• Introduction of polysaccharides
• Polysaccharide sources and characterization
• Polysaccharide structure analysis
• Functions of polysaccharides
• Selecting polysaccharides for food applications
Polysaccharides: Introduction

Definitions of polysaccharides

• “Polysaccharide” is the name given to a macromolecule consisting of a large number of monosaccharide residues joined to each other by glycosidic linkages.

• Polysaccharides composed of only one kind of monosaccharide are described as homopolysaccharides (homoglycans). Similarly, if two or more different kinds of monomeric unit are present, the class name heteropolysaccharide (heteroglycans) may be used.

• A general term for a homopolysaccharide is obtained by replacing the ending “-ose” of the sugar name by “-an”. For example: xylan for polymers of xylose, mannan for polymers of mannose, and galactan for polymers of galactose. Cellulose and starch are both glucans, as they are composed of glucose residues.

Adapted from IUPAC Nomenclature of Carbohydrates (1996) http://www.chem.qmul.ac.uk/iupac/2carb/
**Shorthand Notation**

- Glycosyl units are represented by the first 3 letters of their names, except for glucose which is Glc
- Sometimes D is omitted; if it is an L sugar, the L is put in the designation
- Ring size: $p$ or $f$
- Uronic acids are indicated by a suffix A
- $\alpha$ and $\beta$ are designated where appropriate
- **Examples**
  - Cellbiose = $\beta$-Glc$p$(1$\rightarrow$4)-Glc or $\beta$Glc$p$1,4Glc
  - Lactose = $\beta$-Gal$p$(1$\rightarrow$4)-Glc or $\beta$Gal$p$1,4Glc
  - Maltose = $\alpha$-Glc$p$(1$\rightarrow$4)-Glc or $\alpha$Glc$p$1,4Glc
  - Gellan = \((3)$-\beta$-D-Glc$p$-(1$\rightarrow$4)$-\beta$-D-Glc$p$A-(1$\rightarrow$4)$-\beta$-D-Glc$p$-(1$\rightarrow$4)$-\alpha$-L-Rhap-(1 $\rightarrow$)n
Polysaccharides: Introduction

Classification of Polysaccharides

Polysaccharides by source

- Seaweed extracts: Agars, alginates, carrageenans
- Higher plant cell walls insoluble: cellulose
- Higher plant cell wall soluble: pectin
- Higher plant seeds: cereal starch, guar gum, locust bean gum
- Higher plant tuber & root: potato starch, tapioca starch
- Higher plant exudates: gum arabic, gum tragacanth
- Microorganism: Xanthan gum, Gellan gum
- Derived: modified starch, carboxymethyl cellulose, propylene glycol alginate
Classification of Polysaccharides

Polysaccharides by structure

• Linear: amylose, cellulose, pectin, alginates
• Short branched: guar gum, locust bean gum, Xanthan gum
• Branch-on-branch: amylopectin, gum arabic, arabinoxylan

Polysaccharides by monomers

• Homoglycans: starch, cellulose
• Diheteroglycans: agars, alginate, carrageenans,
• Triheteroglycans: Xanthan, Gellan, arabinoxylan

Polysaccharides by charge

• Neutral: amylose, amylopectin, cellulose, guar gum, etc
• Anionic: alginates, carrageenans, Gellan, gum arabic, Xanthan
• Cationic: chitosan
Molecular weight and degree of polymerization

- Molecular weight (MW):
  - The mass of one molecule of the substance, relative to the “unified atomic mass unit” (equal to 1/12 the mass of one atom of carbon-12)

- Degree of polymerization (DP):
  - The number of monomeric residues in a polymer molecule

- “Chain length”, expressed in DP, is used to quantify the size of polysaccharide chains
Polydisperse and polydispersity

This collection of molecules is polydisperse

Polydispersity index (PDI):

- Ratio of the weight average molecular weight to the number average molecular weight
- Indicating the overall distribution of individual molecular weight in a batch of polymers
- PDI equal to 1 indicates only one length of polymer is present
- In polysaccharides (e.g. starch), PDI may vary significantly.
Number average molecular weight ($M_N$)

- $M_N = \Sigma_i N_i M_i / \Sigma_i N_i$, where $N_i$ is the number of molecules of molecular weight $M_i$

- Can be determined by osmometry, end group titration, and colligative properties

- $M_N$ is more weighted by the small molecules in the molecular population
Weight average molecular weight ($M_W$)

- $M_W = \Sigma_i N_i (M_i)^2 / \Sigma_i N_i M_i$, where $N_i$ is the number of molecules of molecular weight $M_i$
- Can be determined by light scattering, small angle neutron scattering (SANS), X-ray scattering, and sedimentation velocity
- $M_W$ is more weighted by the large molecules
Polydispersity index $= \frac{M_W}{M_N}$
An example of $M_W$, $M_N$, and polydispersity index

<table>
<thead>
<tr>
<th>$M_i$ (DP)</th>
<th>$N_i$</th>
<th>$N_iM_i$</th>
<th>$N_i(M_i)^2$</th>
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<tbody>
<tr>
<td>100</td>
<td>10</td>
<td>1,000</td>
<td>100,000</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>100</td>
<td>1,000</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>20</td>
<td>1,100</td>
<td>101,000</td>
</tr>
</tbody>
</table>

$M_W = \frac{\Sigma N_i(M_i)^2}{\Sigma N_iM_i}$

$101,000/1100 = 91.8$ (DP)

$M_N = \frac{\Sigma N_iM_i}{\Sigma N_i}$

$1,100/20 = 55$ (DP)

So, polydispersity index $= 91.8/55 = 1.67$
Chain length distribution of starch: HPSEC & FACE

High performance size-exclusion chromatography

Fluorophore-assisted carbohydrate electrophoresis
Amylopectin branching analysis

Debranching → amylopectin → β-limit dextrin → Debranching

CL profile of AP

DEGREE of POLYMERIZATION, DP

Normalized D.R.I.

B3 ICL + 2.5

B1-a ICL + 2.5

Average CL

Cluster amount

CL profile of BLD

DEGREE of POLYMERIZATION, DP

Normalized D.R.I.

B2 ICL + 2.5

B1-b ICL + 2.5

B1-a ICL + 2.5

Cluster amount

A chain amount
Branched structure of amylopectin

ICL of B3 (53.5 DP)

Average number of branches per cluster (ANBPC)

ICL of B2 (26.5 DP)

Cluster repeat distance (26.5 DP)

B chain stub
1 or 2 DP

A chain stub
2 or 3 DP

ICL of B1-a (3.2 DP)

Polysaccharides from seed, tuber, or root: Starch

- A most abundant carbohydrate
- Major component of human diet
- Various digestibility
- Numerous applications as ingredients
- Comprising linear molecules, amylose, & branched molecules, amylopectin
- Subjected to genetic, chemical, physical, and enzymatic modifications
- Subjected to acidic and enzyme hydrolysis to maltodextrins and syrups
- Starting material of many food and non-food industries

Adopted from: http://www.oci.unizh.ch/edu/lectures/material/AC_BII/Kap14/kap14.html
Polysaccharides from seed: Guar gum

• Galactomannan obtained from the seed of guar plant, *Cyanaposis tetragonolobus*, mostly in India and Pakistan

• Chains of (1→4)-linked β-D-mannopyranosyl units, with averagely 1.8 chain units attached with single α-D-galactopyranosyl units via (1→6)-linkages

• Distribution of side units is relatively even along the main chain

• Neutral polysaccharide with molecular weight: 150,000 – 1,500,000

• Soluble in cold water

• Showing pseudoplastic (shear thinning) behavior in solution
Polysaccharides from seed: Locust bean gum

- Galactomannan obtained from the seed of carob tree, *Ceratonia siliqua*, around the Mediterranean Sea
- Chains of (1→4)-linked β-D-mannopyranosyl units, with averagely 3.9 chain units attached with single α-D-galactopyranosyl units via (1→6)-linkages
- Distribution of side units is highly uneven along the main chain
- Neutral polysaccharide with molecular weight: 400,000 - 1,000,000
- Requires heating to hydrate completely
- Showing pseudoplastic behavior in solution
Polysaccharides from seed: Tara gum

- Galactomannan obtained from the seed of Tara shrub, *Caesalpinia spinosa*, mostly in northern Africa and South America (Peru)
- Main chain of (1→4)-linked β-D-mannopyranosyl units, with single α-D-galactopyranosyl units attached with average three main chain units via (1→6)-linkages
- Molecular weight may fall between 300,000 to 1,000,000
- 70% soluble in cold water and 100% hydrated at >80°C
- Showing pseudoplastic behavior in solution
Polysaccharides: sources and characterization

Polysaccharides from tuber: Konjac flour

• Glucomannan obtained from the tuber of *Amorphophallus konjac* grown in Asia

• Chain of mannose and glucose units in a molar ratio of 1.6:1 connected with $\beta$-(1$\rightarrow$4)-linkages. One acetyl group presents at the C-6 for about 6 to 20 sugar units

• Neutral polysaccharide with molecular weight: 200,000 - 2,000,000

• Swells in cold water, fully hydrates after heating

• Showing pseudoplastic behavior in solution
Polysaccharides from exudates: Gum Arabic

• A gummy exudate obtained from *Acacia* trees in Africa, primarily Sudan

• Highly branched polysaccharide constructed from both neutral monomers and uronic acids

• Covalently attached with proteinaceous fractions, rendering its excellent function as emulsifier

• Molecular weight about 250,000

• Highly soluble, low viscosity even at 40% concentration

• Solution showing *Newtonian* behavior (constant viscosity at different shear rate)
Polysaccharides from exudates: Gum Tragacanth

- An exudate of *Astragalus*, a perennial short brush in Asia
- Slightly acidic and occurred as Ca, Mg, or Na salt
- Contains neutral highly branched arabinogalactan and tragacanthis acid (linear (1→4)-linked α-D-galacturonopyranosyl units, with some substitutions)
- Highly viscous, some emulsification properties
- Showing pseudoplastic behavior in solution
Polysaccharides from exudates: Gum Karaya

- An exudate of *Sterculia urens*, a tree in India
- Main chain composed of D-galactose, D-glucuronic acid, and L-rhamnose. Partially acetylated
- Slightly acidic and occurred as Ca, Mg, or Na salt
- Molecular weight of 300,000 to 1,000,000
- Not completely water soluble, but swell extensively
- Highly viscous
Polysaccharides extracted from seaweed: Carrageenan

- Obtained from the red seaweeds of the class Rhodophyceae, as a structural material
- A group of linear galactan with ester sulfate content of 15-40% (w/w) and containing alternating (1→3)-α-D and (1→4)-β-D-galactopyranosyl (or 3,6-anhydro-α-D-galactopyranosyl) linkages
- Three types of commercially available carrageenans are κ, ι, and λ
- Anionic polysaccharides with molecular weight: 100,000 – 1,000,000
- Form gels with potassium or calcium ions
- More effective gel formation in milk than in water due to incorporation of casein micelles into the gel network
Polysaccharides: sources and characterization

Polysaccharides extracted from seaweed: Agar

- Obtained from the red seaweeds of the class Rhodophyceae, as a structural material
- Linear chain similar with carrageenans, consisting of repeating sections of (1→3)-linked β-D-galactopyranosyl units joined to 3,6-anhydro-α-L-galactopyranosyl units via (1→4)-linkages
- Has very few sulfate groups
- Up to 21% of C-6 carbon on β-D-galactopyranosyl units may contain methoxyl groups, affecting the gelation properties
- Unique gelation properties: gelation occurs at temperature (30-35C) far below the gel melting temperature (90-95C)
Polysaccharides: sources and characterization

Polysaccharides extracted from seaweed: alginate

- Obtained from the brown seaweeds of the class Phaeophyceae, as a structural material
- Linear polysaccharide composed of $\beta$-D-mannuronopyranosyl and $\alpha$-L-guluronopyranosyl units. The units occur in M blocks (containing solely mannuronopyranose residues), G blocks (containing solely guluronopyranose residues), or MG blocks
- Ratio of G-, M-, and MG-blocks affects the gel strength, calcium reactivity, and other properties
- Form gels with calcium ions
- Alginate with high G-blocks results in greater gel strength
- Alginate with high M-blocks is more calcium tolerant and less likely to have problems with syneresis
Polysaccharides extracted from plant: Pectin

- Found in virtually all land-based plant as a structural material
- Commercial pectin extracted from citrus peel, apple pomace, sugar beet, or sunflower heads
- A linear chain of galacturonic acid units with molecular weight about 110,000-150,000
- In native pectin one free galacturonic acid units is followed by 5 methyl esters of galacturonic acid, with degree of esterification (DE) of 83.3%
- DE can be controlled during extraction processing, to obtain low ester (low methoxyl) pectin (DE<50%) or high ester (high methoxyl) pectin (DE>50)
- Low ester pectins gel with calcium, and high ester pectins gel with high sugar solids at low pH
Polysaccharides extracted from microorganism: Xanthan gum

• Prepared via culturing *Xanthomonas campestris*, a single-cell organism producing gum as protective coating
• Having a backbone chain identical to cellulose
• A trisaccharide side chain is attached to alternate D-glucosyl units at the O-3 position. The side chain consists of a D-glucuronosyl unit between two D-mannosyl units
• Approximately 50% terminal mannosyl units contain a pyruvic acid moiety as a 4,6-cyclic acetal. The non-terminal mannosyl units are substituted at the O-6 position with an acetal group
• Molecular weight about 2,000,000-3,000,000
• Showing pseudoplastic (shear thinning) behavior in solution
• Viscosity stable at wide temperature and pH
Polysaccharides extracted from microorganism: Gellan gum

- Prepared via culturing *Pseudomonas elodea*
- composed of a four-sugar repeating sequence containing one D-glucuronopyranosyl, two D-glucopyranosyl, and one L-rhamnopyranosyl unit
- Native gellan has high content of acyl groups (acetyl and L-glyceryl groups)
- Native gellan produces elastic gel, deacylated gellan produces firm and brittle gel
- Molecular weight about 1,000,000-2,000,000
- Requires either monovalent or divalent cations to form a gel. Calcium ions have the most effect on gel strength
**Cellulose and its derivatives**

- **Microcrystalline cellulose**
  - Extracted from wood cellulose
  - Amorphous regions removed under high shear/acid to release small crystalline bundles of cellulose fibers
  - Stable with relatively wide range of temperature and pH

- **Carboxymethyl cellulose (CMC)**
  - Prepared by soaking cellulose in aqueous sodium hydroxide and reacting with monochloroacetic acid

- **Methylcellulose (MC)**
  - Prepared by soaking cellulose in aqueous sodium hydroxide and reacting with methyl chloride
Cellulose and its derivatives

- Hydroxypropylcellulose (HPC)
  - Prepared by soaking cellulose in aqueous sodium hydroxide and reacting with propylene oxide

- Methylhydroxypropylcellulose (MHPC)
  - Prepared by soaking cellulose in aqueous sodium hydroxide and reacting with a mixture of methyl chloride and propylene oxide

- CMC, MC, HPC, and MHPC solutions are optically transparent and pseudoplastic

- MC and MHPC solutions gel if heated to incipient gelation temperature (50-90°C) and revert to the liquid state upon cooling

- HPC solution precipitates if heated to its cloud point and redissolves upon cooling
Chitin and Chitosan

- Chitin is a structural polysaccharide of animal outer skeleton, component of cell walls of certain fungi and algae
- Deacetylation of chitin produces chitosan: film-forming, antibacterial effects, dietary fiber and lipid absorption reducer
Purification of starches

- Starches are isolated as non-soluble granules
- Steeping, grinding, and centrifugations are major steps to separate starch granules from germ, fiber, protein, or solubles
- Starch granule is a mixture of amylose and amylopectin
- Special protocols are needed to isolate amylose and amylopectin
- Starch molecules can be completely dispersed in 90% DMSO

Purification of non-starch polysaccharides

- Non-starch water soluble polysaccharides are usually isolated by dissolving-purification-alcohol precipitation process
- Lipids can be removed by solvent extraction of raw materials
- Protein can be removed by enzyme digestion
- Insoluble fiber can be removed by centrifugation of polysaccharide solutions
- Most of purification cost comes from alcohol consumption
Structure determination of non-starch polysaccharides

- Polysaccharide fractionation
- Monosaccharide composition
- Linkage types
- Anomeric configuration
- Presence and location of substituent groups
- Degree of polymerization/Molecular weight
Polysaccharide fractionation

- Starting material is dissolved in water, purified by solvent precipitation or chromatographic separation, and dried
- A degree of purity & homogeneity should be attained. Polydisperse (chemically homogenous but varying in molecular weight) and polymolecular (varying not only in molecular size but also in chemical composition) are major challenges for structure analysis
- Homogeneity: the absence of extraneous contaminants and “discontinuities in molecular size and structure”
  - Homogeneity of size can be shown by SEC (size-exclusion chromatography)
  - Homogeneity of chemical composition requires the consistency of certain parameters, e.g. sugar ratio, sugar/functional group ratio, physical properties, spectroscopic data (e.g. NMR), before and after an attempted fractionation
Polysaccharides: Structure Analysis

Overview

Fractionated polysaccharide

- **Complete hydrolyzation**
  - HPLC/derivation-GLC
  - Reduced to alditols + acetylated
  - GLC analysis
  - Monomer compositions

- **Complete methylation**
  - Complete hydrolyzation
  - Structure analysis
  - Position of linkages

- **Partial hydrolyzation**
  - Oligomers purification
  - Oligomers structure
  - Molecular weight distribution

- **HPSEC**
  - Enzymatic specificity or NMR for anomeric configuration determination
Monosaccharide composition

- Acid-catalyzed hydrolysis
  - Maximum depolymerization
  - Minimum destruction of monomer
- Monomer detection
  - Direct HPLC analysis of hydrolysates
  - Conversion to volatile derivatives (e.g. alditol acetates) followed by GLC analysis
Polysaccharides: Structure Analysis

Linkage & ring size determination

- Methylation
  - Polysaccharide is methylated with methyl iodide (CH₃I) in strong base and DMSO
  - All exposed hydroxyl groups are converted to methyl ethers

- Hydrolysis
  - Methylated polysaccharides are hydrolyzed to expose the hydroxyl groups involved in glycosidic linkages

- Reduction
  - To release the hydroxyl group involved in ring formation, e.g. C-5 for aldopyranosyl or C-4 for aldofuranosyl unit

- Acetylation
  - To form partially methylated alditol acetates for GLC analysis

- Determination by GLC-MS
  - To identify the structure of methylated alditol acetates and determine the positions of linkages
Polysaccharides: Structure Characterization

Sequence characterization

- Polysaccharide is partially depolymerized by acid or enzymes to obtain oligosaccharides
- Oligosaccharides are purified
- Structure of each oligosaccharide is determined
- Individual oligosaccharide units are fitted together using the linkage information obtained
- Monomer sequences of polysaccharide are determined
Anomeric configuration

- Done from intact polysaccharides or from oligosaccharides
- Done by
  - Enzymatic analysis--enzyme is specific for a particular type of linkage, e.g., β-galactosidase
  - Nuclear magnetic resonance (NMR)--measurement of coupling constants
Starch structure characterization

Starch granule isolation

Granular structure
- Surface morphology
  - Internal structure
    - Protein & lipid complex

Molecular structure
- AP structure
  - CL distribution
  - AP cluster
  - AP branching pattern
- AM content
  - AM structure
  - AM-AP interaction

Crystallinity and crystalline type

AM: amylose
AP: amylopectin
CL: chain length
Derivatization

Major approach to make modified starch & non-starch polysaccharides

Mostly associated with etherification and esterification of hydroxyl groups

Degree of substitution (DS) and molar substitution (MS)

- **DS**: average number of hydroxyl groups per glycosyl unit derivatized by etherification or esterification. Maximum DS can be 3 for polysaccharides with average 3 hydroxyl groups for each glycosyl unit

- **MS**: when hydroxyethyl or hydroxypropyl groups are introduced, the resulting substituent group contains a hydroxyl group that can undergo further reaction. The average number of moles of substituent added to a glycosyl moiety is denoted as molar substitution
Derivatized food starch

Stabilized food starch

• The primary purpose is to stabilize amylose and amylopectin from retrogradation (that results syneresis of starch gel)

• By reacting with monofunctional reagents, substituent groups are introduced to amylose and amylopectin

• Formation of junction zones by linear sections is hindered by chemically introduced substituent, rendering the stability of starch paste or gel

• Starch esters includes: starch acetates, starch phosphates, and starch sodium octenylsuccinate (DS<0.1)

• Starch ethers includes: hydroxypropyl starches (DS<0.2)
Derivatized food starch

Cross-linked starch

• The primary purpose of cross-linking is to reinforce with chemical bonds the hydrogen bonds responsible for granule integrity against heating, shear, and low pH

• Two types of cross-linked food starches: distarch-phosphates and distarch-adipates

• DS is usually very low (DS<0.001) to achieve desirable properties
Cellulose etherification

- Preparation of alkali cellulose

\[
R_{\text{cell}}\text{OH} \xrightarrow{\text{NaOH}} R_{\text{cell}}\text{OH} \cdot \text{NaOH} \xleftrightarrow{} R_{\text{cell}}\text{ONa} + \text{H}_2\text{O}
\]

- Alkylation of alkali cellulose

\[
R_{\text{cell}}\text{ONa} + \text{CH}_3\text{Cl} \rightarrow R_{\text{cell}}\text{OCH}_3 + \text{NaCl}
\]

Methyl chloride

\[
R_{\text{cell}}\text{ONa} + \text{ClCH}_2\text{CO}_2\text{Na} \rightarrow R_{\text{cell}}\text{OCH}_2\text{CO}_2\text{Na} + \text{NaCl}
\]

Sodium salt of chloroacetic acid

- Hydroxyalkylation of alkali cellulose

\[
R_{\text{cell}}\text{OH} + \text{CH}_2\text{CHCH}_3 \xrightarrow{\text{NaOH}} R_{\text{cell}}\text{OCH}_2\text{CHCH}_3 + \text{NaOH}
\]

Propylene oxide
Polysaccharide hydrolysis

Hydrolysis may be catalyzed by acid or enzymes

- Acidic hydrolyzation of glycosidic linkage is random (e.g. starch liquefaction by acid)
- Enzymes attack specific linkages (e.g. starch beta-amylolysis to produce maltose)
- Both pH and temperature may affect the hydrolysis
- Hydrolysis may be conducted (e.g. to produce corn syrup) or prevented (e.g. to retain molecular weight and viscosity after thermal treatment)

Hydrolysis (degradation) may be caused by microorganism

- Commercial gums may not be sterile, leading to degradation during food processing

Digestion of starch is typical acid-enzyme-microorganism catalyzed process

- Resistant starch escapes enzymatic digestion in small intestine, but degraded by microorganisms in colon
Acid-catalyzed hydrolysis

Methyl β-D-glucopyranoside
Catalytic mechanism of $\alpha$-amylase

Aspartic acids, the nucleophile

Glutamic acid, the proton donor

Oxocarbenium ion-like transition state

The first displacement

- $\alpha$-amylases shares a similar action mechanism, using same group of catalytic amino acid residues
- Anomeric configuration is retained after conversion
- The reaction proceeds by a double displacement mechanism
- During the first displacement, glutamic acid protonates the glycosidic oxygen, bringing about scission of the $C_1$-$O$ bond and formation of an oxocarbenium ion-like transition state
- Aspartic acid attacks at the sugar anomeric centre to give a $\beta$-glycosyl enzyme intermediate, while the aglycone of the substrate leaves the active site

E.A. MacGregor et al. / Biochimica et Biophysica Acta 1546 (2001) 1-20
Catalytic mechanism of $\alpha$-amylase, the second displacement

In **hydrolysis**, during the second displacement, the anomeric centre is attacked by a water molecule activated by the carboxylate form of glutamic acid.

This second stage of the reaction proceeds via an ion-like transition state, as before, to yield a product with $\alpha$-anomeric configuration and reprotonation of the original acid group.

**Transglycosylation** can occur if the attacking group in the second displacement of the reaction is a free hydroxyl of a sugar residue rather than water.

E.A. MacGregor et al. / Biochimica et Biophysica Acta 1546 (2001) 1-20
Oxidation-elimination

- Oxidation of a hydroxyl group to a carbonyl group
- Usually catalyzed by a transition metal ion
- These reactions may produce off-flavors and aromas
- Several mechanisms have been proposed (refer to W&B page 84-88, and online chapter 4)
- Leads to depolymerization
Dispersion and hydration

Sugar

Gum

All gone

All gone

Time
Fish eyes

A group of gum powders

Water diffusion to the center is hindered by hydrated gum matrix at the surface
To prevent fish eyes

- Sift the gum slowly into a vortex of rapidly stirred water (high shear)
- Disperse with another hydrophilic (but lower molecular weight) material, e.g., sucrose, glycerol, propylene glycol
- Use an agglomerated gum which hydrates more slowly
- Raise the temperature after initial dissolution
Solution of linear and branched polysaccharides

Both molecules have the same DP
Degradation may reduce viscosity or gel strength
Conformation determined by monomeric type & anomeric linkages

Linear (e.g. amylose)
- High hydrodynamic radius
- High viscosity
- Aggregate, form gel, or precipitate

Branched (e.g. amylopectin, gum arabic)
- Low hydrodynamic radius
- Low viscosity
- Relatively stable in solution
Polysaccharides: Functions

Chain interactions affected by glycosidic linkages, steric hindrance, & charge

Native cellulose
• Hydrogen bonds between 1,4-linked β-D-glucopyranosyl units restrict free rotation of rings along glycosidic linkages
• Flat, ribbonlike character forms for entire molecule and allows adjacent chains to fit closely in crystalline regions

Native starch
• Hydrogen bonds between 1,4-linked α-D-glucopyranosyl units also restrict free rotation of rings
• The chains adopt a helical shape involving either one or two chains. Double helices may aggregate to form crystalline regions

Derivatives of cellulose and starch
• Substituent groups by derivatization hinders the formation of hydrogen bonds and chain ordering, leading to stabilized solution of polysaccharide

Sodium alginate
• In neutral solutions, uronic acid units repel each other by coulombic repulsion, leading to highly viscous and stable solutions of linear polysaccharide
• At pH<3, the ionization of carboxylic group is repressed, chains may associate to gel or precipitate
Polysaccharides: Functions

Junction zone, gel, syneresis, & fringed micelle

Polymers can be amorphous (totally lacking positional order on the molecular scale) or semi-crystalline (containing both crystalline and amorphous regions in the same sample). The semi-crystalline can be pictured according to the "fringed micelle" model.
## Thickening agents & gelling agents

<table>
<thead>
<tr>
<th>Thickening/viscosity agents</th>
<th>Gelling agents</th>
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<tbody>
<tr>
<td>Locust bean gum</td>
<td>Agar</td>
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<tr>
<td>Guar gum</td>
<td>Carrageenan</td>
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<tr>
<td>Tara gum</td>
<td>Pectin</td>
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<tr>
<td>Konjac (with acetyl groups)</td>
<td>Konjac (without acetyl groups)</td>
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<tr>
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<td>Gellan gum</td>
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<td>Xanthan gum</td>
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<td>Tragacanth</td>
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<td>Propylene glycol alginate</td>
<td>Methylcellulose (at 40-70C)</td>
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<td>Methylcellulose (at 25C)</td>
<td>Methylhydroxypropylcellulose (at 40-70C)</td>
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<tr>
<td>Cellulose gum</td>
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<td>Gum karaya</td>
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</table>
Outcome of polysaccharide combinations

- In some cases, there is an additive effect when a gelling gum is used with a thickening gum. Each gum contributes to the food system, and the result reflects the two effects, e.g.
  - Pectin and LBG are used in yogurt preparations

- In certain cases, the combination of two different thickening gums gives more viscosity than additive, e.g.
  - CMC and guar
  - Xanthan gum + CMC (or MCC)
Outcome of polysaccharide combinations

- In a few cases, a synergistic gelation occurs when two gums are combined
  - The best known is LBG + xanthan gum, which gives rubbery but rigid gel
  - Also, Xanthan + tara gum

- One gum may change the gel strength of another gum, e.g.
  - Agar has lower gel strength with sodium alginate and higher gel strength with LBG
  - LBG modifies the texture of κ-carrageenan gel, making it more elastic with higher break strength
Incompatibility of polysaccharides

(Read attached material to understand the following concepts)

Concepts

- Two types of phase separation
- Phase separation threshold
- Thermodynamic incompatibility
- Phase diagram
- Effect of structure and composition on compatibility
  - Use amylose and amylopectin mixture as an example
What do we expect gum to do for our applications?

- Make products more stable over the time (shelf life) or under specific conditions (e.g. high temperatures)
- Create, improve, or modify food texture
- Improve both texture & stability
- Provide additional nutrition (dietary fibers)
Questions related to gum selections?

- Does the product contain a significant amount of proteins? What proteins?
- What’s the pH of the product?
- Is it a dry mix or liquid product?
- What’s content of soluble solids?
- Does the system become unstable when heated? Separate over time?
- Does the undesirable crystal growth appear over storage?
- Does the syneresis appear?
Obtained from the brown seaweeds of the class Phaeophyceae, as a structural material

Linear polysaccharide composed of $\beta$-D-mannuronopyranosyl and $\alpha$-L-guluronopyranosyl units. The units occur in M blocks (containing solely mannuronopyranose residues), G blocks (containing solely guluronopyranose residues), or MG blocks.

Ratio of G-, M-, and MG-blocks affects the gel strength, calcium reactivity, and other properties.

Form gels with calcium ions.

Alginate with higher G-blocks results in greater gel strength.

Alginate with higher M-blocks is more calcium tolerant and less likely to have problems with syneresis.
Monomers and alginate chain

Monomers:
- β-D-mannuronate
- α-L-guluronate

Alginate chain

Symbolic representation of alginate chain

*Food Polysaccharides and their applications, 2nd edition*
Egg-box model of calcium binding with G blocks

*Food Polysaccharides and their applications, 2nd edition*
How to form an alginate gel?

**Diffusion setting, neutral pH**
Alginate-containing mix is dipped into (or sprayed with) a calcium salt solution. The calcium ions diffuse into the mix and form calcium alginate gel. Raising the concentration of calcium and using a strongly calcium-reactive alginate (with a high proportion of G-blocks lead to strong gel.

**Diffusion setting, acid pH**
A calcium salt insoluble at neutral pH is mixed with the alginate. When an acid is added to the mass, the calcium salt is solubilized and reacts with the alginate to form the gel.

**Internal setting, neutral and acid pH**
Calcium is released within the product under controlled conditions. Alginate, a slowly soluble calcium salt, and a suitable calcium sequestrant (e.g. phosphate or citrate). The sequestrant is needed to bind free calcium and prevent pre-gelation of the alginate during processing. The acidity accelerates the solubility of calcium salts.

**Setting after heat treatment**
Alginate is dissolved in hot water with calcium salt and a sequestrant. The high temperature prevents gelation due to alginate chains’ thermal motion. When cooled, the calcium alginate reaction leads to a heat stable gel.
Pectin

- Found in virtually all land-based plant as a structural material
- Commercial pectin extracted from citrus peel, apple pomace, sugar beet, or sunflower heads
- A linear chain of galacturonic acid units with molecular weight about 110,000-150,000
- In native pectin one free galacturonic acid units is followed by 5 methyl esters of galacturonic acid, with degree of esterification (DE) of 83.3%
- DE can be controlled during extraction processing, to obtain low ester (low methoxyl) pectin (DE<50%) or high ester (high methoxyl) pectin (DE>50)
- Low ester pectins gel with calcium, and high ester pectins gel with high sugar solids at low pH
Hypothetical structure of apple pectin showing I xylogalacturonan region, II region with arabinan side chains, III rhamnagalacturonan region making up the ‘hairy region’. (From H. Schols et al. ‘Structural Features of Native and Commercially Extracted Pectins’, in Gums and Stabilisers for the Food Industry 9 ed P. A. Williams and G. O. Phillips, RSC Cambridge, 1998, by permission of the authors.)
Gelation properties of pectins

- Gelation of high methoxyl pectins
  - The presence of sugars is required
  - At a sufficiently low pH
  - Reduced pH leads to increased gel strength and setting temperature
  - Nature of sugars affects pectin performance (e.g. replacement of sugar by glucose syrup leads to increased setting temperature and pH for gelation, but reduced maximum gel strength)
  - Increased sugar amount leads to increase of setting temperature and optimum pH

- Gelation of low methoxyl pectins
  - Governed mainly by interaction between pectin and calcium ions
  - Thus the presence of sequestrant has effects (citrate, di-/poly-phosphate) on gelation, and can be used to produce workable gel system
  - Reactivity increases with decreasing degree of esterification
  - Increased solubles and reduced pH favors gelation
Gelation properties of pectins

<table>
<thead>
<tr>
<th>Classification</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapid set</td>
<td>Acid milk products, jam</td>
</tr>
<tr>
<td>Slow set</td>
<td>Jellies, bakery, confectionery</td>
</tr>
</tbody>
</table>

- High methoxyl
- Low methoxyl
- Calcium reactivity

- Reduced sugar products
- Low sugar or low acid products
Gum Arabic

- A gummy exudate obtained from *Acacia* trees in Africa, primarily Sudan
- Highly branched polysaccharide constructed from both neutral monomers and uronic acids
- Covalently attached with proteinaceous fractions, rendering its excellent function as emulsifier
- Molecular weight about 250,000
- Highly soluble, low viscosity even at 40% concentration
- Solution showing *Newtonian* behavior (constant viscosity at different shear rate)
Putative structure of gum arabic:

A: arabinosyl
R1: rhamnose-glucuronic acid
R2: galactose-1,3-arabinose
R3: arabinose-1,3-arabinose-1,3-arabinose

Filled circle: 1,3 linked galactose
Open circle: 1,6 linked galactose

*Handbook of hydrocolloids*
Gum arabic can be used as an emulsifier

Hydrophilic carbohydrate blocks

Hydrophobic polypeptide chain

Handbook of hydrocolloids