Behaviors of Polysaccharide Solution, Dispersions and Gels

Gums--Food functions
- Gums can control or determine the texture of many food products

Gums--General functions
- Thickening
  - All gums do this to some extent
- Gelling
  - Only a few gums (agar, algin, carrageenan, etc.) can do this
Gums--Food functions

- Principally gums do their jobs by controlling the structure and mobility of liquid water.
- Gums can
  - alter water retention
  - reduce water evaporation
  - alter water freezing rate
  - modify ice crystal formation
  - participate in chemical reactions

Food Rheology

- Rheology -- the science of the deformation and flow of matter.
- Rheos (Greek) -- to flow

Viscoelastic foods

- Elastic
- Plastic
- Viscous
Elastic foods
- Deformation occurs the moment stress is applied, is proportional to stress, and disappears instantly and completely when stress is removed.

Plastic foods
- Deformation begins when the yield stress value is exceeded.
- Deformation is permanent, i.e., there is no recovery of initial shape.
- Example: Crisco.

Viscous foods
- Deformation occurs at the moment stress is applied, is proportional to the rate of change of strain, and there is no recovery when stress is removed.
Viscosity may be thought of as the internal friction of a fluid. Shear stress = force applied over an area/area = F/A. When stress is applied, this produces a shearing strain (movement).

Viscosity (\( \eta \)) is defined as the ratio of shear stress to the rate of change of strain. If we let the rate of change of strain be represented by D, then \( \eta = (F/A)/D \), or, solving for \( F \), \( F = \eta AD \).

Graphical representations of flow behavior typically plot D vs. F (or F vs. D) and \( \eta \) vs. D. In experiments using the Brookfield viscometer, plot the spindle speed for D, plot the scale reading for F, and plot \( \eta \) for \( \eta \).
Newtonian Flow

Viscosity is independent of shear rate

Few polysaccharides show this type of flow
Examples that do: gum arabic and low molecular weight alginate
Mostly this type of behavior is shown by true solutions of low molecular weight compounds

Bingham Plastic

Yield Value

Mostly this type of behavior is shown by true solutions of low molecular weight compounds
A ketchup poem

You shake and shake the ketchup bottle.
First, none will come; and then, a lot 'll.
Some messy guy

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Pseudoplastic

- Mainly a characteristic of linear polymers
- The more stiff or rod-like, the more pseudoplastic the flow
- Degree of pseudoplasticity depends on concentration, polymer charge and salt form, viscosity, pH and molecular weight
- These dispersions may have yield value (like Bingham plastics)

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Pseudoplastic

These are called shear thinning fluids.
Pseudoplastic fluids

Change in viscosity on shearing is not time dependent

- Lower shear
- Greater shear
- Lower shear

Time

Log viscosity

Log shear rate

Break point

Log molar concentration

As concentration and molecular weight increase, degree of pseudoplasticity does as well.

Flow properties affect mouthfeel and processability.
**Long and short flow**

- Gum dispersions that are less pseudoplastic exhibit “long” flow
  - They tend to be slimy
- Gum dispersions that are more pseudoplastic exhibit “short” flow
  - They tend to be less slimy or non-slimy

**Dilatant**

These are known as shear thickening fluids.

**Thixotropic**

Note the hysteresis loop -- a characteristic of thixotropic flow
Thixotropic fluids

- Shear rate 2 is greater than shear rate 1
- Very weak gel
- Sol
- Constant shear rate 1
- Constant shear rate 2
- Constant shear rate 1

Thixotropy

- Depends on
  - Degree of substitution
  - Uniformity of substitution
    - Non-uniformity promotes junction zone formation
  - Molecular weight

Thixotropy example

- Fruit juice containing pulp is a thixotropic fluid
- Dry fruit drink mixes should mimic this thixotropic behavior
Rheopectic

- These are characterized by an increase in viscosity at constant shear rate.
- Examples: beaten egg white or whipping cream

Food Rheology -- Examples

- Newtonian: Corn syrups, broths, skim milk
- Bingham plastics: Chocolate, butter
- Pseudoplastic: Gelled desserts, puddings
- Thixotropic: Honey, mayonnaise
- Dilatant: Honey containing dextran impurities
- Rheopectic: Beaten egg whites, whipping cream

Viscosity grades of gums

- Most gums are available in a range of viscosity of grades
- For thickening, use a high viscosity grade at low solids
- For binding, stabilization, and coating, use low viscosity grade at high solids
Viscosity grades

Gum dissolution depends on
- Gum type
- Viscosity grade
- Particle size
- Temperature
- pH
- Presence of other solutes
- Counterions (if anionic)
- Means of dispersion
- Surface treatment (if any)

Dissolution process
- Fully swollen
- Partially dispersed
- Molecular dispersion
- Time (Degree of disaggregation)
Influence of particle size

- Fine mesh
- Coarse mesh

Viscosity vs. Time

Influence of charge

- Generally, ionic gums are more soluble and dissolve faster than neutrals of the same molecular weight.
- But solubility of ionic gums is decreased more by certain salts than is the solubility of neutral gums.

Effect of other hydrophilic molecules

- Salts decrease gum hydration
- If salts increase intermolecular interaction, viscosity will increase
  E.g. Ca++
- If salts increase intramolecular interaction, viscosity will decrease
- Polyols and sugar generally decrease viscosity
Effect of solutes

- Gum dispersion, no added solute
- Gum dispersion, solute added after a time
- Gum added to a solution

Time (degree of hydration)

Temperature dependence

- Generally, viscosity decreases with increasing temperature of dispersion
- Exceptions are xanthan, gellan, methylcellulose, and hydroxypropyl methylcellulose
- Prolonged heating may cause degradation, thus a decrease in viscosity
- However, some gums must be heated to obtain full viscosity (locust bean gum)

General temperature dependence

Log viscosity

Temperature
Effect of pH

- Most dramatic effect occurs with anionic gums
- Viscosity increases markedly below pH 2.5-5.0
- Some gums may gel or become insoluble
  - This reflects increased intermolecular interaction as a result of decreasing Coulombic repulsion

Effect of pH

- Typical neutral gum
- Typical ionic gum
- Increased intermolecular association
- β-elimination

Synergism

- Synergism occurs when the viscosity or gel strength of a particular system is greater than would be predicted by summing the properties of the individual components
Viscosity-enhancing synergisms

- CMC + Guar
- CMC + Casein
- CMC + Soy protein
- κ-carrageenan + κ-casein
- Xanthan + Agarose
- Xanthan + κ-carrageenan
- Xanthan + Guar

Gelling synergisms

- κ-carrageenan + Locust bean gum
- Xanthan + Locust bean gum

Gels

- A continuous three-dimensional network of molecules of particles, entrapping a large volume of water
To effect this transformation we may:
- Add a non-solvent
- Evaporate the solvent
- Add a cross-linking agent
- Change temperature
- Change pH

This is a GEL
Gelation

- The effect of these treatments is to decrease intramolecular interaction and to increase intermolecular interaction
- Gels have some characteristics of elastic solids but also share some of the characteristics of viscous liquids
- Consequently, they are classified as a viscoelastic semisolid

Junction zone types

- Intermolecular interactions between regular, linear segments of molecules of the same polysaccharide
  - Hydrogen bonds
    - HPMC
    - Pectin
    - Starch
  - van der Waals bonds

Junction zone types

- Intermolecular interactions between, regular, linear segments of polyanionic polysaccharide molecules effected by a cation
  - Ionic
    - Alginate
    - LMP
    - Carrageenan
Junction zone types

- Interactions between linear chain segments of two different polysaccharide molecules
  - Ion-dipole
  - Hydrogen bond
    - LBG and carrageenan
    - LBG and xanthan

Junction zone types

- Interactions between ionic polysaccharide molecules and protein molecules
  - Ionic
    - Kappa-carrageenan and kappa-casein

Junction zone types

- Cross-linking of neutral polysaccharide molecules with a multivalent ion
  - Covalent
    - LBG or guar with borate
    - This type of junction zone formation is not used in foods
Junction zone types

- Chain entanglements, especially in the case of branch-on-branch polymers
  - Physical
    - Gum arabic
    - Starch

Junction zone size

- If the junction zones are relatively small, a gel will be formed
- If the junction zones are large (or grow from small to large) a precipitate may be formed

Junction zone growth and syneresis

Water

Junction zones relatively small
Junction zone growth and syneresis

- Water
- Large junction zones; Significant change in texture; formation of precipitate
- Loss of water from the gel = syneresis

Level of gum to gel

- Gels generally contain 1% or less of gum

Acid set gels

- Sodium alginates
- High-DM pectins + sugar
Chemically set gels
- Sodium alginate + Ca^{2+}
- Iota-type carrageenans and Ca^{2+}
- Low-DM pectins and Ca^{2+}
- Kappa-type carrageenans and K^{+}
- Carrageenans and protein (above pI)
- Carrageenans + pectin + protein (above pI)

Thermally set gels
- Agar
- Calcium alginates
- Gellan
- High-DM pectins + acid + sugar
- Calcium pectinates
- Kappa-type carrageenans + LBG

Thermally set gels (cont.)
- Xanthan + kappa-type carrageenans
- Xanthan + locust bean gum
- Xanthan + agarose
- Starches
Thermogelation

- Curdlan (irreversible)
- HPMC (thermoreversible)
- Methylcelluloses (thermoreversible)

Gels with addition of solutes

- High-DM pectins + acid

Shear reversible gels

- Iota-type carrageenans (above pH 5.0, 20-80 Brix)
- Low-DM pectins (below pH 5.0, 20-80 Brix)
Texture Profile Analysis

- Can use an Instron Universal testing machine or a Texture Analyzer to do this
- Much of this type of analysis is due to the work of Malcolm Bourne

Parameters

- **Modulus**
  - Proportional to sensory firmness
- **Hardness**
  - Maximum force during first compression (before gel failure)
  - Proportional to gel strength
- **Brittleness (fracturability)**
  - Percent compression when the gel breaks
**Parameters**

- **Elasticity (springiness)**
  - Measure of return to undeformed condition after the force of the first compression cycle is removed
  - Proportional to rubberiness

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**Texture Profile Analysis**

- **Cohesiveness**
  - A measure of how much the sample is broken down in the first compression cycle
  - Proportional to the ratio of Area 2/Area 1

- **Adhesiveness (resilience)**
  - Sticky, tacky, gooey
  - Proportional to Area 3
Texture Profile Analysis

Parameters

- Chewiness
  A combination of hardness, cohesiveness, and elasticity
  Hardness x cohesiveness x elasticity

Texture Profile Analysis
**Parameters**

- **Gumminess**
  - A combination of hardness and cohesiveness
  - Hardness x cohesiveness
  - Energy required to disintegrate a semisolid food to a state ready for swallowing

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**Texture Profile Analysis**

Presenting TPA data
Choosing a gum

Consider
- Available viscosity grades
- Amount of the proper viscosity grade to give the specified viscosity or gel strength
- Cost/functionality (cost of the amount needed to impart the desired functional characteristics)
- pH of the system (effect on hydration rates and stability)
- Temperatures during processing and times at those temperatures (effect on hydration rates and stability)
- Times at each processing and storage temperature (effect on hydration rates and stability)
- Interactions with other ingredients, e.g., competition with other dissolved substances for available water
- Desired texture
- Ease of dispersion with available equipment
Gel characteristics to examine in choosing a gum

- Means of gelation
  - Heat, acid, cation
- Shear reversibility
  - Maybe yes, more likely no
- Heat reversibility
  - Generally
- Texture profile
  - Elastic, brittle, etc.

- Gel strength
  - Firm, soft
- Syneresis
  - Yes or no?
- Clarity
  - Depends on the application
- Freeze-thaw stability
  - Syneresis?