Aspects of Raw Materials and Processing Conditions on the Production and Utilization of Microfibrillated Cellulose

Kelley L. Spence, Richard A. Venditti, Youssef Habibi, Orlando J. Rojas, and Joel J. Pawlak

Microfibrillated Celluloses (MFCs) are generally considered to be fibrils with diameters in the range of 10-100 nm liberated from larger plant-based cellulose fibers. MFCs have garnered much attention for the use in composites, coatings, and films because of high specific surface areas, renewability, and unique mechanical properties. Many of the recent studies of MFC generated from wood pulp have focused on fully bleached chemical pulps; however, these materials must be further modified to be incorporated in hydrophobic matrices for composite reinforcement. The production of MFCs containing hydrophobic lignin may reduce the need for surface modifications and generate MFCs with new properties for use in other applications. To investigate, wood pulps of different chemical compositions were used to produce MFCs to determine the effect of lignin on microfibril and film properties.

The energy requirement of the processing of these materials is a major drawback for industrial scale-up. Chemical pretreatments can be implemented to reduce the energy consumption, but further analysis of the processing equipment has not been preformed. This study will investigate the differences in MFC characteristics as well as the energy consumption of the three common processing methods, homogenization, microfluidization, and micro-grinding.

Pulp samples were used as received from pulp mills in the southeastern United States. These samples included bleached hardwood, bleached softwood, unbleached hardwood, two unbleached softwoods, and thermo-mechanical pulp. Pulps were subjected to a refining pretreatment with a Valley beater in order to shorten the fibers and reduce equipment plugging. The pretreated pulps were then processed with a homogenizer, a microfluidizer, or a micro-grinder. Films were generated using a casting-evaporation technique and were tested using TAPPI standard methods. Film characterization included thickness, roughness, optical properties such as opacity, brightness, and scattering coefficient, mechanical properties, and water interaction properties such as water vapor transmission rate and water adsorption. The MFC slurries were evaluated using water retention value, hard-to-remove water content, and the Congo red specific surface area method.

It was found, after homogenization, that the presence of lignin significantly increased film toughness, tensile index, and elastic modulus, contrary to physical properties of paper, Figure 1. It was also found that MFC films had similar surface roughness values to the surface upon which casting occurred. Unexpectedly, the lignin-containing films had higher water vapor transmission rates than the bleached samples, even though the initial contact angle of these materials was higher. This can be explained by the internal hydrophobic pore structures likely formed in the materials containing lignin; this structure allows for the water vapor to rapidly pass through the film.

Further, three different types of mechanical processing equipment were used to generate MFCs from the bleached and unbleached hardwood samples. Film densities were approximately 900 kg/m^3 for all samples and specific surface area of the processed materials ranged from approximately 30 to 70 m^2/g for bleached hardwood and from 70 to 200 m^2/g for unbleached hardwood. Preliminary results show that the microfluidizer resulted in significantly tougher films than both micro-grinding and homogenization and required less energy to obtain these properties, offering great promise for producing MFC materials with lower energy input, Figure 2. Analysis of the processing methods further allow for process optimization

with regards to energy consumption. Unexpectedly, increasing processing pressure and number of passes with the microfluidizer did not improve mechanical properties, suggesting that the optimum processing conditions may be less than 10,000 psi and 5 passes. The refining pretreatment was found to reduce the minimum number of homogenizer passes required to approximately 8 passes from the standard 20 passes, and processing with the grinder was found to eliminate the need for the pretreatment.

These results show that it is possible to produce MFCs containing lignin with properties similar to MFCs made from purified cellulose. The ability to produce MFCs containing lignin could potentially provide new markets for MFC such as composite reinforcements in hydrophobic matrices without surface modification while production with the microfluidizer and the micro-grinder could provide a more economically feasible production method as compared to the homogenizer.

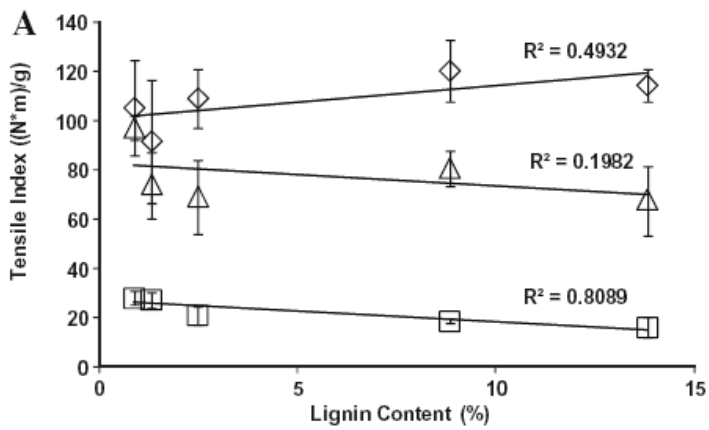

Figure 1: Mechanical properties of films with varying lignin contents for (□) original pulps, (Δ) pretreated materials, and (◊) homogenized samples (Bioresource Technology 101 (2010) 5961–5968)

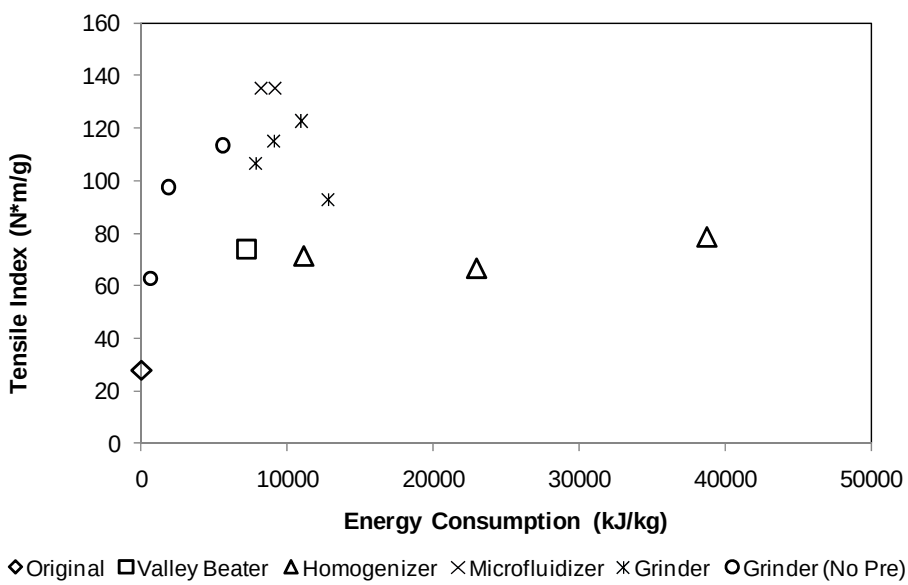

Figure 2: Mechanical properties for bleached hardwood MFC samples processed with the three types of equipment

TAPPI VTT
INTERNATIONAL CONFERENCE ON NANOTECHNOLOGY FOR THE FOREST PRODUCTS INDUSTRY
September 27-29, 2010 • Otaniemi, Espoo, Finland
Technical Advances and Applications in Nanotech Products

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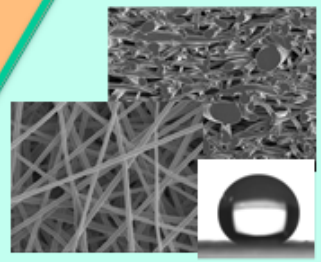
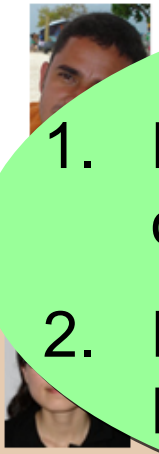
Dr. Jose M. Carbajo, Univ. Complutense Dr. Young Jun Lee, Hansol, Korea Takashi Yamaguchi, Nippon Paper Maria Vallejos, Univ Misiones, Argentina

1. Effect of chemical composition on MFC and film properties
2. Effect of Processing method on MFC and Film properties

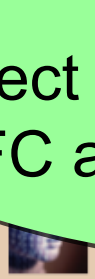


Lignocellulosics as Precursors of Biopolymer Structures
USDA-NRI

Maria Peresin (Rojas/Pawlak)



Xiaomeng Liu Rojas/Genzer (COE)



Kiran Goli Genzer (COE)/Rojas

The Generation and Stability of Organic Films on Surfaces
Nonwovens Cooperative Res. Center

Surface activity & Surface Modification

Lignin and cellulose composites

Interfaces Group
.edu/~ojrojas

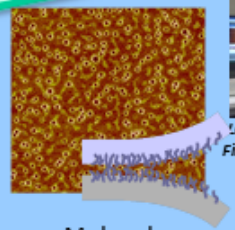
Thin films & soil removal

Protein adsorption & polysaccharide suprastructures

Bioactive surfaces

Cellu mo-structu & stimuli-resp nsive materia

Mir Quddus (Pasquinelli (COT)/Rojas)



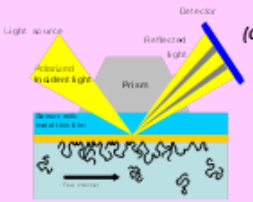
Laura Nyfors, Aalto Finland, Spring 2010 (Rojas)

Molecular assembly , ultra thin films & adhesion
National Textile Center, Whirpool, Academy of Finalnd

Bioactive surfaces and click chemistry
National Center for Food Protection and Defense, TEKES

Dr. Ilari Filpponen, Aalto (Rojas)

Nafisa Islam (Carbonell/Rojas)



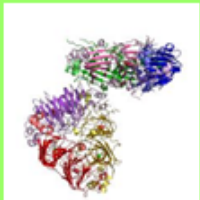
Justin Zoppe (Rojas/Venditti)

Kelley Spence (Venditti/Rojas)

Carlos Salas (Rojas/Lucia)

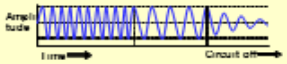
Julio Arboleda (Rojas/Saloni)

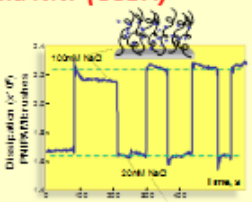
Sugar Surfactants
USDA



Surface modification with proteins and polysaccharides assemblies
United Soy Board and USDA

Cellulose nanocrystals &nanocellulo
Hofmann Fellowship and NNF (USDA)

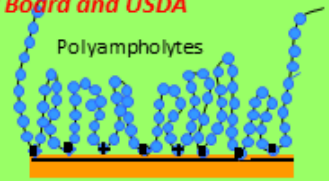




Polymer brushes (ATRP, TEMPO)
NNF (USDA)

Abdelrahman Abdelgawad (Hudson/Rojas)

Polyampholytes



Luis G.Castillo& Belkis Sulbaran, Univ. Guadalajara & SCA Catalina Alvarez, UPB Colombia Dr. Hongyi Liu Prof. Niangui Wang, Hubei University Raquel Martin, Univ. Complutense Jordi Garcia, UPC, Barcelona

Where do plastic bottles go??

- Americans throw out 2.5 million plastic bottles **EVERY HOUR**
- Americans make enough plastic wrap **ANNUALLY** to shrink-wrap the state of Texas (696,241 km^2)
- **ANNUAL** world consumption of plastic is almost 100 million tons

http://www.cleanair.org/Waste/wasteFacts.html
http://www.wasteonline.org.uk/resources/InformationSheets/Plastics.htm

www.greatergoods.com

- Petroleum

  - Cheap
  - Widely produced
  - Non-renewable
  - Lifespan of 100 years in a landfill
  - Variable market price

- Cellulosic

  - Renewable
  - Tunable properties
  - Compostable
  - Hydrophilic & dispersion in non-polar media
  - **Energy consumption**
  - Production costs
  - Production scalability
  - $

Overall Goal

- Develop plastic alternatives using cellulose from wood pulps
  - Minimize waste in landfills
  - Reduce dependence on petroleum

http://www.cleanair.org/Waste/wasteFacts.html
http://www.ecofriendlymag.com/general-green-news/urban-farmer-cited-in-la-for-illegal-composting/

1. EFFECT OF CHEMICAL COMPOSITION ON MFC AND FILM PROPERTIES

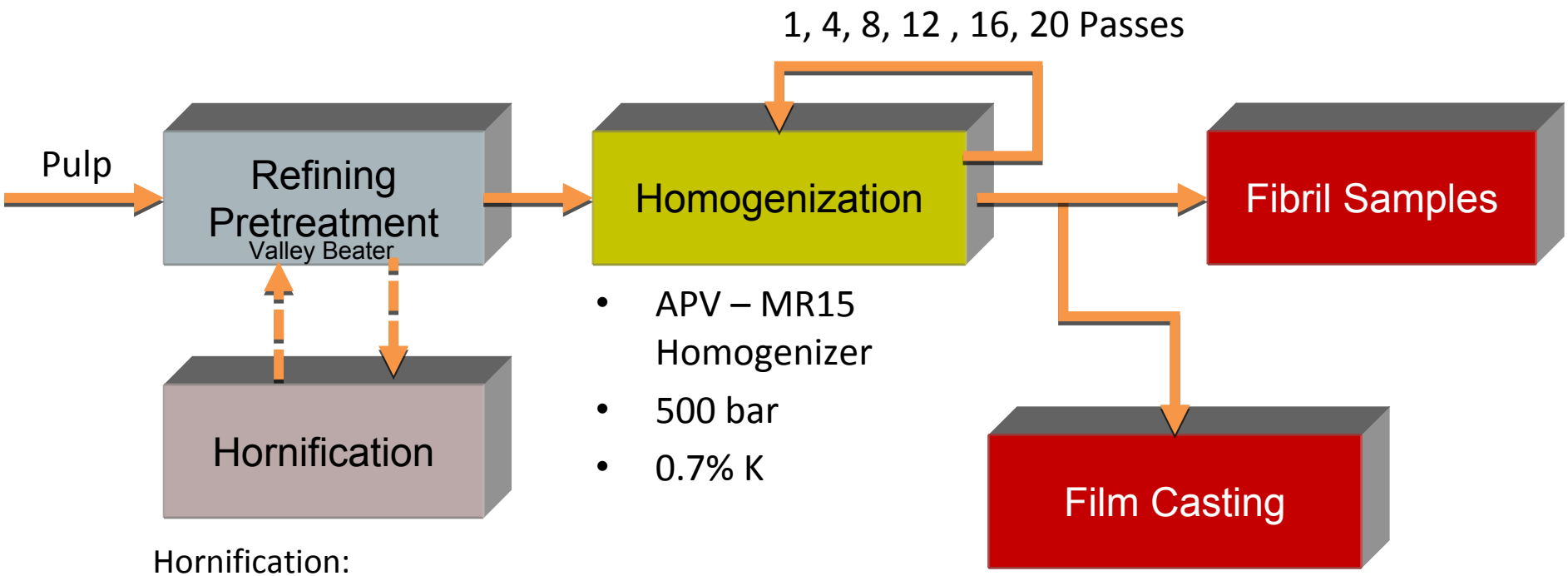
Spence et al., *The effect of chemical composition on microfibrillar cellulose films from wood pulps: processing and physical properties*. **Bioresource Technology**, 101, 5961 (2010)

Spence et al. *The effect of chemical composition on microfibrillar cellulose films from wood pulps: water interactions and physical properties for packaging applications*, **Cellulose**, 17, 835 (2010)

Pulps obtained from local pulp mills

Pulp Type	Extractives (%)	Hemicellulose(%)	Cellulose (%)	Total Lignin (%)
BSW	0.0	20.0	79.2	0.8
BHW	0.5	20.3	78.0	1.3
UBHW	0.3	19.3	78.0	2.4
UBSWloK	0.2	22.0	69.0	8.8
UBSWhiK	0.8	20.1	65.2	13.8
TMP	1.9	29.2	37.7	31.2

MFC Production



- APV – MR15 Homogenizer
- 500 bar
- 0.7% K

Hornification:

- Refined to ~ 300 CSF
- Dried completely at 105 °C
- Dispersed with TAPPI disintegrator
- Refined to total refining time

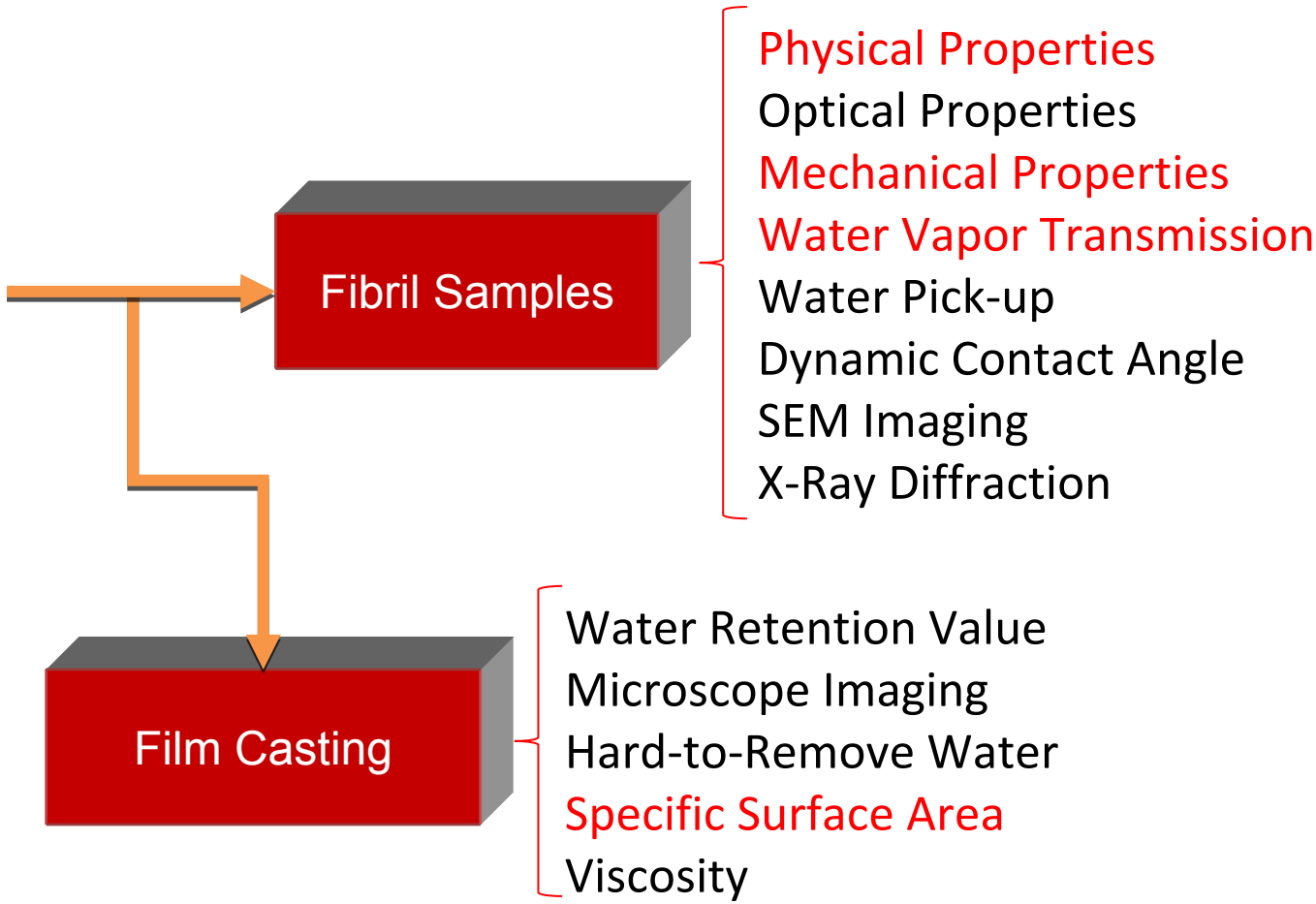
Chemical pulps:

- Cast at 1% K
- Dried at 25°C, 50% RH

TMP:

- Cast at 1%K in Teflon dish
- Dried at 50 °C

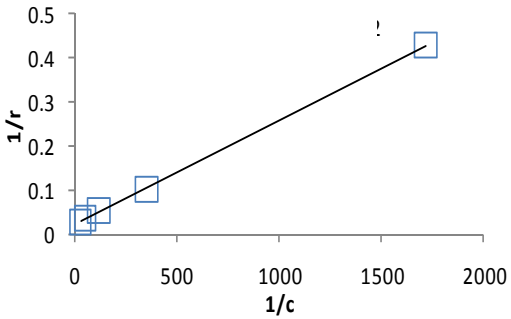
MFC Production (Cont'd)

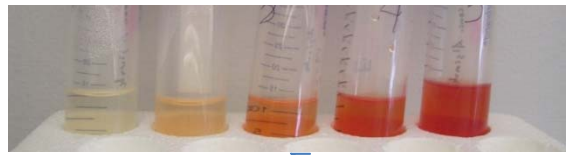


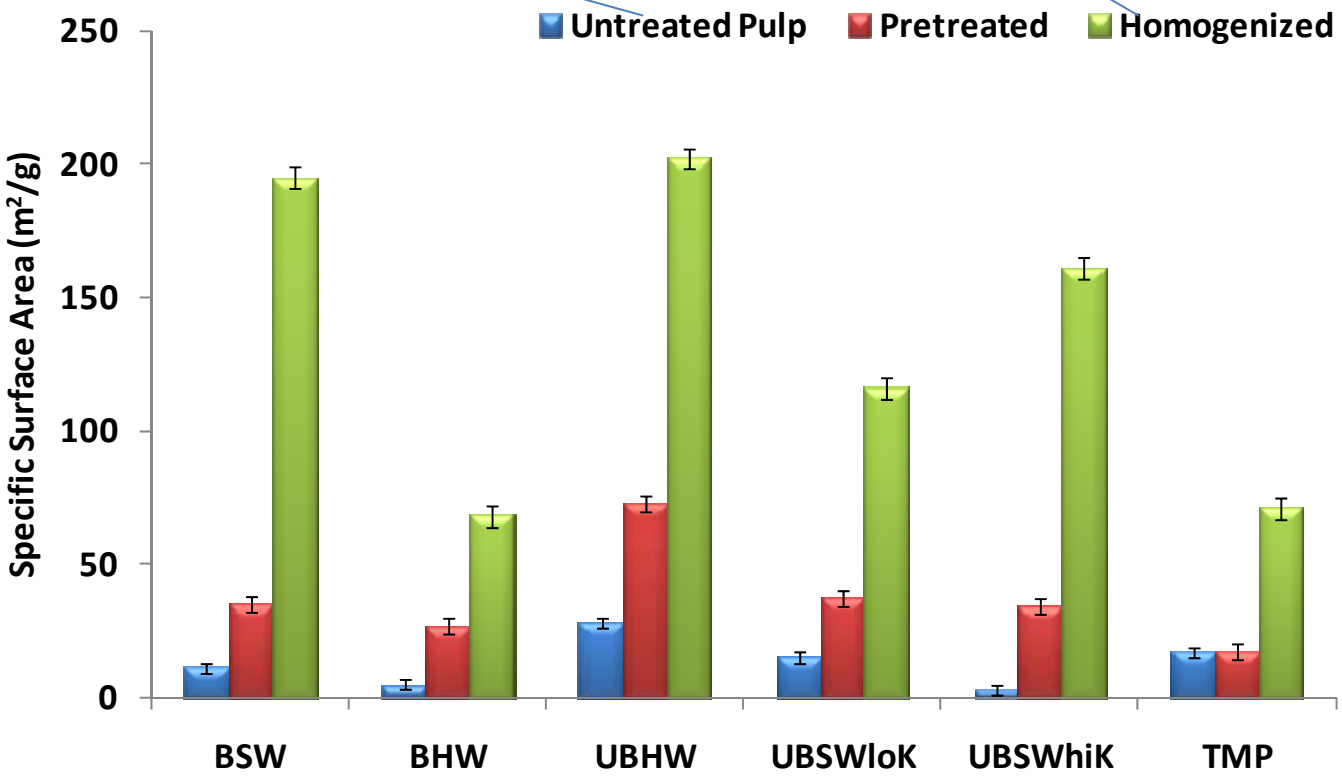
Specific Surface Area

Direct Dye 28 (Congo Red)

- Monolayer adsorption
- Langmuir Isotherm

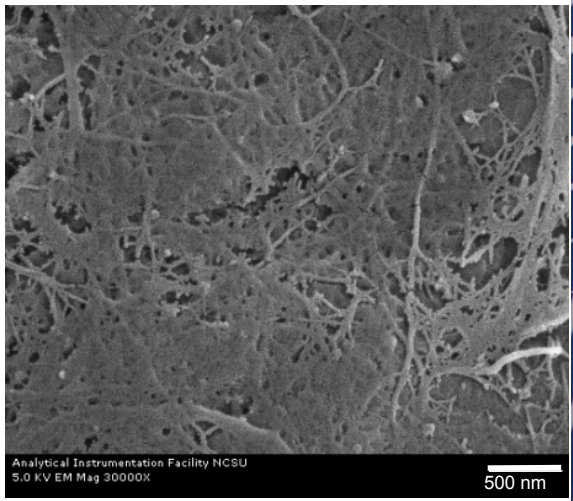


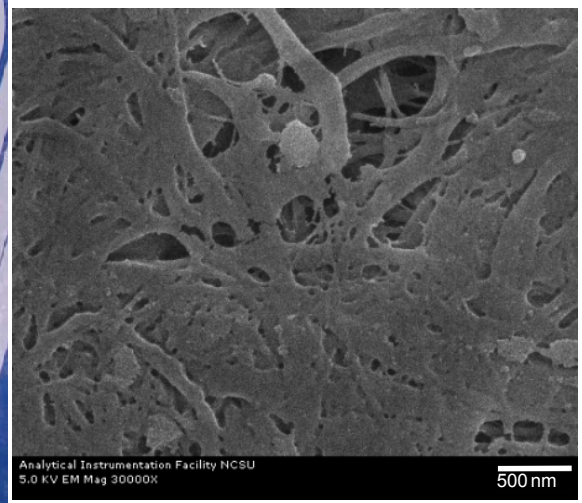




Film Optical Properties

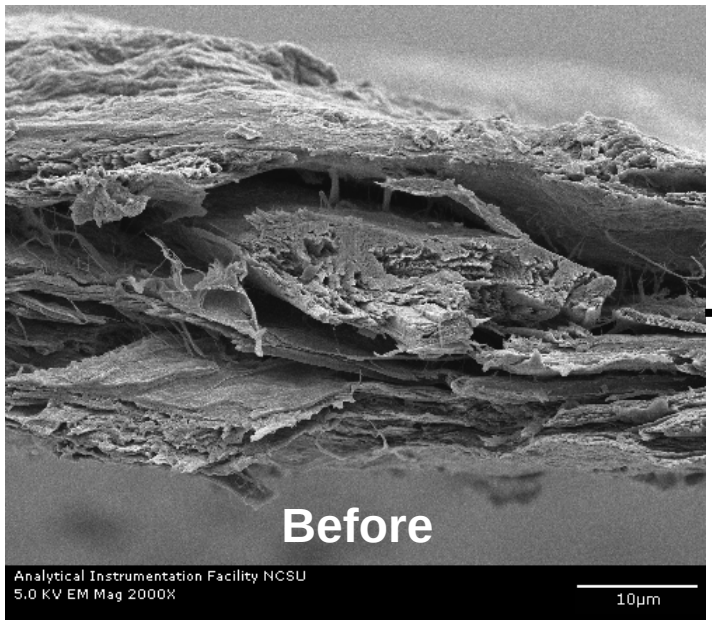
UBSWloK BSW





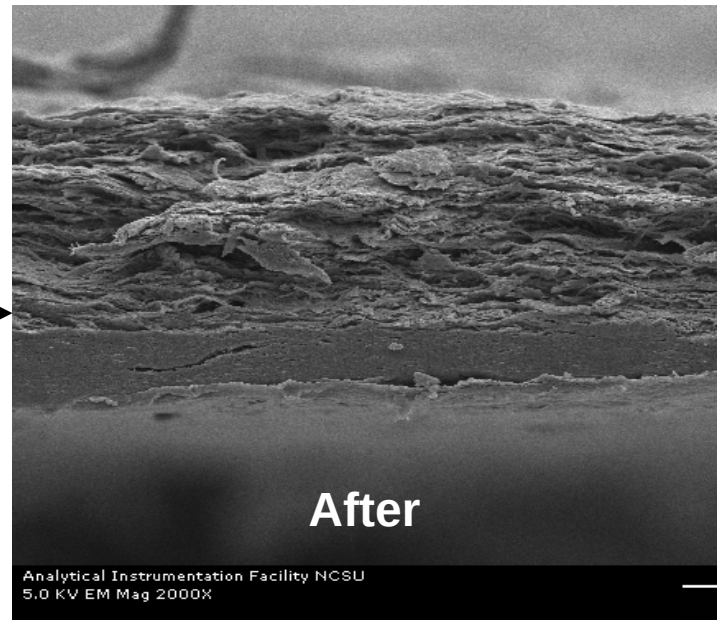
UBSWhiK Hornified BSW

Film Density



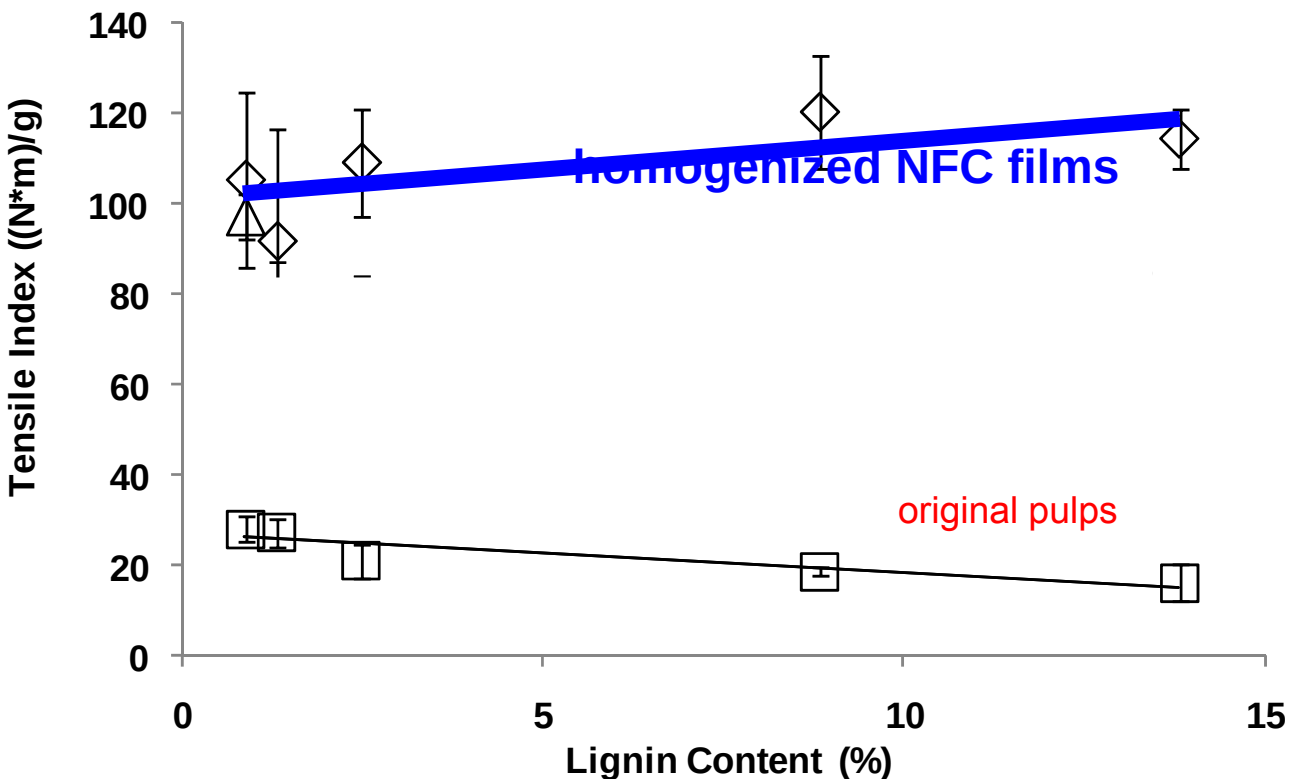
Homogenization

UBSWloK



	BSW	BHW	UBHW	UBSWloK	UBSWhiK	TMP
Original	210 ± 12	273 ± 14	228 ± 10	165 ± 8	142 ± 7	134 ± 15
Pretreated	637 ± 75	697 ± 87	717 ± 87	622 ± 48	465 ± 26	455 ± 16
Homogenized	860 ± 74	903 ± 44	972 ± 36	784 ± 58	792 ± 32	514 ± 25

Mechanical Properties & Lignin Content



Bioresource Technol, 101, 596 (2010)
Cellulose, 17, 835 (2010)

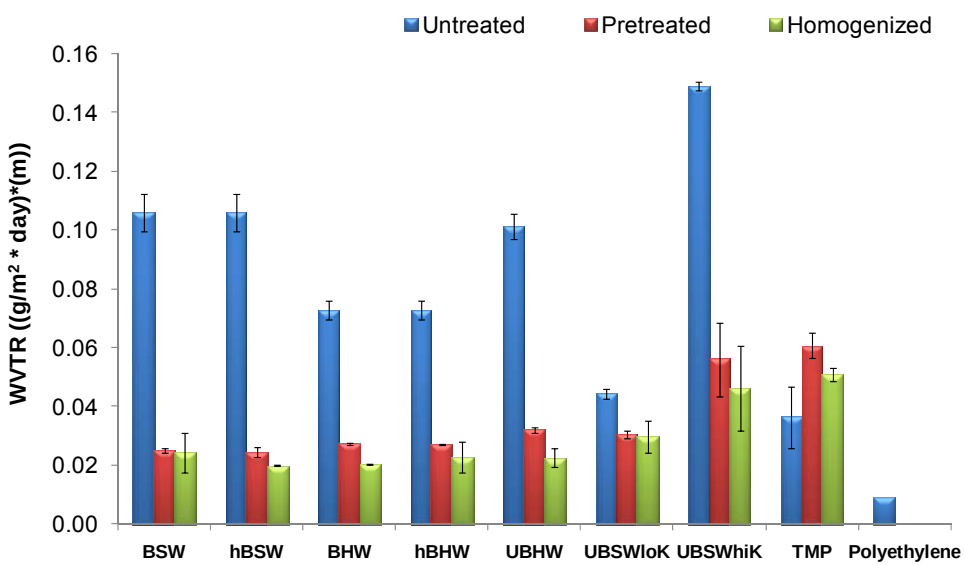
Comparison to Other Polymers

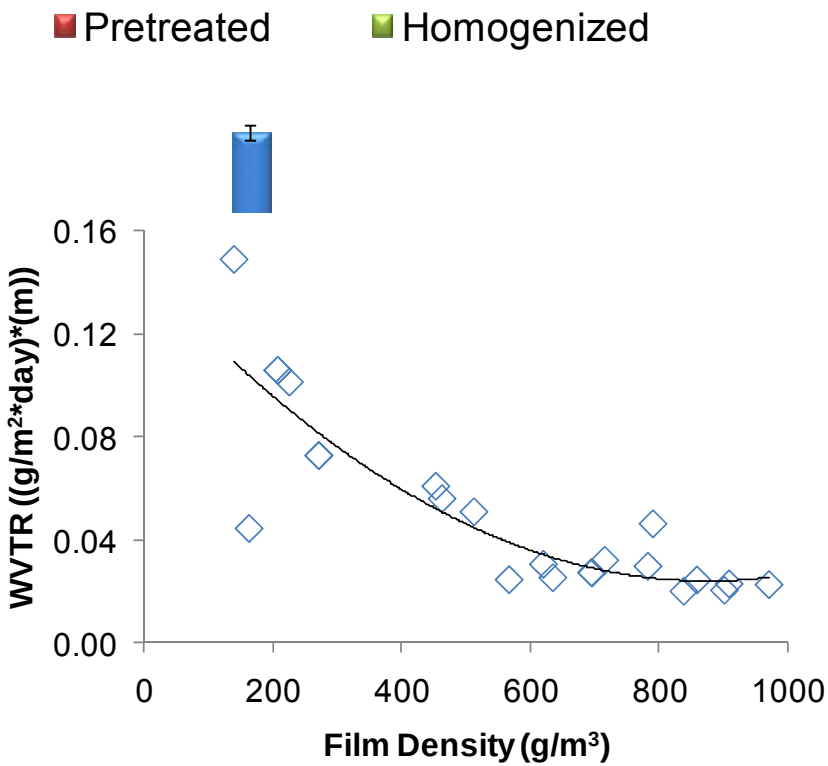
Material	Tensile strength (MPa)
Regenerated cellulose film	170.3[a]
Regenerated cellulose/MCC composite film	215.1–242.8[a]
Cellophane	50–120[b]
30 g/m^2 MFC films, prepared by free drying	136[c]
Original pulp handsheets	2.2–5.9
MFC films	82.2–90.3
Nylon 6,6	75.9[d]
Low density polyethylene	8.3–31.4[d]
High density polyethylene	22.1–31.0[d]

[a] Gindl and Keckes (2005).
[b] Mark et al. (1968).
[c] Syverud and Stenius (2009).
[d] Callister (2003).

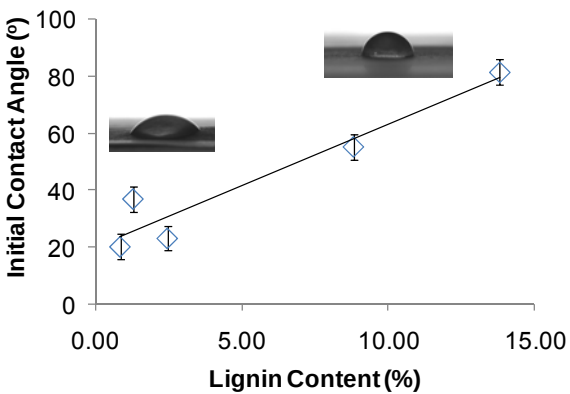
Bioresource Technology. 101 (2010) 5961-5968.

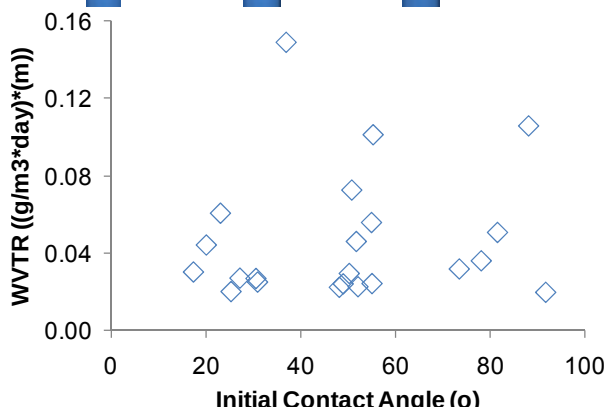
Water Vapor Transmission Rate (WVTR)





Did not correlate to contact angle





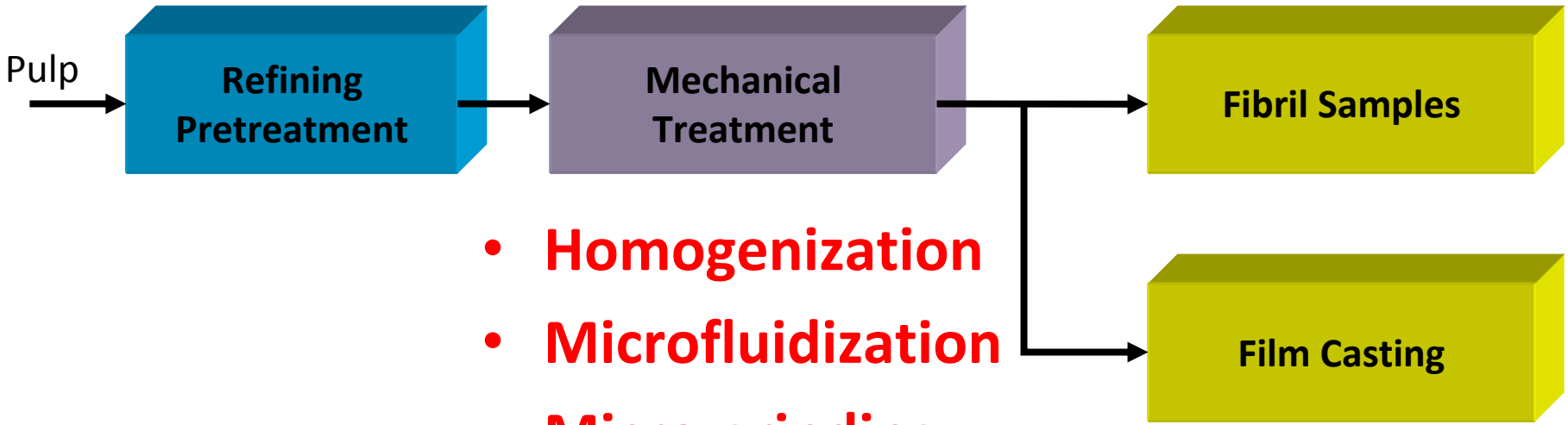
Correlated strongly to film density

2. EFFECT OF PROCESSING METHOD ON MFC AND FILM PROPERTIES

Spence et al., **Applied Physics**, Submitted

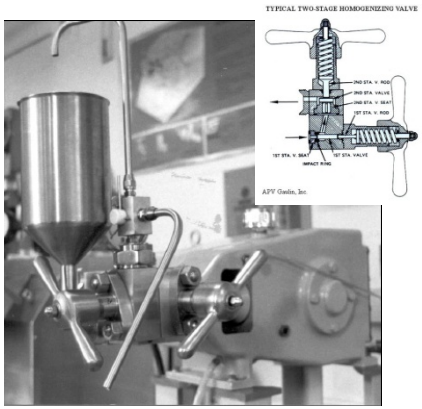
Pulp Type	Cellulose (%)	Hemicellulose (%)	Extractives (%)	Total Lignin (%)
Bleached Hardwood	78.0	20.3	0.5	1.3
Unbleached Hardwood	78.0	19.3	0.3	2.4

MFC Production



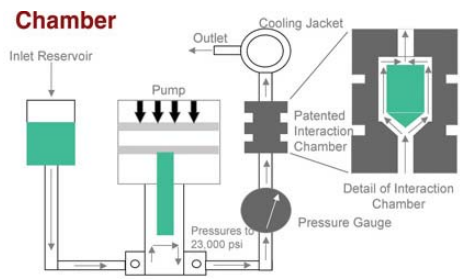
- **Homogenization**
- **Microfluidization**
- **Micro-grinding**

- Cast at ~1% K
- Dried at 23°C and 50% RH
- 30g/m²



Homogenization

Manton-Gaulin15MR
0.7% K, 550 bar
3940 kJ/kg (per pass)
Scale-ability
Continuous operation
Energy intensive
Clogging



Microfluidization

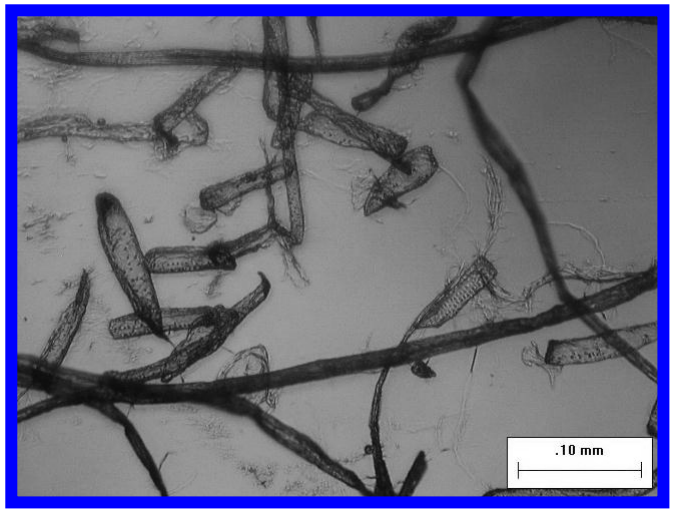
Microfluidics, Inc
0.7% K,10, 20, 30 kpsi
200, 390, 630 kJ/kg (per pass)
Operates by rapid pressure drop
No moving parts
Changeable chambers
Continuous operation
Energy intensive
Clogging

Grinding

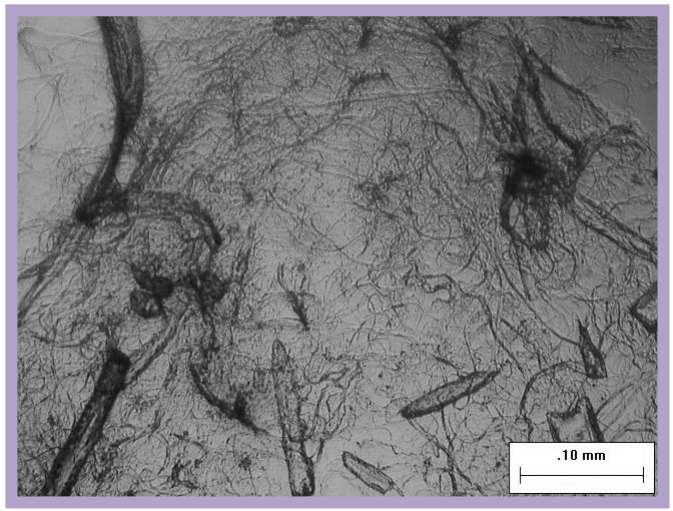
Masuko Super Masscolloider
0.7% K, 25 Hz
620 kJ/kg (per pass)
Operates by friction between disks
No clogging
Batch operation
Energy intensive

http://www.emt-india.net/process/dairy/img/homogenizer.gif
www.drugdeliverytech.com/Media/PublicationsArticle/001077.jpg

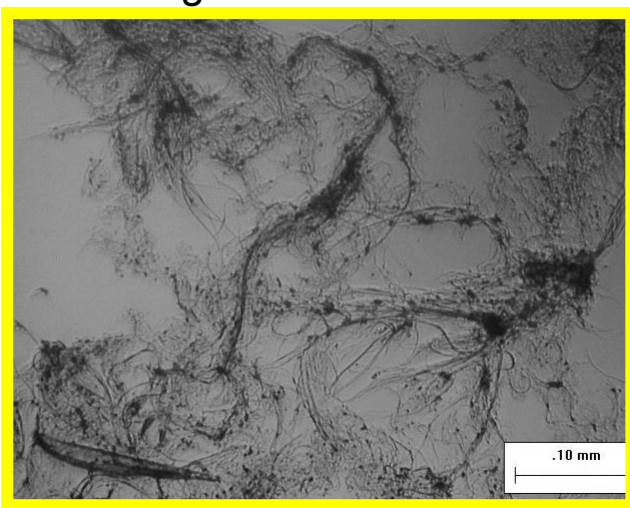
BHW Original Pulp



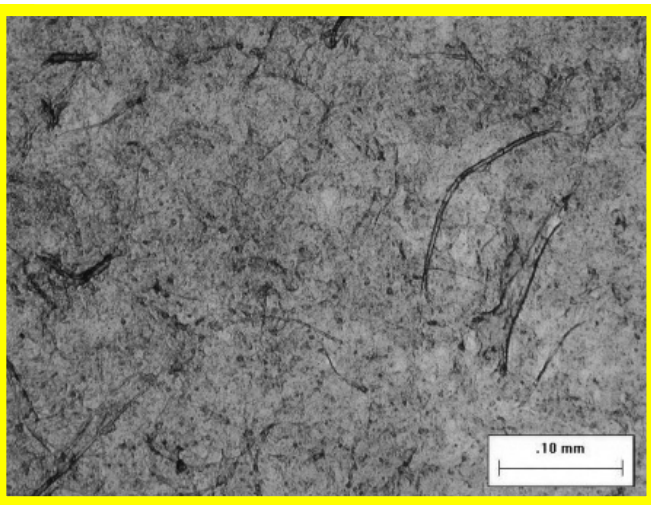
Pretreated (Refined)



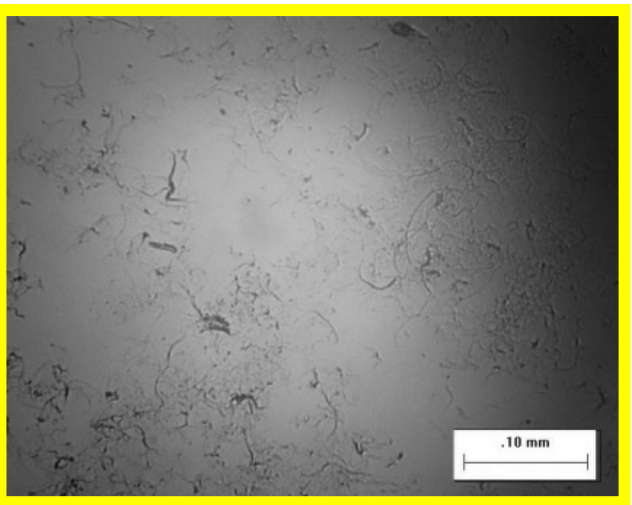
Homogenizer – 20 Passes



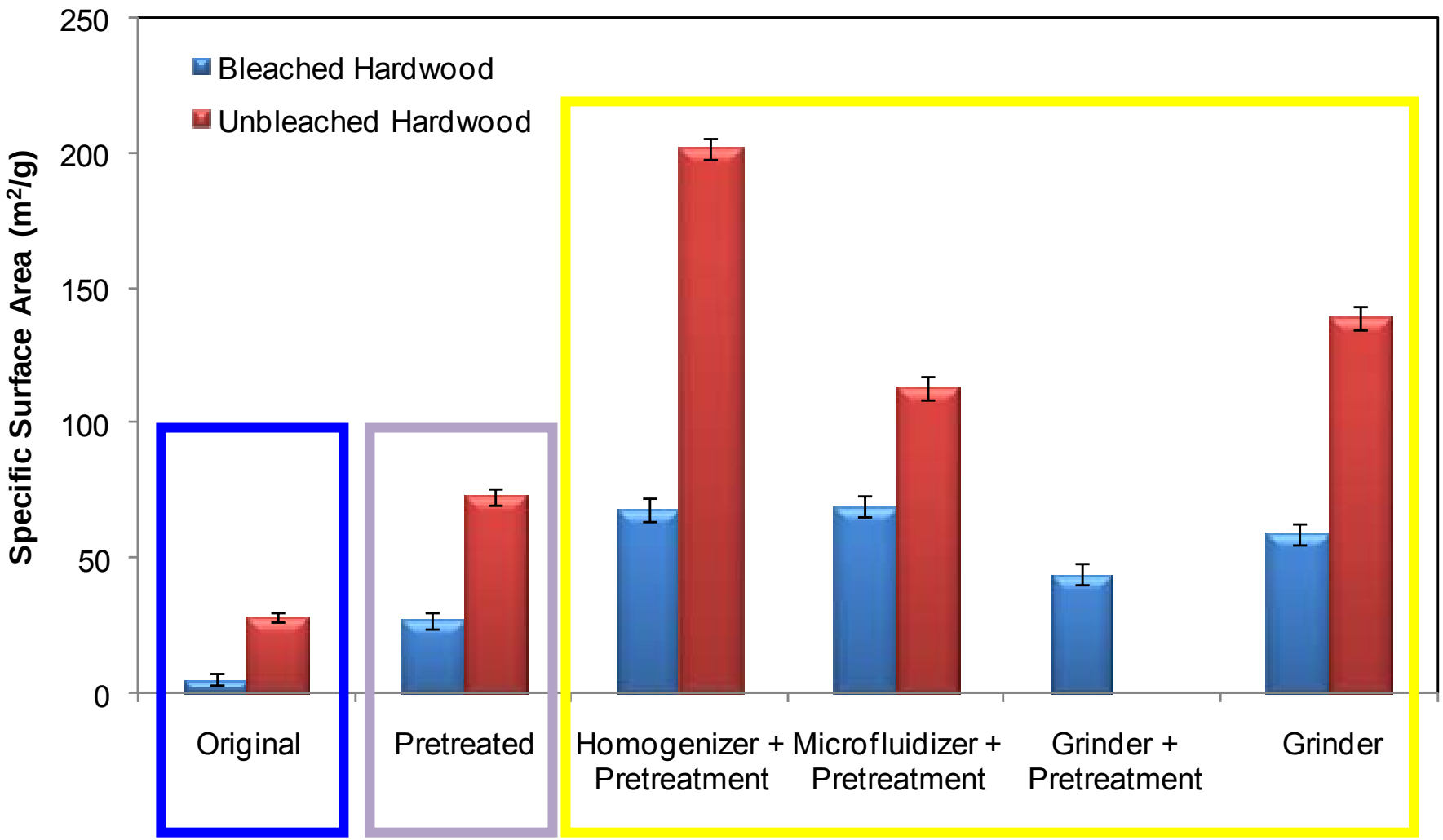
Microfluidizer – 5 Passes



Grinder – 9 Passes



Specific Surface Area



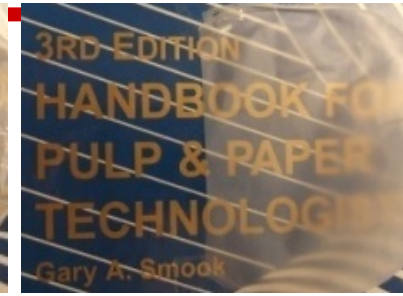
Film Optical Properties

BHW Original

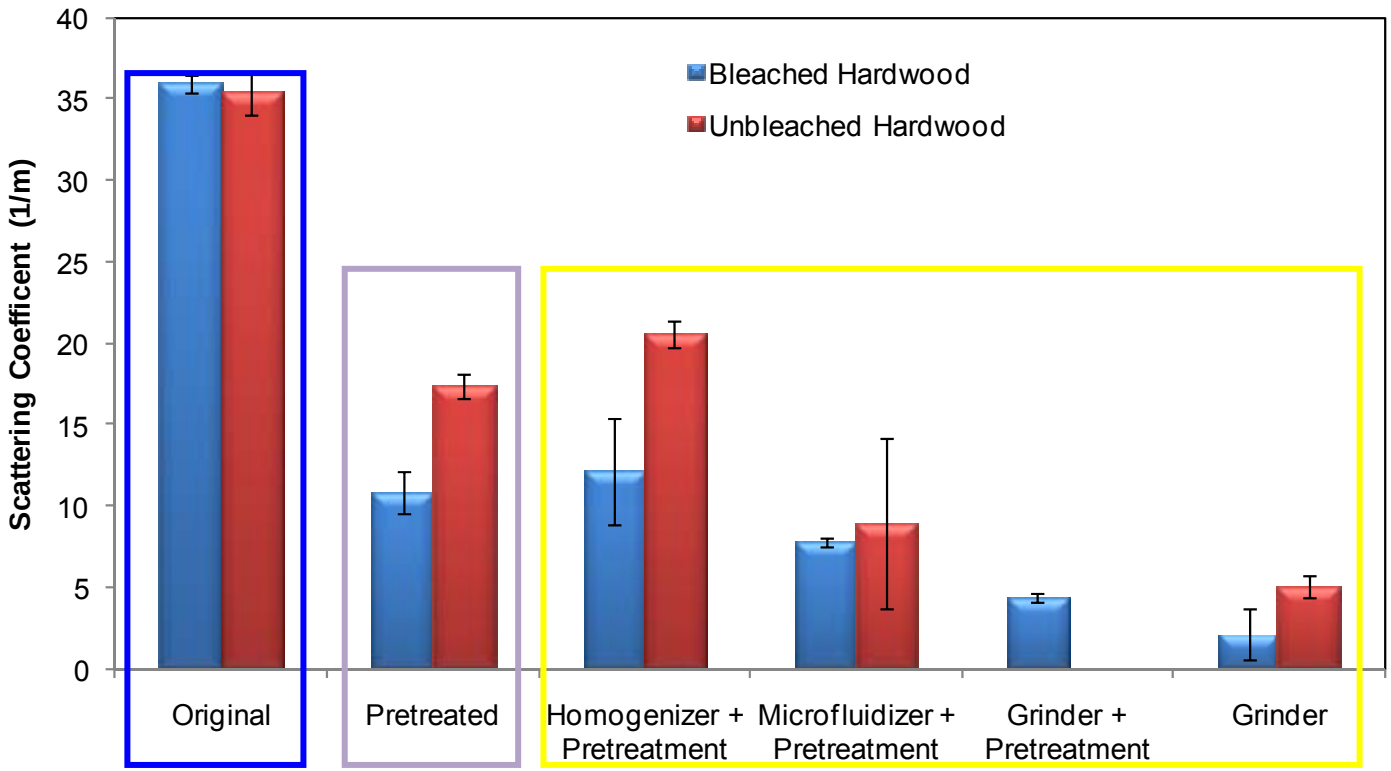
BHW Pretreated

BHW Homogenizer + Pretreatment

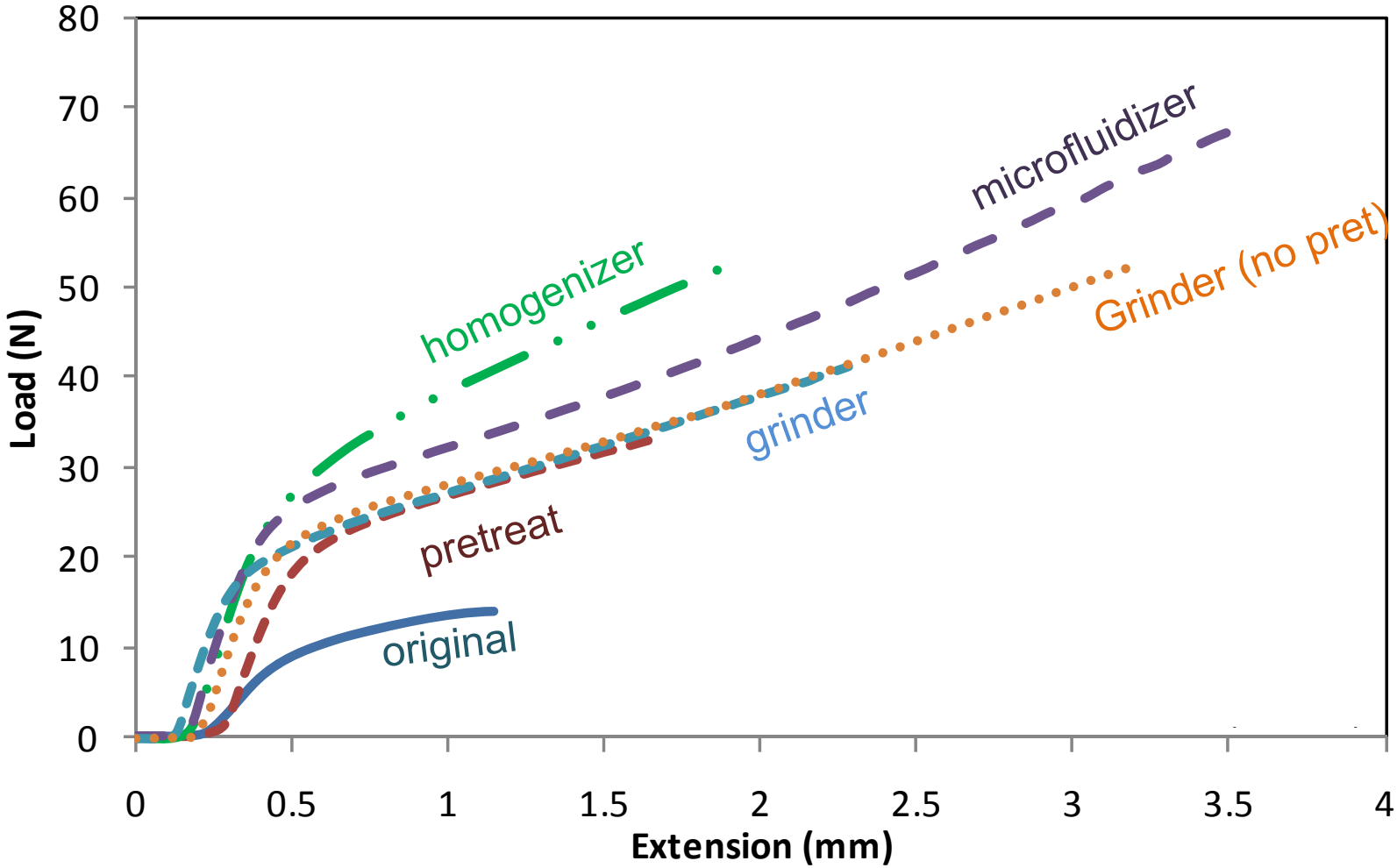
BHW Grinder + Pretreatment



BHW Grinder

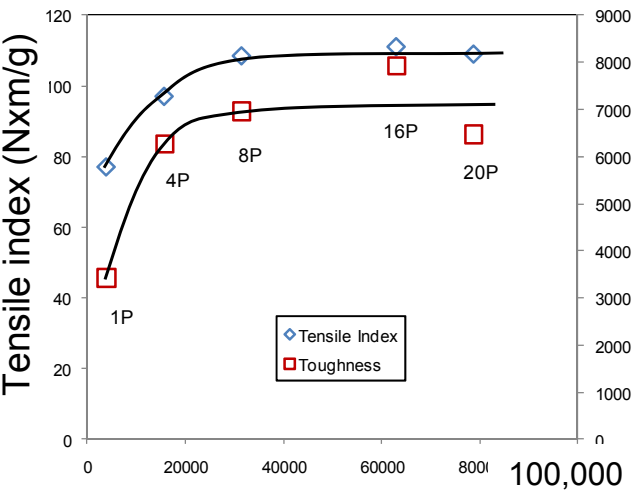


Film Mechanical Properties

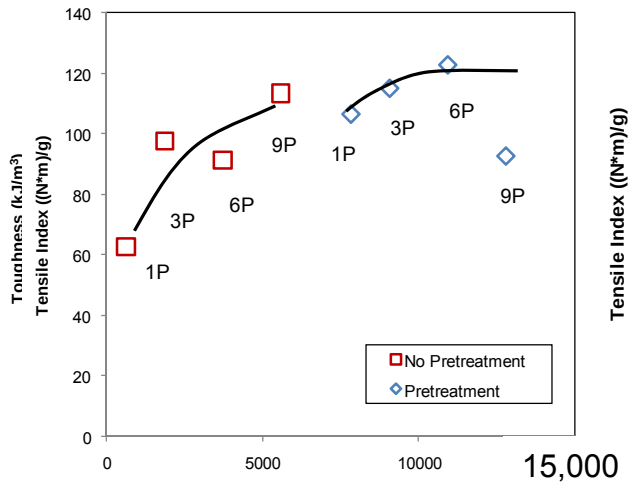


Energy Consumption

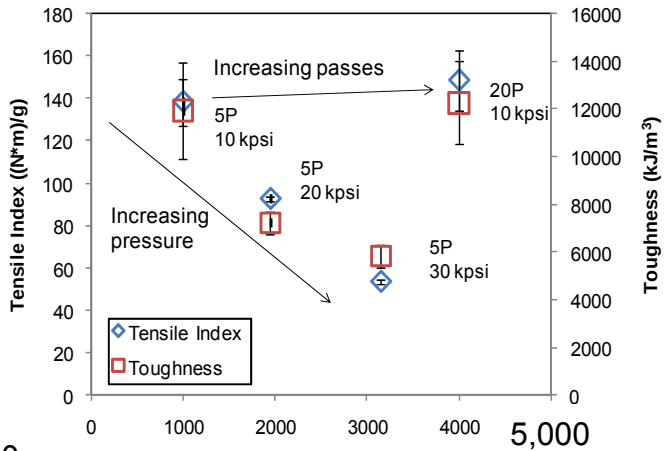
Homogenizer



Grinder



Microfluidizer



Energy consumption (kJ/Kg)

"Rough" Economics

Material	Process	Energy Cost per Ton	Cost per Ton
Bleached Hardwood (BHW)	Homogenizer 8 Pass + Pre	$650	$1,300
	Microfluidizer 5 pass + Pre	$140	$790
	Grinder 9 Pass + Pre	$210	$860
	Grinder 9 Pass	$95	$745
	Homogenizer 20 Pass	$1,310	$1,960
Unbleached Hardwood (UBHW)	Homogenizer 8 Pass + Pre	$650	$1,000
	Microfluidizer 5 pass + Pre	$140	$490
	Grinder 9 Pass + Pre	$210	$560
	Grinder 9 Pass	$95	$445
	Homogenizer 20 Pass	$1,310	$1,660
Recycled Fiber	Grinder 9 Pass	$95	$195
Sludge	Grinder 9 Pass	$95	$115

Material	Market Price
LDPE*	$1,500
HDPE*	$1,400
PP*	$1,840
PS*	$1,600
PLA**	$1,900

* www.ptonline.com/pricing

**Biopolymers strive to meet price/performance challenge. www.thefreelibrary.com

- Energy assumption: $60/ MWh
- Pulp assumption: $350/ton UBHW , $650/ton BHW, $100/ton recycled, and $20/ton sludge

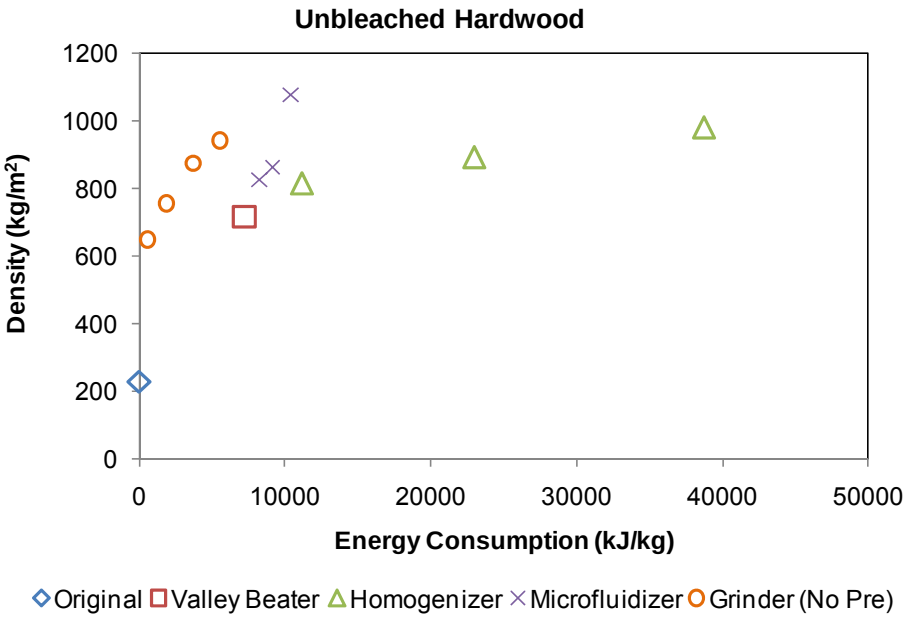
Final Remarks

- Lignin-containing fiber: significant mechanical property improvement with pretreatment and homogenization
- Hornification did not significantly impact final film properties
- Production method has significant impact on film properties
  - Microfluidizer – highest toughness and tensile index
  - Homogenizer – highest specific surface area (SSA)
  - Micro-grinder – lowest scattering coefficient

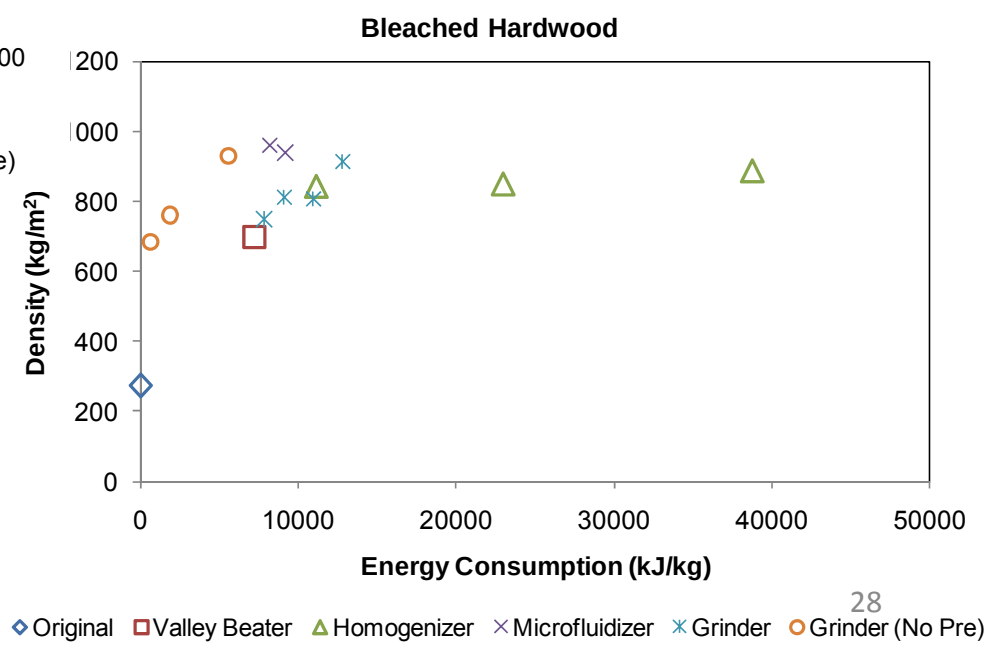
Acknowledgements

- Support for this student training project was provided by USDA National Needs Graduate Fellowship Competitive Grant No. 2007-38420-17772 from the National Institute of Food and Agriculture.
- Microfluidics, Inc.
- Kevin Daniel for assistance in film testing
- Linda McMurray, Ricardo Santos, and Ewellyn Capanema for assistance in pulp chemical composition analysis.

Film Physical Properties

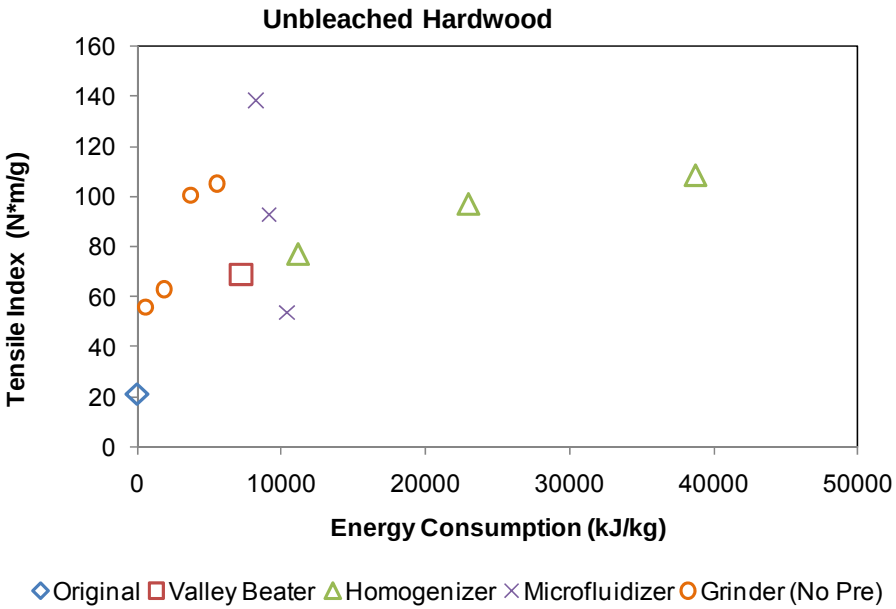


- Processing resulted in similar densities for both (bleached and unbleached) samples



- All films resulted in similar final densities, regardless of processing method

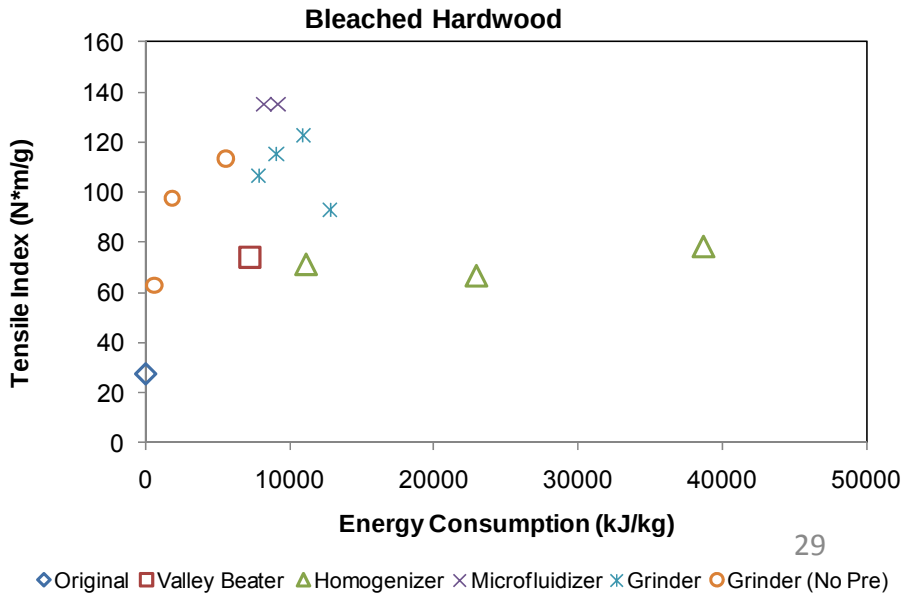
Tensile Index



$$\text{Tensile Index (TI)} = \frac{\text{Tensile Strength (N/m)}}{\text{Basis Weight (g/m}^2\text{)}}$$

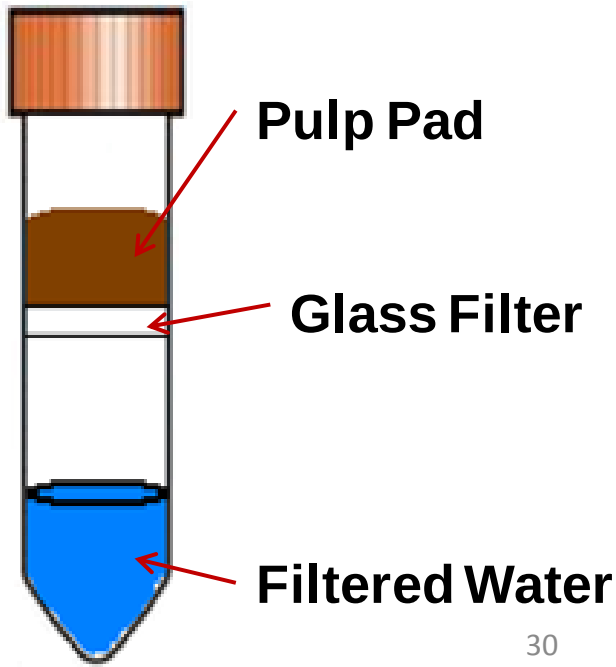
$$\text{Tensile Strength (TS)} = \frac{\text{Max Load (N)}}{\text{Sample Width (m)}}$$

- Microfluidization (10kpsi) resulted in significantly higher T.I.
- Grinder sample without pretreatment was similar to pretreated sample



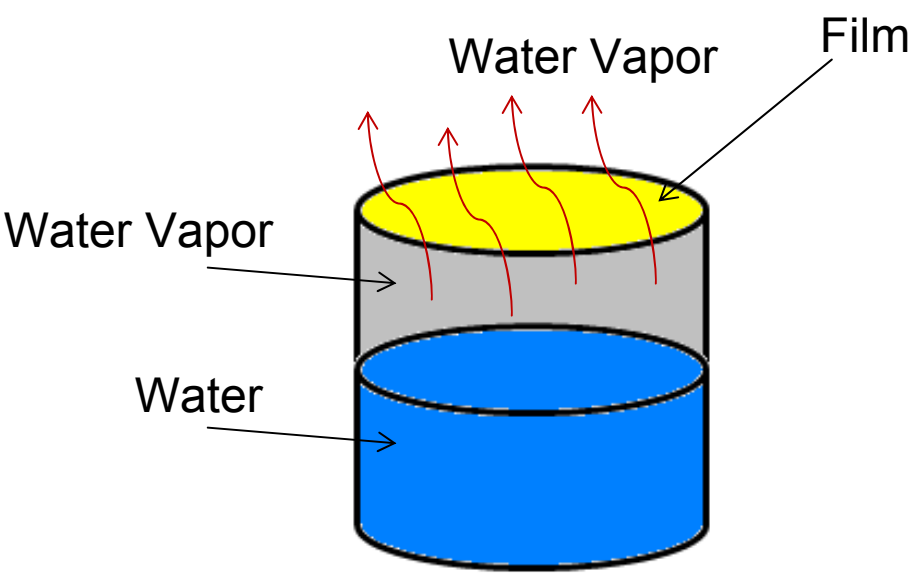
Water Retention Value (WRV)

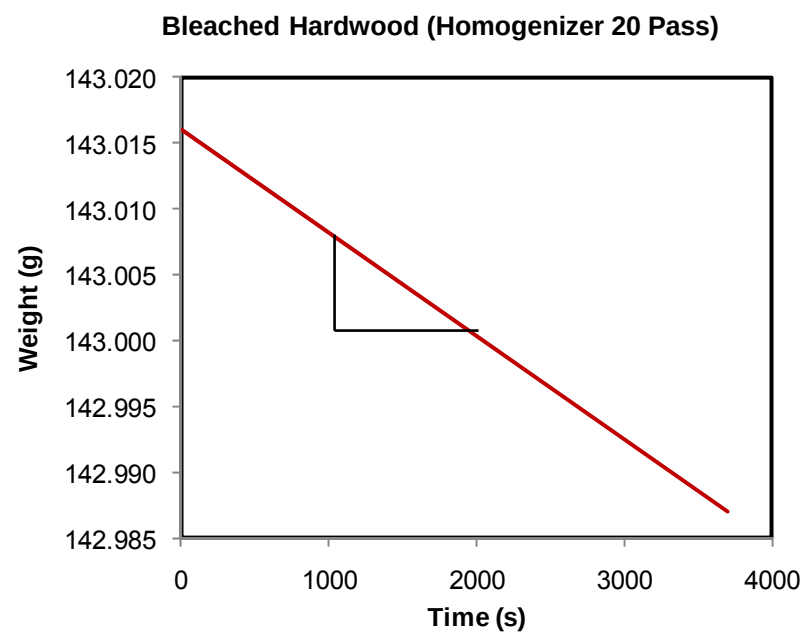
- TAPPI Useful Method 256 (modified)
  - 900 G (2400 rpm)
  - 30 minutes
  - 700 g/m^2 pulp pad
  - Oven dried overnight at 105°C



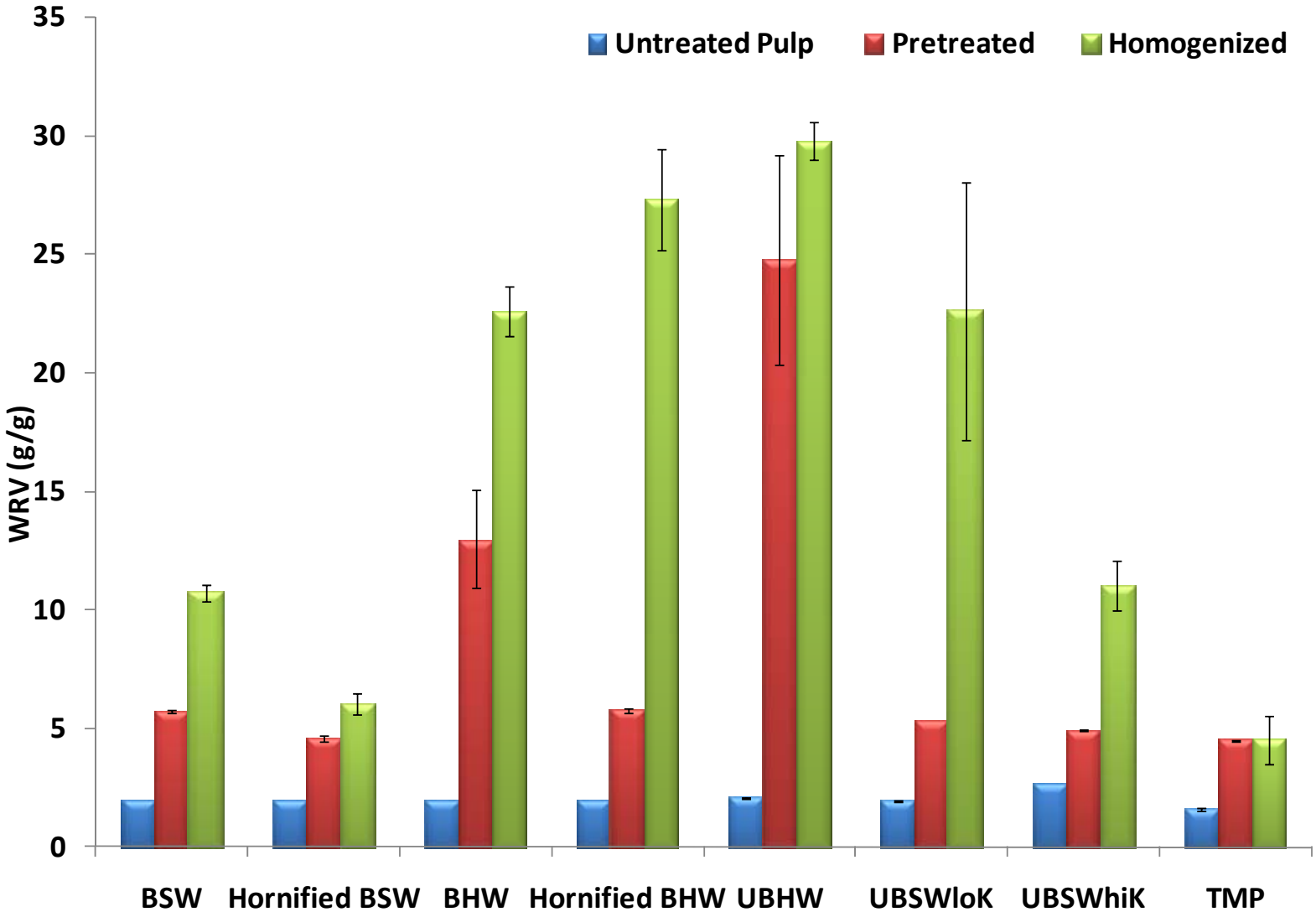
Water Vapor Transmission Rate (WVTR)

- Measured with Dynamic Wetting Apparatus in TAPPI standard conditions (23°C and 50% RH)
- 3.9 cm diameter circle
- 50 ml of water

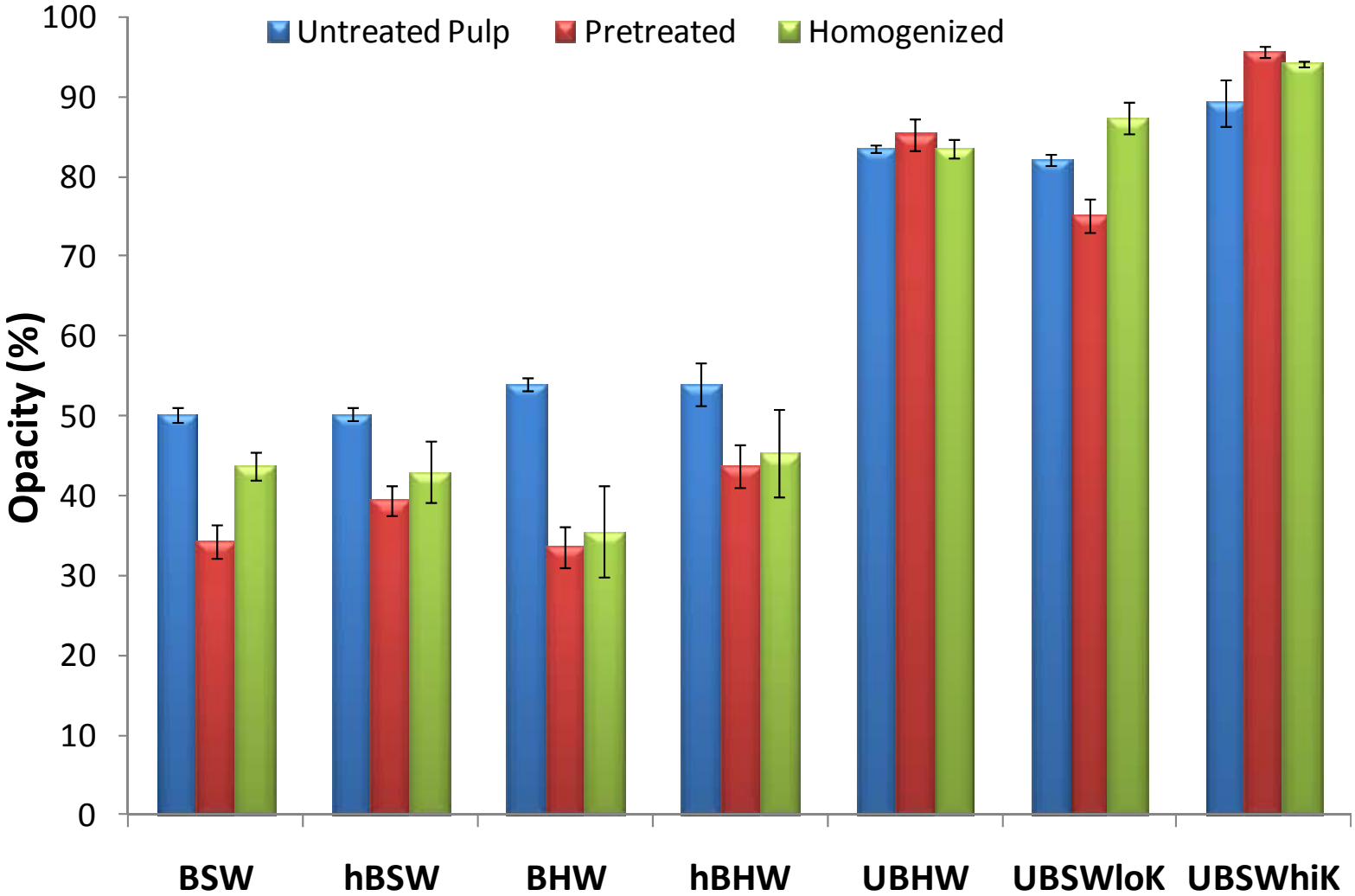




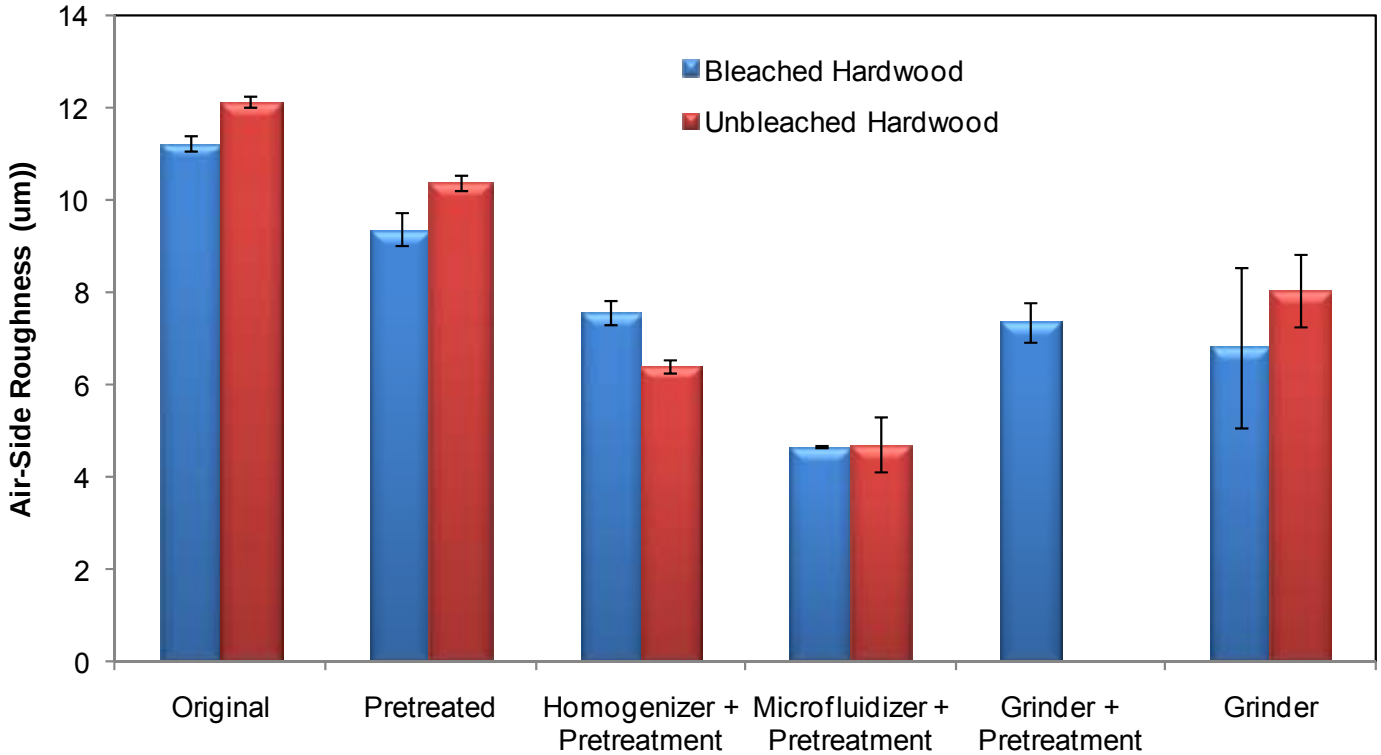
Water Retention Value (WRV)



Film Optical Properties

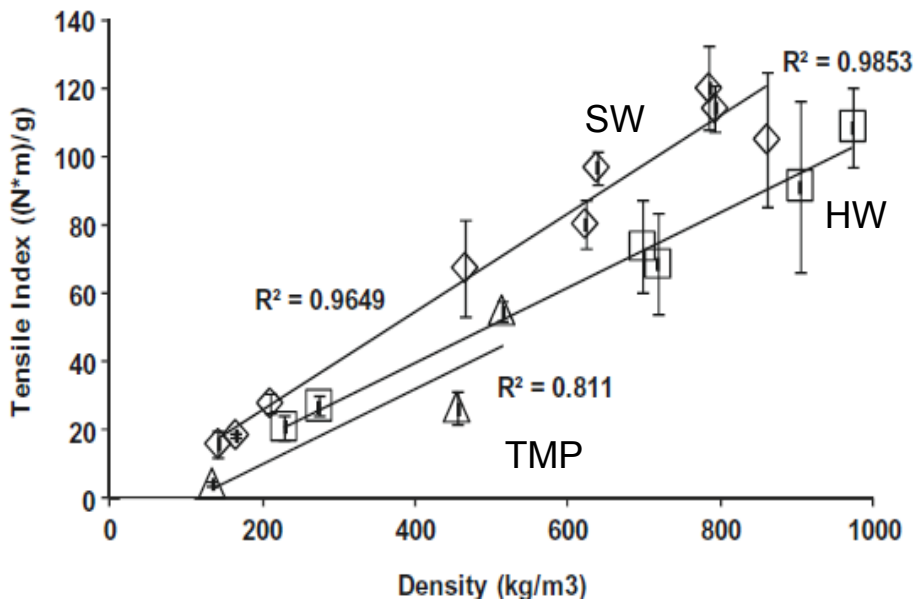


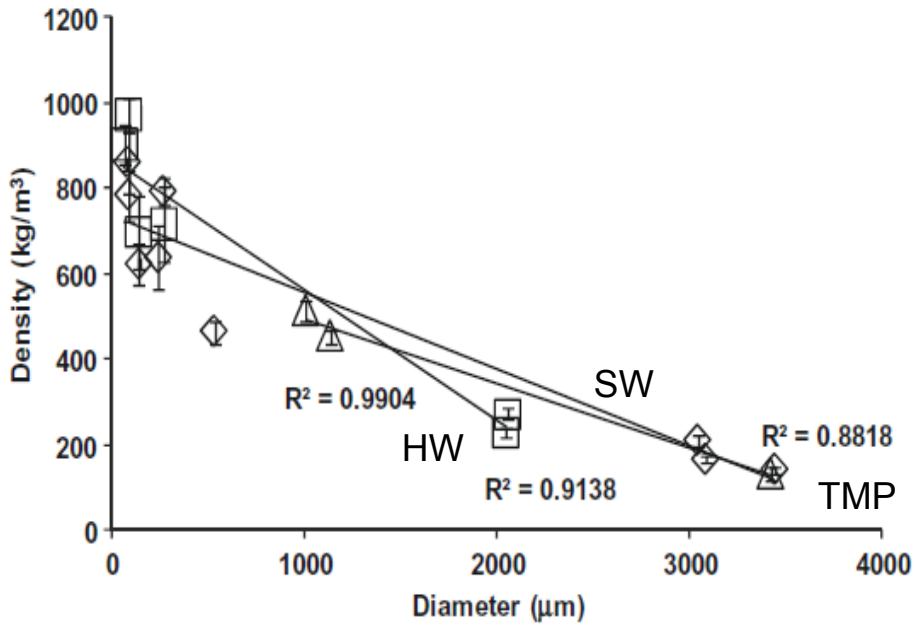
Film Physical Properties



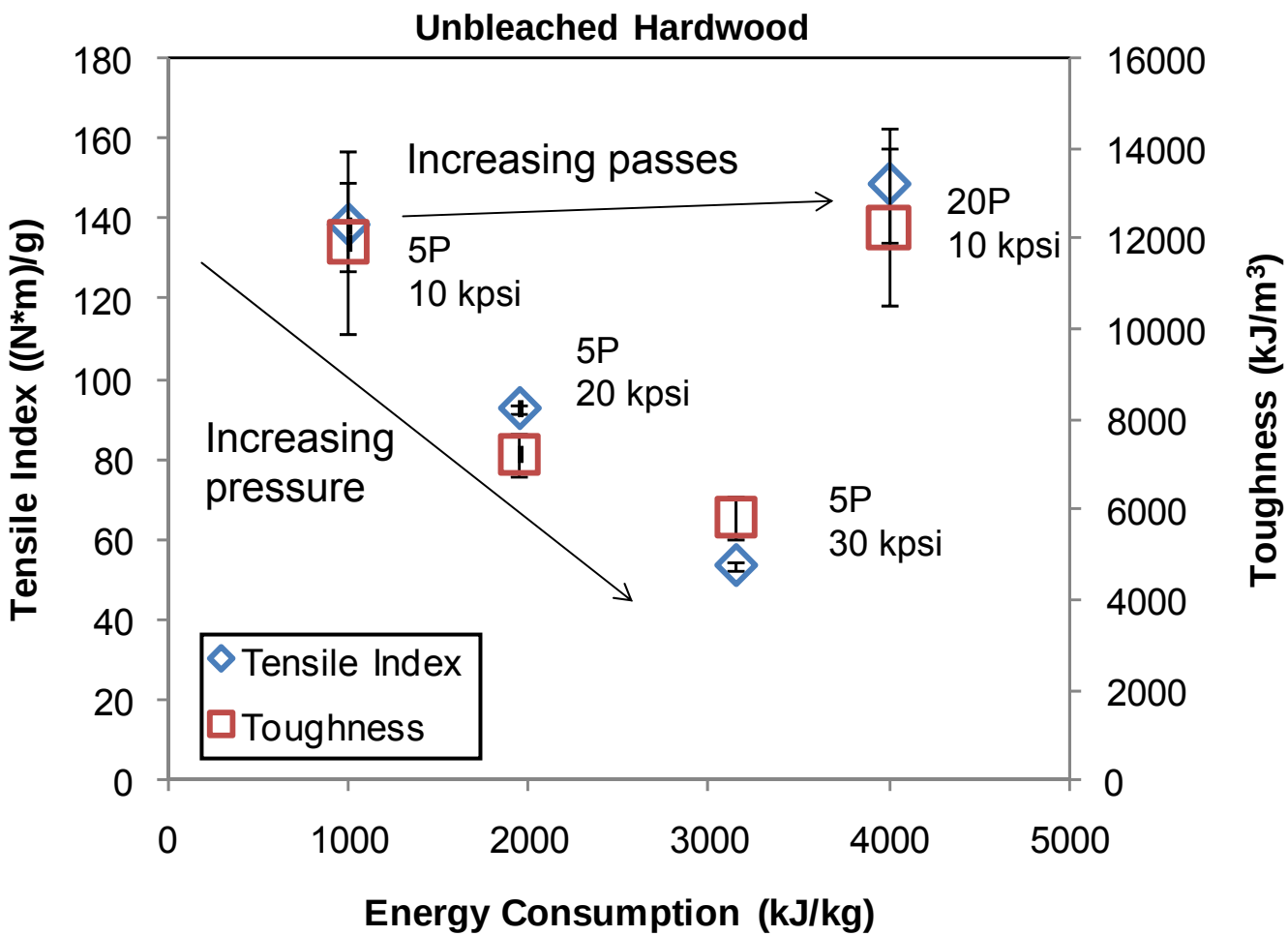
- Microfluidizer resulted in smallest surface roughness, suggesting smaller particle size
- Unbleached samples had a larger reduction of surface roughness

Film Mechanical Properties

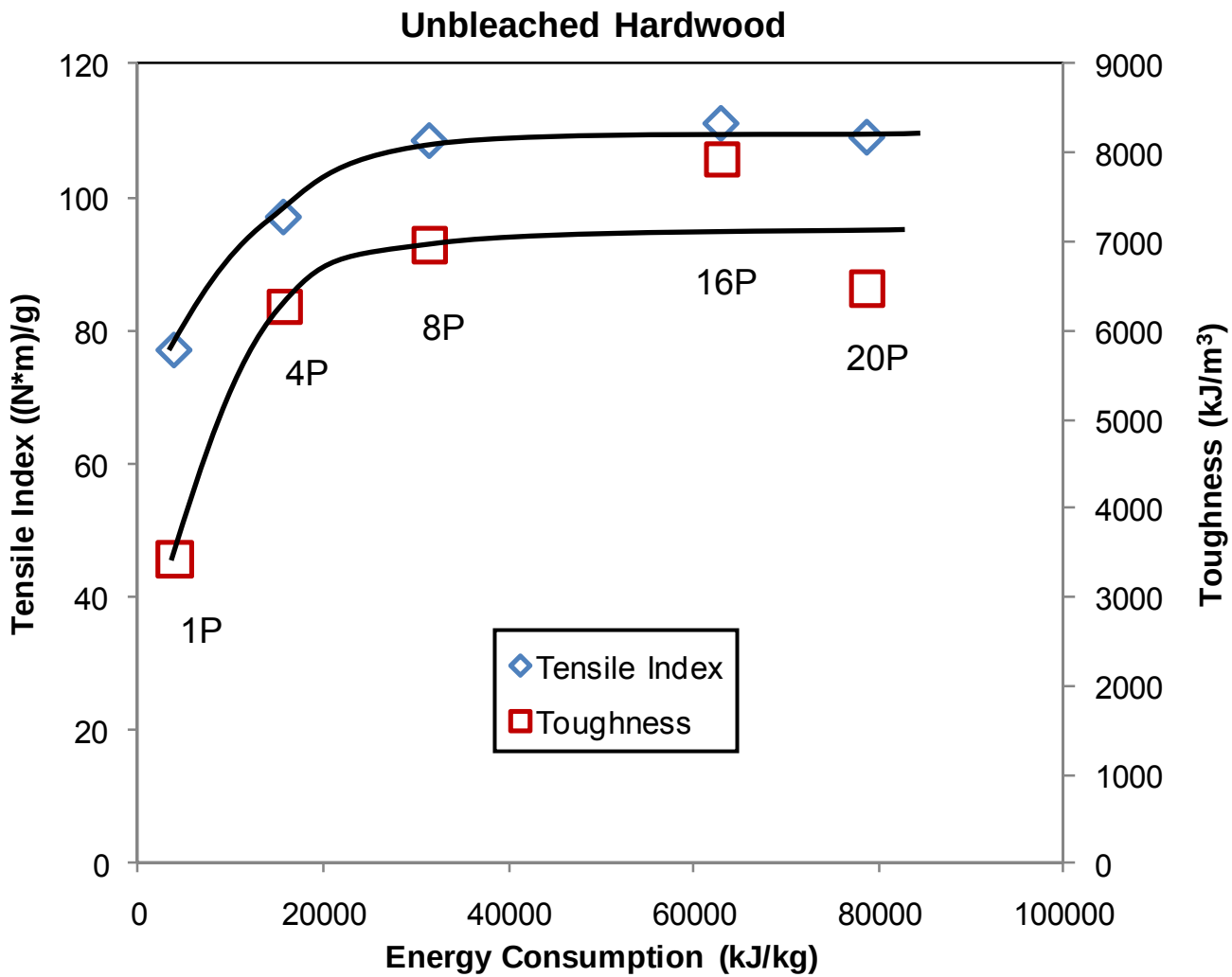




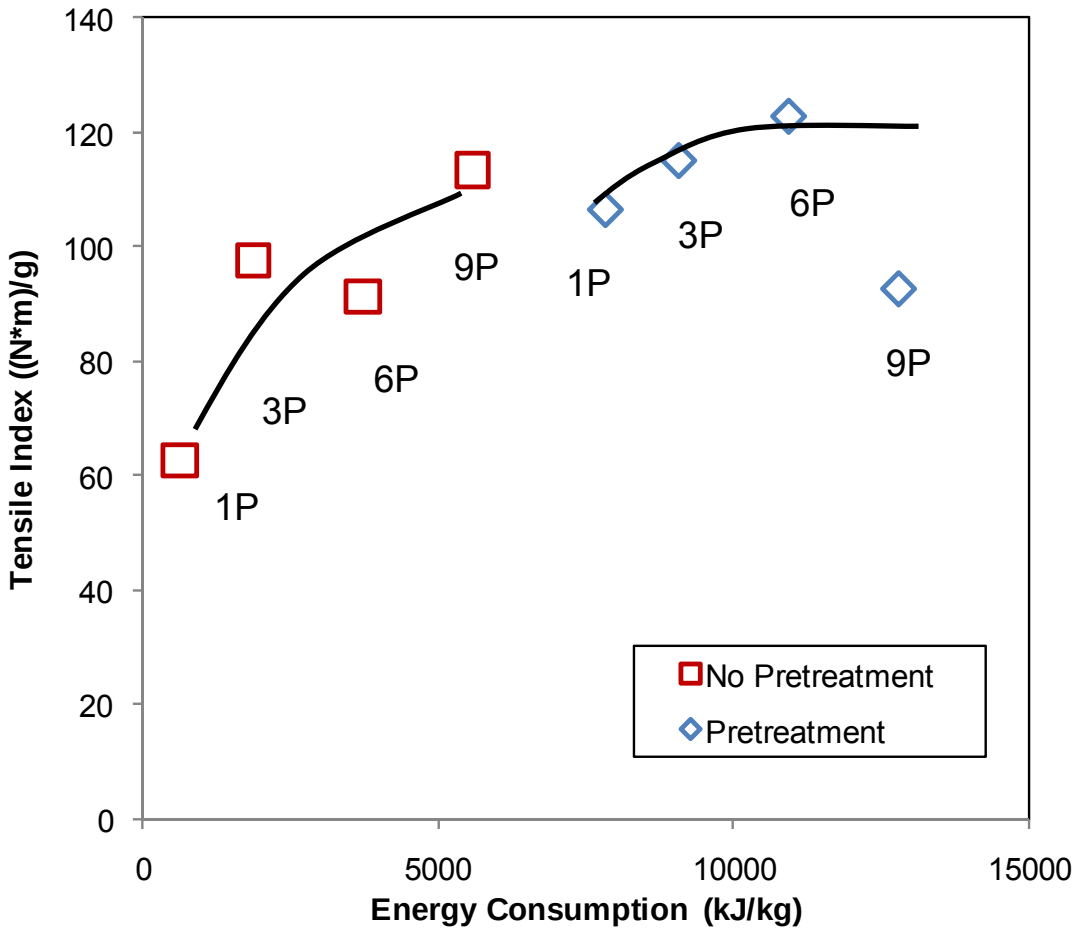
Energy Consumption: Microfluidizer



Energy Consumption: Homogenizer



Energy Consumption: Grinder



Potential Uses of Microfibrillated Cellulose

- Emulsifiers[1]
- Thickening agents[1]
- Food additives[1]:
  - Soups
  - Gravies
  - Mayonnaise

- Cosmetics[1]
- Paints and coatings[1]
- Films/coatings for packaging[2]:
  - Dry food products
  - Frozen foods and beverages
  - Fresh foods
- Composite reinforcements[3]:
  - Shipping crates and pallets
  - Toys
  - Storage bins
  - Outdoor furniture

[1]Turbak, Snyder et al. 1983
[2]Kirwan and Strawbridge 2003
[3]Kokta, Chen, et al. 1983

Objectives

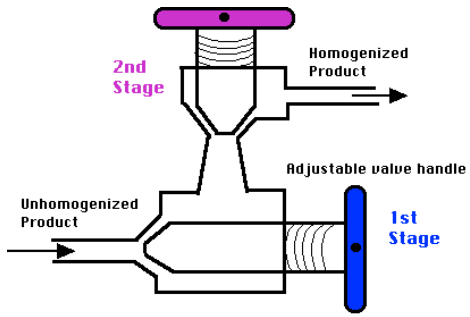
- Produce microfibrillated cellulose from fibers with different chemical compositions
- Determine the effects of fiber type, lignin content, and harsh drying on MFC film properties

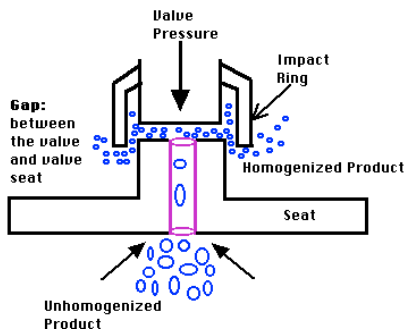
Film Properties

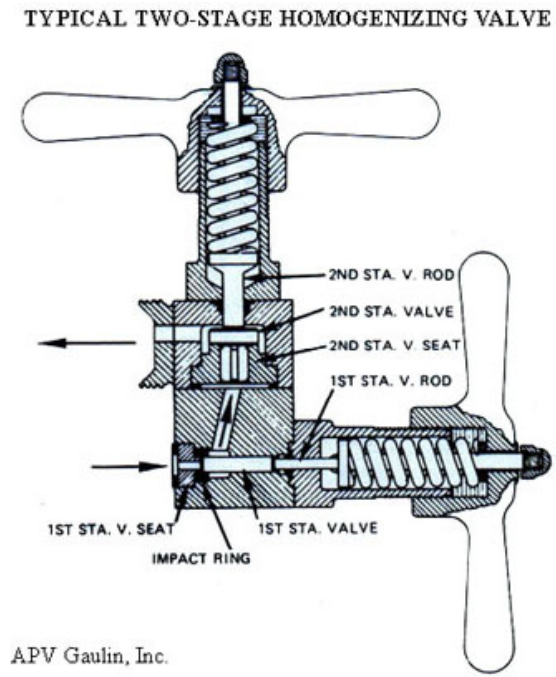
- Thickness – L&W Micrometer 51
- Roughness – L&W Parker Print Surf
  - Clamp pressure 0.5 psi
- Density – calculated from basis weight and thickness
- Optical – Technidyne Spectrophotometer
- Tensile strength
  - Instron
  - Sample width: 15mm
  - Gap width: 25.4 mm
  - Crosshead speed: 4 mm/min

Production of Microfibrillated Cellulose

- Homogenization
  - Operates by rapid pressure drop and shearing
  - Manton-Gaulin 15MR
  - 3940 kJ/kg (per pass)
  - Advantages:
    - Scale-ability
    - Continuous operation
  - Disadvantages:
    - Energy intensive
    - Clogging



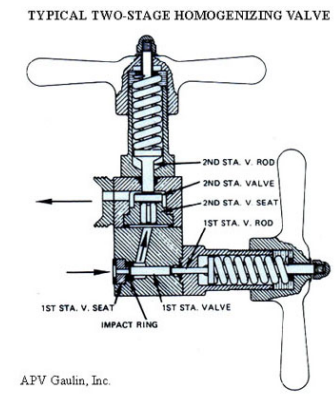


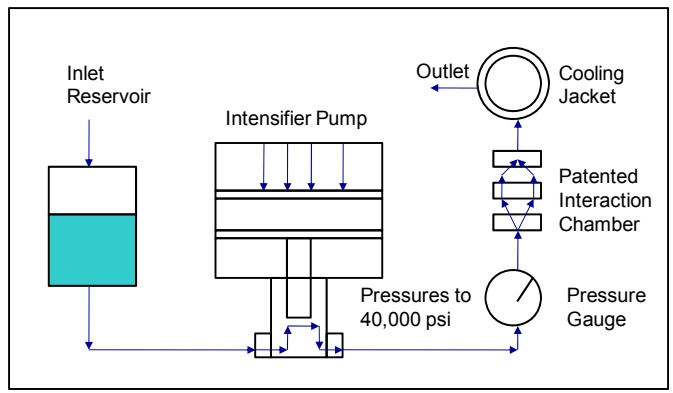


http://www.emt-india.net/process/dairy/img/homogenizer.gif

Equipment Comparison

- Homogenizer:
  - Friction losses: elbows, valves
  - Issues: plugging at ball valve, large ΔP
  - Pretreatment reduced required passes to 8 from 20
- Microfluidizer:
  - Friction losses: elbows, chamber walls
  - Issues: plugging in chamber, large ΔP
  - Increasing P resulted in T.I. decrease
  - Increasing no. passes from 5 to 20 did not significantly improve props
- Micro-grinder:
  - Friction losses: disk-disk interactions
  - Pretreatment not required

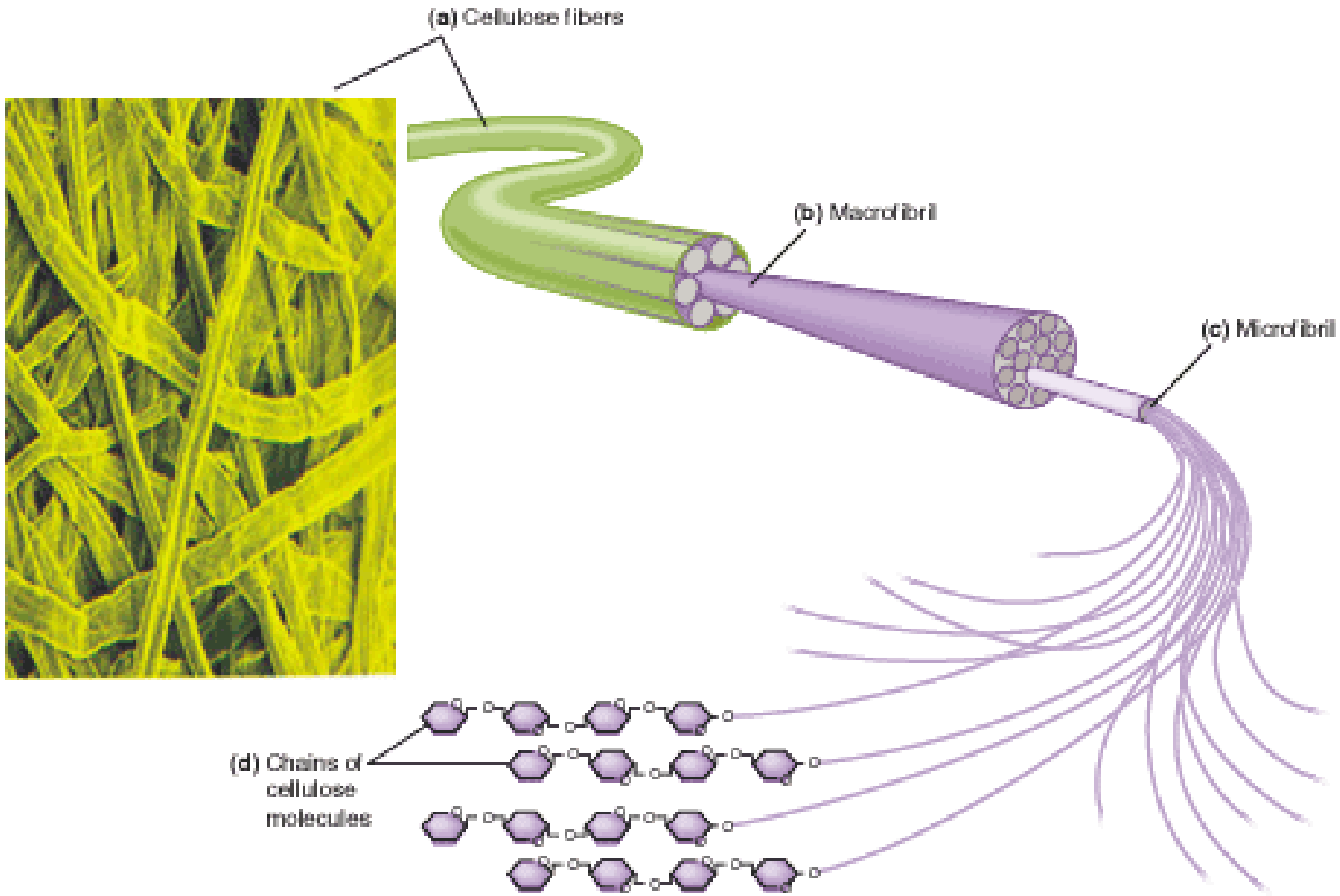




Processability of Fibers

- Unbleached pulps:
  - 0.7% K
  - Plugged constantly – some passed without having to stop and clean out machine
- Bleached pulps:
  - Initial plugging (1st several passes)
- Hornified bleached pulps:
  - No plugging
- TMP:
  - Initial plugging (1st several passes)

Introduction to Microfibrillated Cellulose



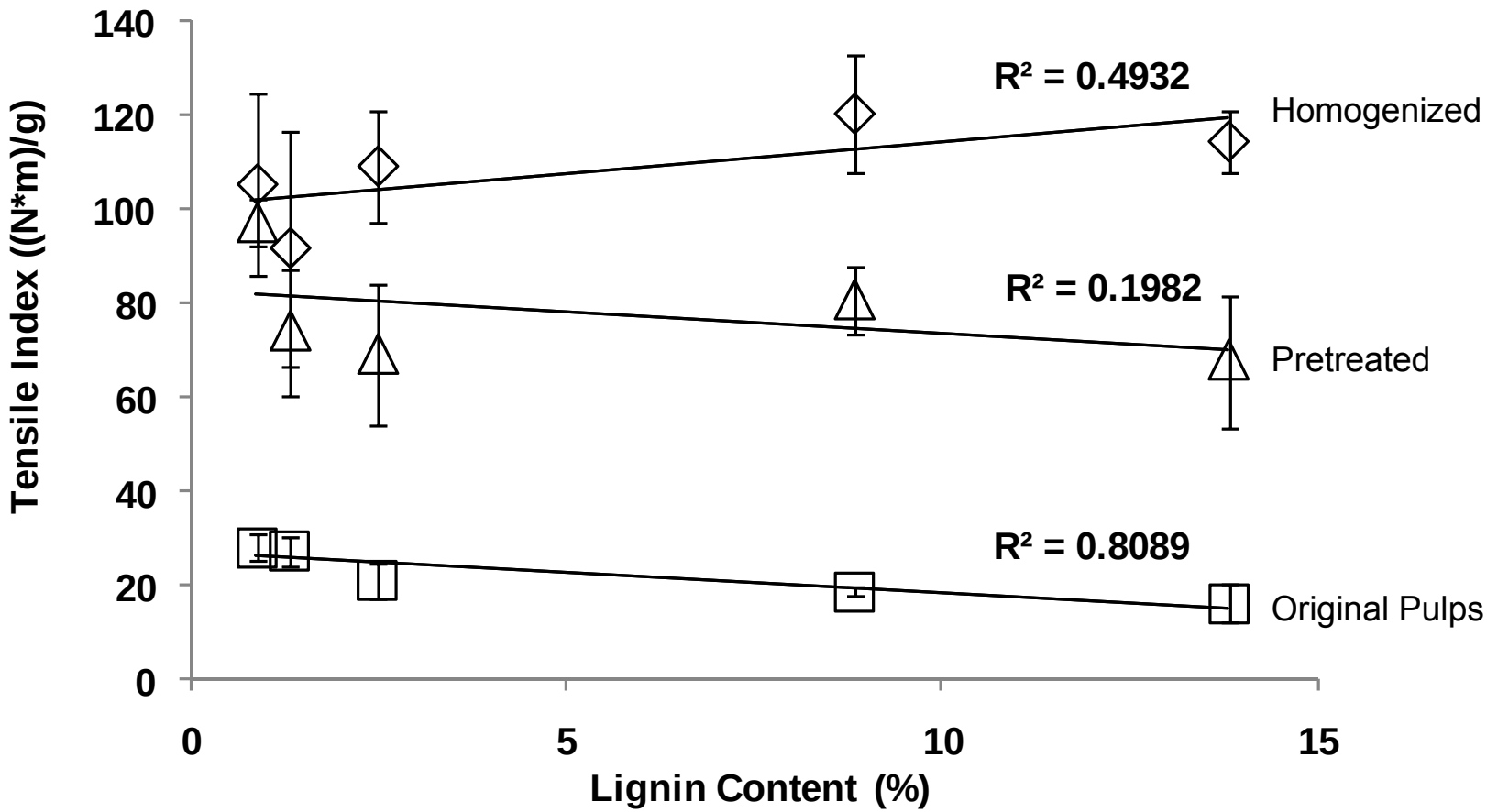
Nutrition Resources: Carbohydrates: http://nutrition.jbpub.com/resources/chemistryreview9.cfm Jones and Bartlett Publishers, 2006

Introduction to Microfibrillated Cellulose

- Gel-like properties at 2%K
- Have diameters ranging from 25-100 nm
- Advantages of these materials:
  - Renewability
  - Abundant fiber precursor
  - High surface area
  - Mechanical properties
    - More hydrogen bonding
    - More distributed defects
    - Crack stopping mechanism
- Typically purified cellulose

"Turning Science into Reality" Presentation by STFI-PACKFORSK

Film Mechanical Properties



original pulps (□), pretreated materials (Δ),and homogenized samples (◊)