Cellulose Derivatives in Food Applications

Dow Wolff Cellulosics

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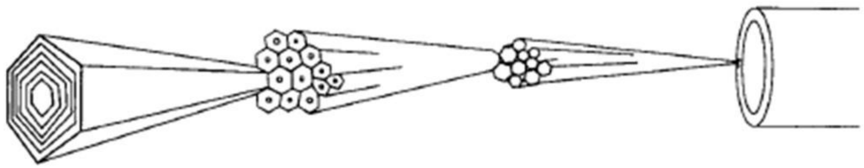
Agenda

- **Introduction to Cellulose**
- **Food Approved Cellulose Derivatives**
  - *Key Properties*
  - *Functions*
  - *Common Applications*
- **Most Widely Used Cellulose Ethers in Food Industry**
  - Methylcellulose (MC)
  - Hydroxypropyl Methylcellose (HPMC)
  - Sodium Carboxymethylcellulose (CMC)
- **Q&A**

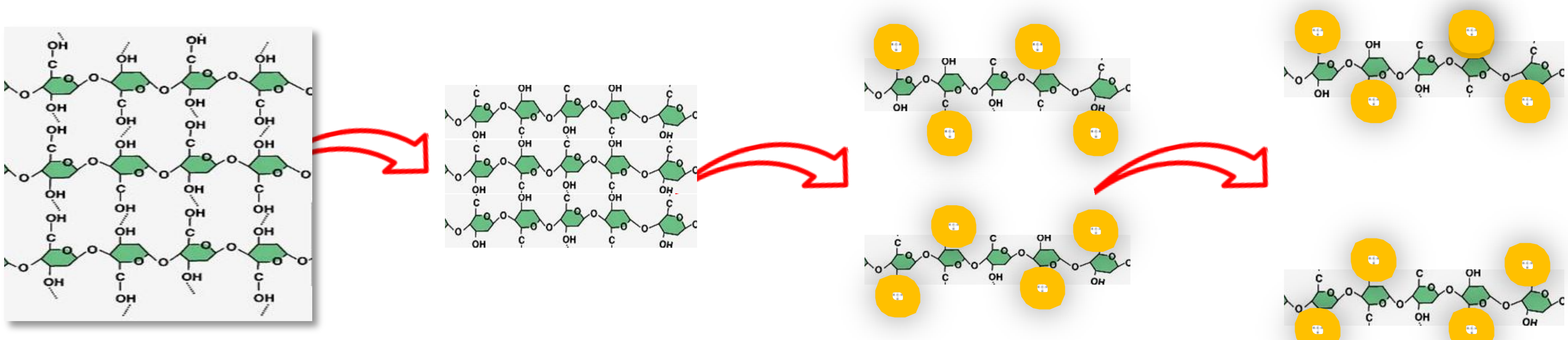
What is Cellulose?



Cell walls are made up of cellulose microfibrils (~70%) in a matrix of hemicelluloses (15%), pectins (10-15%), and lignins (2-5%), with a hierarchical structure.

- Worlds most abundant naturally occurring organic substance
- Cellulose comes from plants, trees and vegetable matter
- As such, it has always been part of the human diet and a source of dietary fiber
- In its natural state, cellulose is not soluble in water (chains of cellulose are very tightly bound to each other by H-bonding)

Cellulose Ethers



Water Insoluble

Water Soluble

Cellulose Derivatives for Food

- First cellulosics research work begun in 1920's in Germany
- Applications in foods (USA) starting in late 1940's.
- High purity (≥ 95% water-soluble dietary fiber)
- Non-digestible
- Non-fermentable - no gas
  - Related to form of 1,4-β-glycosidic bonds between glucose units
- Non-allergenic
- GRAS status

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- Q&A

Types of Cellulose Derivatives for Food

Physically Modified Cellulose

- Microcrystalline Cellulose (MCC)

Cellulose Ethers

- Hydroxypropylcellulose (HPC)
- Ethylmethylcellulose (MEC)
- Ethylcellulose (EC)
- **Methylcellulose (MC)**
- **Hydroxypropyl Methylcellulose (HPMC)**
- **Sodium Carboxymethylcellulose (CMC)**

Microcrystalline Cellulose (MCC)

Properties

- **Thixotropic**
- **Shear Thinning – Reversible**
- Heat Stable
- Nonionic
- Powdered & Dispersible Grades

Functions/Applications

- Opacifying Agent
- Foam Stabilizer
- Anti-caking agent
- Emulsifier
- Freeze Thaw Stability

Cheese (powdered,shredded) Beverages, Confections, Salad Dressings, Sauces, Whipped Toppings

*Labeled as Microcrystalline Cellulose or Cellulose Gel

Hydroxypropyl Cellulose (HPC)

Properties

- Nonionic
- Surface Active
- **Insoluble in Hot Water >40 C**
- **Soluble in Organic Solvents**
- **Thermoplastic**

Functions/Applications

- Foam Stabilizer
- Film Former (Flexible)

Whipped Toppings, Edible Coatings, Confection Glazes, Extruded Foods

*Labeled as Hydroxypropyl Cellulose or Modified Cellulose

Ethylmethyl Cellulose (MEC)

Properties

- Nonionic
- pH Stable
- **Precipitates From Solution Above 60C – (reversible upon cooling)**
- Not widely used

Functions/Applications

- Thickening Agent
- Filler
- Anti-Clumping Agent
- Emulsifier

Non Dairy Creams, Low Calorie Ice Creams, Whipped Toppings, Mousse

*Labeled as Ethylmethylcellulose, methylethylcellulose or Modified Cellulose

Ethylcellulose (EC)

Properties

- Nonionic
- **Hydrophobic**
- **Soluble in Organic Solvents**
- **Thermoplastic**

Functions/Applications

- Film Former
- Flavor Fixative
- Limited Food Approval

Flavor Encapsulation,
Moisture Barrier Films,
Fruit/Vegetable Inks

*Labeled as Ethylcellulose

Methylcellulose & Hydroxypropyl Methylcellulose (MC & HPMC)

Properties

- **Reversible Thermal Gelation**
- Cold Water Soluble
- pH Stable
- Wide Viscosity Range

Functions/Applications

- Binding
- Boilout Control
- Film Former
- Freeze Thaw Stability

Formed Foods, Fillings, Sauces, Whipped Toppings, Gluten Free Baked Goods

*Labeled as Methylcellulose, Hydroxypropyl Methylcellulose, Modified Cellulose

Sodium Carboxymethylcellulose (CMC)

Properties

- **Anionic**
- **pH Sensitive**
- **Interacts with Proteins**
- High Water Holding Capacity

Functions/Applications

- Freeze Thaw Stability
- Protein Protection
- Thickener
- Texture Control

Frozen Foods, Baked Goods, Tortillas, Soups, Sauces, Beverages

*Labeled as Sodium Carboxymethylcellulose or Cellulose Gum

Agenda

- Introduction to Cellulose

- Food Approved Cellulose Derivatives
  - *Structure – Function Relationships*
  - *Common Applications*

- **Most Widely Used Cellulose Derivatives in Food Industry**
  - **Methylcellulose (MC)**
  - **Hydroxypropyl Methylcellose (HPMC)**
  - Sodium Carboxymethylcellulose (CMC)

- Q&A

Methylcellulose (MC)
Hydroxypropyl Methylcellulose (HPMC)

MC & HPMC Common Applications

- Bakery, Gluten Free
- Fillings
- Sauces
- Formed/Extruded Foods
- Salad Dressings/Marinades
- Whipped toppings
- Batters/Coatings
- Meat/fish preparations
- Beverage Emulsions

MC & HPMC – Advantages

- Broad viscosity range – from very low to extremely high
  - *19 – 250,000 cPs (2 %, Brookfield)*
- Always available in high quality (not dependant on harvesting)
- High degree of purity (> 99.5 %)
- Conformity of all standards for food and pharmaceutical applications
- Narrow specifications for all relevant product parameters
- Prepared from wood pulp → GMO free

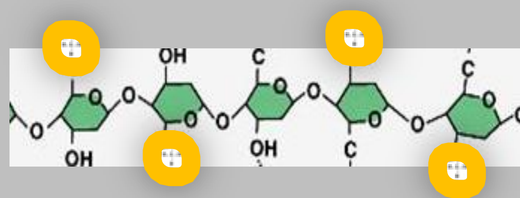
MC & HPMC - Key Properties/Functions

- ***Reversible Thermal Gelation – (varying gel strengths)***
- Wide Viscosity Range
- Thickening
- Moisture Control (Cold Water Binding)
- Emulsification, Encapsulation & Film Formation
- Binding
- Air Entrainment & Foam Stability
- Freeze Thaw Stability
- Provides Soluble Fiber

MC & HPMC Chemistry

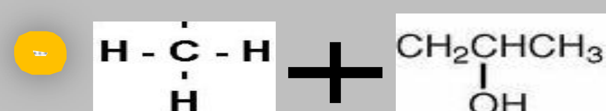
- Methylcellulose (MC)
- Hydroxypropyl methylcellulose (HPMC)

Based on the substituent group



Methyl Group

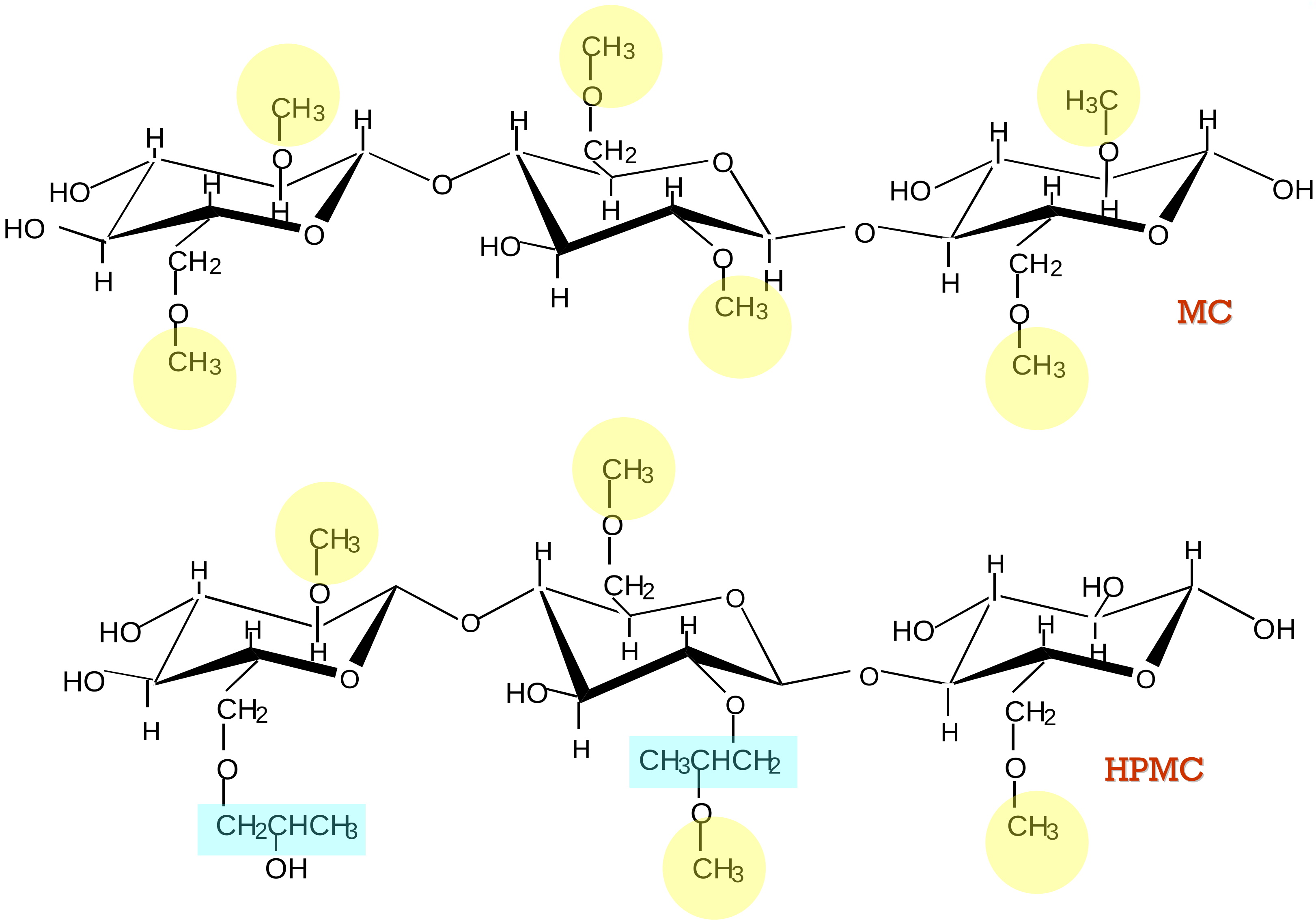
Methylcellulose (MC)



Methyl Group Hydroxypropyl Group

Hydroxypropyl methylcellulose (HPMC)

MC & HPMC - The Chemistry



Chemistry- Functionality

Different chemistries have differences in physical properties

- Dissolution temperature
- Gelation Temperature
- Gel Strength
- Surface Activity

Differences are caused by:

- The substituent group (Ratio of methyl/hydroxpropyl groups)
- Relative numbers of the groups (Degree of Substitution: DS)
- Average chain length of the product (Molecular Weight)

MC & HPMC - Different Viscosities

Thick

~ 50,000 mPa.s

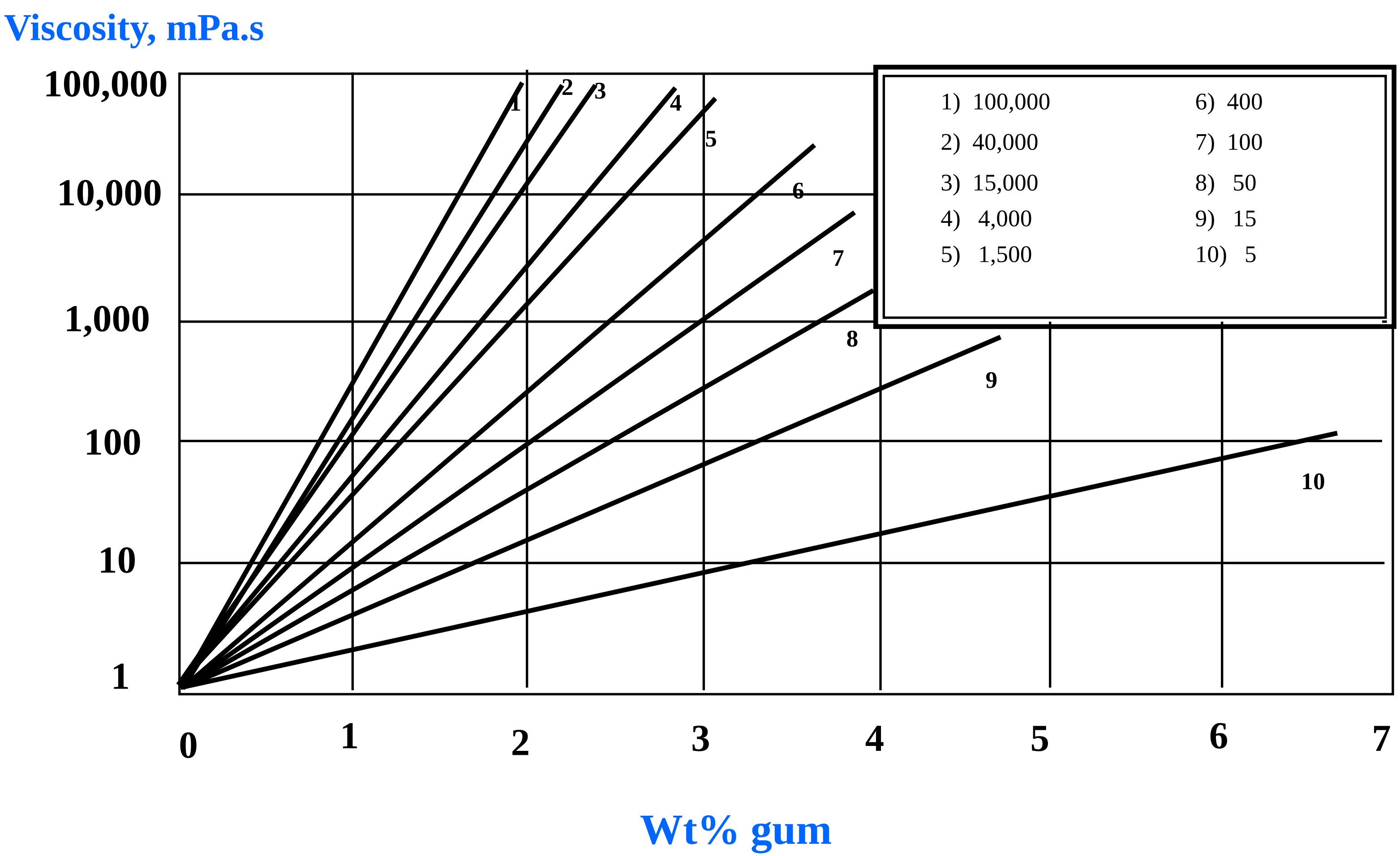
Medium

~ 4000 mPa.s

Thin

~ 50 mPa.s

Viscosity Range



- A rough rule -- For every 1% increase in concentration you will see a 8*x* increase in viscosity

MC & HPMC

Effect of Concentration

- Viscosity build is not linear

Effect of pH

- Viscosity is stable between pH = 3 and 11

Effect of Temperature

- MUST reach set hydration temperatures to become fully functional.

Effect of Salt and Sugar:

- May delay hydration and hinder viscosity development
- May precipitate MC & HPMC out of solution if too much salt or sugar
- May lower gelation temperature

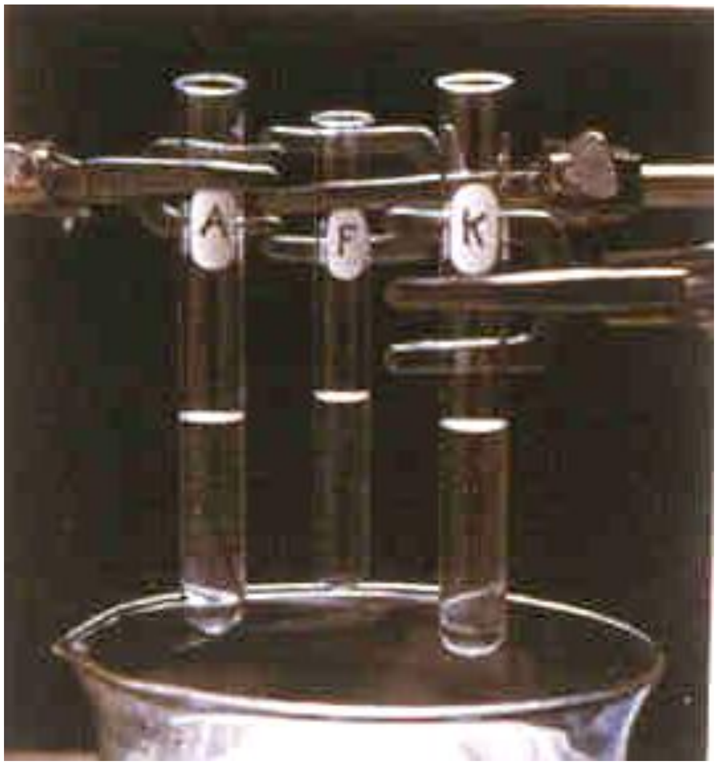
MC & HPMC – Effect of Temperature

	Hydration Range	Gelation Range	Gel Strength
High Gel MC	<50° F (10° C)	100 - 114° F (38 - 44° C)	Very Firm
Conv. MC	<55° F (13° C)	122 - 131° F (38 - 44° C)	Firm
HPMC	< 77° F - 85° F (25° C - 30° C)	143 - 194° F (62° C - 90° C)	Semi-Firm - Soft

REVERSIBLE THERMAL GELATION

MC & HPMC Reversible Thermal Gelation

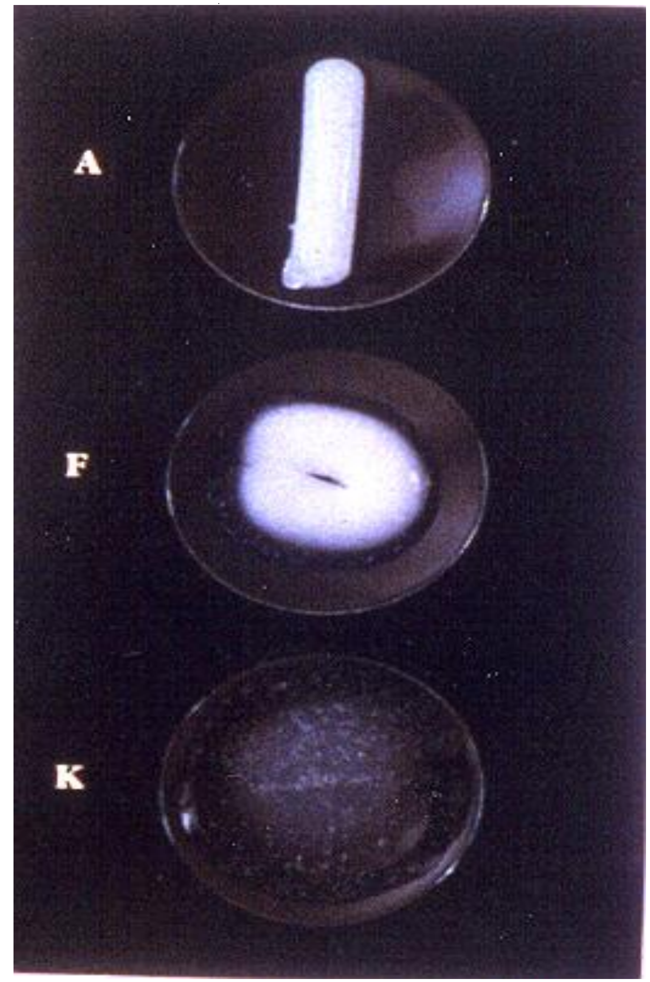
dowwolff CELLULOSICS Dow



2% MC & HPMC Solutions

Heating

Cooling

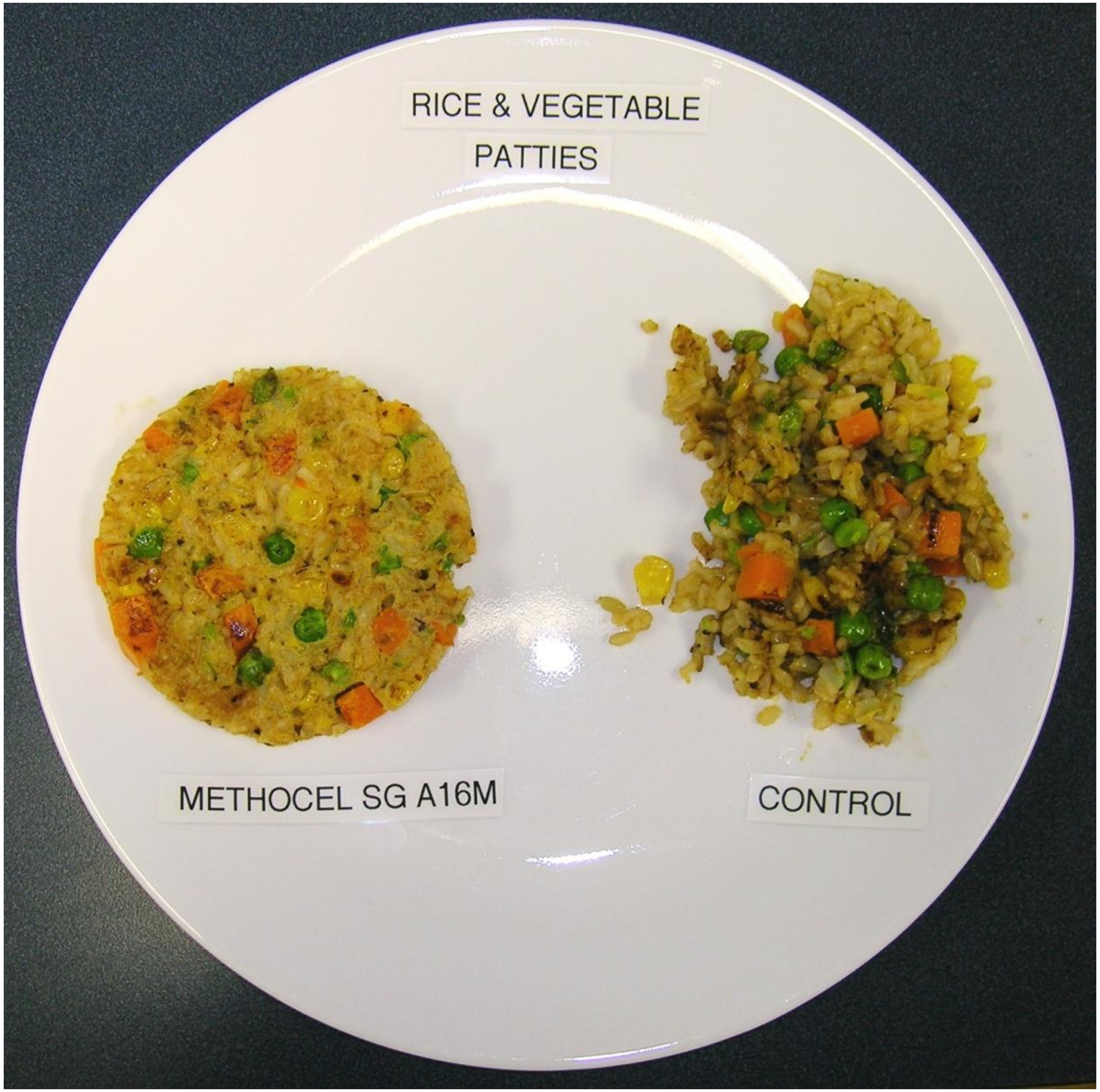


Gels obtained by heating 2% MC and HPMC Solutions

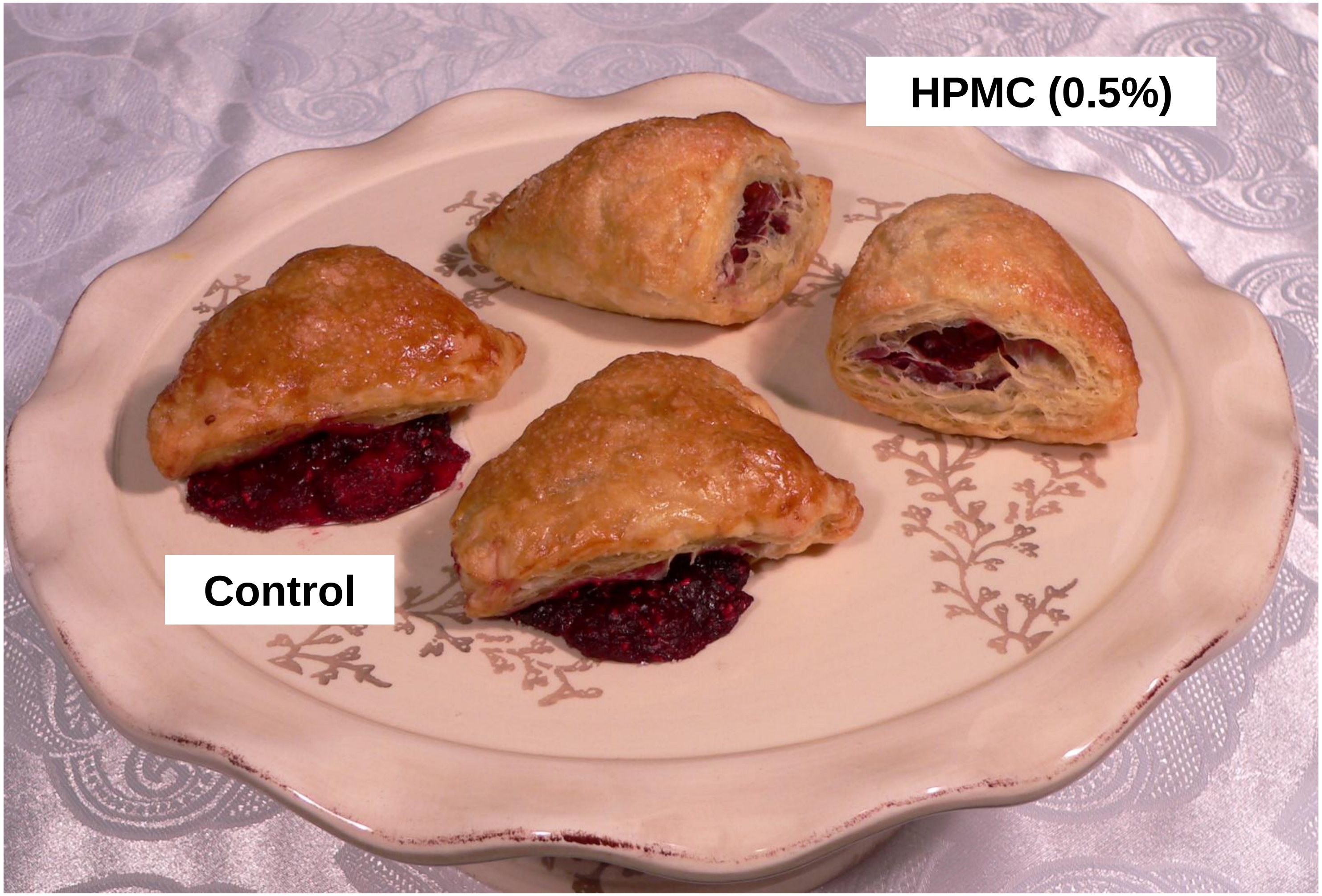
MC & HPMC – Thermal Gelation Benefits

- Controls moisture movement
- Retains shape at high temperatures (Boil out control)
- Reduces oil uptake
- Improves coating adhesion (along with film formation)
- Works alone (no other additives necessary)

MC & HPMC - Thermal Gelation - Binding/Shape Retention



MC & HPMC – Thermal Gelation – Boil Out Control



*Note: maximum sugar content must be less than 50%.

MC & HPMC – Thermal Gelation – Boil Out Control

0.4% MC–vs- 0.15% Xanthan, 0.15% Guar, and starch control

Before Baking

MC & HPMC – Thermal Gelation – Boil Out Control

After Baking

MC & HPMC – Thermal Gelation – Fat Reduction

In French Fry Coatings:

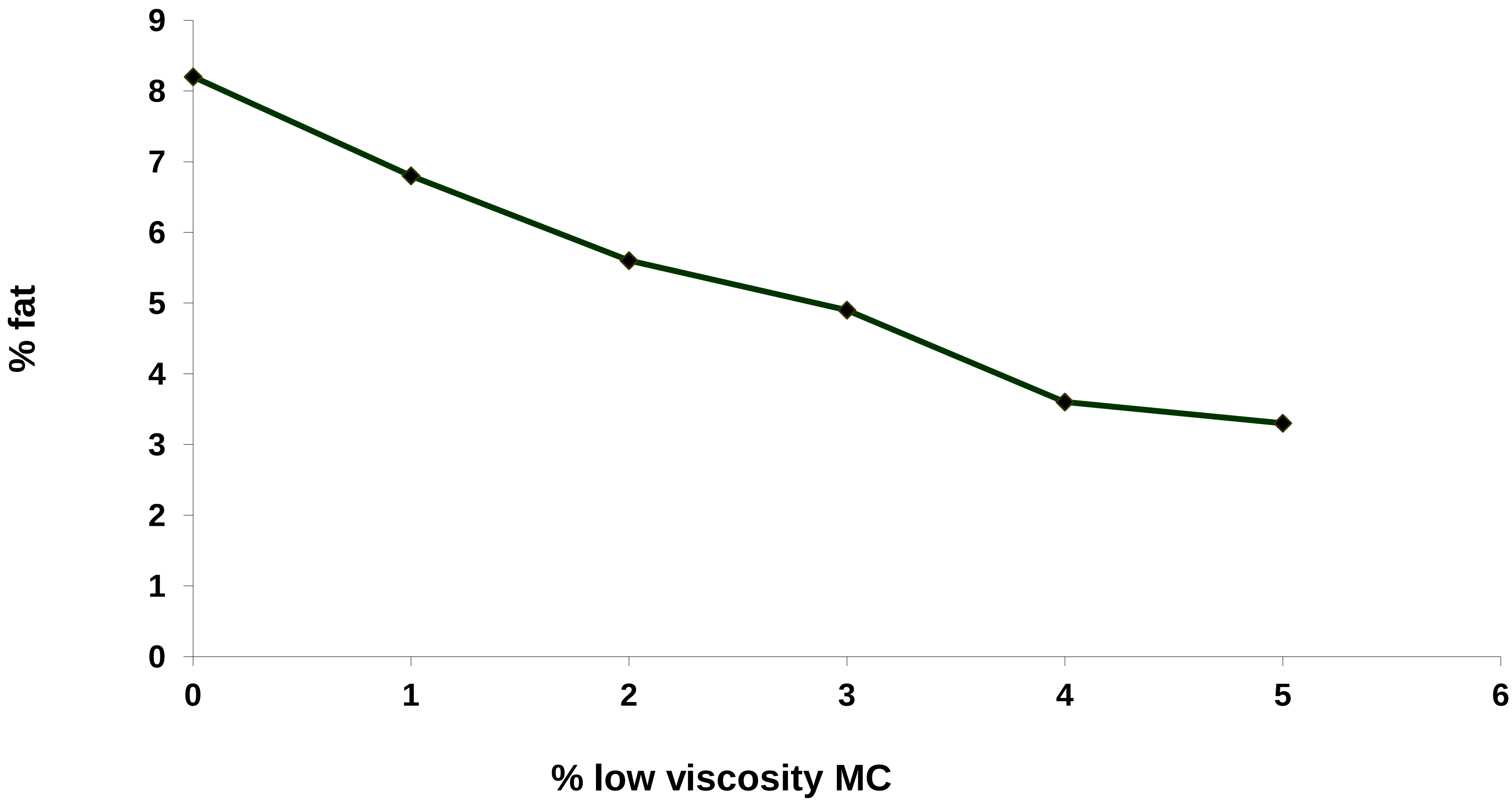
Most important property is gel strength → gel maintains its integrity during frying

- MC has the highest gel strength of the chemistries
- Least surface active

MC will also gel at the lowest temperature

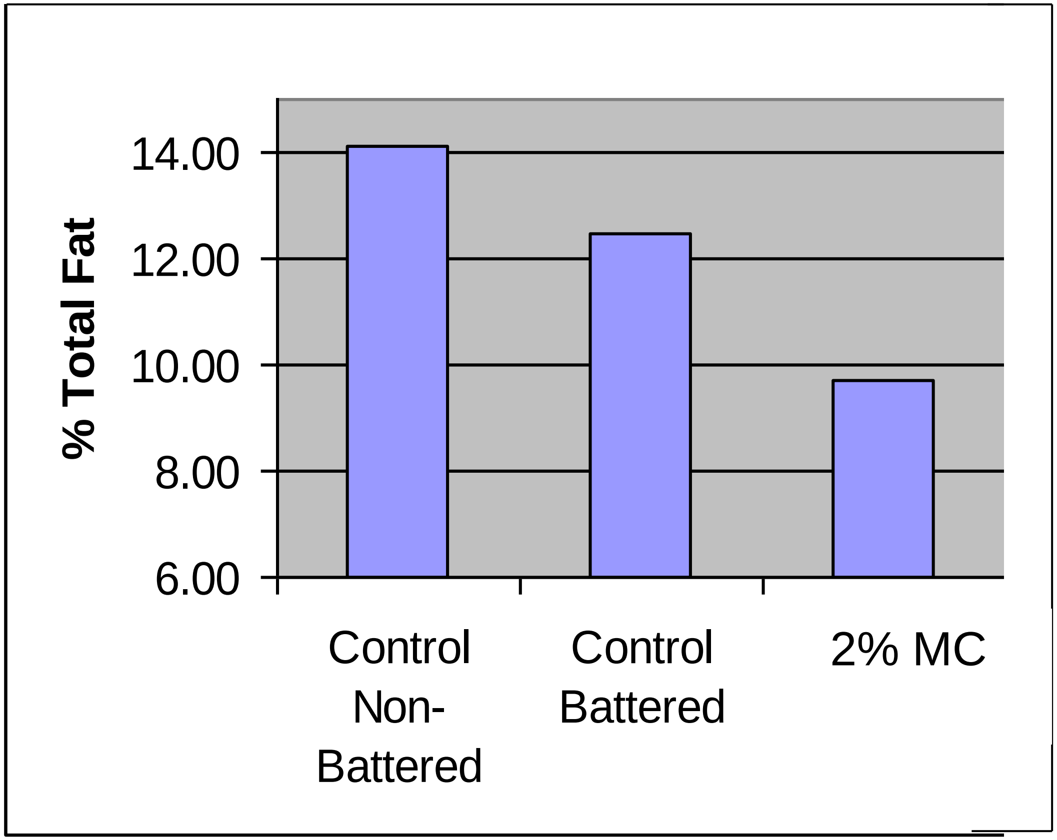
- Ensures film is formed prior to fat being absorbed

Fat Uptake Reduction With Increasing Methylcellulose Solution Strength



Fat Reduction in French Fry Batters

- Achieves ~30% reduction in fat
- Will enable a "***Reduced Fat***" claim in retail markets
- Note that the batter alone does provide some barrier function~11%



MC & HPMC – Thermal Gelation – Fat Reduction

Cinnamon Buns

A4M Reverse Emulsion 09/26/11

Ingredient	Grams	Weight %
Butter	50.00	19.23
METHOCEL A4M	2.00	0.77
Hot Water	48.00	18.46
Brown Sugar	150.00	57.69
Cinnamon	10.00	3.85
TOTALS	**260.00**	**100.00**

Control 09/26/11

Ingredient	Grams	Weight %
Butter	100.00	38.46
Brown Sugar	150.00	57.69
Cinnamon	10.00	3.85
TOTALS	**260.00**	**100.00**

MC & HPMC – Thermal Gelation – Fat Reduction

Methylcellulose be used to improve the juiciness and mouthfeel of an already lean beef patty (without adding extra fat)

Formulation

- 88.4% Lean beef (90% fat free)
- 10.0% Cold water (<40F)
- 1.2% **Methylcellulose**
- 0.4% Salt

Total fat**: 10% fat (from meat)* ***(11.3g fat per ¼ lb patty)

Store bought patty = ***20% (22.6g fat per ¼ lb patty) = 50% fat reduction***

FILM FORMATION

Surface Activity - 1% Gum Solutions

Chemistry	Surface Tension (Dynes/cm)
Water	72
Xanthan	69
CMC	68
Na Alginate	62
PG Alginate	58
MC	53-59
HPMC	45-55

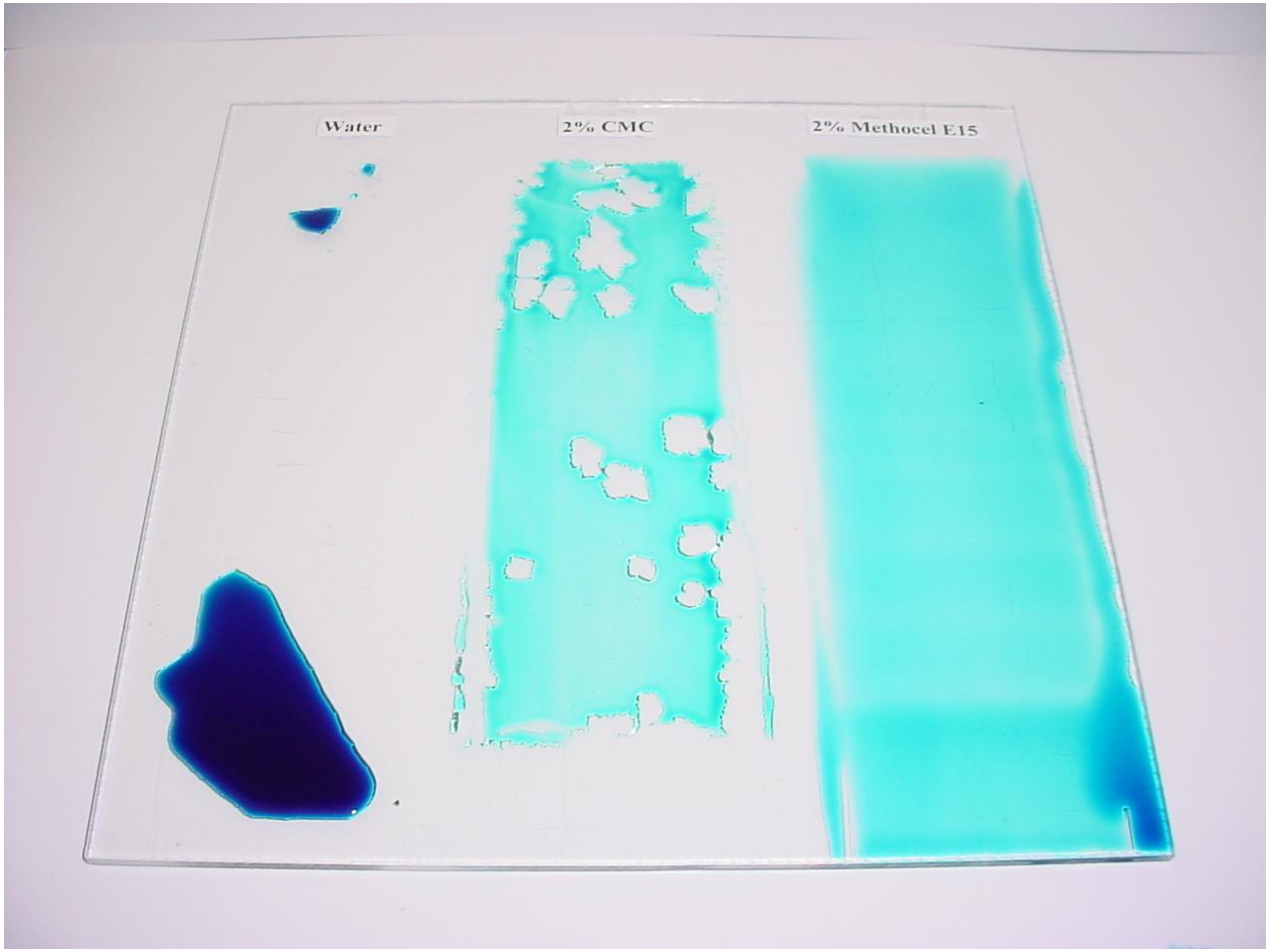
Chemistry	Surface Activity
MC	Least
HPMC	Most

N. Sakar – CRI Report #823965, 1982

MC & HPMC – Film Formation Benefits

- Improved adhesion of coatings
- Reduced oil pick up (also a function of thermal gelation)
- Increased “hold time” under heat lamp
- Reduced runoff in oven
- Reduced browning

MC & HPMC – Film Formation

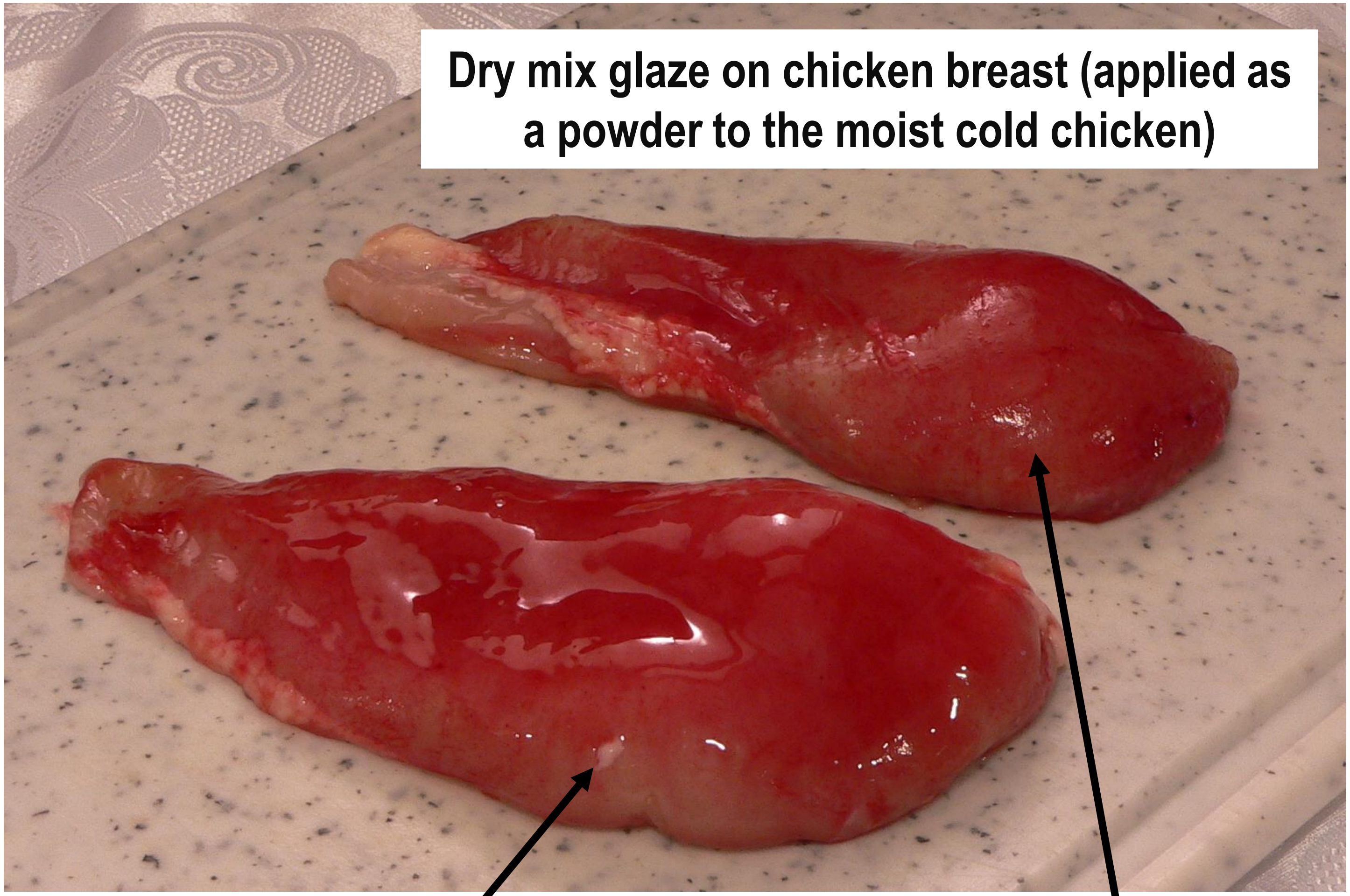


MC & HPMC are very surface active

MC & HPMC – Film Formation

Tri-colored/tri-flavored film for a coating, as an insert between layers, encapsulation, etc

MC & HPMC – Film Formation - Glazes

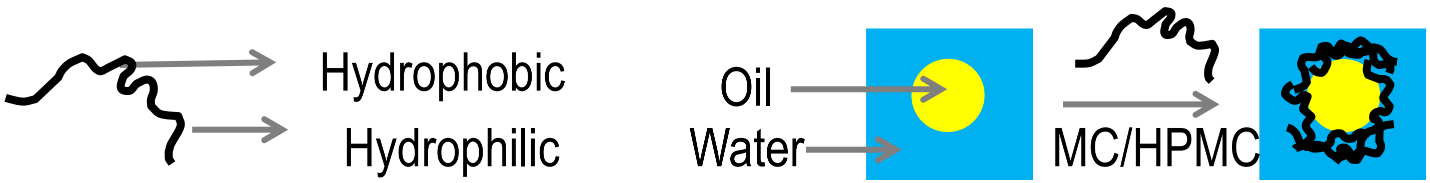


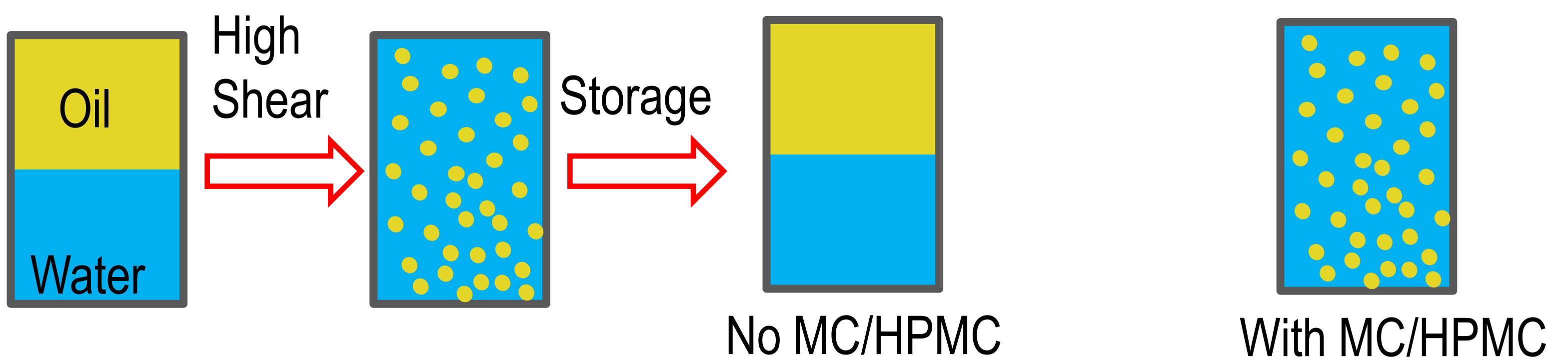
with METHOCEL   **<u>and</u>**   **without METHOCEL**

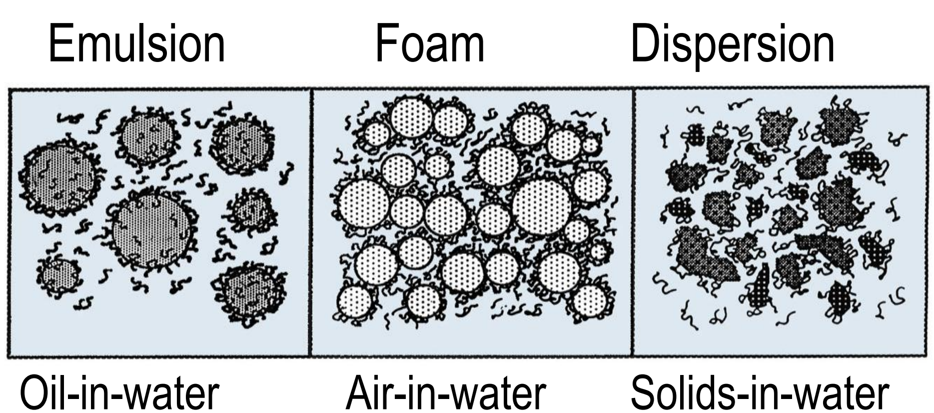
FOAM
STABILITY

Surface Activity of MC & HPMC

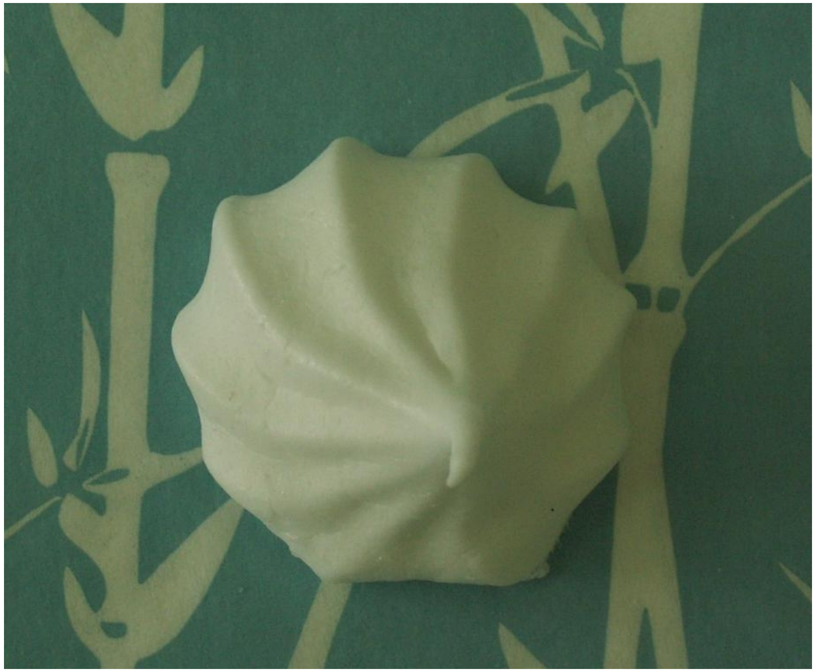
MC & HPMC stabilize emulsions, foams and dispersions by both decreasing the surface tension and increasing the viscosity



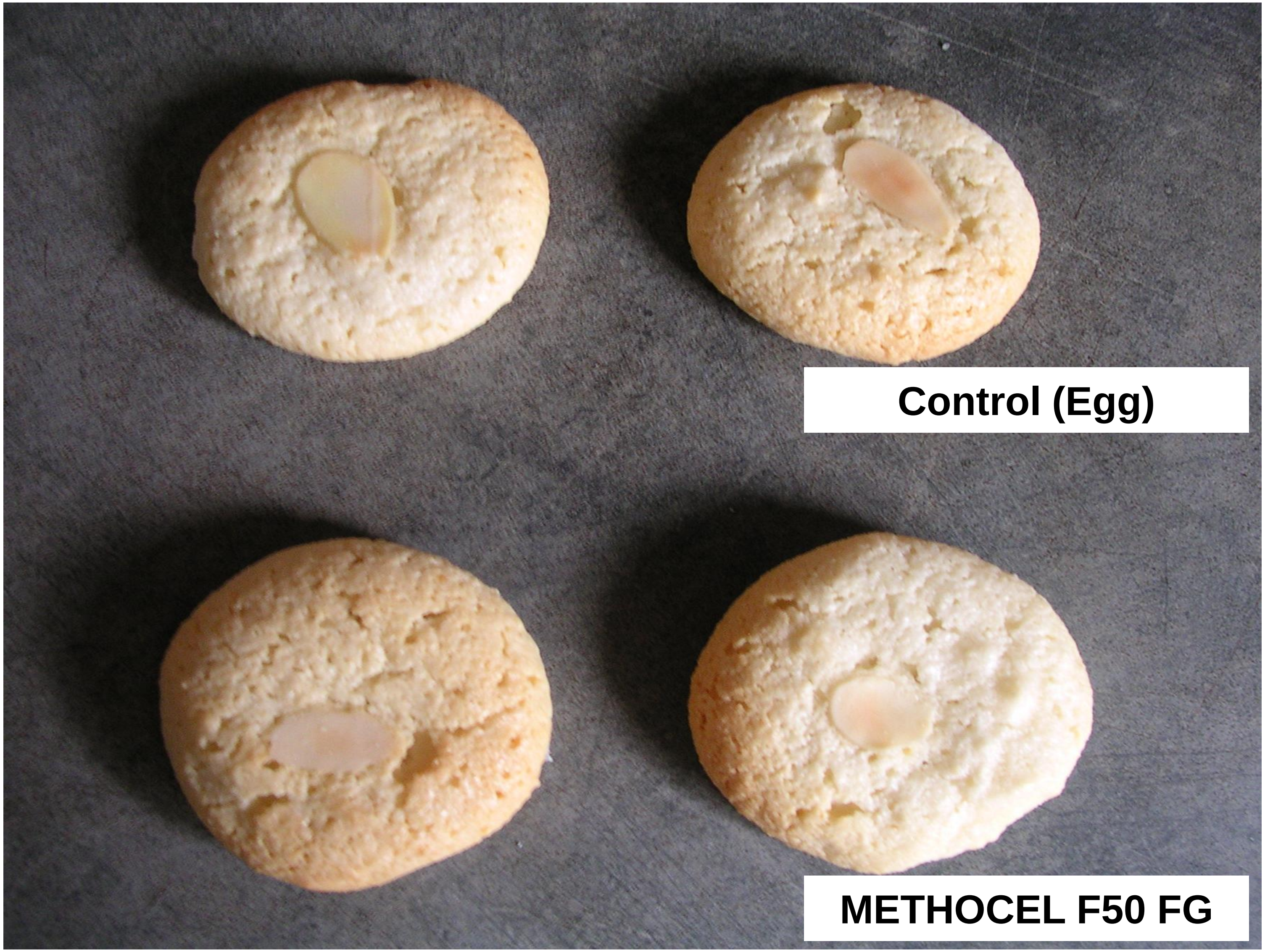




Eggless Meringue



MC & HPMC – Foam Stability



Moisture

Control

MC & HPMC – Moisture Migration Control

- MC & HPMC reabsorb moisture when food cools after heating and retains moisture during shelf storage.
- Cold moisture migration – in chilled and frozen storage (ice crystal control)

- **Where cold moisture migration control might be used**?
  - Baked goods (reduce staling)
  - Frozen doughs and batters (Cookie, Brownie, Rolls & Bread)
  - Frozen Cakes and Muffins
  - Fillings on dough based substrates

Moisture Control and Retention with MC & HPMC

Use of Multiple Properties

MC & HPMC – Using Multiple Properties

Gluten Replacement

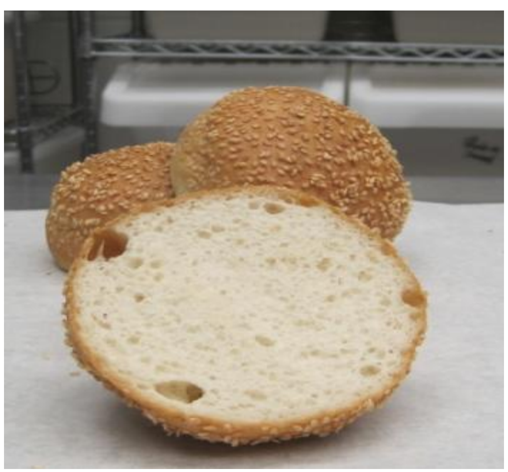
✓*Gel Strength*
Weaker Gel to ensure the bread can rise

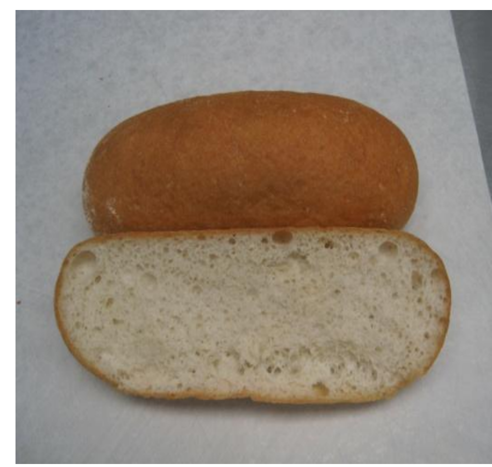
✓*Medium Viscosity*
Needs to be able to thicken dough
Too thick - Will not raise during proving or baking & difficult to work with

HPMC

✓*Gelation Temp*
Higher Gelation Temp (70-90 ^{0}C) -to gel later during the baking process

✓*Surface Activity*
Enhances and stabilizes air pocket structure in dough





MC & HPMC – Using Multiple Properties

In Reformed Potato Products:

- Make **mash formable** in the cold (viscosity control)
- **Maintain shape** when fried and re-cooled (thermal gelation & viscosity)
- Dramatically **reduce bursting** leading to improved yields and better safety (thermal gelation, moisture management)
- Make mash slippery reducing starch damage during extrusion
- **Reduce oil uptake** (thermal gelation, film formation)

MC & HPMC – Using Multiple Properties

In Predusts:

- Increases **Batter Pick-up** (Viscosity)
- **Manages moisture** migration (thermal gelation, film formation)
- Prevents **batter blow-offs** (thermal gelation, film formation)

In Batters:

- **Reduced fat uptake** (thermal gelation, film formation)
- Increases **"hold time"** (thermal gelation, film formation)
- Preserves **crispiness** in oven reconstituted products (film formation)

How to Incorporate MC & HPMC in Food Systems

MC & HPMC - Incorporation Methods

- Dry Blending (flour, sugar,salt, spices, etc.)
  7:1 Dispersant/MC or HPMC ☺

- Food Oils (soy, corn, canola, cottonseed)
  5:1-8:1 Oil/MC or HPMC ☺

- Other Liquids (corn syrup, HFCS, glycerin) 😐

- Hot Processing Steps ☺ ☺

- Direct Cold Water ☹

MC & HPMC – Delayed Hydration Technique

Add MC or HPMC to hot system

- MC or HPMC won't hydrate in hot conditions
- Product (dips/soups/etc) will stay thin during hot HTST or UHT; thicken upon cooling

- Improves pumpability of hot filled products
- Better efficiency of heat transfer during processing – lower processing time
- Less burn on

MC – Starch Synergy

Methylcellulose has a synergistic effect when used in combination with modified waxy maize starches

- Reduce MC and starch levels – save on cost
- Fewer calories
- Increased hot cling
- Greater hot viscosity
- Less “starchy” mouthfeel in sauces

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Sodium Carboxymethylcellulose (CMC)

CMC – Common Applications

- Gluten-free and conventional breads
- Pancakes, wraps, tortillas
- Cakes and cookies: Dough and dry mixes
- Bakery creams, fruit preparations
- Glazes, coatings and toppings of bakery products
- Dairy products
- Soups, sauces, dressings, marinades
- Beverages and Wine
- Meat Products

CMC - Advantages

- Broad viscosity range – from very low to extremely high
  - *30 – 60,000 cPs (2 %, Brookfield)*
- Always available in high quality (not depending on harvesting)
- High degree of purity (> 99.5 %)
- Conformity of all standards for food and pharmaceutical applications
- Narrow specifications for all relevant product parameters
- Prepared from wood pulp → GMO free

CMC - Advantages

- Absolutely odorless and tasteless (e.g. Guar smells like beans)
- Absolutely clear and transparent solutions in water (unique in the world hydrocolloids)

CMC & HPMC

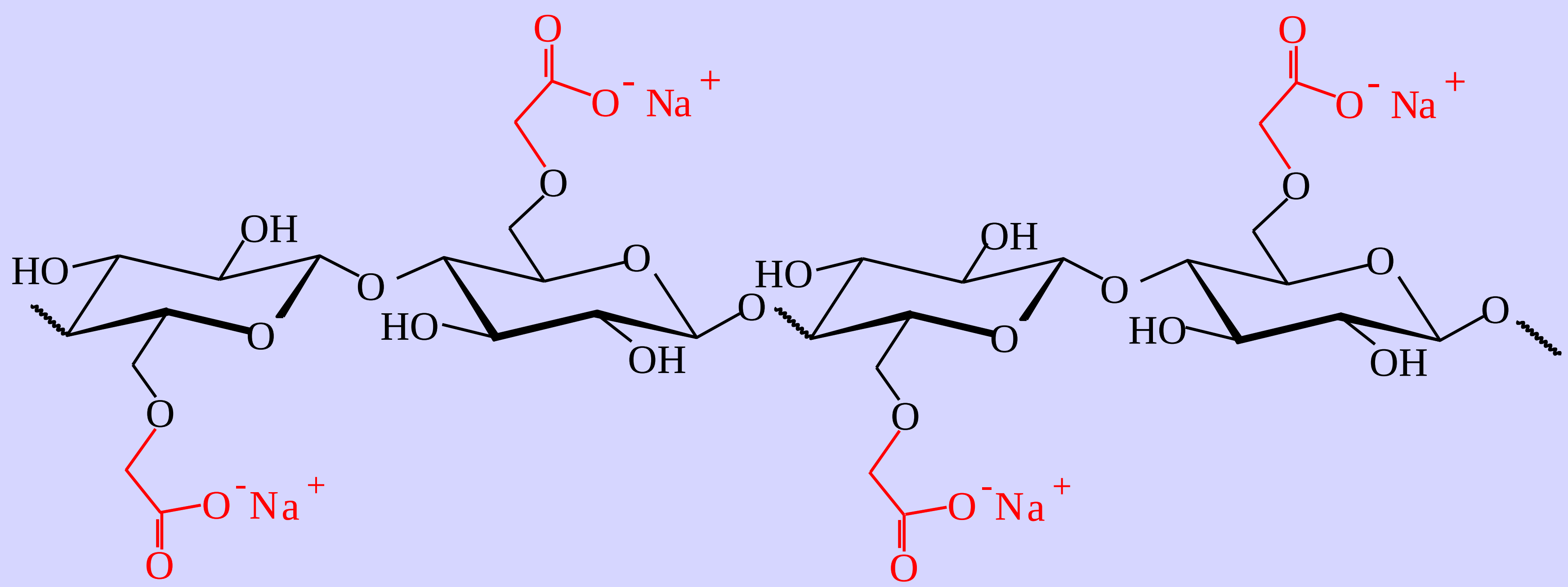
Guar Gum

Agar

CMC – Key Properties

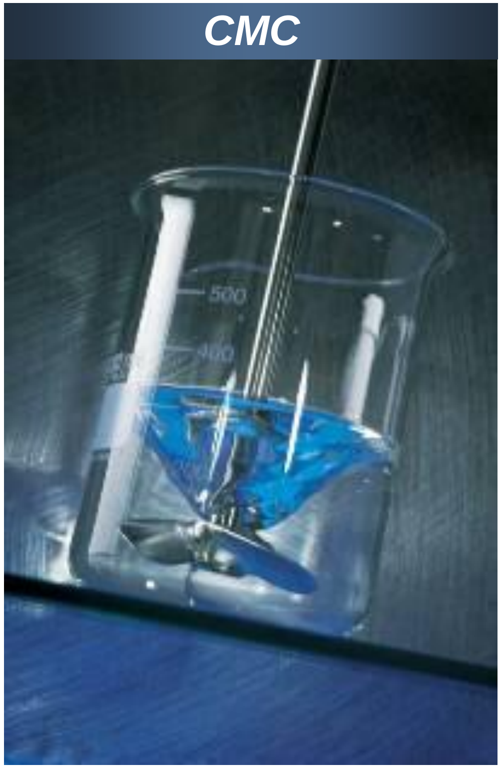
- Soluble in Cold and Hot Water
- Thickener
- Increased Plasticity and Elasticity (improved machinability)
- Freeze Thaw Stability
- High Water Binding
- Emlulsifier
- Protein protection
- Compatible With Other Hydrocolloids

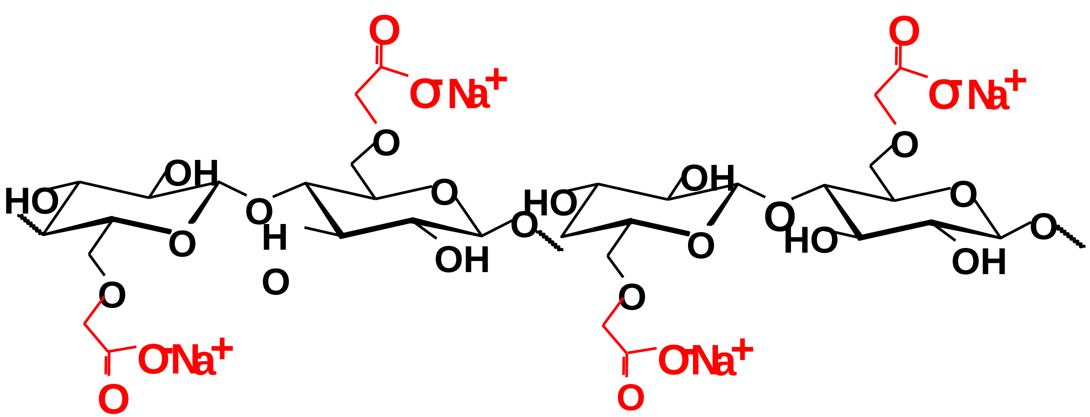
CMC – The Chemistry



CMC - Production

- CMC products are tailor made
- Main product characteristics are controlled by:
  - *degree of polymerisation (DP)*
  - *degree of substitution ⇨ DS*
  - *particle size*



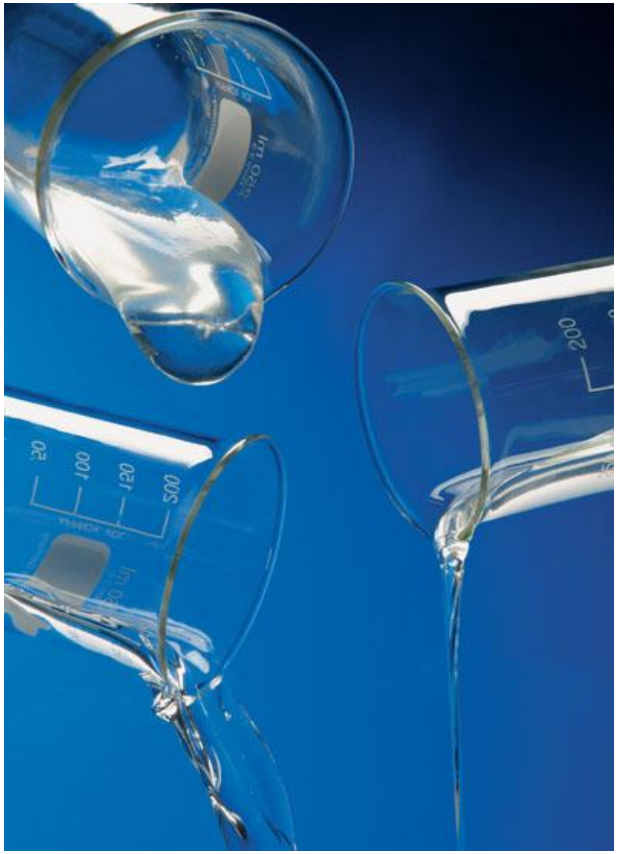


Sodium Carboxymethylcellulose (CMC)

CMC - Degree of Polymerization (DP)

DP = (Average Chain Length)

- Is controlled by the manufacturing process raw material (cellulose) source
- **Determines the viscosity** development of the CMC
- Range includes grades from low to extremely high viscosity



CMC - Degree of substitution (DS)

DS ⇨ Average Number of CM-groups per Glucose Unit

Impact of increasing DS 0.7 → 0.9

- Higher gloss
- Smoother flow behavior, less pseudoplastic
- Clearer solutions (no fibers)
- Higher stability in low water content products
- Higher salt tolerance

CMC - Particle Sizes

Powdered Grades

- Will Clump if attempt to put directly into solution
- Requires dry blending agent

Granular Grades

- Goes into solution without clumping
- Takes longer to hydrate

Instantized Grades

- Very good dispersibility in cold water
- Fast viscosity build up
- No lumping

CMC

Effect of Concentration

- Viscosity build is not linear (doubling will increase viscosity 6-10X)

Effect of Heat

- With increasing temperature the viscosity of the CMC solution decreases (reversible)
- At temperatures above 90C (194 F) **all CMC grades are thin flowing.**

Effect of Shear

- The higher the shear, the greater the thinning effect.
- Reverses and builds back viscosity after shear is removed

Effect of Salt Concentration

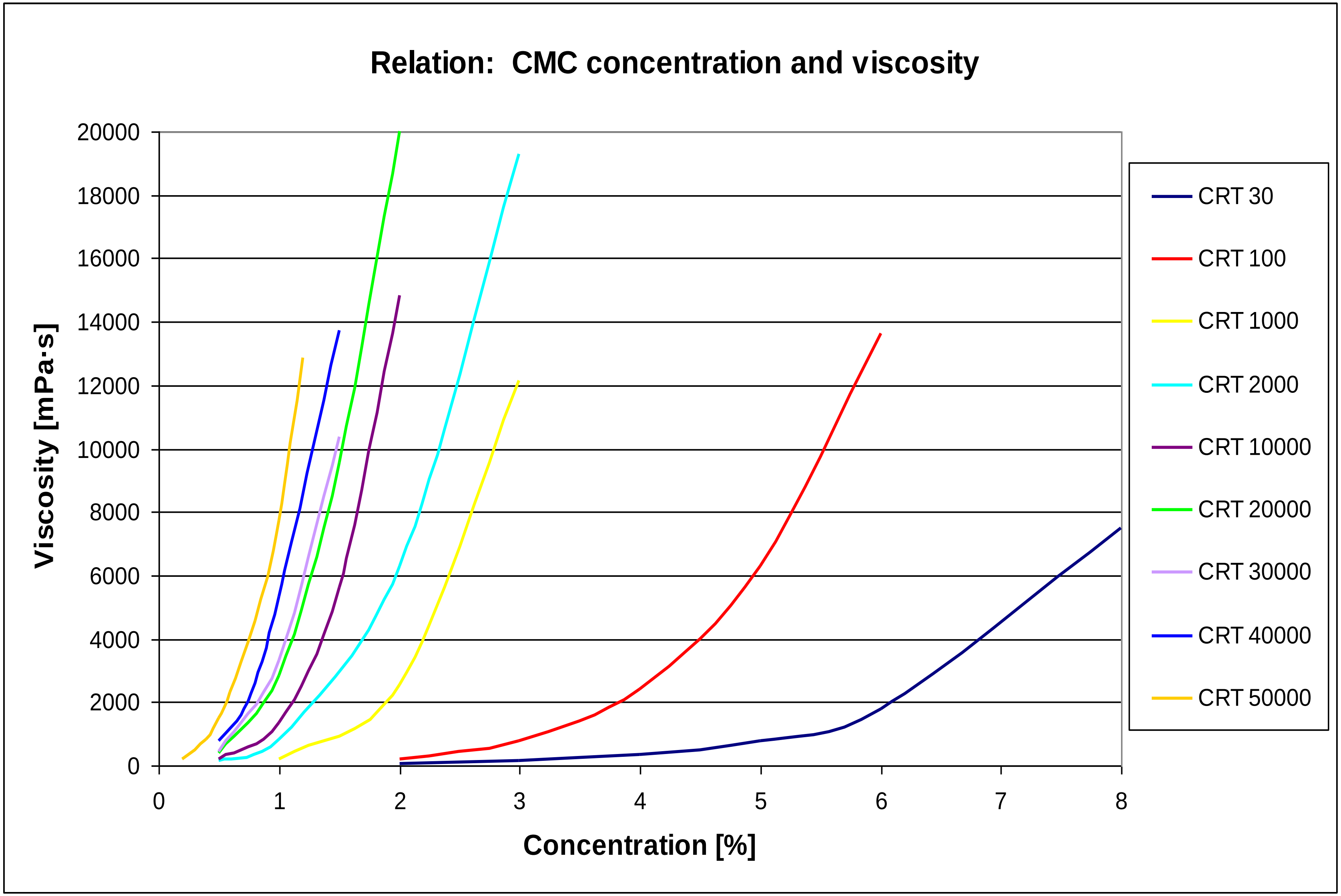
- Viscosity decreases as salt concentration increases

Effect of pH

- Maximum viscosity between pH 6.5 - 8.5
- Viscosity falls on each side of that range

CMC - Viscosity

dowwolff CELLULOSICS

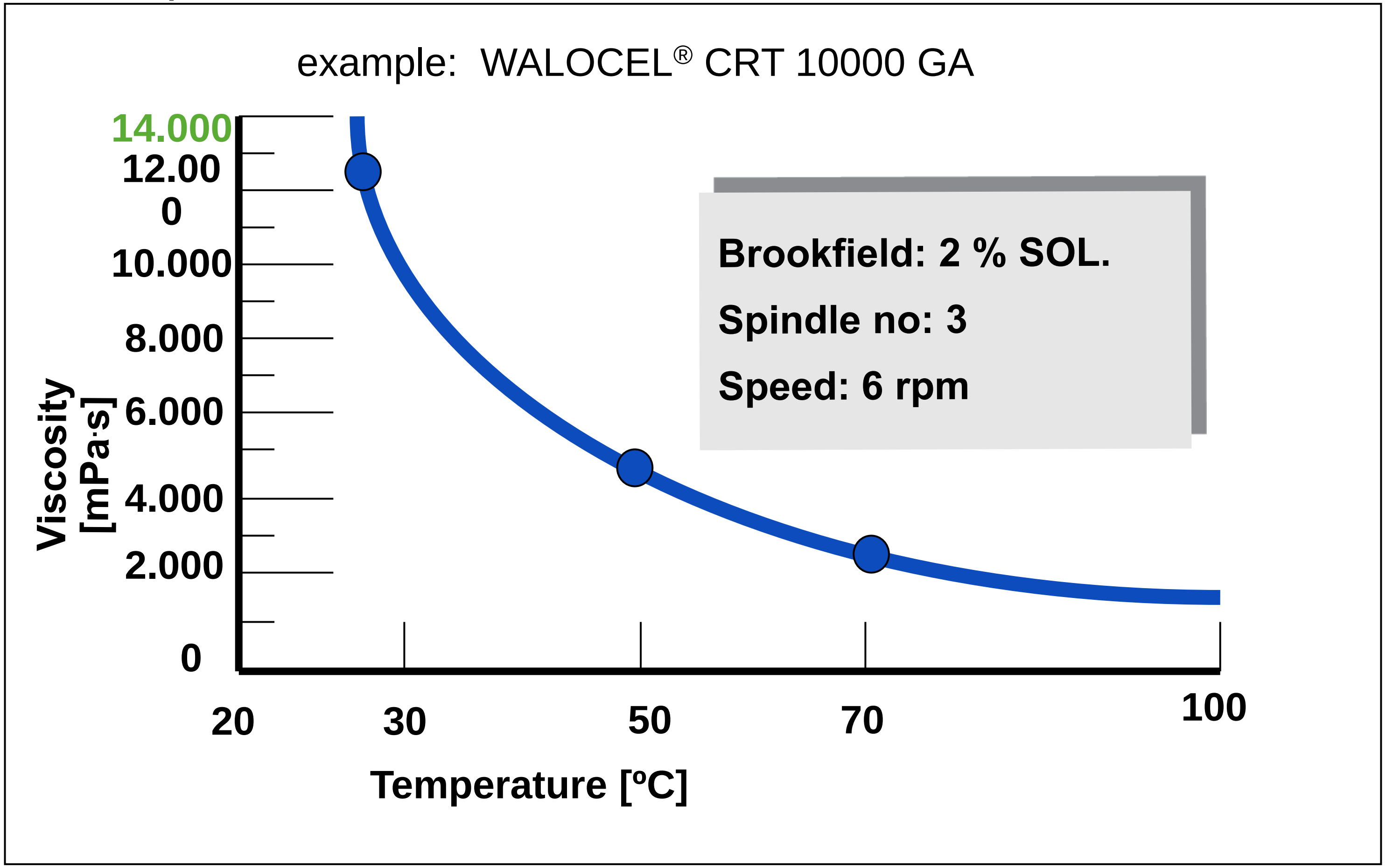


in water, 15 ° C, BF LVT

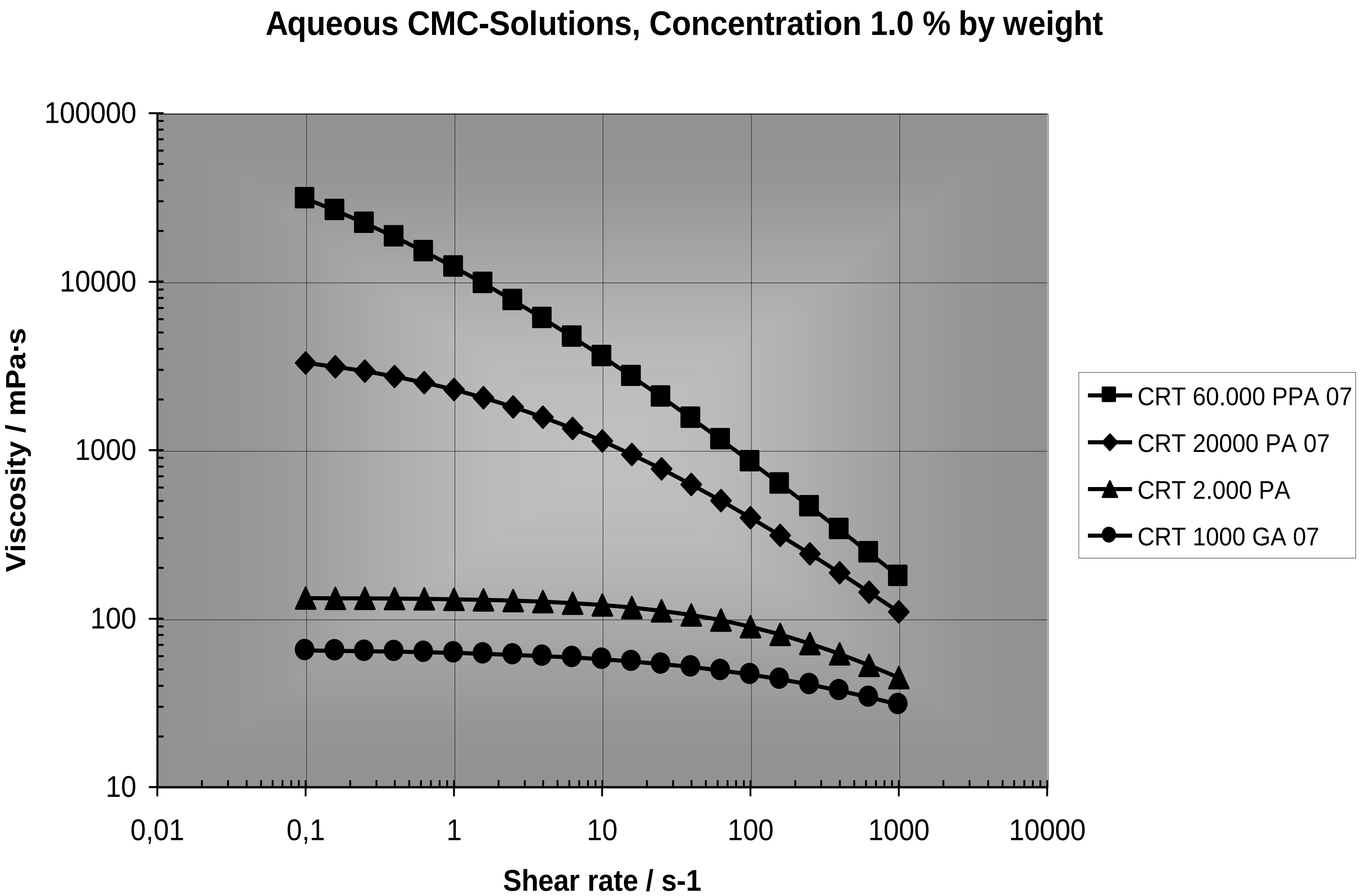
CMC - Heat Impact

The viscosity decreases during heating process.

→ Reversible Process – viscosity increase again by decreasing the temperature!



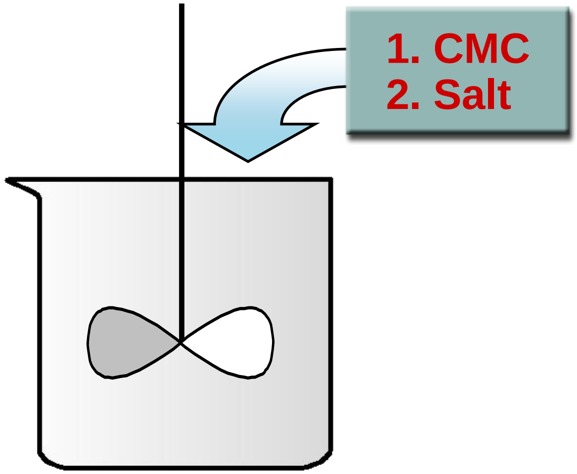
CMC - Impact of Shear



CMC - Salt Tolerance

General behavior in the presence of salts:

- Tolerance is limited
- Viscosity decreases with increasing salt levels
- Higher DS CMCs are more stable than lower

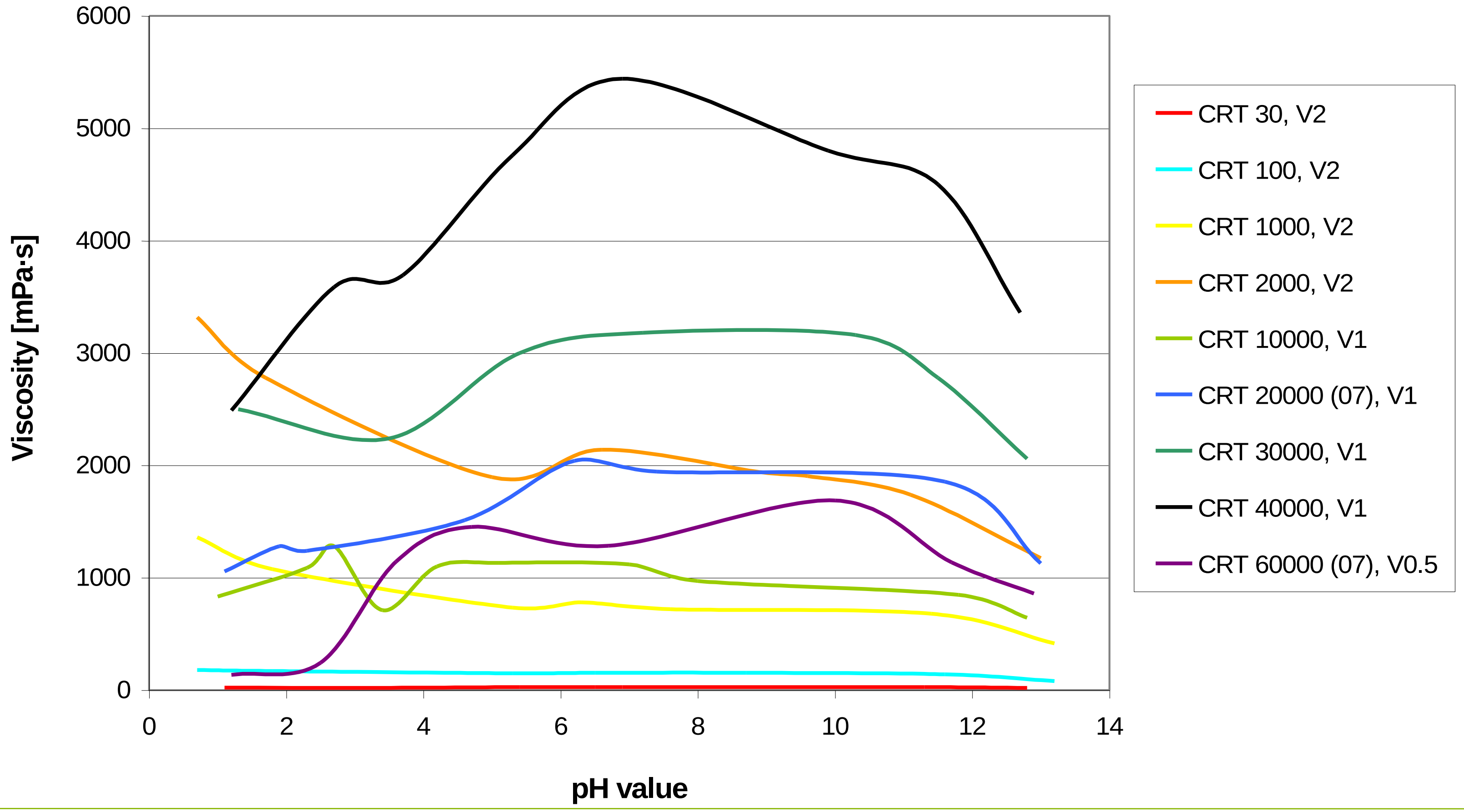


The moment of salt (e.g. table salt) addition is important

- Dissolved CMC is more stable against salts than CMC which is integrated in salt water
- The viscosity development of CMC is suppressed due to salt water

CMC - Effect of pH on Viscosity

- Maximum viscosity between pH 6.5 - 8.5
- Insoluble at pH ≤ 3 (free acid form)
- Strong viscosity decrease at pH < 6
- Slight viscosity drop at pH > 9

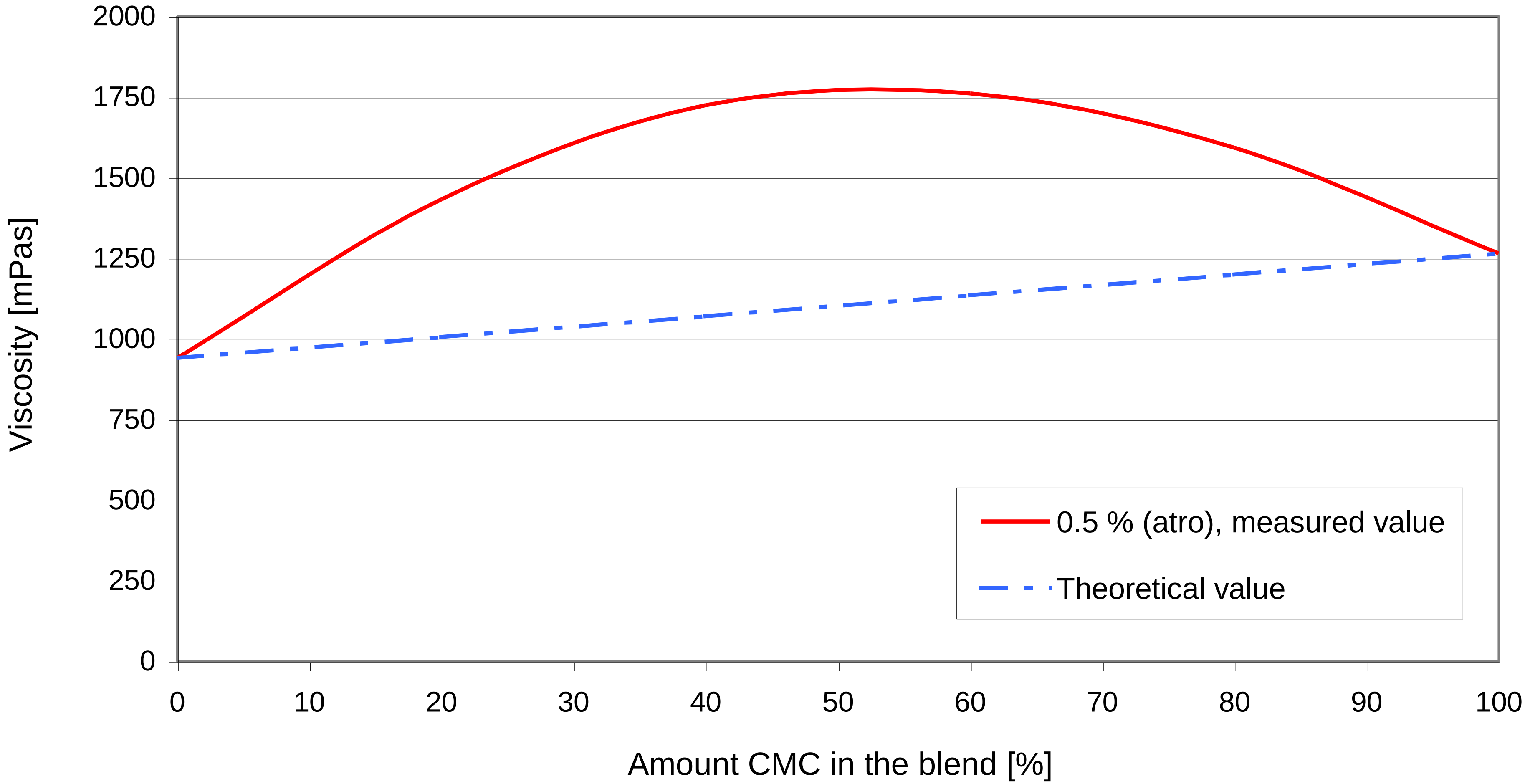


Synergistic Combinations of CMC With Other Hydrocolloids

CMC + Guar ⇨ Viscosity increase

Synergism CMC - Guar without shear stress

Walocel CRT 60000 PA 07 - Guar 5000, concentration: 0.5 % in sum



CMC + Locust Bean Gum

⇨ Improved stability and functionality

Synergism of blends (50 : 50)

- Improved heat resistance compared to pure CMC
- Increased cold functionality compared to pure LBG
- Viscosity win (10 % at low shear)
- Good shear stability

CMC + Gelforming Hydrocolloids

⇨ Improved stability and functionality

"Synergism" between CMC and classic gelformers such as κ-Carrageenan, Agar, Starch …)

- ⇨ Improved gel quality
- ⇨ Prolonged stability
- ⇨ No / less syneresis
- ⇨ Increased elasticity

CMC - Overview on Food Applications

CMC - Functions in Food

Thickener, Viscosifier (e.g. beverages, soups, dressings, sauces)

→ *Gives viscosity to aqueous solutions*

Texturizer (e.g. beverages, fruitpreparation)

→ *Improves body and mouthfeel, keeps consistency stable over storage time*

Improve elasticity and plasticity
(e.g. extruded products, bakery products)

→ *Good machinability / simplified post-processing*

CMC - Functions in Food

Crystallisation control (e.g. ice cream, frozen dough products)

→ *Slows down the crystallisation speed, reduced crystal growth/size*

→ *Delayed retrogradation of amylose (anti staling agent)*

Waterbinding (e.g. meat products, bakery products)

→ *Prevents water loss, suppressed syneresis*

→ *Prolonged freshness*

Mouthfeel enhancer (e.g. fat-reduced products like fresh cheese preparations, soups, sauces, beverages)

→ *Simulates a "fatty" mouth feel, improved creaminess*

CMC - Functions in Food

Protein protection (e.g. fresh cheese, acidified dairy drinks)

→ *CMC protects proteins against the effects of acid and heat*

Stabilizer (e.g. soups, dressings, sauces)

→ *Keeps molecules stable and suspends particles*

"Emulsifier" (e.g. spreadable cheese, dressings)

→ *Stabilizes hydrophilic and lipophilic components, support of classic emulsifiers*

CMC - Functions in Food

Gelling support (e.g. fresh cheese preps, desserts)

→ *CMC improves the quality of gels and supports gel-forming hydrocolloids*

Foam stabilization

→ *Fixing of foams, constant density, prolonged stand-up*

Partial replacement of traditional additives

→ *Fat and oil*

→ *Proteins (Proteins from milk/whey, meat, soy, wheat)*

→ *Sugar and lactose*

Guar Replacement with CMC

Guar Gum

- Guar provides thickening, texturizing, moisture-binding and freeze-thaw stability
- 70-80% of guar gum is being used oilfield applications
  - ✓ Gum gum supply short of demand by ~25% in 2012
- Current prices roughly $7/lb
- 1% viscosity = 3500 – 5000 cPs

- **CMC is a suitable, cost effective replacement**
  - ✓ 40,000 or 50,000 viscosity grade – 1:1 replacement
  - ✓ Synergy: 20/80 & 35/65 Guar/CMC offers a 2x viscosity gain vs expected value

Guar Replacement with CMC

Properties	Guar gum	Cellulose gum
Cold and hot water soluble	√	√
Dissolution time	Medium - Fast	Fast
Solution Transparency	Cloudy	Clear
Flavor	Beany	Neutral
Viscosity range	5000 -7000 @1%	30 to 50,000 @ 2%
Viscosity w/Shear	Shear Thinning	Shear Thinning
Viscosity w/Heat	Heat Thinning	Heat Thinning
Synergy	Xanthan	Guar, MC
pH Stability	5 – 7, loss below 3.5	Loss below 3.2
Moisture Holding	Good	Good
Freeze Thaw Stability	√	√
Ionic	Non Ionic	Ionic
Milk Interaction	Not Known	Protective

CMC - Incorporation Methods

Procedure	Physical Form			Recommended Preparation
	Granular Type (GA)	Powder Type (PA)	Fine Powder Type (PPA)	
Separate Solution	+	–	–	High speed mixer should be used and CMC grades should be added slowly to aqueous solution. The dissolution time is about 30 – 60 minutes.
Dry Blend Mixture	–	+	+	Premix CMC grades with other powder ingredients of the formulation to avoid agglomeration or lumps.
Dispersion in organic solvents or oil	+	+	+	CMC grades are dispersed in organic solvents/oil. The CMC dispersion is than added to water while stirring

Thanks for your kind attention !

QUESTIONS??

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