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Thursday, October 23, 2014

"Planet of Viruses"

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"Sweet Science:
Having Fun with Candy Chemistry"

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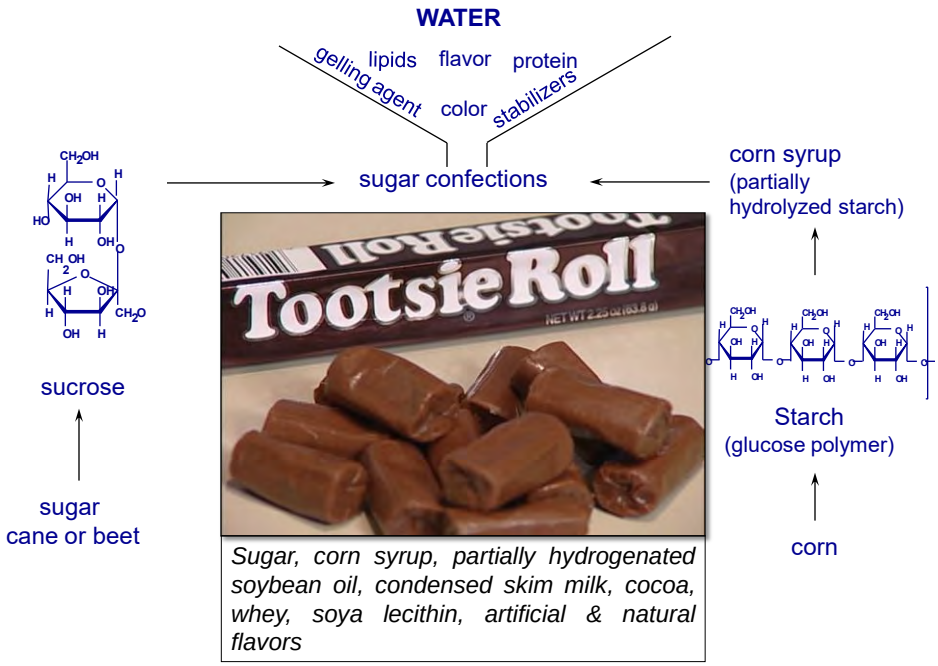
Candy Chemistry

Dr. Rich Hartel
University of Wisconsin-Madison

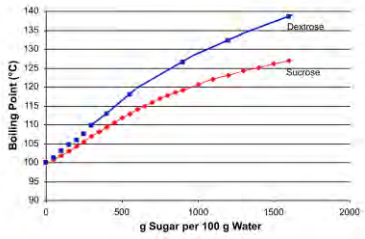
Where's the Chemistry in Candy?

- **Sweetener chemistry dominates all candy**
  - Sweetness, physical state, texture/structure, etc.
- **Hydrocolloid chemistry**
  - Gummies and jellies
- **Flavor/aroma and color chemistry**
  - This is what sells candy
- **Rubber chemistry**
  - Chewing and bubble gum
- **Reaction chemistry**
  - Caramelization, Maillard browning, inversion/hydrolysis
- **And more**



General Process of Candy-Making

- **Mix sugar and corn syrup with excess water**
  - Heat to dissolve granulated sugar
- **Add other ingredients for specific confections**
  - Milk, fats, hydrocolloids, colors, flavors, acids, etc.
  - May be added either before or after cooking
- **Boil to remove excess water**
  - Target water content
  - Specific chemical reactions
- **Cool, process and form**
  - Aeration, crystallization, etc.



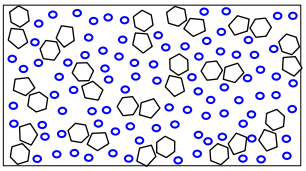
Candy Thermometer

Boiling Temperature	Description
110-112° C (230-234° F)	Thread
112-116° C (234-240° F)	Soft ball
ball that does not hold its shape when pressed	
117-120° C (244-248° F)	Firm ball
ball that holds its shape when pressed	
121-130° C (250-266° F)	Hard ball
ball that holds its shape, but is pliable	
132-143° C (270-290° F)	Soft crack

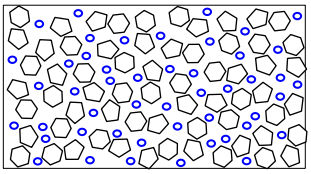
http://www.inspiredtaste.net/8947/salted-caramels-recipe/

Fluid Sugar States

- **Liquid sugar**
  - concentrated (65%) sugar solution
    - random organization of molecules

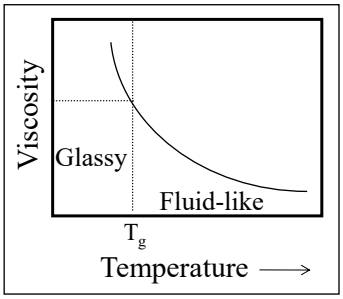


- **Amorphous liquid**
  - highly concentrated (≈85-95%) sugar solution
  - very viscous ($T > T_g$)
    - Still above the zone of transition from amorphous (more fluid-like) to a glassy (more solid-like) state
- **Sugar glass**
  - extremely concentrated (> 95%)
  - extremely high viscosity ($T < T_g$)
    - effectively acts like a solid
  - low molecular mobility



Glass transition temperature, T_g

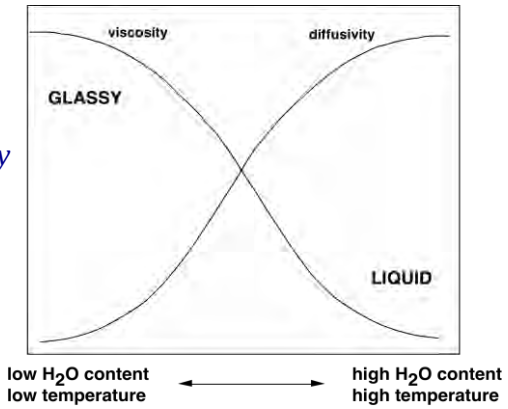
- **Defined as the temperature at which a sugar syrup undergoes a transition from a fluid to being solid-like**
  - Can be measured by mechanical properties
  - More commonly measured by calorimetry as a second order phase transition (ΔC_p)
- **Viscosity of glassy state is about 10^{12} to 10^{14} Pa-s**
- **T_g is dependent on:**
  - Types of sugars present
  - Molecular weight of sugar
    - In general, higher MW, higher T_g
  - Water content
    - Higher water content, lower T_g



Glass Transition

- In some systems, the decrease in diffusivity and associated increase in viscosity as concentration increases or temperature decreases leads to formation of a glass state
  - No crystallization from glassy state

Limited molecular mobility inhibits crystal formation in glassy state



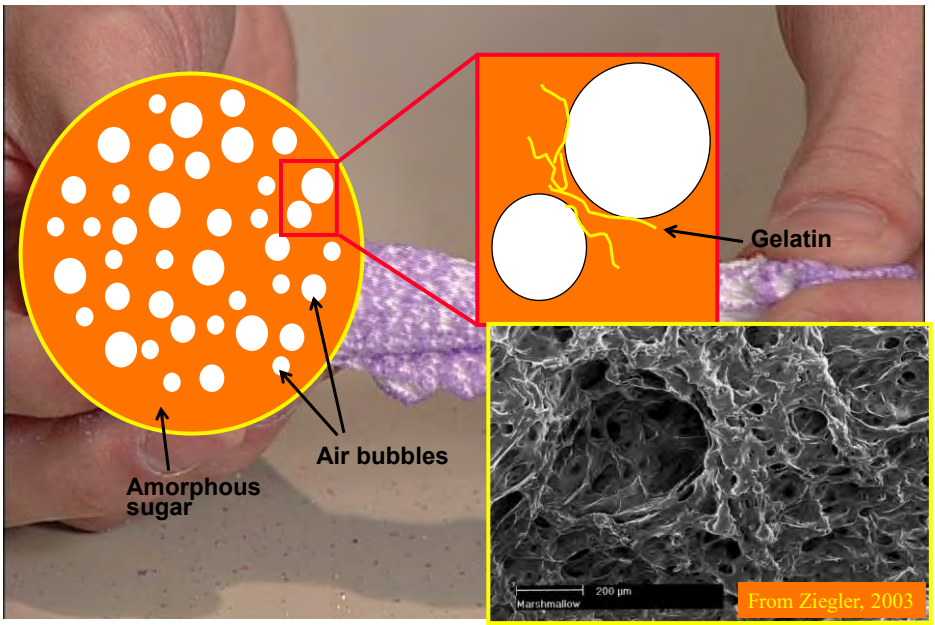
Marshmallow Peeps

Ingredients:

Sugar
Corn syrup
Gelatin
Potassium sorbate
Artificial flavors
Yellow #5
Carnauba wax
Air

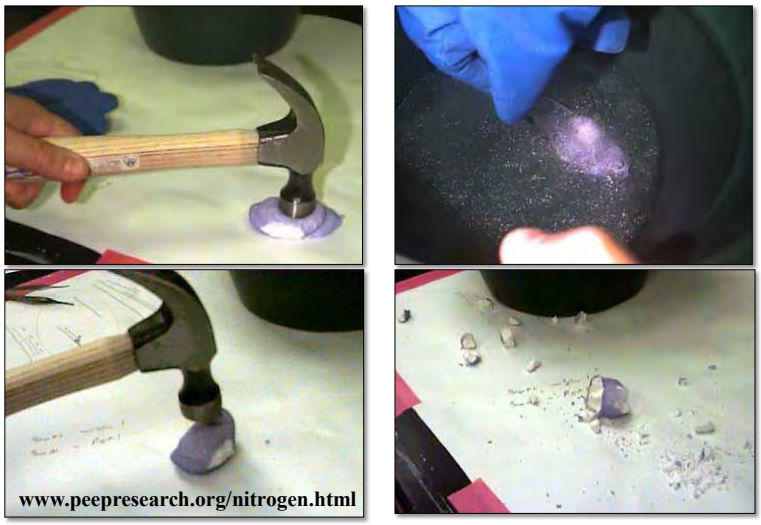
- More than half the volume of marshmallow
  - Marshmallow with a density of about 0.7 g/mL contains about half the volume in air
  - Lower density means more volume in air

Ungrained Marshmallow



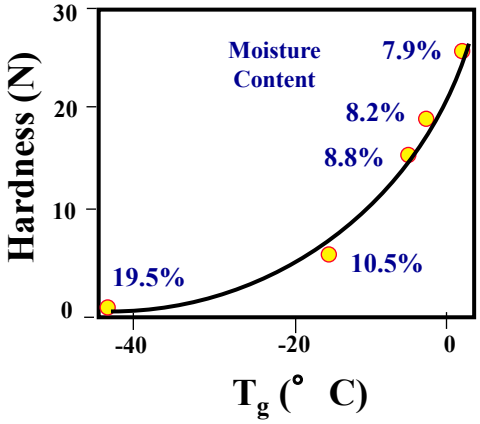
Amorphous or Glassy

- What happens when you dunk Peeps into LN2 and whack with a mallet? Why?



Marshmallow Texture

- Hardness (applied force) dependent on glass transition temperature (T_g)
  - In this study, T_g was changed by varying moisture content for same sugar matrix
  - The same thing happens when you let your Peeps sit in an opened package



From: Lim, Jia and Heenan (2004)

Sugar-Based Confections

- **Noncrystalline**
  - Liquid: Sugar-syrup confections
  - Glassy: Cotton candy, **Hard candy**
  - Amorphous: Ungrained **caramel**, nougat and marshmallow, taffy, etc.

- **Crystalline**
  - Rock candy, Powders, Tablets
- **Partially crystalline**
  - Grained mints, Fondant and creams, Grained caramel, nougat and marshmallows, Fruit chews, Panned candies, etc.

Hard Candy

- **Sugar glass - viscous, solid-like liquid**
  - Similar in molecular organization to window glass, except based on sugar instead of silica
  - Colors and flavors distributed uniformly

LifeSaver and Jolly Rancher

Sugar Glass

- **Clear, transparent – used in old Westerns**
  - Not stable to heat or humidity
  - Now replaced by polyurethane breakaway glass

Sugar Profile in Hard Candy

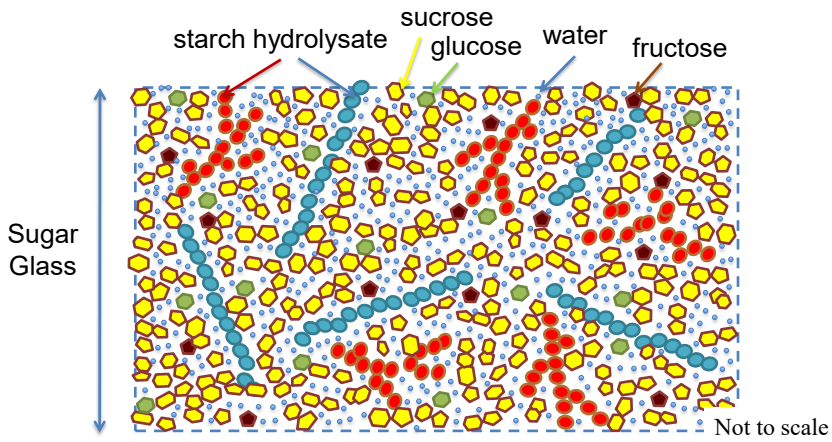
A recent analysis of 24 hard candies from Europe gave the following results:

Component	Content Range (%)	Average (%)
Water	2.1 - 5.1%	3.5
Fructose	0.2 - 8.6%	2.1
Glucose	1.1 - 12.4%	6.7
Sucrose	31.7 - 87.7%	49.2
Maltose	0.7 - 33.2%	7.0
Higher saccharides	12.9 - 44.9%	30.4

Smidova et al., Czech. J. Food Sci. 21(5), 185-191 (2003)

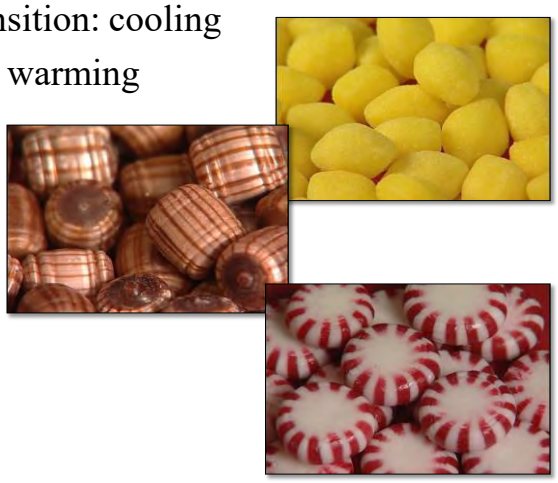
Complex Sugar Glass

- **Molecules have liquid-like disorder, but are packed tightly together in random arrangement**
  - Strong hydrogen bonding interactions also limit mobility



Hard Candies

- **Stability/quality of hard candy is directly related to the glass transition temperature (T_g)**
  - Fluid – solid transition: cooling
  - Or, solid – fluid: warming
- **Depends on:**
  - Types of sugars
  - Water content



Commercial Hard Candies

Sample	Moisture (%)	T_g (° C)
Brand 1 (5 flavors)	4.1±1.0	26.6±2.2
Brand 2 (5 flavors)	3.5±1.0	40.3±4.4
Brand 2 Sour Balls	2.8±0.5	41.2±1.6
Brand 2 Blue Mints	4.8±0.9	33.2±0.5
Brand 3 Wild Cherry	3.8	37.1
Brand 4 Cherry	1.7	40.2
Brand 5 Throat Lozenges	3.8±2.5	36.3±0.4

LifeSaver and Jolly Rancher?

T_g Affects Sensory and Stability

LifeSaver and Jolly Rancher

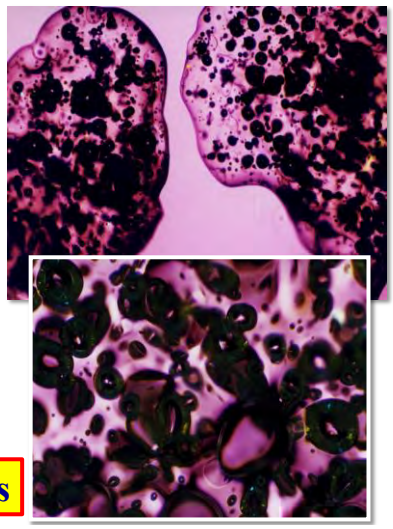
- **What differences between these two?**
  - Flavor release
  - Hardness/brittleness/crunchiness
  - Stability/end of shelf life
    - Moisture uptake – stickiness or graining
    - Flavor loss

Pop Rocks®

How are Pop Rocks® made?

Carbonated Hard Candy

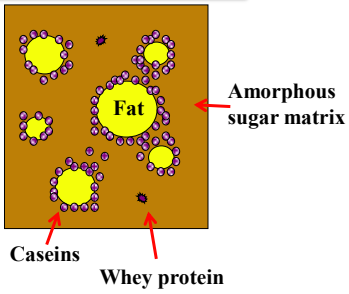
- **Hard candy syrup is gasified while still liquid**
  - 115° C (240° F), 4.1 MPa (600 psi) CO_2
- **Cool under pressure**
  - Solidifies bubbles in glassy matrix
  - Depressurization breaks candy into pieces
- **Bubbles pop when matrix wall dissolves in mouth**
- **Lactose increases hardness by raising T_g**



Pop Rocks

Caramel

- **Chewy candy based on dairy ingredient**
- **Ingredients:**
  - Corn syrup, sugar
  - Skim milk, palm oil
  - Whey, butter, salt
  - Artificial flavor
  - Lecithin



Browning of Sugars

- **Two classes of reactions that cause brown color and caramel flavor development**
  - Caramelization:
    - Sugars heated to elevated temperatures undergo degradation reactions.
    - In fact, caramel colors and flavors are produced by heating sugars under controlled conditions
  - Maillard browning:
    - Reducing sugars and proteins react, leading to color/flavor development

Louis Camille Maillard (1878-1936)

http://www.food-info.net/uk/colour/maillard.htm

Maillard Browning

- **Reaction between reducing sugar and protein**
  - Produces volatile flavors and aromas
  - Production of melanoidins (color compounds)
- **Complex series of reaction steps**
  - Sugar-amine condensation followed by Amadori rearrangement
  - Sugar dehydration and fragmentation, and amino acid degradation by Strecker reaction
  - Formation of heterocyclic N-containing polymers and copolymers

Maillard Browning

- **Rate of reaction depends on many parameters**
  - Nature of substrates
    - Type/concentration of sugars
    - Type/concentration of protein/amine source
  - Water
    - Optimal browning rate at intermediate a_w (0.5-0.8)
  - Temperature
    - Occurs even at room temperature, but faster rate at higher T
  - pH
    - Occurs faster at higher pH

Caramelization

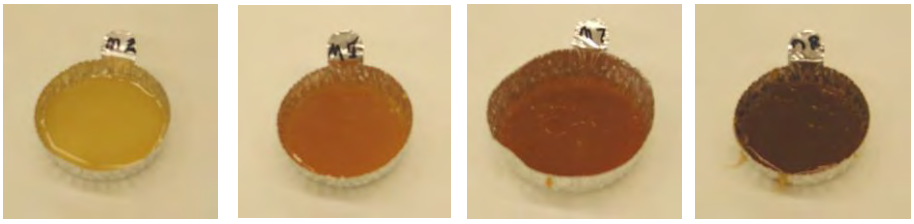
- Reaction of reducing sugars when heated to high temperatures to produce color, flavor and aroma products
  - Typically over 132-138° C (270-280° F)

Caramelization

- **Rate of reaction dependent on many factors**
  - Type/concentration of sugars
  - Temperature – needs very high temperatures > 270-280° F
  - Water content
  - pH

http://whatscookingamerica.net/Sauces_Condiments/CarmelizingSugar.htm

Effect of Protein on Browning



Sugar, corn syrup and (<1%) evaporated milk
Sugar and corn syrup only

230° F | 240° F | 250° F | 260° F

Caramel Cooking Methods

- **Gourmet caramel**
  - Brown sugars, add cream, heat to 115-118° C
    - Based primarily on caramelization of sugars

- **Commercial caramel**
  - Mix everything together, heat slowly to 115-118° C
    - Based on Maillard browning reaction

Where's the Chemistry in Candy?

- Sweetener chemistry dominates all candy
  - Sweetness, physical state, texture/structure, etc.
- Hydrocolloid chemistry
  - Gummies and jellies
- Flavor/aroma and color chemistry
  - This is what sells candy
- Rubber chemistry
  - Chewing and bubble gum
- Reaction chemistry
  - Caramelization, Maillard browning, inversion/hydrolysis
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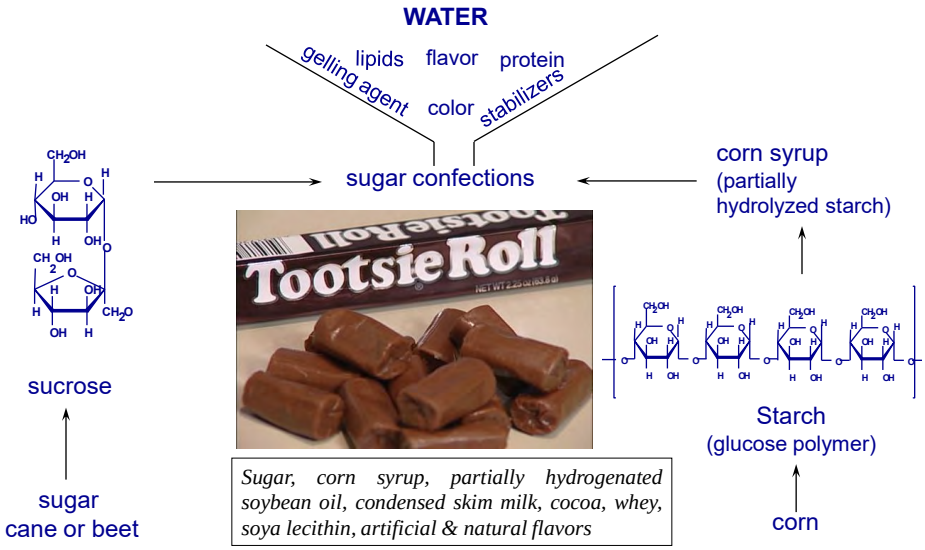
Exam Question
What type of candy are Tootsie Rolls?



Tootsie Rolls

1) Chewy candy
2) White caramel flavored with cocoa
3) Partially crystalline with a “short” texture
4) All of the above

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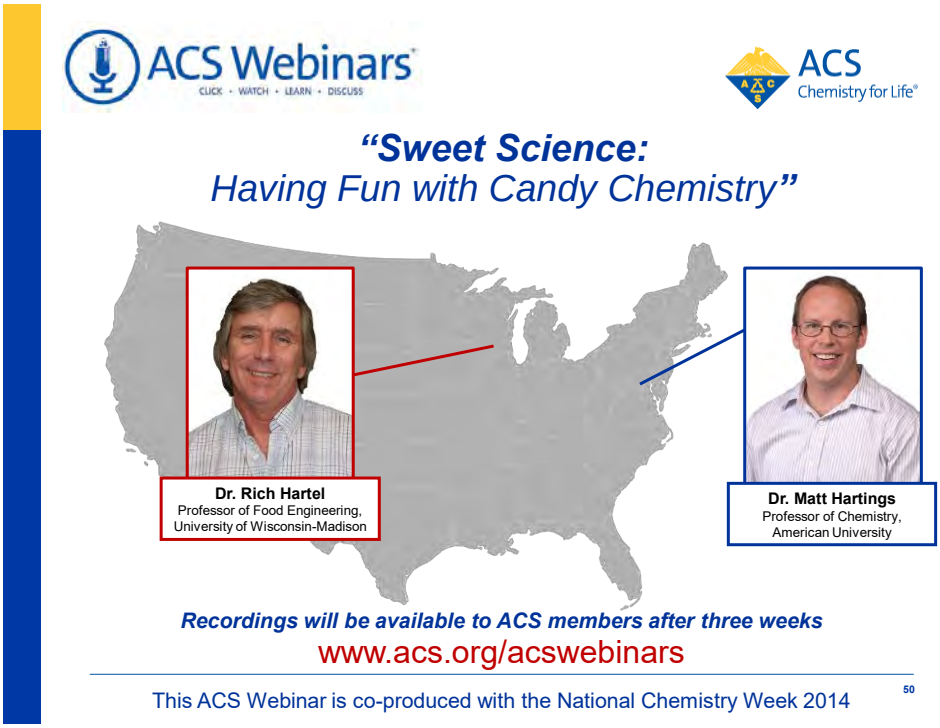

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