LbL Nanocoating for Fiber Recycling
Improved Paper Recycling through Fiber Polycation/Polyanion Multilayer Nanocoating

J. Y. Zhu¹, M. Fleischmann¹, Z. Zheng², E. Lvov³, G. Grozdits³, ⁴, J. Chapman⁵ and Y. Lvov², ³

¹ USDA Forest Service, Forest Products Laboratory, Madison, WI, ² Institute of Micromanufacturing at Louisiana Tech University, Ruston, LA, ³ Nano Pulp and Paper LLC, Ruston, LA; ⁴ School of Forestry at Louisiana Tech University, Ruston, LA, ⁵ Smurfit-Stone Paper Corp. Hodge, LA

Tappi - 8th Research Forum on Recycling
Niagara Falls, ON, Canada
September 23-26, 2007
Paper Recycling is driven by economic incentives and societal pressures.

It requires modified/new fiber preparations and paper making.

Recycling in part requires used fiber rejuvenation.

But it allows creation and operation of small and specialty mills close to resources and market,

Damaged Fibers (green positive), virgin fiber (red negative), they electrostatically attract each other.

Niagara Falls, ON, Sept. 23-26, 2007
In this paper we report on the rejuvenation of fibers from recycled paper by Layer-by-Layer Self Assemblies of polyelectrolytes onto fibers to create enhanced electrostatic bonding potentials.

**Micro-Emulsion Technologies**
- $10^{-6}$ m droplets
- Spot-welding of fiber

**Layer-by-Layer Nanocoating**
- $10^{-9}$ m thick continuous coatings
- Fiber surface contact bonding

Emulsified electrolytes

Short fibers

Whole fibers

Niagara Falls, ON, Sept. 23-26, 2007
Basics of Layer-by-Layer Assembly by Alternate Adsorption of Oppositely Charged Linear Polyions and Nanoparticles

G. Decher, H. Moehwald, Y. Lvov,
M. Rubner, J. Fendler, J. Schlenoff, P. Hammond,
N. Kotov, T. Kunitake, F. Caruso, G. Sukhorukov

The LbL-assembly regimes for more than 50 compounds were established at IfM (using the “dipping automate” equipment).


Niagara Falls, ON, Sept. 23-26, 2007
Nano assemblies change cellulose fibers properties

Confocal images

Presence of nano-layers shown labeled electrolyte

Zeta (ξ) potential approximation

Fiber surface properties, as well as, mechanical & physical properties

Niagara Falls, ON, Sept. 23-26, 2007
History and Development of
The Louisiana Tech Nano Pulp and Paper Initiative

Established LbL nanocoating feasibility in clean-lab conditions

1. Used positive & negative LbL treated unbeaten bleached Kraft commercial pine pulp

2. Used unbeaten bleached Kraft commercial pine pulp with LbL treated broke and fines in clean lab conditions

3. Used machine stock with LbL treated mill broke, LbL treatment in DI water

4. Used machine stock with LbL treated mill broke, LbL treatment in mill process water

This work report on the use of 100 % recycled linerboard pulps, in a limited pilot plant study can, done at USDA-FS-FPL at Madison, WI.

To demonstrate how we move from clean lab conditions to practical paper recycling and linerboard production

Niagara Falls, ON, Sept. 23-26, 2007
Tensile strength (Tappi-T205 standard) of hand sheets made from LbL-treated (with \{PAH/PSS\},.5 electrolytes) softwood unbeaten commercial pulp. LbL nanocoating was done under “clean-lab” conditions. The commercial pulp was washed and treatments done in DI water.

100 % increase in paper tensile index

Tensile strength (Tappi-T205 standard) of hand sheets made from unbeaten softwood commercial pulp with the additions of 10% and 30% LbL-treated (with \{PAH/PSS\}$_{3.5}$ electrolytes) short fibers and fines (simulated broke). LbL nanocoating was done in “clean-lab” conditions. 50 % increase in tensile index.


Niagara Falls, ON, Sept. 23-26, 2007
Tensile strength (Tappi 205 Standard) of handsheets made from southern pine virgin machine stock and paper mill broke from Hodge Paper mill, LA. The pulps were washed in DI water, then treated with \( \{\text{PAH/PSS}\}_{3.5} \) electrolytes. Each electrolyte self-assembly was done in “clean lab” conditions (electrolyte in 0.5N NaCl DI water solution).

**LbL nanocoated papermill stock increased tensile index by 50 to 15%**

<table>
<thead>
<tr>
<th>Broken Fiber ratio (%)</th>
<th>Tensile Index (N•m/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control (0%)</td>
<td>50</td>
</tr>
<tr>
<td>10%</td>
<td>80</td>
</tr>
<tr>
<td>20%</td>
<td>70</td>
</tr>
<tr>
<td>30%</td>
<td>60</td>
</tr>
<tr>
<td>40%</td>
<td>50</td>
</tr>
</tbody>
</table>
Tensile strength (Tappi 205 Standard) of handsheets made from Southern pine virgin machine stock and paper mill broke from Hodge Paper mill, LA. The pulps were not washed before treatment and LbL nanocoated with \( \{\text{PDDA/PSS}\}_{3.5} \). LbL nanocoating was done in mill process waters (“dirty water”) with electrolyte concentration control.

Nanocoating in unwashed pulps in mill process waters “dirty water” increased tensile index by 15 %
The objectives:
Effect of washing
Effect of refining
Partial coating

Old corrugated cardboards (OCC) under close to practical paper recycling conditions were recycled with LbL treatment with \((\text{PAH/PSS})_{1.5}\) electrolyte layers.

6-inch diameter handsheets were made from using 50 % untreated and 50 % LbL treated pulp with one or three self-assembled layers.

Pulp and handsheet properties; Canadian standard freeness, sheet density, basis weight, paper thickness (caliper), stiffness, tensile index, bulk, tear index, stiffness index, and modulus, were measured or tested.

This work was done at the USDA-FS-Forest Products Laboratory, Madison, WI
Tensile index of handsheets made with refined (negative,) and with refined-LbL nanocoated (positive) recycled linerboard pulps from old container linerboards.

Niagara Falls, ON, Sept. 23-26, 2007
Effect of pulp washing between and after LbL polyelectrolyte nanocoating on tensile index handsheets made from old container linerboards.
Effect of LbL on sheet densification

- Unrefined control, uncoated
- 50% refined, uncoated
- 100% refined, uncoated
- 50% refined uncoated + 50% unrefined coated, washed
- One layer
- Three layers
- 50% refined uncoated + 50% refined coated
- One layer, unwashed
- One layer, washed
- Three layers, washed
- Three layers, unwashed
Limited Pilot Scale Experiments - Conclusion

1. Refining (beating) itself can improve paper bonding significantly as it is known.

2. LbL nanocoating with PAH/PSS polyelectrolytes of recycled linerboard pulps also improved paper strength.

3. Washing of the nanocoated pulps between and after polyelectrolyte applications has a negative effect because washing actually removes fines.

4. Multiple LbL nanolayering can improve paper strength, when using 50:50 mix of positive and negative surface potential pulps.
Are the LbL molecular layers really separated in the LbL multilayer?

Or we creating a composite layer with new “composite” properties?
Recycled fiber surfaces adsorbed different, smaller amounts of PSS electrolyte, than virgin pulp
THANK YOU

Louisiana Tech Nano Pulp and Paper Initiative in Cooperation with USDA-FS-Forest Products Laboratory, Madison, WI

Niagara Falls, ON, Sept. 23-26, 2007