How can cellulose ethers play a role in a more sustainable future?

The 9th Workshop on Cellulose, Regenerated Cellulose and Cellulose Derivatives

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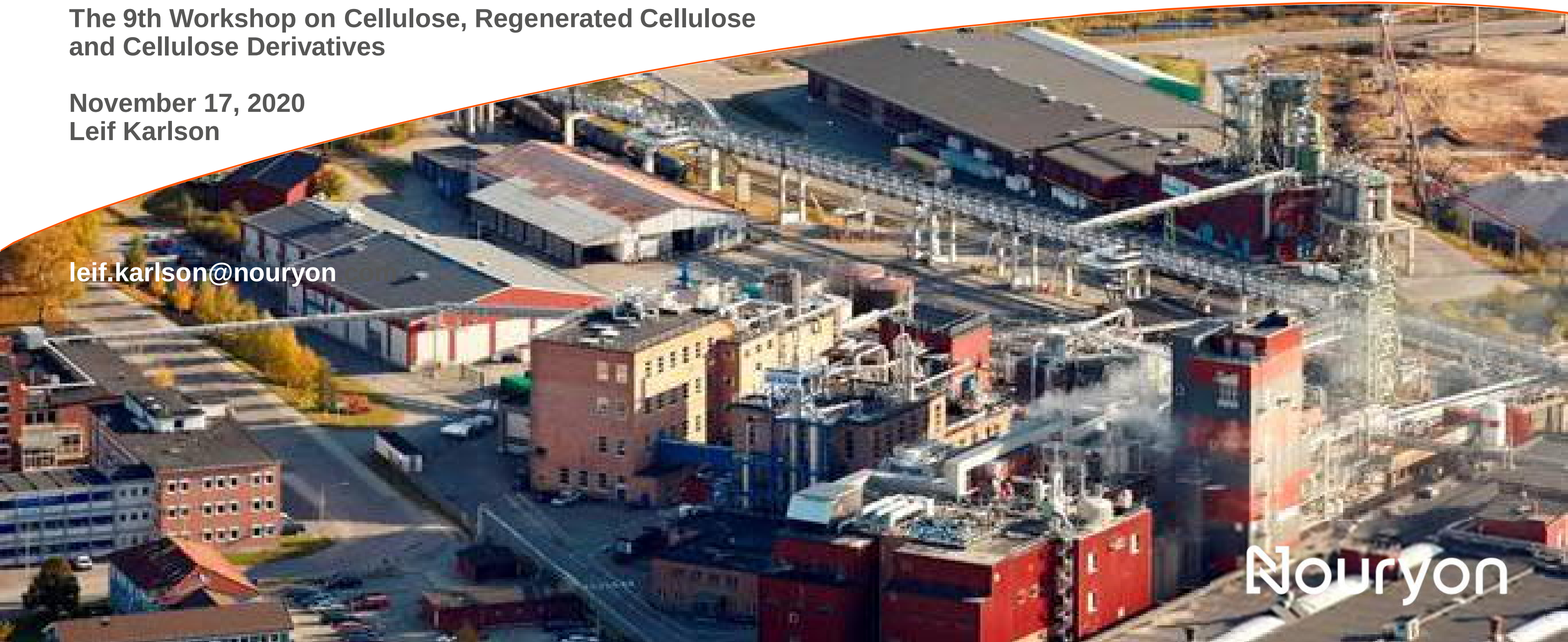

Outline

- Background and history of cellulose ethers
- Chemistry and manufacturing process
- Cellulose ethers in water solution
- Market trends
- Future needs

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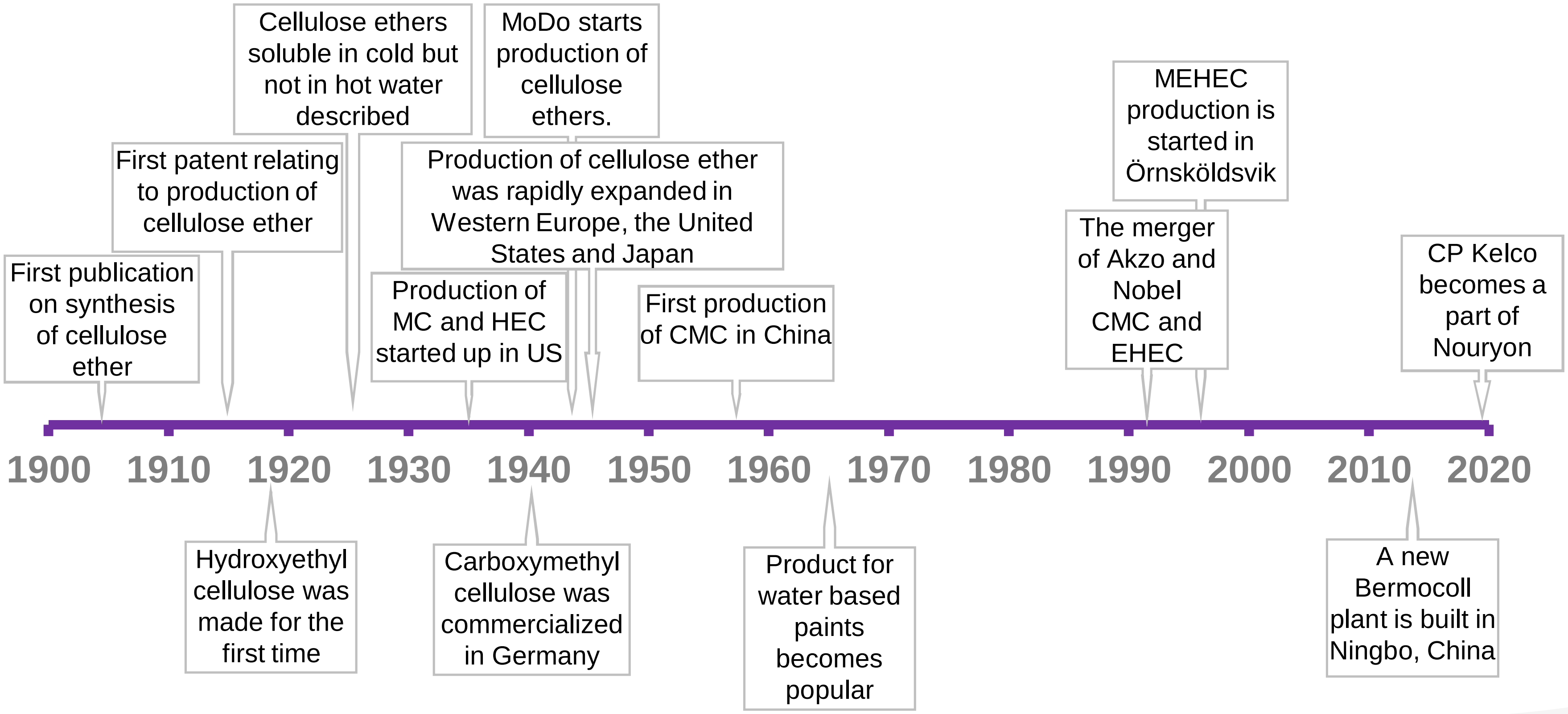
The history of cellulose ethers



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How do you mean?
Dad, do you know we have
at home?
For example as thickener in drinking yoghurt
… or in the
… or in the water borne paint
For water retention in tile adhesives
… or in bread
Also in tablets as disintegrants or in the coating

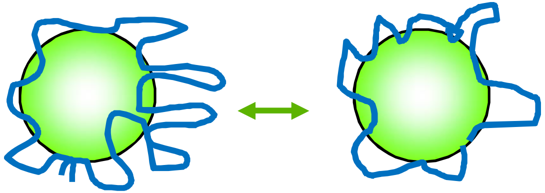
Cellulose ethers

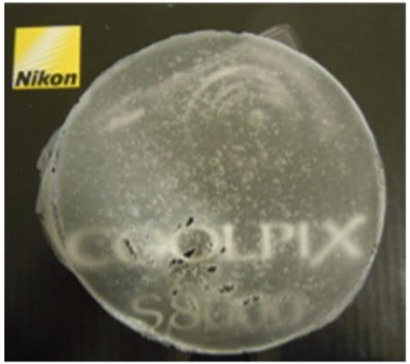
Cellulose ethers are:

- made from renewable resource - cellulose
- biodegradable
- non-toxic

Properties cellulose ethers bring

- Thickening of water solutions
- Water retention
- Dispersion and emulsion stabilization
- Film formation





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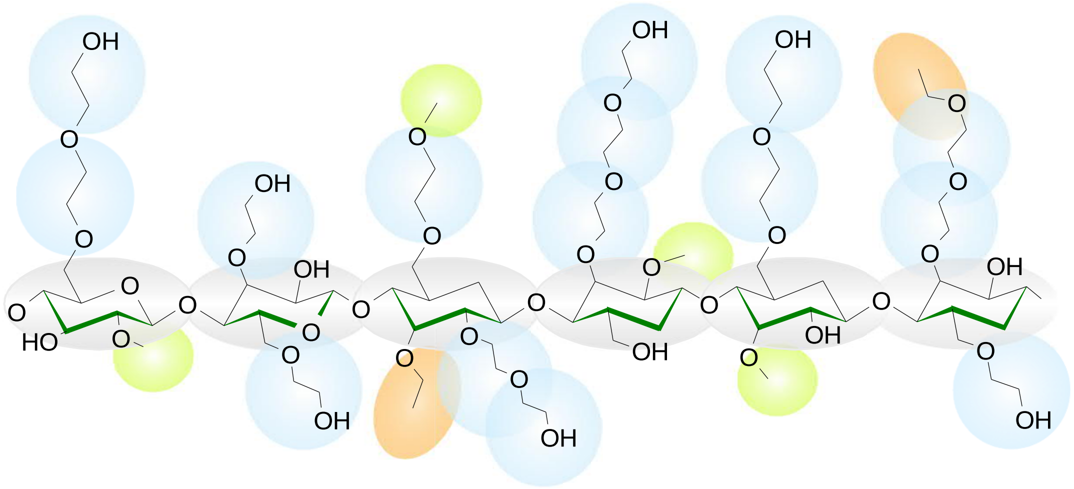
Cellulose ethers used in industrial applications

CMC	Carboxymethyl cellulose
MC	Methyl cellulose
HPMC	Hydroxypropyl MC
HEMC	Hydroxyethyl MC
HEC	Hydroxyethyl cellulose
EHEC	Ethyl HEC
MEHEC	Methyl EHEC
HPC	Hydroxypropyl cellulose
EC	Ethyl cellulose
HM-(E)HEC	Hydrophobically modified (E)HEC



Industrial applications for cellulose ethers

Building formulations

HEMC, HPMC

Detergents

CMC

Food

CMC, MC, HPMC

Oil field

CMC, HEC

Paper

CMC, MEHEC

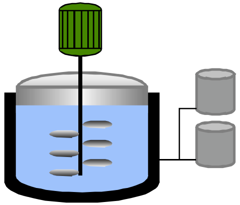
Pharma

HPC, EC, HPMC, HEC, CMC

Personal care

CMC, HPMC, HEC

Polymersization



HEC, HPMC

Coatings

HEC, MEHEC, HM-(E)HEC

Textiles

CMC

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Reagents used in cellulose ether production

Cellulose

Sodium hydroxide

MCA	Mono chloro acetic acid
EC	Ethyl chloride
MC	Methyl chloride
EO	Ethylene oxide
PO	Propylene oxide

EC, MC, EO, PO: volatile compounds and a pressurized reaction vessel is required

Synthesis of nonionic cellulose ethers

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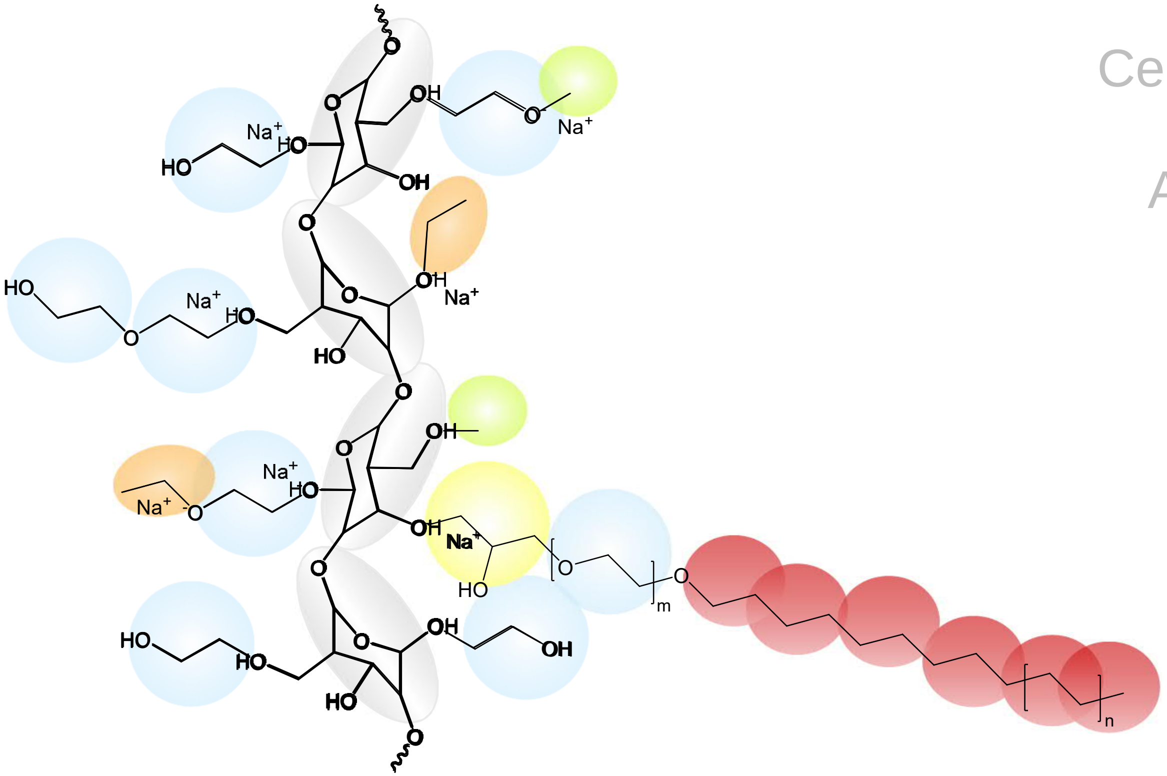

Cellulose - crystalline

Alkali cellulose - swelled

HEC

MEHEC

HM-MEHEC

MEHEC process

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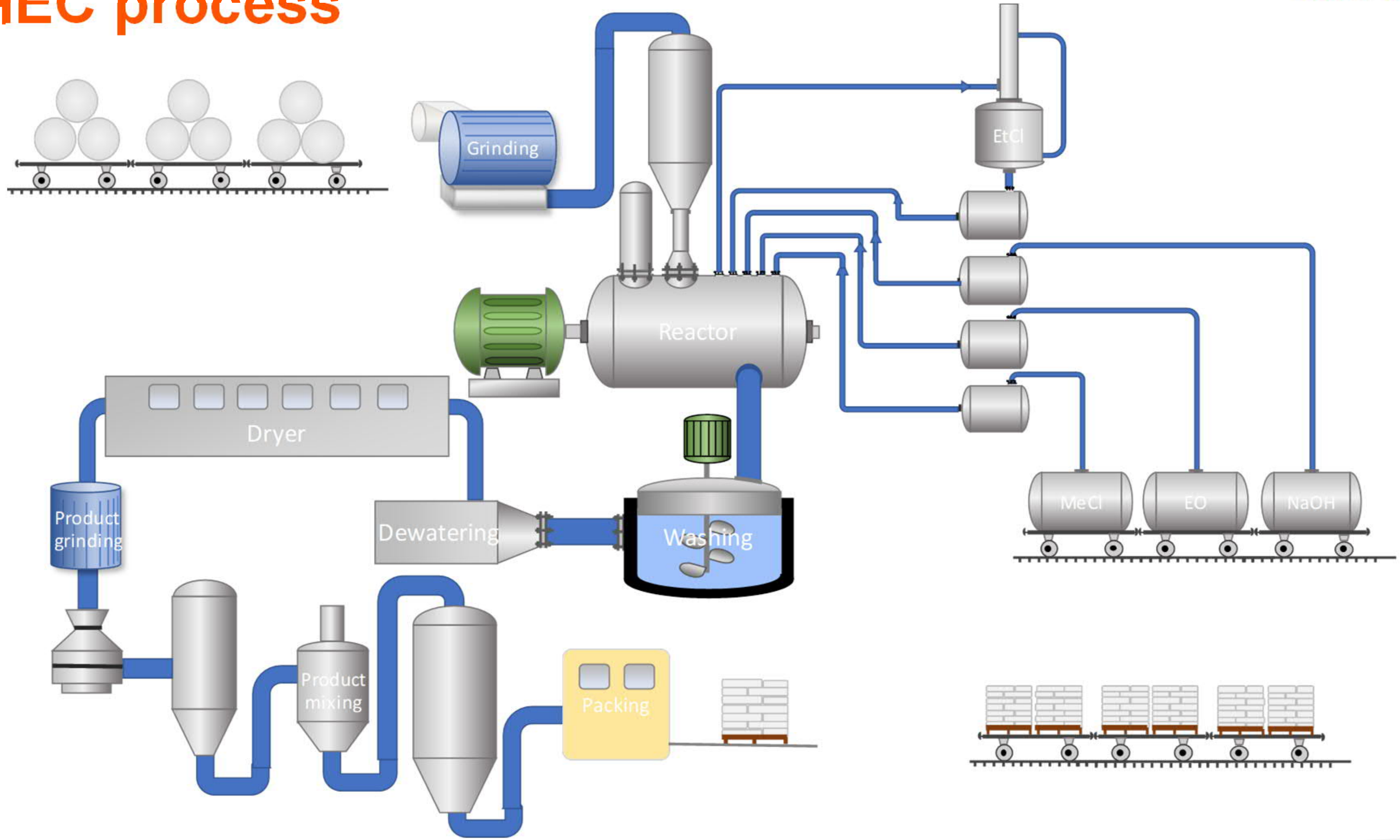

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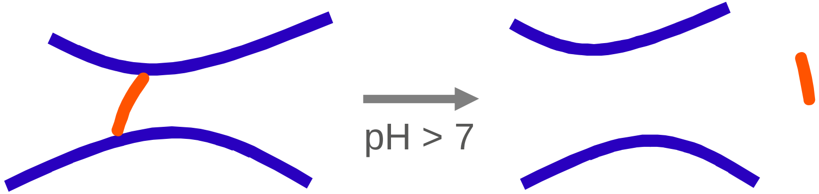
Dissolution time and lump free dissolution

The powder is added slowly under stirring

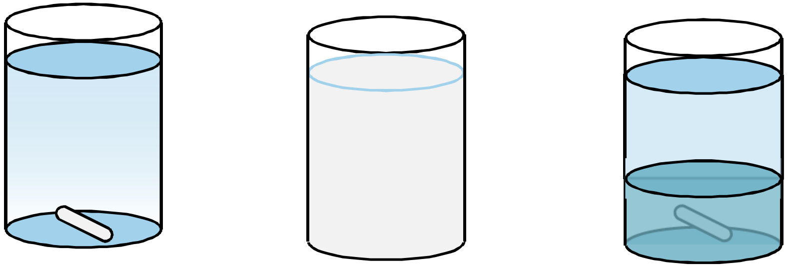
pH adjusted to > 7
Continue mixing for 30 – 180 min



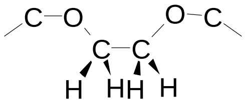
Glyoxal cross-linked cellulose ether

Cloud point

- Nonionic cellulose ethers have a cloud point (Tcp)
- The polymer solution separates into two phases at T>Tcp
- Tcp is influenced by:
  - Degree of substitution MS_{EO}, MS_{HP}, DS_{Et}, DS_{Me}
  - Hydrophobically modified or not
  - Polymer concentration
  - Salt concentration
  - Presence of surfactants and/or particles

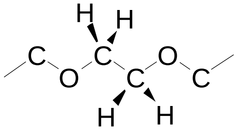


$T < T_{Cp}$ $\quad$ $T > T_{Cp}$ $\quad$ $T > T_{Cp}$ kept for long time



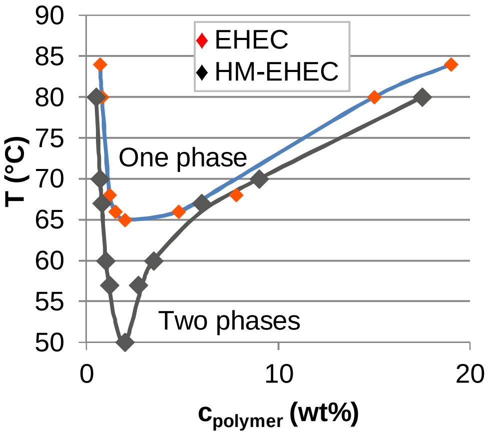
A

A. Low temperature
Polar
High solubility

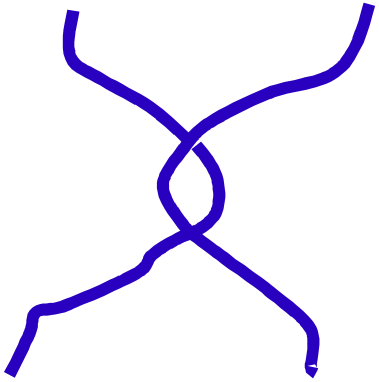


B

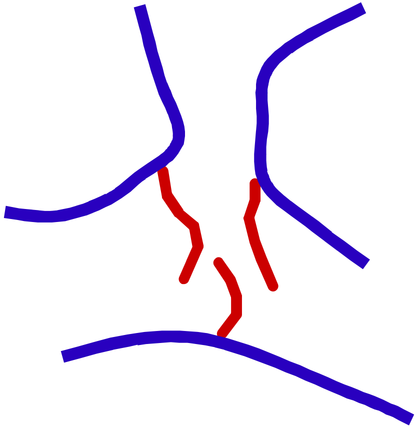
B. High temperature
Unpolar
Low solubility



The thickening mechanisms



Entanglements of polymer chains

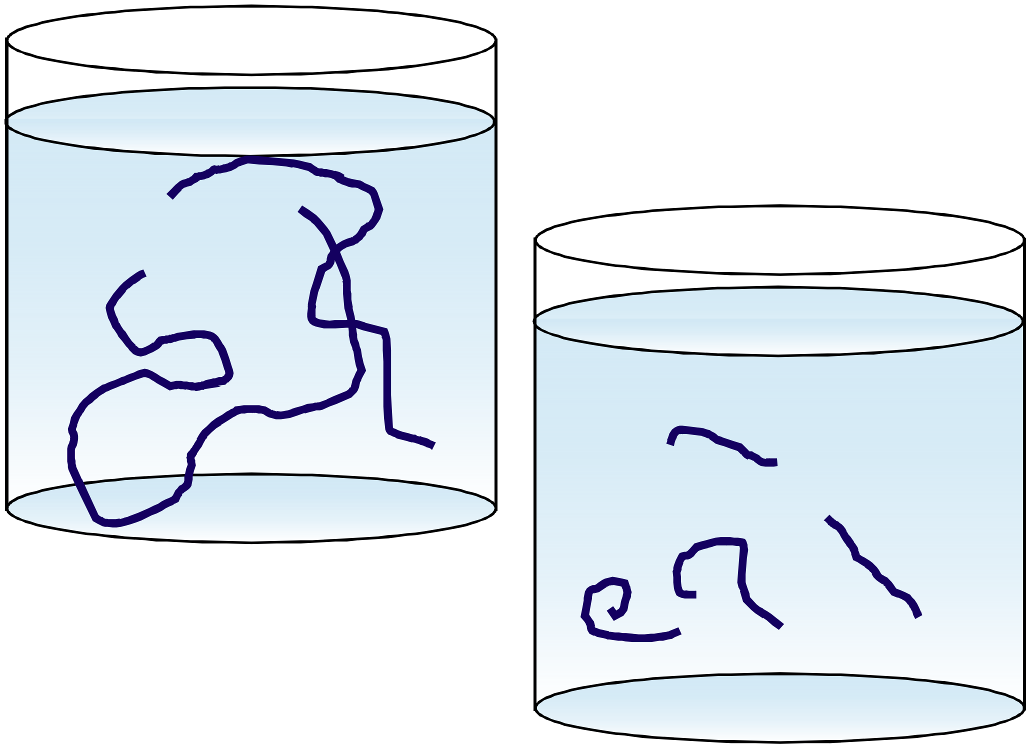


Physical bonds of associating hydrophobic tails

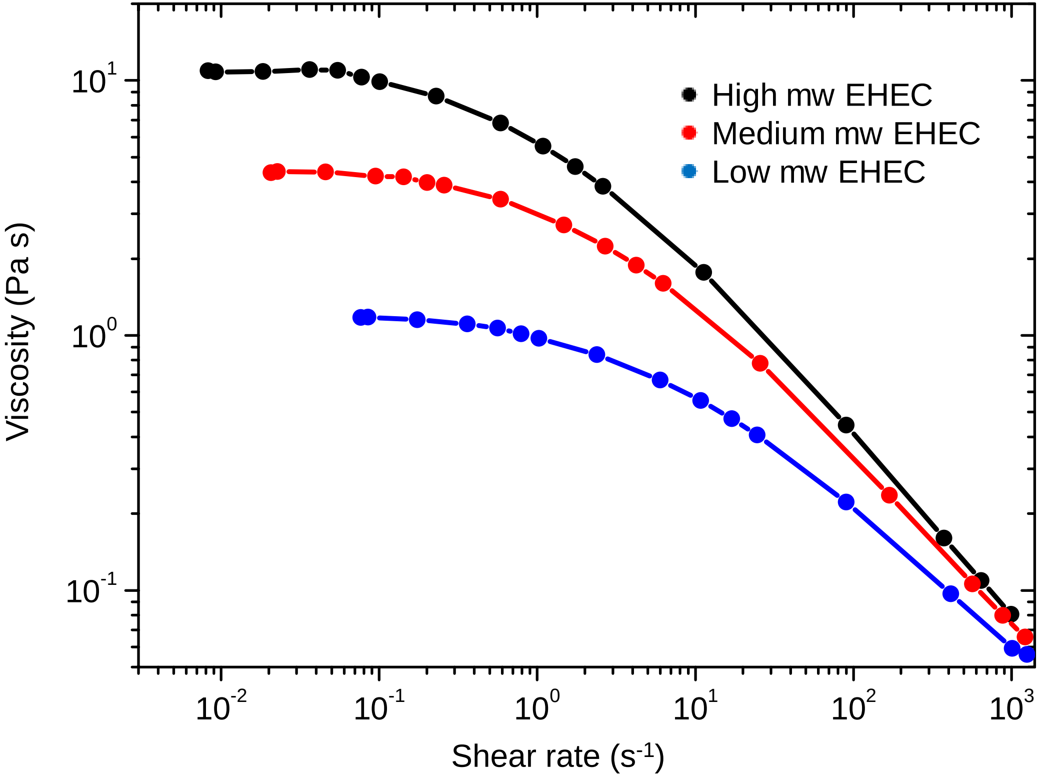
Molecular weight and molecular weight distribution

Viscosity is influenced by:

- Polymer concentration
- Mw (DP of the cellulose backbone)
- Hydrophobically modified or not

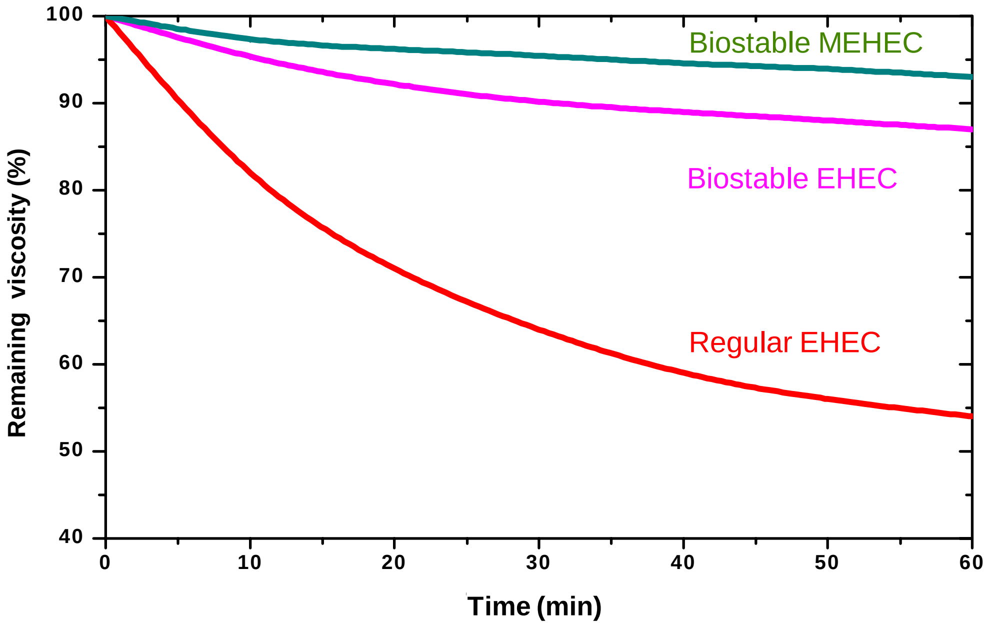


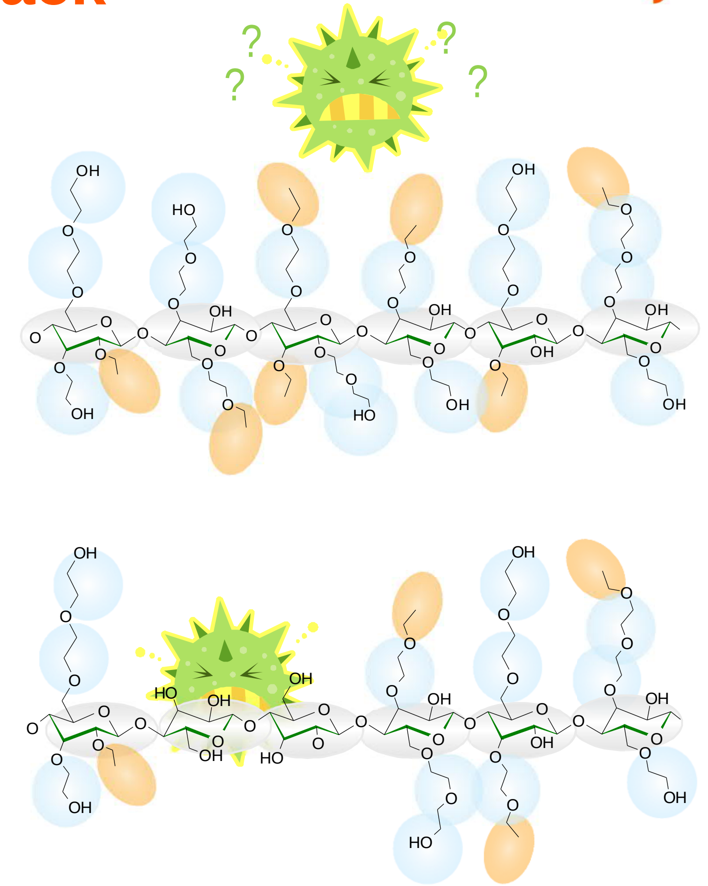
Viscosity as function of shear rate



Resistance against enzymatic attack

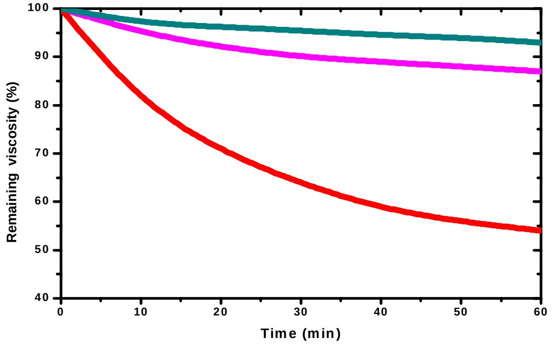
- 1 % solution, 20°C, pH 7
- Viscosity drop 60 min after enzyme addition

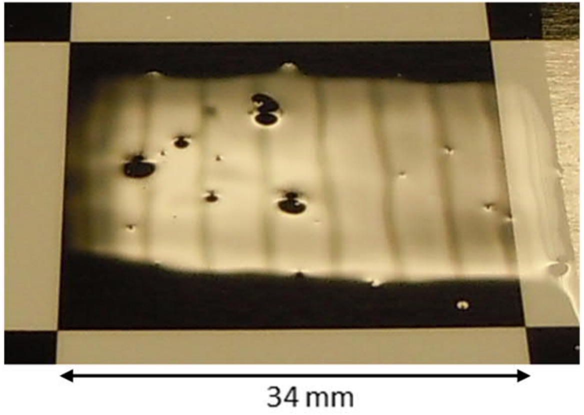




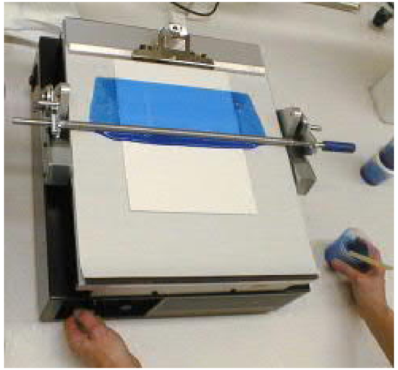
Even or blocky substitution

Even distribution results in high biostability, low gel and low wet bits





Wet bits



Gel particle measurement

Gel particles

Quality requirements on cellulose ethers

Application driven quality requirements on cellulose ethers

- Viscosity
- Thickening efficiency
- Dissolution time and lump free dissolution
- Biostability/biodegradability
- Content of insolubles, gel particles and wet bits
- Cloud point
- Content of impurities

Outline

Background and history of cellulose ethers

Chemistry and manufacturing process

Cellulose ethers in water solution

Market trends

Future needs

Cellulose ether trends

Trend 1

Trend 2

Trend 3

Trend 4

Trend 5

Trend 6

Trend 7

New producers and consolidation

- Increased number of new low cost competitors
  - New small cellulose ether producers in China and Turkey
  - Cellulose producers forward-integrating into cellulose ether production

- Consolidation - Few and large producers of high quality products
  - Dow acquire Dupont (MCC)
  - Nouryon acquire CP Kelco

Producer	CMC	HEC	EHEC	MEHEC	HM-CD	HPMC	HEMC	HPC	MC	EC
Dow	X	X				X	X	X	X	X
Ashland	X	X			X		X	X	X	X
ShinEtsu	X	X				X	X	X	X	
Nouryon	X		X	X	X		X			
Lotte		X			X	X	X		X	

Strong growth in regulated markets
pharma, health care, food, feed

- The need for larger quantities of processed food in future
  - Population growth drives the need for processed food (and food additives)
  - Drive for healthy & natural products / clean label in western markets
  - Regional differences in growth rate and requirements

- Growth in Pharma products
  - More generic drugs will drive excipient growth
  - Strongest growth in China and India

- Large potential in the Health Care market
  - E.g. colostomy bags and plasters

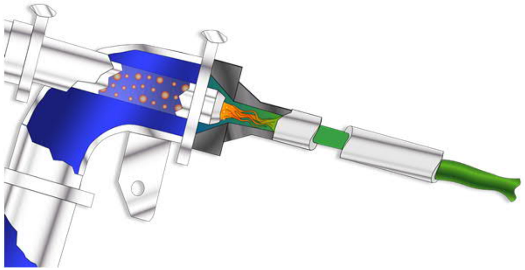
- Strong future growth in Animal feed products

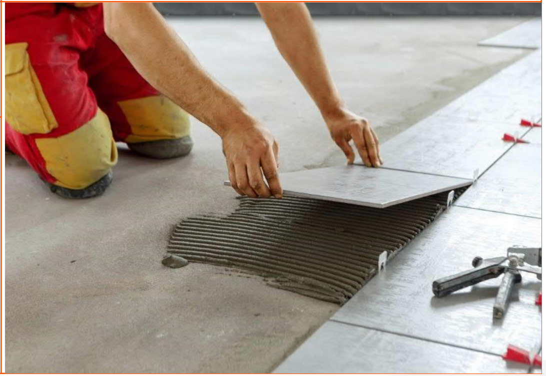
Strong growth in emerging markets

- Strong growth in China, India, South America and Africa
  - Growing middle class
    - Strong drive for building better housings and decorating them
    - High demand on health care products

Downstream process changes

Cost effective and more flexible paint manufacturing process	
• Continuous paint production processes (inline dispersion)	more consistent thickening efficiency
• Use of new equipment to streamline the process (e.g. eductors)	different dissolution properties
Construction time reduction and cost savings	
• Fast setting systems are more and more used (e.g. reduced walk-on time for cementitious floorings)	Reduced cement retardation





Downstream product reformulation

- New paint effects
  - new paint types to replace more heavy and expensive building materials
- Renewed architectural influence on construction materials
  - Use of larger and larger tiles and elimination of grouts between large tiles.
  - Non-covered cement based flooring.
- New construction methods
  - 3D printing of building parts
  - Expansion of prefabrication of facade elements for commercial and residential buildlings
- Use of binders in Li-batteries
- Intelligent materials
  - Functional-textiles, smart coatings, self-healing concrete, etc

Multi color paint (MCP)

MCP or stone paint

Real stone

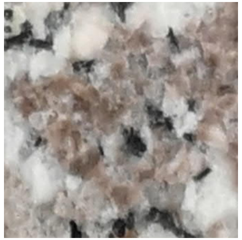
Fast growing segment in China

MCP partly replaces stone paints

Used above the 3rd floor in high-rise buildings

Granite MCP

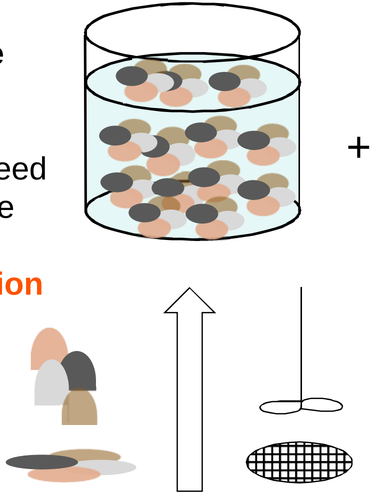
Multi color paint production process

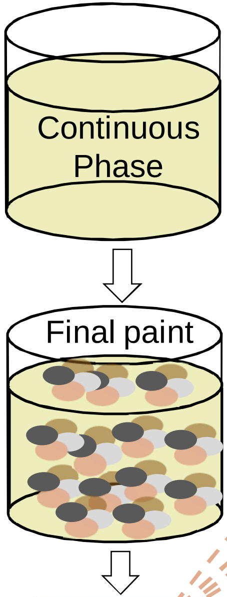


Color analysis of real stone

- Percentage
- Size
- Shape
- Distribution

Droplet size matching
- Shearing
  - Speed
  - time
- Sieving
- **Formulation**

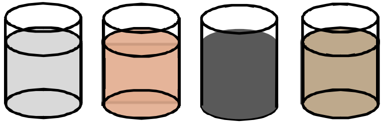


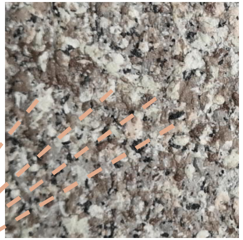


Continuous phase

- PAA latex
- Thickener

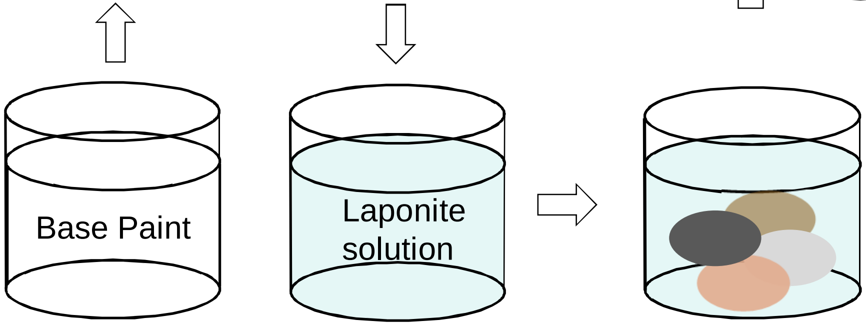
Color matching





Base paint

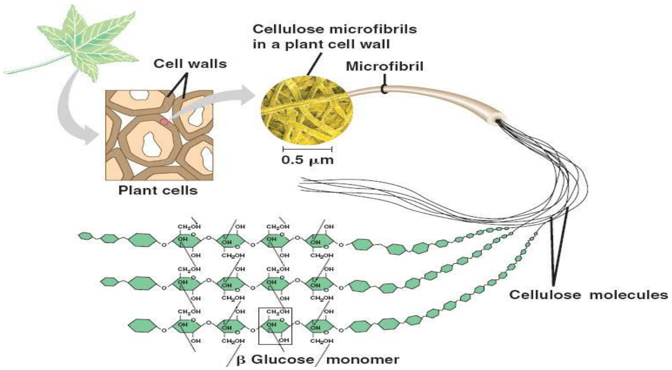
- PAA latex
- **Cellulose ether**
- (+sand)



Rapid change in technology

- New processes to make new or more efficient products
  - Synthesis of cellulose ethers in liquid state
  - Use of enzymes to icrease accessability of the cellulose

- A boom in new cellulose based materials that can compete or be complementary
  - Nanocrystalline, Microcrystalline cellulose and Microfibrillated cellulose



Fiber	3 mm x 30 µm
Microfibril	5 µm x 100 nm
Nanofibril	1 µm x 5 nm
Nanocrystal	200 nm x 5 nm

Increasing drive towards sustainable chemistry

- Push for lower human and environmental impact of products and processes by governments and by consumers
- Circular economy – alternative feedstocks; greater recycling;
- More emphasis on sustainability certificates (e.g. EcoVadis, LCA)
- Low energy use in production
- Biomass and biorefinaries

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The cellulose supply chain

- Cellulose - Normally from wood or cotton linters
  - Scan viscosity 400 – 2400
  - DP 1200 – 10000
  - Mw 200 000 – 1 600 000

Wood pulp

Cotton linters

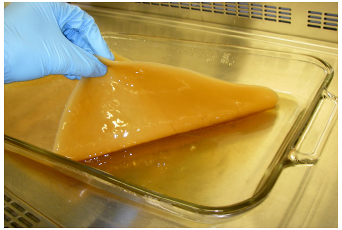
- New cellulose sources to investigate

Sugar cane

Food waste

Sea weed

Bacterial cellulose



Elephant grass

Recycled paper or clothes

Sustainability of cellulose ethers

- 50 – 70% is bio-based (cellulose)

- Cellulose ethers are well positioned to partly replace synthetic water soluble polymers
  - Synthetics have many broad and good properties that are challenging to match
    - depending on polymer they can be e.g. water resistant, thermoplastic, highly charged, flexible/stretchy etc.
  - Cost price / Cost efficiency of synthetics may also be a challenge to match

- Examples of synthetic polymers where cellulose ethers can compete
  - Polyacrylamide (PAM) and copolymers
  - Polyvinyl alcohol (PVOH)
  - Polyacrylic acid (PAA) and copolymers
  - Polyethylene glycols (PEGs)
  - Polyamines, polyethyleneimines, and quaternary ammonium compounds
  - Associative thickeners: nonionic polyurethanes and similar

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Future needs: Improved raw materials

To improve the sustainability and to compete with synthetic polymers we need:

- Higher mw
  - Higher DP cellulose
  - Chain extension reactions

- Lower DP
  - Low DP cellulose
  - Well controlled degradation reactions

- New biobased substituents
  - MCA, EO, PO, EtCl, MeCl from renewable sources
  - New substituent - not necessarily the same reagents as now

Future needs: Improved process

- We need to work constantly to reduce our own environmental footprint from the production process
  - Lower energy demand
  - Low waste
  - Use of more environment friendly raw materials and energy sources
  - Improved raw material efficiency etc.

- We have interest in ideas for an improved process
  - Improved accessibility of the cellulose
  - Alternative to NaOH for catalyzation
  - More reactive substituents
  - Reaction in dissolved state

Conclusions

Cellulose ethers

- Are made from renewable resource, cellulose, are biodegradable and non-toxic
- Are excellent in thickening of water solutions and can contribute with water retention, stabilization of dispersion and emulsion and act as film former
- Can replace synthetic polymers in many applications
- Can play a role in a sustainable future

Thank you very much for listening!

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