BI O-BASED NANOCOMPOSITES: CHALLENGES AND OPPORTUNITIES

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Outline

- What is the difference between composites and nanocomposites?
- Nanocrystalline cellulose (NCC, CNXL)
- Experimental results
  - Polyhydroxyoctanoate
  - PVOH
  - PUR
  - Polysulfone (PSf)
  - CMC
- Challenges and opportunities
- Acknowledgements
Polymer Composites

- Generally consists of a polymer “matrix” and a particulate “filler”
- Filler (dispersed phase) is dispersed in matrix (continuous phase)
- Can also have continuous filler (graphite fiber pultrusion, used for aerospace, etc.), but not yet used in nanocomposites
Wood flour in HDPE

0.1 mm
Synergism in Polymer Composites

- **Function of matrix:**
  - Disperse fibers
  - Transfer load to filler
  - Load sharing between broken and intact filler particles
  - Increases toughness

- **Function of filler**
  - Carry load, increase properties
  - Lower cost
What makes a nanocomposite different?
Reduced impurities

- As the size of a particle is reduced, the number of defects per particle is also reduced
- Mechanical properties rise proportionately
## Properties of fibers and nanoparticles

<table>
<thead>
<tr>
<th>material</th>
<th>Density, g/cm³ (ρ)</th>
<th>Theoretical strength, GPa</th>
<th>Whisker strength (S), GPa</th>
<th>Bulk strength, GPa</th>
<th>Specific whisker strength S/ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>iron</td>
<td>7.68</td>
<td>20</td>
<td>13</td>
<td>4.1</td>
<td>1.68</td>
</tr>
<tr>
<td>Carbon (graphite)</td>
<td>1.38</td>
<td>98</td>
<td>21</td>
<td>1.7</td>
<td>12.4</td>
</tr>
</tbody>
</table>
An historical nano-example:

Carbon black
Addition of nano-sized carbon to rubber

- Particle size 10-75 nm
- Strength can increase 1000 X
- Stiffness increases 7 X (in accordance with modified Einstein equation)
- Abrasion resistance 4-5 X
- Without carbon black, tires would not be made from rubber!
## Surface Area

<table>
<thead>
<tr>
<th>Material</th>
<th>m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-glass fibers*</td>
<td>~1</td>
</tr>
<tr>
<td>Paper fibers</td>
<td>4</td>
</tr>
<tr>
<td>Graphite</td>
<td>25-300</td>
</tr>
<tr>
<td>Fumed silica</td>
<td>100-400</td>
</tr>
<tr>
<td>Fully exfoliated clay</td>
<td>~ 500</td>
</tr>
<tr>
<td>Cellulose nanocrystals**</td>
<td>250</td>
</tr>
<tr>
<td>Carbon nanotubes***</td>
<td>~ 100 - ?</td>
</tr>
</tbody>
</table>


** Winter, W. presentation at ACS meeting, San Diego, March 2005

Polymer-clay nanocomposites

mechanical and barrier properties
The step-assist on the 2002 GMC Safari (shown) and Chevrolet Astro vans is the automotive industry's first exterior applications for thermoplastic polyolefin-based nanocomposites. The part won General Motors the 2001 Grand Award for plastics innovation from the SPE's Automotive Division. (Photo courtesy of Wieck Photo Database).

Nano-PA6
Using Nanomer 1.24 TL - *In Situ* Polymerization

Nylon 6 Nanocomposite
Aspect ratio > 100

intercalation

Confined polymer

exfoliation

U. Southern Miss. Macrogalleria http://www.psrc.usm.edu/macrogs/mmpm/composit/nano/struct2_1.htm
Barrier Platform
Mitsubishi gas chemical and Nanocor Alliance Imperm®
Nano-Nylon MXD6
Barrier Film for packaging
Nano-PA6 using Nanomer 1.24 TL - *In situ polymerization*
Relative electrical conductivity ($\rho_c/\rho_m$) of the carbon black filled LDPE (circles) or HDPE (squares) as a function of the filler content ($\phi$).

FIG. 3. Inverse of the critical volume fraction for percolation ($1/p_c$) plotted vs aspect ratio of ellipsoids of revolution. The solid line is a Padé-type approximant described in the text. It is fit to both asymptotic limits, the value of $1/p_c$ for the sphere, and is forced to have zero slope at $a/b = 1$. 

Nanocomposite Concepts

- Reduced defects
- Surface area
- Percolation
- Interphase volume
  - Polymer morphology
Cellulose
Cellulose Nanocrystal (CNXCL) Production

Native cellulose → Crystalline regions → Acid hydrolysis → Amorphous region → Individual nanocrystals

Individual cellulose polymer
Sources of nanocrystalline cellulose

- Microcrystalline cellulose (wood)
- Bacteria (Nata de coco)
- Cotton
- Ag wastes
- Tunicates
# Cellulose nanocrystals

<table>
<thead>
<tr>
<th>Cellulose source</th>
<th>Length</th>
<th>Cross section</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tunicate</td>
<td>100 nm - microns</td>
<td>10-20 nm</td>
<td>5 to &gt; 100 (high)</td>
</tr>
<tr>
<td>Algal (Valonia)</td>
<td>&gt; 1000 nm</td>
<td>10 to 20 nm</td>
<td>50 to &gt; 10 nm (high)</td>
</tr>
<tr>
<td>Bacterial</td>
<td>100 nm - microns</td>
<td>5-10 x 30-50 nm</td>
<td>2 to &gt; 100 (medium)</td>
</tr>
<tr>
<td>Cotton</td>
<td>200-350 nm</td>
<td>5 nm</td>
<td>20 to 70 (low)</td>
</tr>
<tr>
<td>Wood</td>
<td>100 – 300 nm</td>
<td>3 – 5 nm</td>
<td>20 to 50 (low)</td>
</tr>
</tbody>
</table>

COST OF CELLULOSE NANOCRYSTALS

- Microcrystalline cellulose (MCC)
  - ~ $7/kg
  - HCl based process

- Nanocrystalline Cellulose (CNXL)
  - Target ~ $10/kg
  - H₂SO₄ based process
  - Do you need the purity of MCC starting material?
  - Can acid be recovered?
  - Uses for byproduct (sugar in acid)?
TEM image of cellulose nanocrystals
Polymer systems
Battery Separator, CNXL in Polyhydroxyoctanoate

BACTERIAL CELLULOSE/
POLYVINYLALCOHOL
Slide from Wankei Wan, U. W. Ontario, London, ON, Canada
Bacterial cellulose has very high modulus

Fiber diameter: 27-88 nm
Crystallinity: 60%
Young’s modulus: 78 ± 17 GPa

Eichhorn and Young, Cellulose 8:197 (2001)
Guhados et al, accepted Langmuir (2005)
Bacterial cellulose – PVA nanocomposite

Millon et al, submitted to JBMR (B), (2005)

Slide from Wankei Wan, U. W. Ontario, London, ON, Canada
Aorta – tensile properties

Millon et al, submitted to JBMR (B), (2005)
Slide from Wankei Wan, U. W. Ontario, London, ON, Canada
Some prototypes

Wan et al, JBMR (B), (2001)

Slide from Wankei Wan, U. W. Ontario, London, ON, Canada
Cellulose nanocrystal-filled polyurethane
Composites: Unreacted Mixture

Rheology of the Hydrolyzed Crystals + Polyol Mixture + MDI

\[ G' \propto (m - m_{cG'})^{\beta_{G'}} \]


Calculated parameters
- \( m_{cG'} \approx 0.88 \) wt%
- \( \beta_{G'} \approx 1.2 \)

Theoretical Percolation Threshold
- \( \approx 1.07 \) wt%


Slide from Mirta Aranguren, UNMdP-CONICET, Buenos Aires, Argentina
Even after mixing and sonication some “bundles” and aggregates are observed (2.5%). Aggregation becomes an important problem at higher concentrations (see 10 % sample).
Polysulfone/cellulose nanocomposites

Sweda Noorani
John Simonsen
TGA-16% CNXL

Sample: sample2_dec 30_tga
Size: 1.9800 mg
Method: Ramp

File: C:\Data\sweda\sample2_dec30_tga.001
Operator: sweda
Run Date: 30-Dec-04 12:02
Instrument: 2950 TGA HR V6.0E
TGA (Psf film with 2% CC)

Sample: psf film (ncc) nov 17, 04
Size: 2.0540 mg
Method: Ramp

File: C:\sweda\psf film(ncc) nov 17,04.001
Operator: sweda
Run Date: 17-Nov-04 17:07
Instrument: 2950 TGA HR V6.0E
Nanocrystalline cellulose in PSf

The graph shows the relationship between the modulus of elasticity (MOE) in GPa and the percentage of nanocrystalline cellulose (NCC) (w/w). The MOE increases significantly as the percentage of NCC increases from 0% to 2%. There is a notable decrease in MOE for NCC percentages above 2%. The error bars indicate the variability in the measurements.
WVTR of CNXL-filled PSf

Flux (g/m²·dy) vs. %NCC

Flux values range from 0 to 400 g/m²·dy, and %NCC values range from -2 to 13.
CELLULOSE NANOCRYSTAL-FILLED CARBOXYMETHYL CELLULOSE

YongJae Choi
John Simonsen
Comparison of Microcrystalline Cellulose (MCC) to NCC in CMC

10% MCC
10% glycerin plasticizer
200X optical (crossed polars)

10% NCC
CROSS SECTION OF FILM

90%CMC/10%Gly

80%CMC/10%NCC/10%Gly
Mechanical properties

- **Tensile Strength (MPa)**
  - Control
  - CNXL
  - MCC

CNXL or MCC content (% w/w)

30% increase
Mechanical properties

85% increase

Tensile modulus (GPa)

Control
CNXL
MCC

CNXL or MCC content (% w/w)
Extension at failure

60% increase

Elongation (%)

CNXL or MCC content (% w/w)

control
CNXL
MCC
HEAT TREATMENT

5% NCC in CMC (H form)
No plasticizer
Heat treatment, \(0^\circ\text{C}\) for 3 h, 5% NCC-filled CMC

- Tensile strength, MPa
- MOE, GPa
- Elongation

16% increase
Water Dissolution

![Graph showing weight loss over water immersion time for different temperatures: 120°C, 100°C, 80°C, and no heat. Each line represents a different temperature, with the graph showing the percentage weight loss over time from 0 to 75 hours. The legend identifies the temperatures by their respective lines.](image-url)
Water vapor transmission rate

- Control: g/m² dy
- Heat treated: 11% reduction

WVTR, g/m² dy

- Control
- Heat treated
CHALLENGES

- Dispersion of nanoparticles
- Production scale-up of nanoparticles
- Coupling of filler to matrix
- Where are the high stiffness, high strength composites we should have?
- Improving knowledge base to allow intelligent design of products which capture the advantages of this exceptional nanomaterial
OPPORTUNITIES - APPLICATIONS

- Membranes
  - Fuel cells
  - Kidney dialysis
  - Reverse osmosis
  - Protein separation
  - Pervaporation
- Barrier films
APPLICAT I ONS

- Advanced textiles – fibers
  - If properties of CNXLs can be accessed efficiently
- Biomedical
  - Tissue engineering
    - Heart valves
    - bone replacement materials
    - Skin grafts
APPLICATONS

- Advantages
  - Biocompatible
  - Biodegradable
  - Exceptional mechanical properties
  - Chemical modification straightforward
  - Self-assembling?
Acknowledgements

- This project was supported by a grant from the USDA National Research Initiative Competitive Grants Program
QUESTIONS?