Building Leadership Excellence

Biobased Materials for Paper Coating

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RETHINK PAPER:
Lean and Green

Summary of Presentation

- Biobased product definition
- Drivers for emphasis on biobased materials
- Historical use of biobased materials
- Recent developments
- Trends and path forward

Biobased Products Definition

Biobased product was defined by the United States Secretary of Agriculture in the Farm Security and Rural Investment Act of 2002 as follows: "The term ‘**biobased product**’ means a product determined by the Secretary to be a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal, and marine materials) or forestry materials OR an intermediate feedstock.”

Drivers for Use of Biobased Materials

- Sustainability
  - Made from renewable resources
  - Reduced carbon footprint
- Increasing costs of crude oil and petrochemical feed stocks
- Developments in biobased materials that:
  - Improve coated paper and paperboard quality and properties
  - Provide improved runnability and efficiency of coating operations
  - Reduce energy consumption in coating operations

Historical Uses of Biobased Materials in Papermaking and Paper Coating

- Starches (generally acid thinned or low degree of chemical modification)
  - Wet end additive for strength and retention
  - Surface sizing chemical for strength, film forming and coating holdout
  - Co-binder for latex in pigmented coating
  - Primer for barrier coating
- Soy protein
  - Co-binder for coating – improves coating structure and water holding
  - Calender sizing
- Casein
  - Co-binder for coating and water holding agent
- Alginate
  - Rheology modifier and water holding agent

Historical Use of Biobased Materials in Papermaking and Paper Coating

- Cellulose derivatives
  - Methyl cellulose and carboxymethyl cellulose
  - Rheology modifier and water holding agent
- Lecithin derivatives
  - Coating lubricant

Annually Renewable Bio feed stocks

Direct Extraction

Cellulosics & Lignocellulosics

Products:

- •Cellulose (Cellophane)
- •Cellulose Derivatives (CA, CAB)
- •Cellulose graft copolymers & blends
- •Engineered wood Products

Natural Fibers

Examples:

- •Kenaf
- •Sisal
- •Jute
- •Hemp
- •Flax

Products:

- •Biofiber Composites

Starches

Examples:

- •Corn
- •Potato
- •Tapioca

Products:

- •Industrial Mod. Starches
- •Thermoplastic Starch
- •Starch Foams
- • Starch graft copolymers & reactive blends
- •Starch nanoparticles

Other Polysaccharides

Example:

- •Pectin
- •Chitin
- •Levan
- •Pullulan

Fats & Oils

Examples:

- •Soybean
- •Lesquerella
- •Rapeseed

Products:

- •Biodiesel
- •lubricants
- •Polyols – urethanes
- •Plasticizers / Process aids

Proteins

Examples:

- •Casein
- •Zein
- •Soy protein

Source: R. Narayan

Examples of Recently Developed Biobased Materials

- Nanocrystalline cellulose
- Nanofibrillated cellulose
- Nanoparticle biopolymer coating binders
- Starch based pigments
- Polylactic acid (PLA) resins and dispersions (synthetic polyesters with monomers from fermentation)
- Polyhydroxyalkanoates (PHA, bacterial polyesters)
- Zein (corn protein)

Nano Crystalline Cellulose (NCC)

TEM image of cellulose nanocrystals

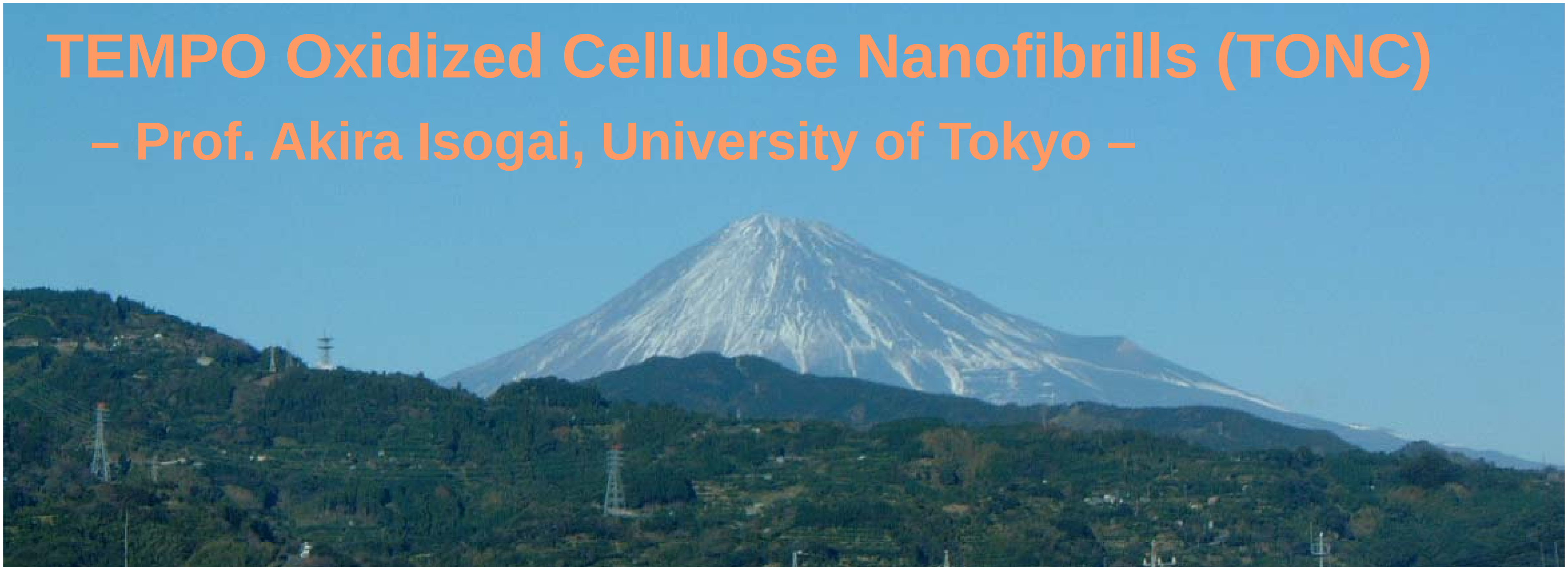
From: John Simonsen, Oregon State University, *Bio-Based Nano Composites Challenges and Opportunities*

Nanocrystalline Cellulose (NCC)

- Research and process development focus at FP Innovations
- Demo plant being built at Windsor, QC by joint venture of FP Innovations and Domtar with Quebec government grant
- Early stage application development shows
  - Improved gloss in coated papers
  - Improvements in tensile strength, stiffness, bulk and smoothness
- NCC is affected by magnetic and electrical fields
  - Potential use in printed electronics
    - Magnetic inks
    - Electric memory cards
    - Printed RFID antennae
- Barrier film for packaging materials

TEMPO Oxidized Cellulose Nanofibrills (TONC)

– Prof. Akira Isogai, University of Tokyo –



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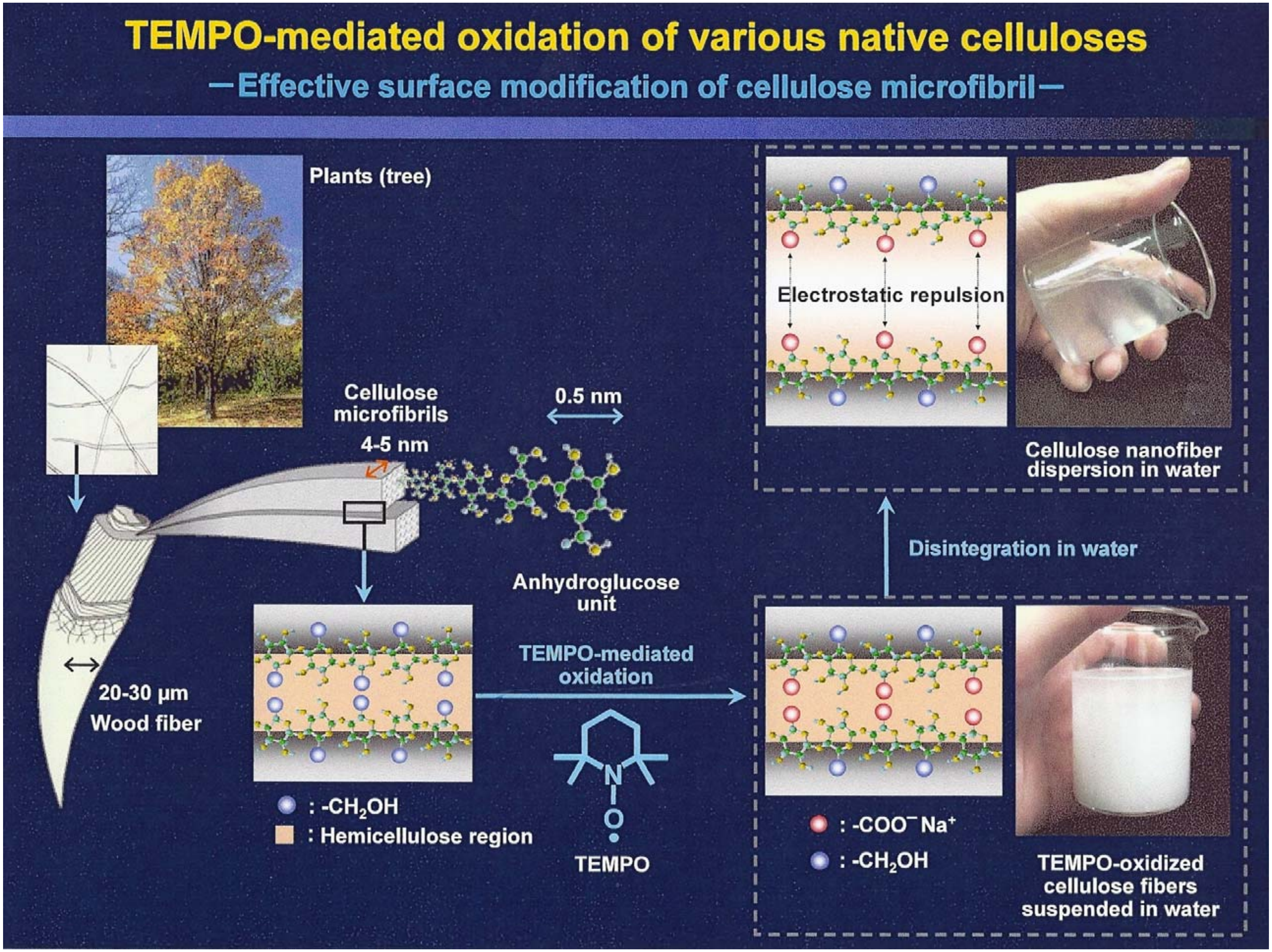
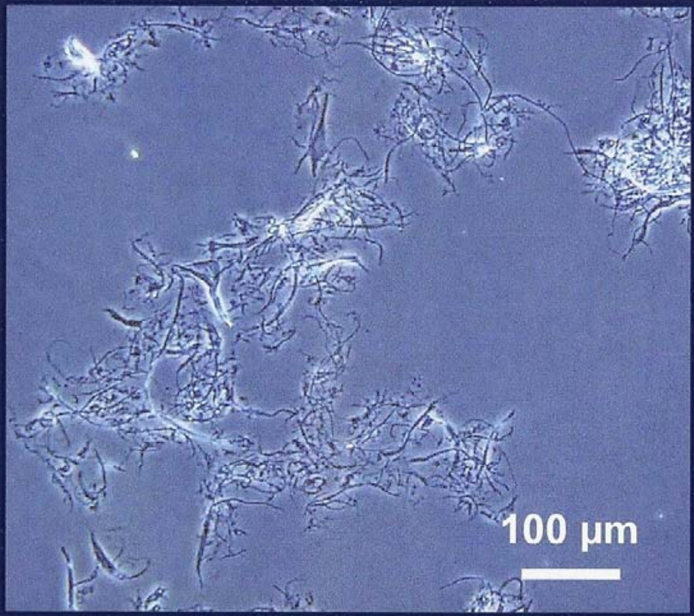


Source: Akira Isogai

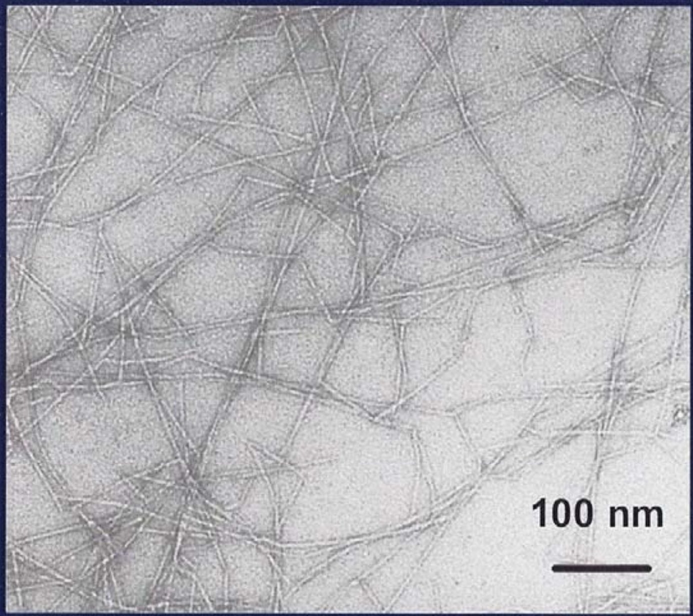
Differences in morphology and consumed energy between micro-fibrillate cellulose and TEMPO-oxidized cellulose nano-fibers

Micro-fibrillated cellulose



Disintegration energy > 200 khw / kg
More than 10 times cycles by high-pressure homogenizer

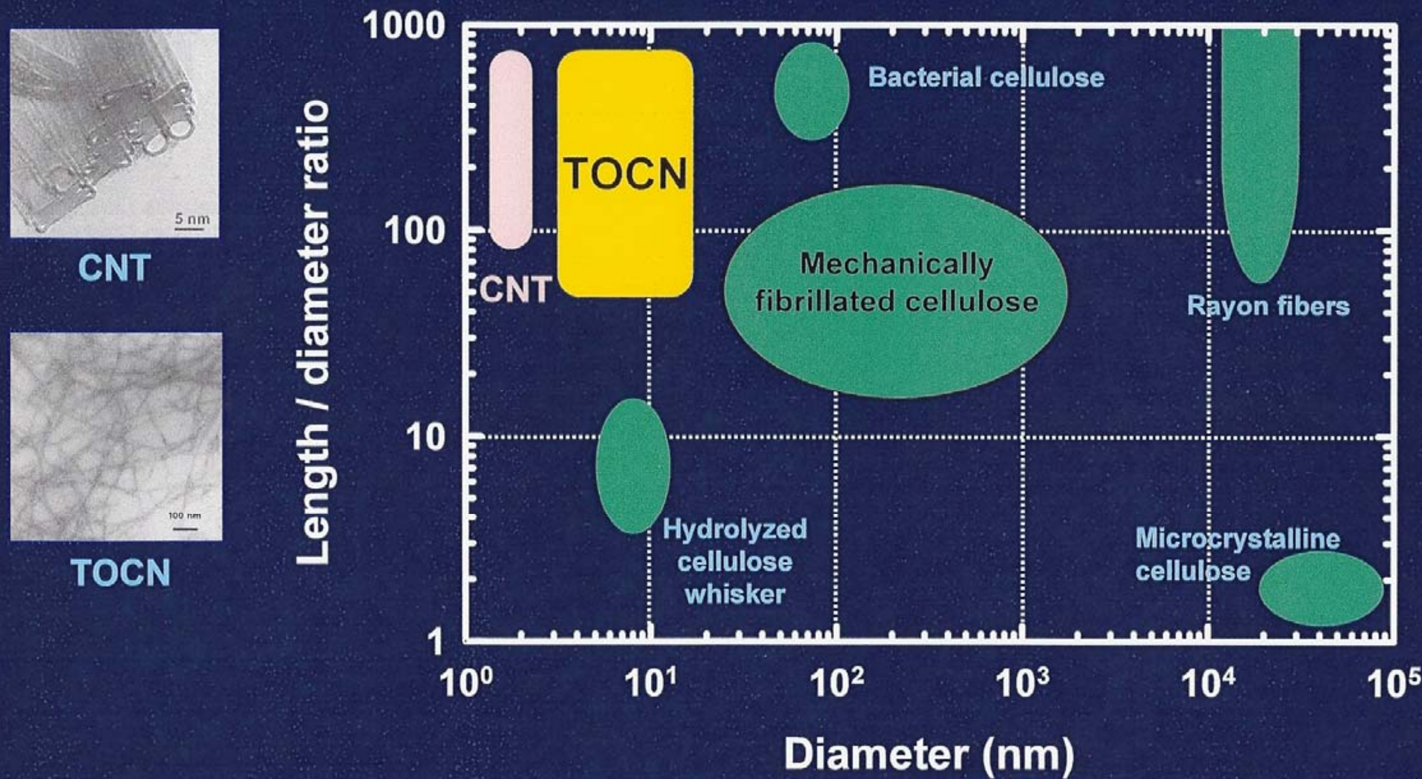
TEMPO-oxidized cellulose nanofibers



Disintegration energy < 2 khw / kg

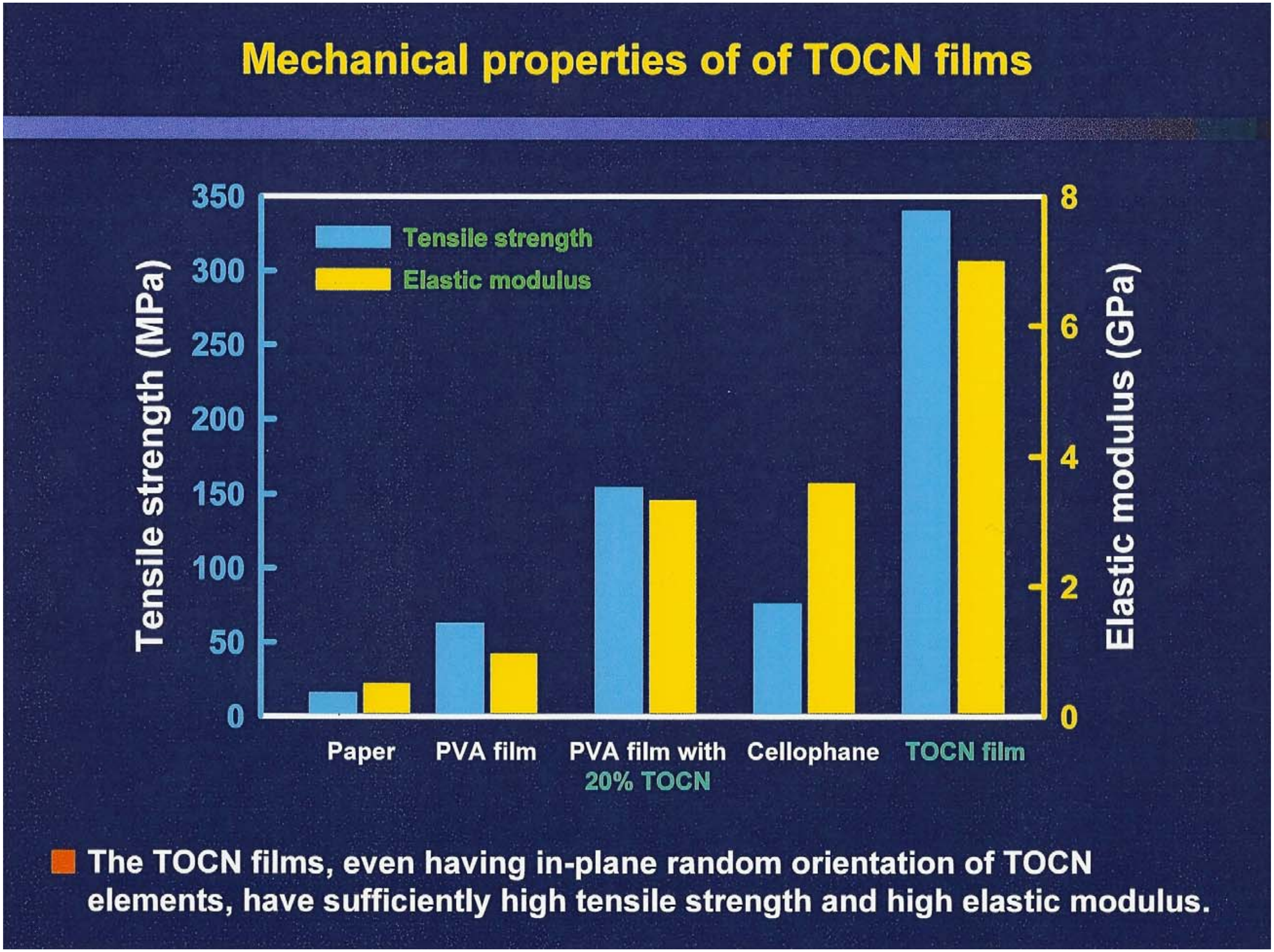
Source: Akira Isogai

Size map of new TEMPO-oxidized cellulose nano-fibers (TOCN) prepared from native celluloses



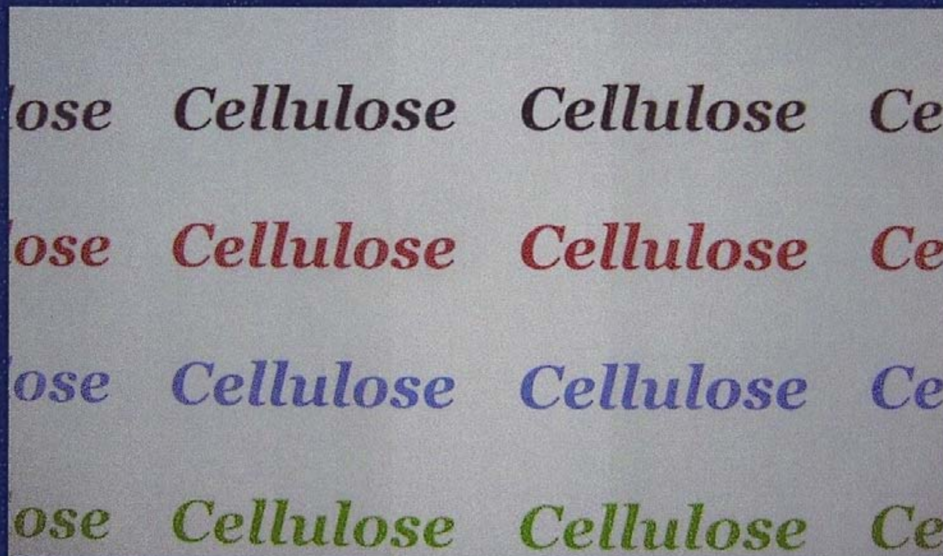
- TOCN covers new nano-fiber region at nm-level diameters in the map, which has not been prepared from other polymers or by other processes.

Source: Akira Isogai



Source: Akira Isogai

Optical transparency and oxygen-barrier property of TEMPO-oxidized cellulose nanofiber-coated PLA film



PLA film (25 µm) PLA film coated with TOCN (1 µm)

Oxygen permeability 746 → < 0.1 (mL m^{-2} day^{-1} atm^{-1})

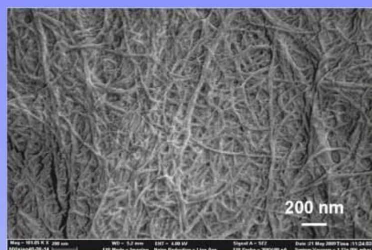
- Highly transparent, bendable and high-oxygen barrier films can be obtained by casting TOCN on a polylactic acid film.

Source: Akira Isogai

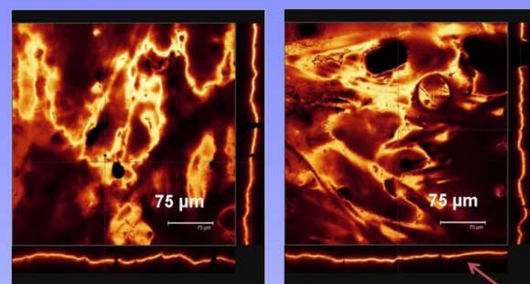
Nano Fibrillated Cellulose (NFC)

Nano-fibrillated Cellulose (NFC) in Coatings and Latex Films

Gerard Gagnon, Hitomi Hamada, Rikard Rigdal, Michael Bilodeau, and Doug Bousfield
Department of Chemical and Biological Engineering and Process Development Center, University of Maine, Orono, ME 04469



FE-SEM image of nano-fibrillated cellulose.

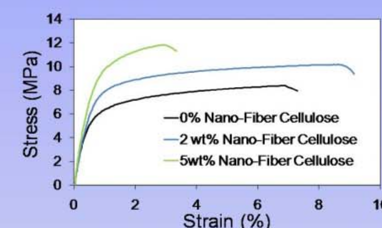


Confocal laser scanning microscopy of the distribution of pigment ink printed on NFC coated samples.

Cross section shows good pigment hold-out

NFC incorporated into latex films **increases** strength properties.

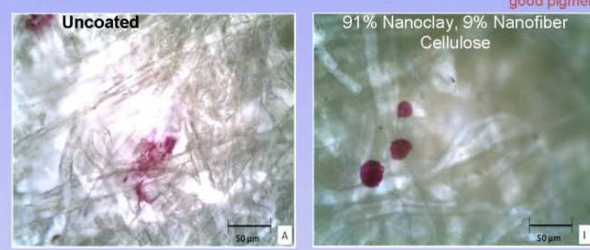

Tensile test strips, composed of SBR latex and NFC.



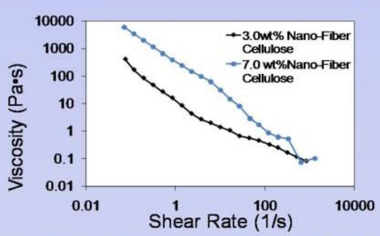
Tensile stress of latex/kaolin pigment films containing NFC.

Low-Cost Large Scale Production is now possible of Nano-fibrillated Cellulose (NFC)

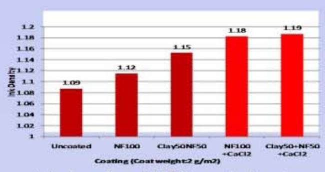

NFC in water suspension



Images of the distribution of pigment ink jet ink printed on NFC coated samples.

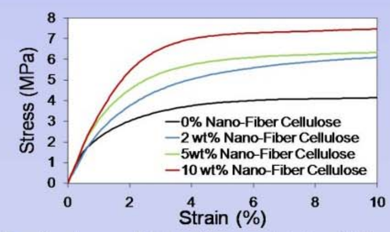


Suspension viscosity at various shear rates.



Ink density of NFC coated onto paper

NFC coated onto paper **improves** printing properties.



Tensile stress of latex films containing NFC.

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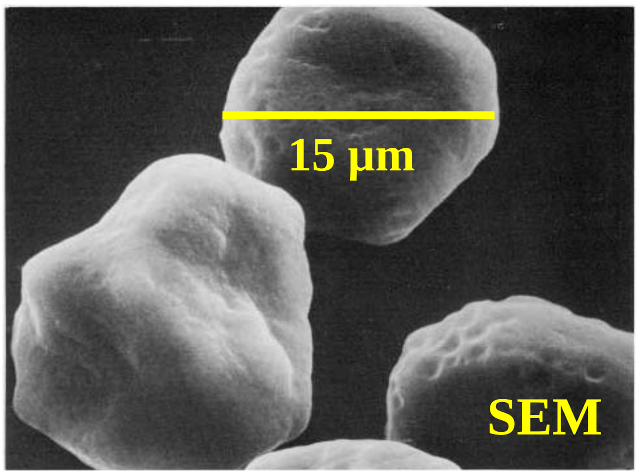
Nano Fibrillated Cellulose (NFC) Potential Coating Additive Applications

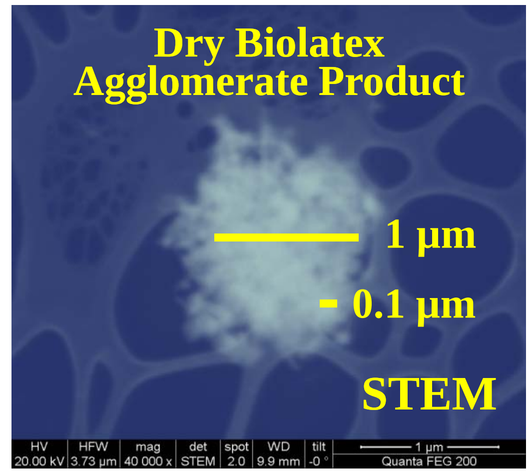
- Improvement of coating micro surface structure
- Improved ink jet and LEP papers
- Improvement of print quality and fidelity in direct print flexo without smudging

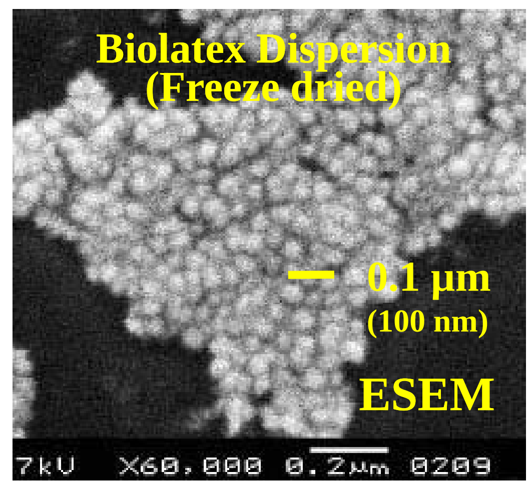
Nanoparticle Biopolymer Coating Binder Production



Native Starch Granules

“Patented” Reactive Extrusion Process





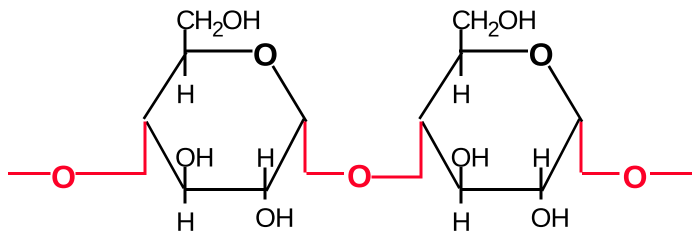
Nanoparticle Biopolymer Coating Binder

- Produced by reactive extrusion process to make ~100 nm nanoparticles
- Readily dispersible in water
- Binding strength about equivalent to SB latex
- Improved water holding
- Improved coating structure – nanoparticles don't shrink back when dried – yields good optical properties
- Can facilitate higher solids coating
- Commercially available and in regular use

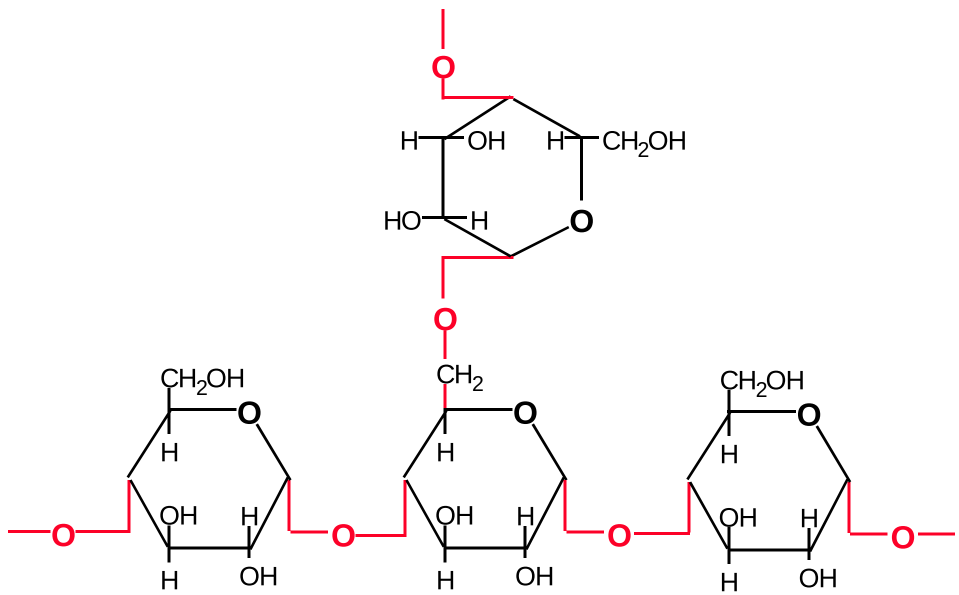
Starch-based Pigments

- Research at University of Helsinki in cooperation with Western Michigan University
- Objective was to replace mineral fillers and coating pigments to
  - Reduce formation of deinking sludge
  - Make a combustible pigment to reduce usage of fuel oil
  - Reduce ash and minerals in landfill – starch-based pigment is biodegradable
- Spherical particles formed by chemically cleaving potato starch acetate with DS value 2 to 3 and T_g 158-160°C
  - Particle size 250 nm with narrow particle size distribution
  - Refractive index 1.47
  - ISO Brightness 94%
- 20 – 30% solids as produced

Starch-based Pigments – structure of starch

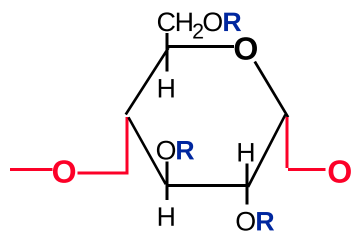


Linear α-1,4-glucan -- AMYLOSE
(200 to 2000 anhydroglucose units)

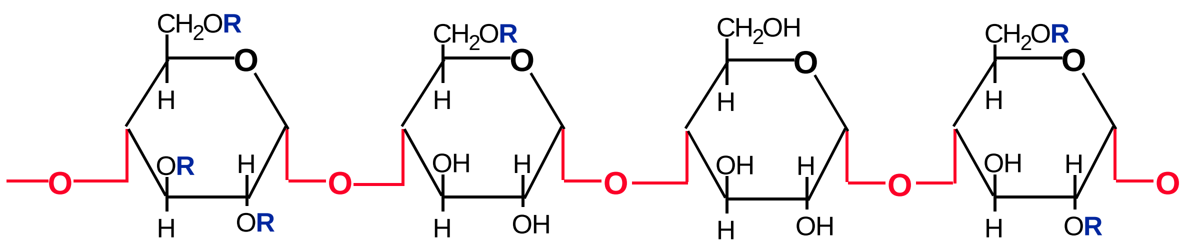


Branched polymer -- AMYLOPECTIN
α-1,4-glucan with 1,6-glycosidic linked branches containing 20-30 anhydroglucose units

Structure of starch esters



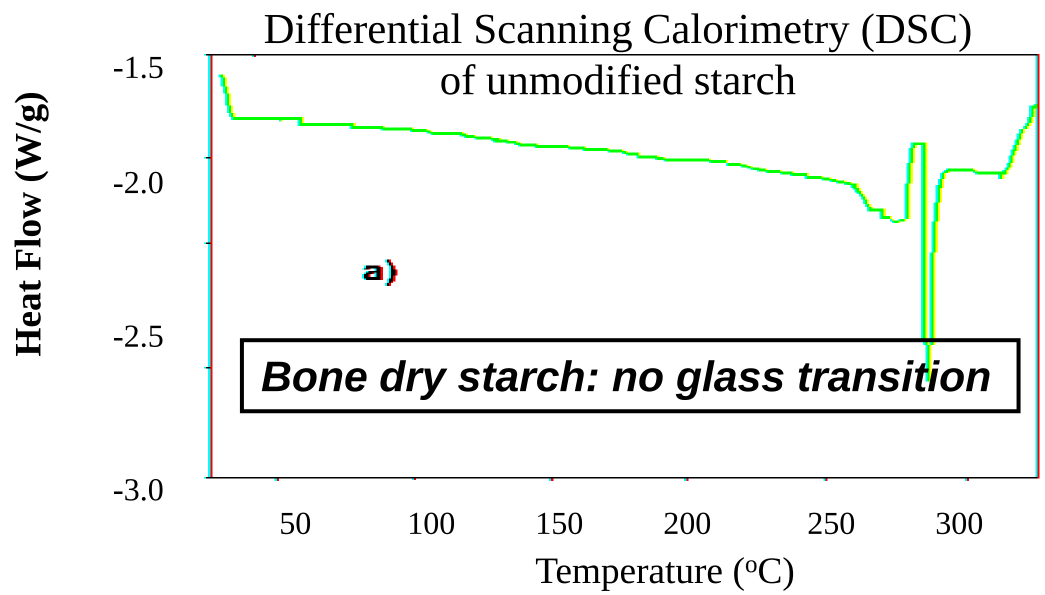
Starch triester

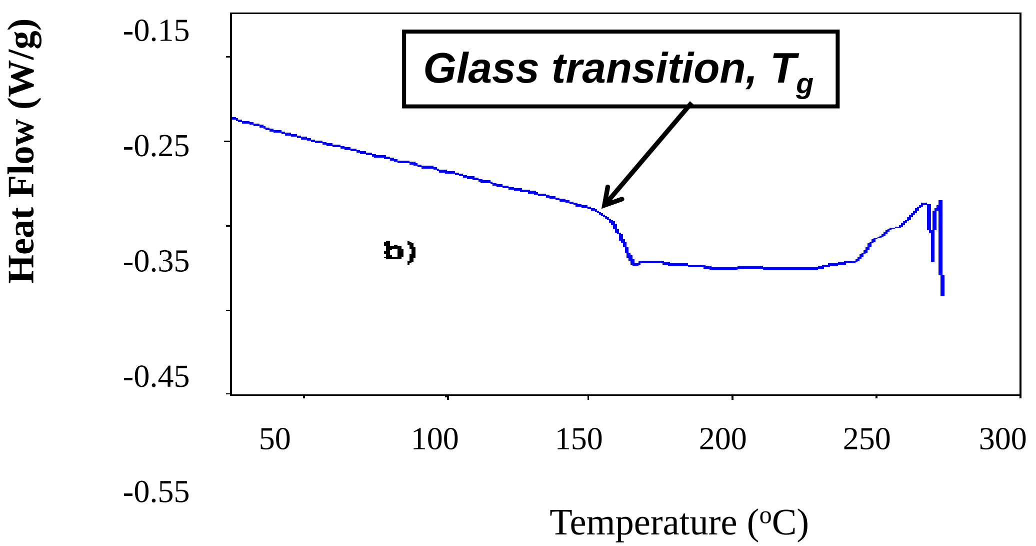


Random copolymer of mono, di, and tri-substituted starch ester

[R = $-COCH_3$; $-CO(CH_2)_nCH_3$ (n = 2 to 18); maleate, succinate]

Starch esters: thermoplastic polymers





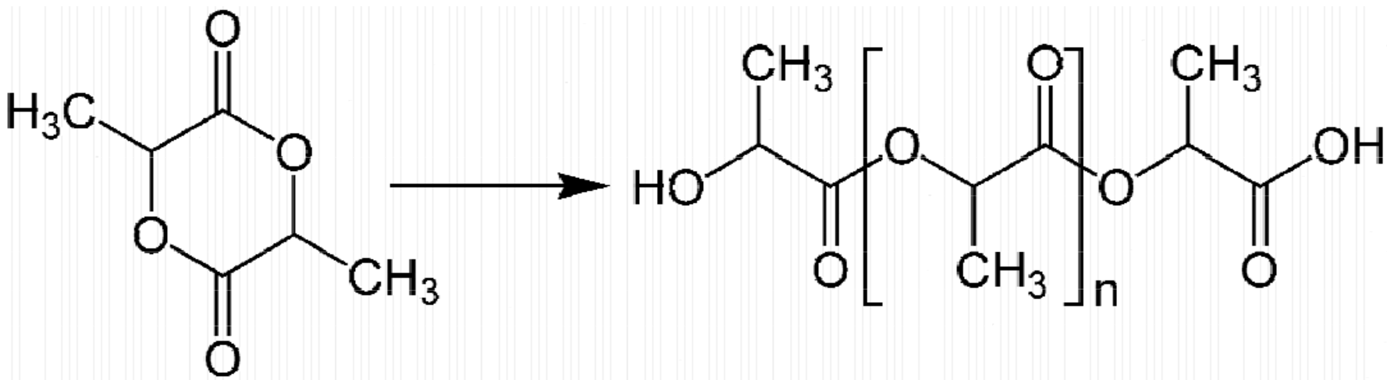
Source: S. Bloembergen

Starch-based Pigments
Results of CLC and Pilot Coating Trials

- At 25% substitution for kaolin clay, starch-based pigment showed
  - Improved response to supercalendering
  - Higher gloss
  - Higher calendered opacity
  - Decreased roughness
  - Higher print gloss
  - Equal pick resistance
- Major impediment is higher price than mineral pigments
- Further research may show benefits at lower substitution rates

PLA – Polylactic Acid

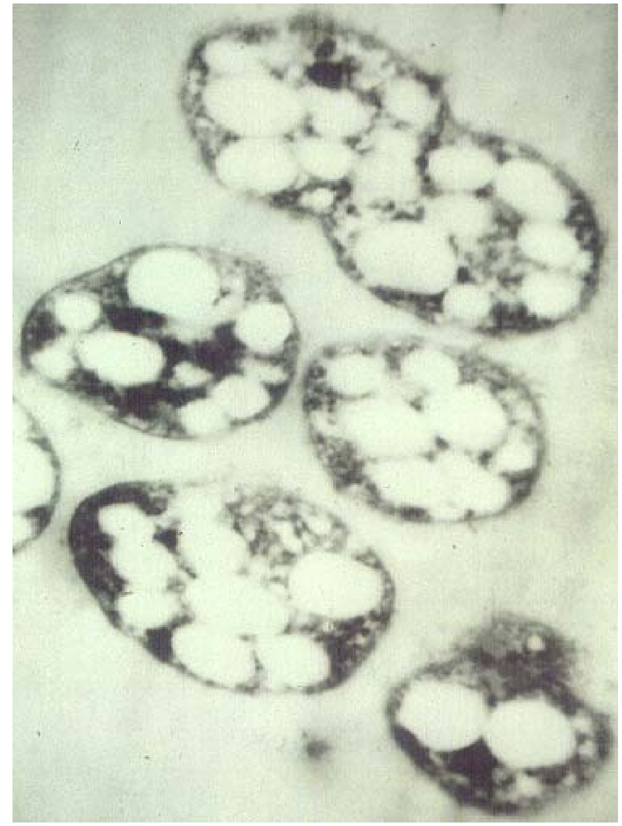
- Polylactic acid (PLA) is a thermoplastic aliphatic polyester derived from starch or sugar cane
- Bacterial fermentation is used to make lactic acid from corn or sugar cane
- Lactic acid or lactide dimer is polymerized to form PLA resin

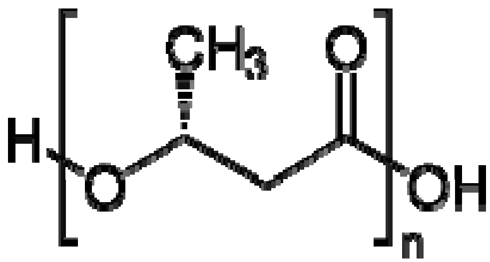


- Currently used in thermoplastic molding for use in drink cups, etc.
- Being used for extrusion coating of paper and board
- Aqueous dispersions being developed for barrier coating

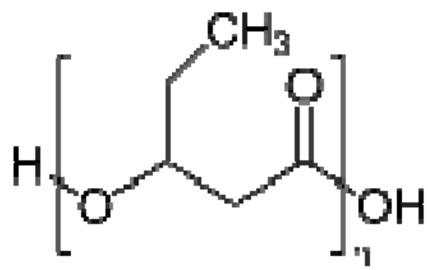
PHAs – Polyhydroxyalkanoates

- Polyhydroxyalkanoates (PHAs) are a family of aliphatic polyesters
- Poly-β-hydroxybutyrate (PHB), the simplest PHA, was discovered by Maurice Lemoigne in 1926 as an energy storage granule in *Bacillus megaterium*
- The most common PHAs are PHB/V (hydroxybutyrate/hydroxyvalerate) copolymers, thermoplastics being introduced to the market by Metabolix





PHB



PHV

Source: S. Bloembergen

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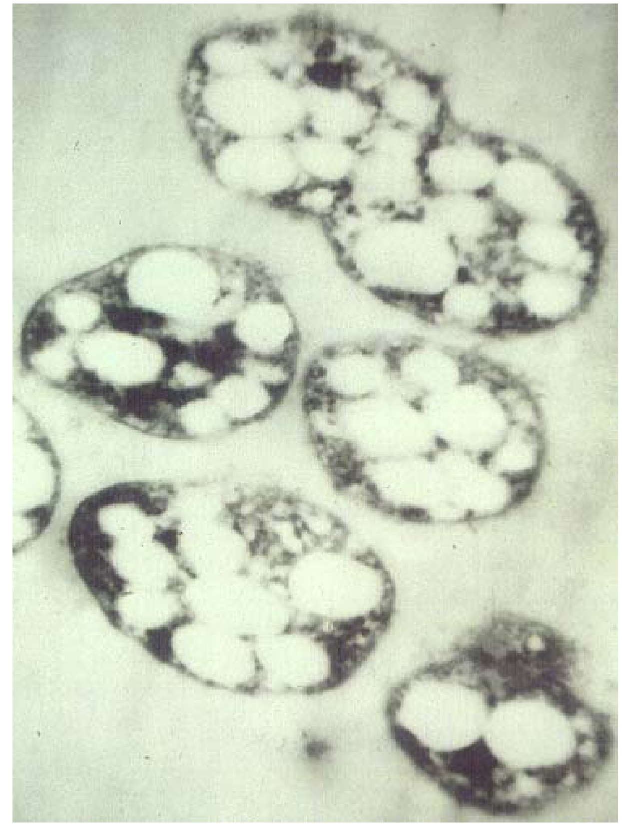
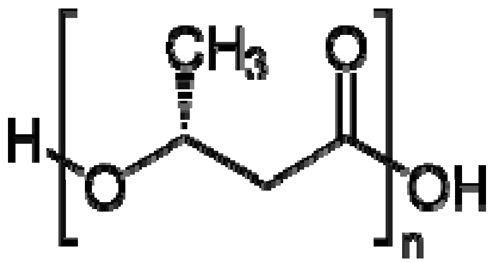
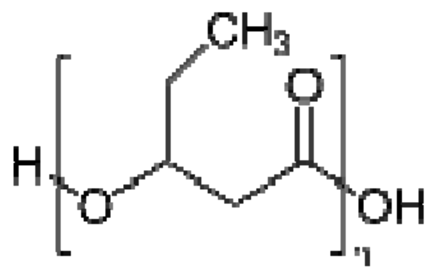
PHAs – Polyhydroxyalkanoates

- PHB has a high melting point (Tm=180 °C) and its high degree of crystallinity renders it fully water resistant
- PHB has become the “gold standard” for biodegradability of high molecular weight polymers
- PHB/V copolymers have lower Tm’s yet still have high crystallinity and are more readily processable than PHB itself





PHB



PHV

- Currently the scale of production and economics are not in line with coated paper manufacturing

Source: S. Bloembergen

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Zein (Maize Protein)

- Zein: A class of prolamine protein found in maize
- Has been used in food and pharmaceutical applications
- Subject of USDA laboratory research on potential paper industry applications
  - Shows promise as a barrier coating material to provide oil and grease resistance and WVTR barrier applications
  - Shows promise as a biobased dry strength resin
  - USDA issued patented technology is available for license

Source: R. Narayan and USDA Philadelphia Laboratory

Path Forward

- Research and commercialization on biobased coating materials is in early stages, but some products are already commercialized
- Emphasis on sustainability and reduction of carbon footprint – along with upward movement in crude oil and petrochemical material prices – will likely continue to make biobased materials priority R&D objectives
- Applications are likely to extend beyond conventional coated paper and paperboard – especially in recyclable and biodegradable barrier coated paper-based packaging materials
- Other biobased materials are on the horizon for use by the paper industry, provided advances in scale and economics are realized

Acknowledgements

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- Dr. Akira Isogai, University of Tokyo
- Dr. Steven Bloembergen, ECOSYNTHETIX INC.

Thank you for your attention!

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