



## Crystalline starch based nanoparticles

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### ABSTRACT

Starch is an abundant, natural, renewable, and biodegradable polymer produced by many plants as a source of stored energy. Because of the multiscale structure of starch granules consisting of alternating crystalline and amorphous concentric layers, the controlled acid hydrolysis treatment of starch disrupts this organization and releases crystalline platelet-like particles with nanoscale dimensions. This paper intends to provide a comprehensive overview of their preparation, characterization, properties, and applications.

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### 1. Introduction

Fossil energy depletion and growing environmental concerns have brought up increasing interest in bio-based eco-efficient and high technology materials. In this context, an increasing demand is made for products made from renewable and sustainable non-petroleum based resources. It has brought two scientific fields together, viz. nanotechnologies, which allow the development of innovative and efficient materials, and biomaterial processing, with the use of renewable raw materials for more environmentally-friendly and sustainable solutions.

Starch is a natural, renewable, and biodegradable polymer produced by many plants as a source of stored energy. It is therefore a promising material because of its versatility, low price, availability, and numerous industrial applications. It is the major carbohydrate reserve in plant tubers and seed endosperm, and it is found in plant roots, stalks, crop seeds, and staple crops such as rice, corn, wheat, tapioca and potato [1]. In 2000, the world starch market was estimated to be 48.5 million tons, including native and modified starches, but also the large volume of starch that is converted into syrups for direct use as glucose and isoglucose, and as substrates in the form of very high dextrose syrups (known as starch hydrolysates) for fermentation into organic chemicals, including ethanol [2]. The value of the output is worth € 15 billion per year, explaining the interest of the industrialists and researchers seeking new properties of high value application. The major categories to be considered while mapping the starch processing industry are food and non-food products. Use of starch in food products includes

food processing and beverages. Non-food products of starch include paper, glue, thickening agent, and stiffening agent, among others.

Starch consists of amorphous and crystalline domains. The amorphous regions are highly susceptible to hydrolysis and, under controlled conditions, may be dissolved leaving the rigid crystalline regions intact. The acid hydrolysis of native starch granules releases platelet-like nanoscale highly crystalline residues. As the size of a particle is decreasing down to the nanometer scale important changes occur. Both specific surface area and total surface energy increase. Moreover, starch nanoparticles display a highly reactive surface with plenty of hydroxyl groups. When blended with a polymeric matrix, ensuing nanocomposites show unique properties, because of the nanometric size effect, compared to conventional composite even at low filler content. Indeed, nanofillers have strong reinforcing effect and studies have also shown their positive impact in barrier effect. However, for decades studies have been conducted with non-renewable inorganic fillers. Increasing environmental concerns have led to investigating the potential uses of renewable resources for such application.

### 2. Native starch

Starch is the major energy reserve of higher plants. The starch industry extracts and refines starches by wet grinding, sieving and drying. After its extraction from plants, starch occurs as a flour-like tasteless and odorless white powder insoluble in cold water. This powder called native starch consists of microscopic granules with diameters depending on the botanic origin, ranging from 2 (for wheat and rice) to 100  $\mu\text{m}$  (for potato), and with a density around  $1.5 \text{ g}\cdot\text{cm}^{-3}$  [1].

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## 2.1. Starch composition

The composition of starch was originally determined by studying the residue of its total acid hydrolysis. It mainly consists of a combination of two glucosidic macromolecules, namely amylose and amylopectin. In most common types of starch, the amylopectin content ranges between 72 and 82%, while the amylose content ranges between 18 and 28%. However, some mutant types of starch have very high amylopectin content (99% for waxy maize), and some very high amylose content (up to 70% and more for amylo maize). Other trace elements are lipids, proteins, minerals, phosphorous, enzymes, amino acids, and nucleic acids.

Amylose is essentially a linear polymer consisting of glucose units linked by  $\alpha$ -(1  $\rightarrow$  4) glycosidic bonds, slightly branched by  $\alpha$ -(1  $\rightarrow$  6) linkages. Amylopectin is a highly branched polymer constituted of relatively short branches of  $\alpha$ -D-(1  $\rightarrow$  4) glycopyranose that are interlinked by  $\alpha$ -D-(1  $\rightarrow$  6) glycosidic linkages.

## 2.2. Multiscale structure of starch granule

The starch granule displays a multiscale structure as shown in Fig. 1. It consists of the (a) starch granule (2–100  $\mu$ m), into which we find (b) growth rings (120–500 nm) composed of (d) blocklets (20–50 nm) made of (c) amorphous and crystalline lamellae (9 nm) [4] containing (g) amylopectin, and (h) amylose chains (0.1–1 nm). When observed under a microscope and polarized light, starch shows birefringence. The refracted characteristic “Maltese cross” corresponding to the crystalline region is typical of a radial orientation of the macromolecules. The so-called onion-like structure of starch granule with more or less concentric growth rings is composed of alternating hard crystalline and soft less ordered shells growing by apposition from the hilum (center of the granule). The thickness of the combined repeated crystalline and amorphous lamellae is 9 nm regardless the botanic origin [4].

Native starches contain between 15% and 45% of crystalline material [5]. Depending on their X-ray diffraction pattern, starches are

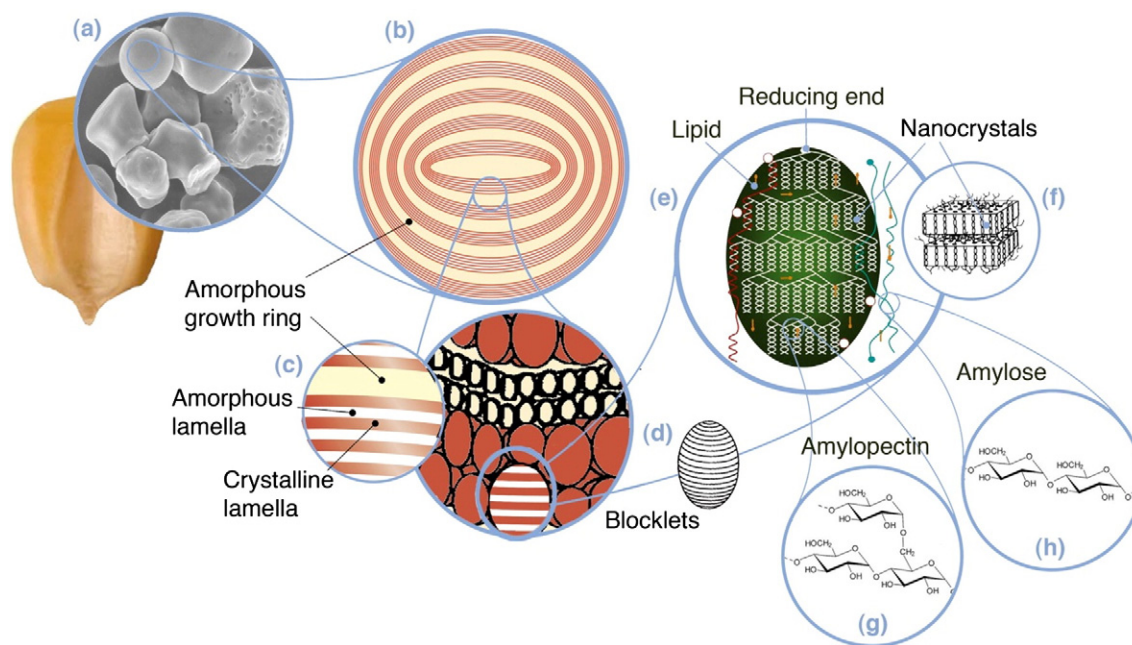
categorized in three crystalline types referred to A, B and C. A-type is characteristic of cereal starches (wheat and maize starch). B-type is typical of tuber and amylose-rich cereal starches. C-type is characteristic of leguminous starches and corresponds to a mixture of A and B crystalline types. V-type is observed during the formation of complexes between amylose and a complexing molecule (iodine, alcohols, cyclohexane, fatty acids, ...). The appearance of starch X-ray diffraction pattern depends on the water content of granules during the measurement. The more starch is hydrated, the thinner the diffraction pattern rings up to a given limit. Water is therefore one of the components of the crystalline organization of starch. The crystalline to amorphous transition occurs at 60–70 °C in water and this process is called gelatinization.

## 3. Preparation of starch nanocrystals

Nanoparticles can be prepared from starch following different strategies involving regeneration and precipitation and leading to particles with different properties, crystallinities, and shapes [3]. Moreover, the method for producing nanofibrillated cellulose (NFC) has been transferred for producing starch colloids [6]. Diluted slurry of high amylose corn starch was run through a Microfluidizer for several passes (up to 30). The particle size of the sample obtained from more than 10 passes was below 100 nm with a yield close to 100% and the gel-like suspension remained stable for more than one month. However, the ensuing starch colloids were obtained from breaking down both amorphous and crystalline domains, rendering amorphous nanoparticles after 10 passes. Nevertheless, the classical and most investigated procedure for preparing starch nanoparticles is acid hydrolysis yielding highly crystalline nanoparticles or starch nanocrystals.

### 3.1. Acid hydrolysis of starch

Acid hydrolysis is a chemical treatment largely used in industry to prepare glucose syrups from starch. Nägeli reported the preparation of a low molecular weight acid-resistant fraction of potato starch after the hydrolysis with a 15% (w/v) sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) suspension at



**Fig. 1.** Starch multiscale structure: (a) starch granules from normal maize (30  $\mu$ m), (b) amorphous and semi-crystalline growth rings (120–500 nm), (c) amorphous and crystalline lamellae (9 nm): magnified details of the semi-crystalline growth ring, (d) blocklets (20–50 nm) constituting unit of the growth rings, (e) amylopectin double helices forming the crystalline lamellae of the blocklets, (f) nanocrystals: other representation of the crystalline lamellae called starch nanocrystals when separated by acid hydrolysis, (g) amylopectin's molecular structure, and (h) amylose's molecular structure (0.1–1 nm). Reproduced with permissions from [3].

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