Green Materials and Processes in Fibers and Fabrics

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Presented at the CIFFI Symposium
Cornell University, Ithaca, NY
May 18, 2015
Types of Composite Materials based on Reinforcement

(ASTM Standardization News)
Composite Applications

Aerospace

Transportation

White Night 2
Composite Applications

Sports

Electronics

Medical
Production, Sales & Use of Resins (US-2013) (Millions of pounds)

<table>
<thead>
<tr>
<th>Plastics</th>
<th>U.S. Production</th>
<th>Total Sales &amp; Captive Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermosets</td>
<td>14,975</td>
<td>14,917</td>
</tr>
<tr>
<td>Thermoplastics</td>
<td>92,547</td>
<td>93,743</td>
</tr>
<tr>
<td>TOTAL</td>
<td>107,522</td>
<td>108,660</td>
</tr>
</tbody>
</table>

Source: American Chemical Council, March 2014

*Most Derived from Petroleum  *Not Biodegradable
*Not Sustainable  *Not Environment-Friendly
*About 94% of composites end up in landfills

6-8% of Petroleum is used for producing Plastics, Polymers, Fibers, etc.
Today’s Environmental ‘Mantras’
Or Guiding Principles

- ‘Green’ Chemistry
- Environment-Friendly, Fully Sustainable ‘Green’ Materials
- Recyclable Materials,
- ‘Cradle-to-Cradle’ Design
- Life Cycle Assessment
- The 4 ‘R’s
‘Green’ Materials Research

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Value Added Products from Agriculture & Food Wastes

Seed Coating Hydromulch Bacterial Cellulose

Sporting Goods Skateboards

Structural Components

Chemical & Engineering News

Gearing up for Biofuels
Brazil-U.S. partnerships aim to boost production P.15

Specialty Chemicals
Dawn of the renewables

C&EN
Change Agents Formulating a modus operandi for pharma P.27
Boston is on Preliminary program for ACS national meeting F.61

Hair Treatments Nanofilters

Green Buildings Ballistic Components

Research Netravali lab Cornell University ann2@cornell.edu

Nanofilters

Hair Treatments

Nanofilters

Ballistic Components

Structural Components

Sporting Goods Skateboards

Seed Coating Hydromulch Bacterial Cellulose

Value Added Products from Agriculture & Food Wastes

‘Green’ Materials Research

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Val...
Biodegradable Resins

Biodegradable Polymers

Natural

1. Polysaccharides
   • Starch
   • Cellulose
     • Chitin
     • Pullulan
     • Levan
     • Konjac
     • Elsinan

2. Proteins
   • Collagen/Gelatin
   • Casein, Albumin, Fibrogen, Silks, Elastins
   • Protein from grains

3. Polyesters
   • Poly(hydroxyalkanoates)

4. Other Polymers
   • Lignin
   • Shellac
   • Natural Rubber

Synthetic

1. Poly(amide)
2. Poly(anhydrides)
3. Poly(amide-enamines)
4. Poly(vinyl alcohol)
5. Poly(ethylene-co-vinyl alcohol)
6. Poly(vinyl acetate)
7. Polyesters
   • Poly(glycolic acid)
   • Poly(lactic acid)
   • Poly(caprolactone)
   • Poly(ortho esters)

8. Poly(ethylene oxide)
9. Some Poly(urethanes)
10. Poly(phosphazenes)
11. Poly(imino carbomates)
12. Some Poly(acrylates)
Why Soy Protein?

- Plant-based resource
- Yearly renewable - Sustainable
- Fully Biodegradable
- Inexpensive and Worldwide Availability
  - SF, SPC, SPI
- Benign Process of Separating Protein

Also

➢ Multi-functional protein
Polar Amino Acids in Soy Protein

- Aspartic acid (anionic)
- Glutamic acid (anionic)
- Arginine (cationic)
- Lysine (cationic)
- Histidine (cationic)
- Serine (hydroxyl)
- Threonine (hydroxyl)
- Tyrosine (hydroxyl)
- Cystine (sulfhydryl)
Ways of Modifying Soy Protein as Resin

- Cross-linking ✔
- Internal plasticization ✔
- Blending with other resins ✔
- Hydrophobicity Enhancers ✔
- Forming Interpenetrating Network (IPN) or IPN-like Structures ✔
- Nano-Composites with clay and other nano-particles and fibrils ✔️

✔ = Methods used in our lab
Why Natural Fibers?

- Biodegradable → Environment-friendly
- Annually renewable → Fully sustainable
- Many varieties → Available throughout the world
- Good tensile properties → Comparable to glass
- Hollow structure → Insulation against noise and heat
- Can be easily processed → No new equipment needed
- Can be microfibrillated → Resin & composite strengthening
Properties of Some Natural Fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Density (gm/cc)</th>
<th>Moisture Content (wt. %)</th>
<th>Elongation at Break (%)</th>
<th>Fracture Stress (MPa)</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>1.5</td>
<td>-</td>
<td>7.0-8.0</td>
<td>287-597</td>
<td>5.5-12.6</td>
</tr>
<tr>
<td>Jute</td>
<td>1.3</td>
<td>12.6</td>
<td>1.5-1.8</td>
<td>393-773</td>
<td>26.5</td>
</tr>
<tr>
<td>Flax</td>
<td>1.5</td>
<td>10.0</td>
<td>2.7-3.2</td>
<td>345-1035</td>
<td>27.6</td>
</tr>
<tr>
<td>Hemp</td>
<td>-</td>
<td>10.8</td>
<td>1.6</td>
<td>690.0</td>
<td>-</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.5</td>
<td>11.0</td>
<td>2.0-2.5</td>
<td>511-635</td>
<td>9.4-22.0</td>
</tr>
<tr>
<td>Coir (Coconut)</td>
<td>1.2</td>
<td>8.0</td>
<td>30.0</td>
<td>175.0</td>
<td>4.0-6.0</td>
</tr>
<tr>
<td>Bamboo</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>391-1000</td>
<td>48-89</td>
</tr>
<tr>
<td>Soft Wood</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>1000.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Pineapple</td>
<td>-</td>
<td>11.8</td>
<td>1.6</td>
<td>413-1627</td>
<td>34.5-82.5</td>
</tr>
<tr>
<td>Ramie</td>
<td>1.5</td>
<td>8.0</td>
<td>3.6-3.8</td>
<td>400-938</td>
<td>61.4-128</td>
</tr>
</tbody>
</table>

Most fibers are commercially available
Engineering of Natural Fiber ‘Hybrid’ Composites

**Resin process**
- Dissolving SPI powder (at room temperature)
- Control pH-value
- Pre-curing + modification (at around 75°C)
- Cross-linker and other additives

**Composite process**
- Soy Resin
- Resin impregnation
- Oven dry
- Hot press
- Curing at 120°C
- Reinforcing yarns
# Tensile Properties of Flax Yarn/MSPI Composites

(Yarns kept under stress, 45% yarn content by wt)

<table>
<thead>
<tr>
<th>Composites</th>
<th>Fracture Stress (MPa)</th>
<th>Fracture Strain (%)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td>256.4</td>
<td>13.3</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>(370.0)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transverse</td>
<td>10.2</td>
<td>3.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Tested as per ASTM D3039M-00 procedure

- Strength estimated for 65% fiber content
Use of Green Composites for Cabinetry and Shelving at Cornell University
Developments in ‘Green’ Fibers

**Cellulosic**
- Microfibrillar Cellulose (MFC)
- Nanofibrillar Cellulose (NFC)
- Bacterial Cellulose
- Liquid Crystalline Cellulose

**Protein**
- Spider Silk-like Fibers
SEM of Micro-Fibrillated Cellulose (MFC)

Plant cell wall

Cellulose nanofibril

Cellulose molecule

4nm

NFC

\[ E = 140 \text{ GPa} \]

\[ 2 \text{ GPa} < \sigma < 10 \text{ GPa} \]

Kevlar 49

\[ E = 131 \text{ GPa} \]

\[ \sigma = 3.8 \text{ GPa} \]
Effect of Glycerol on Mechanical Properties of the MFC modified SPC resin (40% MFC)

<table>
<thead>
<tr>
<th>Glycerol Content %</th>
<th>Fracture Stress MPa</th>
<th>Fracture Strain %</th>
<th>Young’s Modulus MPa</th>
<th>Toughness MPa</th>
<th>Moisture Content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>77.2</td>
<td>11.8</td>
<td>2146</td>
<td>5.9</td>
<td>12.9</td>
</tr>
<tr>
<td>10</td>
<td>80.2</td>
<td>9.0</td>
<td>2949</td>
<td>5.3</td>
<td>11.7</td>
</tr>
<tr>
<td>7</td>
<td>84.5</td>
<td>8.8</td>
<td>3168</td>
<td>5.0</td>
<td>11.4</td>
</tr>
<tr>
<td>4</td>
<td>91.3</td>
<td>6.3</td>
<td>3560</td>
<td>4.5</td>
<td>11.1</td>
</tr>
<tr>
<td>1.5</td>
<td>95.3*</td>
<td>4.9</td>
<td>3848*</td>
<td>3.9</td>
<td>11.0</td>
</tr>
<tr>
<td>0</td>
<td>91.0*</td>
<td>3.6</td>
<td>4127*</td>
<td>3.2</td>
<td>11.0</td>
</tr>
</tbody>
</table>

*These properties are better than commonly used DGEBA based Epoxy Resin
## Fiber Tensile Properties

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Fracture Stress (MPa)</th>
<th>Fracture Strain (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC Cellulose</td>
<td>1483</td>
<td>6.8</td>
<td>47.8</td>
</tr>
<tr>
<td>Kevlar®</td>
<td>3500</td>
<td>4.5</td>
<td>140</td>
</tr>
</tbody>
</table>
Modification of LC Cellulose by KOH Treatment

<table>
<thead>
<tr>
<th>Treatment Condition</th>
<th>Tensile strength (MPa)</th>
<th>Tensile strain (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1483 (13.1)</td>
<td>6.8 (6.8)</td>
<td>47.8 (15.5)</td>
</tr>
<tr>
<td>LC-KOH-Slack</td>
<td>1588 (10.5)</td>
<td>6.5 (8.8)</td>
<td>53.7 (6.5)</td>
</tr>
<tr>
<td>LC-KOH-Load</td>
<td>1749 (9.2)</td>
<td>5.2 (8.6)</td>
<td>63.7 (9.1)</td>
</tr>
</tbody>
</table>

- 18% Increase in strength
- 33% increase in modulus/stiffness
Tensile Properties of LC Cellulose Reinforced Advanced Green Composites
Fiber content of all specimens is 41.5% by wt.

<table>
<thead>
<tr>
<th>Fibers used</th>
<th>Tensile strength (MPa)</th>
<th>Tensile strain (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCRC- Control</td>
<td>Experimental</td>
<td>540 (10.3)</td>
<td>6.4 (5.8)</td>
</tr>
<tr>
<td></td>
<td>Theoretical</td>
<td>624</td>
<td>-</td>
</tr>
<tr>
<td>LCRC- Slack</td>
<td>Experimental</td>
<td>583 (6.4)</td>
<td>5.7 (9.9)</td>
</tr>
<tr>
<td></td>
<td>Theoretical</td>
<td>668</td>
<td>-</td>
</tr>
<tr>
<td>LCRC- Load</td>
<td>Experimental</td>
<td><strong>625 (4.8)</strong>*</td>
<td>5.2 (6.6)</td>
</tr>
<tr>
<td></td>
<td>Theoretical</td>
<td>735</td>
<td>-</td>
</tr>
</tbody>
</table>

*At 65% Vol. estimated composite strength is over 1000 MPa
Over 6 times stronger (per unit wt) than most varieties of STEEL!
Green Composite Construction

tradition platform wood construction

post and beam with structural skin

Green Composite Molded Walls

Advanced Green Composite Frame

reducing layers
Green Composite Cabin Construction
Biorefinery: The Soybean Model

Soybean Field → Soybeans → Soybean oil → Defatted Soy Flour → Fiber mat

- MFC
- NFC

Soy Foam → Food

Biodiesel → Epoxidized Soy Oil

Hydromulch, Soil Rehabilitation & Seed Coating

Bacterial Cellulose

Carbohydrates → Soy Protein

Green Composites

NanoFilters

= Research in Netravali Lab
ann2@cornell.edu
Bacterial Cellulose Based Composites

Hydrogel-like fresh bacterial cellulose (BC) specimens

SEM image of bacterial cellulose

BC-SPI resin composite

BC-poly (vinyl alcohol) composite
What’s Next?

Starch Extraction from Wastes
Mango Seed Kernel and
Raw Plantains
for
Advanced Composites and Textile Applications

Protein Extraction from Wastes
neem (*Azadiractha Indica*) seed and
Karanja (*Pongamia Pinnata*)
for
Advanced Composites
Effect of COC Treatment on Hair Straightness and Straightness Retention
Characterization of hair curliness

Results - 0 Day of Conditioning*

A: As received (not treated)
   Brazilian Curly Hair

B: - Hand washed with soap
   - Flat ironed -dried (not treated)

C: - Hand washed with soap
   - Air dried (not treated)

D: - Hand washed with soap
   - COC** treatment
     (pH 10.5, 50°C, 30 min)
   - Flat ironed (crosslinking)
   - Washed (removal residuals)
   - Flat ironed (possible additional crosslinking)

*Hung vertically @ 21°C and 65% RH
**COC = Cornell Oxidized Carbs
Results - 1 Day of Conditioning*

A: As received (not treated)  
   **Brazilian Curly Hair**

B: - Hand washed with soap  
   - Flat ironed -dried (not treated)

C: - Hand washed with soap  
   - Air dried (not treated)

D: - Hand washed with soap  
   - COC** treatment  
     (pH 10.5, 50°C, 30 min)  
   - Flat ironed (crosslinking)  
   - Washed (removal residuals)  
   - Flat ironed (possible additional crosslinking)

*Hung vertically @ 21°C and 65% RH  
**COC = Cornell Oxidized Carbs
Results - 16 Days of Conditioning*

A: As received (not treated)
   Brazilian Curly Hair

B: - Hand washed with soap
   - Flat ironed -dried (not treated)

C: - Hand washed with soap
   - Air dried (not treated)

D: - Hand washed with soap
   - COC** treatment
     (pH 10.5, 50°C, 30 min)
   - Flat ironed (crosslinking)
   - Washed (removal residuals)
   - Flat ironed (possible additional crosslinking)

*Hung vertically @ 21°C and 65% RH
**COC = Cornell Oxidized Carbs
Results - 40 Days of Conditioning*

A: As received (not treated)
Brazilian Curly Hair

B: - Hand washed with soap
- Flat ironed -dried (not treated)

C: - Hand washed with soap
- Air dried (not treated)

D: - Hand washed with soap
- COC** treatment
  (pH 10.5, 50°C, 30 min)
- Flat ironed (crosslinking)
- Washed (removal residuals)
- Flat ironed (possible additional crosslinking)

*Hung vertically @ 21°C and 65% RH
**COC = Cornell Oxidized Carbs
‘Green Methods’ to Obtain Ultrahydrophobic Cotton
Wetting on a Flat Surface

- Young’s equation:

\[
\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}
\]

- \(\gamma\) is interfacial tension
- \(\theta\) is highly depend on liquid surface tension (energy).

(\(\gamma_{lv}\) of water = 73mN/m and oil < 35mN/m)

\[\text{H́, Bellanger, etc., Chemical Reviews, 2014, 114 (5), pp 2694–2716}\]
Wetting on a Flat Surface

Hydrophilic: $\theta<90^\circ$
Hydrophobic: $\theta>90^\circ$
Superhydrophobic: $\theta>150^\circ$
Wenzel state:
\[
\cos \theta^* = r \cos \theta
\]

Roughness factor \( r = \frac{\text{specific area}}{\text{projected area}} \)

- Liquid completely fills the grooves of the solid
- Hydrophilic substrate will be more hydrophilic, whereas a hydrophobic substrate will be more hydrophobic
- Described as “Sticky”, due to the strong adhesion between liquid and solid

H́, Bellanger, etc., *Chemical Reviews*, 2014, 114 (5), pp 2694–2716
Cassie–Baxter state:

\[ \cos \theta^* = \phi_s (\cos \theta + 1) - 1 \]

\( \phi_s \) is liquid-solid contact surface area

- Liquid “sits” on the surface roughness
- Described as “Non sticky”
Natural Superhydrophobic Surface

1) Low surface energy:
   Epicuticula wax

2) High surface roughness:
   Micro and nanometer scale roughness: one around 10 µm and the other around 100 nm

Zhiguang Guo, Plant Science 172, no. 6 (2007): 1103-1112.
Techniques to Obtain Hydrophobic Surfaces

- Lower Surface Energy
  - Low surface energy materials:
    - Fluorocarbon: Teflon
    - Silicones: PDMS
    - Inorganic material: ZnO
    - Organic material: Polyethylene

- Rough Surface
  - Methods to fabricate rough surface
    - Lithography and etching
    - Mechanical abrasion
    - Crystal growth
    - Self-assembly
Our Objectives

• **Develop ‘greener’ method** to fabricate hydrophobic cotton surface
  – **Graft fatty acid onto cellulosic backbone** to reduce surface energy
  – **Disperse micro- and nano-particles** onto cotton fiber to increase surface roughness
  – **Crosslink particles deposited on cotton fabric** for ‘permanent’ surface topography and hydrophobicity & in order to reduce the environmental concerns of nanoparticle washing away.

• **Challenges:**
  1. Low reactivity of fatty acid toward cellulosic hydroxyl groups
  2. Common method for activation fatty acid involves toxic and hazardous reagents and solvents \(\rightarrow\) Formation of benign intermediates
  3. High energy consumption for reaching desired reaction temperature \(\rightarrow\) Microwave
Effect of Microwave Power Level and Heating Time on Hydrophobicity of Fatty Acid Treated Cotton Fabric

a) Fixed microwave heating time (10 min)  
b) Fixed microwave power level (900 Watts)
## Laundry Durability of Fabric Hydrophobicity

*Each cycle is equivalent to five hand or home launderings

** 37 laundry cycles is equivalent to 185 washings

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Cycle of laundry test*</th>
<th>Average</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% Power/10 min</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>60% Power/10 min</td>
<td>10</td>
<td>12</td>
<td>11.3</td>
</tr>
<tr>
<td>80% Power/10 min</td>
<td>23</td>
<td>22</td>
<td>24</td>
</tr>
<tr>
<td>100% Power/10 min</td>
<td>31</td>
<td>29</td>
<td>33</td>
</tr>
<tr>
<td>100% Power/3 min</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>100% Power/6 min</td>
<td>17</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>100% Power/15 min</td>
<td>35</td>
<td>35</td>
<td>37**</td>
</tr>
</tbody>
</table>
SEM Images for Cotton Fabric

a) As received                      b) Ethanol washed                   c) Hydrophobic treated
Preparation of Micro- and Nano-Particles

Diameter of Particles  a) 458 nm b) 107 nm
Cotton Fabrics Treated with Single Size Particles

SEM images of size particles (d = 107 nm) deposited cotton fabric. Cotton fabric was immersed in:

a) and b) 0.5% particle dispersion;

c) 0.1% particle dispersion;

d) 0.02% particle dispersion
Effect of Hydrophobic Treatment on Deposited Particles

SEM images of a) cotton fabric with physically deposited particles before hydrophobic treatment; b) after hydrophobic treatment

*No significant particle loss was observed
<table>
<thead>
<tr>
<th>Specimens</th>
<th>Water contact angle (°)</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (no particle)</td>
<td>135.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Treated in 0.02% particle dispersion</td>
<td>139.3</td>
<td>2.7</td>
</tr>
<tr>
<td>Treated in 0.1% particle dispersion</td>
<td>143.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Treated in 0.5% particle dispersion</td>
<td>144.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Cotton Fabric With Dual-size Particles Treatment
Cotton Fabric with Crosslinked Dual Size Particles

SEM images of cotton fabric with dual size particles crosslinked by: A (left) and by B (right)
# Water Contact Angle Results of Hydrophobic Cotton Fabric with Dual-size Particles

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Water contact angle (°)</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic Control (no particles)</td>
<td>135.51</td>
<td>1.19</td>
</tr>
<tr>
<td>Crosslinked cotton fabric (A) with dual sized particles</td>
<td>150.81</td>
<td>3.81</td>
</tr>
<tr>
<td>Crosslinked cotton fabric (B) with dual-size particles</td>
<td>152.73</td>
<td>3.09</td>
</tr>
<tr>
<td>Cotton fabric with physically deposited dual-size particles</td>
<td>153.41</td>
<td>2.33</td>
</tr>
</tbody>
</table>
Acknowledgements

• Mr. S. Chabba, Dr. P. Lodha, Mr. Y. Yamamoto
• Dr. S. Nam, Dr. J-T. Kim Dr. D. Lubasova
• Dr. X. Huang Dr. K. Qiu Mr. J. Hoiby
• Dr. H. Kumar Ms. A. Sonis Mr. K. Mizuta
• Dr. D-W. Cho Ms. Y. Yong Dr. T. Ghosh Dastidar
• Mr. M. Rahman Ms. N. Patil Ms. V. Vaidya

• Prof Mike Hoffman (Cornell)
• Mr. Jeffrey Gardener (Cornell)
• Prof. Hiro Yano (Kyoto)
• Dr. H. Boerstoel (Rijksuniversiteit, Groningen)
• Dr. Luiz Farah
• Mr. Pat Govang (e2e Materials)
• Mr. Jason Salfi (Comet Skateboards)

Materials
• Archer Daniels Midland (ADM) Company, IL

Funding/Facilities
• National Textile Center (NTC)
• NSF (through CCMR, CREST & PREM)
• NYSTAR
• NYSERDA
• Nissan
• Wallace Foundation
• e2e Materials/Comet Skateboards
• CCMR and FSAD
Future of ‘Green’ Materials Looks Very Promising!

To my biased green eyes!
Future of ‘Green’ Materials Looks Very Promising!

Perhaps because there is no alternative!
Questions