Green ionic liquids for the production of fully biobased and biodegradable all-cellulose composites

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All-cellulose composites

• Fully biobased and biodegradable composite material composed solely of cellulose.
• Manufactured by:
  – (i) mixing fully dissolved cellulose and undissolved cellulose
  – (ii) by consolidating partially dissolved cellulose.
• The material needs to be regenerated (precipitated) and dried.
• Excellent mechanical properties.
Outline

• Background:
  – General idea
  – Partial dissolution
  – Comparison with other materials
  – Solvents

• Experimental procedures:
  – Materials
  – Characterization
  – Manufacturing

• Results:
  – XRD
  – Mechanical properties
  – SEM
  – DP

• Conclusions
  – Schematic
  – General remarks
The philosophy behind all-cellulose composites

Composite → Matrix → Reinforcement

Regenerated cellulose obtained by cellulose dissolution, insureing excellent interfacial chemical bonding

Natural fibre from ramie, wood pulp, rice husk, MCC, BC, etc

Regenerated fibre: high-strength, high modulus, high orientation fibres

Cellulose I crystallites: $E_{\text{cellulose I}} > E_{\text{cellulose II}}$

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{cellulose I}}$ (GPa)</th>
<th>$E_{\text{cellulose II}}$ (GPa)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>138</td>
<td>88</td>
<td>Nishino 1995</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>75</td>
<td>Ishikawa 1997</td>
</tr>
</tbody>
</table>
Manufacturing by partial dissolution: step 1

- Crystallites ~3-7 nm initially present in the material.
- Non-crystalline phase surrounding the crystallites and making the microfibrils.
- Solvent
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Manufacturing by partial dissolution: step 2

- Crystallites
- Non-crystalline phase
- Solvent
- Dissolved cellulose
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Manufacturing by partial dissolution: steps 3 and 4

- Crystallites
- Dissolved cellulose
- Precipitation medium
- Regenerated cellulose
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What all-cellulose composites are not

- Tracing paper
- Vulcanized paper
- Cellophane
- Regenerated films from NMMO

Specialty papers

Regenerated cellulose
Mechanical properties of all-cellulose composites compared

Regular paper, GF weave/epoxy, regenerated cellulose films, MFC composites (low resin content), nanofibrillated cellulose paper, all-cellulose composites
Mechanical properties of all-cellulose composites compared

- Young's modulus (GPa)
- Strain (%)

Regular paper, GF weave/epoxy, regenerated cellulose films, MFC composites (low resin content), nanofibrillated cellulose paper, all-cellulose composites
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The *greenness* of all-cellulose composites...

...is determined by the choice of solvent

<table>
<thead>
<tr>
<th>Factors</th>
<th>Efficiency</th>
<th>Temperature</th>
<th>Viscosity</th>
<th>Recyclability</th>
<th>Hygroscopicity</th>
<th>V.O.C.</th>
<th>Pre-treatment</th>
<th>Toxicity</th>
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</thead>
<tbody>
<tr>
<td>LiCl/DMAc</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✔️</td>
<td>✔️</td>
<td>✗</td>
</tr>
<tr>
<td>Ionic liquids (*)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✔️</td>
<td>✔️</td>
<td>✔️</td>
</tr>
</tbody>
</table>

(*): BmimCl (a.k.a. \([C_4\text{mim}]\text{Cl}\)), BmimBr, BmimSCN, BmPyCl, AmimCl, EmimAc, EmimDEPO, ...
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Materials

- **Whatman filter paper** grade 40 (95 g/m², ash content < 0.007%) from cotton linters, DP = 1240.

- **Microfibrillated cellulose** (Daicel chemicals, lot # 75203) from wood pulp, vacuum filtered and hot pressed at 100°C and 1.5 MPa, DP = 1000.

- **1-butyl-3-methylimidazolium chloride**, [C₄mim]Cl, 95% purity, BASF.
Characterization

- **Mechanical testing:** Shimadzu Autograph AG-X, 55% R.H., 20 °C, 1 mm/min, 20 mm gage length.

- **X-ray diffraction:** Siemens D5000, Cu Kα source ($\lambda = 0.15418$ nm), 40 kV acceleration voltage and 40 mA current. $CrI$ calculated using Segal's method (1959).

- **Scanning electron microscopy:** Jeol JSM 6460LV, 10 kV acceleration voltage, samples gold coated and mounted on carbon tabs.

- **Degree of polymerization:** dissolution in 4.6 wt.% LiOH/15 wt. % urea (Cai 2006).
• Thorough drying at 103°C
• Immersion of MFC or filter paper in [C₄mim]Cl
• Dissolution at 80°C for a time \( t \)
• Cooling for 1 hr at room conditions
• Water exchange for 2 * 24 hr at room temperature
• DI water rinsing
• Drying in a vacuum bag, 60°C overnight and pressure < 0.1 atm.
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XRD: Filter paper

- Initially: highly crystalline cellulose I.
- Broadening of the (200) peak indicative of dissolution.
- Broadening increases with dissolution time.
- (200) peak of cellulose I at ca. 22.8° remains throughout the transformation.
• Initially: highly crystalline cellulose I.
• Slight broadening of the (200) peak indicative of limited dissolution.
• Cellulose I allomorph clearly remains throughout the transformation.
XRD: \( CrI \) changes

- Only very limited change for MFC.
- More drastic decrystallization occurring for filter paper.
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Mechanical properties

- More spectacular changes could be observed for FP (□) than for MFC (■).
- MFC performed the best in terms of tensile strength and stiffness.
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SEM: filter paper

Microfibrillar structure (initially)

Fully consolidated structure (160 min dissolution)
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SEM: MFC

Submicron fibrillar structure (initially)

Partially consolidated, “skin-core” morphology (160 min dissolution)
The DP is reduced by ~40%!
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Schematic of the differences in solvent penetration

Filter paper

Microfibrillated cellulose

Initially

Solvent penetration

Final composite
Parameter interaction

- DISSOLUTION TIME
- LEVEL OF DEFIBRILLATION
- DEGREE OF POLYMERIZATION
- AMOUNT OF MATRIX & CONSOLIDATION
- CRYSTALLINITY
- HOMOGENEOUS OR SANDWICH STRUCTURE
- MECHANICAL PROPERTIES
Conclusions

• **Filter paper:**
  – Impressive increase in strength, stiffness and strain at break
  – CrI losses
  – Excellent consolidation.

• **MFC:**
  – Moderate increase in strength and stiffness
  – Highest mechanical properties
  – Limited solvent penetration due to tight interfibrillar network and high solvent viscosity.
  – High crystallinity.

• **[C₄mim]Cl:**
  – Depolymerized the cellulose
  – Could be recycled by evaporation and re-used.
Acknowledgments & references

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The greenness of all-cellulose composites...

...is determined by the choice of solvent.

- LiCl/DMAc: has been used so far for most all-cellulose composites, but...
- NMMO: is considered as being the greenest solvent industrially. However...
- Low temperatures solvents NaOH, NaOH/urea, LiOH...
- Strong acids
- Ionic liquid: not perfect (yet) but already very advantageous

FACTORS: EFFICIENCY; PRICE; AVAILABILITY; RECYCLABILITY; TOXICITY; PRESENCE OF V.O.C.; OTHER HAZARDOUS ASPECTS; EASINESS OF USE (WORKING TEMPERATURE, VISCOSITY, HYGROSCOPICITY)....
IL naming

- BmimCl (a.k.a. [C4mim]Cl): 1-butyl-3 methylimidazolium chloride
- BmimBr: 1-butyl-3 methylimidazolium chloride
- BmimSCN: 1-butyl-3 methylimidazolium sulfocyanate
- BmPyCl: 1-butyl-3-methylpyridinium chloride
- AmimCl: 1-allyl-3 methylimidazolium chloride
- EmimAc: 1-ethyl-3 methylimidazolium acetate
- EmimDEP: 1-ethyl-3 methylimidazolium diethylphosphate
- DmimDMP: 1,3-dimethylimidazolium dimethylphosphate
Isotropic biocomposites: comparison chart
Unidirectional composites: comparison chart