Recent Advances in Thermoplastic Puncture-Healing Polymers

Keith L. Gordon
Philip B. Bogert
Dennis C. Working
Kristopher E. Wise
Janice Y. Smith
Crystal C. Topping
Sean M. Britton
Paul R. Bagby
Emilie J. Siochi

NASA-Langley Research Center
Advanced Materials and Processing Branch
Hampton, VA 23681

AIAA Infotech@Aerospace 2010 in
Buckhead, GA
April 20, 2010 – April 22, 2010
Background
Self-Healing Polymeric Materials

Autonomic Self healing of Polymeric Composites
University of Illinois

Advantages
• Fast polymerization of DCPD
• Inexpensive DCPD
• Recovery of 60-90% of initial fracture load

Disadvantages
• High cost of catalyst
• Amount of catalyst
• Stability of catalyst?
• Healing of crack along previous crack?
• Capsules may have detrimental effects on composite performance.

Advantages
- Easy and fast polymer synthesis
- Transparent material
- Retro-Diels-Alder reaction allows for remending of sample

Disadvantages
- Crack initiation led to fracture of sample—could not stop crack propagation
- Samples had to be held in intimate contact at high temperature for several hours for sample to remend
- A maximum of 50% of initial fracture load could be recovered
- Subsequent cracks propagate along original crack plane, with additional cracking adjacent to this crack

Background
Self-Healing Polymeric Materials

Brittle glass fiber reinforced plastics containing hollow fibers filled with epoxy hardener and uncured resin in alternate layers, with fluorescent dye

University of Bristol

(a) Hollow glass fibres, (b) Hollow glass fibres embedded in carbon fiber reinforced composite laminate, (c) Damage visual enhancement in composite laminate by the bleeding action of a fluorescent dye from hollow glass fibres


Hucker MJ, Bond I, Bleay S, Haq S., Composites A, 34(11), (2003), 1045-1052
Motivation

• Develop self-healing polymeric materials to enable damage tolerant systems.
  - Tailor puncture healing for use temperatures and applications.

• Benefit in environments and conditions where access for manual repair is limited or impossible, or where damage may not be detected.
Approach

- Survey commercially available materials capable of puncture self healing.

- Determine puncture healing mechanism.

- Understanding guides design of range of new puncture self-healing materials.

Ballistics testing assembly
Methods

- Thermal and mechanical analysis of polymers
- Mid-velocity projectile tests on various commercially available polymers at various temperatures
- Measured initial and final bullet velocities with chronographs
- Measured site of impact temperatures with thermal imaging cameras
- Dynamic Mechanical Analysis
  Time Temperature Superposition (TTS) master curve.
- High speed video

Ballistics testing assembly
Puncture Self-Healing Concept Background

- Puncture healing in these materials is dependent on how the combination of the polymer’s viscoelastic properties responds to the energy input from the puncture event which results in an increase of temperature in the vicinity of the impact.

- Self-healing behavior occurs upon projectile puncture whereby energy is transferred to the material during impact both elastically and inelastically thus establishing two requirements for puncture healing to occur:
  1. The need for the puncture event to produce a local melt state in the polymer material and
  2. The molten material has to have sufficient melt elasticity to snap back and close the hole


  Collaboration with Emilie Siochi with NASA-Langley Research Center

*2nd ICSHM 2009*
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>Elongation (%)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surlyn</td>
<td>-100</td>
<td>54.95</td>
<td>309</td>
<td>27.2</td>
<td>308.5</td>
</tr>
<tr>
<td>Affinity EG 8200</td>
<td>-68</td>
<td>46.66</td>
<td>947</td>
<td>9.3</td>
<td>5.9</td>
</tr>
<tr>
<td>PB-g-PMA-co-PAN</td>
<td>85</td>
<td>-</td>
<td>7.5</td>
<td>37.3</td>
<td>2472.5</td>
</tr>
<tr>
<td>Lexan</td>
<td>150</td>
<td>-</td>
<td>2.0</td>
<td>59.0</td>
<td>2900</td>
</tr>
<tr>
<td>PBT</td>
<td>70</td>
<td>210</td>
<td>250</td>
<td>50.0</td>
<td>2000</td>
</tr>
<tr>
<td>PBT-co-PAGT</td>
<td>66</td>
<td>180</td>
<td>500</td>
<td>6.9</td>
<td>188</td>
</tr>
</tbody>
</table>
## Ballistic Testing Results

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Test Temp (°C)</th>
<th>Site of Impact Temp (T)&lt;sub&gt;i&lt;/sub&gt; (°C)</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>Hole Diameter (mm)</th>
<th>Self healing (Y or N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surlyn</td>
<td>25</td>
<td>127</td>
<td>-100</td>
<td>54,95</td>
<td></td>
<td>Y</td>
</tr>
<tr>
<td>Affinity EG 8200</td>
<td>25</td>
<td>77</td>
<td>-68</td>
<td>46,66</td>
<td></td>
<td>Y</td>
</tr>
<tr>
<td>PB-g-PMA-co-PAN</td>
<td>25</td>
<td>133</td>
<td>85</td>
<td></td>
<td>.5</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>127</td>
<td></td>
<td></td>
<td></td>
<td>Y</td>
</tr>
<tr>
<td>Lexan</td>
<td>25</td>
<td></td>
<td>150</td>
<td></td>
<td></td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
<td>N</td>
</tr>
<tr>
<td>PBT</td>
<td>25</td>
<td></td>
<td>70</td>
<td>210</td>
<td></td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td>3.0</td>
<td></td>
<td>N</td>
</tr>
<tr>
<td>PBT-co-PAGT</td>
<td>28</td>
<td></td>
<td>66</td>
<td>180</td>
<td></td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td>N</td>
</tr>
</tbody>
</table>
Ballistic Testing Results

(PB-g-PMA-co-PAN)

Test temperature: \((25^\circ C)\)

Test temperature: \((50^\circ C)\)

2\(^{nd}\) ICSHM 2009
Time Temperature Superposition Results

Master Curve - Surlyn

29°C  50°C  70°C  90°C
Bullet penetration schematic diagram of puncture healing mechanism
High Speed Video

PB-g-PMA-co-PAN

2nd ICSHM 2009
Conclusions and Future Work

• Several commercially available polymers possessing unique puncture self-healing functionality at low to mid range temperatures have been identified.

• Puncture self-healing improved with increasing temperature for the commercially available polymer, PB-g-PMA-co-PAN.

• Puncture self-healing was more effective when site of impact temperatures were above glass transition temperatures and melting temperatures of respective polymers.

• High speed video confirmed puncture healing mechanism in Surlyn and PB-g-PMA-co-PAN.

• Incorporate computational methods in the design of new compositions.
Cross Cutting Applications

Fuel Tanks

Space Structures

2nd ICSHM 2009