Polymer and Nano-Material Research in the Polymers Branch at NASA Glenn Research Center

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Future Exploration Mission Requirements Cannot Be Met with Conventional Materials

**Satellites and rovers**
- Reduced mass and volume
- Reduced power requirements
- Increased capability, multifunctionality

**Vehicles and habitats**
- Reduced mass
- High strength
- Thermal and radiation protection
- Self-healing, self-diagnostic
- Multifunctionality
- Improved durability
- Environmental resistance (dust, atmosphere, radiation)

**EVA Suits**
- Reduced mass
- Increased functionality and mobility
- Thermal and radiation protection
- Environmental resistance
RXP Nanomaterials Research

Synthesis

Giannelis group - Cornell

NASA Nanotechnology Gallery

Dispersion/Processing

Incorporation into Composite Structures

Characterization

Relative Intensity

30B in API resin

30B in PES1

2 Theta
Outline

• Nanocomposites for Highly Loaded Structures

• Nanocomposites for Cold Temperature Applications (cryogen storage)

• Nanocomposites for High Temperature Applications (300°C)
Composite Fan Blade

Goal: Enable Reduced Blade Thickness through Improved Composite Fracture Toughness and Interlaminar Strain

Approach:
1. Investigate the influence of a wide range of nanoparticles on epoxy toughness.
2. Design materials to best utilize the various nanoparticles.
Composite Fan Blades

**Background**

**Materials:**

- **Epon 826**

  ![Structure of Epon 826](image)

  - Tensile strength and ductility are improved when nanoparticles can align in the direction of applied load.
  - Pre-dispersion forces clay into the more mobile components of the resin.

- **Araldite DY3601**

  ![Structure of Araldite DY3601](image)

- **Jeffamine D230**

  ![Structure of Jeffamine D230](image)

  - $M_n < 385$
  - $x = 2.6$

- **Materials:**

  - Neat Resin
  - Neat Resin + 2% clay
  - Neat Resin + 5% clay
  - 2% clay- premixed
  - 2% clay- premixed + Neat Resin
  - 2% clay- premixed + 2% 30B in 100% DY3601
  - 2% clay- premixed + 2% 30B directly dispersed
  - 2% clay- premixed + 2% 30B in 100% E826

- **Performance Metrics:**

  - **Stress** vs. **Strain**

  ![Graph: Stress vs. Strain](image)

  - Baseline: 3000 psi
  - 2% matrix: 3500 psi
  - 2% preswell: 4000 psi
  - 5% matrix: 4500 psi
  - 5% preswell: 5000 psi

- **Relative Intensity** vs. **2 Theta**

  ![Graph: Relative Intensity vs. 2 Theta](image)

  - 2% 30B pre-dispersed
  - 2% 30B in 100% DY3601
  - 2% 30B directly dispersed
  - 2% 30B in 100% E826
Strain in Un-Toughened Epoxy-Clay Nanocomposites

Glassy at Room Temperature

Rubbery at Room Temperature

Stress (MPa) vs. Strain (%)
Nanocomposites Based on Aerospace Grade Epoxies

Fracture surface of nano-reinforced samples indicate increased material toughness.

Graphite particles were epoxy functionalized via solvent-based wash. CNF particles were not functionalized.
1. Epoxy Nanocomposite film laid up with between plies of base laminate.
2. Autoclave cured using vendor recommended cure cycle
3. Characterized for panel quality
   1. C-scan
   2. Acid Digestion
   3. Optical Microscopy
4. Mechanical Testing
Composite Testing: Thermal and Mechanical Testing Results

Short Beam Shear

Nanoclay interleave shows drop in short beam shear strength, but comparable or improved ductility.

Little difference in dynamic mechanical data.
Next Steps - Improved Nano-Incorporation

- **Need Better Dispersion**
  - Do not have the facilities to handle this scale of dispersion.
  - Contract in place with Nanosperse to aid in dispersion

- **Exploring Alternative Mechanisms to Include Nanoparticles**
  - Purchases in place with Nanocomp to incorporate CNT sheets
  - Working with North Carolina A&T University to electro-spin PES for interleave material.
Composite Tanks

Goal: Reduce Permeation through Composite

- The majority of this effort has focused on clay nanoparticles.
- Reduced material permeability following nanoclay dispersion is well documented.
- Expected that the platelet structure of clay contributes to the improved barrier performance.

Clay layer dispersion and alignment, with respect to the permeation direction, greatly influence the barrier performance of the matrix.

Bharadwaj, R.K. *Macromolecules* 2001, 34, 9189
High Temperature Polymer Nanocomposites

Goal: Improve High Temperature Durability of Matrix Resin

Elevated PMR-15 processing temperatures led to development of unique nanoclay modifier.

PMR-15 processing temperature

MDA-C12 co-ion exchange
Thermal and Physical Properties of PMR-15/Clay Nanocomposites

- Glass transition temperature was maintained with increased clay loading.
- Weight loss with thermal aging reduced with increased clay loading.
- Oxygen permeation through nanocomposite reduced compared to baseline material.

<table>
<thead>
<tr>
<th>Silicate (%)</th>
<th>PGV-(MDA-C12)</th>
<th>PGV-C12</th>
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<tbody>
<tr>
<td>0%</td>
<td>335</td>
<td>335</td>
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<tr>
<td>1%</td>
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<td>338</td>
<td>311</td>
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Oxygen Permeability of Carbon Fiber Composites

- 0% silicate
- 1% silicate
- 3% silicate
- 5% silicate
- 7% silicate

1000 hours (288°C)
High Temperature Polymer Nanocomposites

CNF dispersion results in weight loss comparable to clay

0.5 wt% CNF

Neat Resin
Carbon Nanotube Efforts- Focus on Functionalization

SWCNTs Non-Covalent Functionalization

Pyrene derivative

Schematic illustration of the SWCNTs/Pyrene complex

FT-IR

TGA

(a) SWCNTs

(b) SWCNTs/Pyrene

(c) Pyrene

FT-IR spectra and TGA curves for SWCNTs, SWCNTs/Pyrene, and Pyrene.
SWCNTs Non-Covalent Functionalization

Agglomeration of SWCNTs is clearly visible in the SEM image of the SWCNT nanocomposite film.

Complexes form stable colloidal dispersion in polar solvents – enables production of homogeneous polymer films.

The addition of 3.5 wt% SWCNT/complexes increased the tensile strength of the polyimide from 61.4 to 129 MPa; higher loading levels led to embrittlement and lower tensile strengths.
Results: Photo-Oxidation of SWCNTs

- The oxygen content of the SWCNTs (i.e., photo-oxidation, acid treatment) has been studied by X-ray photoelectron spectroscopy (XPS).
- **Photo-oxidation adds nearly 2X the oxygen to the SWNTs than acid treatment alone.**

(a) Overlay of oxygen peaks from the survey scan after normalizing the carbon peaks.
(b) Oxygen concentration of SWCNTs oxidized by photo-oxidation (with and without sensitizer) and by acid treatment.
Results: Photo-Oxidation of SWCNTs

- XPS is sensitive to matrix effects and is able to provide both oxidation and chemical state information about the elements detected.
- An overlay of all of the carbon regions after normalization revealed the presence of a shoulder on the main carbon peak (284.8 eV) of the photo-oxidized.
- Peaks at 286.3 eV, 287.9 eV, and 289.3 eV are indicative of C-O, C=O, and O-C=O, respectively.
- Analytical characterizations by FT-IR also confirmed the presence of oxygen groups.

XPS: Curve-fitting of the carbon region of the photo-oxidized SWCNTs with RB.

FT-IR: (a) SWCNTs and (b) photo-oxidized SWCNTs.
Additional Nanomaterials Efforts

• Magnetic nanoparticle synthesis and dispersion
• Nanoparticle influence on shape memory polymer
• Nanoparticle modified carbon fibers
• Boron Carbide Nanotube materials (radiation shielding)
• Graphene nanocomposites for improved electrical conductivity.