INTEGRATION OF LIGNIN WITH RESIDUAL SOY PROTEINS IN THE FABRICATION OF FIBER WEBS

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Outline

Background

Lignin

Soy fibers

Wettability improvement

Conclusions

Lignin-Soy fibers
Soybean Proteins

Molecular weight: 320-360 kDa

Molecular weight: 180-200 kDa

Applications

- Wood adhesives
- Building materials
- Plastics
- Textile fibers
- Cosmetics
- Printing ink

• Readily available
• Low cost (~$0.2/lb)
• Commercial forms: Flour, isolates, concentrates
Lignin

Building blocks

Typical uses

- Burned to produce energy.
- Small amount (~3%) goes to the production of dispersants, adhesives and surfactants.

Emerging applications

- Carbon fibers
- Composite materials

Lignin soy protein interactions

- Non-specific interactions between soy proteins and lignin: Important on wood adhesives, animal feed, dispersants, and enzymatic inhibition.

**Adsorption**

![Graph showing adsorption mass (mg/m²) vs. concentration (mg/ml) for Glycinin, pH 7.0, with different modifiers: +100 mM NaCl, +10 mM 2-ME, +8M Urea, Native.]

**Surface modification**

![Bar graph showing % Reduction on contact angle for Glycinin and β-conglycinin at concentrations: 0.01 mg/ml, 0.1 mg/ml, 1 mg/ml.]

Salas et al. *Biomacromolecules* 2012, 13, 387
Salas et al. ACS Appl. Mater. Interfaces, 2013, 5, 199
Soy protein-lignin composites

Alkaline lignin proved to be an effective filler, increasing the mechanical strength and thermal stability soy protein plastics.

Soy protein plastics reinforced with lignin and lignosulfonates.

Lignin-soy protein fibers
Important variables

- Solution Viscosity
- Surface tension
- Conductivity of solution
- Distance to collector
- Applied voltage
- Humidity
## Electrospinning of soy proteins

<table>
<thead>
<tr>
<th>Material</th>
<th>Solvent</th>
<th>Coadyuvant</th>
<th>Experiment conditions</th>
<th>Fiber diameter</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soy isolate</td>
<td>1% NaOH</td>
<td>PEO, TritonX-100</td>
<td>Heating 60 °C, 2h, 20-30 kV, 26 cm, 0.04 ml/min</td>
<td>~240 nm (95wt% isolate)</td>
<td>1</td>
</tr>
<tr>
<td>Soy Isolate</td>
<td>Hexafluoroisopropanol</td>
<td>PEO</td>
<td>8 days to dissolve protein, 25 kV, 25 cm, 1.5 ml/min</td>
<td>200-300 nm (94% SPI)</td>
<td>2</td>
</tr>
<tr>
<td>Soy Isolate</td>
<td>NaOH</td>
<td>PVA, triton X-100</td>
<td>80 C, 30 min, pH 12.15-20 kV, 20 cm, 0.015 ml/min</td>
<td>0.6-4.5 μm</td>
<td>3</td>
</tr>
</tbody>
</table>

3 Xu et al. ACS Appl. Mater. Interfaces 2012, 4, 4331
Electrospinning of lignin

<table>
<thead>
<tr>
<th>Material</th>
<th>Solvent</th>
<th>Coadjutant</th>
<th>Experiment conditions</th>
<th>Fiber diameter</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Alcell Lignin</td>
<td>Ethanol</td>
<td>None</td>
<td>12 kV, coaxial electrospinning</td>
<td>400 nm-2μm</td>
<td>4</td>
</tr>
<tr>
<td>Kraft lignins, Organosolv</td>
<td>DMF</td>
<td>PEO</td>
<td>10-50 wt%, 60 °C, 1-5 wt% PEO</td>
<td>700-1650 nm (1% PEO)</td>
<td>5</td>
</tr>
<tr>
<td>Kraft Lignin</td>
<td>Water</td>
<td>PVA, CNCs</td>
<td>19 kV, 8 μL/min</td>
<td>61-500 nm</td>
<td>7,8</td>
</tr>
<tr>
<td>Kraft lignin</td>
<td>DMF</td>
<td>PEO</td>
<td>15 kV, 20 cm,</td>
<td>400-3200 nm</td>
<td>9,10</td>
</tr>
</tbody>
</table>

The addition of polyethylene oxide or polyvinyl alcohol improved intermolecular interactions, leading to uniform fibers.

5 Dallmeyer et al. J. Wood Chem. Technol. 2010, 30, 315
6 Ruiz-Rosas et al. Carbon 2010, 48, 696
Experimental

- Kraft lignin
- Solvent: Acetonitrile in dilute NaOH.
- Proteins: commercial isolate and glycinin (11S)

- Co-adjuvant: Polyethylene oxide (PEO)
- 8 ul/min, 19 kV, 22 cm
Rheology of precursor solutions

G: Glycinin

0.1 1 10 100 1000
0.01 0.1 1

Viscosity (Pa.s)
Shear rate (s
-1
)

G4 (70% lignin)
G2 (50% lignin)
G1 (20% lignin)
G3 (60% lignin)

Bead-free fibers

Morphology of electrospun fibers

<table>
<thead>
<tr>
<th>Lignin Content</th>
<th>Diameter (nm)</th>
<th>SEM Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% Lignin</td>
<td>125±27</td>
<td><img src="image1" alt="Image 1" /></td>
</tr>
<tr>
<td></td>
<td>113±26</td>
<td><img src="image2" alt="Image 2" /></td>
</tr>
<tr>
<td>50 wt% Lignin</td>
<td>191±31</td>
<td><img src="image3" alt="Image 3" /></td>
</tr>
<tr>
<td></td>
<td>246±38</td>
<td><img src="image4" alt="Image 4" /></td>
</tr>
<tr>
<td>60 wt% Lignin</td>
<td>280±27</td>
<td><img src="image5" alt="Image 5" /></td>
</tr>
<tr>
<td></td>
<td>222±29</td>
<td><img src="image6" alt="Image 6" /></td>
</tr>
<tr>
<td>70 wt% Lignin</td>
<td>392±50</td>
<td><img src="image7" alt="Image 7" /></td>
</tr>
<tr>
<td></td>
<td>438±49</td>
<td><img src="image8" alt="Image 8" /></td>
</tr>
</tbody>
</table>

Salas et al. Reactive and Functional Polymers 2014, 85, 221
Water resistance of fiber mats

Salas et al. Reactive and Functional Polymers 2014, 85, 221
Improvement of wettability by crosslinking

Crosslinking with glutaraldehyde (GA)

Carried out in two ways

**Vapor phase**

To vacuum

Sample

Glutaraldehyde solution

**Liquid phase**

GA in solution (5, 10 or 20 mM)
Crosslinking: GA in precursor solution

GA
In solution 5 mM
Glycinin

GA
In solution 5 mM
Isolate
Crosslinking: exposure to GA under vacuum

Vapor phase
10% wt GA solution

1 min

3 min

5 min
Conclusions

• Favorable interactions of soy proteins with lignin: synthesis of uniform nanofibers.

• Increase in fiber diameter and hydrophilicity of fiber mats with lignin loading.

• Crosslinking improve the stability on water of the fibers
Acknowledgments

• United Soybean Board (USB).

• ADM for soybean flour and isolate samples.

• Robina Hogan, and Tom Theyson at Omni Tech International.

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Thanks for your kind attention

Any Question?