Biobased Materials for Paper Coating

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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

Examples:
- Kenaf
- Sisal
- Jute
- Hemp
- Flax

Products:
- Biofiber Composites

Natural Fibers
- Examples:
  - Corn
  - Potato
  - Tapioca
  - Industrial Mod. Starches
  - Thermoplastic Starch
  - Starch Foams
  - Starch graft copolymers & reactive blends
  - Starch nanoparticles

Starches
- Examples:
  - Pectin
  - Chitin
  - Levan
  - Pullulan

Other Polysaccharides
- Example:
  - Biodiesel
  - Lubricants
  - Polyols – urethanes
  - Plasticizers / Process aids

Fats & Oils
- Examples:
  - Soybean
  - Lesquerella
  - Rapeseed

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 –
TEMPO-mediated oxidation of various native celluloses
— Effective surface modification of cellulose microfibril —

Source: Akira Isogai
Differences in morphology and consumed energy between micro-fibrillate cellulose and TEMPO-oxidized cellulose nano-fibers

Micro-fibrillated cellulose

TEMPO-oxidized cellulose nanofibers

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

Disintegration energy < 2 kwh / 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
The TOCN films, even having in-plane random orientation of TOCN elements, have sufficiently high tensile strength and high elastic modulus.

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 Rigidal, Michael Bilodeau, and Doug Bousfield
Department of Chemical and Biological Engineering and Process Development Center, University of Maine,
Orono, ME 04469

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.

NFC incorporated into latex films increases strength properties.

Tensile stress of latex/kaolin pigment films containing NFC.

Tensile test strips, composed of SBR latex and NFC.
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

Dry Biolatex Agglomerate Product

1 µm

- 0.1 µm

STEM

Biolatex Dispersion (Freeze dried)

- 0.1 µm (100 nm)

ESEM
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

\[
R = -\text{COCH}_3; \ -\text{CO(CH}_2\text{)}_n\text{CH}_3 (n = 2 \text{ to } 18); \text{ maleate, succinate}
\]
Starch esters: thermoplastic polymers

Differential Scanning Calorimetry (DSC) of unmodified starch

Bone dry starch: no glass transition

Glass transition, $T_g$

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

![Chemical structure of PLA](image)

- 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
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

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

Source: S. Bloembergen
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.
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Thank you for your attention!

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