Over View of Ragauskas' Fiber Research Program

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Ragauskas Research Vision

Focused on Exploiting Lignocellulosics Chemistry To Develop Innovative Sustainable Solutions For The Pulp and Paper Industry

Research Program Initiated 1989


Ragauskas Team
Exploiting
Lignocellulosic
Chemistry - Engineering
Material Research
Paper
Board
Material Research
Fillers
Composites
Energy
Integrated
Biorefinery

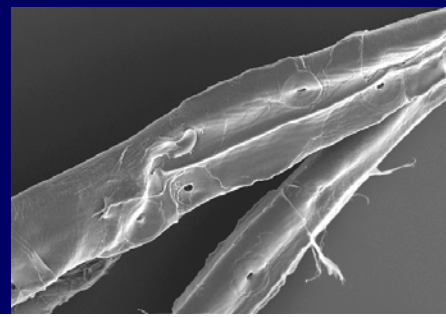
Highlights of Current Research Portfolio

Ongoing Research: Fiber Engineering

Program Objective:

Identify topochemical fiber properties that enhance physical properties of fibers, paper and board. Research activities include:

- Innovative pulping and bleaching technologies to control fiber charge and enhance refinability, tensile, tear, stiffness, bulk, STFi
- Curl/Kink control strategies
- Enhanced extractives control
- Crosslinking and sulfonating fibers for enhanced water absorbency



Ongoing Research: Advanced Pulping/Bleaching

Program Objective:

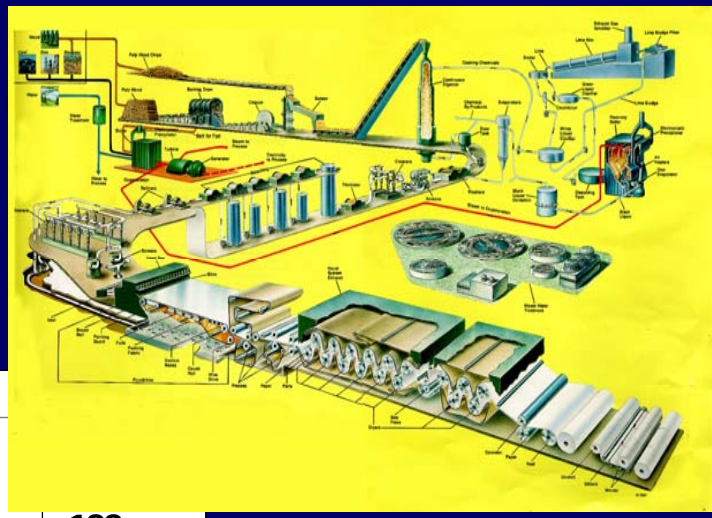
Integration of kraft pulping and bleaching operations for reduced cost and improved pulp properties.

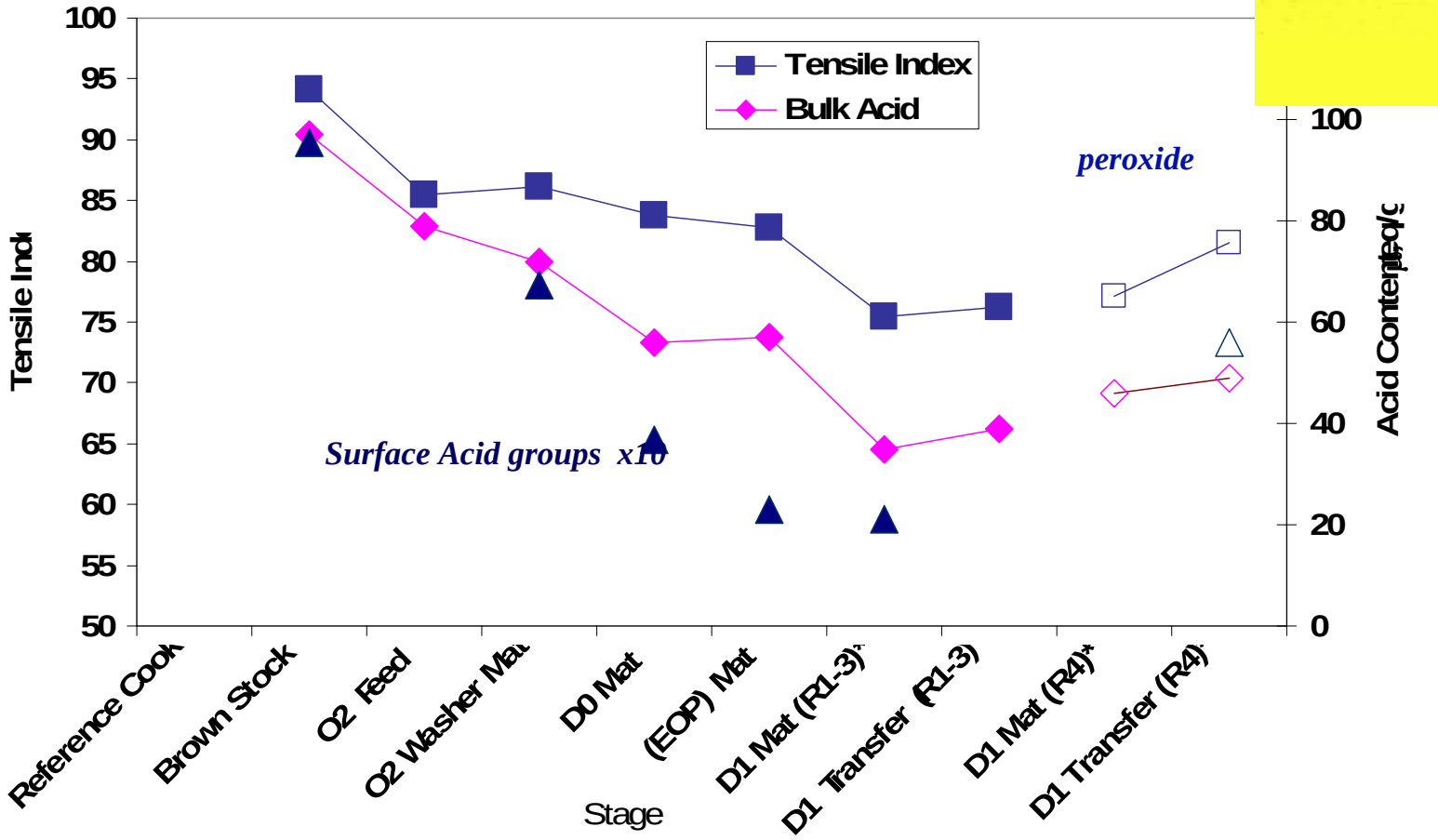
- High kappa pulping/extended oxygen delignification for enhanced yield
- Optimized ECF pulp bleaching
  - Minimizing bleaching chemicals
  - Minimize corrosivity of bleaching equipment
- Hexenuronic acid control strategies
- Reduced reversion of fully bleached kraft pulps

Fiber Modification/Fiber-Fiber Bonding

HIGHLIGHTS

- **OD(EOP)D Mill Tensile Strength and Bulk/Surface Acid Groups**





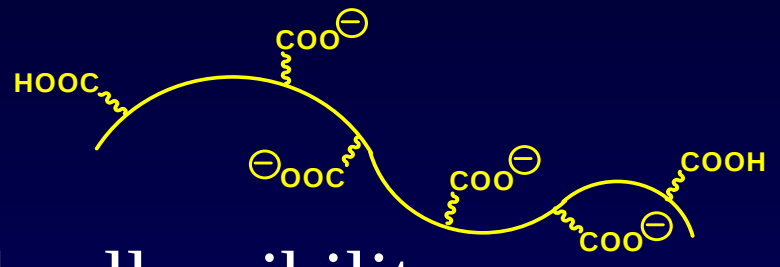
Gradual loss of acid groups due in part to degradation of lignin

Finally P increases Brightness - Known

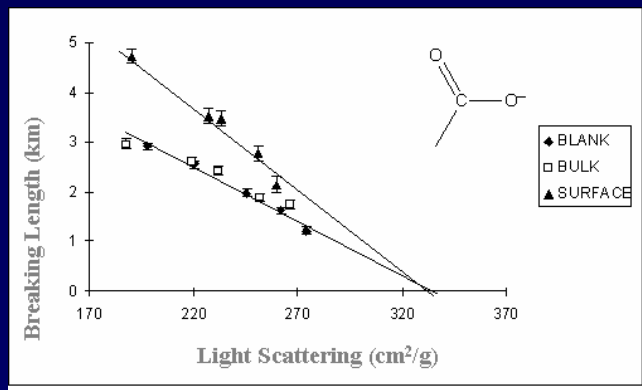
Previously not documented Strength-acid groups Due to terminal P-stage

Fundamentals of Fiber Modification Chemistry: Importance of Carboxylate Groups

- Main group responsible for surface and bulk charge of kraft fibers.
- Important for pulp swelling.
- Increase pulp fiber softness and collapsibility
- Improve pulp strength properties.
- Improve beatability.
- Capable of ion-exchange reactions.



$$K_{specific} = \frac{[\text{-COO}^-][\text{H}^+]}{[\text{-COOH}]}$$



Barzyk, Page, and Ragauskas (1996)

Fiber Modification/Fiber-Fiber Bonding

Program Strengths

1. Extensive mill expertise
2. Internationally recognized in relationship between fiber chemistry – physical properties
3. Fiber Imaging capabilities: SEM/TEM/AFM/ESCA/TOF-SIMS
4. Established team with leading expertise in mill pulping/bleaching/refining, paper physics, fiber chemistry, imaging

Improved/New Tissue

Liquid Packaging

Boxes

Magazine

Writing/Printing Paper

Modified Filler Studies IPST@GT

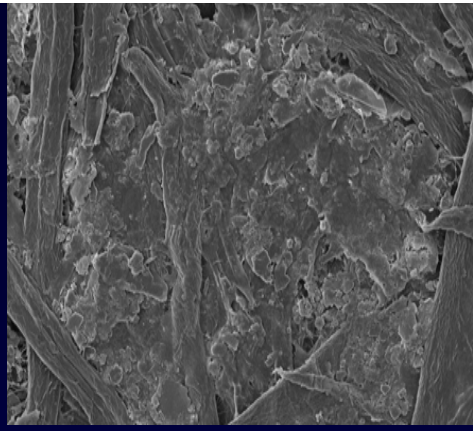
Program Team

Program Leader: Ragauskas
Task Team Leaders: Y. Deng, A. Ragauskas

Program Objective:

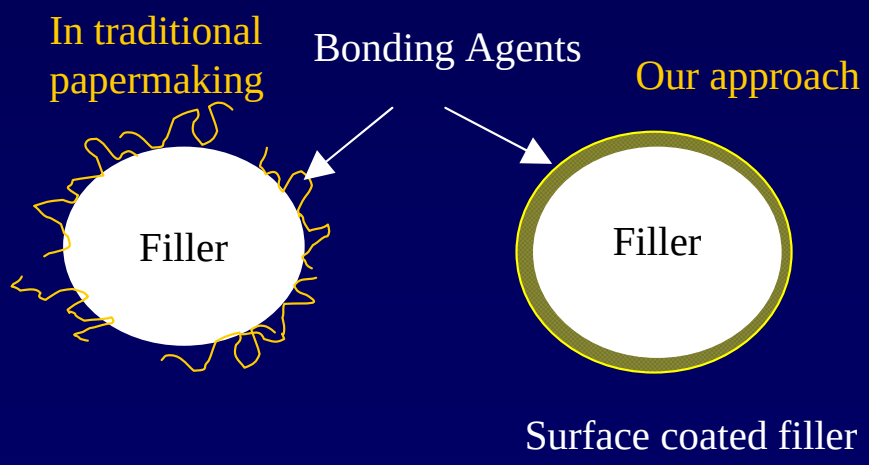
- Increase the value of pulp products by 50% by identifying new composite paper product platforms that will dramatically improve existing sheet properties and develop new applications for pulp fibers.
- Develop non-brittle synthetic fibrous fillers with the ability to bond with fibers and fillers.
- Applications include printing, packaging, food, and sanitary products.

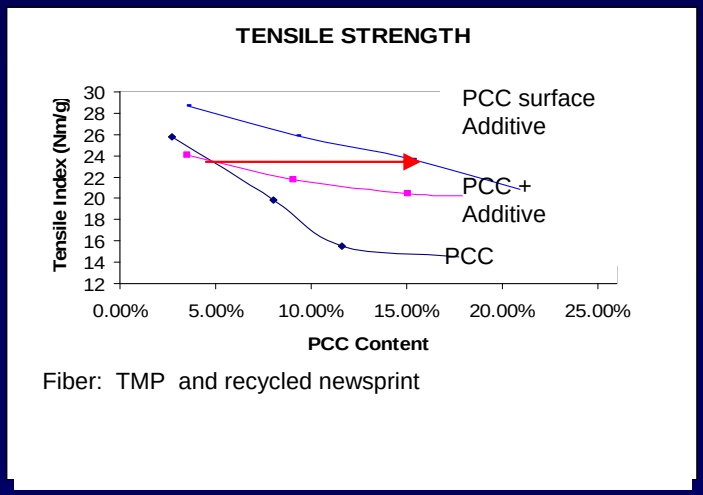
Modified Filler Studies:



FY 2004 – 08 Program Goals:

Research directed at determining the important topochemical parameters for developing new PCC/clay fillers that permit increased filler application levels without additional sheet strength losses

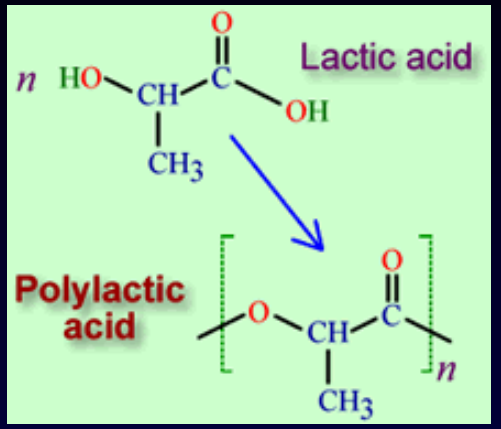


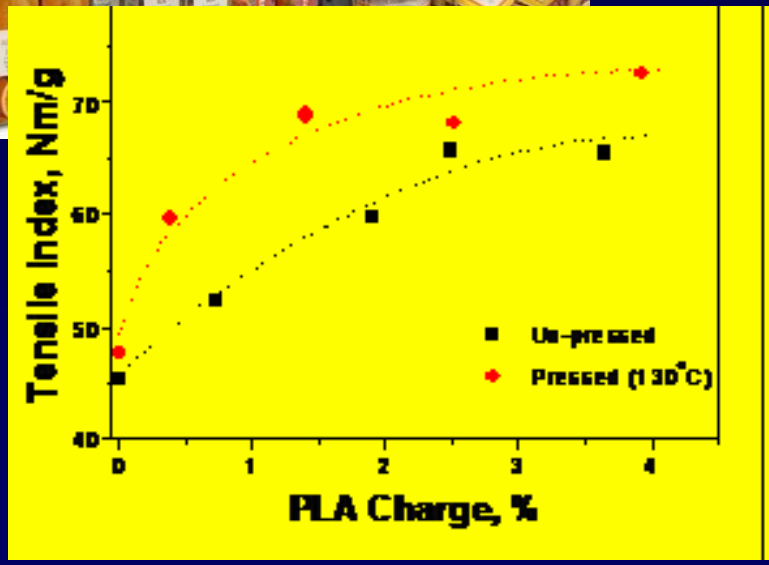


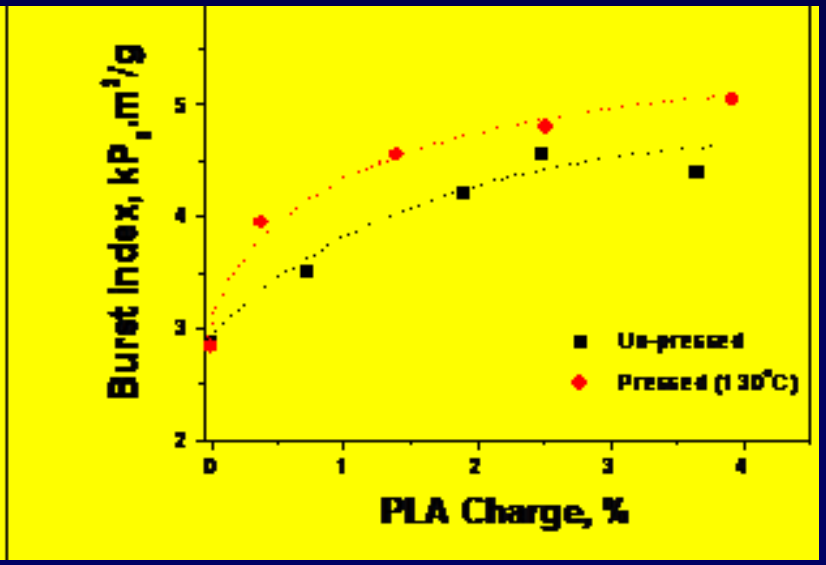
Lower Cost Packaging and Writing Paper


Industry Sponsored
Composite Research Program
New Fiber Applications

PLA – Pulp Composites







Product Platform Research

Developing New Markets for Kraft Pulps

- Innovative biocomposites: pulp + plastics

- Total plastic filler market is 5.5 billion lbs
- Approx. 1.7 billion lbs is reinforced with fiber glass

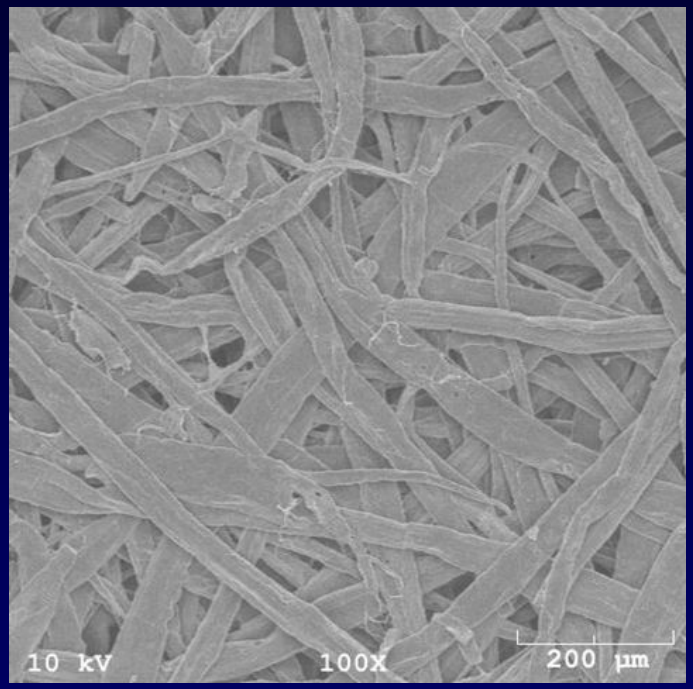
Glass fiber is ~ $1800/ton

- Plastic wood with wood flour is about a 400 million lb market growing 10-20% year, wood flour provides little if no strength benefits

Research directed at using kraft pulp fibers

Nano-Enhanced Paper: Coatings

Application of Polyelectrolyte Coating Technologies
Layer-by-Layer Self-Assembly

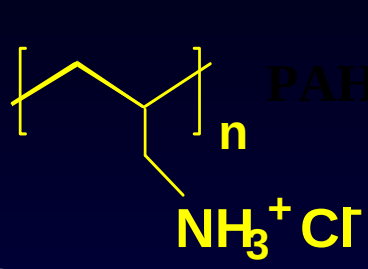


General Considerations:

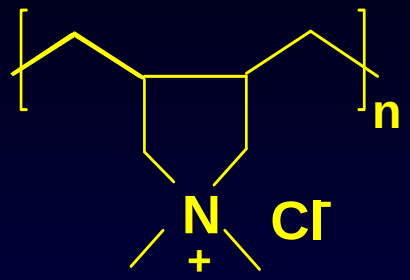
- Assembly via electrostatic and H-bond interactions
- Aqueous Processing
- Process Parameters:
    - pH; salt concentration
    - Polymer charge/DP
- Wide range of materials can be employed
    - Paper
    - Board
    - Tissue
    - Fillers

Nano-Enhanced Paper: Coatings

Current Studies



PAH



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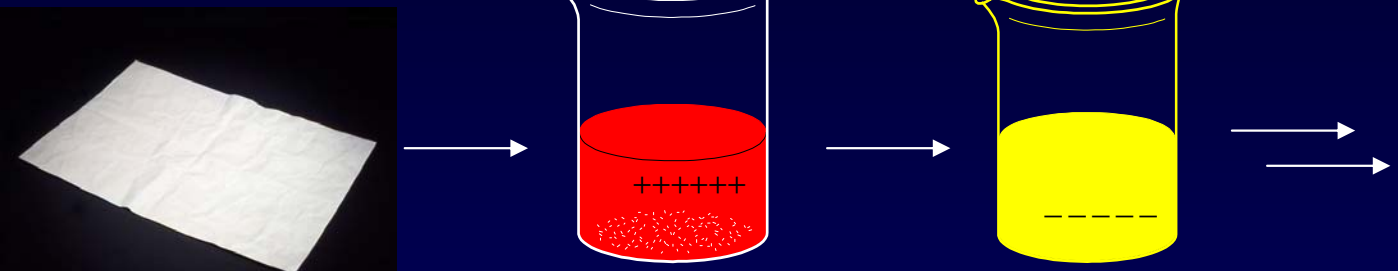
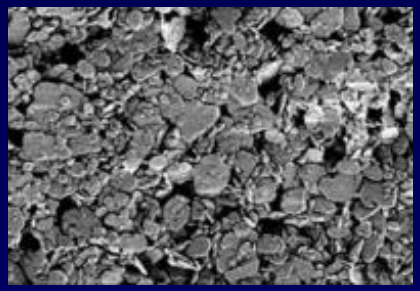
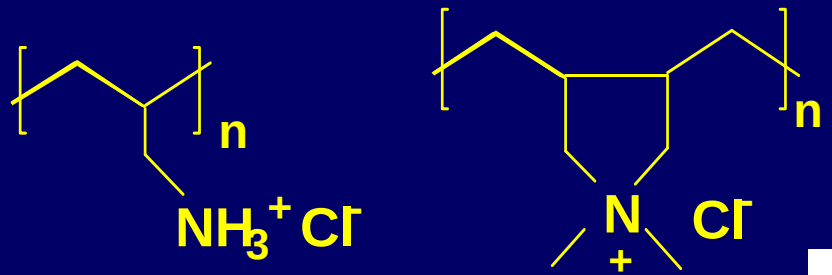
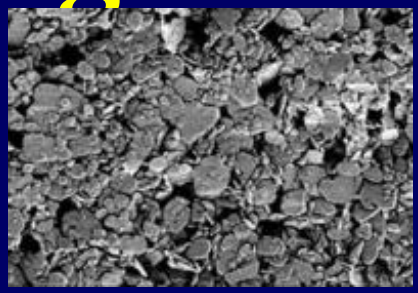




Nano-Enhanced Paper: Coatings

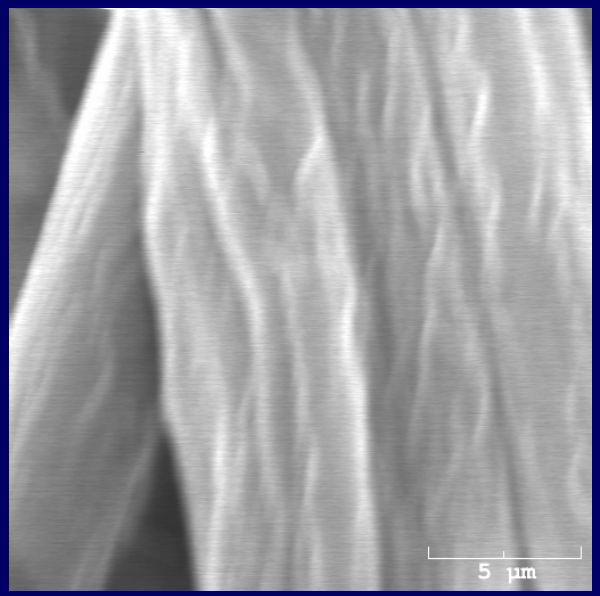
Current Studies

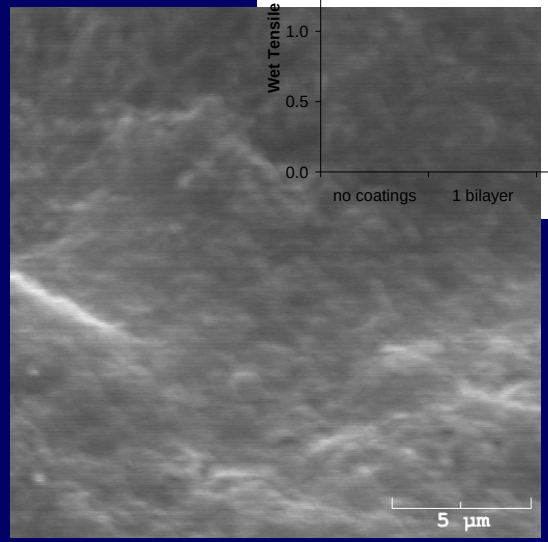


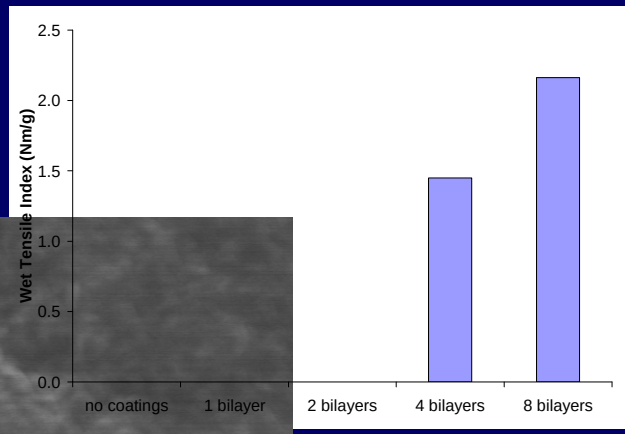


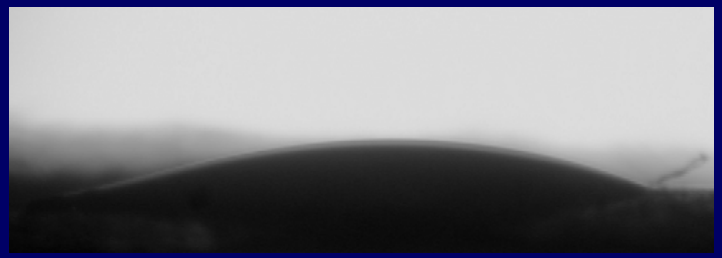
Initial Fibers

8 Bilayers of PAH
Kaolin





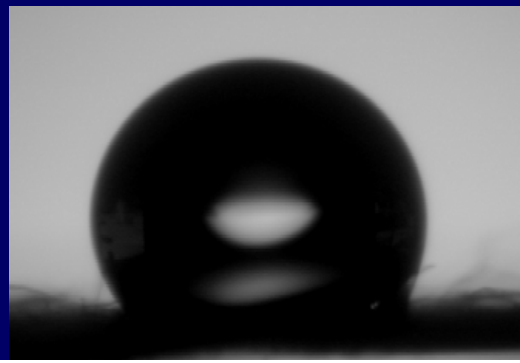




Water Contact Angle

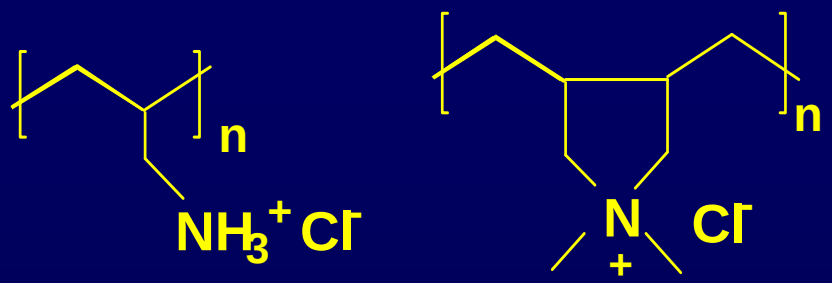
← Untreated

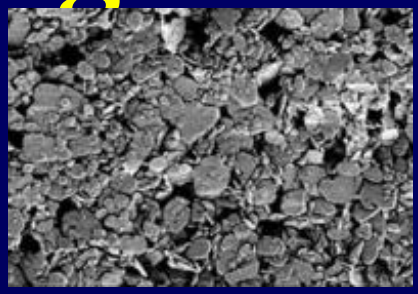
Treated →



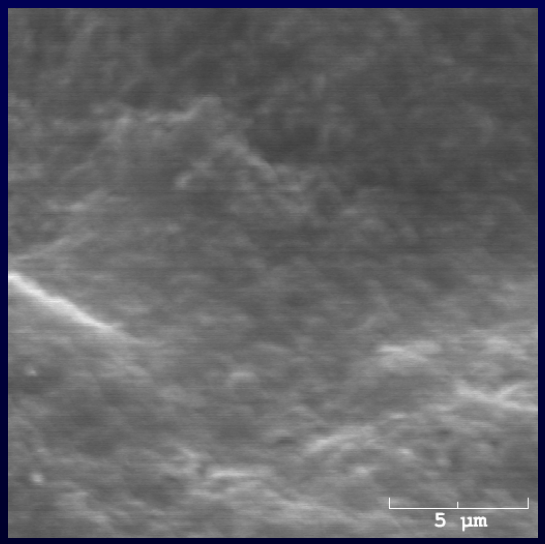
Nano-Enhanced Paper: Coatings

Current Studies





Bilayers of PAH/Kaolin



Ongoing Studies

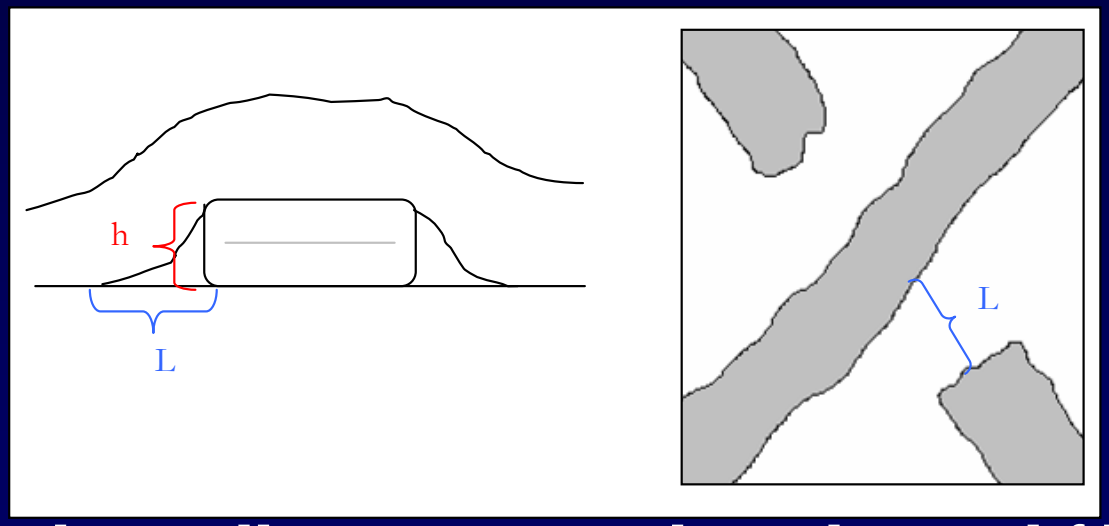
- *Enhance hydrophobic effect*
- *Optical properties*
- *Alternative barrier properties*
- *Self-cleaning nano-coatings*

Fiber/Sheet Modification

Research Programs

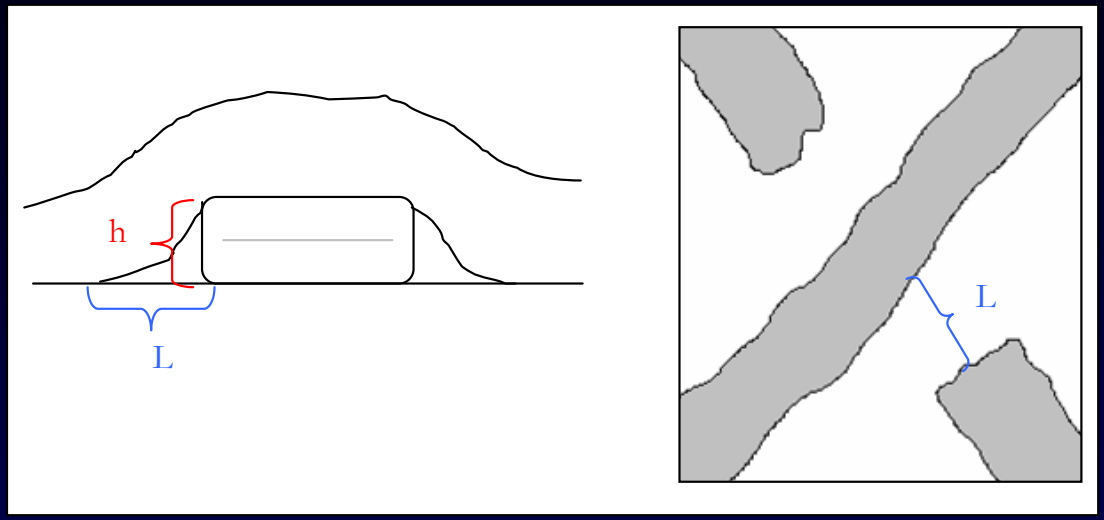
Determining Fundamental Principles of Wet Fiber Deformability

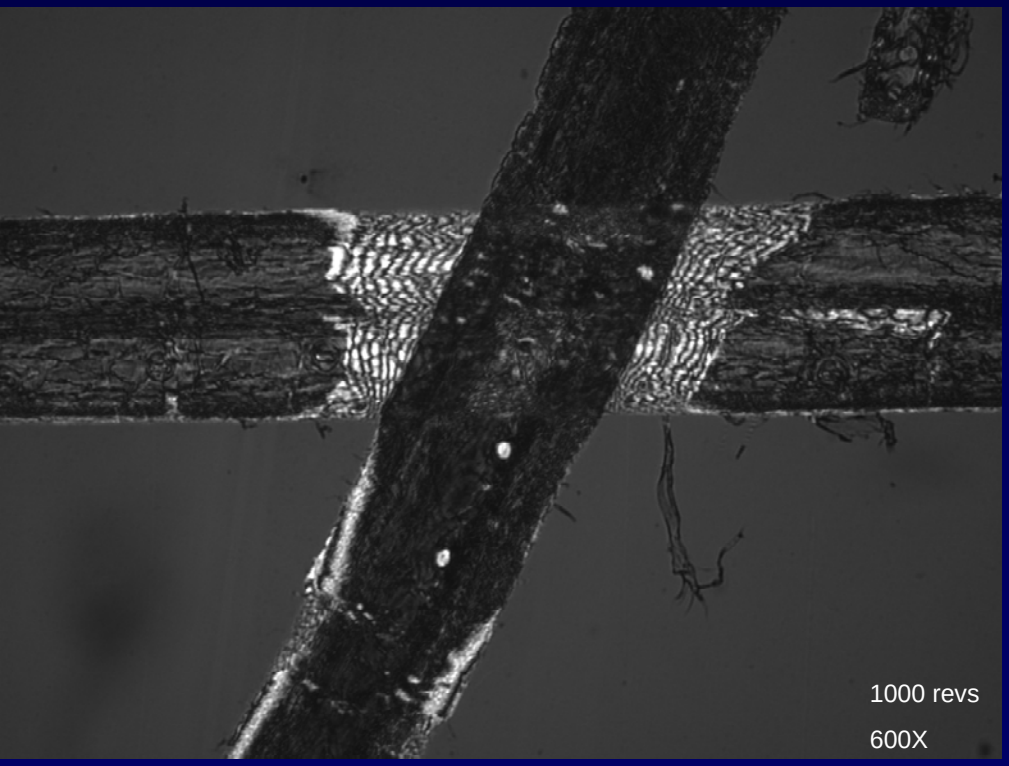
Research Objective: Establish fundamental principles controlling wet fibre *flexibility* (deformability) is important for the physical and optical properties for paper/tissue. The response of fibres to the forces of wet pressing and surface tension determines the ultimate sheet structure and properties.

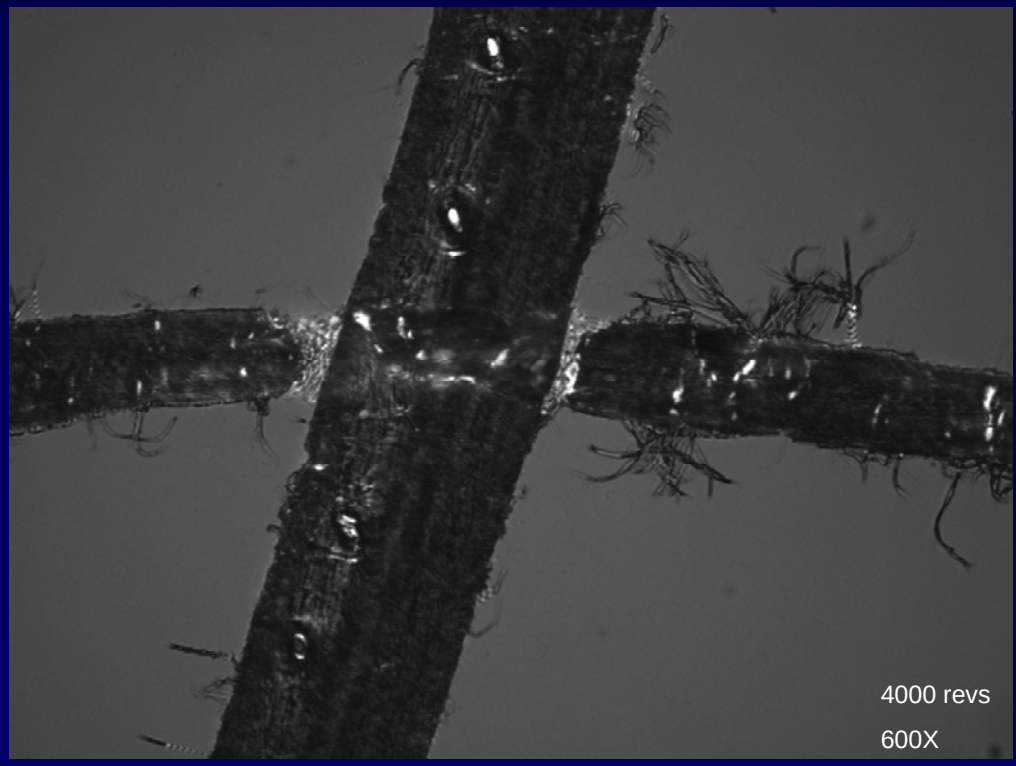


Research studies will examine employ advanced fiber concepts on flexibility vs deformability and determine role of surface charge, refining, and wet end chemical

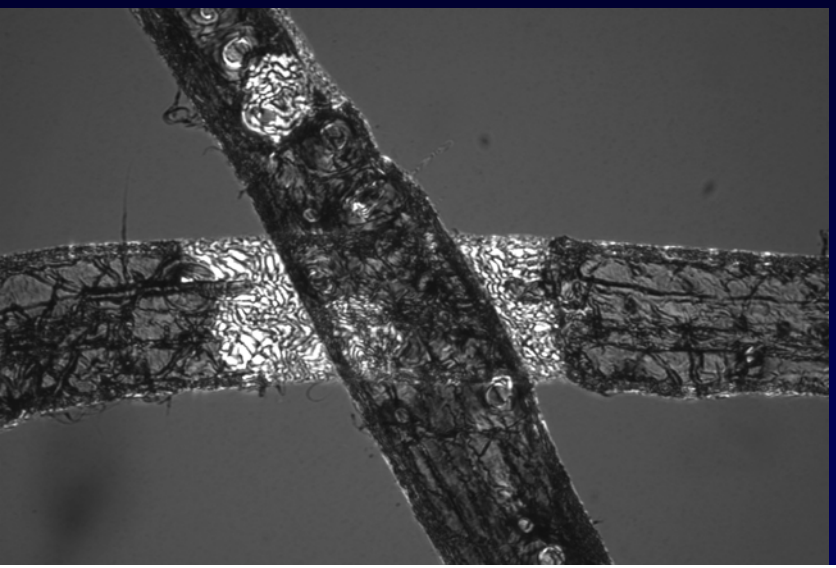
Determining Fundamental Principles of Wet Fiber Deformability

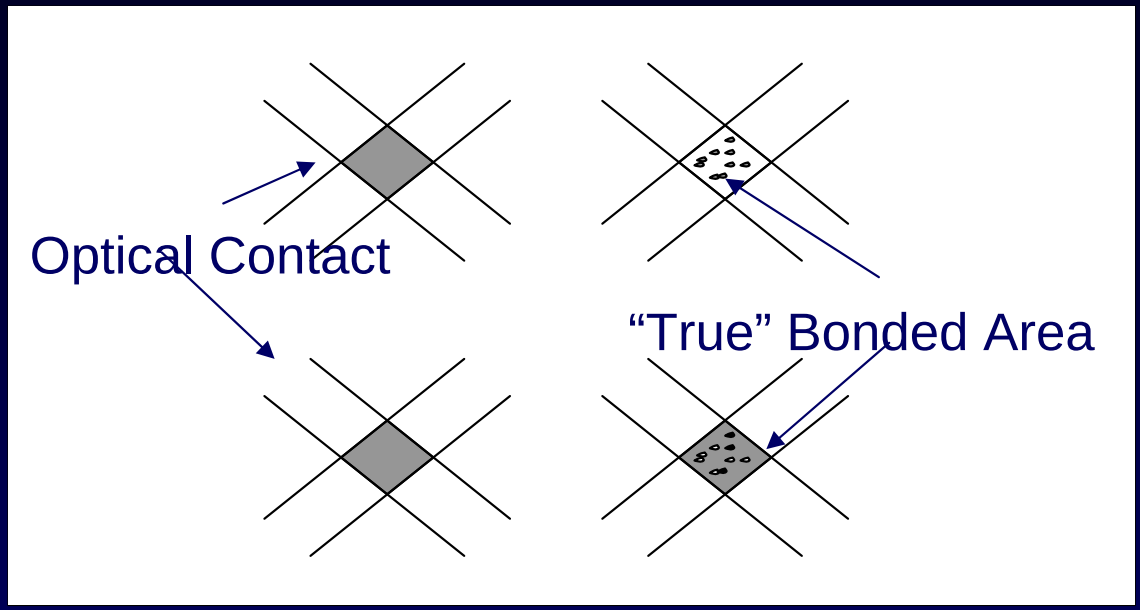


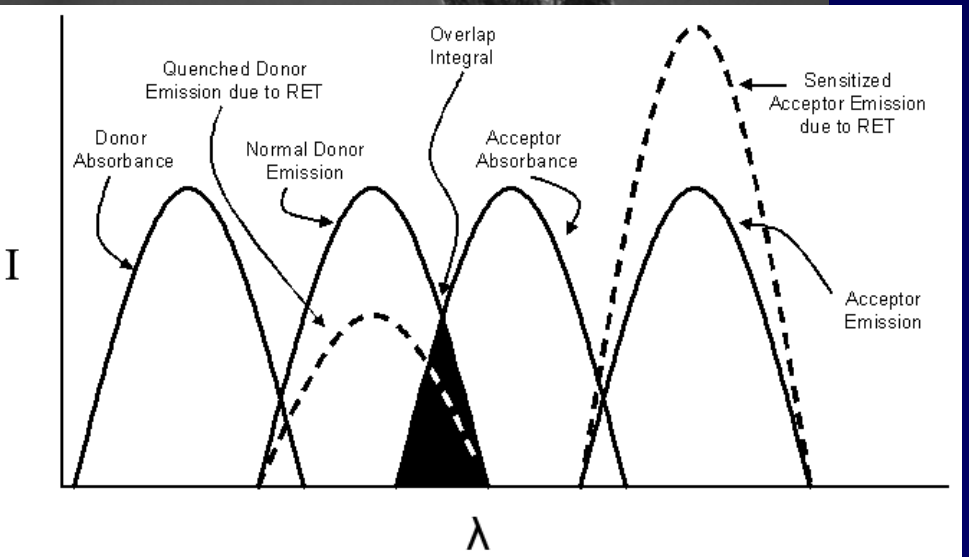


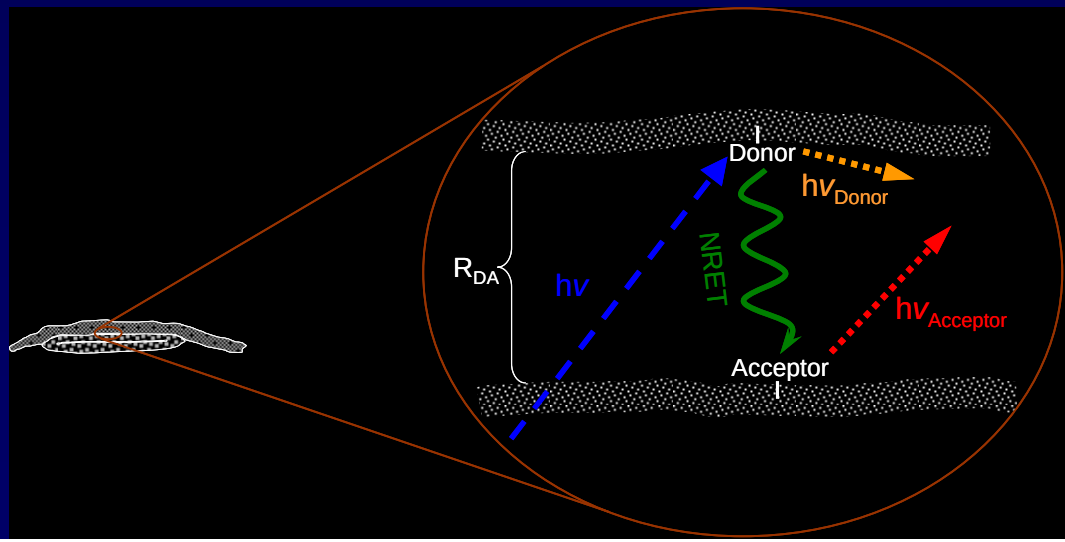


Novel Visualization of Fiber-Fiber Bonding with FRET









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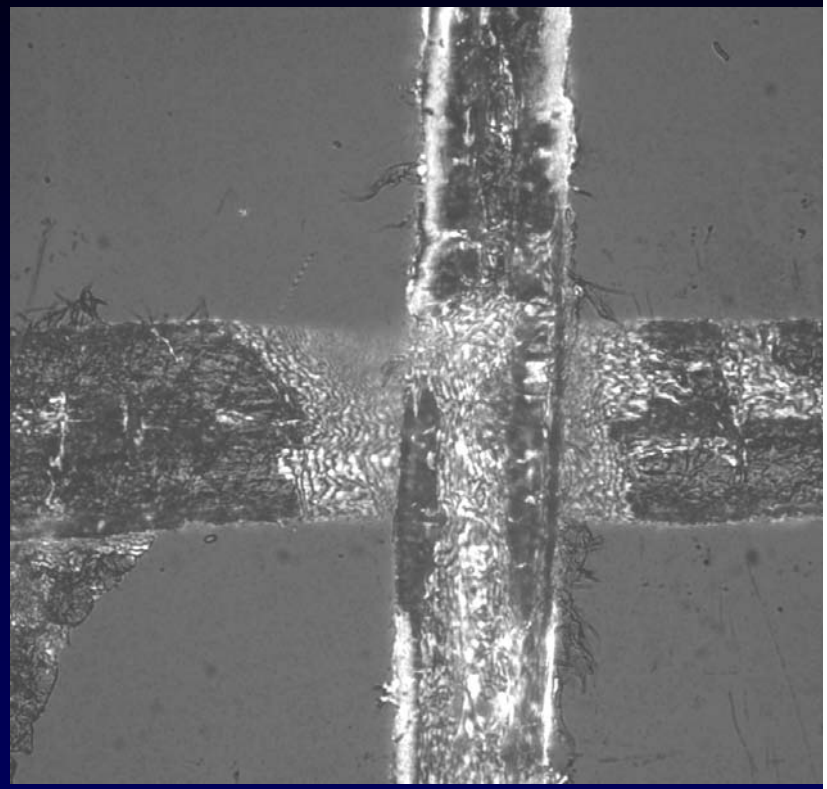
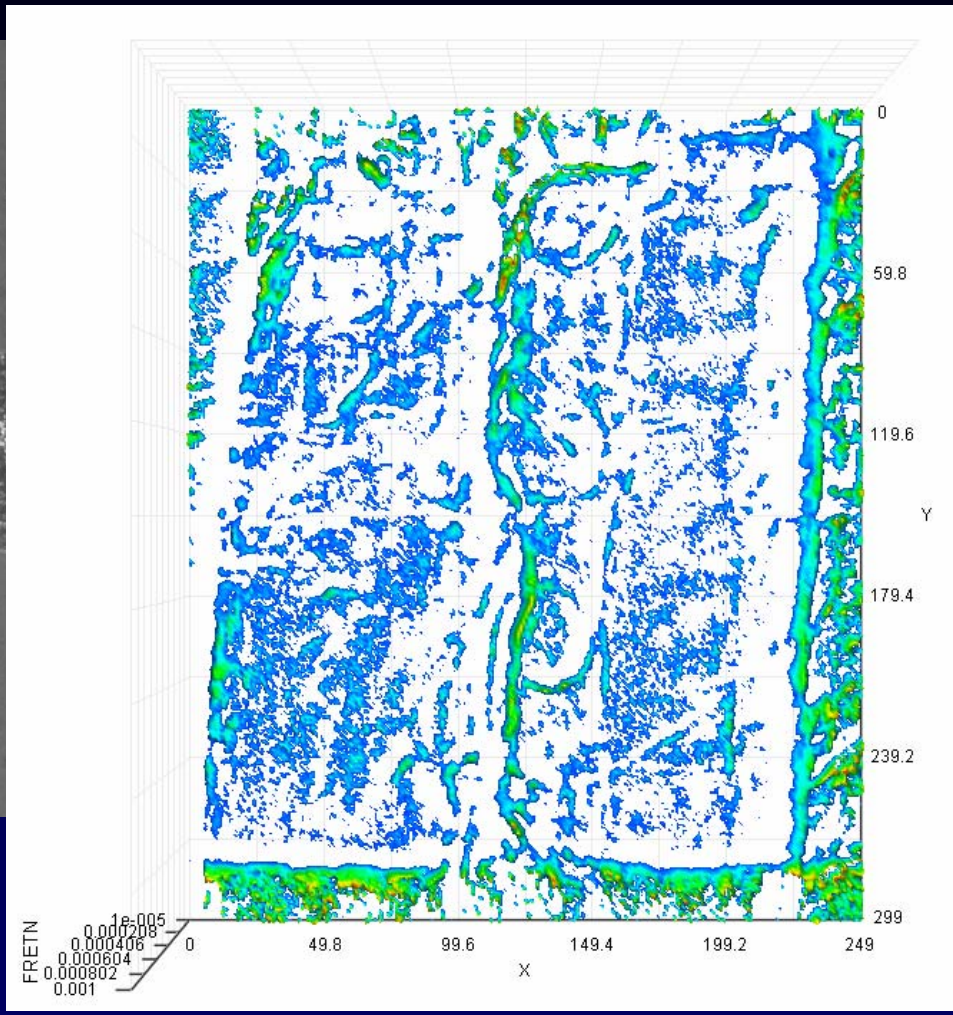
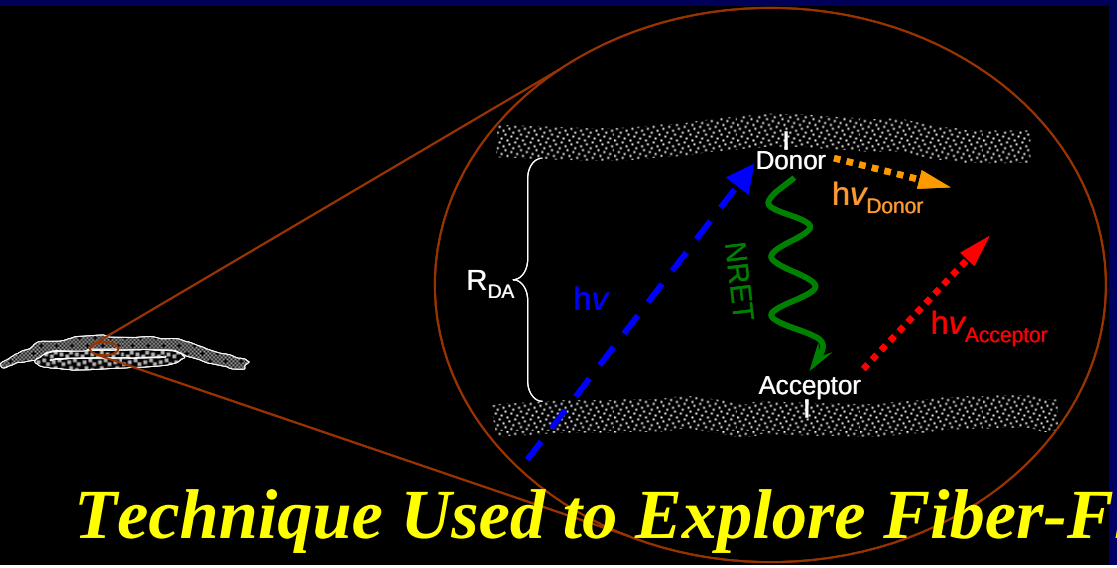


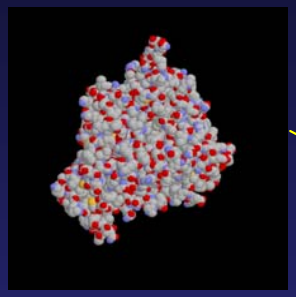




First Picture of
True Fiber-Fiber Bonded Area

Technique Used to Explore Fiber-Fiber Treatments

BioGrafting SW Kraft Fibers



Laccase

Enzymatic Grafting

Phenolic Additives

Amino Acids

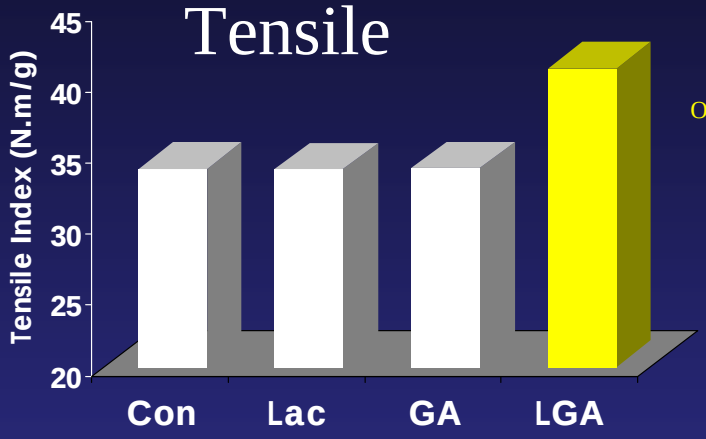
Charged structures

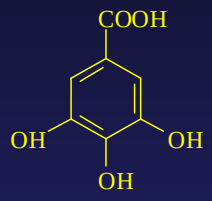
Dyes

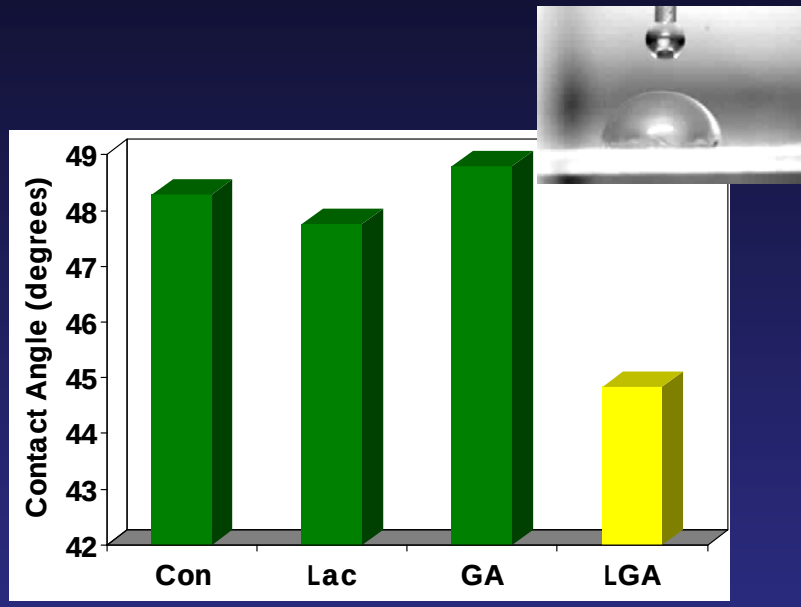
Hydrophobes

New Properties

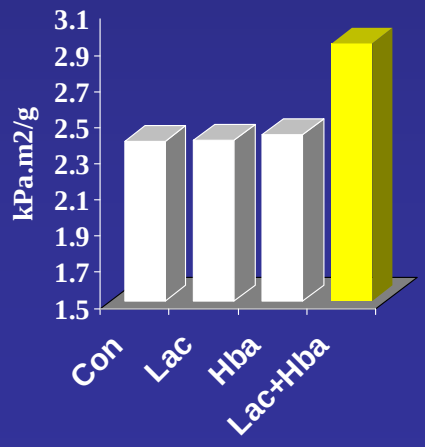
BioGrafting SW Kraft Fibers







Burst Improvements

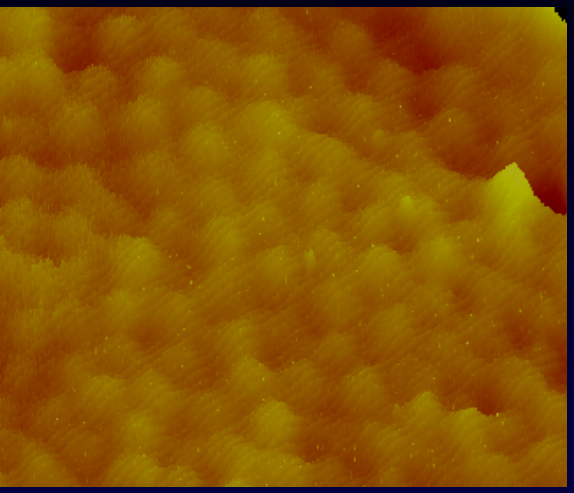


Future Opportunities

- Enzymatic control of fiber/sheet properties
- Modification of sheet friction
- Functional paper

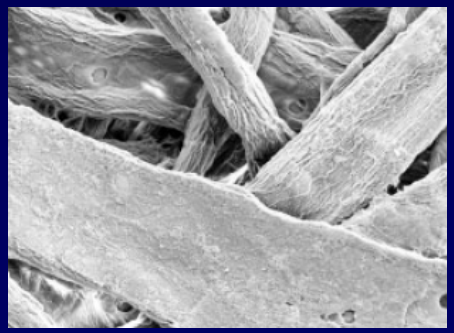
Related Research Programs

Nanotechnology/Pulp and Paper



Nanocellulose Whiskers/Balls

- New cellulosic composites
- New papermaking additives
- Novel viscosity modifiers



Homeland Security

- Tamper proof
- Counterfeit resistance
- Smart Packaging

Provide controllable inner environment for packages:

- CO_2, O_2, H_2O, N_2

Self-assembly Coatings

- Enhanced wet strength
- New Barrier Properties
- Novel Optical Properties
- Superhydrophobic

- **Spoilage/Flavor Control**
- Long Term Storage
- Spoilage Indicators
- New biocomposite packaging materials

Nanotechnology/Pulp and Paper

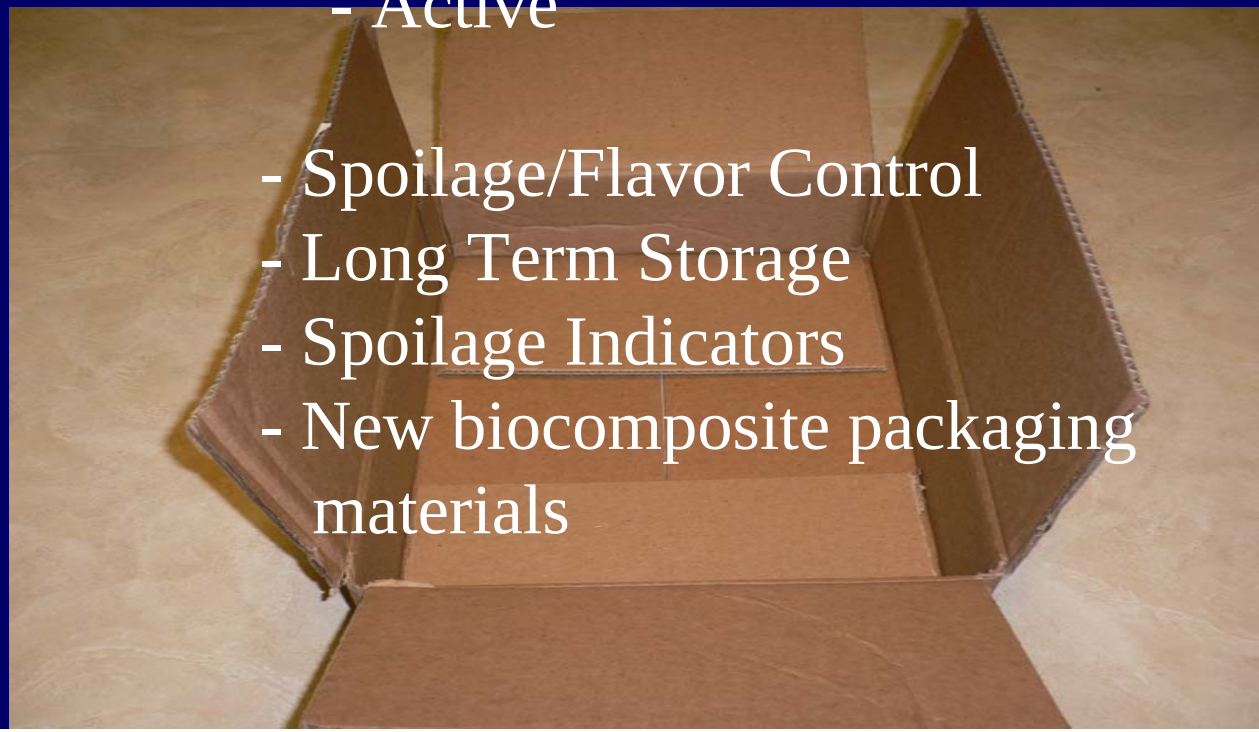
vironment

Provide controllable inner environment for packages:

- CO_2, O_2, H_2O, N_2

Defense systems for bacterial/fungus growth

- Passive
- Active



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Product Platform Research

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Glass fiber is ~ $1800/ton

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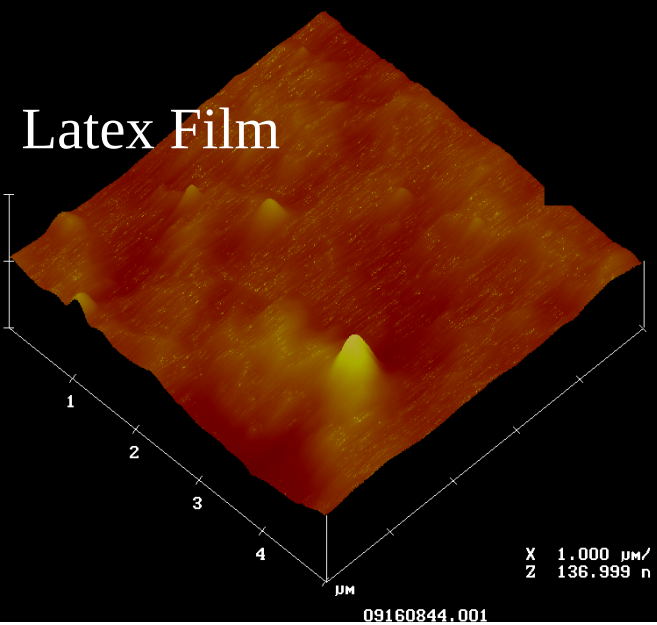
Research directed at using kraft pulp fibers

NanoCellulosic Structures

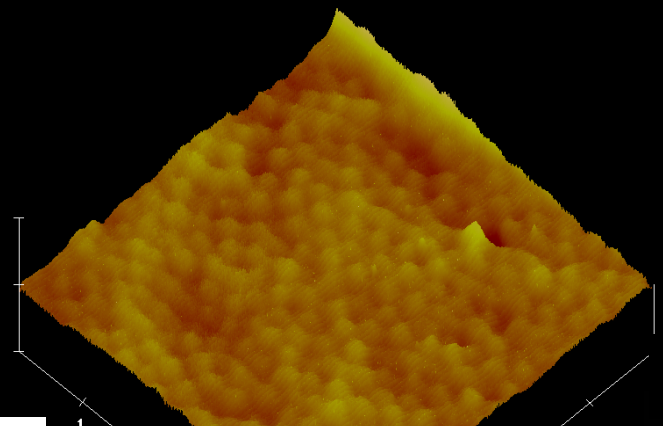
Nanocellulose Whisker:Acrylic Acid Composite Film

Interest from Consumer Packaging Companies

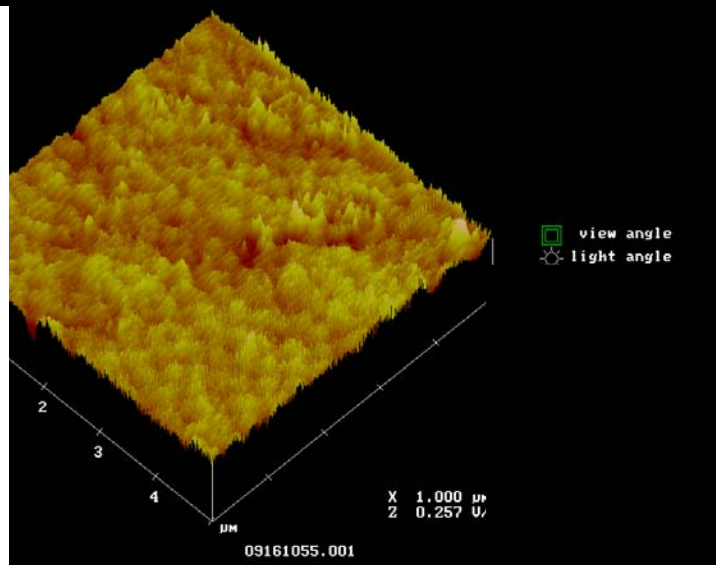
Latex Film

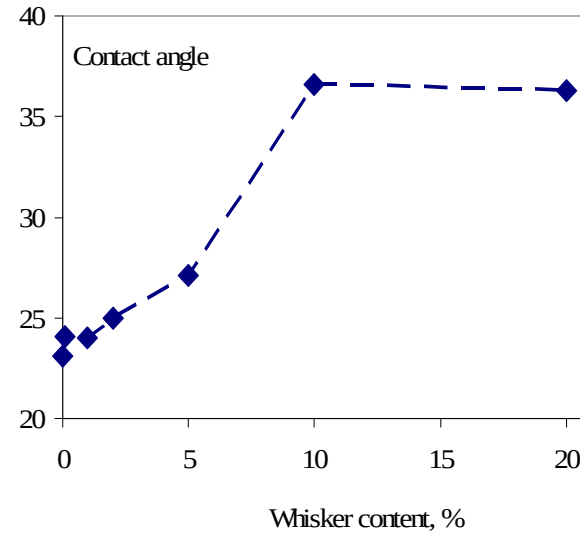


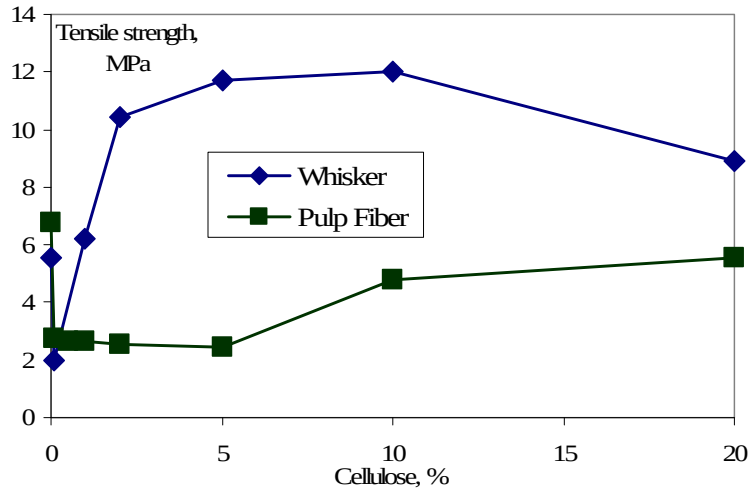
20% Cellulose Whiskers:Latex Film



5% Cellulose Whiskers:Latex Film

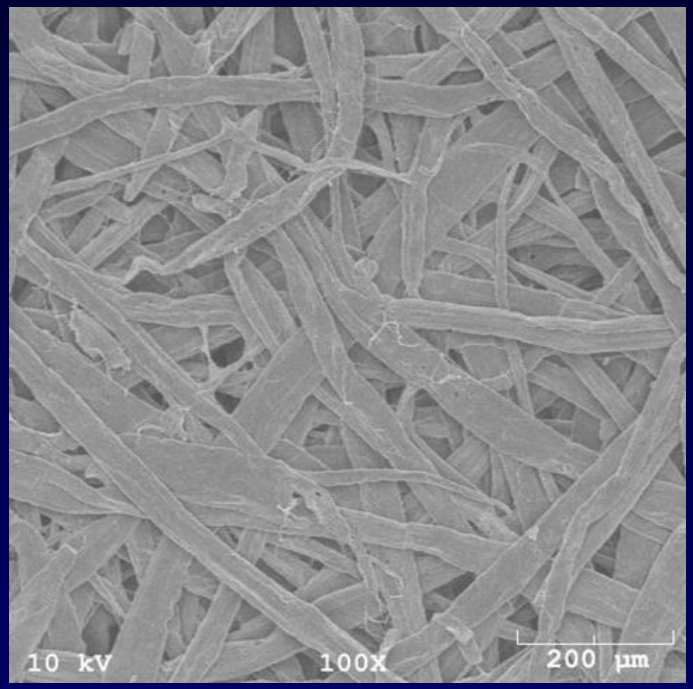






Nano-Enhanced Paper: Coatings

Application of Polyelectrolyte Coating Technologies
Layer-by-Layer Self-Assembly

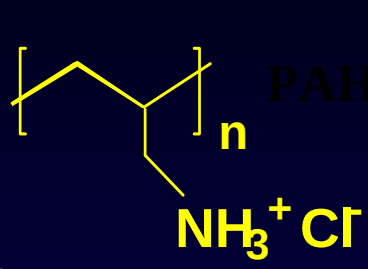


General Considerations:

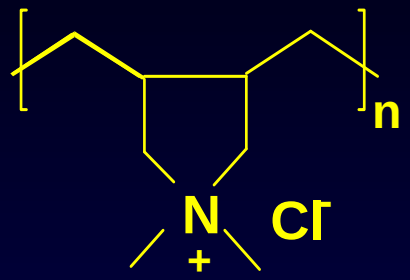
- Assembly via electrostatic and H-bond interactions
- Aqueous Processing
- Process Parameters:
    - pH; salt concentration
    - Polymer charge/DP
- Wide range of materials can be employed
    - Paper
    - Board
    - Tissue
    - Fillers

Nano-Enhanced Paper: Coatings

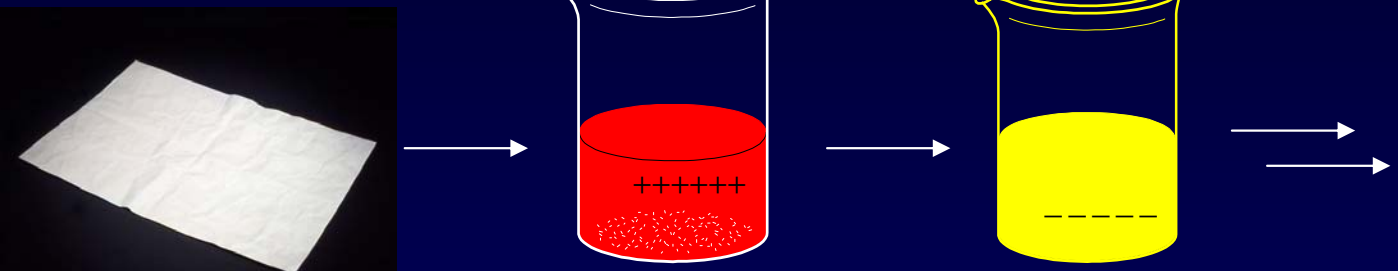
Current Studies

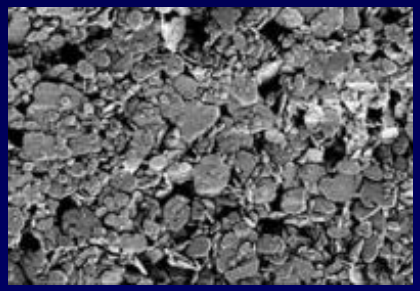


PAH



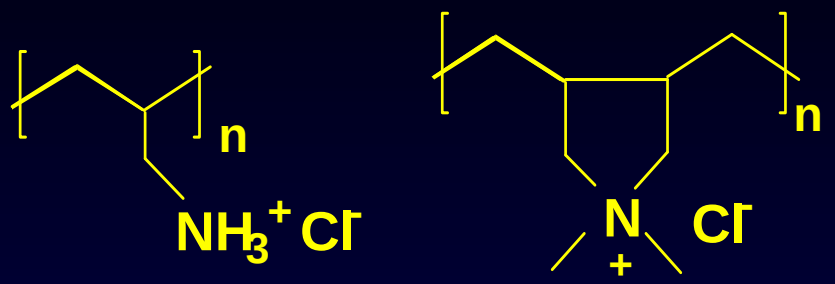
PDDA

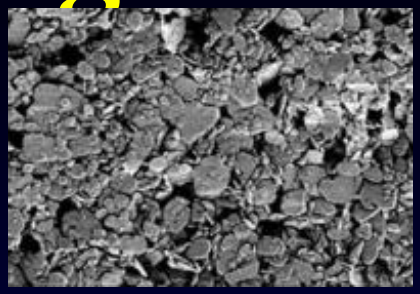




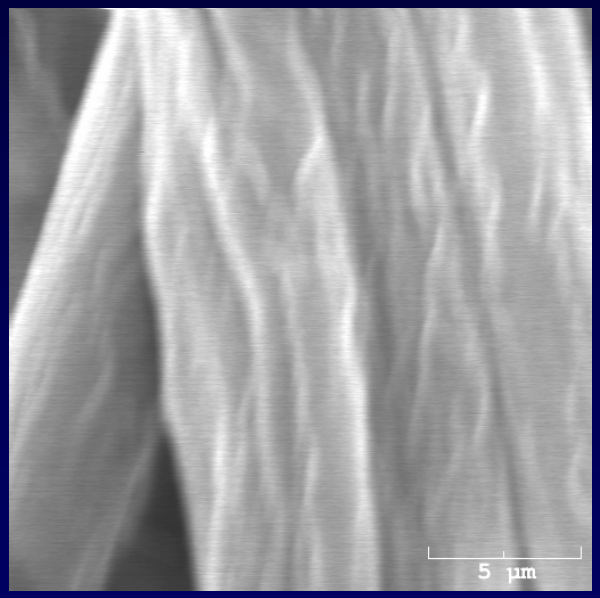
Nano-Enhanced Paper: Coatings

Current Studies

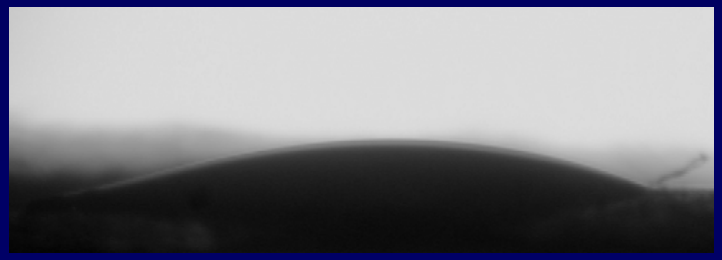




Initial Fibers



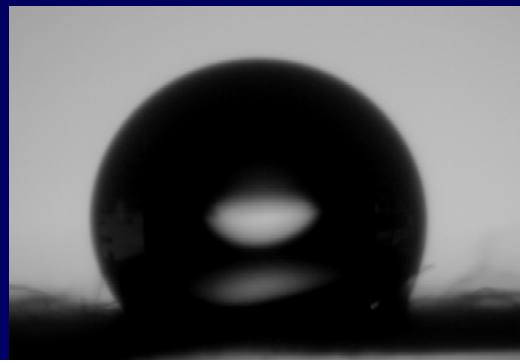
8 Bilayers of PAH
Kaolin



Water Contact Angle

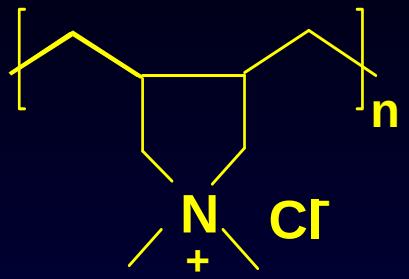
← Untreated

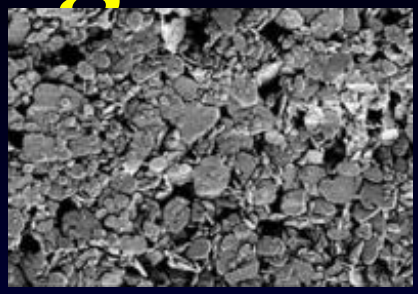
Treated →



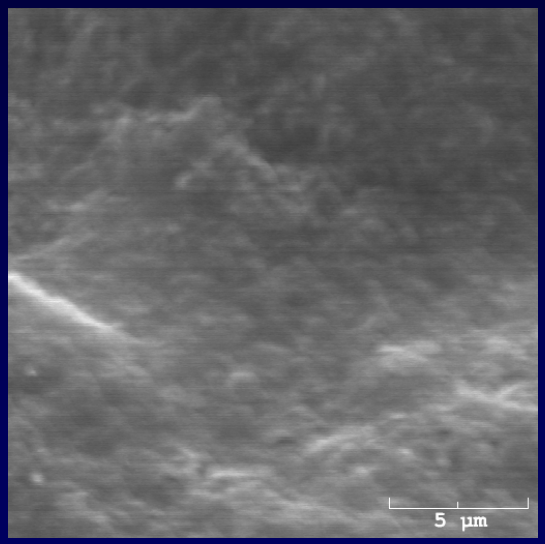
Nano-Enhanced Paper: Coatings

Current Studies





Bilayers of PAH/Kaolin



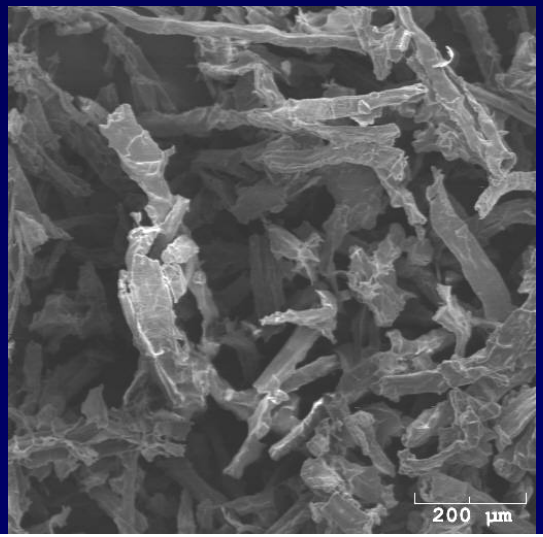
Ongoing Studies

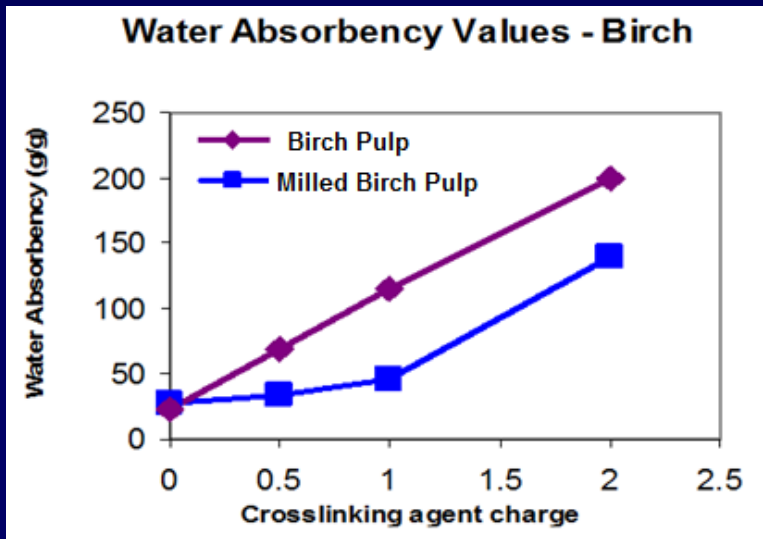
- *Enhance hydrophobic effect*
- *Optical properties*
- *Alternative barrier properties*
- *Self-cleaning nano-coatings*

Additional Material Studies

- Biomaterials/chemicals from wood biopolymers
  - Superabsorbers from pulp
    - Crosslinked
    - High Fiber Charge

Water





New Infrastructure Capabilities: Nanomaterials Analysis and Characterization Center

- ✓ Environmental SEM
- ✓ 4 TEMs including High Resolution and Cryogenic TEMs
- ✓ 3 SEMs including a High Resolution SEM
- ✓ Digital STM/AFM Facility
- ✓ 200 KeV STEM/TEM
- ✓ 2 Dual Beam Focused Ion Beam Units
- ✓ Scanning Probe Microscope
- ✓ 3 XRDs

BioEnergy BioFuels Research Efforts

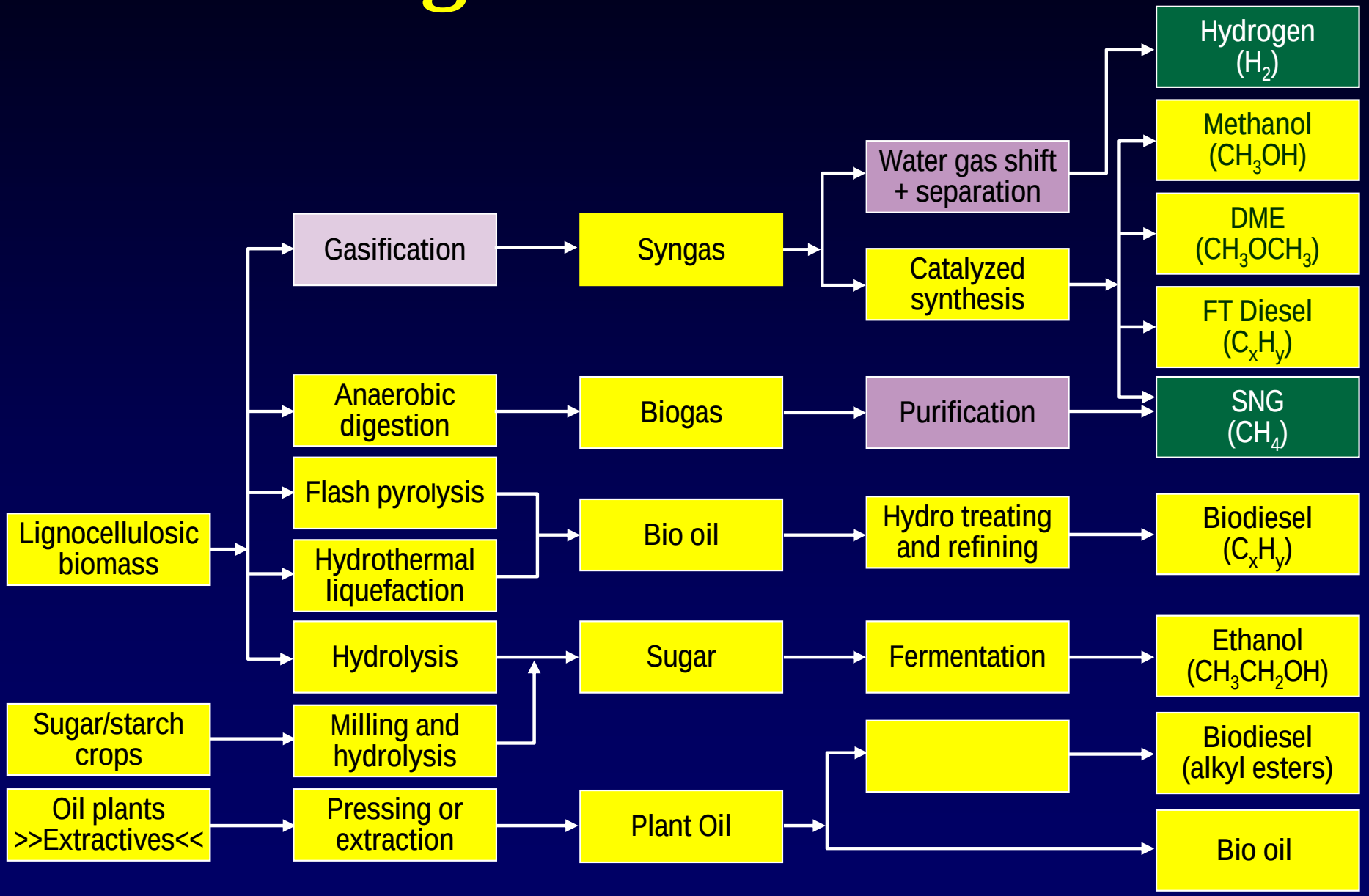
Next Generation Forest Pr

Fulbright Chair Alternative Energy Ragauskas Mission

- **Swedish-US Industry-Governmental Partnerships**
  - ***Student Exchange***
  - ***Collaborative Research Programs***
  - ***Technology Demonstrations***

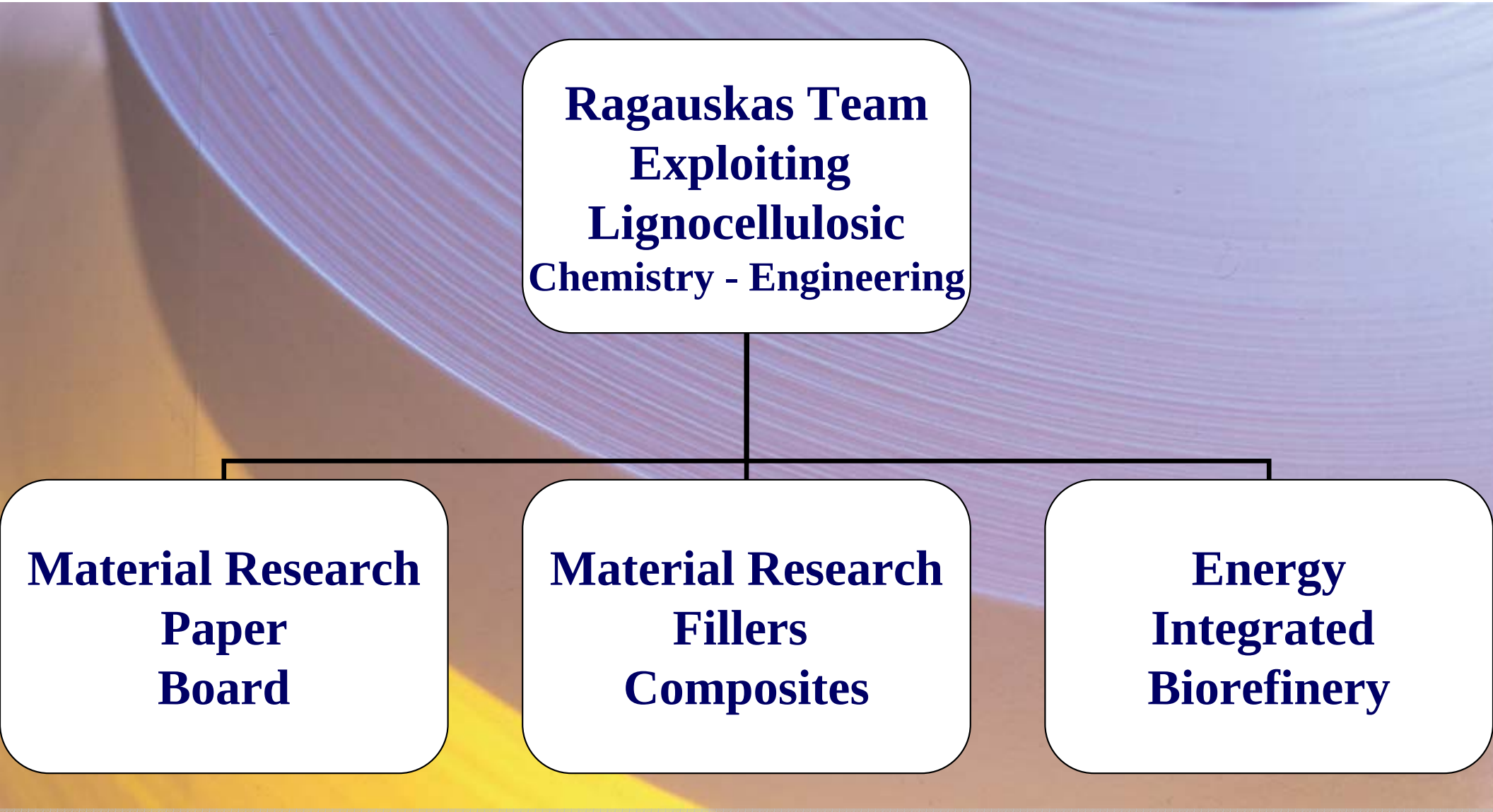
Innovative Swedish/US Forest BioRefinery Technologies Addressing The Challenge of Sustainable BioEnergy/BioFuels

Related BioMass-BioFuels Activities
Ragauskas Team



Past Research Accomplishments:

- Characterization of mature and thinning wood, relationship to final pulp properties
- Photostabilization – Photoreversion studies
- Fundamental and process chemistry of ECF – TCF bleaching
  - D, D_{HT}, A, O, OO, P*, E*, Z, X, and biological agents
  - Scale formation, NPE
- Mechanical Pulp Bleaching
- Relationship between kraft pulping and fiber chemistry
  - Yield, Strength, Brightness, Pulp bleachability
- Extended Oxygen Delignification high-kappa kraft pulps>Yield
- Extensive experience on northern HW and SW
- Expertise on MHW, Acacia, Eucalyptus
- Visiting Professor to KTH, STFi, Chalmers, University of Beira Interior /Portugal
- Visiting researchers/collaboration with Chalmers, STFI, NTNU, UBI, VTT, SCUT/Guangzhou NCSU, Auburn University, USDA, ORNL, GT ICL, Latvia, Lithuania, China, Indonesian



Established Experience

Wood Resources, Pulping, Bleaching, Papermaking

Process Chemistry, Engineering, Paper Physics

Nanotechnology, Biotechnology, Material Science/Chemistry

Ragauskas Research