Outline

• General introduction
• Viscosity & Gelation
• Structure-function relationships in a few examples - Cellulose, Xanthan, Galactomannans, Gum Arabic, Alginate and Carrageenans
• Beyond food applications...
Some food products maintain the structure, how?
What are Hydrocolloids?

• Natural
• Water-soluble or -dispersible polysaccharides and modified polysaccharides
• Also called as Food Gums
• Generally, they produce viscous dispersions and gels (in some cases)
Hydrocolloids: A few uses

To:
- thicken
- form gels
- stabilize suspensions
- bind/hold water
- improve texture
- stabilize emulsions
- form films and coatings
- encapsulate
Hydrocolloids: A few applications

- Emulsification (o/w or w/o)
  - Salad dressing
    - Gum Arabic, xanthan
- Suspension/dispersion
  - Chocolate milk
    - Carrageenan
- Foams
  - Whipped toppings
    - Locust bean gum
Hydrocolloids: A few applications

- Crystallization control
  - Ice cream
    - many gums
- Flavor fixation
  - Powdered drink mixes
    - Gum Arabic
- Protective films
  - Sausage casings
    - Alginate
- Syneresis inhibitor
  - Processed cheeses
    - Locust bean gum, guar
Polysaccharides

- Plant
  - Cellulose
  - Curdlan
  - Galactomannan
  - Starch
  - Arabinogalactan

- Seaweed
  - Alginate
  - Pectin
  - Gellan Family
  - Xanthan

- Seed
  - Carboxylate
  - Amino
  - Chitosan

- Bacterial
  - Sulfate
  - Carrageenan
Chemical Repeats

Cellulose: \( \rightarrow 4\)-\(\beta\)-D-Glc-(1\(\rightarrow\))

Amylose: \( \rightarrow 4\)-\(\alpha\)-D-Glc-(1\(\rightarrow\))

Curdlan: \( \rightarrow 3\)-\(\beta\)-D-Glc-(1\(\rightarrow\))

Galactomannan: \( \rightarrow 4\)-\(\beta\)-D-Man-(1\(\rightarrow\))4\(\beta\)-D-Man-(1\(\rightarrow\))6

\[\uparrow\]

1 \(\alpha\)-D-Gal

Gellan: \( \rightarrow 3\)-\(\beta\)-D-Glc-(1\(\rightarrow\))4\(\beta\)-D-GlcA-(1\(\rightarrow\))4\(\beta\)-D-Glc-(1\(\rightarrow\))4-\(\alpha\)-L-Rha-(1\(\rightarrow\))

Welan: \( \rightarrow 3\)-\(\beta\)-D-Glc-(1\(\rightarrow\))4\(\beta\)-D-GlcA-(1\(\rightarrow\))4\(\beta\)-D-Glc-(1\(\rightarrow\))4\(\alpha\)-L-Rha-(1\(\rightarrow\))3

\[\uparrow\]

1 \(\alpha\)-L-Rha or \(\alpha\)-L-Man
Hydrocolloids: Properties

• Solutions behaviors are related to the associative properties of hydrocolloids

• Hydrocolloid with regular repeating-unit sequence has a natural tendency to adopt a helical conformation

• Interactions between helices are affected by surrounding water molecules and cations (in the case of anionic hydrocolloids)

• Interactions between helices are responsible for the associative properties of hydrocolloids
Viscosity

- Hydrocolloids become hydrated upon dispersion in water
- Hydrocolloids and water molecules interact via hydrogen bonds or ion-dipole interactions
- Upon hydration they interact with each other leading to viscosity
Viscosity

• Is dependent on molecular size, shape and charge

• Influenced by the presence of polyelectrolytes and counter ions

• Linear chain requires more volume for tumbling (hydrodynamic volume) and gyration than branched molecule of the same molecular weight
Junction Zones

• If the interactions are substantial, junction zones are formed and might lead to gelation.

• Junction zone bonds include:
  – Hydrogen bonds
  – Ionic bonds
  – Covalent bonds
What controls the functionality, and How?

Molecular Shapes & Interactions!
Molecular Shapes

- Helices are the preferred structures
- Nuclear Magnetic Resonance (solution)
- Atomic Force Microscopy: low resolution
- Diffraction techniques: high resolution
Chemical Structures

Arise from different

- Monosaccharides such as glucose, mannose and galactose
- Configurations (e.g. L, D, α and β)
- Linkages (e.g. 1→3, 1→4 and 1→6)
- Distributions of all of the above
Hydrocolloids: A few examples

1. Cellulose
2. Xanthan
3. Galactomannans: Guar gum & Locust bean gum
4. Gum Arabic
5. Alginate
6. Carrageenans
Cellulose: Chemical structure
Cellulose

- Four crystalline allomorphs: I, II, III and IV
- I: Native fibers from *Valonia, ramie, cotton and wood*
- II: Fibers produced after regeneration (using alkali)
Cellulose: Molecular structure

- 2-fold helix of pitch 10.4 Å
- Stabilized by O$_3$H···O$_5$ bonds across each glycosidic bridge oxygen atom
Cellulose I vs. II
Cellulose: Effect of Substitution

Cellulose

Hydroxypropylmethylcellulose (HPMC)
Xanthan

- A bacterial gum
- Source
  - *Xanthomonas campestris*
- Structure
  - Basically a derivatized cellulose
Xanthan

Bulky side group

Bulky side group
Xanthan

- **Uses**
  - Temperature and pH independent viscosity
  - **Beverages**
    - Good flavor release
    - Cloud stabilizer
  - **Frozen foods**
    - Pie fillings-increases freeze-thaw stability
  - **Relishes**
    - Good acid stability (0.1%)
Galactomannans

- Mannan backbone contains $(1\rightarrow 6)$-linked $\alpha$-D-galactose residues as random side groups
- Galactose/Mannose ratio: Varies from 0.3 in carob, 0.6 in guaran to 0.9 in fenugreek
- Solubility: Most galactomannans are water soluble and produce highly viscous solutions. Used as thickening agents in a variety of food systems
Guar gum

- **Source**
  - Grown in India, Pakistan and the U.S.
  - Seed endosperm

- **Structure**
  - Mannose:Galactose = 2:1
  - MW = 1-2 x 10^6 Daltons

- Hydrates rapidly in water and yields highly viscous dispersions
- Neutral gum & pH has little effect
Guar gum

- Uses
  - Ice cream
  - Baked goods
  - Meat
  - Beverages
  - Dressings and sauces
Locust bean gum

- **Source**
  - Grows in the near East and Mediterranean

- **Structure**
  - A galactomannan (Man:Gal = 4:1)
  - MW 300,000 to 360,000 Daltons
  - Side chains are not uniformly distributed
  - Some parts of the backbone are highly substituted: "hairy" regions, while other parts are not substituted at all: "bare" regions
Locust bean gum

- Ice cream
- Cheese products
- Meat products
- Chocolate substitute
Galactomannan: Molecular structure

- **Mannan-like 2-fold helix** of pitch 10.4 Å; the side group is turned towards the reducing end
Galactomannan: Molecular structure

Considerable increase in chain width causes voids in the sheet structure; ability to trap water leads to solubility
Galactomannan: Packing arrangement
Gum Arabic

- An exudate gum
- Source
  - *Acacia* trees
  - Sudan and other African countries
  - Produced naturally as teardrop shaped globules from tree barks
- Structure
  - D-galactose, L-arabinose, L-rhamnose, D-glucuronic acid
  - MW 50,000 to 3,500,000 Daltons
Gum Arabic

- **Uses**
  - Candies: decreases sugar crystallization
  - Baked goods: reduces moisture absorption
  - Frozen desserts: formation and maintenance of small ice crystals
  - Flavor fixation: retains volatile flavors and protects from degradation
Alginate

- **Source**
  - Brown algae, *Macrocystis pyriforma*

- **Structure**
  - D-mannuronic acid, L-guluronic acid
  - Poly($M$) blocks
  - Poly($G$) blocks
  - Alternating $M$-$G$ blocks
  - $M$/$G$ ratio differs depending on the source
Alginate

- Ice cream
- Bakery icings
- Bakery jelly
- Meringues
- Salad dressings
- Pimento stuffed olives
- Frozen reformed onion rings
Carrageenans

• **Fifteen Carrageenans:** κ, τ, λ, θ, μ, ν, ξ, α, β, ω, ό, π, γ, δ and ψ

• κ-, τ- and λ-carrageenans are utilized extensively due to their greater versatility

• κ- and τ-carrageenan gel in the presence of mono (K⁺) and divalent (Ca²⁺) cations but trivalent ions (Fe³⁺) are needed for λ-carrageenan
Structural-function relationships: iota-carrageenan

\[
\rightarrow 3) \beta-D-Gal-4-SO_3^- \rightarrow (1 \rightarrow 4)-3,6-anhydro-\alpha-D-Gal-2-SO_3^- (1 \rightarrow 4)
\]

Janaswamy et al., Unpublished results
Iota-carrageenan: Molecular Structure
Iota-carrageenan: Helix–Helix association

Na$^+$

$\rightarrow$

Ca$^{2+}$

$\downarrow$

$\leftarrow\text{13.9 Å}\rightarrow$

$\leftarrow\text{13.6 Å}\rightarrow$
Carrageenans

• Uses

Puddings
  – “Eggless” custards
Chocolate milk
  – Particle suspension
Cheese products
  – Prevents whey separation
Ice cream
  – Crystallization control
Meat
  – Protective coating
Salad dressing
  – Stabilizer
Recap

• Defined & Categorized Polysaccharides
• Discussed hydration, viscosity and junction zones
• Discussed chemical structure and solution properties of a few Hydrocolloids
• Role of hydrocolloids in developing novel functional foods, food supplements and medicinal foods
Food for Thought

• Do you think alginate and carrageenans would display cation dependent solution properties? If so, why?

• In a food product development, if you were given an opportunity to choose between carrageenan and xanthan which one you would prefer and why?