'Green' Bio-Composites: Moving Towards More Eco-friendly Structural Automotive Parts

Lawrence T. Drzal

Dept of Chemical Engineering and Materials Science

A.K. Mohanty, M. Misra

Composite Materials & Structures Center

Michigan State University

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Contents of Presentation

- Introduction to BioComposites
- BioFibers as Reinforcements
- BioPolymers as Matrices
- Processing of BioComposites
- Surface Modification to Enhance Properties
- BioComposite Properties
  - Modulus, Strength and Impact Properties
- Summary

"SUSTAINABLE" GREEN MATERIALS

Renewable

Recyclable

Triggered Biodegradable

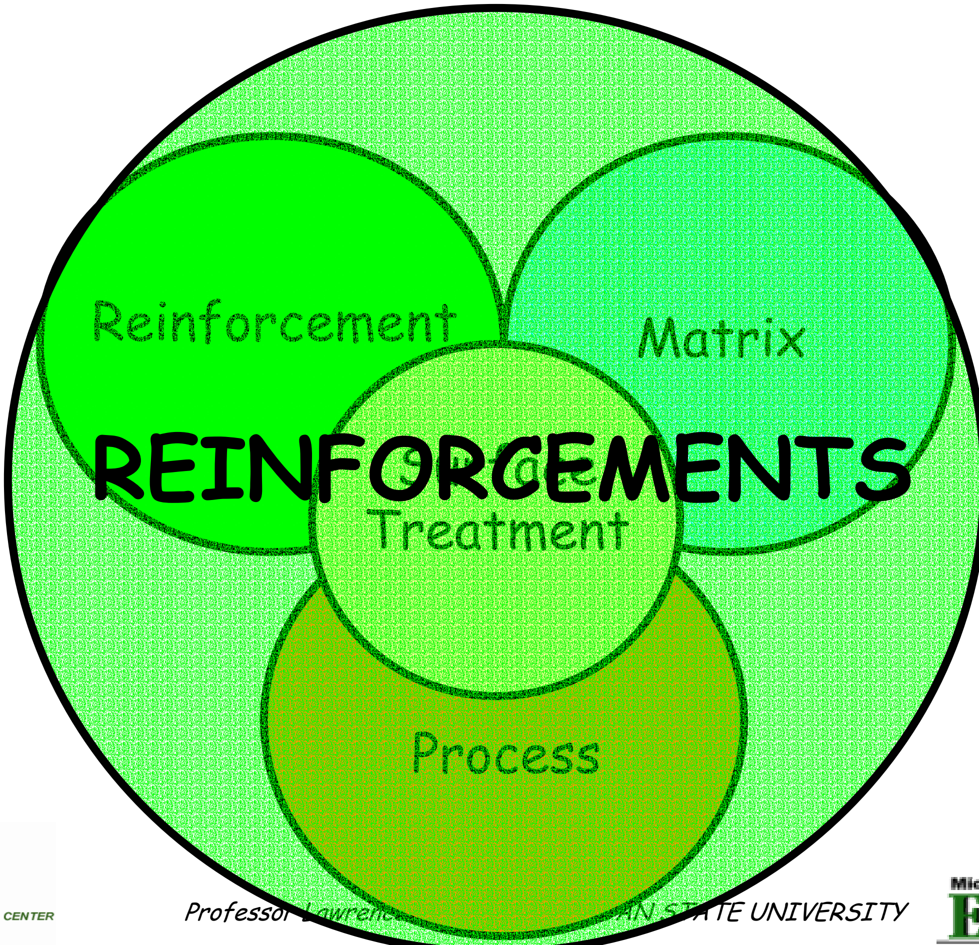
Commercial Viability & Environmental Acceptability

SUSTAINABLE

Why BioComposites?

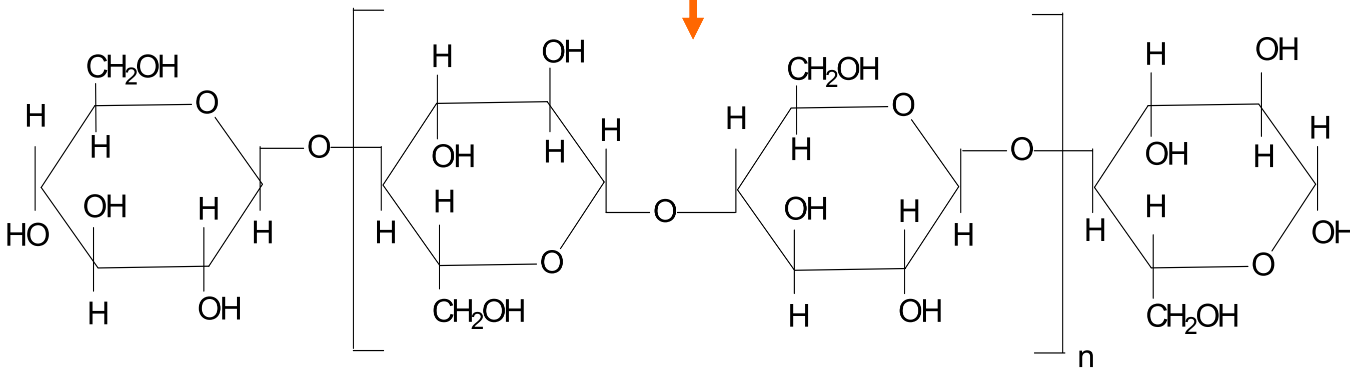
- Natural Products have an inherent high variability
  - Composition, properties, quality
- EcoFriendly MUST be extended to structural applications
  - Beyond 'picnic' goods and garbage bags
- Bioplastics alone are 'marginal' materials
- Addition of reinforcing fibers increases structural potential
- Control of fiber orientation 'optimizes' properties
- Improve Thermal, Moisture and Mechanical Durability

Factors Necessary for Development of a BioComposite System

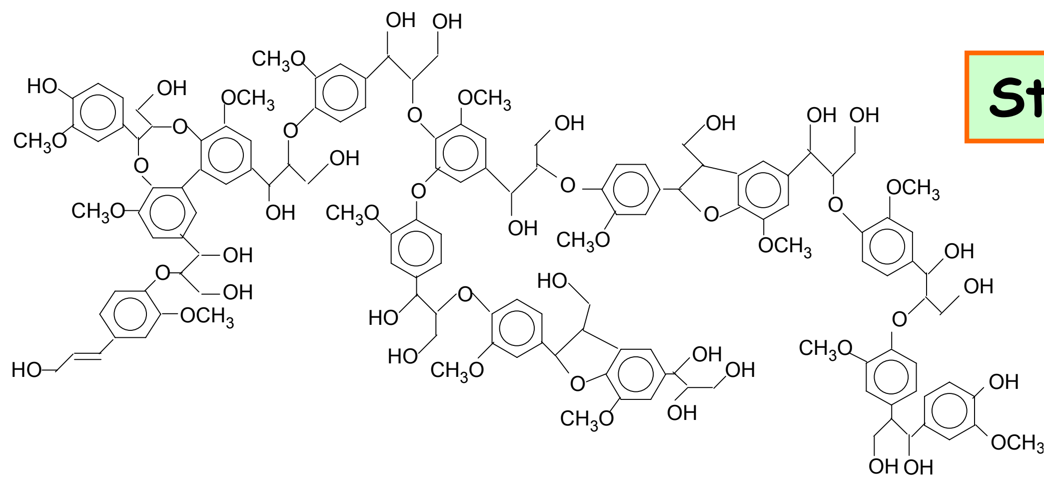


BIOFIBERS- Cellulose + Lignin

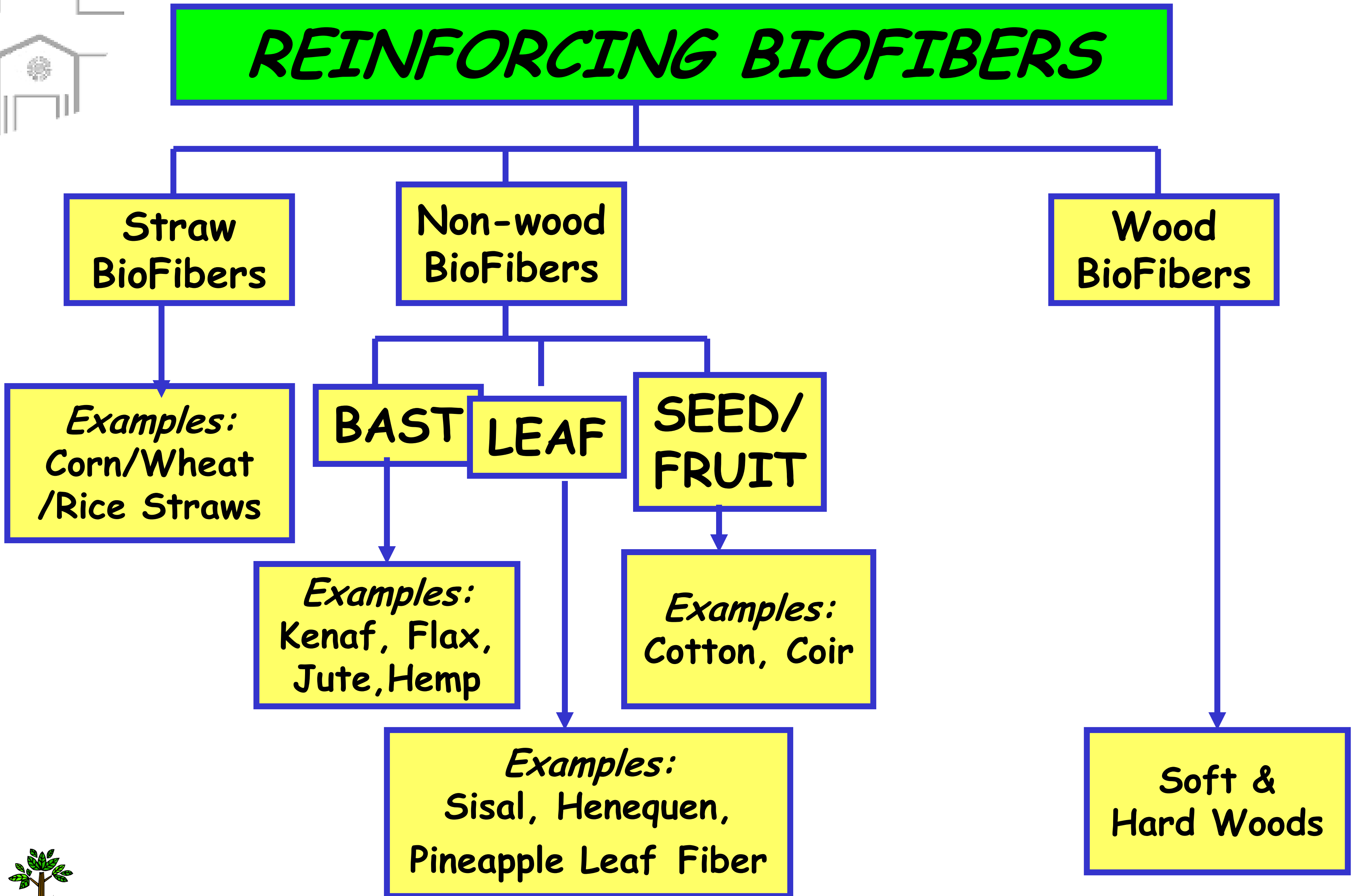
Structure of cellulose



Structure of lignin

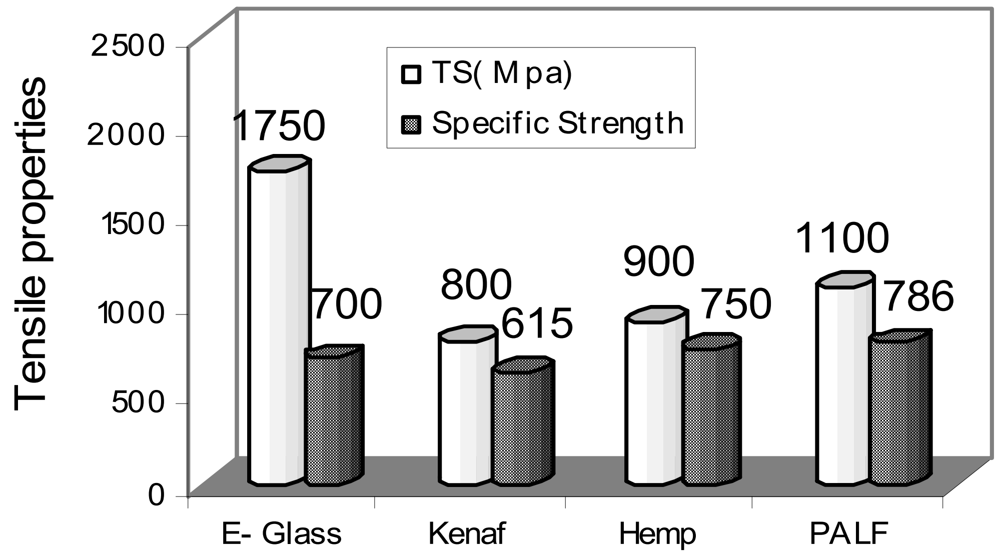


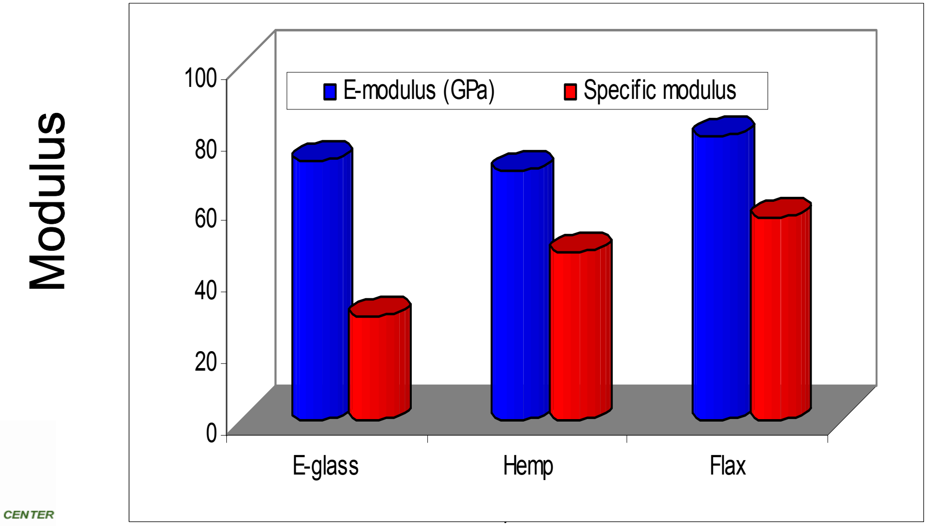
NATURAL FIBERS


REINFORCING BIOFIBERS
Straw BioFibers
Non-wood BioFibers
Wood BioFibers
Examples: Corn/Wheat /Rice Straws
BAST
LEAF
SEED/ FRUIT
Examples: Kenaf, Flax, Jute,Hemp
Examples: Cotton, Coir
Examples: Sisal, Henequen, Pineapple Leaf Fiber
Soft & Hard Woods

BIOFIBERS vs. GLASS

(Specific Strength/Modulus)





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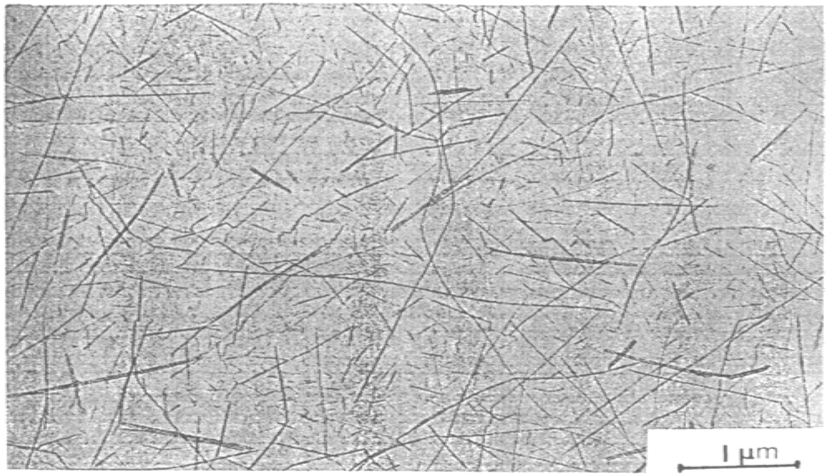
REINFORCING BIOFIBERS

- **Straw BioFibers**
  - *Examples:* Corn/Wheat /Rice Straws
- **Non-wood BioFibers**
  - **BAST**
    - *Examples:* Kenaf, Flax, Jute, Hemp
  - **LEAF**
    - *Examples:* Sisal, Henequen, Pineapple Leaf Fiber
  - **SEED/ FRUIT**
    - *Examples:* Cotton, Coir
- **Cellulose Nano-whiskers**
  - *Sources:* Wood & Non-wood Fibers Through Explosion
- **Wood BioFibers**
  - Soft & Hard Woods

Cellulose Nanowhiskers as Reinforcements for Polymer Composites

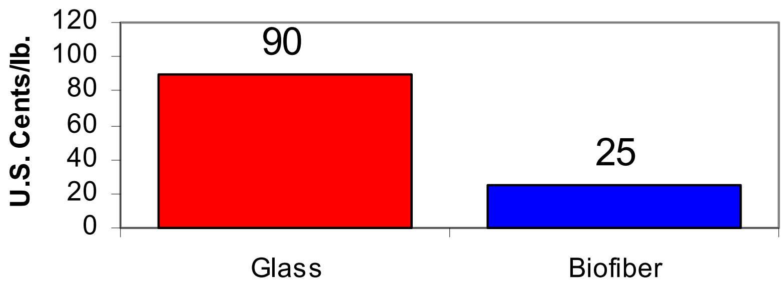
- Cellulose microfibrils
  - (5nm x 150-300nm)
  - monocrystalline cellulose domains parallel to the microfibril axis composed of cellulose chains in a cellulose lattice bonded laterally and surrounded by surface chains forming a paracrystalline envelope
  - devoid of defects, linked by amorphous domains having a strength of 10 GPa
  - tensile modulus of 130 GPa
  - reinforcement for polymers



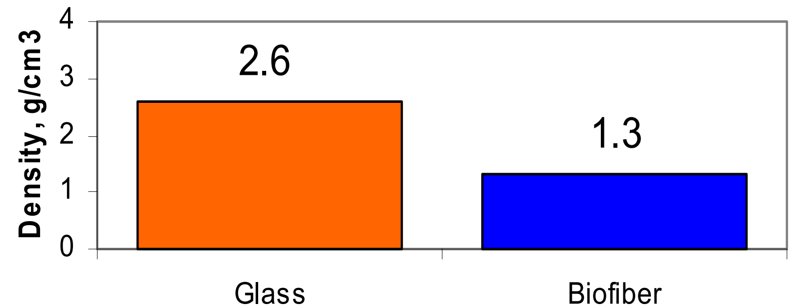
TEM micrograph of cellulose whiskers from tunicate (Favier, et. al)

Motivation for BioFibers

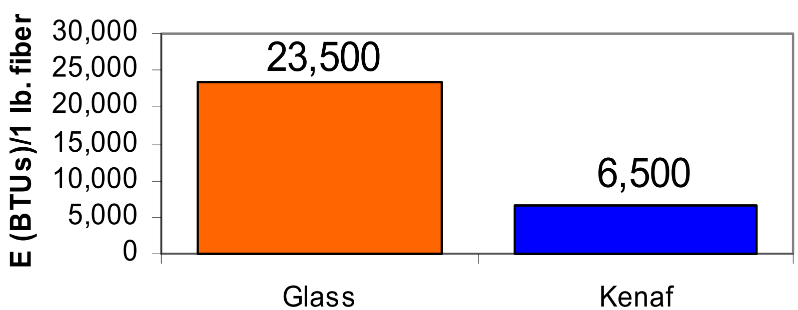
Cost comparison in average



Weight savings

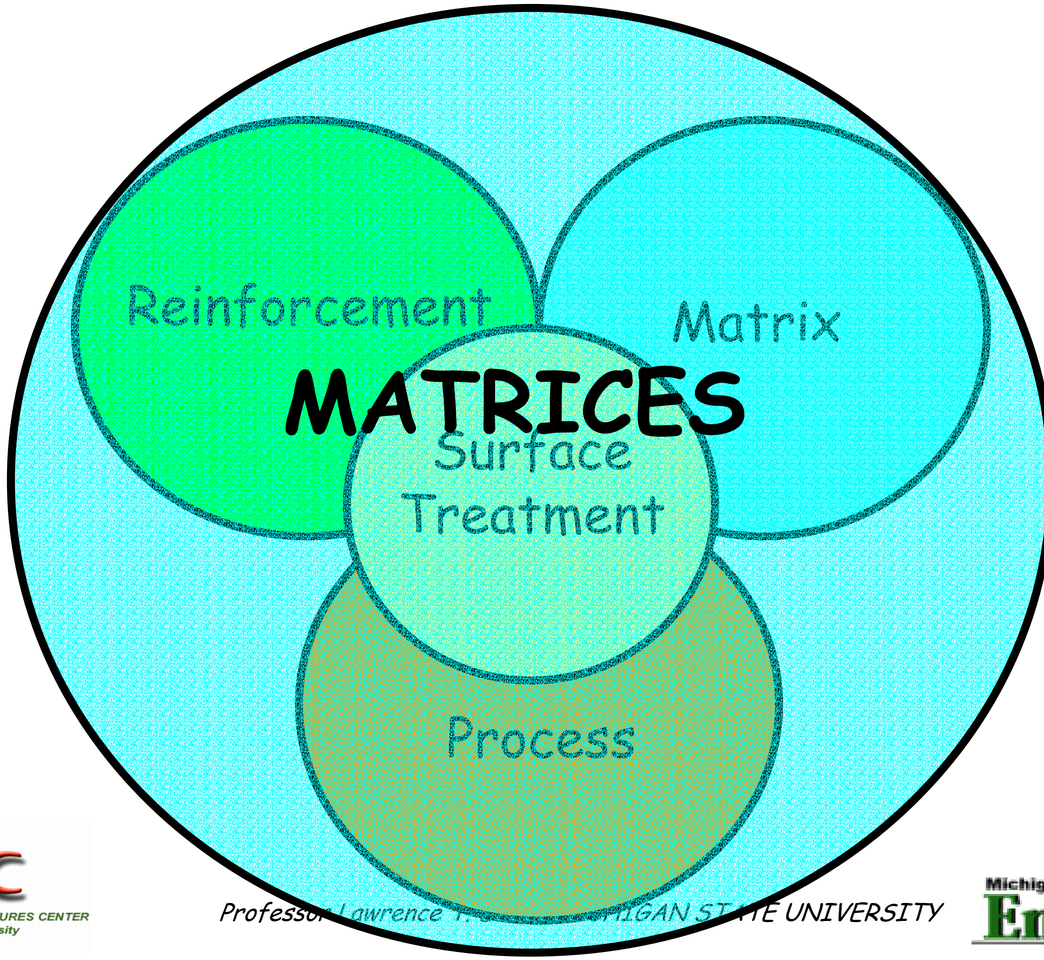


Energy savings



- Biodegradability and Recyclability
- EcoFriendly 'GREEN' Material
- CO_2 Sequesterization
- Mechanical PERFORMANCE

Factors Necessary for Development of a BioComposite System



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BIODEGRADABLE POLYMERS

Renewable Resource-based

- PLA Polymer
- Cellulosic plastics
- Soy-based plastics
- Starch plastics

Petro-based synthetic

- Aliphatic polyester
- Aliphatic-aromatic polyesters
- Polyesteramides
- Polyvinyl alcohols

Microbial synthesized

- Polyhydroxy-alkanoate (PHA)
- Polyhydoxy-butyrate co-valerate (PHBV)

BIOPOL Polymers

Biopolymer blends

- Starch blends
- Polyester
- other blends

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A. K. Mohanty, L. T. Drzal, R. Narayan, M. Misra, **Progress in Polymer Science** 2001

Professor Lawrence T. Drzal, MICHIGAN STATE UNIVERSITY

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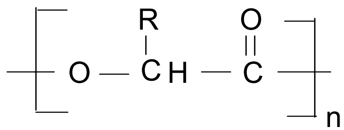
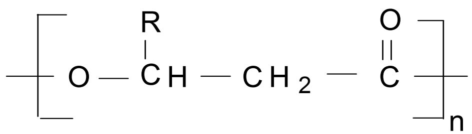
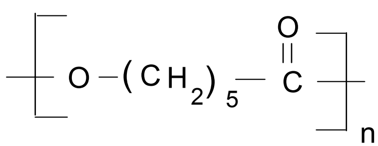
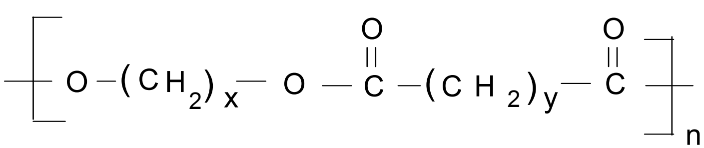
Chemical Structure of some Biopolymers

Chemical Structure	*Examples*
 Poly(alpha-hydroxy acid)	R = H, Poly(glycolic acid), PGA R = CH_3, Poly(lacticacid), PLA
 Poly(beta-hydroxy alkanoate)	R = CH_3, Poly(beta-hydroxybutyrate), PHB R = CH_3, C_2H_5, Poly(betahydroxybutyrate-co-valerate) PHBV (BIOPOL)
 Poly(omega-hydroxy alkanoate)	x = 5, Poly(epsilon-caprolactone), PCL
 Poly(alkylene dicarboxylate)	x = 2, y = 2, PES x = 4, y = 2, PBS x = 4, y = 2,4, PBSA (BIONOLLE)

Protein And Soybean Oil: Source of Plastic Resin For Bio-Composite

In 1924 - - 5 million bushels of soybean
In 2000 - - 2.8 billion bushels processes in U.S.

Composition of Whole Soybean

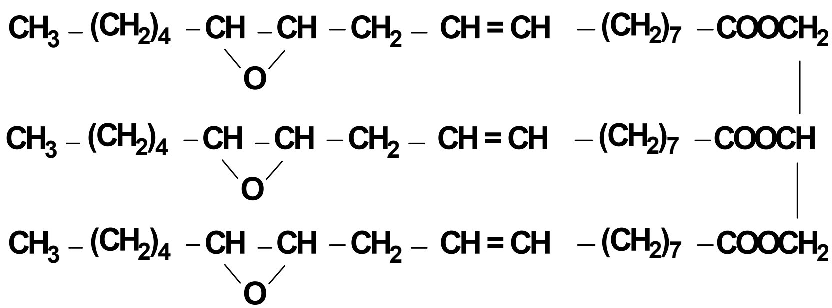
- Protein: 43%
- Oil: 20%
- Carbohydrate: 26%
- Hulls: 8%
- Other: 3%

Soy protein	Protein content	Cost/lb.
Defatted Flour	50-55%	$0.20
Protein Concentrate	65-72%	$0.55
Protein Isolate	90+%	$1.10

Soy Oil:	$0.20-0.25
Epoxidized Soy Oil :	$0.60-0.65

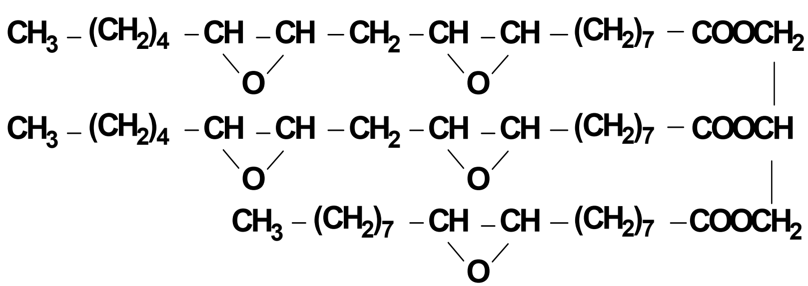
EPOXIDIZED OIL: A SOURCE OF PLASTIC RESIN TO REPLACE PETRO-BASED SYNTHETIC THERMOSET RESIN

VERONIAN OIL (VO) : Naturally epoxidized vegetable oil



VO has a lower average epoxy functionality of 2.4

EPOXIDIZED SOYBEAN OIL (ESO)



ESO has a higher average epoxy functionality (4.5)

- Triacylglycerol oil, very much similar to other vegetable oils, such as corn oil, soybean oil, sunflower oil, coconut oil, castor oil etc.
- VO contains triglycerols in which the fatty acid moieties are mostly epoxidized – thus VO is nature made epoxidized vegetable oil.

Vernonian Oil (VO): Natural made Epoxidized Vegetable Oil Abundantly Available in Tropical Parts of AFRICA

Biopolymers Are Becoming Commercial Products

- Poly(lactic acid) — *Cargill-Dow & Mitsui Chemicals*
- Starch plastics — *Novamont, National Starch*
- Cellullosic Plastic — *Eastman Chemical*
- Aliphatic / aliphatic-aromatic copolyester

Easter Bio	Eastman
Biomax	DuPont
Ecoflerx	BASF
BAK	Bayer
Bionolle	Showa High Polymer

PLA
300 million lb./yr. – Nebraska
1 billion lb./yr. - World by 2006

Natural/Bio-Fiber Composites (BioComposites)

Partial Biodegradable

- **Thermoplastic BioComposites**
  (Biofiber+Poly-propylene/Poly-ethylene etc.)
- **Thermoset BioComposites**
  (Biofiber+Epoxy, Polyester, etc.)

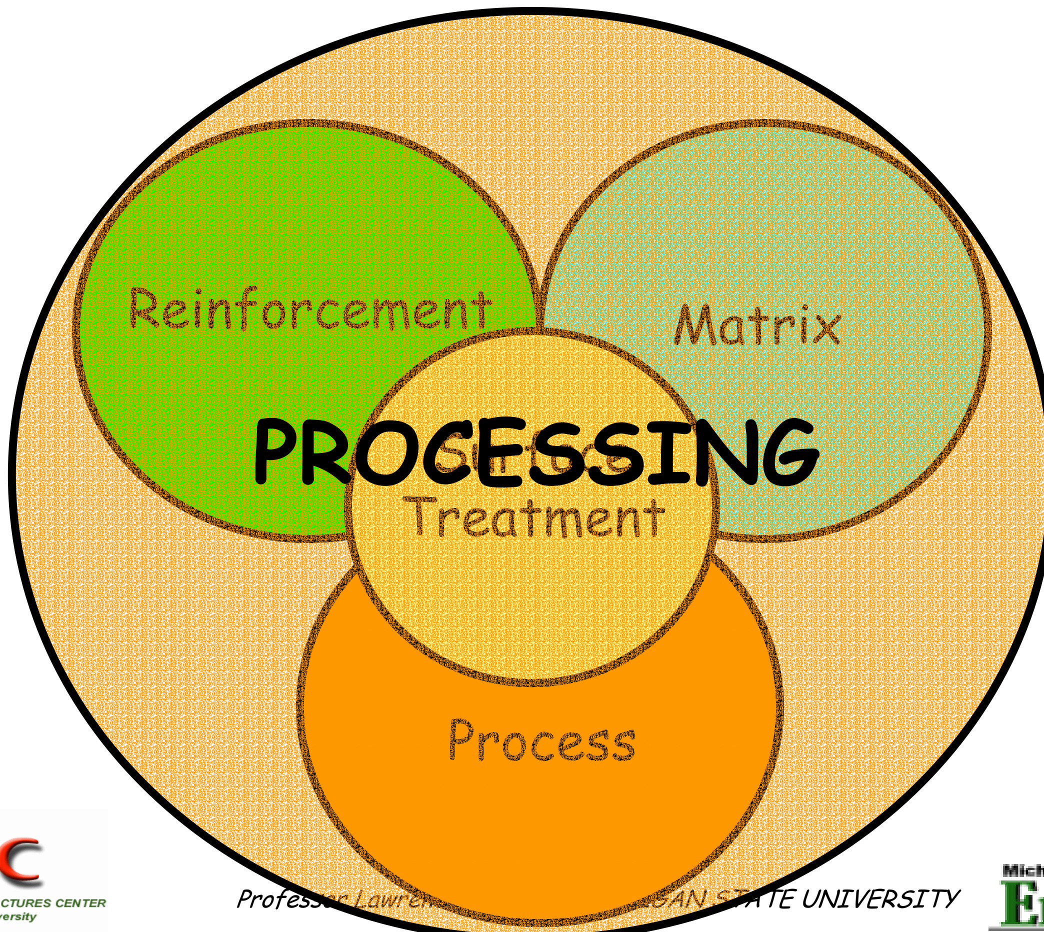
Completely Biodegradable (Optional)

- **Biofiber-Biopolymer BioComposites**
  (Biofiber+Soy plastic/ Starch plastic/ Cellulosic Plastic/PLA
- **Biofiber-PetroPolymer BioComposites**
  (Biofiber+aliphatic co-polyester Polyesteramides

HYBRID BIO-COMPOSITES

Thermoplastic/Thermoset/bio-polymers Reinforced with Two or more Bio-fibers to Manipulate BioComposite Properties & To Maintain Balance Among Ecology-Economy-Technology

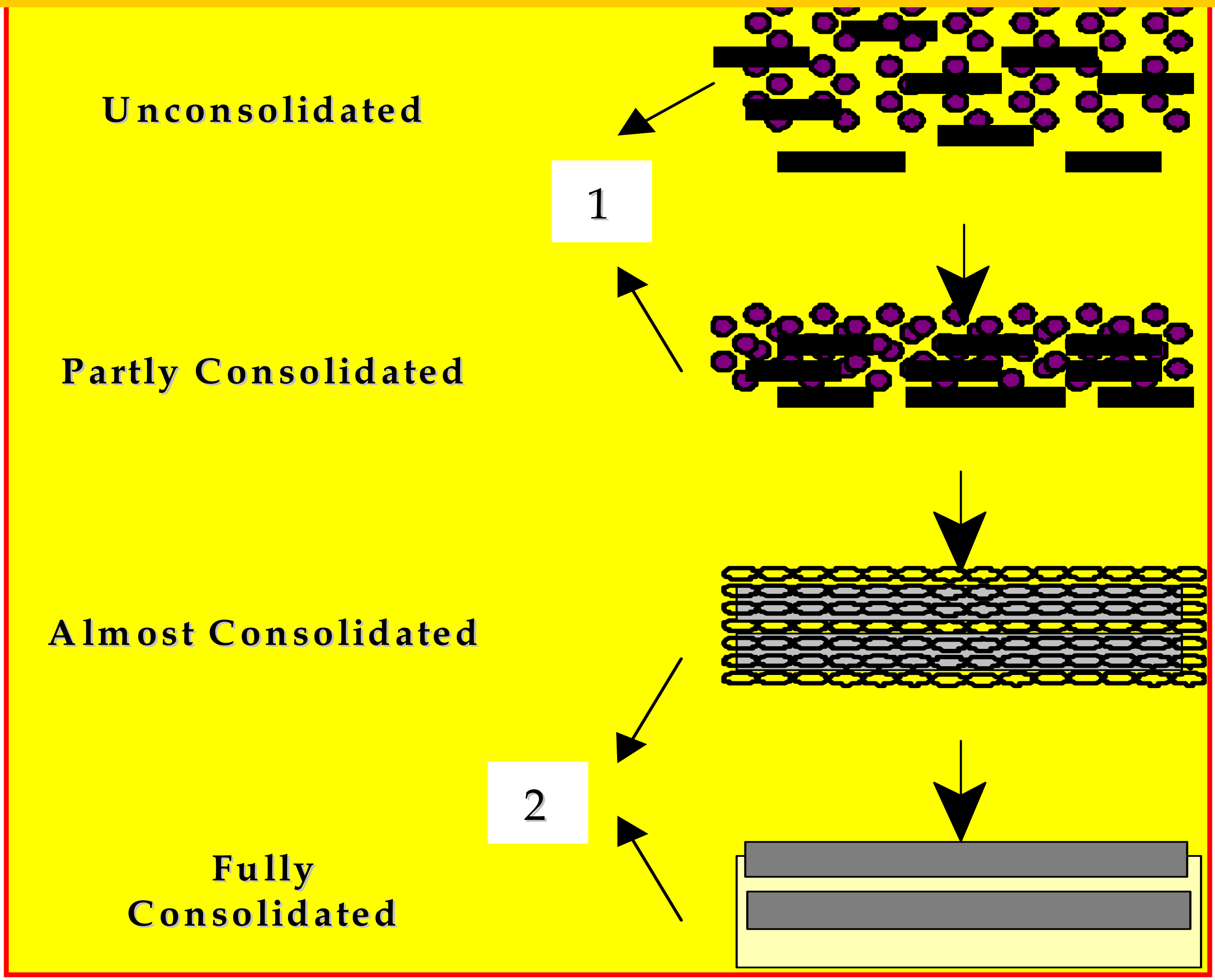
Factors Necessary for Development of a BioComposite System



BioComposite Process Requirements

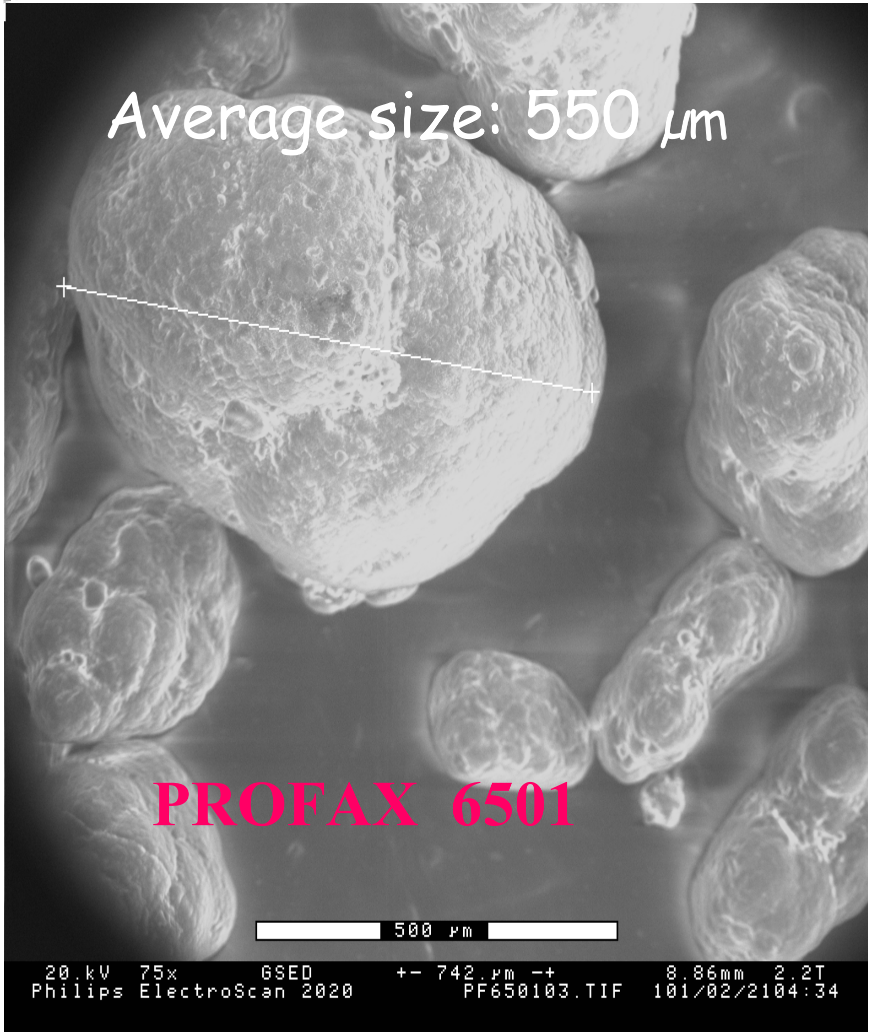
- Preserve BioFiber Mechanical Properties
  - minimize attrition
  - minimize mixing degradation
- Attain a High Degree of BioFiber Dispersion
- Insure BioFiber Wettability
- Maximize BioFiber Volume Fraction
- Control BioFiber Orientation
- High Speed
- Low Cost

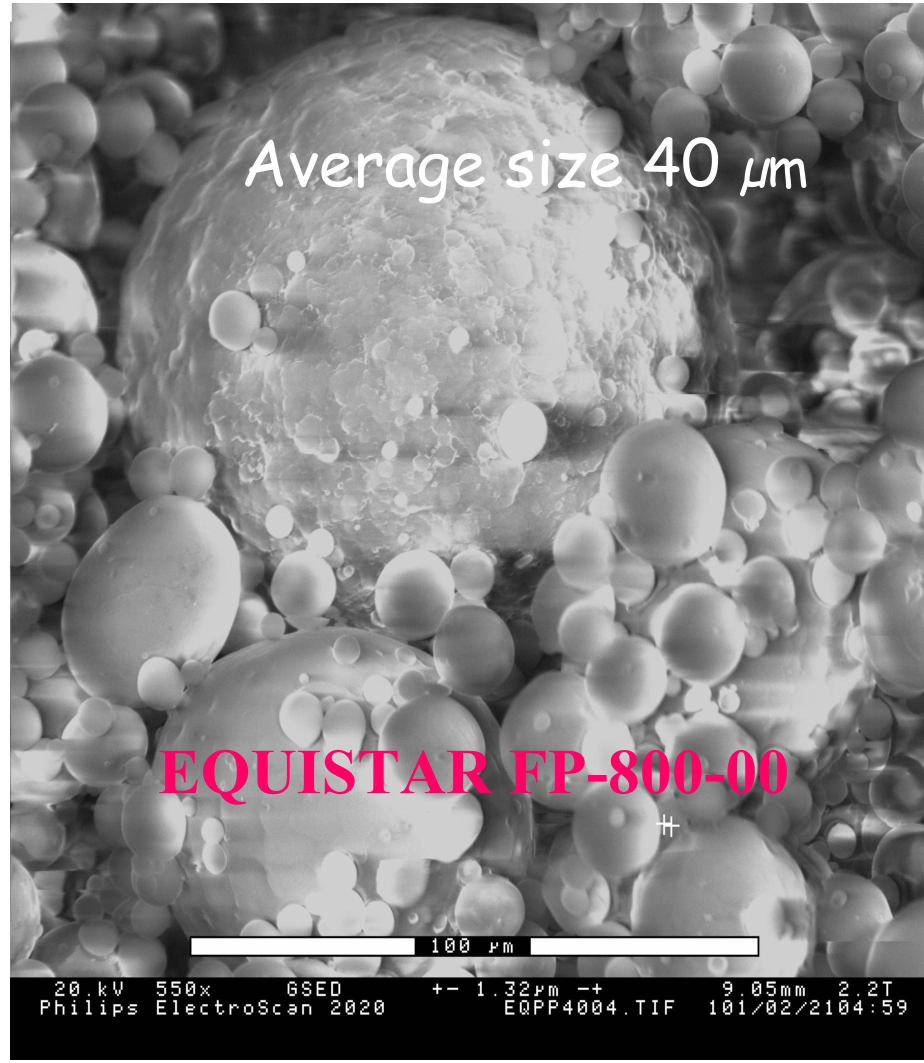
Various Stages of Consolidation



Drzal et al. US Patent, 5,102,690 (1992); 5,123,373 (1992); 5,128,199 (1992)

POWDERED PolyPROPYLENE





Mixing of PP powder and Paper Stock

Hollander Beater

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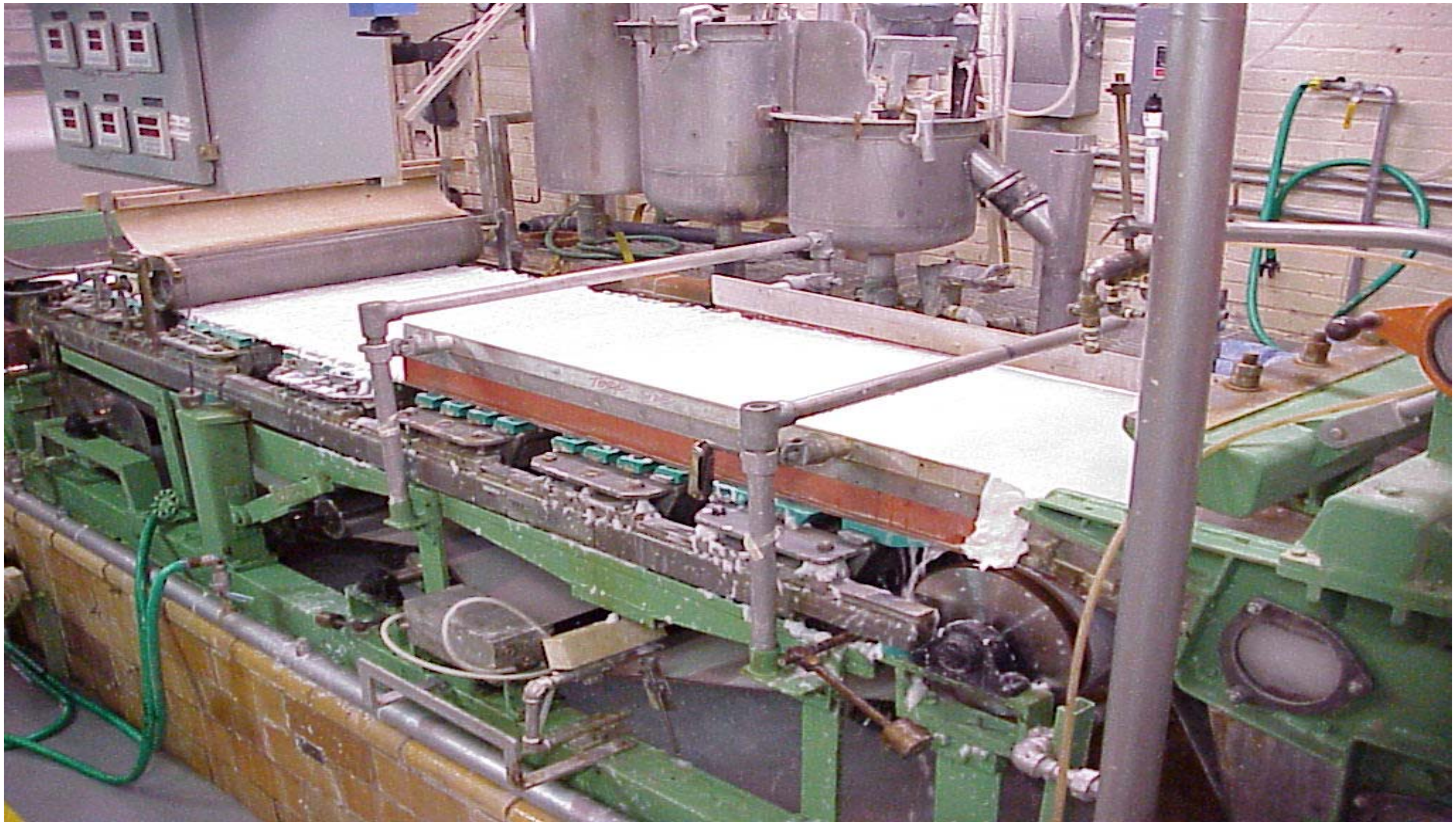
Fourdrinier (Wet) Continuous Process: 160 lb/h



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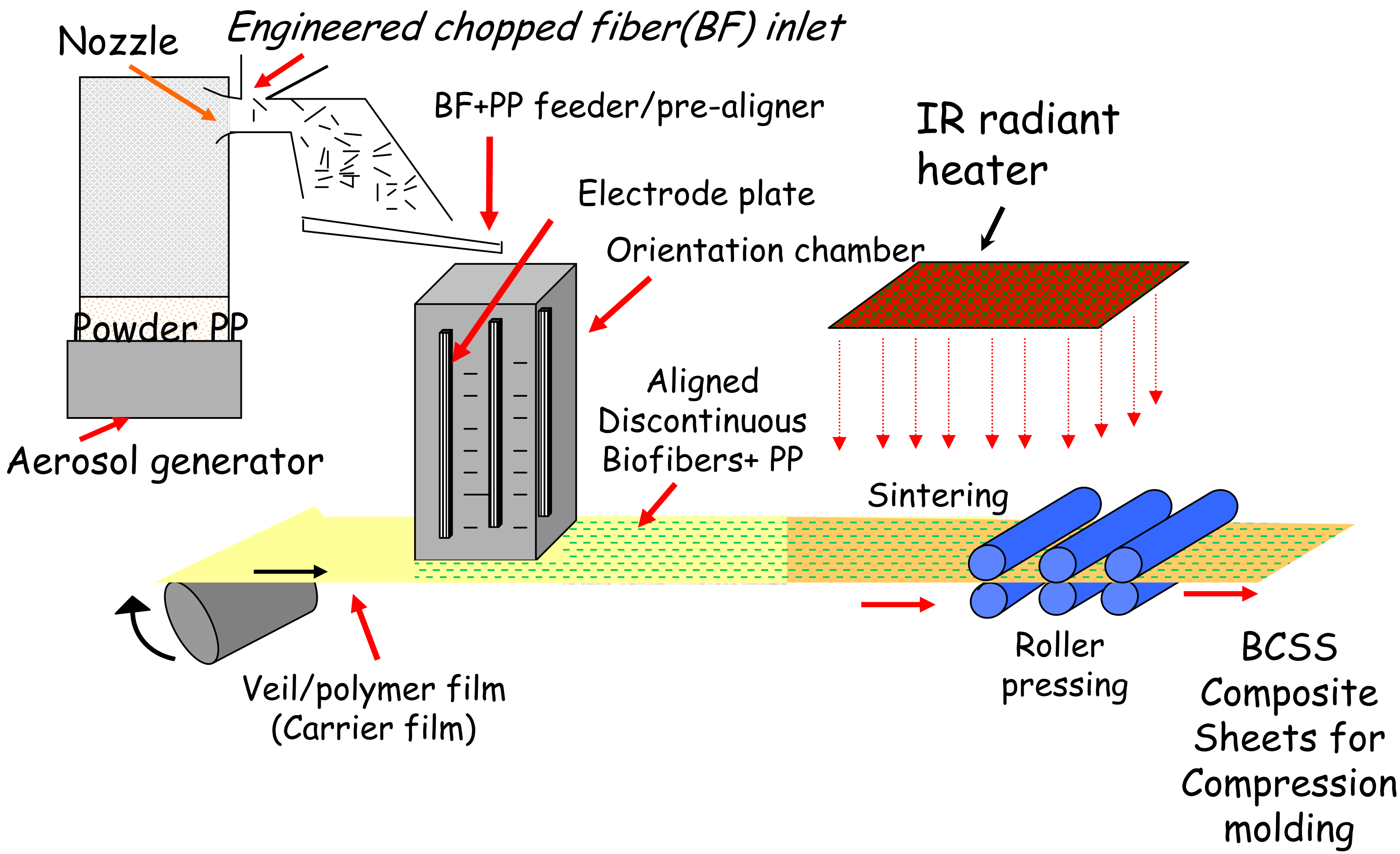
Thin sheets of Cellulose fiber-pp sheet composite



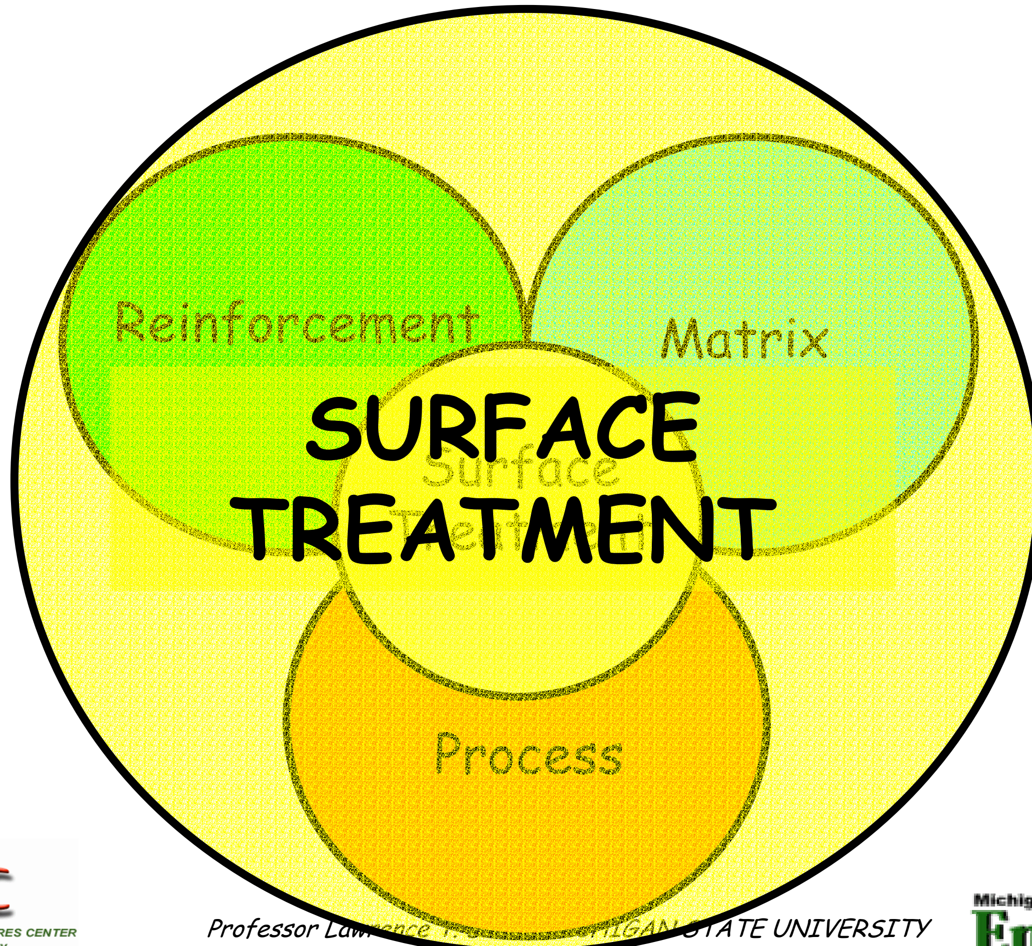
Environmentally Benign Powder (DRY) Processing

Powder Impregnation Technology

ADVANTAGES

- Environmentally Benign
- No organic solvent (WET or DRY)
- Low Void-composites - better properties
- Mixing and dispersion of multiple components of is easy
- Low cost processes
- Low energy consumption
- High Process Speed
- Powders are recyclable

Factors Necessary for Development of a BioComposite System



Surface Modification of BioFibers

Why surface modification?

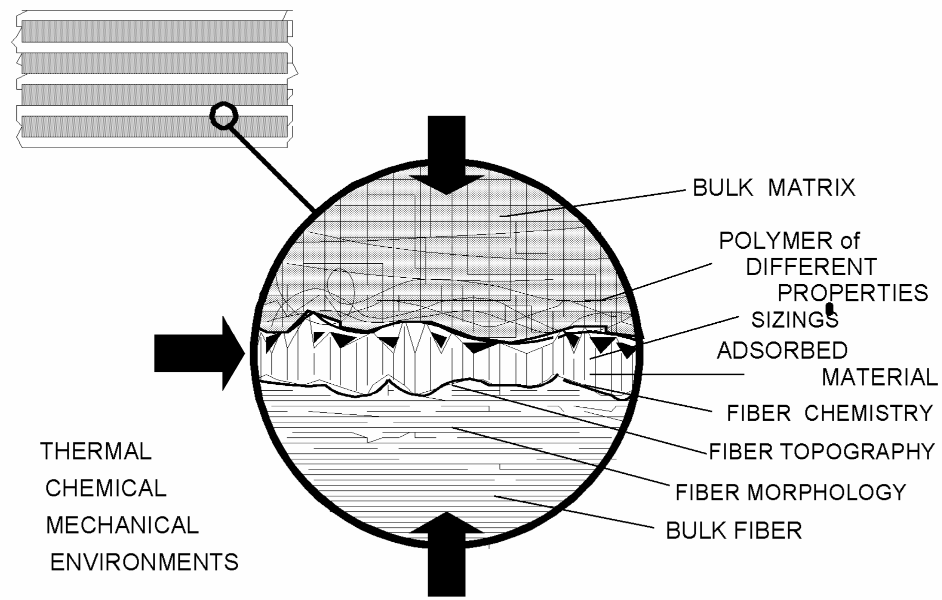
Improve:

- Wettability
- Adhesion
- Strength
- Impact
- Durability

Modification Strategies?

* Alkali treatment
* Silane treatment
* Maleated Polyolefins
* Ammonia Explosion

Isocyanate, Bleaching, Plasma, Grafting, Acetylation

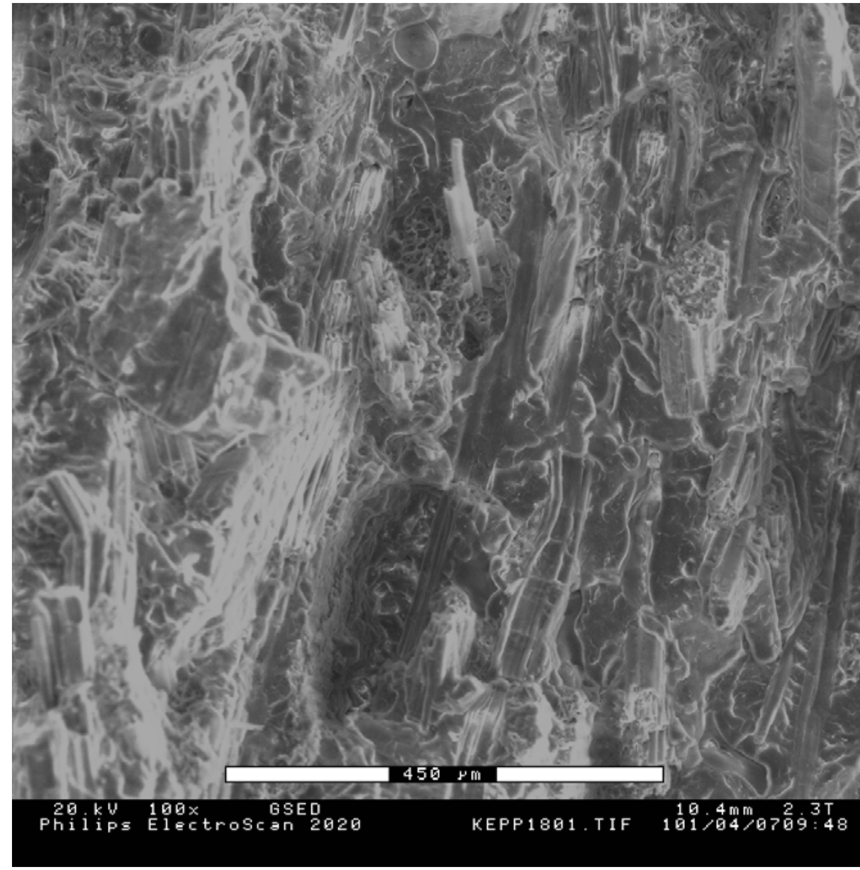


BioComposites utilizing Engineered Natural Fibers

ESEM pictures of Kenaf - PP Composites

scale bar 450 μm

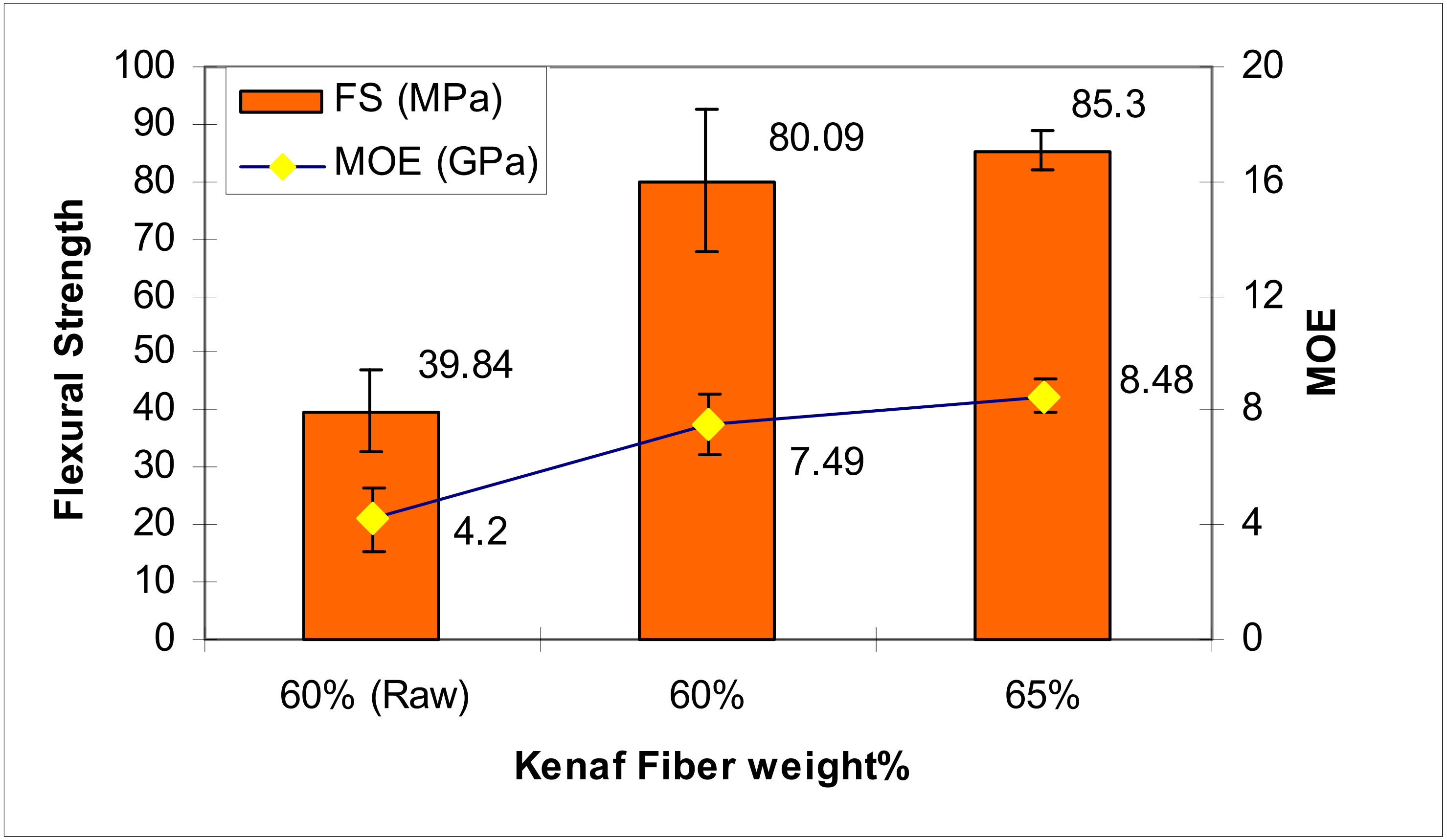
Raw Kenaf-PP 100X



Hybrid coupling agent treated Kenaf-PP 100X

Optimum Surface Treatment for HIGH FIBER CONTENT BIO-COMPOSITES

Used Optimum Content Of Coupling Agent: 3% MAPP



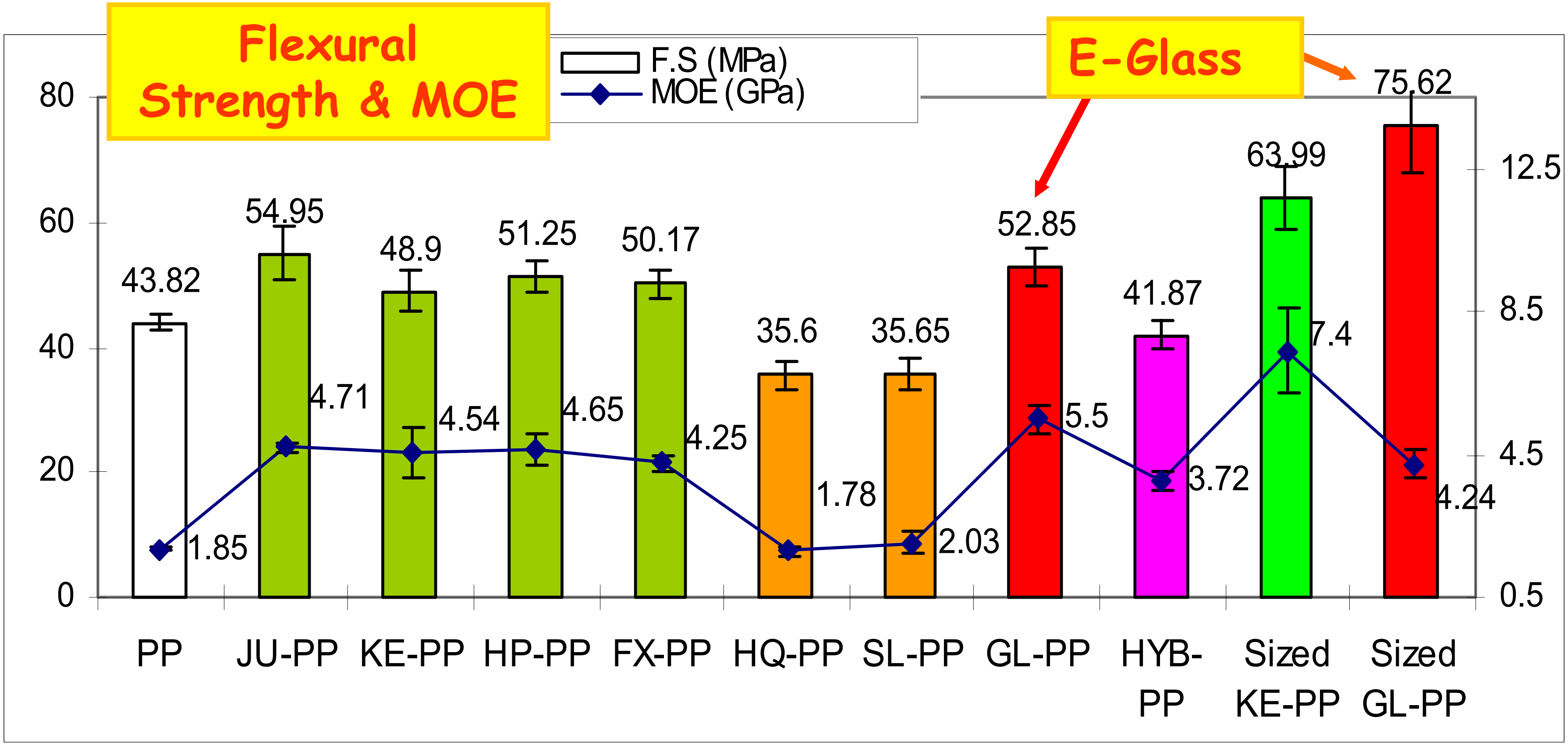
Result: (High Fiber content) FS: 85 MPA, MOE: 8.5 GPa

ACCEPTANCE CRITERIA for BIOCOMPOSITES

1. Performance
1. Cost

2. Natural Resource Based
3. Renewable
4. Recyclable
etc.

BIOFIBER – POLYPROPYLENE COMPOSITES (40 wt.% Fiber –Powder Processing)

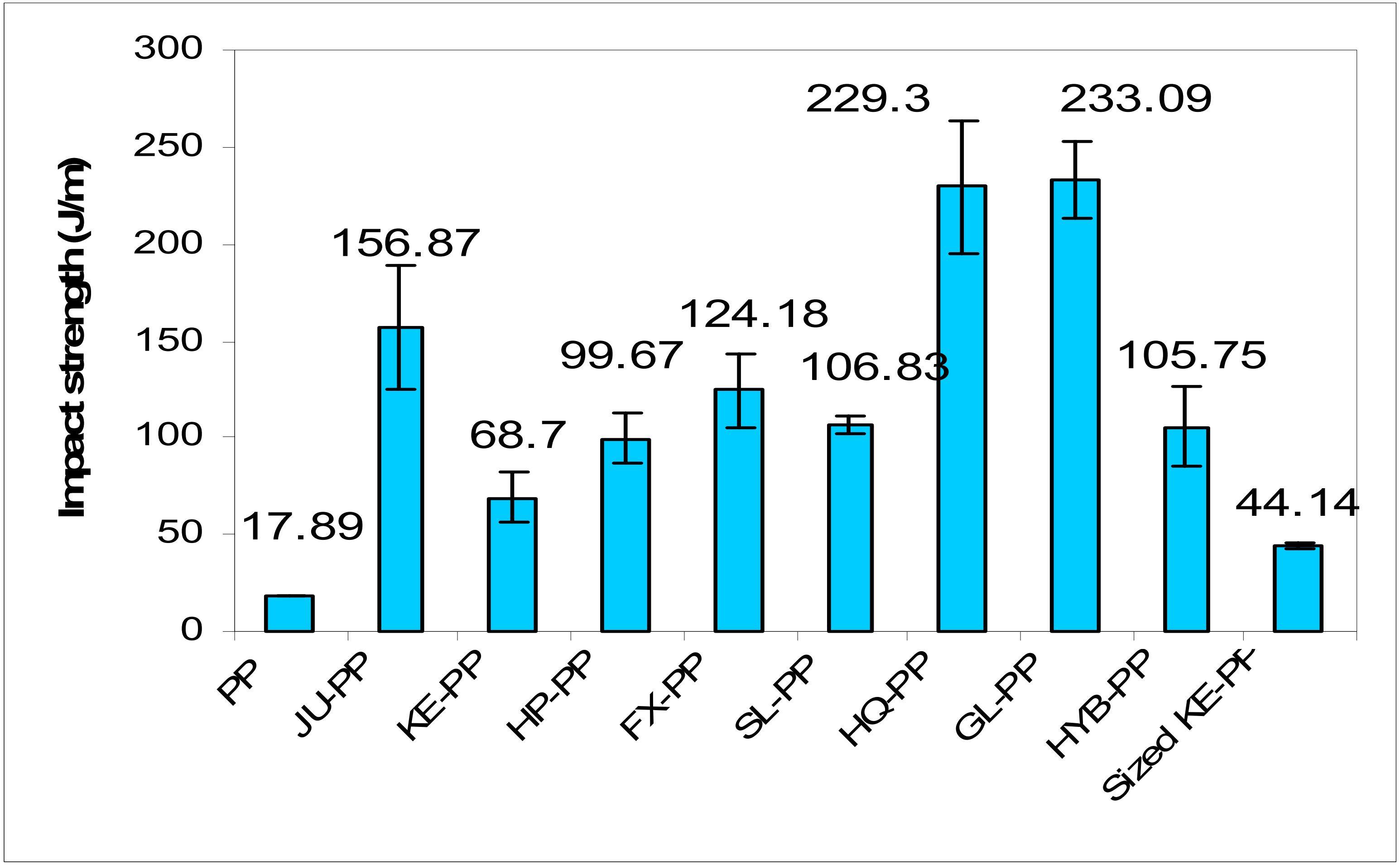


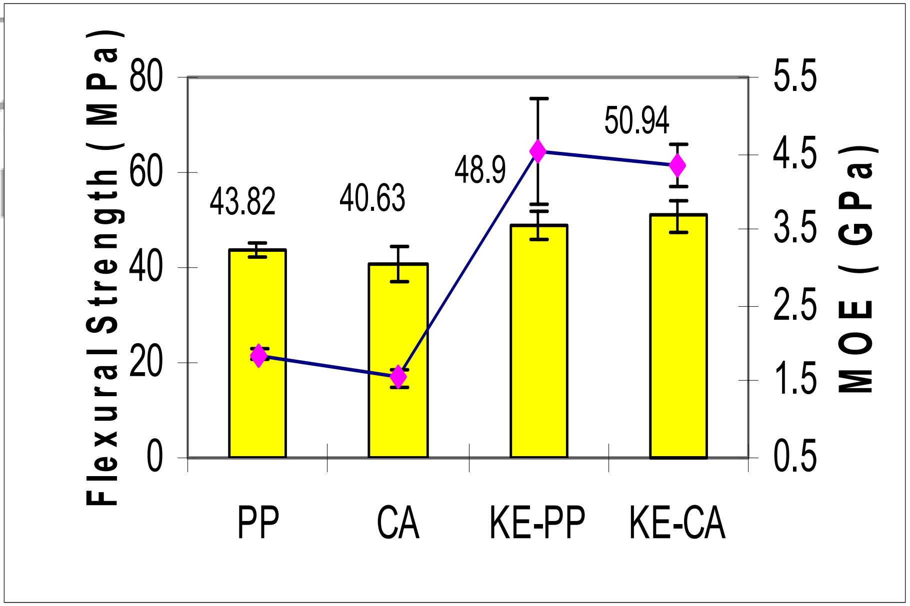
HYB: 15% KE, 15%FX, 10% SL

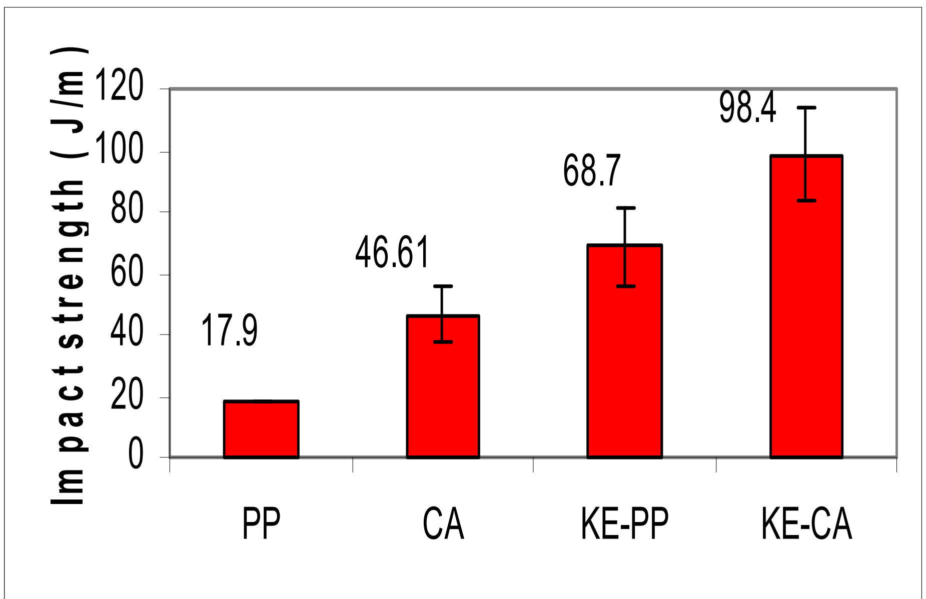
Sized: Hybrid water-based sizing (Silane + Maleated PP Emulsion)

Bio-composites show: Comparable FS & superior MOE over Glass Fiber Composites

IMPACT STRENGTH OF HENEQUEN BIO-COMPOSITES COMPARABLE TO GLASS FIBER COMPOSITES



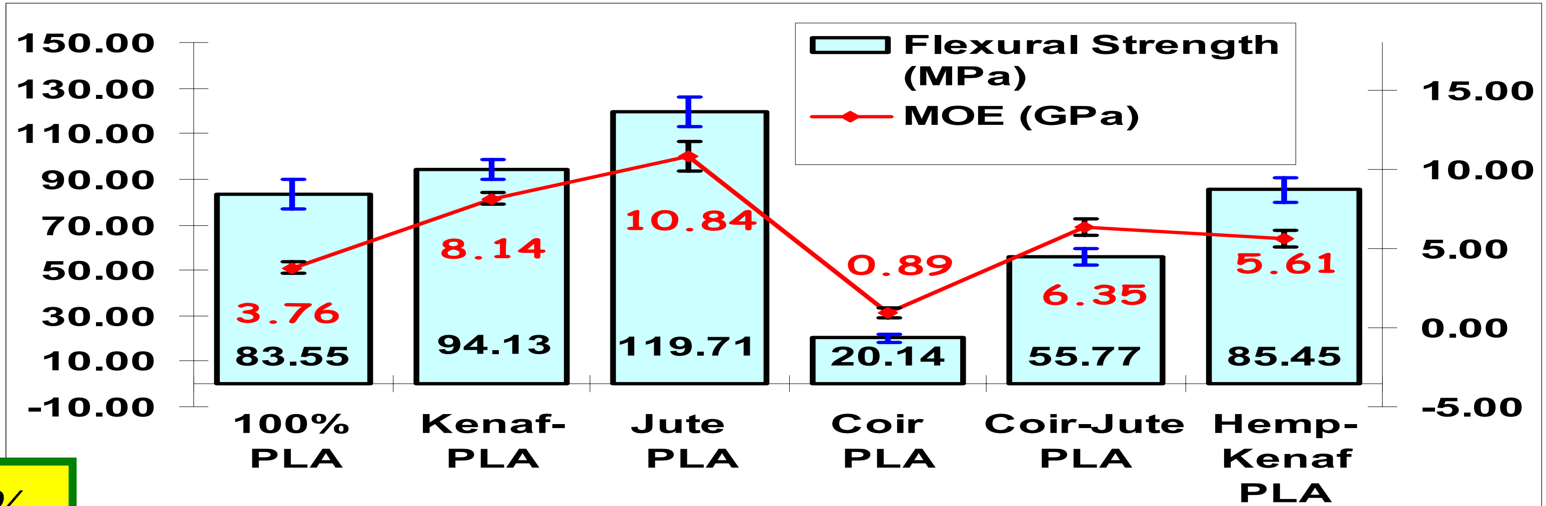




Natural Fiber (40 wt.%) PP Vs. Cellulose Acetate (CA) Green Bio-Composites (Powder Processing -- Short fiber)

- **Need for more Eco-friendly Green Composite materials**
- **Bioceta/Cellulosic plastic shows better Impact over PP**
- **KE/Cellulose–based composites: best flexural and modulus**
- **Ultimate Goal: Engineered Natural Fiber and Continuous BCSS Process**

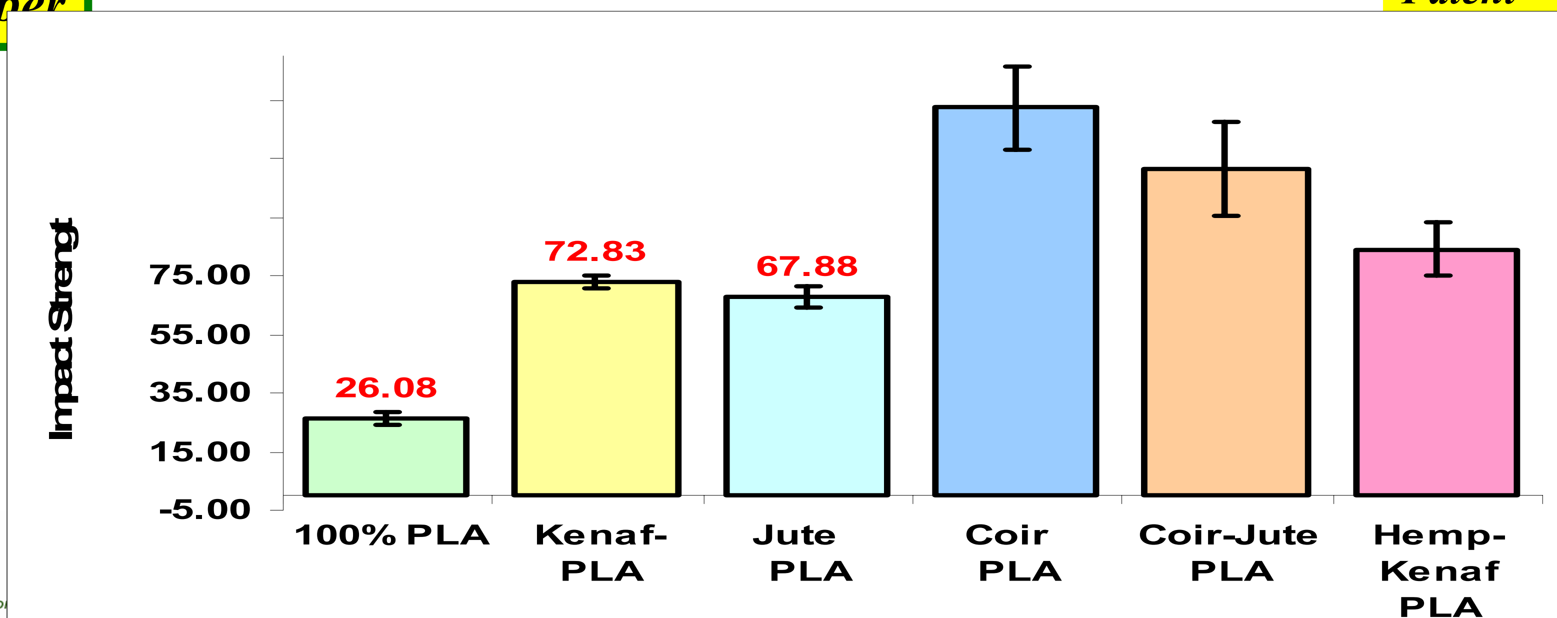
PLA-BASED BIO-COMPOSITES



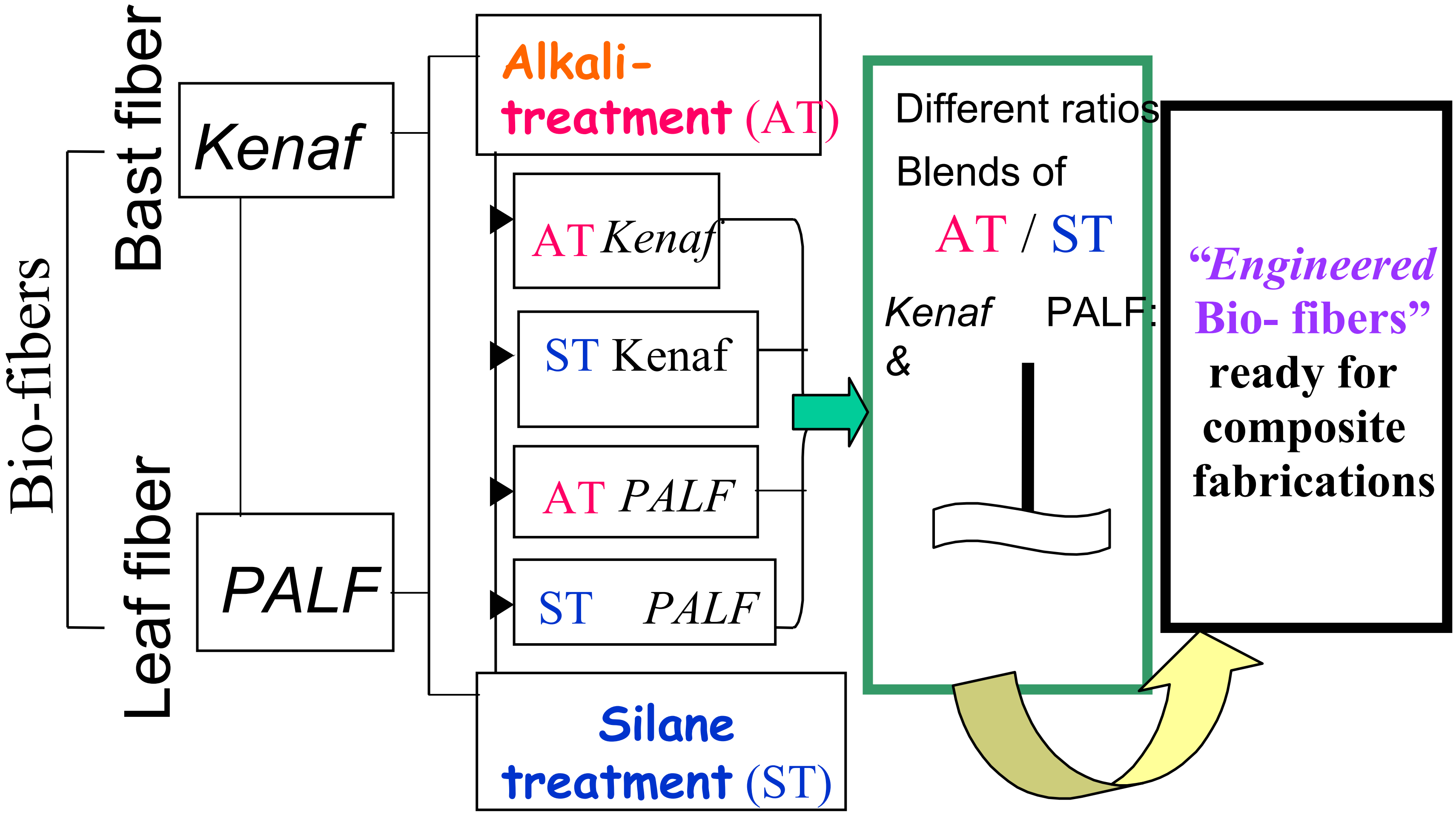
45 wt.% Bio-fiber

Enhancement: 44% in FS and 188% in MOE

Patent



THE CONCEPT OF ENGINEERED NATURAL/BIO-FIBERS



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SUMMARY

- ***Plant Derived Fiber and Crop Derived Plastics ARE the Materials of 21st Century: Eco-friendly BioComposites***
  - ✓ Replace/Substitute Glass Fiber Petroleum Based Composites
  - ✓ Energy benefit
  - ✓ Renewability, potential to replace/supplement of PP, PE
  - ✓ Biodegradability,
  - ✓ CO_2 sequestration
  - ✓ Reduce Dependence on Petroleum Resources
  - ✓ Value-Added Opportunity for Agricultural Industry
- ***Challenges***
  - ✓ Consistent Material Properties
  - ✓ Stable during storage, shipment, use
  - ✓ Biodegradable/Recyclable after disposal
  - ✓ Large-scale and new processing technology
  - ✓ Hybridization of Matrix and Reinforcement
  - ✓ Design with Higher degree of variability

MSU BIOCOMPOSITES RESEARCH GROUP