Rigid Polyurethane Foam/Cellulose Whiskers Nanocomposites: Preparation, Characterization and Properties
Cellulose structure and characteristics

- Polymeric chains of $\beta$-(1,4)-D-glucose units
- Abundance - Annual biomass production of $1.5 \times 10^{12}$ tons
- Renewability - Environment biocompatible products

Inter- and intra-molecule hydrogen bonding

Cellulose molecule

Plant cell

Fiber

Microfibril

Elementary fibril

Macrophibril
Preparation of cellulose whiskers

- Under certain acid hydrolysis conditions, transverse cleavage happens along the amorphous regions and releases needle-like monocrystals, which refer to whiskers.

10-20 nm in diameter
100-200 nm in length
Bending strength ~10 GPa
Elastic modulus ~143 GPa
Polyurethane structure

- Polyurethane (PU) is any polymer consisting of a chain of organic units joined by urethane links.
- Rigid PU foam is a highly crosslinking polymer with a closed-cell structure.

\[
\begin{align*}
O&=C\equiv N-R^1-N=C=O + OH-R^2-OH + O&=C\equiv N-R^1-N=C=O + OH-R^2-OH + \cdots \\
\rightarrow C&-N-R^1-N&-C&O-R^2-O& C&-N-R^1-N&-C&O-R^2-O & \cdots
\end{align*}
\]

But not as stiff as traditional materials

Strong but with
Significantly lower density
Dimensional stability
Thermal insulation
Good adhesive properties
Impervious to moisture
Low cost
Objective-improve mechanical properties

- Solar energy
- Feedstock
- Physical, chemical or enzyme treatment
- Rigid PU nanocomposite foam
- Other polymers e.g. PU
- Cellulose whiskers
- Other polymers e.g. PU

Other polymers e.g. PU
Reagents

Sucrose-based polyol (S polyol), $F = 4.4$
Glycerol-based polyol (G polyol), $F = 3$
Polymeric methylene diphenyl diisocyanate (MDI), $F = 2.7$
Dimethylcyclohexylamine (DMCHA)
Potassium octotate
Silicon surfactant
n-pentane (boiling point 36.1$^\circ$ C)

Sucrose

Polymeric MDI
Preparation of pure PU foam (control)

Polyols, surfactant and catalysts → Polymeric MDI → Polymerization → Self-rising → Solidification

<table>
<thead>
<tr>
<th></th>
<th>S polyol</th>
<th>G polyol</th>
<th>MDI</th>
<th>DMCHA</th>
<th>octotate</th>
<th>pentane</th>
<th>surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>27.9</td>
<td>16.7</td>
<td>40.6</td>
<td>1.30</td>
<td>0.900</td>
<td>11.2</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Preparation of PU nanocomposite foam

Freeze dried whiskers in DMF
Foam structure characterization

- Rigid PU Foams reinforced with 0, 0.25, 0.50, 0.75 and 1.0 wt% whiskers were prepared.
- Closed cells had a homogeneous dispersion, and cell sizes were all around 200 µm.

<table>
<thead>
<tr>
<th>Whisker wt%</th>
<th>0</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>537.6</td>
<td>414.4</td>
<td>461.6</td>
<td>535.9</td>
<td>820.1</td>
</tr>
<tr>
<td>(kg/m³)</td>
<td>±5.1</td>
<td>±5.1</td>
<td>±5.6</td>
<td>±3.3</td>
<td>±5.7</td>
</tr>
</tbody>
</table>

Scale bar: 100 nm.
Fourier transform infrared spectroscopy

- Urethane linkage
- Polyether polyols
- Cellulose whiskers
- Interrupt H-bonding
Whiskers and PU interactions

Crosslinking happens between cellulose whiskers and isocyanates during polyurethane synthesis.

![Absorbance vs Wavenumber Graph]

- Control + 1.0 wt% whiskers
- 1.0 wt% nanocomposite
Tensile stress-strain curves

- **Tensile modulus**: $4.37 \pm 0.14$ MPa
- **Yield strength**: $0.316 \pm 0.031$ MPa
- **Tensile strength**: $0.485 \pm 0.043$ MPa

Changes (%):
- $-30.4 - 34.2 - 27.0$
- $-20.6 - 22.8 - 21.4$
- $36.8 15.2 13.8$
- $227 112 99.2$

Graph showing stress-strain curves for different foam concentrations.
Compressive stress-strain curves

- Control foam
- 0.25 wt%
- 0.50 wt%
- 0.75 wt%
- 1.0 wt%

**Modulus**: 3.29 ± 0.85 MPa
**Strength**: 0.145 ± 0.045 MPa

**Gain (%):**
- 210 270
- 180 143
- 118 131
- 66.6 29.0
Thermal stability

<table>
<thead>
<tr>
<th>Whiskers (wt%)</th>
<th>0</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (°C)</td>
<td>88</td>
<td>94</td>
<td>100</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>$T_d$ (°C)</td>
<td>333</td>
<td>329</td>
<td>331</td>
<td>336</td>
<td>343</td>
</tr>
</tbody>
</table>
Conclusions

- Novel nanocomposites of rigid PU foam reinforced with cellulose whiskers up to 1 wt% have been prepared.
- The well-dispersed closed cells of different foams were all around 200 µm in diameter.
- Additional H bonding were developed in the nanocomposite, and crosslinking occurred between the whiskers OH groups and NCO groups.
- A substantial improvement of mechanical properties was obtained.
- Thermal stability of the nanocomposites was also enhanced.
Acknowledgements

THANK YOU!