Polymeric Materials for Aerospace Power and Propulsion-
NASA Glenn Overview

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Use of lightweight materials in aerospace power and propulsion components can lead to significant reductions in vehicle weight and improvements in performance and efficiency. Polymeric materials are well suited for many of these applications, but improvements in processability, durability and performance are required for their successful use in these components. Polymers Research at NASA Glenn is focused on utilizing a combination of traditional polymer science and engineering approaches and nanotechnology to develop new materials with enhanced processability, performance and durability. An overview of these efforts will be presented.
Polymeric Materials for Aerospace Power and Propulsion – NASA Glenn Overview

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Polymers Branch R&D Efforts

- Propulsion
- Power
- Nanotechnology
- Stimuli Responsive Materials
- Thermal Control Materials

Nanotechnology

- 16 nm
GRC Polymeric Materials Research Efforts in Aeronautics

• Subsonic Rotary Wing Aircraft
  – Multifunctional acoustic insulation – gearbox noise
• Subsonic Fixed Wing Aircraft
  – Multifunctional materials for acoustic lines for aircraft engine
  – Adaptive materials
• Supersonics
  – RTM processable 600°F resins for bypass ducts and containment systems, includes nanocomposites
  – High temperature containment (500-600°F)
• Hypersonics
  – Thermal protection systems
  – High temperature ballutes – Mars landing
• Aging Aircraft
  – Effects of aging on ballistic impact behavior of composites
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 fillers to enhance TOS and properties

Partners:
Boeing, Clark Atlanta U, M&P Technologies
Nanocomposites

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

- 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, Clark Atlanta U
Multicomponent Nanocomposites

**Layered silicate clays:**
Platelet morphology provides barrier to oxygen diffusion and oxidative degradation.
   - Exfoliated morphology optimizes permeability reduction.
Commonly modified with alkyl ammonium ion
   - Degradation at polyimide processing temp.
   - Thermally stable modifier is necessary.

**Carbon nanofibers:**
Thermally stable - will not contribute to resin degradation
   - Imparts mechanical strength and stiffness to the resin.
   - Thermally conductive
Nanocomposite Synthesis

Clay loading: 5 wt%, CNF loading: 0.5 – 1.0 wt%
Use of Synthetic Clay Improves Resin TOS

Melt Viscosities Increase with Clay Addition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Minimum Viscosity* [cP]</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Resin</td>
<td>~ 10</td>
<td>250</td>
</tr>
<tr>
<td>5% TPPB</td>
<td>~ 60</td>
<td>250</td>
</tr>
<tr>
<td>5% MSU</td>
<td>~ 40</td>
<td>250</td>
</tr>
</tbody>
</table>

*Measured by Brookfield

• Examined TPPB modified MMT and synthetic clay
• Used BAX-TAB RTM processable polyimide
• Evaluated TOS, melt viscosity and Tg

Pre-exfoliated Clay Gives Better Dispersion

30% Reduction in Weight Loss

Weight Loss after 1000 h at 288°C (550°F)
Clay and Nanofiber Dispersion

Clay and CNF dispersion characterized by TEM

CNF separation of over 100 nm.

Clay dispersion comparable to clay only nanocomposites
Synergistic Effects of Clay and CNF Addition on Resin TOS Investigated

CNF containing nanocomposites increases temperature of 5% and 10% weight loss by 30°C.

Nanocomposites containing PR-19 reduce polyimide weight loss on aging by up to 38%.
Thermal Conductivity of CNF Nanocomposites

Increased conductivity observed in PR-19 and PR-19/TPPB nanocomposites
## Effect of Nanoscale Additive on Melt Behavior

<table>
<thead>
<tr>
<th>Sample</th>
<th>Minimum Viscosity [P]</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Resin</td>
<td>3.5</td>
<td>250</td>
</tr>
<tr>
<td>0.5% PR-19</td>
<td>0.5</td>
<td>250</td>
</tr>
<tr>
<td>1% PR-19</td>
<td>95</td>
<td>250</td>
</tr>
<tr>
<td>1% PR-19/5% TPPB</td>
<td>28</td>
<td>250</td>
</tr>
<tr>
<td>0.5% PR-24</td>
<td>10</td>
<td>280</td>
</tr>
<tr>
<td>1% PR-24</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1% PR-24/5% TPPB</td>
<td>0.78</td>
<td>250</td>
</tr>
<tr>
<td>5% TPPB</td>
<td>0.04</td>
<td>165</td>
</tr>
</tbody>
</table>

Measured by Parallel Plate Rheology
## Dynamic Mechanical Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage Modulus (MPa), 100°C</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Resin</td>
<td>1558</td>
<td>328</td>
</tr>
<tr>
<td>5% TPPB</td>
<td>1558</td>
<td>318</td>
</tr>
<tr>
<td>0.5% PR-19</td>
<td>1622</td>
<td>316</td>
</tr>
<tr>
<td>1% PR-19</td>
<td>2174</td>
<td>318</td>
</tr>
<tr>
<td>1% PR-19/5% TPPB</td>
<td>2351</td>
<td>318</td>
</tr>
<tr>
<td>0.5% PR-24</td>
<td>1674</td>
<td>323</td>
</tr>
<tr>
<td>1% PR-24</td>
<td>1829</td>
<td>315</td>
</tr>
<tr>
<td>1% PR-24/5% TPPB</td>
<td>2639</td>
<td>313</td>
</tr>
</tbody>
</table>

Increased storage modulus observed with increasing CNF concentration, and on dispersion with clay.
**Durable Polymer Cross-Linked Aerogels**

**Conventional Aerogels**
- Low densities
- High porosity and surface area
- Good electrical and thermal insulators

**Application in NASA missions limited because of poor mechanical and environmental durability**

**Polymer Cross-linked Aerogels**
- Significantly enhanced mechanical properties (up to 300X increase in strength)
- Improved durability – some formulations are flexible
- Slightly increase in density and thermal conductivity

**New aerogels offer multifunctional solution for many NASA Mission Needs**

Capadona, Leventis, Meador, Nguyen, Vivod

Collaborations with: Clark Atlanta, U of Akron, Parker Hannifin, ASI, Aspen Aerogels
Surface Modification of Silica Particles Opens Doors to Other Polymer Systems

TMOS, \((\text{EtO})_3\text{-Si-X, Solvent}\)

Water, catalyst, Solvent

\(X = \text{amines, acrylate, double bond, etc.}\)

Acrylates
Polyacrylate
Anhydrides
Polyimide
Epoxy
Epoxies
Styrene
Polyurea
Polystyrene
Compression test of crosslinked aerogels

Katti et al, Chemistry of Materials, 2006, 18, 285-296
Enhanced Mechanical Properties Through the Addition of Carbon Nanofibers

Pyrograph® Fibers with Proprietary Surface Treatment to Enhance Solvent Compatibility

- Nanofibers incorporated in the sol – form stable suspensions in acetonitrile containing APTES and TMOS
- Some fiber dissolution observed upon addition of water
- Nanofiber settling observed in gels with higher nanofiber content

Wet Gels with (right) and without (left) Carbon Nanofibers

Dry Gels – Those with Nanofibers Have Gray or Blue Appearance
Flex-Link Aerogels Have Improved Flexibility and Durability

Incorporation of Flexible Linkages in Silica Backbone Enhances Flexibility and Durability

Flex-Link Aerogels Easier to Handle in “Green” State – Better Processability

Flex-Link Aerogels Show Better Recovery After Compression
Polyimide Cross-linked Aerogels

3 Variable DoE Study to assess effects of:
- Am’t of total silane (aminopropyl + TMOS0 in initial sol
- Two different co-reactants – APTES and APDMES
- Am’t of co-reactant as mole % of total

On:
- Density – no effect of co-reactant type, interact of co-reactant and total silane
- Porosity – slightly higher for APTES
- Compressive Modulus – depends on total silane
- Compression Set – APDMES more sensitive to co-reactant %
- TOS – see figure

Corrected for weight loss due to solvent

Weight Loss after 1000 h at 200°
Compression tests

- Samples compressed to 25% strain and allowed to recover
- APMDES aerogels more sensitive to mole fraction

- Modulus dependent mostly on total silane concentration
- No effect of co-reactant type
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
Large Scale Aerogel Manufacturing

joint with Aspen Aerogels

- Thermal conductivities as low as 20mW/mK
- Mechanical properties – TBD
- Cross-linking eliminates shedding
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: Panels
- Materials screening
- Composite material and failure models

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

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
High Temperature PMC Radiators and Heat Exchangers

- 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!
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

• Innovative Partnership Program
  – Started in FY06, expect opportunity in FY08
  – Fund partnerships between NASA Center and industry – emphasis on both commercialization and NASA mission needs
  – Up to $250K funding/year, requires industry and NASA program cost match