with granule growth, the shells are thinner in the interior granule parts and the hilum is shown off center. Blocklets in association with amorphous radial channels are present at a higher level of structure, where blocklet size is larger in the crystalline shells than in the semi-

crystalline shells. At the next highest structural level one blocklet with its amorphous and crystalline lamellae is shown.

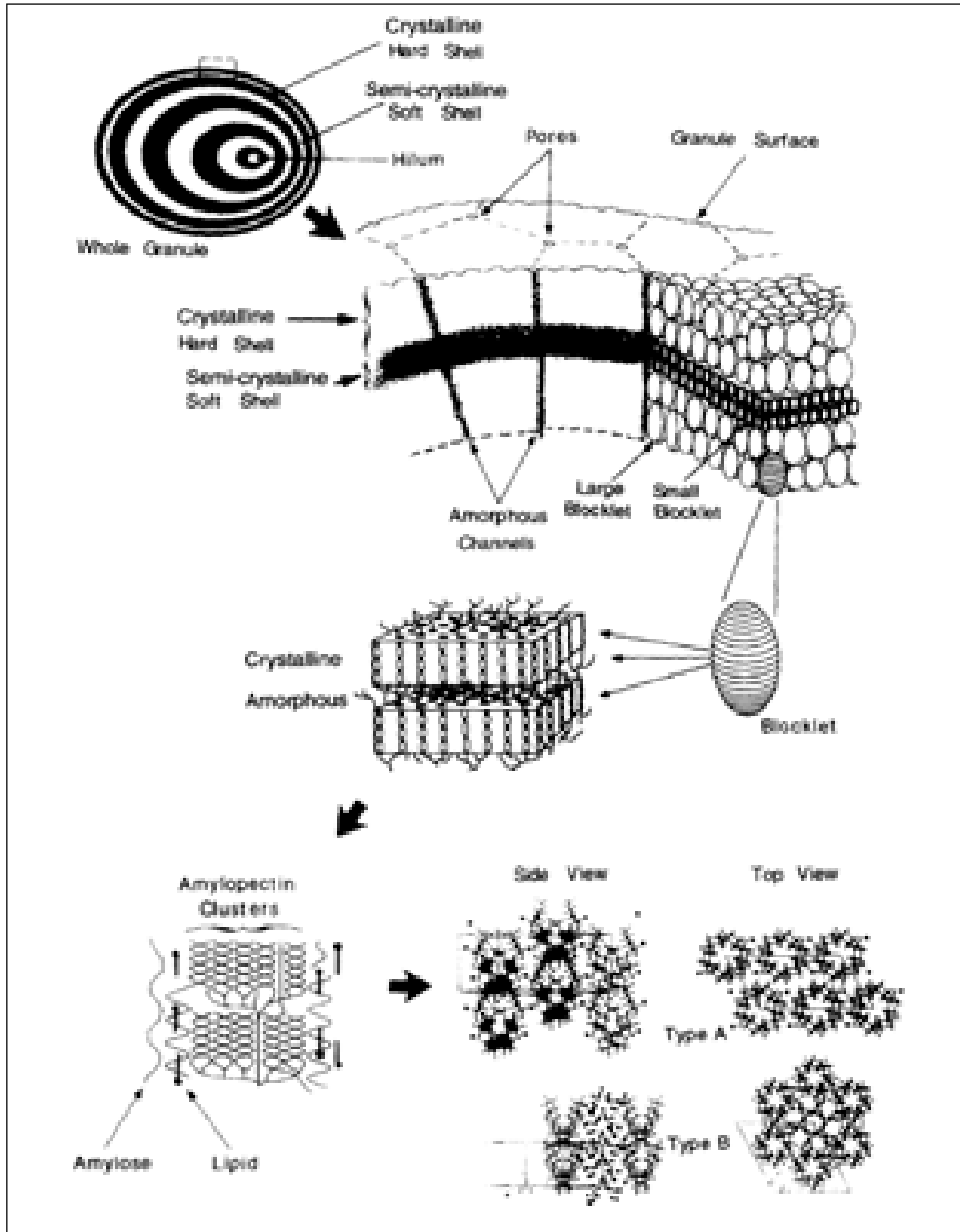


Figure 1-3: Overview on the structure of a starch granule according to Gallant et al. [14]

Also, the amylopectin polymer in the lamellae and the amylose-lipid complex formation are shown. The type A and B crystal structures of starch represent the highest level of order. A-type polymorphs are packed more densely. In the lower density B-type crystal structure there is a higher amount of water included substituting one amylopectin helix.

### **1.1.2 Application**

Nature creates these perfectly structured molecules highly organized in granules, why do we have the wish to excel this perfection?

Traditionally, starch is used in the food sector. As a major component in cereal grains with a portion of 50 to 60 % of the dry weight it is present in all baked goods (bread, tortillas, cakes), in extruded snack foods, pasta and in unprocessed food such as rice and potatoes. The gelatinization and retrogradation of starch is responsible for important structural and textural features of food, e.g. staling of bread, stability of gels and emulsions, freeze-thaw stability. Additionally starch serves as energy source as it is easily digestible to glucose by the human saline and intestinal enzymes (amylase). The use of native, unmodified starches from variable botanical origins is practically limited to its application in food. Modification of starch provides a useful tool to broaden the range of utilization within the food sector as well as opening new possibilities for the use in other sectors.

### **1.1.3 Derivatives**

Starch can be modified physically, e.g. by pre-gelatinization, extrusion or redrying, or chemically by the introduction of substituents, e.g. by esterification, etherification, or by oxidation [15]. Due to their tailor-made properties, modified starches have gained an increasingly important role during the past years [3]. In this study only the chemical possibilities of modifying starch will be elucidated closer.

The free hydroxyl groups at the glucose monomer provide a reactive site for chemical reactions. Figure 1-4 schematically shows a monomer section of an amylose or amylopectin molecule with its three hydroxyl moieties. Substitution can take place at position 2-, 3- and 6-O of the glucose unit.