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STARCH PROPERTIES, MODIFICATIONS, AND APPLICATIONS

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ABSTRACT

Starch is the second largest biomass produced on earth. Starch consists mainly of amylose and amylopectin. The chemical structures of starch molecules, polymers of α-1-4 linked glucopyranose with α-1-6 branches, render a natural tendency for starch in aqueous systems to crystallize to double helices. Depending on botanical origin and genetic background, starch has different chemical structures, such as branch-chain lengths and phosphate derivatives, and different functional properties. This structural and functional diversity makes these starches suitable for different applications. High-amylose starch produces strong films and is suitable for making biodegradable plastics, and small-granule starch is an appropriate polyethylene film filler. Various physical, chemical, and enzymatic modifications will change and improve functional properties of starch and facilitate its utilization for different purposes. Pregelatinized and cold-water-soluble starches enable users to disperse starch without going through a heating process. Hydrophobic starch derivatives enhance the compatibility between starch and hydrophobic components. Dialdehyde starch facilitates crosslinkages between starch and other components carrying functional groups, such as amino, hydroxyl, and sulfurhydryl groups.

STARCH STRUCTURES AND PROPERTIES

Starch is the major form of carbohydrate storage in green plants and is considered the second largest biomass, next to cellulose, produced on earth. Starch is a polymer that consists of six-member-ring glucose units (glucopyranose). The molecular weight of starch varies from 10^4 to 10^7 daltons [1]. In contrast to cellulose, glucose units in starch are linked by α-1-4 bonds instead of the β-1-4 bonds found in cellulose. The α-1-4 linked starch displays a random-coil conformation, whereas the β-1-4 linked cellulose displays a ridged linear structure. The majority of starch molecules (e.g., up to 100% in waxy starches, 72% in normal maize starch, and 80% in potato starch) have highly branched structures, known as amylopectin [2]. Amylopectin has an α-1-4 linked backbone and ca. 5% α-1-6 linked branches. Branch chains in amylopectin are arranged in clusters [3, 4], and the branch-chain lengths vary with the species and genetic background of the starch. The branch chains are present in double helical, crystalline structures [3-5]. Amylose is a primarily linear molecule that has few branches [6]. In certain high-amylose varieties, the amylose content can be as high as 50 or 70%.

Starch Gelatinization

Native starches are present in semicrystalline granular forms with densities ca. 1.5 g/cm^3 [5]. Granular starch can be solvated to dispersed and amorphous molecules by heating with plasticizers (mainly water), or by treating them with organic solvents (e.g., dimethylsulfoxide), aqueous alkaline [7], or salt solutions (e.g., $CaCl_2$, KI) [8, 9]. The conversion from crystalline, granular starch to the dispersed and amorphous state is known as gelatinization [1].

Starch Retrogradation and Crystalline Structures

Solvated, amorphous starch has a tendency to return to an insoluble, aggregated, or crystalline state when being stored at a temperature above its glass transition temperature. This is known as retrogradation [1]. Retrogradation of starch dispersions is enhanced by a low temperature (0-5°C) and by high starch concentrations. Linear molecular chains have an extremely high tendency to retrograde. The retrogradation rate of linear molecules also depends on the chain length. Studies have shown that amylose with a chain length of ca. 100 glucose units has the greatest tendency to retrograde [10]. Retrograded branched molecules (amylopectin) can be more easily reversed than highly crystallized amylose. The latter requires high temperature (ca. 150°C) processing or chemical treatments (e.g., 90% DMSO, 0.5 N KOH).

X-ray crystallography of retrograded starch has revealed a double helical structure with a 10.5 Å repeat distance, indicating six glucose units per pitch (21 Å) [11]. In this structure, two parallel strands of starch are intertwined and the helix is stabilized by hydrogen bonds between the hydroxy groups and by hydrophobic interactions between the hydrocarbon moieties of the two strands. The double-helical crystalline starch is resistant to acidic and enzymatic hydrolyses. 55% of retrograded amylose sustained acid hydrolysis in 16% H_2SO_4 at 25°C for 40 days.

The resistant amylose consists of fragments of rather narrow molecular size distribution with the peak chain-length of ca. 31 glucose units [12].

Chemical Structures of Starch

Chemical structures of starch, such as molecular sizes of amylose, branch-chain lengths of amylopectin [13], and the proportion of amylose and amylopectin, are found to affect the functional properties of starch [13, 14]. Amylopectin of long branch-chains interacts more effectively with amylose and, thus, generates greater viscosity and gel strength. When the amylose content of the starch increases, the viscosity and gel strength of the starch paste also increase. Amylose alone and high-amylose maize starch produce strong films [14, 15].

In addition to amylose and amylopectin, starch also contains lipids (up to 1%), residues of protein (ca. 0.4%), and trace amounts of phosphorus (up to 0.09%) [16]. Lipids, particularly phospholipids, have great tendencies to form helical complexes with starch (mainly with amylose). Amylose-phospholipid complexes are so tightly bound that the lipids cannot be completely removed after 24 hours extraction with water-saturated butanol or 75% propanol solution in a Soxhlet extractor [16]. The amylose-lipid complex restricts the swelling of starch granules during cooking and results in a paste of reduced viscosity and increased opaque appearance. An example is wheat starch. Wheat-starch paste has significantly less viscosity than other starches because of its high phospholipid content.

Phosphate monoester derivatives are commonly found in starch. Potato starch is known for its great phosphate monoester content. A method to determine and differentiate phosphorous of different chemical structures in starch by using ^{31}P-NMR was developed [16]. The ^{31}P-NMR studies showed that most tuber and root starches, such as potato, sweet potato, arrowroot, and many legume starches, such as mung bean and green pea, have substantial amounts of phosphate monoester derivatives. Cereal starches, such as wheat, maize, and oat, have little or none [16]. Phosphate monoesters, carrying multiple negative charges which repel one another, enhance starch gelatinization and dispersion and retard starch retrogradation. The charged groups also have enhanced ionic interactions with proteins and other cationic groups. Starches with phosphate monoester derivatives, such as potato starch, produce pastes of increased clarity and viscosity. The paste also displays enhanced stability and a slow retrogradation rate.

Starch Morphology

Starches isolated from different botanical sources differ in their chemical structures [2] and in their morphologies [17]. Some starch granules, such as amaranth and pigweed, have submicron sizes, whereas others, such as canna and potato, have diameters of some granules larger than 100 μm. Many starches, such as potato and canna, are of oval shape; maize, oats, and rice starches are of polygonal and round shapes; wheat and barley starches are disk shaped and have bimodally distributed granular sizes. Some granules display unusual shapes, for example: diffenbachia starch is extended rod; shoti starch is a point-edged disk; babassu starch is half-spherical; all the legume starches investigated have beanlike granules each with a characteristic indent; and some high-amylose maize starch granules have budlike protrusions, whereas others are snake-like.

STARCH MODIFICATIONS AND APPLICATIONS

Starch, as an abundant and renewable resource for biodegradable polymers, is environmentally friendly and cost competitive. Properties of native starches may not be desirable for all applications. Many approaches, however, are available to modify the properties of starch to meet specific applications. These approaches include physical, chemical, and enzymatic modifications.

Physical Modifications of Starch

Starch can be physically modified to improve its water solubility and to change particle size. The requirement of heating or chemical treatment to disperse granules may be a hurdle for some applications. For example, the dispersion of high-amylose maize starch requires an extremely high processing temperature (ca. 150°C), which may require a specific equipment design and is not desirable for other ingredients in the mixture. Some active ingredients in starch mixtures are heat labile or volatile and may be destroyed by heating processes intended to disperse starch. In these cases, cold-water soluble starches would be desirable alternatives. Cold-water soluble starches can be prepared by various physical treatments.

Cold-Water-Soluble Starch

Pregelatinized starches can be prepared by precooking and drum-drying or by extrusion [18, 19]. Pregelatinized starch, after being rehydrated, displays a reduced viscosity, less sheen, and grainier paste than a freshly dispersed starch paste, indicating that some degradation and reassociation have taken place during processing.

To improve the viscosity and other physical properties, many technologies have been recently developed to produce granular cold-water-soluble (GCWS) starches. GCWS starch can be prepared by an injection and nozzle-spray drying process [20], high-temperature treatments of starch aqueous alcohol suspensions [21, 22], heating starch in aqueous polyhydric alcohol solutions [23, 24], and by alcoholic-alkali treatments [25, 26]. All these methods can be applied to normal starches. The alcoholic-alkali treatment method has a broader substrate spectrum, which can be used to prepare GCWS waxy as well as GCWS high-amylose starches [25]. The alcoholic-alkali method, however, cannot be applied to chemically-modified starches because most of them are labile at alkaline pH. Heating starch in an aqueous polyhydric alcohol solution has produced highly soluble GCWS chemically-modified starches, such as hydroxypropylated starch [23]. GCWS starches prepared by these methods display up to 95% water solubility at 25°C.

GCWS starches have been recently investigated as controlled-release agents for agriculture chemicals [27, 28]. GCWS waxy, normal, high-amylose V (50% amylose), and high-amylose VII (70% amylose) maize starches prepared by the alcoholic-alkali method were used to encapsulate atrazine for controlled-release studies [27]. Scanning electron micrographs show that atrazine is physically embedded in the starch matrix. Studies indicate that the swellibility of the matrix varies with the amylose content: the greater the amylose content, the less swelling of the matrix. The rate constant of atrazine release is inversely proportional to the amylose content of starch. These results indicate that starches of different amylose contents can be used to control chemical release rates [27].

Small-Particle Starch

Small-granular starch is desirable for use as plastic film fillers [29], cosmetic products, and fat replacements. Native small-granule starch is scarce and inherently expensive. A method has been developed to make small-particle starch from maize or from other abundant starches [30]. The method involves an acid treatment of granular starch to break glycosidic bonds in the amorphous region of the granule. The crystalline regions in the granule remain intact. After mechanical attrition of the acid-treated starch, the granule breaks up into small particles. Particle size of the products can be controlled by the degree of acid hydrolysis. The particle size can be reduced to submicron diameters if so desired.

Chemical Modifications of Starch

Chemical modifications of starch can be conducted to change starch properties [31]. Commonly used chemical modifications include crosslinking to enhance molecular stability against mechanical shearing, and acidic and high-temperature hydrolysis [31]. Hydroxyethylate, hydroxypropylate, phosphorylate, acetate, and succinate derivatives of starch can reduce the retrogradation rate [31]. Starch phosphate and succinate also have enhanced interaction with cationic molecules, whereas cationic starches have better interactions with electronegative substances, such as cellulose. Oxidized and partially hydrolyzed starches display decreased viscosities. Oxidized starches carry carbonyl and carboxyl groups, which also have enhanced interactions with cations or by crosslinks. Octenylsuccinate starch aluminum complex presents a hydrophobic surface of starch granules [31] and, thus, interacts more with hydrophobic matrices. Dialdehyde starch carries two aldehyde groups on each glucose unit [32]. The starch can develop a highly crosslinked network with other molecules through crosslinking reactions with $-OH$, $-NH_2$, and $-SH$ groups.

Starch maleate, octenylsuccinate, succinate, and dialdehyde starch have been investigated for starch-protein-based biodegradable plastics [33]. Starch maleate significantly enhances tensile strength and storage stability of molded plastic specimens [33]. Starch octenylsuccinate, however, increases the percentage elongation [33]. Dialdehyde starches enhance tensile strength and water resistance of molded plastic specimens [34]. Plastic specimens made from polymeric dialdehyde starch (90% oxidation) and zein (4:1/w:w) displays ca. 50 MPa and 2.7% water absorption after 24 hours submersion in water at 25 °C [34].

Enzymatic Modifications of Starch

Starch can be enzymatically modified to produce maltodextrins, cyclodextrins, and oligosaccharides. Maltodextrins, prepared by α-amylase and/or acidic hydrolysis, have widely distributed molecular sizes. The smaller the molecular size, the lower the glass-transition temperature [35, 36]. Maltodextrins have been investigated as plasticizers to reduce the glass-transition temperature of materials [33]. Cyclodextrins have different molecular sizes (e.g., six, seven, and eight-member rings) and can be prepared by enzymes such as that from *B. macerans* [37]. Cyclodextrins consist of donutlike structures which have hydrophobic cavities. The hydrophobic cavity can complex with chemicals carrying hydrophobic moieties. Cylcodextrins have been used to stabilize aroma compounds during extrusion and thermal processing. It is not known how cyclodextrins affect the physical properties of plastics.

CONCLUSIONS

Naturally available starches have diverse properties which may meet different application requirements. Physical, chemical, and enzymatic modifications can tailor the properties of native starch for specific applications, otherwise requiring exotic starches.

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