Bacterial Cellulose as a Building Block for Novel Materials

Jonny J. Blaker, Koon-Yang Lee, Anne Delille, Julasak Juntaro & Alexander Bismarck

Department of Chemical Engineering
Polymer & Composite Engineering (PaCE) Group
Imperial College London

www.imperial.ac.uk/pace

© Imperial College London
Outline

- Why green(er) materials?
- Challenges/problems with renewable
- Bacterial cellulose as building block
- Examples:
  1. Fully renewable nanocomposites
  2. Utilising bacteria to modify fibre surfaces or a route to incorporate nanomaterials into composites ➔ Green hierarchical composites
  3. Renewable macroporous polymer composites
Can we contribute to the future?

City SUV (Ford Model U)
- 2.3 L motor H₂ powered
- 45 miles/gallon
- cradle-to-cradle materials for optimum health

source: http://www.motioncars.com/autobuzz/articles27/ford_modelu.html
What is the problem with our current materials?

Use it ➔ Dump it!
Where to dump our waste?
We are running out of space!
Legal requirements in EU:

  
  Legislation to encourage re-use, recycling and other forms of recovery of ELVs and ban certain hazardous substances

- **Directive on the Landfill of Waste** 1999/31/EC
  
  Legislation to prevent or reduce negative effects on the environment from landfilling of waste

  
  Legislation to tackle rapidly increasing waste stream of EEE & to reduce landfill & incineration of waste. Enforces recycling of EEE to limit the total quantity of waste going to final disposal.

ALL enforce very high recycling targets!
The Biorefinery Concept

Our Motivation

Biobased/renewable polymers  …

Biofuels / Electricity / heat

Our Motivation

Keeping carbon effectively in the loop!

Extend the life of bio-based materials

Biomass

CO₂

Biorefinery

Biofuels / Electricity / heat

Biomass

Compost

Biomass

Oils + Fibres

Cellulose Nano-whiskers

Polymers

Biobased/renewable polymers …

New Materials
Learning from the past!

**Trabant** then produced in GDR by VEB Sachsenring Zwickau

cotton waste reinforced polyester chassis
Our Motivation:

It is clear - new materials are needed!

- Recyclable or made from renewable resources with triggered biodegradability

with mechanical performance of commonly used engineering materials
Challenge to be addressed...
Challenges: Matrix Properties

Comparison of properties of renewable polymers vs. commodity & engineering polymers.

- PLA
- PHB
- Cellulose
- PMMA
- PC
- PVC
- PS
- PP
- CAB
- PCL
- LDPE
- HDPE

Graph showing tensile strength (σ) vs. elongation at break (ε) for various polymers.

Tensile strength σ / MPa
Elongation at break ε / %

- PLA
- PMMA
- Cellulose
- PHB
- PLA
- CAB
- PS
- PP
- PC
- PVC
- PS
- PMMA
- PC
- PVC
- LDPE
- HDPE
- PCL
- PLA

Materials
Example 1:
A possibility to boost the matrix performance...
What Are Composites?

Fibre
parallel strength, E-modulus

Matrix
HT-properties & transverse strength

Interphase
adhesion, load transfer & overall performance
Bacterial cellulose

Medium
(essential nutrients)

Bacteria
(Acetobacter xylinum BPR 200)

Bacterial cellulose biogenesis

Ref.: Iguchi et al., J. Mater. Sci. 35 (2000), 261
Bacterial cellulose

Synthesis of **bacterial cellulose**
(extracellular product)

Medium (essential nutrients) → **Bacteria**
*(Acetobacter xylinum BPR 2001)*

3d old culture

Young’s modulus of single nanofibril:
**78 GPa** (same as glass fibres)
(Guhados et al., 2005)

**89% Crystallinity**
(Czaja et al., 2004)
Source of Bacterial Cellulose

*Nata de coco*

A chewy, jelly-like food product produced by the bacterial fermentation of coconut water.

Originates from the Philippines.

Each 500 g net jar contents gives ~ 1.2 g dry weight bacterial cellulose
Extraction of bacterial cellulose from *Nata de coco*
Purification of Bacterial Cellulose

- Redisperse centrifuged bacterial cellulose in water.
- Add NaOH (0.1 M).
- @ 80°C for 20 min
- Wash until neutral pH
Cellulose functionalisation necessary to boost the matrix performance!
Hydrophobisation of Bacterial Cellulose
via organic acid esterification

Reaction in presence of pyridine at 50°C

Morphology of modified bacterial cellulose

Pure BC

C₂-BC

C₆-BC

C₁₂-BC
Did we modify cellulose? FTIR confirmation

- C=O
- CH₂
- OH
Contact angle (water-in-air)
Crystallinity of modified Bacterial Cellulose: WAXD

Segal's equation:

\[
\text{Crystallinity Index} = \frac{I_{002} - I_{\text{amorphous}}}{I_{002}} \times 100\%
\]
Will interaction between modified nanocellulose and matrix improve?
Interaction between PLLA and BC

0.05 wt% BC in chloroform + 0.06 wt% PLLA in chloroform

Non-solvent bath (80 Chloroform: 20 Hexane)

Collect precipitate by filtration, melt it & then SEM!

US for 1 h

Measuring the receding contact angle using Generalised Drop Length-Height method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact Angle °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat BC</td>
<td>35.4 ± 0.8</td>
</tr>
<tr>
<td>C₂-BC</td>
<td>29.5 ± 2.9</td>
</tr>
<tr>
<td>C₆-BC</td>
<td>27.7 ± 2.0</td>
</tr>
<tr>
<td>C₁₂-BC</td>
<td>20.8 ± 2.5</td>
</tr>
</tbody>
</table>

Dry processing BC nanofibrils: TIPS

- Compounding of never-dried & dried BC nanofibrils difficult

Possibility composite microspheres made by Thermally Induced Phase Separation (TIPS)

90 mL 1,4-dioxane

BC

PLLA (1:12 g mL⁻¹)

Syringe

PLLA+BC droplets

liquid N₂ bath

Freeze drying

Processing via conventional twin-screw extrusion process!!
## Properties of PLLA/PC Nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>M&lt;sub&gt;W&lt;/sub&gt; (kDa)</th>
<th>X&lt;sub&gt;c&lt;/sub&gt; (%)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;c&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;d&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLLA</td>
<td>1.34 ± 0.04</td>
<td>60.7 ± 0.8</td>
<td>3.59 ± 0.07</td>
<td>157</td>
<td>47.5</td>
<td>59</td>
<td>118</td>
<td>165, 170</td>
<td>256</td>
</tr>
<tr>
<td>PLLA/BC (2 wt%)</td>
<td>1.75 ± 0.05</td>
<td>57.5 ± 1.4</td>
<td>2.85 ± 0.12</td>
<td>147</td>
<td>45.1</td>
<td>59</td>
<td>102</td>
<td>168</td>
<td>275</td>
</tr>
<tr>
<td>PLLA/BC (5 wt%)</td>
<td>1.89 ± 0.02</td>
<td>60.9 ± 0.5</td>
<td>2.41 ± 0.08</td>
<td>146</td>
<td>45.0</td>
<td>59</td>
<td>99</td>
<td>167</td>
<td>279</td>
</tr>
<tr>
<td>PLLA/C&lt;sub&gt;2&lt;/sub&gt;BC (2 wt%)</td>
<td>1.71 ± 0.06</td>
<td>53.0 ± 1.4</td>
<td>2.23 ± 0.07</td>
<td>116</td>
<td>45.3</td>
<td>59</td>
<td>104</td>
<td>168</td>
<td>262</td>
</tr>
<tr>
<td>PLLA/C&lt;sub&gt;2&lt;/sub&gt;BC (5 wt%)</td>
<td>1.70 ± 0.03</td>
<td>60.1 ± 0.9</td>
<td>2.62 ± 0.07</td>
<td>135</td>
<td>42.7</td>
<td>59</td>
<td>105</td>
<td>168</td>
<td>270</td>
</tr>
<tr>
<td>PLLA/C&lt;sub&gt;6&lt;/sub&gt;BC (2 wt%)</td>
<td>1.63 ± 0.04</td>
<td>66.1 ± 2.4</td>
<td>3.12 ± 0.09</td>
<td>157</td>
<td>42.5</td>
<td>59</td>
<td>106</td>
<td>169</td>
<td>270</td>
</tr>
<tr>
<td>PLLA/C&lt;sub&gt;6&lt;/sub&gt;BC (5 wt%)</td>
<td>1.79 ± 0.02</td>
<td>65.1 ± 0.9</td>
<td>2.87 ± 0.03</td>
<td>153</td>
<td>41.6</td>
<td>59</td>
<td>106</td>
<td>169</td>
<td>276</td>
</tr>
<tr>
<td>PLLA/C&lt;sub&gt;12&lt;/sub&gt;BC (2 wt%)</td>
<td>1.66 ± 0.05</td>
<td>63.0 ± 1.2</td>
<td>3.21 ± 0.04</td>
<td>149</td>
<td>45.8</td>
<td>59</td>
<td>105</td>
<td>169</td>
<td>271</td>
</tr>
<tr>
<td>PLLA/C&lt;sub&gt;12&lt;/sub&gt;BC (5 wt%)</td>
<td>1.98 ± 0.04</td>
<td>68.5 ± 1.5</td>
<td>2.69 ± 0.06</td>
<td>157</td>
<td>44.3</td>
<td>59</td>
<td>97</td>
<td>167</td>
<td>268</td>
</tr>
</tbody>
</table>

**15% Increase in Tensile Strength!!**

**50% Increase in Tensile Modulus!!**
Summary
Example 2:
A possibility to improve composite performance...
What are hierarchical composites?

Using “hairy” fibres to deliver nano-reinforcement should improve:

- dispersion & alignment of nano-reinforcement
- interfacial area & bonding
- through-thickness strength & other critical properties
Aim: What we want!

Environmentally Friendly Truly Green

Hierarchical Nanocomposites

Recyclable Biodegradable

Made entirely of renewable resources

Composed of:

- Natural fibres (Hierarchical by themselves)
- Bio-polymer (Mesoscale)
- Bacterial cellulose (Nanoscale)

Biopolymer matrix

Modified fibres

Fibre surface

Bacterial cellulose
A green (natural) fibre surface treatment procedure or how bacteria can help us!
A renewable route to nanomaterial enhanced fibre surfaces

Schematic of our method:

- Plant fibres
- Bacteria culture medium
- Inoculation with the cellulose producing bacteria
- Gluconobacter fermentation for 1 week → Strain BRP 2001 (suitable for dynamic culture)

Using Bacteria to enhance fibre surface properties

Photographs of sisal fibres before and after 2 days in the static bacterial culture
Sisal after Cellulose Fermentation
Extraction of modified fibres in NaOH at 80°C
Bacterial Cellulose coated Sisal
How do we do it?

Method

Instrumented fermentor

Cassette with plant fibres

Stoppers

Glass vessel

Ref.: M. Pommet et al., Biomacromol. 9 (2008) 1643.

Culture conditions: T = 37°C; pH 5.5; agitation 700 rpm; aeration 5 l/min; carbon: source fructose
Bacterial Cellulose Modified Natural Fibres

Original Hemp:
- σ = 286 ± 31 MPa
- E = 21.4 ± 2.0 GPa

Modified Hemp:
- σ = 130 ± 12 MPa
- E = 8.0 ± 0.6 GPa

Original Sisal:
- σ = 338 ± 25 MPa
- E = 15.2 ± 0.9 GPa

Modified Sisal:
- σ = 352 ± 27 MPa
- E = 15.2 ± 1.7 GPa
Are nanocellulose modified fibres useful?
Fibre/Matrix Adhesion

– Single Fibre Pull-Out Test

Interfacial Shear Strength \( \tau_{IFSS} \) as Measure of ‘practical’ Adhesion!

\[
\tau_{IFSS} = \frac{F_{\text{max}}}{p \cdot L_e}
\]

\( F_{\text{max}} \) ... max. pull-out force
\( p \cdot L_e \) ... embedded fibre area

Source.: www.bam.de

Single Fibre Pull-out Test  Force-Displacement curve during pull-out

with G. Kalinka

BAM
Nanocellulose enhanced interfaces in green composites

IFSS of (modified) sisal & hemp fibres/PLLA model composites

Ref.: M. Pommet et al., Biomacromol. 9 (2008) 1643.
Does the improved interaction between fibres and matrix translate result in better composite properties?
Nanocellulose Enhanced Composite Interfaces

<table>
<thead>
<tr>
<th>Fibre Orientation</th>
<th>CAB/Hemp FVC = 30%</th>
<th>CAB/Sisal FVC = 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>unmodified 0°</td>
<td>100 ± 13</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>“grafted” 0°</td>
<td>90 ± 14</td>
<td>6 ± 0.5</td>
</tr>
<tr>
<td>unmodified 90°</td>
<td>16 ± 2</td>
<td>2 ± 0.1</td>
</tr>
<tr>
<td>“grafted” 90°</td>
<td>13 ± 1</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>PLLA/Hemp FVC = 30%</td>
<td>110 ± 30</td>
<td>12 ± 4</td>
</tr>
<tr>
<td>“grafted” 0°</td>
<td>105 ± 10</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>unmodified 90°</td>
<td>13 ± 4</td>
<td>3 ± 0.2</td>
</tr>
<tr>
<td>“grafted” 90°</td>
<td>13 ± 2</td>
<td>2 ± 0.3</td>
</tr>
</tbody>
</table>

Parallel (0°) and off-axis (90°) tensile strength σ and Young’s modulus E of original and bacterial cellulose grafted hemp and sisal reinforced CAB and PLLA.

Conclusion! Introduction of bacterial cellulose onto natural fibres allows to create Hierarchical composite structures

This leads to ...

- better Interfacial Adhesion between NF and renewable polymers (CAB & PLLA)
- bacterial cellulose directly reinforces polymer matrix

& eventually to UD sisal/PLLA composites with better performance!!

& even improved short sisal fibre/CAB composites
Example 3:
Making renewable macroporous nanocomposite foams
HIPEs to polyHIPEs

**HIPE**

- continuous *organic* phase: max. 26 vol.-% monomers (DVB, styrene, ...), initiator and 5 – 50 % surfactant (common ≈ 20 %)
- internal *aqueous* phase: electrolyte solution with volume fraction of min. 74 vol.-%
- very viscous, metastable

**polyHIPE**

- foams with an interconnected pore structure
- low materials density
- porosity up to 95%
More (possible) Applications for polyHIPEs:

- Filters
- Absorbents
- Demulsifiers
- Scaffolds for TE
- Static Stirrers
- Catalyst supports

Membranes
Monoliths
Beads
Preparing **High Internal Phase Emulsions**

- **HIPE**: Oil phase (with surfactant) + aqueous phase + agitation

![Diagram showing the preparation of HIPE](image)

- **LIPE**: Dilute emulsion, \( \Phi < 30\% \)
- **MIPE**: Concentrated emulsion, \( 30\% < \Phi < 70\% \)
- **HIPE with deformed droplets**
- **polyHIPE**: interconnected cell structure
Particle Stabilised Emulsions

Static stabilisation by particles
(Ramsdon or Pickering Emulsions)

- Hydrophilic particles: $\theta < 90^\circ$
- Hydrophobic particles: $\theta > 90^\circ$
Making renewable polyPolyPickering nanocomposite foams

1. Greener monomer phase

Acrylated Epoxidized Soybean Oil (AESO)
How we make foams using these esterified cellulose nano-fibrils

50:50 Soybean oil to H₂O + 100 mg Cₓ-BC

Homogenise & shake at 4 Hz + leave for 24 h

Extract ejected phase + replace soybean oil with AESO and UV initiator

UV flood lamp [100 W]
Unmodified cellulose ➔ no foam!

Bacterial cellulose flocculates in aqueous phase
Cured renewable nanocomposite foam

[Graph showing porosity, modulus, and crush strength vs. position in foam]
Conclusions

No Soap Required!

Thank You!

A sponsor that went out of business &

EPSRC
Challenging Engineering

+ 

EPSRC
Engineering and Physical Sciences Research Council

for funding
We hope to receive your contribution soon.