A Step Towards A More Sustainable, Responsible & Profitable Textile Industry

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University of Nebraska-Lincoln
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Acknowledgement

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• Graduate Students

• Collaborators

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Challenges

• Annual fiber consumption: >120 M tons
  – Doubled in 20 years

• Environmental impacts
  – Fiber production
  – Slashing
  – Wet Processing
  – Waste and spent textiles

• Sustainability
  – Reduce, Replace, Reuse and Recycle
Our Efforts

• Fibers
  – Non-traditional biobased fibers

• Sizes
  – Plant/animal proteins to replace PVA

• Coloration
  – Natural dyes from wastes
  – Non-aqueous systems

• Complete recycling of dyes and waste/used textiles
  – Effluent
  – Waste and used textiles
Biofibers

- Non-traditional natural and regenerated fibers
- Challenges
  - Property and cost equivalence
- Lignocellulosics
  - Crop stovers
    - Corn
    - Cotton
- Proteins
  - Distillers grains
  - Meals
  - Feathers
  - Low quality/waste hair fibers
# Worldwide Availability of Raw Materials and Non-traditional Lignocellulosics

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Availability, Million Tons</th>
<th>Source</th>
<th>Fiber/chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw</td>
<td>580</td>
<td></td>
<td>116</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>570</td>
<td></td>
<td>114</td>
</tr>
<tr>
<td>Cornstalk</td>
<td>320</td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>Cornhusk</td>
<td>64</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>Soybean straw</td>
<td>214</td>
<td></td>
<td>43</td>
</tr>
<tr>
<td>Sorghum</td>
<td>59</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>Pineapple leaf</td>
<td>233</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>Sugarcane rind</td>
<td>29</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Total</td>
<td>2069</td>
<td></td>
<td>388</td>
</tr>
</tbody>
</table>

*The potential fiber availability has been calculated based on 20% yield of fibers/chemicals (10% for pineapple leaf fibers and sugarcane rind fibers)
Stress-Strain Properties of Some Non-traditional Natural Cellulose fibers compared with cotton and linen
Examples of Lignocellulosic Textiles

<< AGRI-COUTURE

More than half of the 67 million tons of textile fibers produced annually are petroleum-based synthetics. But with rocketing oil prices, agricultural byproducts are gaining attention as natural fiber sources, scientists reported last week at the American Chemical Society meeting in San Francisco, California.

Textile scientist Yiqi Yang of the University of Nebraska, Lincoln, said he has gotten fibers from rice straw that are “long and fine enough for textiles but still very strong.” Using alkali and enzymes, he and student Narendra Reddy extracted finger-length fibers that they say rival linen and cotton in flexibility and strength. Adding cotton, they spun a yarn and wove it into rice/cotton fabric. Yang estimates that 58 million tons of textile fiber could be produced from half of the 580 million tons of waste rice straw grown each year.

Brian George, a textile engineer at Philadelphia University in Pennsylvania, says the relative stiffness of such fibers makes them hard to work with unless they are blended with cotton or flax, but that the idea seems economically viable if the fibers “can be processed on standard textile equipment.”

Yang says rice-straw fibers are stronger than those from cornhusks, which he managed to make a sweater out of a few years ago. His next project is to get spinnable fibers from chicken leathers, whose honeycomb structure, he says, could potentially make for textiles lighter and warmer than wool.

www.sciencemag.org SCIENCE VOL 313 22 SEPTEMBER 2006
Worldwide Availability of Raw Materials and Protein Fibers/Chemicals

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>World Production (Million tons)</th>
<th>Protein Content</th>
<th>Potential Protein for Biofibers/Chemicals (Million Tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybeans</td>
<td>206.5</td>
<td>44%</td>
<td>9.1*</td>
</tr>
<tr>
<td>Wheat</td>
<td>632.6</td>
<td>13%</td>
<td>8.2*</td>
</tr>
<tr>
<td>Corn</td>
<td>724.6</td>
<td>9%</td>
<td>6.5*</td>
</tr>
<tr>
<td>Milk</td>
<td>622.3</td>
<td>3%</td>
<td>1.9*</td>
</tr>
<tr>
<td>Peanut</td>
<td>30.2</td>
<td>27%</td>
<td>0.8*</td>
</tr>
<tr>
<td>Feather</td>
<td>8</td>
<td>~100%</td>
<td>8.0**</td>
</tr>
<tr>
<td>Total</td>
<td>2224</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Wool</td>
<td>&lt;2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silk</td>
<td>&lt;0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Assumed 10% availability of proteins for biofiber/chemical production
** Assumed 100% availability for biofiber/chemical production
Fabrication of Regenerated Protein Fibers
## Properties of Plant Protein Fibers Compared to Wool

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Breaking Tenacity g/den</th>
<th>Breaking Elongation %</th>
<th>Modulus g/den</th>
<th>Moisture Regain %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat Gluten</td>
<td>1.1 ± 0.07</td>
<td>23 ± 2.7</td>
<td>34 ± 2.2</td>
<td>18</td>
</tr>
<tr>
<td>Wheat Gliadin</td>
<td>1.2 ± 0.9</td>
<td>25 ± 3.2</td>
<td>29 ± 2.8</td>
<td>15</td>
</tr>
<tr>
<td>Soyprotein</td>
<td>1.0 ± 0.12</td>
<td>8.5 ± 1.1</td>
<td>42 ± 1.4</td>
<td>15</td>
</tr>
<tr>
<td>Zein</td>
<td>1.1 ± 0.02</td>
<td>30.0 ± 2.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wool</td>
<td>1.2 -1.8</td>
<td>30-40</td>
<td>30- 45</td>
<td>16</td>
</tr>
</tbody>
</table>
Comparison of feather keratin fibers and wool

<table>
<thead>
<tr>
<th>Fiber source</th>
<th>Dry Properties</th>
<th>Wet Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stress (MPa)</td>
<td>Strain (J cm⁻³)</td>
</tr>
<tr>
<td>Keratin fibers</td>
<td>110-145</td>
<td>8-12%</td>
</tr>
<tr>
<td>Crosslinked keratin fibers</td>
<td>195-215</td>
<td>16-22%</td>
</tr>
<tr>
<td>Wool</td>
<td>150-190</td>
<td>30-40%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Stress (MPa)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keratin fibers</td>
<td>60-90</td>
<td>22-28%</td>
</tr>
<tr>
<td>Crosslinked keratin fibers</td>
<td>120-140</td>
<td>27-35%</td>
</tr>
<tr>
<td>Wool</td>
<td>120-160</td>
<td>42-50%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Toughness (J cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keratin fibers</td>
<td>17-19</td>
</tr>
<tr>
<td>Crosslinked keratin fibers</td>
<td>27-32</td>
</tr>
<tr>
<td>Wool</td>
<td>28-38</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Toughness (J cm⁻³)</th>
</tr>
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<tbody>
<tr>
<td>Keratin fibers</td>
<td>22-28</td>
</tr>
<tr>
<td>Crosslinked keratin fibers</td>
<td>29-35</td>
</tr>
<tr>
<td>Wool</td>
<td>33-40</td>
</tr>
</tbody>
</table>
Size

- PVA for high-speed weaving
  - COD
- Challenges
  - High speed weaving efficiency
- Plant and feather proteins
Industrial Weaving Results
Using Sizes from Soy Protein Isolates

<table>
<thead>
<tr>
<th>Yarn</th>
<th>Sizes</th>
<th>Add-on, %</th>
<th>Relative weaving efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>Soy protein isolate sizes</td>
<td>16</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>PVA sizes</td>
<td>21</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>Modified starch sizes</td>
<td>21</td>
<td>61</td>
</tr>
<tr>
<td>30/70 Poly/cotton</td>
<td>Soy protein isolate sizes</td>
<td>11</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>PVA sizes</td>
<td>17</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>Modified starch sizes</td>
<td>14</td>
<td>90</td>
</tr>
<tr>
<td>Polyester (plant A)</td>
<td>Soy protein isolate sizes</td>
<td>11</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>PVA sizes</td>
<td>17</td>
<td>100</td>
</tr>
<tr>
<td>Polyester (plant B)</td>
<td>Soy protein isolate sizes</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>PVA sizes</td>
<td>7</td>
<td>100</td>
</tr>
</tbody>
</table>
# Desizing Performance

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Soy protein isolates</th>
<th>Soymeal</th>
<th>PVA</th>
<th>Modified starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>95.0 ± 2.1</td>
<td>92.1 ± 1.0</td>
<td>100</td>
<td>62.4 ± 4.3</td>
</tr>
<tr>
<td>30/70 Poly/cotton</td>
<td>100</td>
<td>98.3 ± 0.5</td>
<td>98.2 ± 1.6</td>
<td>65.0 ± 4.9</td>
</tr>
<tr>
<td>Polyester</td>
<td>100</td>
<td>100</td>
<td>94.5 ± 2.6</td>
<td>-</td>
</tr>
</tbody>
</table>

*Three rinses at 90 °C, liquor/fabric = 5/1
Biodegradation-COD

COD, mg/L

Days in activated sludge

Grade II discharge standard:
COD < 120 mg/L
Cost Comparison: Soy protein, Soymeal vs PVA

**Price of PVA sizes:**
Domestic PVA market, Entrepreneur database .
http://www.qiveku.com/xinwen949012.html
Price of Japanese PVOH Kuraray, Poval PVA 205MB, Poval PVA 217,
http://detail.1688.com/offer/1270719815.html

**Price of soy meal and soy protein:**
Corn ethanol-higher value coproducts and recovery of corn oil;
http://www.yptel.cn/qyjj3.asp?ID=60397
http://www.1688.com/jiage/4F3B6B9B7D6C0EBB5B00D7.html
http://www.cofco.com/cn/service/c-269.html

<table>
<thead>
<tr>
<th>Protein Type</th>
<th>Cost of Protein (per ton)</th>
<th>Cost of Meal (per ton)</th>
<th>Price of Sizes (per ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soy protein</td>
<td>$400-4950</td>
<td>$400-550</td>
<td>$3270-3830</td>
</tr>
<tr>
<td>Soy meal</td>
<td>$3270-3830</td>
<td>$655-1020</td>
<td>$3300-4000</td>
</tr>
<tr>
<td>PVA</td>
<td>$400-550</td>
<td>$655-1020</td>
<td>$3300-4000</td>
</tr>
</tbody>
</table>
Traditional Coloration

• Salt and dye in the spent batch dyeing bath
  – Mainly reactives

• Challenges
  – Environmental problems
  • Costs

• Dual liquid system
  – Water: fiber inner phase
  – Oil: outer phase
Our Approach

- Using plant oil/water dyeing system
  - High dye fixation
  - No salt
- Excellent levelness
  - Controlled dye sorption rate
- Reuseable dyebath
- Low costs
  - No needs for 100% recycle of dyebath
- Environmental responsibility
  - Plant oils are safe in use
  - Plant oils are easily degradable by activated sludge commonly used
Principles

- Increased chemical potential of dye in external phase, thus increased affinity of dyes to fabric
Potential Problems and Solutions

• Fast dye sorption rate
  – Problem
    • Uneven dyeing
  – Solution
    • Controlled dye sorption rate
    • Controlled dye migration and diffusion

• Strong oil sorption into fibers
  – Problem
    • Complete removal of oil from fabrics
  – Solution
    • Fill capillaries with water to prevent oil entrance
Dyeing Procedures:
Warm dyeing reactives: Water content/Emulsion

- Oil as the continuous phase.
- Water as the dispersed phase.
- The dispersed phase to dissolve dyes and swell cotton.
- Dyes directly dissolved in water and added into the stirring cottonseed oil with certain weight ratios to form a semi-stable emulsion as the dye stock.
High Dye Uptake and Fixation - Ball milling

3% (owf) of Reactive Red 120, ratio of oil to fabric: 20:1. 100% owf water content. Cottonseed oil
High Dye Uptake and Fixation - Emulsion

2% (owf) of Reactive Blue 19, Ratio of oil to fabric: 20:1. 100% owf water content Cottonseed oil
Coloration with Natural Dyes

• Challenges
  – Cost
  – Colorfastness
  – Shade consistency
  – New environmental concerns

• Natural dyes from agricultural wastes
  – Hulls and peels of grains and fruits
Natural Dyes from Wastes

- Sorghum Hulls
- Orange Peels
- Chlorophyllin
- Granatum
- Banana Peels
Advantages of Natural Dyes from Wastes

• Low cost comparing to planting just for dyes
• No additional environmental problems
• Large availability
• Unique properties
  – Antibacterial
  – UV blocking
  – Fluorescent
Dye Removal from Spent Dyebath

• Challenges
  – Costs
  – New environmental issues

• Solutions
  – High sorption capacity
  – High regeneration capability
    • Ionic interaction with minimal van der Waals attractions
  – Environmentally responsibility
    • Non-toxic in production and regeneration
Efficient Dye Removal and Sorbent Regeneration

• Dyestuff sorption capacity: 7g/g hydrolyzed Reactive Blue 19
• Sorbent regeneration
  – Concentration factor: 19 with 99% dye desorption efficiency.
• Easy salt and dye reuse
  – 8% reduction in dye sorption with 5 g/L NaCl
  – 12% reduction in dye sorption with 10 g/L NaCl
Recycling of Dyes and Fibers from Apparels and Carpets

• Challenge
  – Dye removal from textiles without damages
  – Costs

• Systems for complete dye removal and fiber separation
  – Elimination of dye affinity to textiles
  – Dissolution of dye and fiber polymers
  – Selective sorption/desorption and precipitation for dye and fiber separation and purification
Dye Removal via Fiber Swelling and Fiber Separation via Dissolution

PET/cotton fabric

Solvent 1 to dissolve PET and disperse dyes

Cotton fabric

Separation of PET and cotton

PET & disperse dye solution

Controlled PET precipitation & filtration

PET

Disperse dye solution

Solution of dyes for cotton

Cotton fabric
Credit to the Journals
This presentation is based on our following publications

ACS Sustainable Chemistry & Engineering. 5(6) 4589-4597 (2017); 7(16) 13698-13707 (2019).
Acta Biomaterialia. 6(10) 4042-4051 (2010).
Biomacromolecules, 8(2) 638-643 (2007).
Food Hydrocolloids. 90. 443-451 (2019).
Green Chemistry, 7(4) 190 – 195 (2005); 22(5) 1726-1734 (2020).
Journal of Cleaner Production. 52. 410-419 (2013); 139. 267-276 (2016); 236. 117566 (2019).