Chapter 4 : Carbohydrates in Food

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1. Cellulose and its derivatives

Cellulose is the most abundant renewable polymer on earth and the main structural polysaccharide in plant cell walls. It is a linear homopolysaccharide of β-D-glucopyranose units linked by β (1→4) glycosidic bonds, organized into microfibrils that group to form fibers.

Each glucose unit carries three hydroxyl groups, which form many intra- and intermolecular hydrogen bonds and give cellulose its rigidity and low solubility in water and common solvents.

In the cell wall, cellulose microfibrils (2–20 nm in diameter) are embedded in a matrix of hemicelluloses and lignin, forming a composite material. Each microfibril can be viewed as an alternation of crystalline (ordered) regions and amorphous (disordered) regions along its axis, which influences mechanical and chemical behavior. Although humans cannot digest cellulose, it is widely used: wood and paper, textile fibers (cotton, flax, rayon), nitrocellulose in explosives, and cellulose acetate in films and plastics.

In nutrition, dietary cellulose largely escapes digestion in the stomach and small intestine and is partially fermented by colonic microbiota into short-chain fatty acids, gases and other metabolites. In pharmacy, cellulose and its derivatives are major excipients because they are non-toxic, stable, inexpensive and obtained from renewable plant sources. Microcrystalline cellulose is especially important as a filler and binder for directly compressed tablets and as part of sustained-release matrices.

Cellulose exists in several crystalline allomorphs: native plant cellulose (cellulose I), regenerated or mercerized cellulose (cellulose II), and forms III and IV obtained by treatments with liquid ammonia or by heat. Chemical modification of cellulose (e.g. ethers and esters)

improves processability and generates derivatives with controlled solubility and functionality for textiles, packaging and biomedical uses such as membranes for blood purification.

Natural cellulose fibers include cotton, flax, jute, sisal and hemp, all rich in cellulose and used for paper or textiles. Regenerated cellulosic fibers (rayon, modal, lyocell) are produced from dissolved natural cellulose and offer specific properties depending on the plant source (wood, bamboo, algae, sugarcane bagasse, etc.).
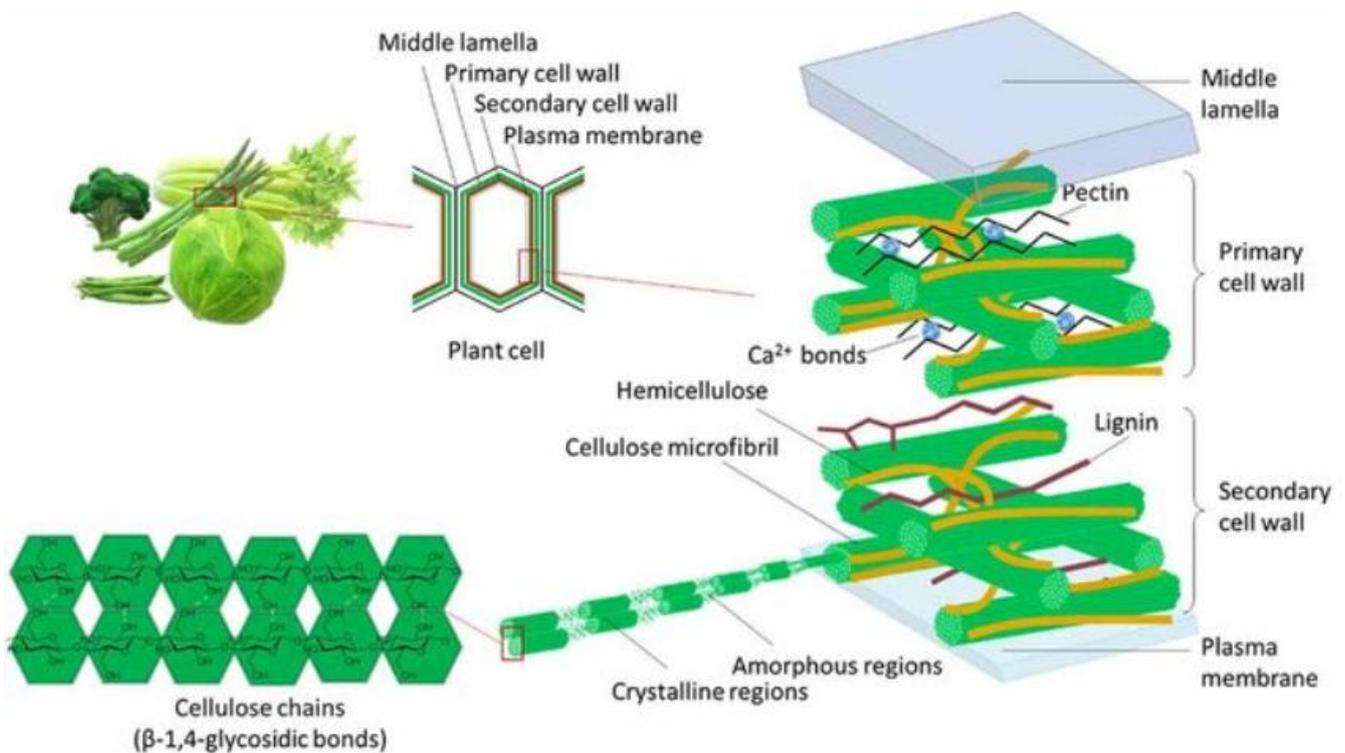

Figure 01 : Schematic representation of the composition and structure of the plant cell wall and cellulose chain. In crystalline cellulose, chains are linked by hydrogen bonds in an orderly and periodic way, whereas in the amorphous cellulose regions, chains are disordered.

2. Starch: structure and composition

Starch is the main storage polysaccharide of higher plants and is accumulated in granules whose size, shape and crystalline type depend on botanical origin. It is a major component of many crops: about 30–70% of cereals, 60–90% of tubers and 25–50% of legumes by weight. When

purified, starch is a white powder of insoluble granules (2–100 μm) that swell and gelatinize when heated in excess water.

Chemically, starch is almost entirely a homopolymer of D-glucose in the $^4C_1$ chair conformation, with hydroxyls in equatorial positions, linked mainly by α (1→4) bonds and a smaller proportion of α (1→6) branch points. It is composed of two main macromolecules:

❖ **Amylose :** essentially linear chains of α (1→4) -linked glucose, with degrees of polymerization around 500 on average and molecular masses of about 2×10^5 to 8×10^5 Da.

❖ **Amylopectin:** a highly branched polymer with α (1→4) main chains and α (1→6) branches, representing 70–80% of most starches and reaching molecular masses up to $10^7 - 10^8$ Da.

Inside the granule, amylopectin and amylose are radially organized in concentric growth rings composed of alternating amorphous and semicrystalline lamellae ("blocklets" of 300–500 nm). Crystalline lamellae contain short amylopectin chains (DP ≈ 15), while amorphous lamellae contain branch points and possibly amylose; this hierarchical structure explains many thermal and mechanical properties. Amylose content generally ranges from 17–35% depending on botanical source, with "waxy" starches containing almost only amylopectin and "high-amylose" starches enriched in amylose.

Native starches are classified into A, B, C and V types based on X-ray diffraction diagrams. Type A is typical of cereal starches, type B of tubers and high-amylose starches, type C of legumes (mixture of A and B), and type V corresponds to amylose–complex structures formed with small molecules such as lipids or iodine. Besides carbohydrates, small amounts of proteins, lipids and minerals (<1% dry matter) affect functional behavior without changing the basic physicochemical nature of starch.

2.1. Gelatinization and retrogradation

When starch granules are heated in excess water above a critical temperature, they undergo gelatinization: granules swell, crystalline order is lost, amylose and part of amylopectin leach out, and viscosity increases strongly. Upon cooling, these macromolecules tend to re-associate and re-crystallize, a phenomenon called retrogradation that leads to gel formation and, over time, to textural changes such as firming and syneresis.

Amylose chains retrograde rapidly at room temperature and are mainly responsible for the initial setting and rigidity of the gel. Amylopectin rearrangements are slower and dominate long-term changes, such as bread staling. The extent and rate of retrogradation depend on amylose content, concentration, temperature profile and storage conditions, which is important for designing stable starch-based foods.

2.2. Rheological behavior of starch pastes

Measuring rheology of ungelatinized starch suspensions is difficult because granules sediment and viscosity is low. After gelatinization, starch pastes behave as complex dispersions of swollen granules in a continuous phase containing dissolved macromolecules, and their flow properties can be characterized more reliably. The rheology of these pastes depends on granule size and shape, their volume fraction, interactions between granules, the viscosity of the continuous phase, and the shear conditions.

Starch pastes typically show shear-thinning behavior: apparent viscosity decreases as shear rate increases, so the relation between shear stress τ and shear rate $\dot{\gamma}$ is non-linear. Flow curves are strongly influenced by botanical origin, amylose/amylopectin ratio and processing conditions such as heating rate and stirring, and provide useful information to optimize texture in sauces, fillings and gels.

3. Native and modified starch: functional properties

Native starch is the starch extracted from plant tissues without chemical modification of the macromolecules. In food, native starches have several limitations: they often form opaque gels, show low resistance to high temperatures, shear and freezing/thawing, and are unstable in acidic media (pH < 5), with loss of viscosity and binding capacity. They therefore require cooking and are best suited for products with mild processing and rapid consumption, such as simple sauces, often using potato or corn starch.

To overcome these drawbacks, food technologists use modified starches obtained by physical, enzymatic or chemical treatments. Cross-linked starches, produced by creating covalent bridges between chains, resist heat, shear and acid better and are widely used in canned foods, acidic sauces and frozen products. Substituted starches (e.g. acetylated, hydroxypropylated) show

improved freeze–thaw stability and clarity and are used in products like instant desserts, dressings or bakery fillings.

Modified starches can be viewed as hydrocolloids: at low concentrations, they bind large amounts of water and modify viscosity, texture and stability of dispersions and emulsions. Their effective use requires good dispersion of dry particles in the aqueous phase to avoid lump formation and sufficient hydration/solubilization of macromolecules. In practice, different modified starches are used in charcuterie, bakery, beverages, dairy, sauces and baby foods to control viscosity, water retention, mouthfeel, gloss and stability over shelf life.

4. Amylolytic enzymes (family GH13)

Many enzymes that hydrolyze or transfer α-glycosidic bonds belong to glycoside hydrolase family 13 (GH13). These enzymes act mainly on α(1→4) and α(1→6) linkages in substrates such as starch, amylose, amylopectin, glycogen, maltooligosaccharides and, more rarely, sucrose or trehalose. GH13 therefore includes several functional groups:

- Glucohydrolases specific for α(1→4) bonds: α-amylases, α-glucosidases and various malto-oligosaccharide-forming amylases that produce maltose, maltotriose or longer fragments.

- Glucohydrolases specific for α(1→6) bonds: debranching enzymes such as isoamylase, pullulanase and oligo α(1→6)-glucosidase.

- Trehalose-6-phosphate hydrolases, which act on phosphorylated trehalose.

- Transglucosidases: enzymes such as amylomaltase and cyclodextrin glucanotransferase that transfer glucosyl units and can synthesize cyclic or branched products.

- Isomerases such as trehalose synthase and isomaltulose synthase, which rearrange bonds within disaccharides.

These amylolytic enzymes are widely used in industry to liquefy starch, produce syrups of defined composition, modify texture and create specific functional carbohydrates.

5. Dietary fiber: roles and types

Dietary fiber is defined as carbohydrate polymers and related substances that form the structural framework of plant cell walls and are resistant to digestion and absorption in the human small intestine. Historically, the term "crude fiber" referred to the residue remaining after harsh chemical treatments, but modern definitions consider dietary fiber as a broader group including cellulose, hemicelluloses, pectins, gums, resistant starch and often lignin.

The physiological effects of dietary fiber cannot be predicted from structure alone; they depend on physicochemical properties such as solubility, viscosity, water-holding capacity and fermentability. Soluble fibers (e.g. pectins, some hemicelluloses, β-glucans) dissolve or swell in water and often form viscous solutions that modestly lower blood cholesterol and triglycerides and attenuate postprandial glycemic responses. Insoluble fibers (e.g. cellulose, many hemicelluloses) are characterized by low solubility, higher porosity and bulk, and primarily increase fecal mass and reduce intestinal transit time, thereby improving bowel function.

One mechanism by which viscous fibers reduce postprandial hyperglycemia is by slowing the diffusion of glucose and other nutrients through the intestinal lumen, delaying absorption. In addition, fermentable fibers are metabolized by colonic microbiota into short-chain fatty acids, which can influence gut health, satiety and metabolic regulation.

5.1. Pectins: structure and solubility

Pectins are a structurally complex family of plant cell wall polysaccharides rich in galacturonic acid and are abundant in primary walls and middle lamellae of many fruits and vegetables. Homogalacturonan (HG), a linear α(1→4)-linked galacturonic acid polymer, makes up around two-thirds of total pectin, while more complex domains such as rhamnogalacturonan I (RG-I), rhamnogalacturonan II (RG-II), xylogalacturonan and apiogalacturonan provide side chains and branching.

Pectins are insoluble in most organic solvents but can dissolve or swell in water, with solubility largely governed by degree of methoxylation and molecular weight. A lower degree of methoxylation and the presence of ionized carboxyl groups promote electrostatic repulsion between chains, reduce aggregation and increase solubility, especially at pH values above the pKa of galacturonic acid (≈3.5). In practice, pH above about 5.5 favors full solubilization, which proceeds through hydration, swelling and then dissolution of the polymer.

Because of their gelling, thickening and stabilizing properties, pectins are widely used in the food and pharmaceutical industries. As stabilizers, they can increase viscosity, form weak networks that suspend particles, or interact with charged components such as casein in acidic dairy drinks to prevent aggregation and sedimentation. At pH below the isoelectric point of casein (≈ 4.6), casein particles are positively charged and can be coated by negatively charged pectin chains, which sterically and electrostatically stabilize the dispersion.

5.2. Pectin gelation and applications

Gelation is the formation of a three-dimensional polymer network that traps a continuous liquid phase, giving a viscoelastic material with both solid-like and liquid-like properties. High-methoxyl (HM) pectins (degree of methoxylation 60–90%) form gels mainly through hydrogen bonding and hydrophobic interactions between non-ionized galacturonic acid units under conditions of low pH and high soluble solids (e.g. traditional jams). At pH below the pKa, carboxyl groups are protonated, which reduces electrostatic repulsion and favors junction-zone formation.

Low-methoxyl (LM) pectins (degree of methoxylation < 50%) can gel in the presence of divalent cations such as calcium, which form "egg-box" coordination crosslinks between chains. This allows gelation at lower sugar content and is important for reduced-sugar jams and many dairy and dessert products. Because pectin gels can be tailored by adjusting degree of methoxylation, pH, ionic strength and solids content, they are key ingredients for designing texture and controlled release in foods and nutraceuticals.

The food industry often prefers soluble dietary fibers like pectins because they can increase viscosity, stabilize emulsions and form gels without strongly altering taste. Pectin and other fibers are used as thickeners in jams, jellies and marmalades, to prevent syneresis, maintain texture and improve overall product quality. For example, adding fruit or cereal fibers to pectin gels can reinforce their viscoelastic properties, which is useful in developing "fruit-candy-like" healthy products.