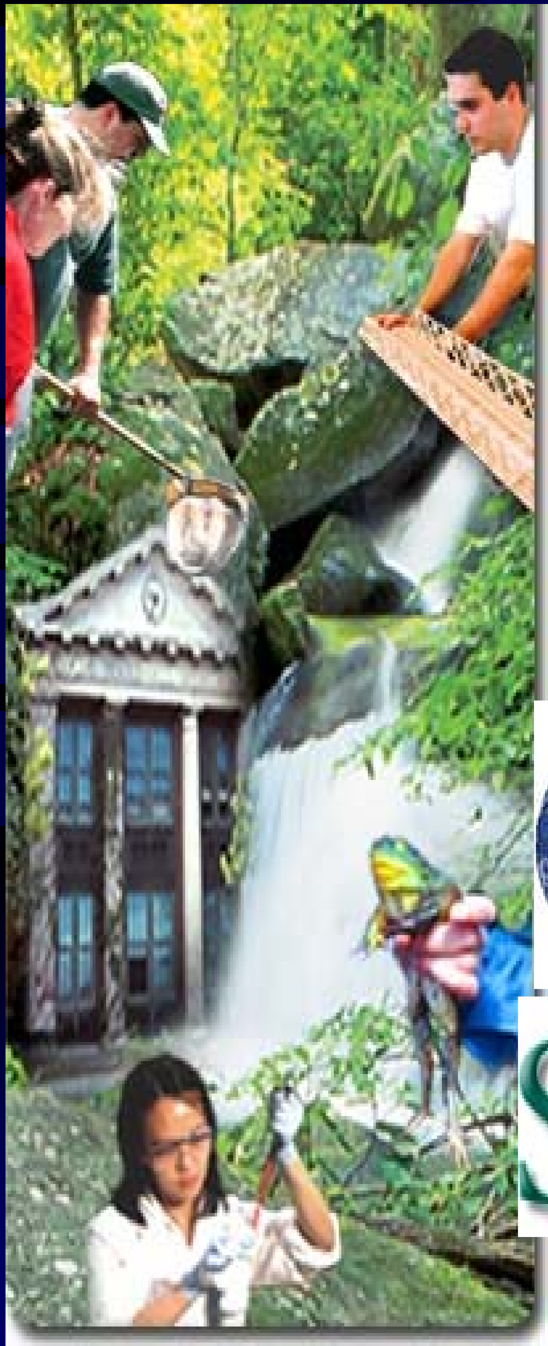
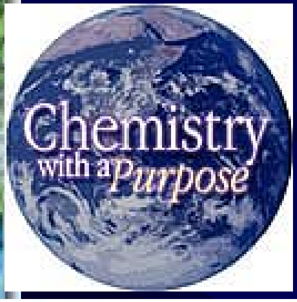
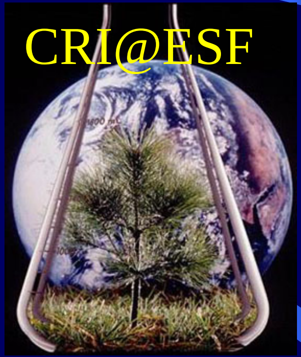
Ecocomposites Reinforced with Cellulose Nanoparticles: An Alternative to Existing Petroleum Based Polymer Composites



EPA Grant Number: R830897 1/15/2004-1/14/2007

WT Winter, Cellulose Res. Inst., SUNY-ESF,
Syracuse, NY, 13210





Philadelphia 8-18-2004

Drivers for This Program

1. Sustainability

   Use renewables

   safely and responsibly

2. Nanotechnology

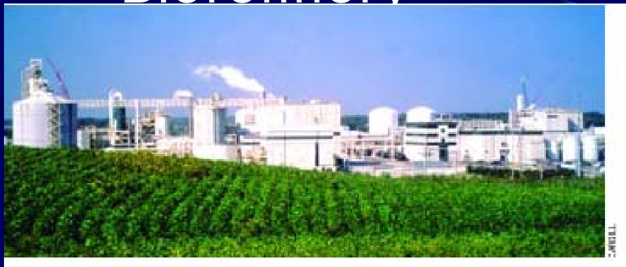
   surface, surface, surface

3. Policy /Regulation

- Biomass R&D Act of 2000
- Farm Bill 2002, Title IX

Willow Project

Biorefinery



Products

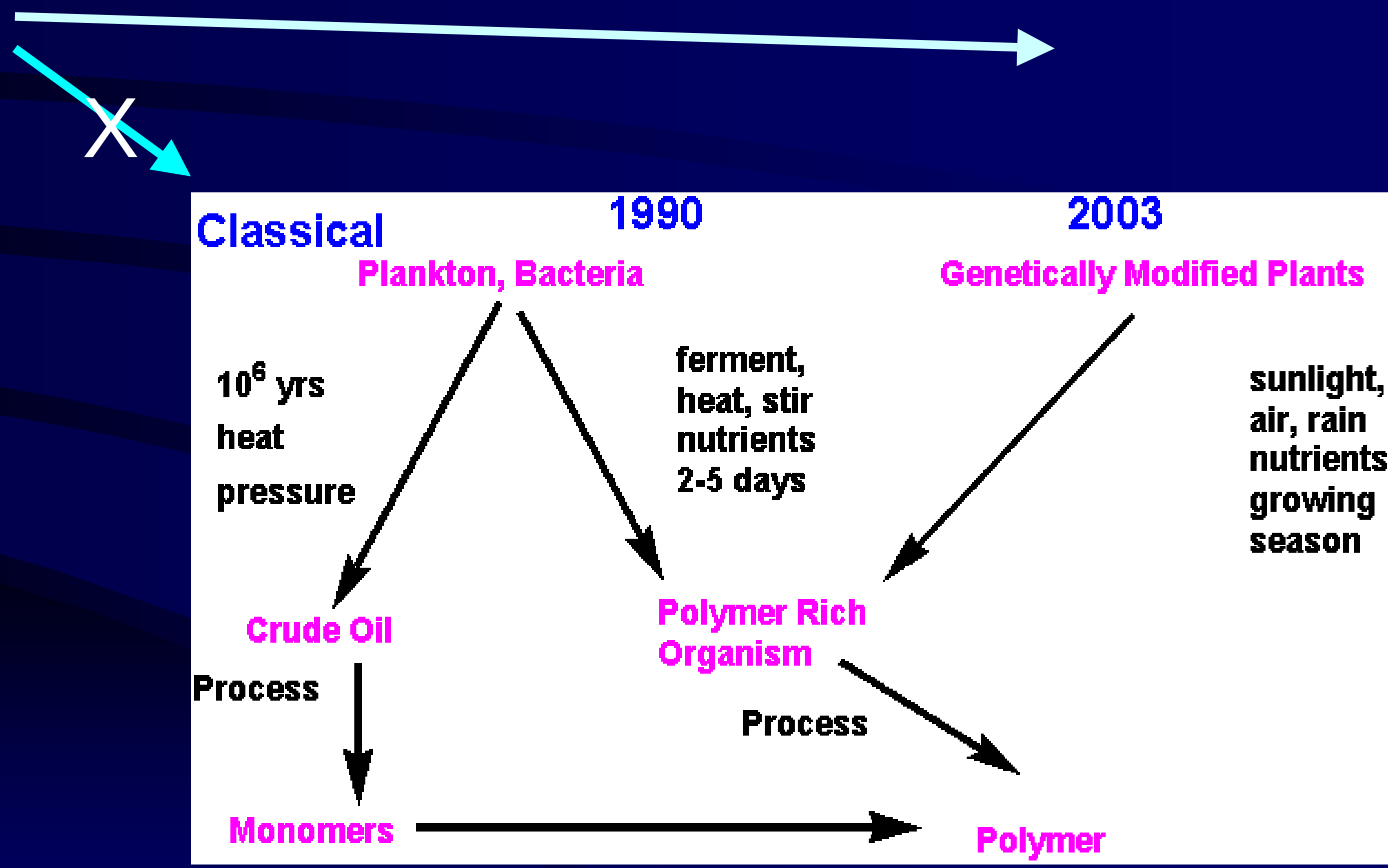
Bioplastic, Biofuels, Nanoparticles for reinforced bioplastics

Driver: UN Agenda 21

- 4.19. ... society needs to develop effective ways of dealing with the problem of disposing of mounting levels of waste products and materials. Governments, together with industry, households and the public, should make a concerted effort to reduce the generation of wastes and waste products by:
  - (a) Encouraging recycling in industrial processes and at the consumer level;
  - (b) **Reducing wasteful packaging** of products;
  - (c) Encouraging the **introduction of more environmentally sound products**.

Why Biodegradable?

- Sustainable
- Regulations on disposal

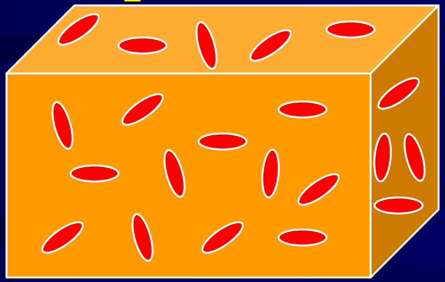


Nanoparticles

- At least 1 dimension < 100 nm (10^{-7} m) - NSF
- 2 Advantages of Nanotechnology
  - **Speed** of light: 3×10^{10} cm/sec * 10^{-9} s/ns
    - **1 ns = 30 cm** (1 foot) mostly useful in electrical applications
  - Increased **specific surface area**
    - Influences catalysis, adhesion

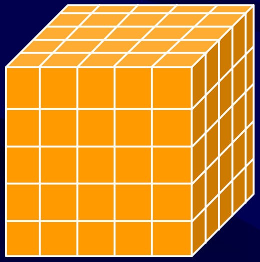
Nanocomposites

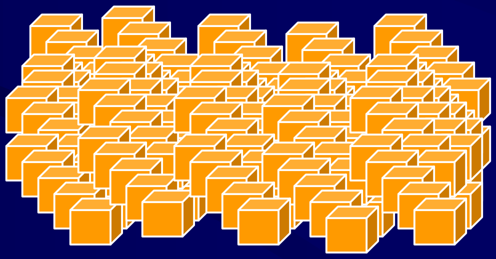
- **Particulate composites**:
  - Matrix
  - Particulate Phase



- Reinforcing particles have at least one dimension (i.e. length, width, or thickness) on the nanometer scale

Why small?





Surface area: 5 x 5 x 6 = 150 125 x (1 x 1 x 6) = 750 = 5 x 150

In proceeding from a μm to nm scale the specific surface area increases by 3 orders of magnitude

Surface Area vs. Aspect Ratio

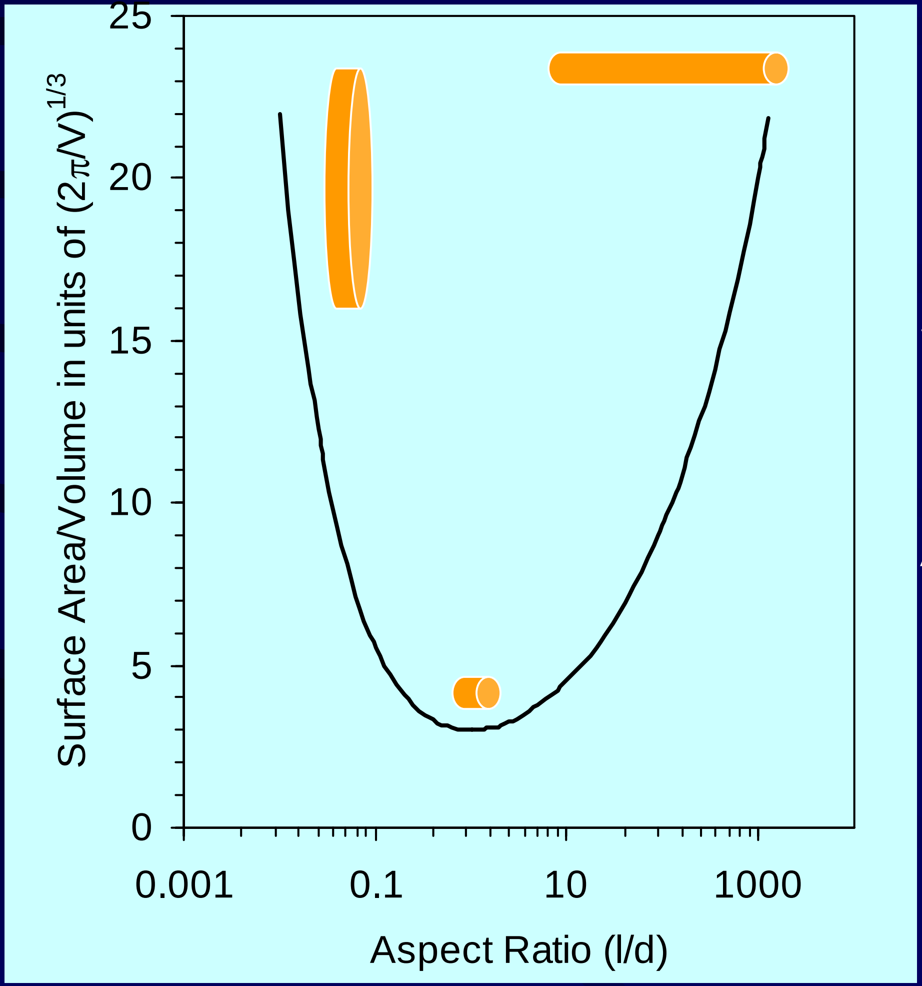
Montmorillonite Clay:

Length: 1 nm

Diameter: 200 – 400 nm

Aspect Ratio:

0.005 – 0.0025 (200 – 400)



Cellulose Nanocrystals:

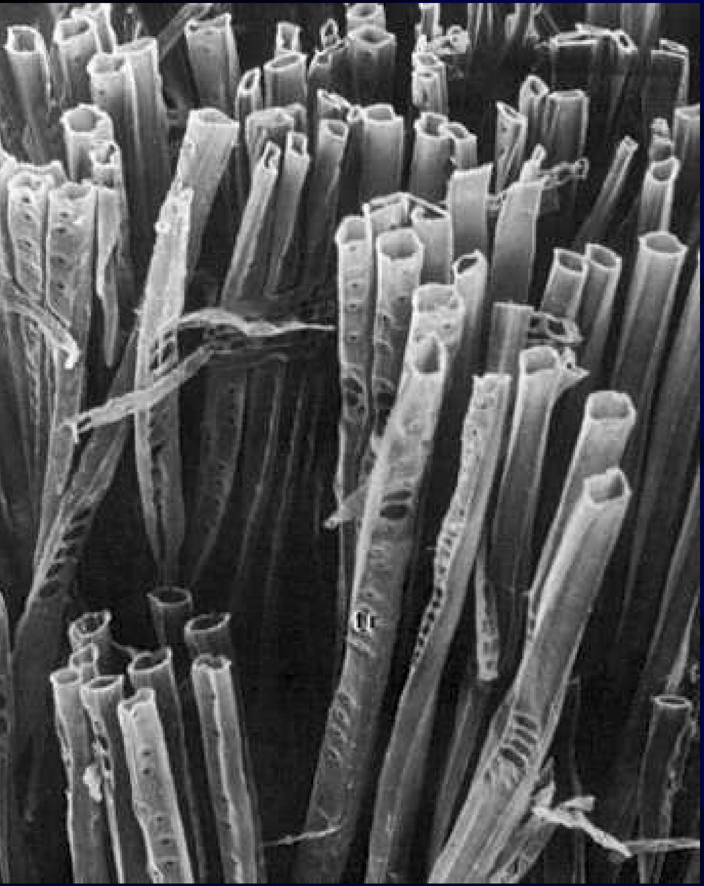
Length: 100 – several μm

Diameter: 3 – 20 nm

Aspect Ratio:

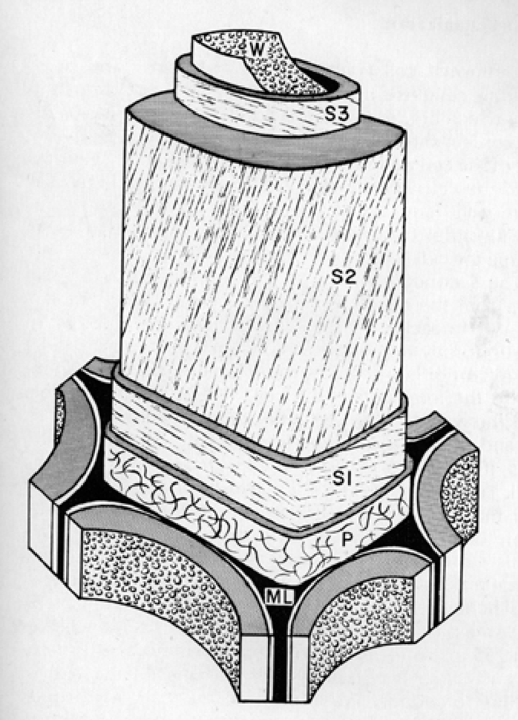
10 – 10,000

Cellulose Morphology

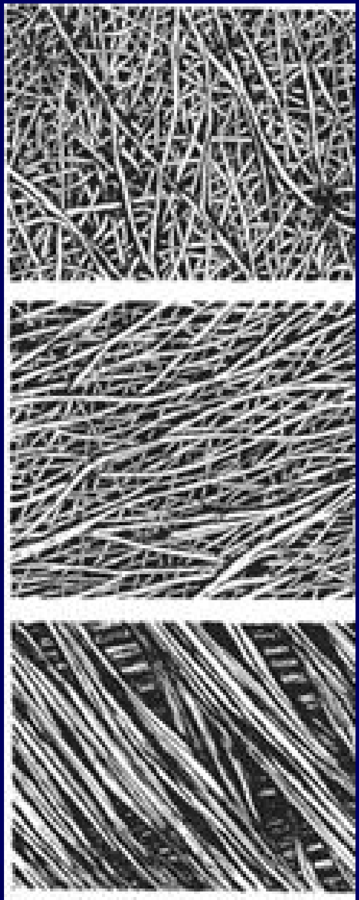


Fiber (cell)

White pine tracheids – Helm, Va Tech



Wood Cell Schematic



Microfibril

Hanna, ESF

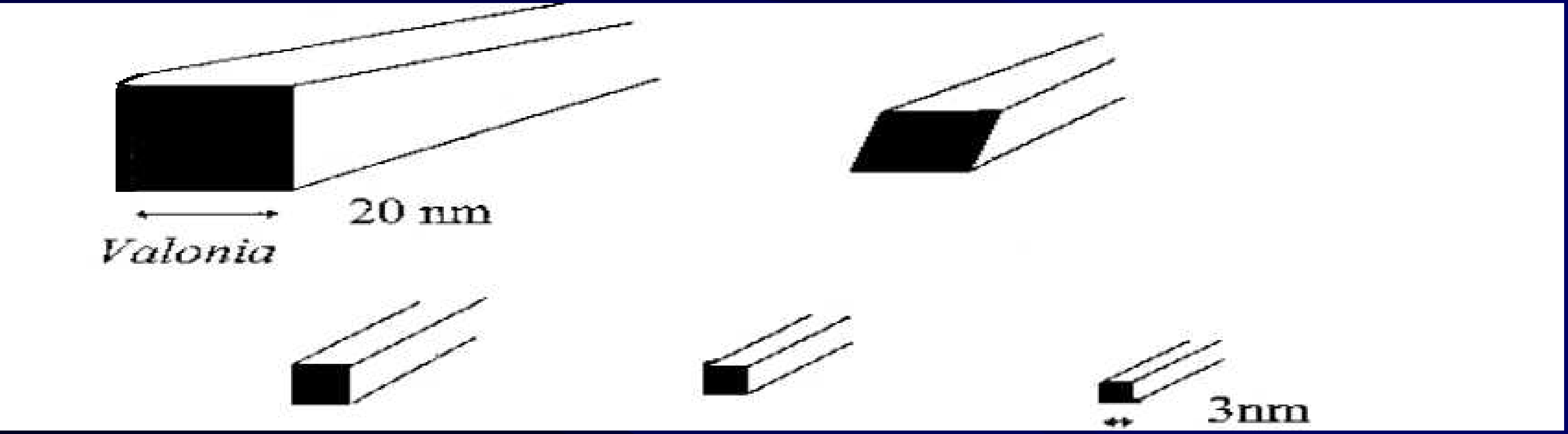
Parenchyma Cells

- Predominant cell type in fruit
- Primary cell wall tissue
- Rays in woody tissue

Microfibril size

Algae

Tunicate



Cotton

Wood

Sugar Beet

Biomass from Fruit and Sugar Processing

4.3 Mt/yr- USDA 2002

40% > juice

12.4 Mt/yr USDA 2002

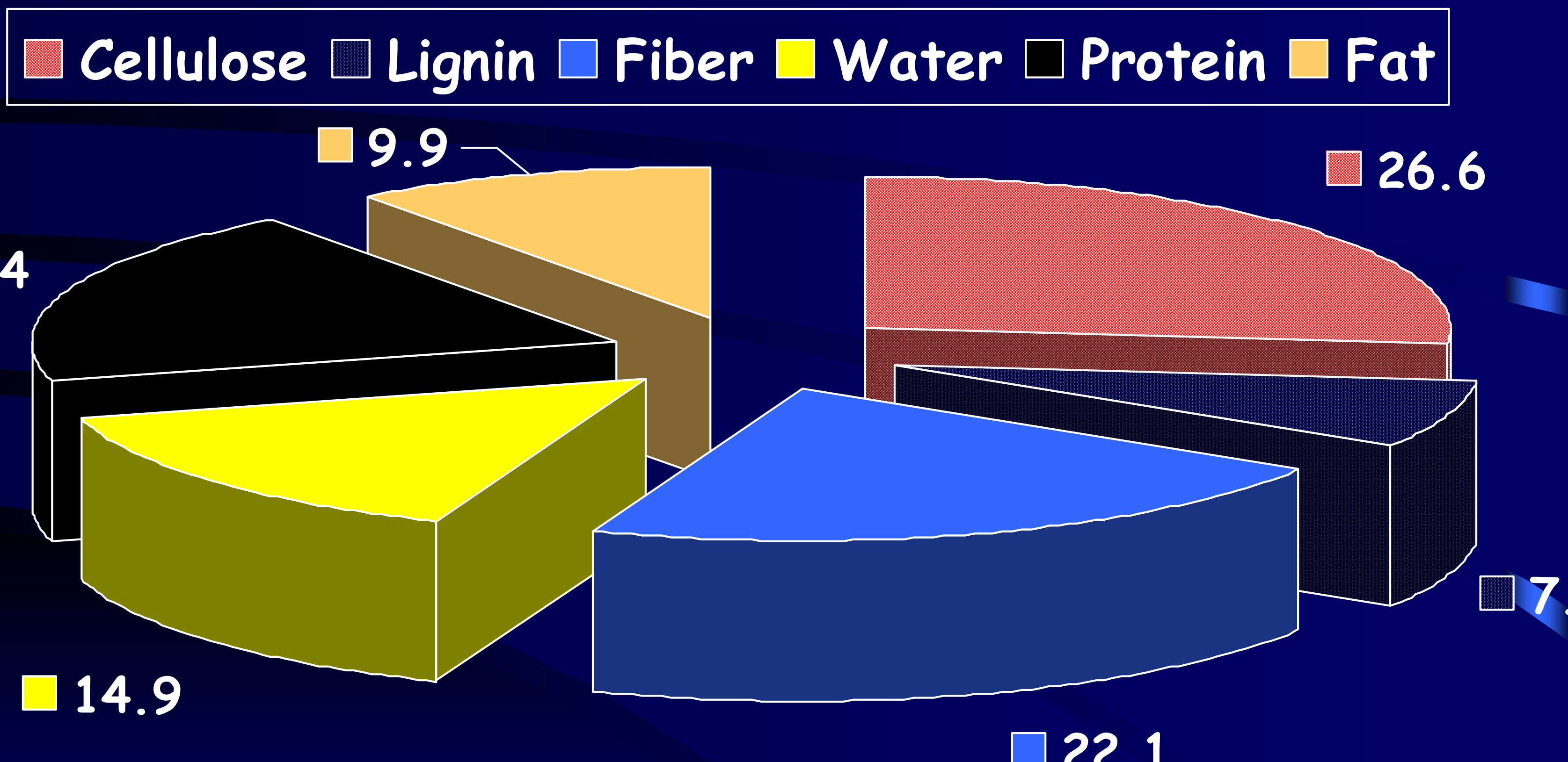
Sugar Beets

27Mt/yr USDA 2002

1 ton beets >110 lb pellets

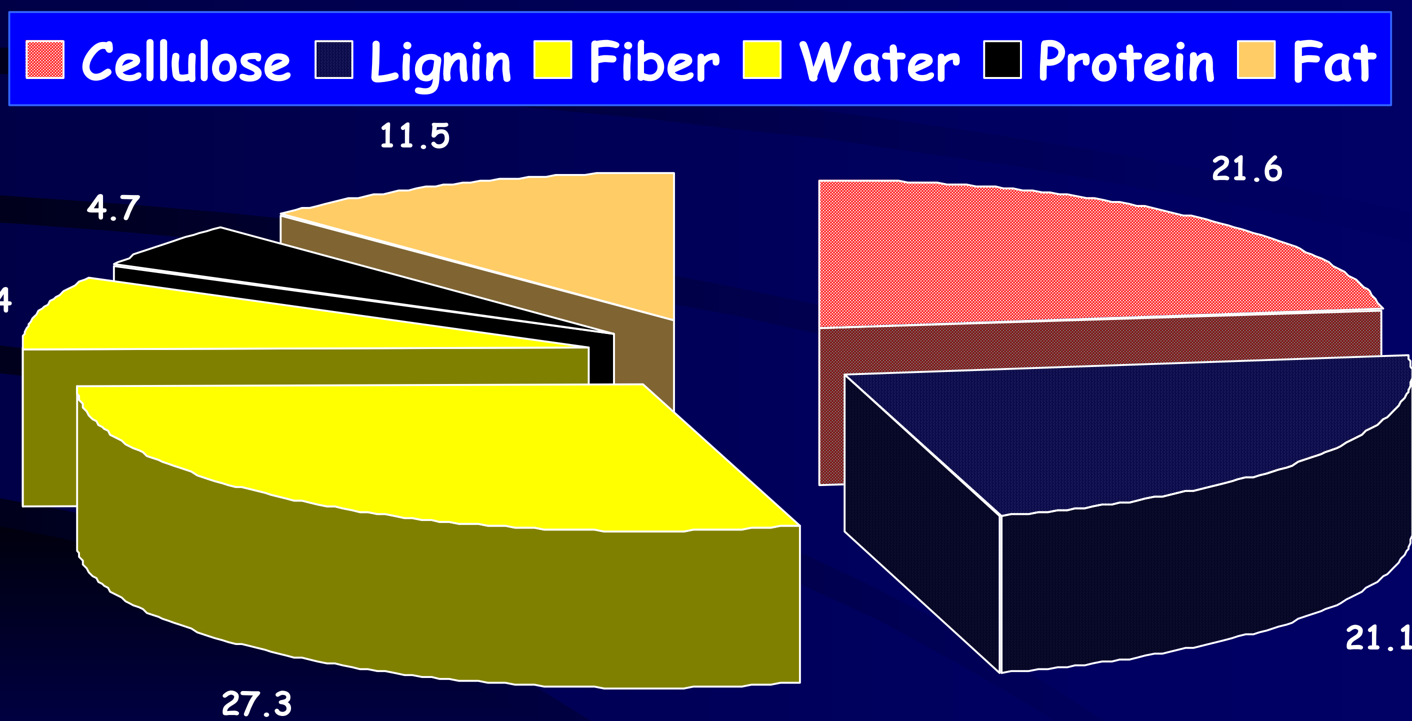
Composition of Orange Byproduct

Weight %



Composition of Apple Pomace

Weight %



Chiellini (2001) *Biomacromol* 2:1029-1037

Sugar Beet Pulp Cellulose

- 20% cellulose, 25-30% hemicellulose and 25-35% pectin, sucrose, proteins, lignin, fat
- Individual microfibrils 2 - 4 nm in diameter

Nanoparticle Samples

Sources Utilized

- Apple Pomace
- Bagasse
- Chitin
- Orange Pulp
- Sugar beet
- Tunicate
- Wheat
- Wood

Derivatives Made

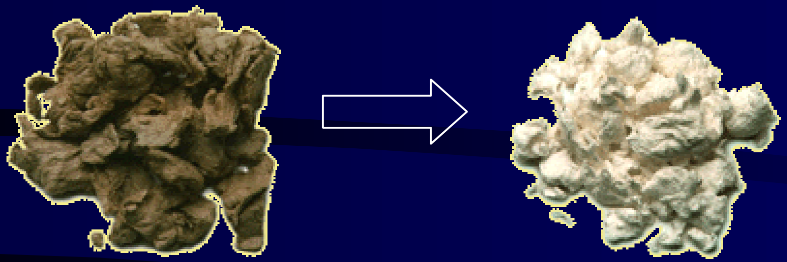
- Acetates
- Maleates
- N-Acetyl (chitin)
- Trimethylsilyl

Derivatives Planned

- Amino
- Carboxylate
- Fatty acid

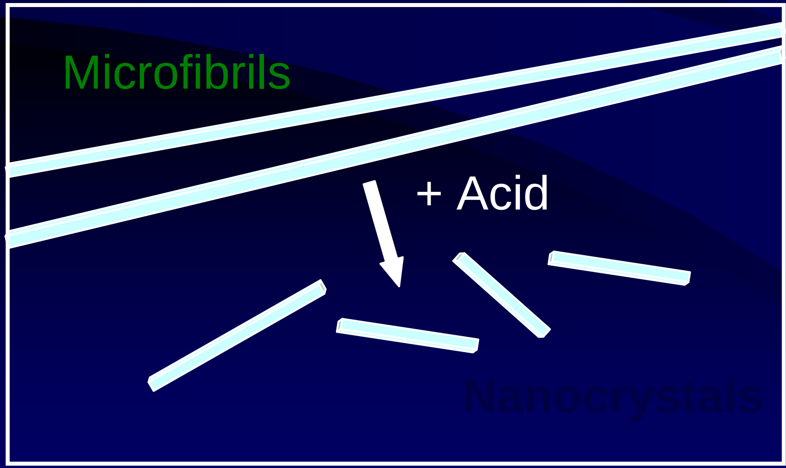
Crystal and Microfibril Preparation

Extraction, Bleaching:



1. Dewax- Soxhlet
2. Mill
3. Alkali solution
4. Sodium chlorite
5. homogenize

Hydrolysis (for nanocrystals):



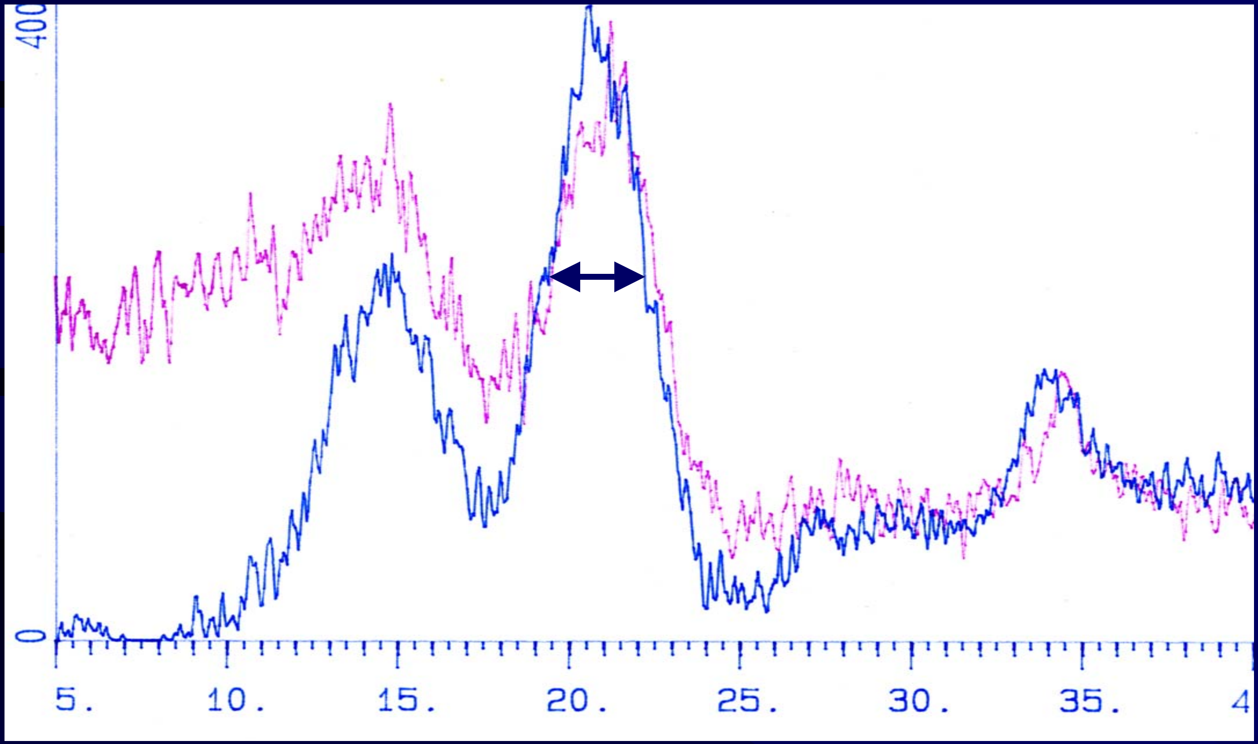
- acid (HCl, H_2SO_4)
- concentrations (65%)
- temperature (40°C)
- hydrolysis time (1 – 2 h)
- acid-to-substrate ratio (0.1

Bacterial Cellulose

- *Acetobacter xylinum*
- Ribbons: rectangular cross-section of 50 x 0.8 nm

Apple Pomace /Cellulose XRD

I



2θ **(deg)**

Cellulose I

Size from

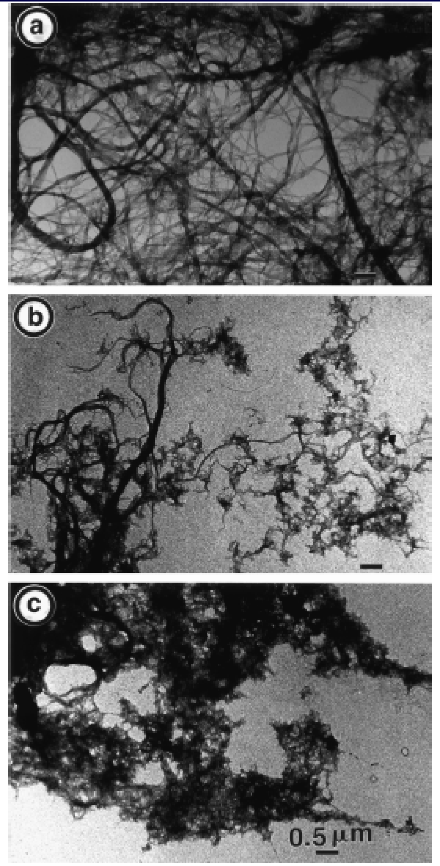
Line broadening

~ 3 nm

As received:

After bleaching, dispersion and re-drying

Are Parenchymal Celluloses Unusual??



After 9% NaOH

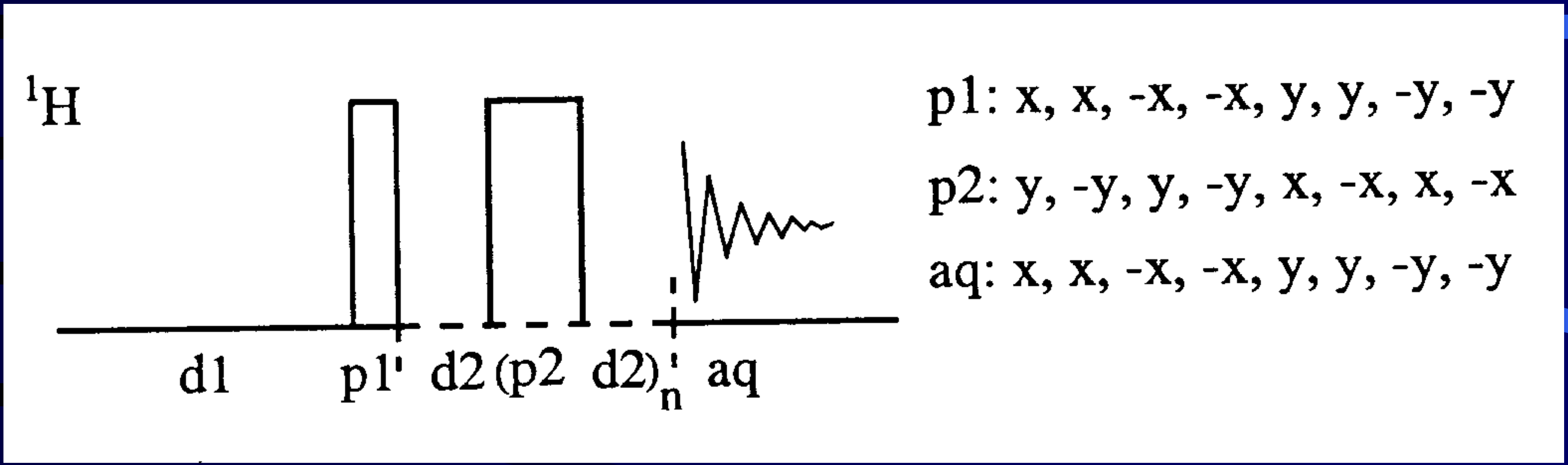
After 10% NaOH

After 12% NaOH

The sudden and essentially complete disappearance of microfibril structure is dramatically different from the gradual loss of microfibril size found in secondary wall mercerization

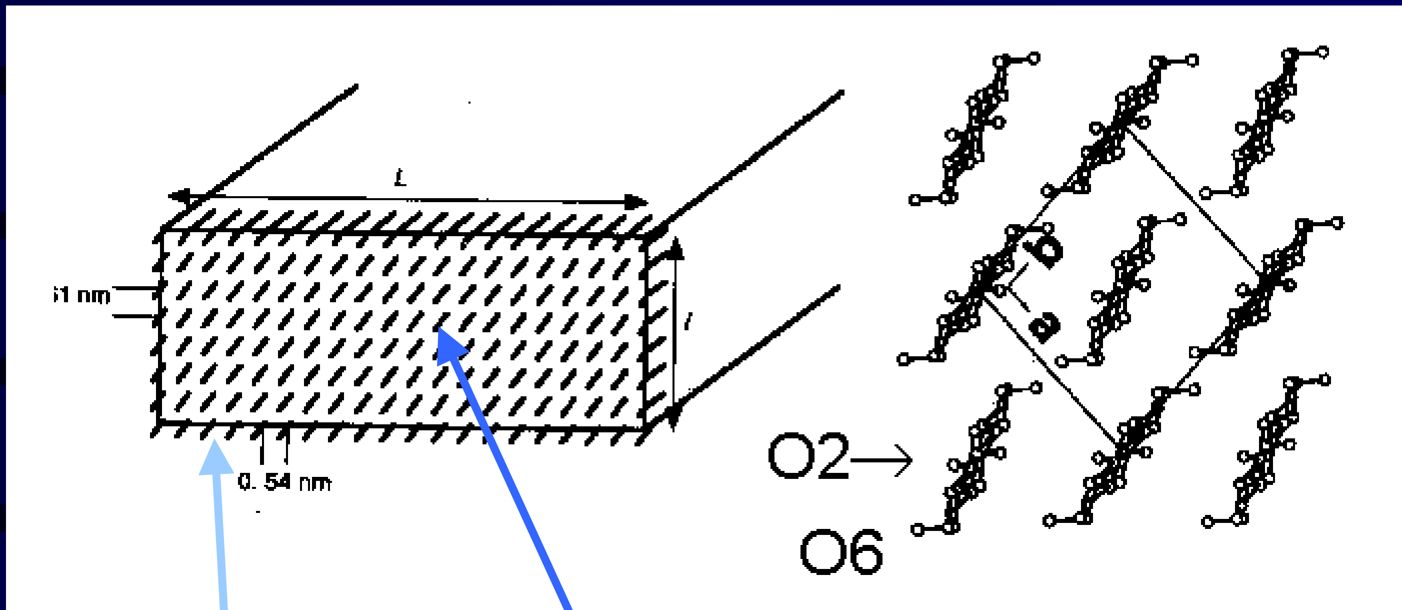
Dinand *et al*., *Cellulose* **9:** 7–18, 2002.

CPMG



n and d2 are variables and act as a T_2 filter which allows the selective removal of signals associated with short T_2 values (rigid components, crystal interior).

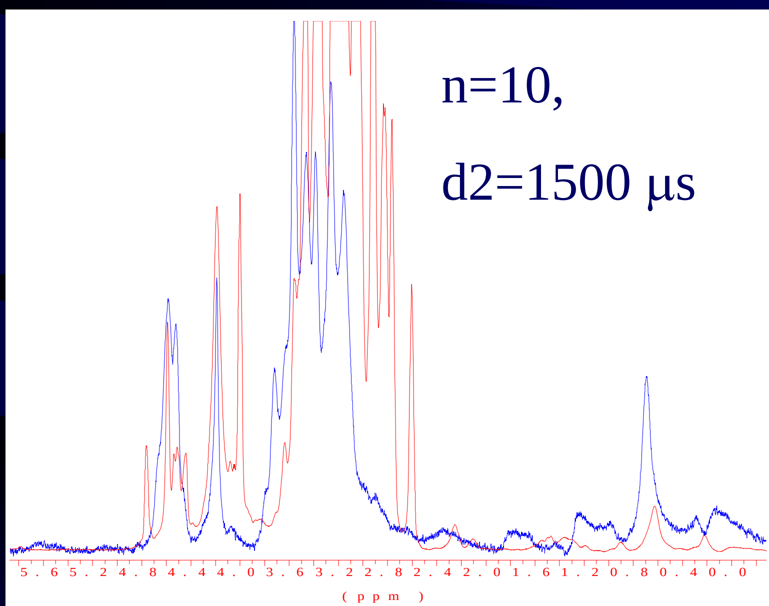
HR vs CP MAS NMR



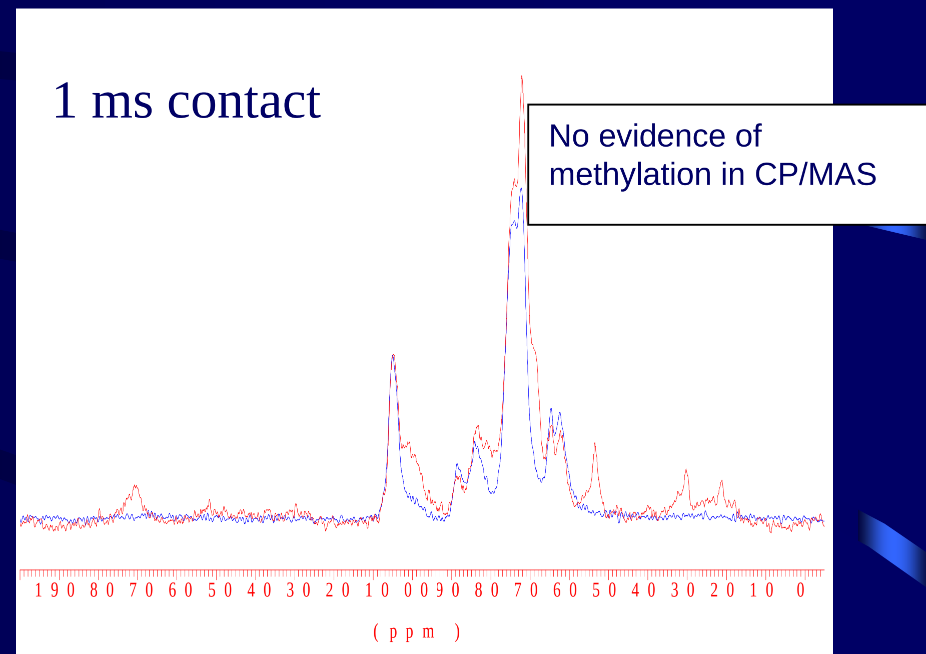
HRMAS CPMG active CPMAS active

Parenchyma Fibers Have Pectin Rich Surfaces

Raw apple pomace Purified Cellulose



^{1}H CPMG HR/MAS NMR

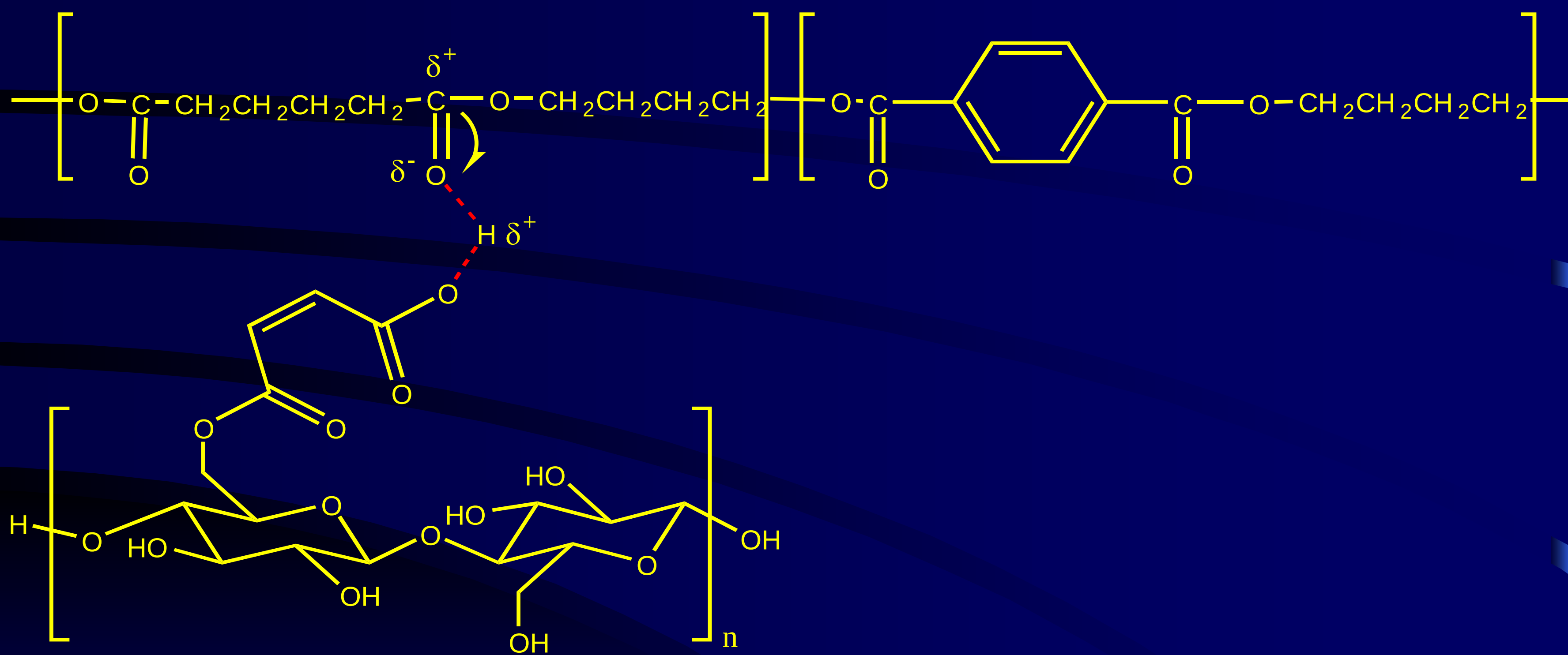


^{13}C CP/MAS NMR

Methyl groups (pectin) reside on the mobile surface seen by HR/MAS, not in the interior.

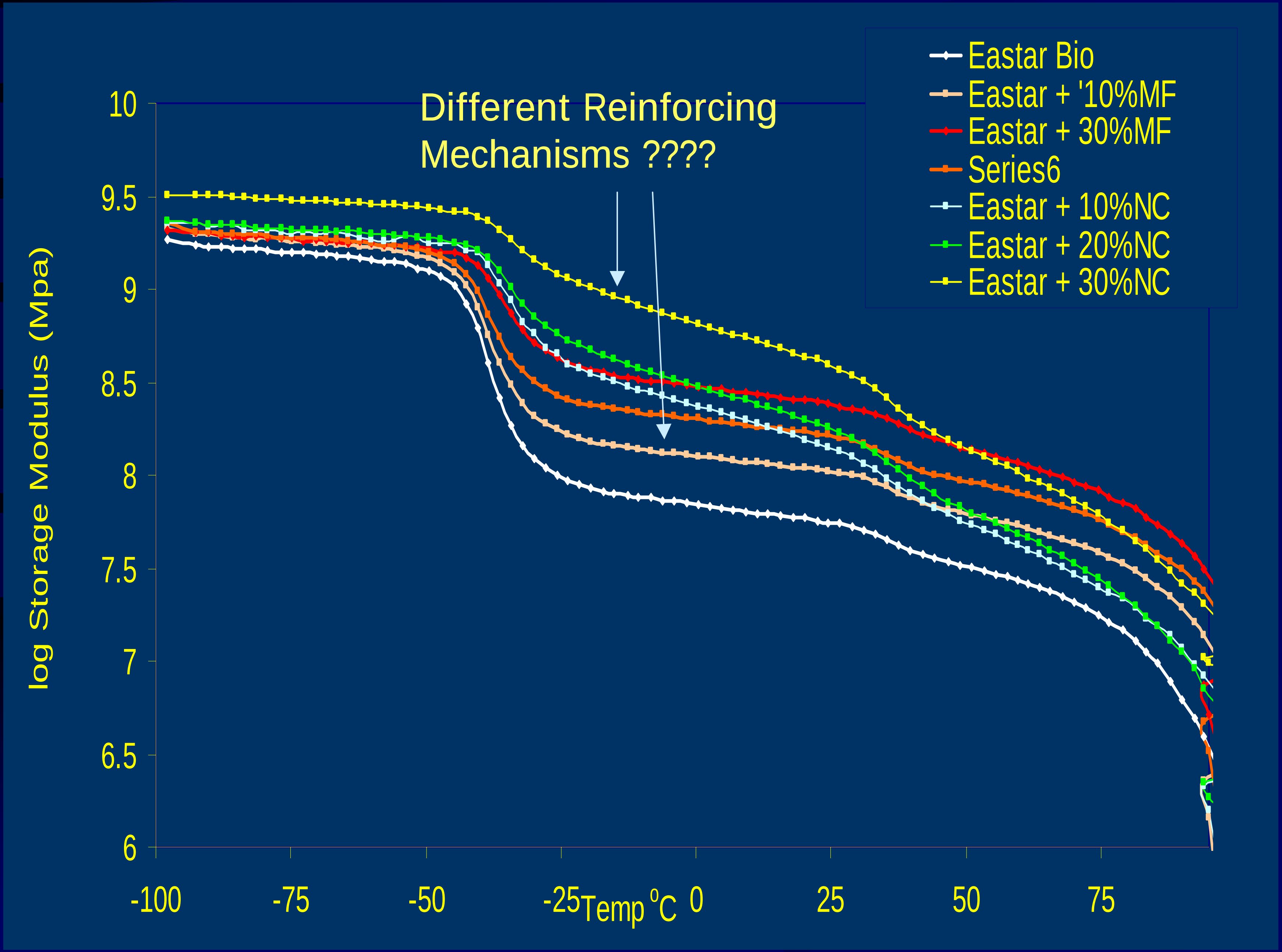
Possible interactions at the filler matrix interface

D43T4 Eastar Bio



Maleated Cellulose MF

Dynamic Mechanical Analysis



Scale Up

June 2004: Purchased a 22 l reactor to make nanoparticles in larger quantities

July 2004: First run

65% H_2SO_4 @ 40° C for 2h

400 gm wood pulp

Final yield = 280 g (70% conversion)

Problems / Challenges

Separation of particles from acid

Acid recycling?

Minimizing reaggregation

TEBOL(t-BuOH) ppt

What's Ahead

1. Reactive Extrusion - Can we improve the association by covalent links from particles matrix molecules?

2. Biodegradability Plastic (GreenPla®???)

   - Currently review ASTM and other standards.

Conclusions

1. Cellulose Nanoparticles can be made from almost any kind of biomass,
2. The properties of the particles may vary with source due to species dependent differences in mean particle size,
3. Scale up of our preps, now in progress, will permit more widespread testing,
4. New techniques are needed to characterize surface chemistry and interactions,
5. Reactive extrusion may provide a route to stronger composites. (speculation at this point),
6. An acid free or reduced process may come from treating the nanoparticles as a coproduct of ethanol production from biomass.

Acknowledgements

Time, Effort, Ideas

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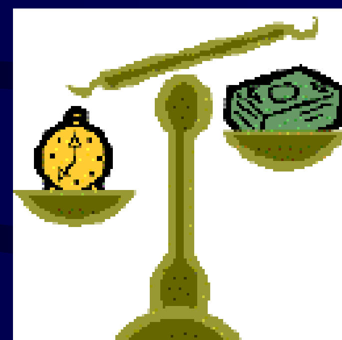
Prof. Arthur Stipanovic,
Ms. Yae Takahashi



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the EPA which is enabling continuation of this work

Edwin C. Jahn Chemistry Laboratory

www.esf.edu/cellulose

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