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# Environmentally friendly wet-end paper reinforcement agents

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**RETHINK PAPER:**  
**Lean and Green**

# SMART, ENVIRONMENTALLY FRIENDLY PAPER

- Today's motto “more for less”

Increase in profit margin by

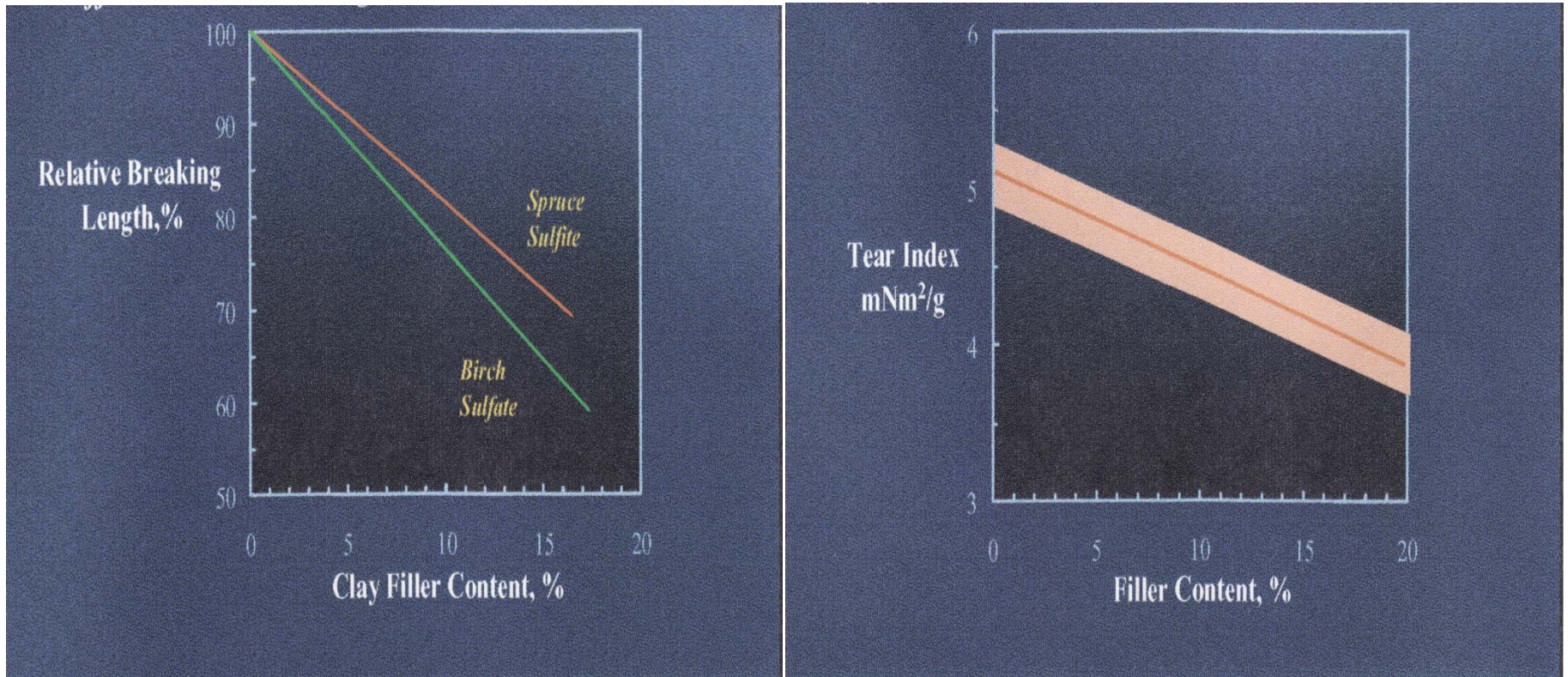
- Reduction of basis weight
  - Replacement of fiber by cheaper materials such as fillers
- 
- Industry of future needs to design its paper without compromising
    - strength
    - bulk



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## REPLACE FIBER?

- Disadvantage of adding fillers



- How to compensate for the strength loss?  
-Additives?

- Society and Government are looking for an industry :

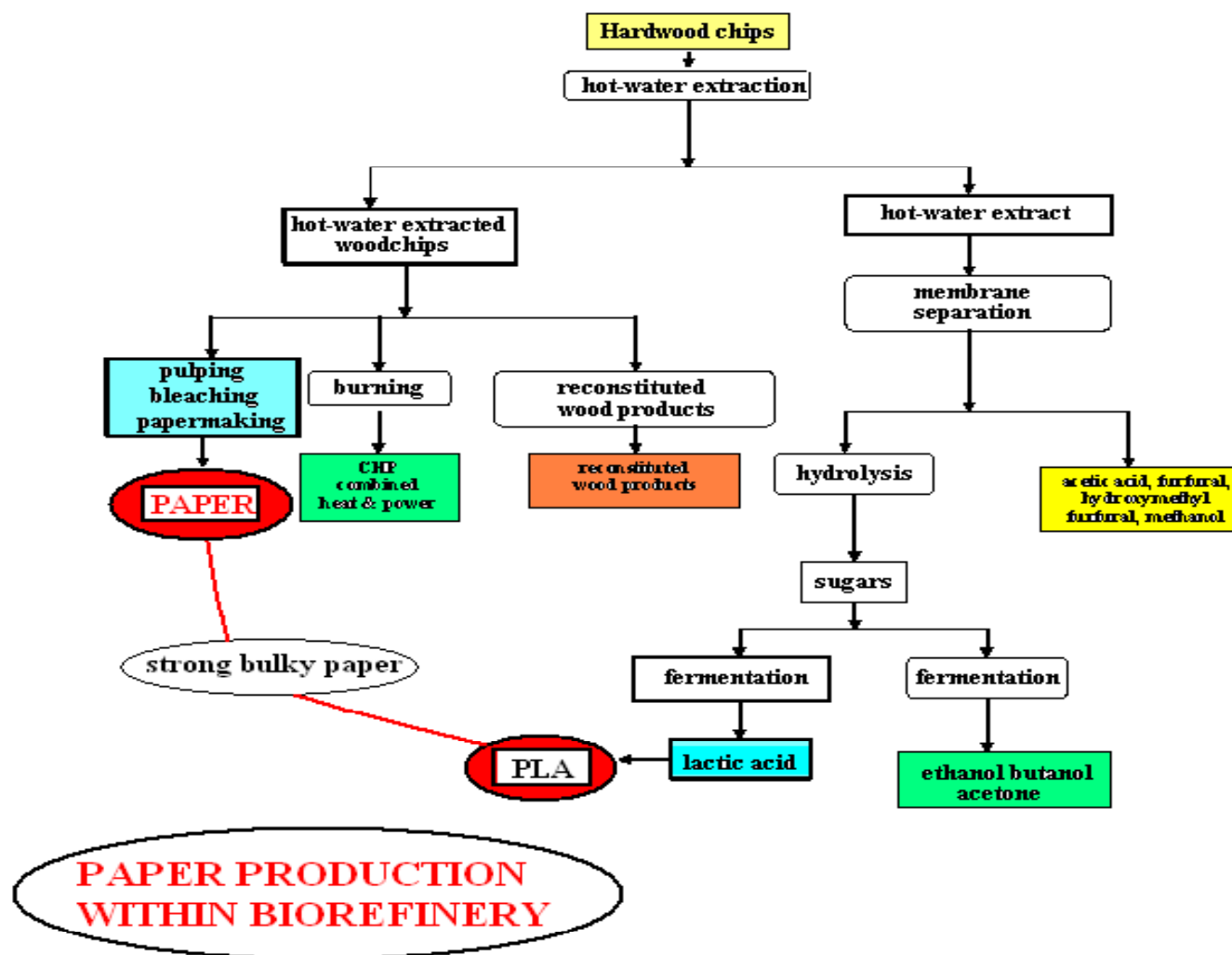
1. More sustainable
2. Based on renewables
3. Environmentally benign
4. Produces net positive energy
5. Green

Consistent with that is the concept of Biorefinery....



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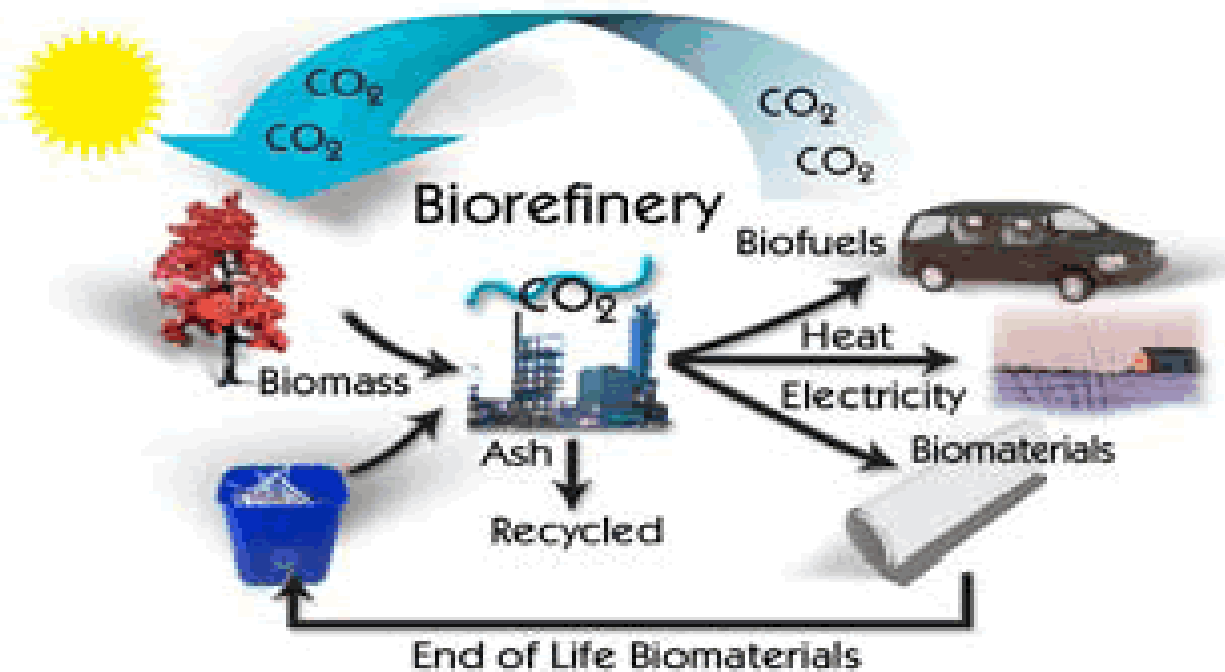
# Pulping within biorefinery: hot water extraction (HWE) of chips before pulping, ESPRI SUNY ESF process



➤ 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)

HW Extracted chips for  
pulp/paper production



# 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

Conventional Additives	Environmentally Friendly Additives
<p><b>❑PAE( Polyamide – Epichlorohydrin) resins</b></p> <ul style="list-style-type: none"> <li>•Compatible with alkaline pulps,</li> <li>•Gives wet strength</li> <li>•produce chlorine compounds</li> </ul>	<p><b>❑Starch:</b></p> <ul style="list-style-type: none"> <li>•Compatible with any pulping system</li> <li>•Gives only dry strength - hydrophillic</li> <li>•Biodegradable</li> <li>•Renewable</li> </ul>
<p><b>❑Urea-formaldehyde resins</b> <b>❑Melamine-fpormaldehyde resins</b></p> <ul style="list-style-type: none"> <li>•Used in acid conditions, in the presence of Alum</li> <li>•Gives wet strength <ul style="list-style-type: none"> <li>• Both linked to respiratory problem and poor air quality</li> </ul> </li> </ul>	<p><b>❑Polylactic Acid (polylactide):</b></p> <ul style="list-style-type: none"> <li>•Compatible with any pulp system</li> <li>•Gives wet strength</li> <li>•Helps dry strength</li> <li>•Compostable</li> <li>•Product of Renewable feedstock</li> </ul>
<p><b>❑Glyoxalated Polyacrylamide:</b></p> <ul style="list-style-type: none"> <li>•Gives dry and wet strength</li> <li>•potentially Carcinogenic in monomeric form</li> </ul>	<p><b>❑Polyhydroxy alkanoates (PHA):</b></p> <ul style="list-style-type: none"> <li>•Product of Renewable feedstock</li> <li>•Potential for dry and wet strength</li> </ul>

## 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).

[Hasan, A. Bujanovic, B. and Amidon, T.(2009): “ Strength properties of Kraft pulp produced from hot-water extracted woodchips within the **biorefinery**” **Journal of Biobased Materials and Bioenergy**, V.4. 1-7 ]



Figure 1: SEM micrograph of paper made from biorefinery pulp

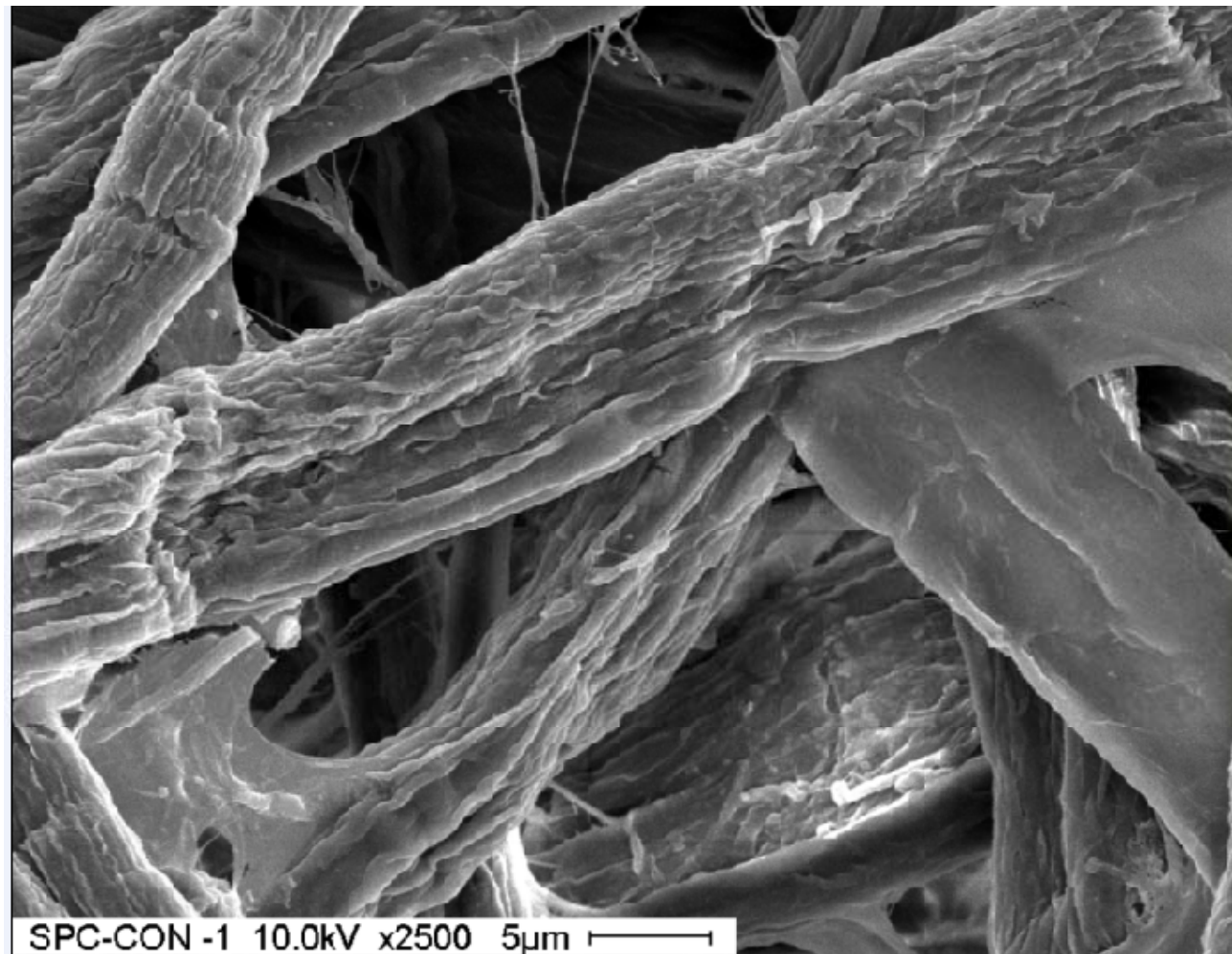
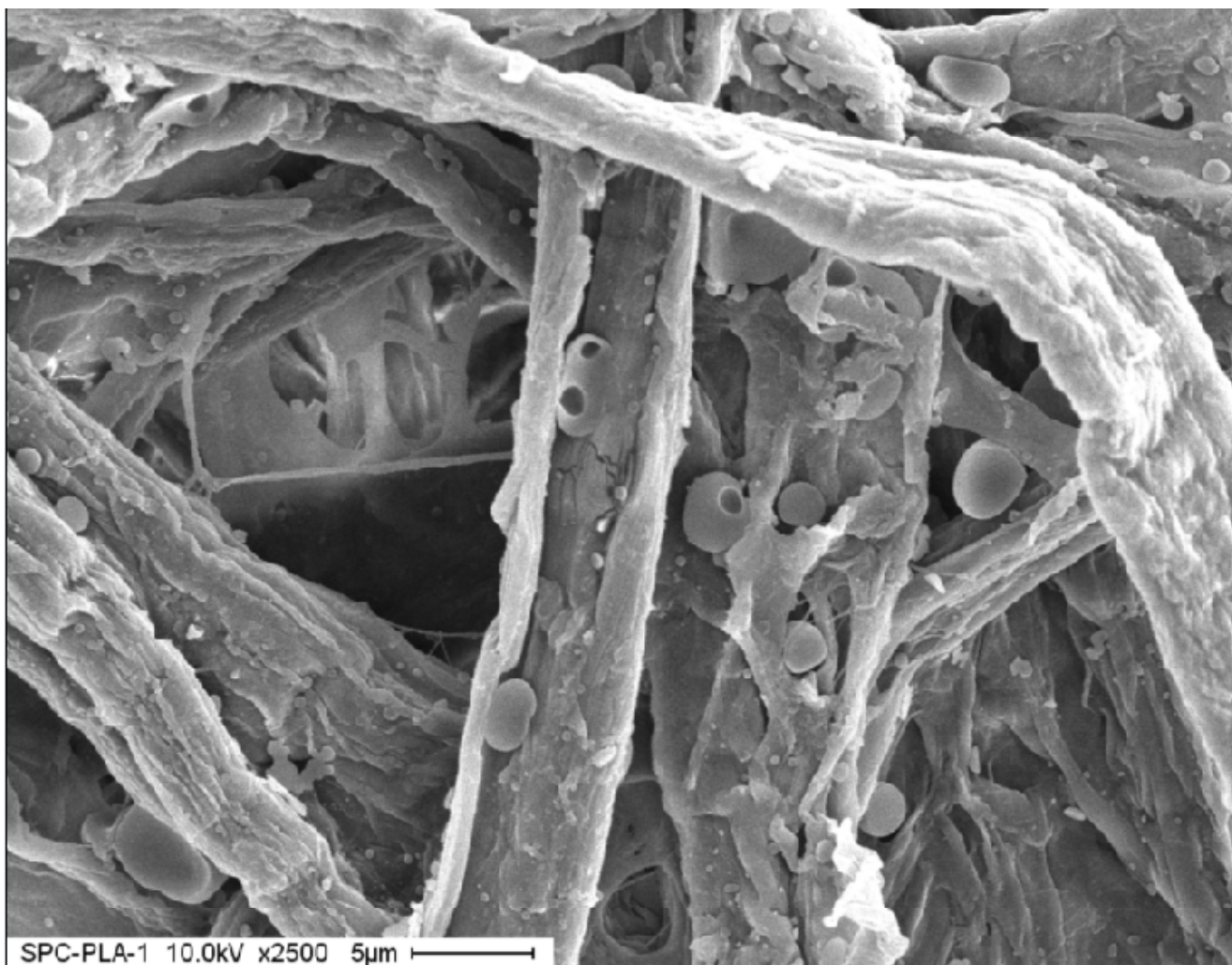


Figure 2: SEM micrograph of paper made from biorefinery pulp and treated in the surface with PLA (2% based on OD fibers)



- **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**



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# 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**

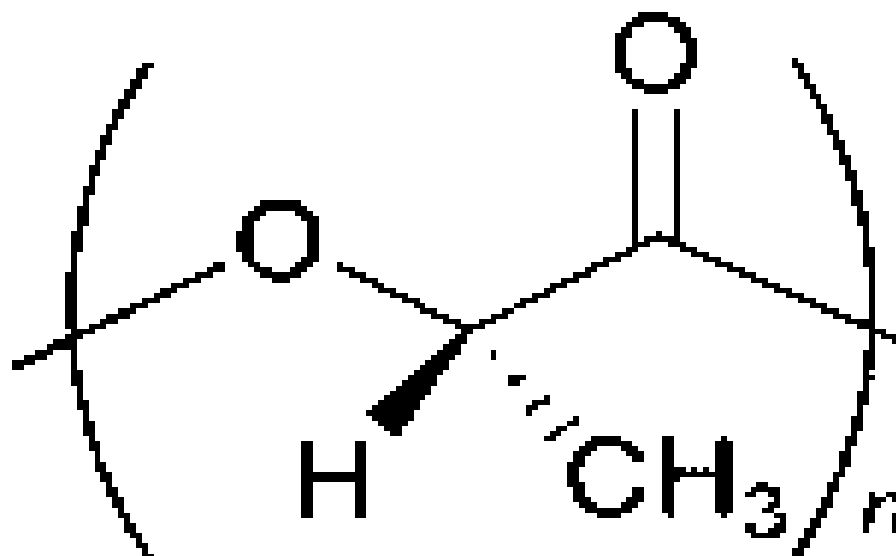
- Internal tearing resistance (Elmendorf type method, T 414 om-04)
- Tensile strength (constant rate elongation apparatus, T494 om-06)
- Wet strength



# MATERIALS AND METHODS: PLA AS A REINFORCING AGENT

- PLA poly (dl-lactic acid)

PLA	Poly (dl-lactic acid)	Supplier
MW	20K-30K	Polysciences, Inc.
Tg	54 C	Cat.#165



- 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

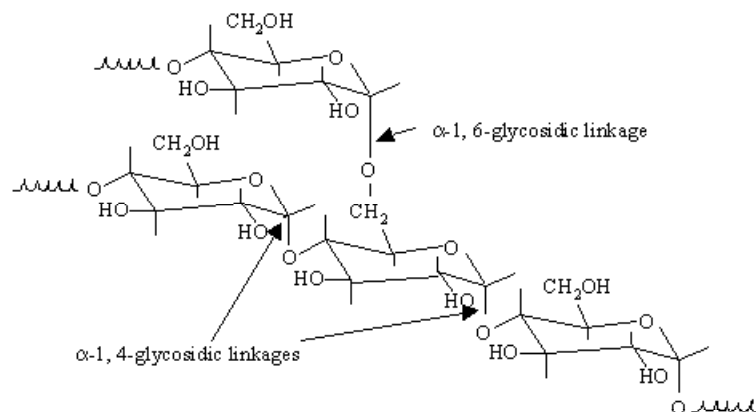
- 0.9% (max)
- 0.5% (min)



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# MATERIALS AND METHODS: Starch AS A REINFORCING AGENT



AMYLOPECTIN	N2 CONTENT (%)	Supplier
Starch A	0.43	Tate & Lyle, Decatur IL 62525
Starch B	0.3	

- Starch was first slurried by mixing dry powder with water
- cooked at 0.3% solids at 95-97°C 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.

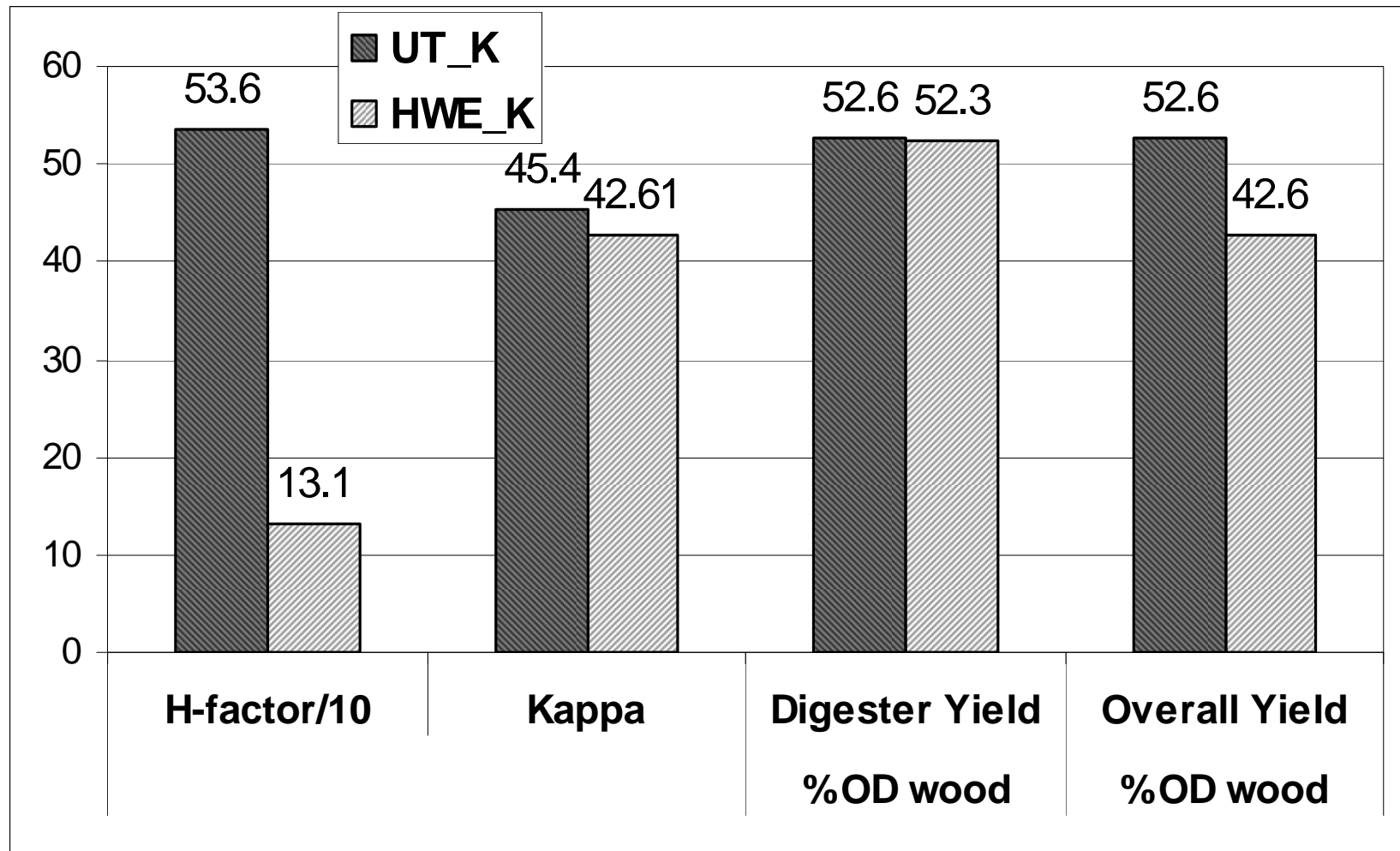
# MATERIALS AND METHODS: ADDITIVE DOSAGE

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



## PULPING RESULTS

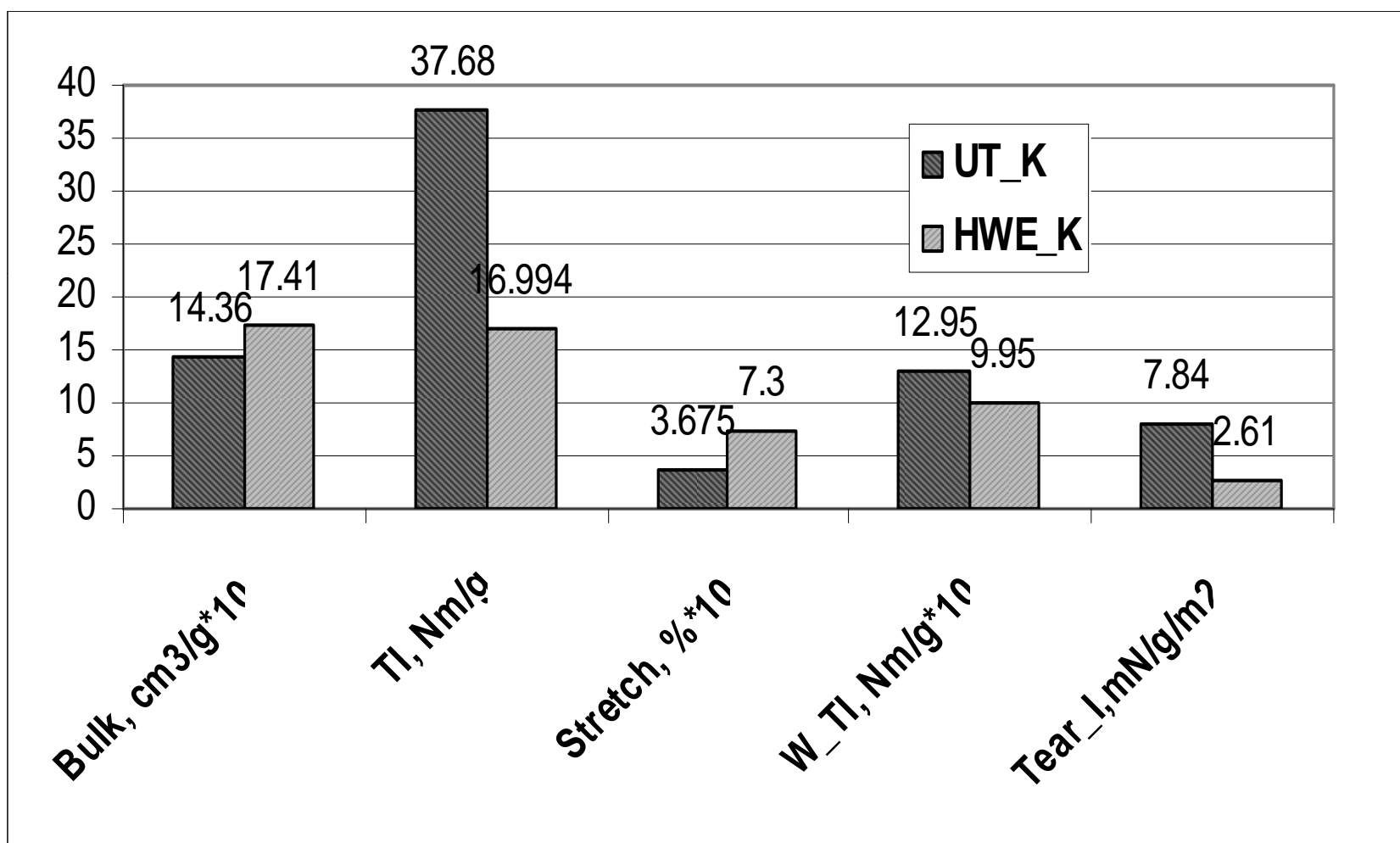
Kraft pulp from HW extracted chips vs. un-extracted chips



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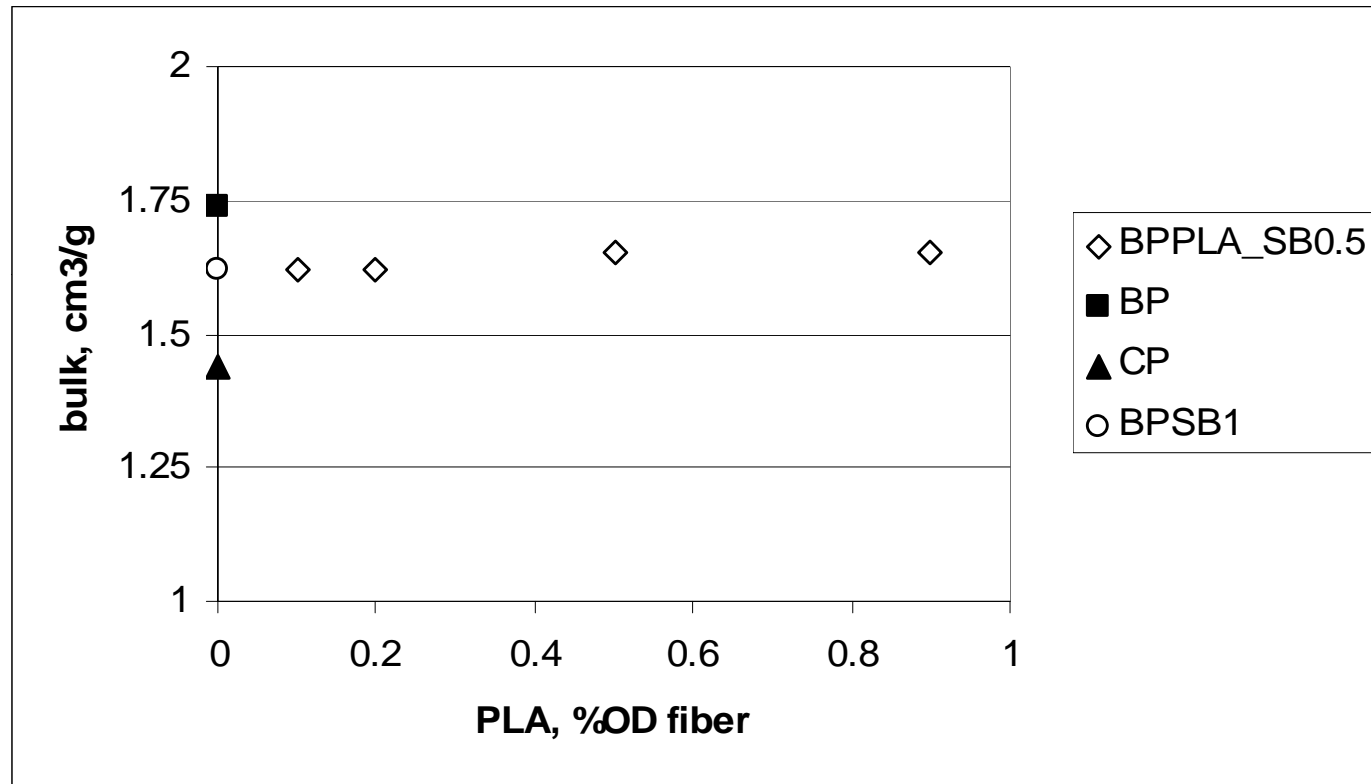
## SHEET PROPERTIES of HWE vs. control pulp ( without any use of Additives)



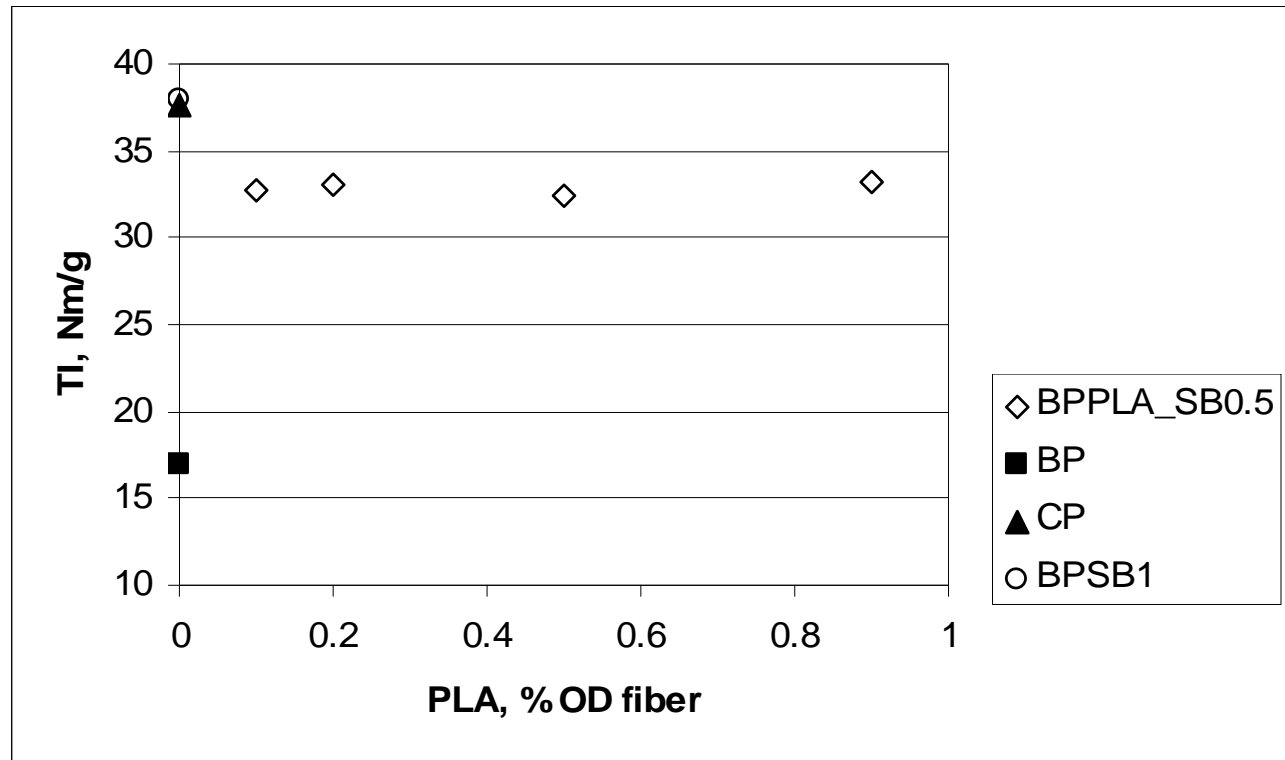
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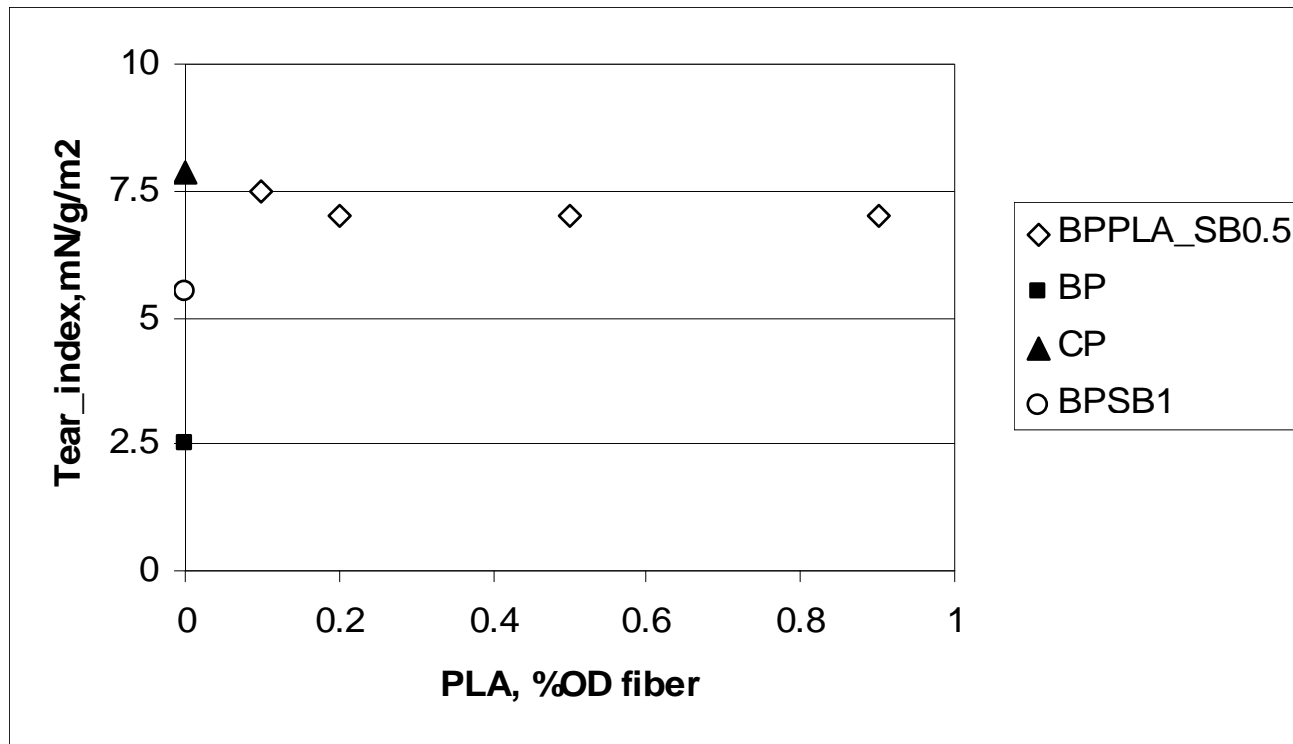
**Figure : Effect of increasing amount of PLA in the PLA-starch B blend at the constant amount of starch B at 0.5% based on OD fiber on the bulk of HWE biorefinery pulp (BPPLA\_SB0.5)**



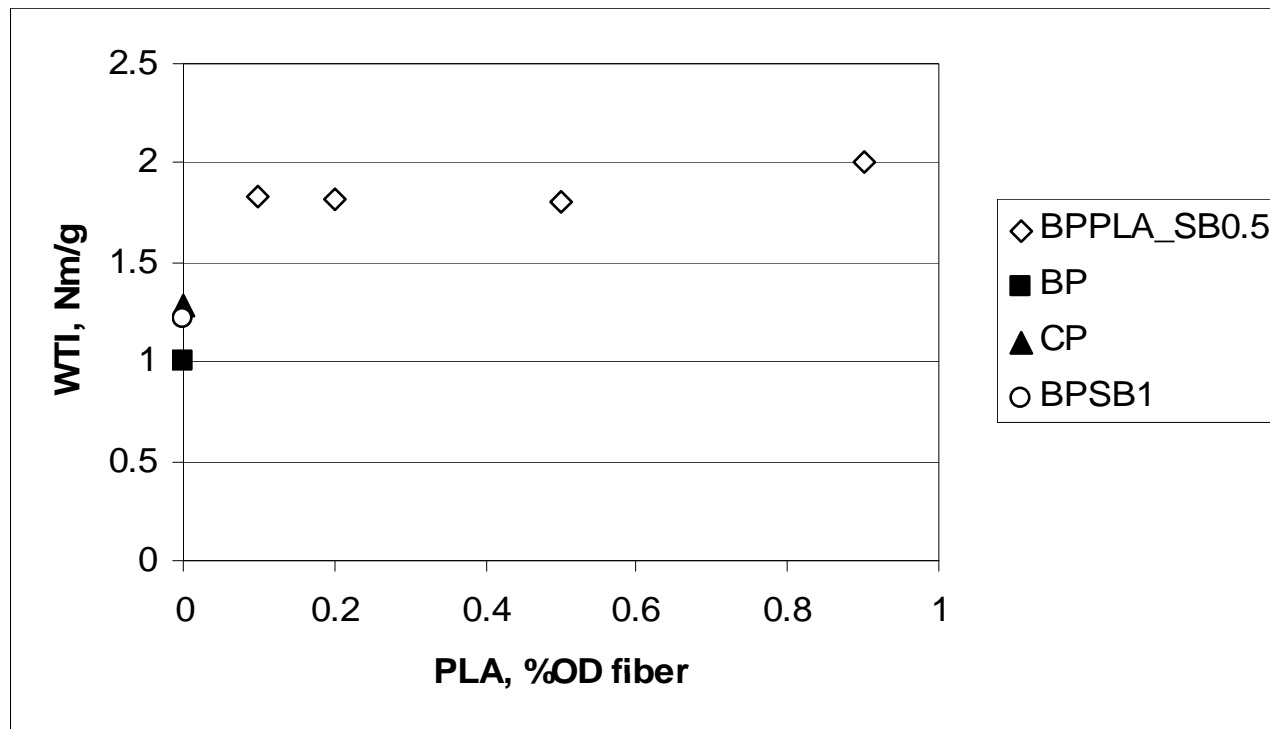
**Figure : Effect of increasing amount of PLA on the Tensile index of HWE biorefinery pulp (BPPLA\_SB0.5) using the PLA-starch B blend for starch B dosage at 0.5% based on OD fiber**



**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 (WTI) 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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Thank you from



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