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

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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
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.

\[
O=C=N-R^1-N-C=O + OH-R^2-OH + O=C=N-R^1-N-C=O + OH-R^2-OH + \ldots
\]

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

But not as stiff as traditional materials
Objective-improve mechanical properties

- Physical, chemical or enzyme treatment
- Rigid PU nanocomposite foam
- Other polymers e.g. PU
- Solar energy
- Feedstock
- Cellulose whiskers
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° 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>
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</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>537.6</td>
<td>414.4</td>
<td>461.6</td>
<td>535.9</td>
<td>820.1</td>
</tr>
<tr>
<td></td>
<td>± 5.1</td>
<td>± 5.1</td>
<td>± 5.6</td>
<td>± 3.3</td>
<td>± 5.7</td>
</tr>
</tbody>
</table>
Fourier transform infrared spectroscopy

- **1.0 wt%**: Urethane linkage
- **0.75 wt%**: Polyether polyols
- **0.50 wt%**: Cellulose whiskers
- **0.25 wt%**: Interrupt H-bonding

**Absorbance**

**Wavenumber (cm\(^{-1}\))**

- 1736
- 1732
- C-O
- O-CO
- NH
- CH\(_3\)
- OC=O
- CO-NH
- Control
Whiskers and PU interactions

Crosslinking happens between cellulose whiskers and isocyanates during polyurethane synthesis.
Tensile stress-strain curves

- Control foam: Tensile modulus 4.37 ± 0.14 MPa
- 0.25 wt%: Yield strength 0.316 ± 0.031 MPa, Tensile strength 0.485 ± 0.043 MPa
- 0.50 wt%, 0.75 wt%, 1.0 wt%:

Changes (%):
-30.4 -34.2 -27.0
-20.6 -22.8 -21.4
36.8 15.2 13.8
227 112 99.2
Compressive stress-strain curves

Gain (%):

- 0.25 wt%: 210
- 0.50 wt%: 180
- 0.75 wt%: 118
- 1.0 wt%: 66.6

Modulus 3.29 ± 0.85 MPa
Strength 0.145 ± 0.045 MPa
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>
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</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

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