Polymer-Matrix Nanocomposites: Selective Research Topics in MSE

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Polymer-Matrix Nanocomposites (PNC)

- **PNC definition:**
  - Polymeric matrix embedded with nanoparticles in lieu of conventional fillers or fibers

- **Nanoparticle definition:**
  - Particle with at least one dimension in the range 1 – 100 nm

- **Examples:**
  - Carbon nanotubes
  - Exfoliated clay particles
  - Cellulose whiskers
  - Metal nanoclusters

- **Advantages of PNCs:**
  - Improved strength – to weight ratio => transportation applications
  - Improved barrier properties => increased thermal stability
  - Improved optical properties => packaging applications
PNC Optimal Characteristics

- **Important PNC characteristics:**
  - Immobilization of polymer chains at nanoparticle surface
  - Influence of the “interphase” region

- **Requirements for PNCs:**
  - Strong bonding between nanoparticle and matrix
  - Good dispersion of nanoparticle in polymer matrix

- **PNCs raise processing challenges:**
  - Nanoparticle synthesis & characterization
  - Overcoming nanoparticle aggregation
  - PNC characterization
Topic 1: Polymer nanocomposites with bio-based filler phase
Nanoparticles from Natural Materials

- Advantages of nanoparticles from natural materials:
  - No need for surface functionalization – functional groups are “built in”

- Some Examples:
  - Cellulose & chitin whiskers from wood and marine animals
  - Clays
  - Silk nanoparticles

- Main processing challenge:
  - Achieving dispersion requires overcoming strong inter-particle interactions
Cellulose Whiskers (CW)

- Biopolymer of D-glucose
  - β (1→4)-glycosidic bonds

- Basic building block in wood, cotton, etc.
  - 5 to 20 nm diameter
  - Typical aspect ratio 60 – 70

- High modulus, crystallinity
  - Defect-free monocrystal 250 GPa
Polymerization of Furfuryl Alcohol (FA)

- Characteristics of furfuryl alcohol (FA) precursor:
  - Furfuryl alcohol derived from furfural in commercial quantities
  - Furfural derived from pentose-rich feedstocks, e.g. oats, wood, etc
  - FA is a difunctional molecule, because it is susceptible to electrophilic attach at the C5 position

Polymerization of FA is catalyzed by acids

![Polymerization Reaction Diagram]
Polyfurfuryl Alcohol (PFA)

- **Characteristics of polyfurfuryl alcohol (PFA) product**
  - Crosslinked polymer, typically hard and brittle like phenolics
  - Black due to chromophores (conjugated double bonds) along backbone
  - Excellent thermal stability – due to aromatic furan ring
  - Excellent insulator

- **Applications of PFA**
  - Binder in foundry cores
  - Chemical resistant coatings
  - FRP (fiberglass reinforced plastics)
Experimental Approach: CW-PNCs

- **Processing of CW – PFA PNCs**
  - Whiskers preparation by hydrolysis, ultracentrifuging, dialysis, freeze-drying
  - Redisperse 0.75 wt% CW in FA by ultrasonication

- **Objectives**
  - Freeze the CW dispersion by achieving polymerization at CW surface
  - Exploit presence of sulfonic acid residues at CW surface as catalyst for polymerization of FA

- **Characterization of CW – PFA PNCs**
  - CW morphology characterization by AFM, cryo-TEM
  - Characterize polymerization by FTIR
  - Thermal analysis by TGA, DSC
  - Mechanical analysis by DMA, nanoindentation
Cellulose Whiskers Preparation

- **AFM imaging of CW:**
  - Well dispersed
  - Length in 0.5 – 1.0 um
  - Average diameter ≈ 10 nm
Processing of CW - PFA PNCs

- **Polymerization of FA:**
  - FTIR internal referencing (the Cp ring at 1500 cm$^{-1}$)
  - $T_{\text{reaction}}$ = 100°C

<table>
<thead>
<tr>
<th>Peak height ratio $I/I_{\text{ref}}$</th>
<th>Pure FA</th>
<th>CW-PFA 0.5h / 100°C</th>
<th>CW-PFA 1h / 100°C</th>
<th>CW-PFA 2h / 100°C</th>
<th>γAl-PFA 12h / 100°C</th>
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<tbody>
<tr>
<td>$I_{1562}/I_{1500}$</td>
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<td>0.465</td>
<td>0.663</td>
<td>1.107</td>
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<td>$I_{1712}/I_{1500}$</td>
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<td>0.455</td>
<td>0.697</td>
<td>1.349</td>
<td>0.424</td>
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</tbody>
</table>

![Graph showing FTIR spectra for various samples](image)
Proposed Mechanism of FA Polymerization Catalyzed by CW

**Initial Mixing**

CW

FA

O-SO$_3^-$

O-SO$_3^-$

Desulfonation at CW surface

$>$60$^\circ$C

OH + H$_2$SO$_4$

$\text{H}_2\text{SO}_4$-catalyzed Polymerization of FA

PFA
Thermal Stability of PFA-Based PNCs

TGA showing onset of degradation for non-oxidative degradation for cured PNCs

Onset of degradation temperature:

- γAl-PFA (control): 246°C
- 30B-PFA: 292°C (+46°C)
- NaMMT-PFA: 297°C (+51°C)
- CW-PFA: 323°C (+77°C)
Thermal Stability of PFA PNCs

TGA showing onset of degradation for oxidative degradation for cured PNCs

Onset of degradation temperature:

- γAl-PFA (control): 260°C
- NaMMT-PFA: 288°C (+28°C)
- 30B-PFA: 330°C (+70°C)
- CW-PFA: 352°C (+92°C)
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Topic 2: Cellulose-based nanocomposites
Gelation of Cellulose Ester Polymers Mediated by Metallic Nanoparticles

Decomposition of CAP in the presence of Fe(CO)$_5$

\[ n\text{Fe(CO)}_5 \xrightarrow{\Delta} \frac{n}{x}\text{[Fe}_x\text{(CO)}_y\text{]} + \frac{n}{y}\text{CO} \xrightarrow{\Delta} \cdots \frac{n}{k}\text{Fe}_k^0 + 5n\text{CO} \]

\[ \text{Fe}_x\text{(CO)}_y + \text{CAP-OH} \xrightarrow{\Delta} \left[ (\mu - \text{H})\text{Fe}_x\text{(CO)}_{y-2}(\mu - \text{OCAP}) \right] + 2\text{CO} \]
Progress of Reaction
Viscosity Behavior During Reaction

Decomposition of Fe(CO)$_5$ with CAP under an oxidative atmosphere

Decomposition of Fe(CO)$_5$ with CAP under an inert atmosphere
Mechanism of Gelation in Inert Environments

\[
\text{Fe(CO)}_5 \xrightarrow{\Delta} \text{Fe(CO)}_4 \quad \text{Fe}_2\text{O}_3 + \text{Polymer chains} \rightarrow \text{Fe}_2\text{O}_3
\]

- \( \text{Fe}^0 \) and other reactive intermediates
- Zero-valent iron clusters
- Metallic clusters associated with the polymer by weak chemical interactions
Applications: Gel Formation in Cellulose Ethers

- Hydroxypropyl methylcellulose (HPMC) is particularly useful in many industries as a water soluble polymeric binder, thickener, film, and matrix former.

- HPMC and other cellulose ethers such as methylcellulose (MC) and hydroxyethylmethylcellulose (HEMC) tend to undergo a reversible sol-gel transition at elevated temperatures in aqueous solutions.

- It is thought that this phenomenon arises from the increasing hydrophobic interactions and exclusion of water from heavily methoxylated regions of the
Validation of Gelation Mechanism

$\text{Co}_2(\text{CO})_8$

$\text{Ru}_3(\text{CO})_{12}$
The layer-by-layer dipping process. A cleaned glass slide is first dipped into the polymer solution, and the excess is rinsed in deionized water. It will then be dipped into a kaolin suspension and rinsed again. The process will be repeated to build the material. Ideally, the material should have >20 layers.
Hydrodeoxygenation of Biomass over Bifunctional Metal Organic Framework (MOF) Catalysts

Difunctional, molecularly porous catalysts with Brønsted acid and metal sites in a well defined distance to each other will be designed, synthesized, characterized and tested. These MOF materials will be based on MOFs, with Rh, Ru, Pt, Pd and Cu as the metallic component.

Strategies for production of fuels from lignocellulosic biomass.