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

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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

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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

Factors:
- Reinforcement
- Matrix
- Process

Treatment

REINFORCEMENTS
BIOFIBERS - Cellulose + Lignin

Structure of cellulose

Structure of lignin
NATURAL FIBERS

FLAX
HEMP
KENAF
JUTE
HENEQUEN
COIR
WOOD
CORN
GRASS
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BIOFIBERS vs. GLASS
(Specific Strength/Modulus)

**Tensile properties**

- E- Glass
- Kenaf
- Hemp
- PALF

**Specific Strength**

- E-Glass: 1750
- Kenaf: 700
- Hemp: 800
- PALF: 900

**Specific Modulus**

- E-glass: 700
- Hemp: 615
- Flax: 750
- PALF: 786

**Modulus**

- E-modulus (GPa)
- Specific modulus

E-glass, Hemp, Flax
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Cellulose microfibrils
- (5nm x 150-300nm)
- monocrystraline 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

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost (U.S. Cents/lb.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>90</td>
</tr>
<tr>
<td>Biofiber</td>
<td>25</td>
</tr>
</tbody>
</table>

Weight savings

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>2.6</td>
</tr>
<tr>
<td>Biofiber</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Energy savings

<table>
<thead>
<tr>
<th>Material</th>
<th>E (BTUs)/lb. fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>23,500</td>
</tr>
<tr>
<td>Kenaf</td>
<td>6,500</td>
</tr>
</tbody>
</table>

- Biodegradability and Recyclability
- EcoFriendly ‘GREEN’ Material
- CO₂ Sequesterization
- Mechanical PERFORMANCE
Factors Necessary for Development of a BioComposite System
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)
- Polyhydroxy-butyrate co-valerate (PHBV)

Biopolymer blends
- Starch blends
- Polyester
- Other blends


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**Chemical Structure of some Biopolymers**

**Chemical Structure**

- Poly(alpha-hydroxy acid)
  \[
  \left[ \begin{array}{c}
  \text{O} \\
  \text{CH} \\
  \text{C} \\
  \text{R} \\
  \text{O} \\
  \end{array} \right]_n
\]

**Examples**

- \( R = \text{H}, \) Poly(glycolic acid), PGA
- \( R = \text{CH}_3, \) Poly(lactic acid), PLA

- Poly(beta-hydroxy alkanoate)
  \[
  \left[ \begin{array}{c}
  \text{O} \\
  \text{CH} \\
  \text{C} \\
  \text{R} \\
  \text{O} \\
  \end{array} \right]_n
\]

**Examples**

- \( R = \text{CH}_3, \) Poly(beta-hydroxybutyrate), PHB
- \( R = \text{CH}_3, \text{C}_2\text{H}_5, \) Poly(betahydroxybutyrate-co-valerate) PHBV (BIOPOL)

- Poly(omega-hydroxy alkanoate)
  \[
  \left[ \begin{array}{c}
  \text{O} \\
  \text{CH}_2 \\
  \text{C} \\
  \text{O} \\
  \end{array} \right]_n
\]

**Examples**

- \( x = 5, \) Poly(epsilon-caprolactone), PCL

- Poly(alkylene dicarboxylate)
  \[
  \left[ \begin{array}{c}
  \text{O} \\
  \text{CH}_2 \\
  \text{C} \\
  \text{O} \\
  \end{array} \right]_n
\]

**Examples**

- \( x = 2, \) Poly(ethylene glycol), PEG
- \( x = 4, \) Poly(butylene glycol), PBO
- \( x = 4, y = 2, \) Poly(butylene glycol-co-caprolactone), PBC
- \( x = 4, y = 2,4, \) Poly(butylene glycol-co-caprolactone), PBCA
- \( x = 2, y = 2, \) Poly(ethylene glycol-co-caprolactone), PPEC
- \( x = 4, y = 2, \) Poly(butylene glycol-co-caprolactone), PBOC
- \( x = 4, y = 2,4, \) Poly(butylene glycol-co-caprolactone), PBOCA
- \( (\text{BIOPOLLE})\)
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

<table>
<thead>
<tr>
<th>Component</th>
<th>Protein Content</th>
<th>Cost/lb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defatted Flour</td>
<td>50-55%</td>
<td>$0.20</td>
</tr>
<tr>
<td>Protein Concentrate</td>
<td>65-72%</td>
<td>$0.55</td>
</tr>
<tr>
<td>Protein Isolate</td>
<td>90+%</td>
<td>$1.10</td>
</tr>
</tbody>
</table>

Soy Oil:
- Defatted Flour: $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

\[
\begin{align*}
\text{CH}_3 \! - \! (\text{CH}_2)_4 \! - \! \text{CH} \! - \! \text{CH} \! - \! \text{CH}_2 \! - \! \text{CH} \! = \! \text{CH} \! - \! (\text{CH}_2)_7 \! - \! \text{COOCH}_2 \\
\bigg/ \bigg/ \\
\text{CH}_3 \! - \! (\text{CH}_2)_4 \! - \! \text{CH} \! - \! \text{CH} \! - \! \text{CH}_2 \! - \! \text{CH} \! = \! \text{CH} \! - \! (\text{CH}_2)_7 \! - \! \text{COOCH} \\
\bigg/ \bigg/ \\
\text{CH}_3 \! - \! (\text{CH}_2)_4 \! - \! \text{CH} \! - \! \text{CH} \! - \! \text{CH}_2 \! - \! \text{CH} \! = \! \text{CH} \! - \! (\text{CH}_2)_7 \! - \! \text{COOCH}_2 \\
\bigg/ \bigg/
\end{align*}
\]

VO has a lower average epoxy functionality of 2.4

EPOXIDIZED SOYBEAN OIL (ESO)

\[
\begin{align*}
\text{CH}_3 \! - \! (\text{CH}_2)_4 \! - \! \text{CH} \! - \! \text{CH} \! - \! \text{CH}_2 \! - \! \text{CH} \! - \! \text{CH} \! - \! (\text{CH}_2)_7 \! - \! \text{COOCH}_2 \\
\bigg/ \bigg/ \bigg/ \\
\text{CH}_3 \! - \! (\text{CH}_2)_4 \! - \! \text{CH} \! - \! \text{CH} \! - \! \text{CH}_2 \! - \! \text{CH} \! - \! \text{CH} \! - \! (\text{CH}_2)_7 \! - \! \text{COOCH} \\
\bigg/ \bigg/ \bigg/ \\
\text{CH}_3 \! - \! (\text{CH}_2)_7 \! - \! \text{CH} \! - \! \text{CH} \! - \! (\text{CH}_2)_7 \! - \! \text{COOCH}_2 \\
\bigg/ \bigg/ \bigg/ \\
\end{align*}
\]

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

- Completely Biodegradable (Optional)

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

- Reinforcement
- Matrix
- Process
- Treatment

PROCESSING
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

1. Unconsolidated
2. Partly Consolidated
3. Almost Consolidated
4. Fully Consolidated

POWDERED PolyPROPYLENE

Average size: 550 µm

PROFAX 6501

Average size 40 µm

EQUISTAR FP-800-00

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Mixing of PP powder and Paper Stock

Hollander Beater

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Fourdrinier (Wet)
Continuous Process: 160 lb/h
Thin sheets of Cellulose fiber-pp sheet composite

Stored for further Compression molding

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Environmentally Benign Powder (DRY) Processing
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

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**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)*

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Flexural Strength (MPa)</th>
<th>MOE (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>43.82</td>
<td></td>
</tr>
<tr>
<td>JU-PP</td>
<td>54.95</td>
<td></td>
</tr>
<tr>
<td>KE-PP</td>
<td>48.9</td>
<td></td>
</tr>
<tr>
<td>HP-PP</td>
<td>51.25</td>
<td></td>
</tr>
<tr>
<td>FX-PP</td>
<td>50.17</td>
<td></td>
</tr>
<tr>
<td>HQ-PP</td>
<td>35.6</td>
<td></td>
</tr>
<tr>
<td>SL-PP</td>
<td>35.65</td>
<td></td>
</tr>
<tr>
<td>GL-PP</td>
<td>52.85</td>
<td></td>
</tr>
<tr>
<td>HYB-PP</td>
<td>41.87</td>
<td></td>
</tr>
<tr>
<td>Sized KE-PP</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>Sized GL-PP</td>
<td>4.24</td>
<td></td>
</tr>
</tbody>
</table>

**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
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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
Enhancement: 44% in FS and 188% in MOE
THE CONCEPT OF ENGINEERED NATURAL/BIO-FIBERS

Bio-fibers

Bast fiber

Kenaf

Alkali-treatment (AT)

AT Kenaf

ST Kenaf

AT PALF

ST PALF

Silane treatment (ST)

Different ratios Blends of

AT / ST

Kenaf & PALF:

“Engineered Bio-fibers” ready for composite fabrications
SUMMARY


√ Replace/Substitute Glass Fiber Petroleum Based Composites
√ Energy benefit
√ Renewability, potential to replace/supplement of PP, PE
√ Biodegradability,
√ CO₂ 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