Environmentally friendly
wet-end paper reinforcement agents

Asif Hasan, Chen Gong, Biljana Bujanovic*, Tom Amidon
Department of Paper and Bioprocess Engineering
SUNY ESF, Syracuse, New York-13210
SMART, ENVIRONMENTALLY FRIENDLY PAPER

• Today’s motto “more for less”
Increase in profit margin by
  - Reduction of basis weight
  - Replacement of fiber by cheaper materials such as fillers

• Industry of future needs to design its paper without compromising
  - strength
  - bulk
REPLACE FIBER?

- Disadvantage of adding fillers

- How to compensate for the strength loss?
  - Additives?
• Society and Government are looking for an industry:

1. More sustainable
2. Based on renewables
3. Environmentally benign
4. Produces net positive energy
5. Green

Consistent with that is the concept of Biorefinery....
Pulping within biorefinery: hot water extraction (HWE) of chips before pulping, ESPRI SUNY ESF process

- **Hardwood chips**
  - Hot-water extraction
  - Hot-water extracted woodchips
    - Pulping, bleaching, papermaking
      - PAPER
      - Strong bulky paper
    - CHP combined heat & power
  - Burning
  - Reconstituted wood products
    - Hydrolysis
      - Acetic acid, furfural, hydroxymethyl furfural, methanol
      - Sugars
        - Fermentation
          - Lactic acid
          - FLA
        - Ethanol butanol acetone
  - Membrane separation
    - Hot-water extract
      - Paper production within biorefinery

Hot water Extraction (HWE) is performed to produce fermentable feedstock by dissolution of hemicelluloses.

Hemicelluloses are worth 3 to 4.5 times as Ethanol than energy in kraft pulping (Restina, Pykannen, 2007).
BENEFICIAL EFFECTS OF EXTRACTION

- Hemicelluloses as fermentable feedstock
- **Lower H-factor** requirement to make the same kappa number of pulp as with un-extracted wood
  - Open substrate structure, penetration of chemicals and diffusion of degraded products become easier
- **Lower alkali consumption**
  - Due to lower hemicellulose content (lower acetyl content)
- **Higher bulk**
  - Resulting in high porosity, high scattering coefficient / good opacity, greater caliper, high stiffness
- **Higher refining energy**
  - Due to higher fiber rigidity, lower response to beating
Lower tensile strength

- There is a need to strengthen paper based on pulp from extracted woodchips to retain the bulk advantage and have compatible strength to unextracted pulp
<table>
<thead>
<tr>
<th>Conventional Additives</th>
<th>Environmentally Friendly Additives</th>
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<tbody>
<tr>
<td><strong>PAE (Polyamide – Epichlorohydrin) resins</strong></td>
<td><strong>Starch:</strong></td>
</tr>
<tr>
<td>• Compatible with alkaline pulps,</td>
<td>• Compatible with any pulping system</td>
</tr>
<tr>
<td>• Gives wet strength</td>
<td>• Gives only dry strength - hydrophillic</td>
</tr>
<tr>
<td>• Produce chlorine compounds</td>
<td>• Biodegradable</td>
</tr>
<tr>
<td></td>
<td>• Renewable</td>
</tr>
<tr>
<td><strong>Urea-formaldehyde resins</strong></td>
<td><strong>Polylactic Acid (polylactide):</strong></td>
</tr>
<tr>
<td><strong>Melamine-fpormaldehyde resins</strong></td>
<td>• Compatible with any pulp system</td>
</tr>
<tr>
<td>• Used in acid conditions, in the presence of Alum</td>
<td>• Gives wet strength</td>
</tr>
<tr>
<td>• Gives wet strength</td>
<td>• Helps dry strength</td>
</tr>
<tr>
<td>• Both linked to respiratory problem and poor air quality</td>
<td>• Compostable</td>
</tr>
<tr>
<td></td>
<td>• Product of Renewable feedstock</td>
</tr>
<tr>
<td><strong>Glyoxalated Polyacrylamide:</strong></td>
<td><strong>Polyhydroxy alkanoates (PHA):</strong></td>
</tr>
<tr>
<td>• Gives dry and wet strength</td>
<td>• Product of Renewable feedstock</td>
</tr>
<tr>
<td>• Potentially Carcinogenic in monomeric form</td>
<td>• Potential for dry and wet strength</td>
</tr>
</tbody>
</table>
In our earlier work

- We demonstrated on Kraft pulp made from Sugar Maple (Acer saccharum) chips that **PLA** applied on surface improved:

- **Tensile Index** (35-100%)
- % **Stretch** (20-40%)
- **Tear Index** (10-100%)
- **Wet Tensile Index** (50-250%)

- **Hot water extracted, unbleached Kraft pulp** which is hemicellulose depleted and lignin rich, responded the most favorably to PLA treatment in strength parameters while being able to retain its bulk.

(Change in the chemical composition has a positive effect on interaction between PLA and fiber).

Figure 1: SEM micrograph of paper made from biorefinery pulp
Figure 2: SEM micrograph of paper made from biorefinery pulp and treated in the surface with PLA (2% based on OD fibers)
• **Unbleached Kraft** pulp from **Hotwater extracted** chips in the Biorefinery is the natural step forward in exploring potential for PLA treatment.

• However the SEM images revealed that the PLA was not uniformly distributed.

• If PLA could be uniformly distributed by application in the **WET END**, it can further improve its prospects.

• PLA by itself is not soluble in water, so if combined with Cationic starch it could be stabilized in papermachine white water stock.
MATERIALS AND METHODS: HOT WATER EXTRACTION

- Wood
  - Sugar maple
    *(Acer saccharum)*

**Hot water extraction conditions**
- Performed in an M/K digester
- OD chips - 500 g
- Water to wood ratio - 4:1.
- Temperature profile - 45 minutes to 160 °C and 120 minutes at 160°C.

At the end of the extraction the liquor was drained, Chips were washed and collected, and kept in plastic bags for pulping

Yield 81.4% OD wood
MATERIALS AND METHODS: KRAFT PULPING

- Pulping Conditions

Temperature profile
- 60 minutes to 165°C,
- 5 minutes at 165°C, H-factor 132 (HW extracted kraft)
- 45 minutes at 165°C, H-factor 536 (Regular kraft)

Active Alkali -16% on OD Chips
Sulfidity – 25%
Liquor to Wood - 4:1

- H-factor was adjusted based on the results of preliminary experiments to produce pulp of kappa number ~40
MATERIALS AND METHODS: PULP CHARACTERIZATION

- Kappa number (Tappi T 236 cm-85)
- PFI beating of pulp (T 248 sp-08) 5000 rev.
- CSF(T227 om-4)
- Hand sheet preparation (T205 sp-06)

** Strength properties tested
- Internal tearing resistance (Elmendorf type method, T 414 om-04)
- Tensile strength (constant rate elongation apparatus, T494 om-06)
- Wet strength
MATERIALS AND METHODS: PLA AS A REINFORCING AGENT

- PLA poly (dl-lactic acid)

<table>
<thead>
<tr>
<th>PLA</th>
<th>Poly (dl-lactic acid)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>20K-30K</td>
<td>Polysciences, Inc.</td>
</tr>
<tr>
<td>Tg</td>
<td>54°C</td>
<td>Cat.#165</td>
</tr>
</tbody>
</table>

- PLA solution in acetone, 0.8-1 g/L concentration
- Experiments were performed at PLA level:
  - On surface based on OD fiber w/w
    - 2%
  - In Stock based on OD fiber w/w
    - 0.9% (max)
    - 0.5% (min)
MATERIALS AND METHODS: Starch AS A REINFORCING AGENT

- Starch was first slurried by mixing dry powder with water.
- Cooked at 0.3% solids at 95-970C for an hour under constant stirring.
- It formed a clear aqueous starch paste ready to be applied in stock.
- PLA-Starch mix: Since PLA is not soluble in water, PLA in acetone was mixed with the aqueous starch paste and together they formed a clear stable solution.

<table>
<thead>
<tr>
<th>AMYLOPECTIN</th>
<th>N2 CONTENT (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch A</td>
<td>0.43</td>
<td>Tate &amp; Lyle, Decatur IL 62525</td>
</tr>
<tr>
<td>Starch B</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>
### MATERIALS AND METHODS: ADDITIVE DOSAGE

<table>
<thead>
<tr>
<th>Test sheets</th>
<th>Description</th>
<th>Reinforcement method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface: PLA % OD fiber</td>
</tr>
<tr>
<td>CP</td>
<td>Control Unextracted</td>
<td>-</td>
</tr>
<tr>
<td>BP</td>
<td>Biorefinery Hot Water Extracted</td>
<td>-</td>
</tr>
<tr>
<td>BPPLA2</td>
<td>BP with 2% PLA sprayed</td>
<td>2</td>
</tr>
<tr>
<td>BPSA1</td>
<td>BP with 1% starch A in wet end</td>
<td>-</td>
</tr>
<tr>
<td>BPSB1</td>
<td>BP with 1% starch B in wet end</td>
<td>-</td>
</tr>
<tr>
<td>BPPLA0.5SA0.5</td>
<td>BP with PLA 0.5% and Starch A 0.5%</td>
<td>-</td>
</tr>
<tr>
<td>BPPLA0.5SB0.5</td>
<td>BP with PLA 0.5% and Starch B 0.5%</td>
<td>-</td>
</tr>
<tr>
<td>BPPLA0.9SA0.1</td>
<td>BP with PLA 0.9% and Starch A 0.1%</td>
<td>-</td>
</tr>
<tr>
<td>BPPLA0.9SB0.1</td>
<td>BP with PLA 0.9% and Starch B 0.1%</td>
<td>-</td>
</tr>
</tbody>
</table>
PULPING RESULTS

Kraft pulp from HW extracted chips vs. un-extracted chips

- **H-factor/10**
  - UT_K: 53.6
  - HWE_K: 45.4

- **Kappa**
  - UT_K: 13.1
  - HWE_K: 42.61

- **Digester Yield**
  - UT_K: 52.6%
  - HWE_K: 52.3%

- **Overall Yield**
  - UT_K: 52.6%
  - HWE_K: 42.6%
SHEET PROPERTIES of HWE vs. control pulp
(without any use of Additives)

\[
\begin{align*}
\text{Bulk, cm}^3/\text{g} & : 14.36, 17.41 \\
\text{Tl, Nm/g} & : 16.994, 37.68 \\
\text{Stretch, \%} \times 10 & : 3.675, 7.3 \\
\text{W_Tl, Nm/g} \times 10 & : 9.95, 12.95 \\
\text{Tear, mN/g/m} & : 2.61, 7.84
\end{align*}
\]
Figure: Effect of increasing amount of PLA in the PLA-starch B blend at the constant amount of starch B at 0.5% based on OD fiber on the bulk of HWE biorefinery pulp (BPPLA_SB0.5)
Figure: Effect of increasing amount of PLA on the Tensile index of HWE biorefinery pulp (BPPLA_SB0.5) using the PLA-starch B blend for starch B dosage at 0.5% based on OD fiber.

![Graph showing the effect of PLA on Tensile index](image-url)
Figure: Increasing amount of PLA in the PLA-starch B blend at the constant amount of starch B at 0.5% and the Tear index of HWE biorefinery pulp (BPPLA_SB0.5)
Figure: Effect of increasing amount of PLA in the PLA-starch B blend at the constant amount of starch B at 0.5% based on OD fiber on the Wet Tensile index of biorefinery pulp (BPPLA_SB0.5)
Conclusion

• Reinforcement of sheets was achieved by adding the PLA-cationic starch blend in the wet end.

-This is important as it is convenient to add PLA-starch emulsion in the wet end stock

• In addition, these experiments demonstrated that five parts of the cationic starch applied as a dry strength agent may be successfully replaced with one part of PLA with minimal loss of Tensile strength and improvement in Tear and Wet tensile strength.

• The PLA/starch combination enhances both wet and dry strength of the biorefinery pulp
Acknowledgment

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- Funding from DOE, BRI, ESPRI

Thank you from

ESF