Polymeric Materials for Aerospace Power and Propulsion
An Overview of Polymers Related Research at NASA Glenn

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Weight, durability and performance are all major concerns for any NASA mission. Use of lightweight materials, such as fiber reinforced polymer matrix composites can lead to significant reductions in vehicle weight and improvements in vehicle performance. Research in the Polymeric Materials Branch at NASA Glenn is focused on improving the durability, properties, processability and performance of polymeric materials by utilizing both conventional polymer science and engineering as well as nanotechnology and bio-inspired approaches. This presentation will provide an overview of these efforts and highlight recent progress.
Polymeric Materials for Aerospace Power and Propulsion

Overview of Polymer Research at NASA Glenn

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Polymers for Aerospace Power and Propulsion

Propulsion

Nanotechnology

Lithium/Polymer Batteries

Fuel Cells
Aeronautics Restructuring at NASA

• New Associate Administrator, Dr. Lisa Porter (DARPA), appointed in 2006
• Changing focus from developing technologies for a specific vehicle
  – Feeling that working toward a single “point design” is not the best use of NASA resources
  – Construction of demonstrator vehicles is expensive
• Associate Administrator wants to develop generic technologies that can support development of a specific class of vehicles and cross-cutting areas
  – Subsonics - Fixed and Rotary Wing
  – Supersonics
  – Hypersonics
  – IVHM, Aging Aircraft, IRAC
• Looking for greater cost-shared partnering with industry
• Using NRA as the primary (only) vehicle for grants and contracts
GRC Polymeric Materials Research Efforts in Aeronautics

• Subsonic Rotary Wing Aircraft
  – Multifunctional materials for acoustic damping

• Subsonic Fixed Wing Aircraft
  – Multifunctional materials for ultralightweight ballistic impact protection
  – Adaptive materials for tip-clearance seals

• Supersonics
  – RTM processable 600°F resins for bypass ducts and containment systems
  – High temperature containment (500-600°F)

• Hypersonics
  – Thermal protection systems

• Aging Aircraft
  – Effects of aging on ballistic impact behavior of composites
RTM/RFI Processable Polymers for Propulsion Components

Objective:
Develop low melt viscosity polymers for RTM, VARTM or RFI processing of high temperature propulsion components
- Melt viscosities below 20Poise
- Tg and TOS suitable for use from 500-600°F

Approach:
• Modify oligomer chemistry to reduce viscosity with minimal effect on Tg and TOS
  - Molecular morphology – branching, twists, asymmetry
  - Formulated molecular weight
  - Endcap chemistry
• Investigate use of nanoscale filers to enhance TOS and properties

Partners:
Boeing, Clark Atlanta U, M&P Technologies
High Temperature RTM Processable Resin Development

- Low Viscosities, Long Pot-Lives
- Good High Temperature Property Retention

- Resin scale-up efforts underway
- Pursuing commercialization through GATE program

Chuang, Criss, McCorkle, Mintz, Nguyen and Scheimann
Composite Materials for Engine Containment Cases

Resin Mechanical Tests
- High strain rate constitutive models
- Toughened material evaluation

Composite Fan Case Fabrication
- A&P Technology- braided preforms
- North Coast Composites- molding (RTM)

Ballistic Impact Tests: Fan Cases
- Simulate blade impact
- Measures resistance to penetration

Ballistic Impact Tests: Panels
- Materials screening
- Composite material and failure models

Engine Blade-Out Simulation
- Define ballistic impact test parameters
- Validate analysis methods for certification

Structural Loading Tests
- Simulate rotor out-of-balance loads
- Measures resistance to crack growth
Nanocomposites

- Investigating effects of a variety of nanoscale fillers on properties of polymers
  - Organically modified clays
  - Functionalized graphene sheets (FEGs aka TEGO)
  - Carbon nanotubes

- Potential applications:
  - Cryotanks – reduced permeability, enhanced microcrack resistance
  - Fan containment – improved toughness
  - High temperature engine structures – improved TOS, mechanical properties

Lebron-Colon, Miller, Gintert
Collaborations with: U of Akron, Princeton, Northwestern, MSU
Nanocomposites Have Potential for Use in Lightweight Cryogen Propellant Tanks

- **Reduced CTE by 25%**
- **Two-fold Increase in Notched Izod Toughness**
- **60% Reduction in H₂ Permeability**
- **Five-fold lower leak rate**

*Miller, Johnston, MSU*
Thermal Oxidative Stability of Clay Influenced by Modifier

TGA Results in Air

<table>
<thead>
<tr>
<th>Modifier</th>
<th>( T_1 )</th>
<th>( T_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl. 30B</td>
<td>280°C</td>
<td>400°C</td>
</tr>
<tr>
<td>APND+C12</td>
<td>365°C</td>
<td>600°C</td>
</tr>
</tbody>
</table>

\( T_1 = \text{Temperature at 5\% weight loss} \)

\( T_2 = \text{Temperature at maximum rate of weight loss} \)

Combination of aromatic and aliphatic clay treatment increases TOS compared to aliphatic treatment alone.

*Gintert, Jana, Miller*
Intercalation of Clay Layers with Low MW Oligomers Promotes Exfoliation

Lower MW produces higher $G'$ during curing due to higher crosslink density.

Difference in \textit{crosslink density} results in

\begin{itemize}
  \item High elastic force \textit{inside} clay layers
  \item Low viscous force \textit{outside} clay layers
\end{itemize}

Exfoliation
Intergallery Spacings Change During Reaction

- Increases during cure reaction for reactive APND-treated clay
- Decreases during cure reaction for aliphatic-treated clay (modifier decomposition)

Full exfoliation results!
Addition of Clays Increases $T_2^*$ in Air

$T_2 = \text{temperature at max rate of weight loss in TGA}$

- Addition of clay protects resin from oxidation by reducing rate of $O_2$ diffusion
- Enhanced exfoliation (addition of PMR-5) creates more tortuous path for diffusion
Enhanced Exfoliation Leads to an Increase in Stiffness

Glassy Region

Near Tg

G' @ 50°C

G' @ 300°C
Carbon Nanotube Based Materials

Purification

Functionalization

Evaluation

Purification

- Weight (%)
- Temperature (ºC)

Functionalization

- SWNTs
- SWNT/Pyrene complex

Evaluation

- Tensile Strength, MPa
- Resistivity Log, Ohm-cm
Issues of Single Wall Carbon Nanotubes

• Poor processability and insolubility in any solvents.
• Their degree of dispersion decreases significantly after the purification process.

• Goal:
  – Development a technique to stimulate dispersion of individual SWNT ropes in organic solvents.

• Objectives:
  – Enable homogeneous dispersion of nanotubes in polymer matrix.
  – Emphasis is on repeatable, simple functionalization methods that do not adversely affect SWNTs properties.

Figure 1.
SWNTs in toluene: (a) as received, (b) after purification

Lebron-Colon
Functionalization of SWNTs

- Oxygen functionalized SWNTs can serve as anchor precursor for further functionalization.

- The most common reagents used to generate acidic functional groups on the ends and walls of SWNTs have been:
  - concentrated HNO₃
  - or a mix of H₂SO₄ with HNO₃, H₂O₂, or KMnO₄

- The continue exposure of SWNTs to acid leads to damage which may affect their properties.
Photooxidation of Single Wall Carbon Nanotubes

Irradiation of oxygen saturated DMF suspension of SWNTs (450W Hg lamp, 18 h)
A decrease in weight of the functionalized SWNTs appears at about 200 ºC as consequence of the photo-oxidation treatment. 

The thermal decomposition of the SWNTs still around 600 ºC very near to the pristine SWNTs.

**Figure 5.** TGA (a) SWNTs and (b) photo-oxidized SWNTs.
Raman Spectra Suggest Regeneration of SWNTs at High Temperatures

• Raman bands diminish in intensity after photooxidation.
• Annealing photooxidized tubes lead to recovery of Raman bands indicating substantial reduction or complete elimination of the oxygen groups.
Graphite Offers Benefits Observed with both Layered Silicate and CNT

- Graphite is composed of a graphene layers held together by van der Waal forces\(^1\).
- Graphite is anisotropic, with good electrical and thermal conductivity within layers, not in perpendicular direction.\(^2\)

- Platelet morphology may provide gas barrier enhancements.
- Sheet edges may be functionalized.

Initial Permeability Measurements Show Reductions Comparable to Layered Silicate

- Dispersion of 1wt% expanded graphite shows over 20% reduction in oxygen permeability.

- Sample is a thermoplastic polyimide that was sonicated with graphite in dichloromethane.

Measurements were made at Michigan State University.
Exfoliated Graphite (EG) and Functionalized Graphene Sheets (FGS)

- Difference in surface area due to the separation of the graphite layers.
- EG exhibits a strong diffraction peak by WAXD, FGS is amorphous.
- FGS particle size is relatively small, making it easier to disperse
FGS Disperses Well in Epoxy

- FGS had good dispersion in Epon resins, both 862 and 826.
- Samples were prepared by sonicating epoxy resin with FGS for several hours.
Reduction in Resin Coefficient of Thermal Expansion

- Cycling composites from low temperature to room temperature builds stresses in a composite due to the mismatch of CTE.

- Reducing the CTE of the matrix may reduce microcracking in the composite.

- CTE reduction similar to that observed in layered silicate-epoxy nanocomposites.

<table>
<thead>
<tr>
<th>FGS Sample Loading (wt%)</th>
<th>Unmodified FGS</th>
<th>C18 Modified FGS</th>
<th>10% Excess Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>270</td>
<td></td>
<td>266</td>
</tr>
<tr>
<td>0.10</td>
<td>163</td>
<td>212</td>
<td>228</td>
</tr>
<tr>
<td>0.25</td>
<td>194</td>
<td>220</td>
<td>231</td>
</tr>
<tr>
<td>0.50</td>
<td>207</td>
<td>218</td>
<td>247</td>
</tr>
</tbody>
</table>
Tensile Tests Show Increase in Mechanical Properties

Interfacial chemistry affects nanocomposite failure during tensile testing.

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<th>C18 Modified FGS</th>
<th>10% Excess Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.875 ± 0.27</td>
<td></td>
<td>0.314 ± 0.11</td>
</tr>
<tr>
<td>0.10</td>
<td>0.914 ± 0.18</td>
<td>0.724 ± 0.11</td>
<td>0.981 ± 0.02</td>
</tr>
<tr>
<td>0.25</td>
<td>0.898 ± 0.10</td>
<td>0.725 ± 0.06</td>
<td>0.804 ± 0.11</td>
</tr>
<tr>
<td>0.50</td>
<td>1.000 ± 0.10</td>
<td>0.395 ± 0.19</td>
<td>1.015 ± 0.56</td>
</tr>
</tbody>
</table>
Electrical Conductivity is Obtained at Higher Loading

<table>
<thead>
<tr>
<th>Sample (wt% FGS)</th>
<th>Resistivity (ohm-cm)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4 E +10</td>
<td>Quickly decays to no current</td>
</tr>
<tr>
<td>0.5</td>
<td>5 E +10</td>
<td>Capacitive</td>
</tr>
<tr>
<td>1.0</td>
<td>1 E + 6</td>
<td>Conductive</td>
</tr>
</tbody>
</table>

FGS disperses well at 1 wt% loading.
Conductivity is observed at the 1wt% loading
Mechanical properties drop-off
Aerogels

- Properties
  - Low density (0.05-0.5 g/cc)
  - High porosity
  - High surface area (300-1000 m²/g)

- Uses
  - Poor thermal conductors; Good insulators (see picture)
  - Good electrical insulators; SiO₂-low dielectric <2
  - Good electrical conductors; RuOₓ, VOₓ
  - Photophysical properties; optics
  - Sensors; Optical, Magnetic and Electronic
  - Catalysts; High surface area increases efficiency of reactions

Capadona, Leventis, Meador, Nguyen
Collaborations with: Clark Atlanta, U of Akron, Parker Hannifin, ASI, Aspen Aerogels
X-Aerogels Have Potential as Structural Materials

Versatile Cross-linking Chemistry

Tailorable properties

Enhanced Mechanical Properties

Simplified (ambient pressure) processing
Other properties of x-aerogels parallel native aerogels…

...but x-aerogels are much stronger
Potential Applications for Durable Aerogels in Aeronautics

- X-aerogel
- Polymer-clay nanocomposite
- Ultralightweight, Multifunctional Sandwich Structures
- Propellant Tanks
- Fan Engine Containment (Ballistic Protection)
Typical Aerogel Cross-linking Process

1. Silanes in solvent
2. H$_2$O/solvent
3. Soak in monomer bath
4. Heat
5. 4 washes (to get rid of water, alcohols)
6. Crosslinked Aerogel
Surface modification of silica particles opens doors to other polymer systems

TMOS, (EtO)$_3$-Si-X, Solvent

Water, catalyst, Solvent

X = amines, acrylate, double bond, etc.

Polyacrylate

Acrylates

Anhydrides

Polyimide

Epoxy

Epoxies

Styrene

Polystyrene

Isocyanates

Polyurea
Process/Property Optimization Through Statistical Experimental Design

Empirical models…

…used for predictions of optima

Low density…

…to high density…

and everything in-between

Meador et al, Chemistry of Materials, in press
Comparison of Properties of X-Aerogels and Various Foams

Can tailor aerogel properties by polymer selection and adjusting silica, polymer and water content during processing.
Simplified processing—one pot preparation of wet gel

- Concept:
  - Introduce latent crosslinker into sol right from the start
  - Must be inert to gelation
  - Heat or light to initiate crosslinking after gelation
- Demonstrated with polyimides, acrylates, isocyanates, bis-maleimides
- Reduces processing time in at least half
Inclusion of carbon nanofibers

Fiber

Fiber in aerogel

Loading at 0.2% Strain (MPa)

- Low polymer data
- High Polymer

Density, g/cm³

Polymer, wt%
Development of large scale manufacturing

• GATE Platform Technology development
  – Parker-Hannifin
    continuous process to manufacture tubing
  – University of Akron CMPD
    thin film casting, incorporation of electrospun fibers
  – Applied Sciences, Inc.
    incorporation of carbon nanofibers

• Partnership with Aspen Aerogels
  – Aerogel composites
  – Early introduction technology
  – Can solve some issues related to other types of manufacturing
GRC Polymers Research for Exploration and Science

- High Temperature PMC Radiators
- Composite Overwrap Pressure Vessels
- Flexible Aerogel Insulation for EVA Suits
Composite Overwrapped Pressure Vessels: Shuttle & ISS

NESC STRUCTURES & MATERIALS TEAM:

- Investigating stresses in liners and overwraps
- Determining reliability of Kevlar overwrap subjected to constant stress
- Computing survival probability of individual and system-level COPVs
- Investigating damage tolerance (analysis and testing)
- Establishing reliability of the individual as well as the system of vessels is of paramount importance
- Investigating various combinations of Weibull-based analyses to arrive at a system-level survival probability
- Provided improved composite overwrap repair methods
- Revised COPV material recertification
- Identified Kevlar®49 failure mechanisms based on material impurities
- Linked importance of Kevlar®49 vintage to COPV quality issues
- Team Integrated with Orbiter Office
High Temperature PMC Radiators

- Larger area, significant mass driver
- Wider range of temperatures (200 – 550°F)
- Sophisticated deployment, possibly similar to ISS
- PMC with high thermal conductivity carbon fibers (Coal tar pitch-based w/ up to 1000 W/mK)

Higher potential!
Approaches to PMC Radiator

Utilizing Conventional Carbon Fibers and Nanoscale Fillers

Weight, Durability and Conductivity are Critical
- Investigating various design concepts for reduced weight
- Exploring new materials to control CTE, maximize thermal conductivity

Shin, Bowman, Beach, Quade
Lower density x-aerogels

- Lowest densities approaching 36 mg/cm³
- Samples <50 mg/cm³ are flexible

Capadona et al, Polymer, 2006, 47, 5754-5761
How to get more flexibility in the aerogels

- Use more flexible polymer crosslinks
  - Rubbers
  - Block copolymers

- Make the underlying silica more flexible
  - Less bonds to silica
  - Incorporation of short chains

Collaborations and Tech Transfer
Glenn Alliance for Technology Exchange (GATE)

- Funded by Congressional Earmark in 2005 to NASA/OAI/Glitech Team
- Commercialization of NASA Glenn developed technologies
  - Partner Grants (Glitech) – NASA and industry ($50K each)
    - UV Cured Polymers
    - Aerogels
  - Technology Platforms (OAI)-
    - Cost-shared industry consortia
      - Aerogels
      - High Temperature Polymers
      - Fluorescence Based Molecular Sensors
Funding Opportunities

• Aeronautics Mission Directorate NRA
  – [http://www.aerospace.nasa.gov/nra.htm](http://www.aerospace.nasa.gov/nra.htm)
  – Topics already listed for Supersonics and Subsonics Rotary Wing, Subsonics- Fixed Wing expected soon

• SBIR/STTR
  – Phase I- 6 months, $100K; Phase II – 2 years, $600K
  – Dates -TBD
  – SBIR Submission Deadlines - Typically Late Summer/Early Fall
    • 2006 deadline for SBIR Phase I proposals was September 7