Recent Advances in Thermoplastic Puncture-Healing Polymers

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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.

**Background**

Self-Healing Polymeric Materials

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**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
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*
# Thermal and Mechanical Property Characterization Results

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<th>Polymer</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
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<td>Tg (°C)</td>
<td>Tm (°C)</td>
<td>Hole Diameter (mm)</td>
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Ballistic Testing Results

Test temperature: (25°C)

Front

Test temperature: (50°C)

Back

(PB-g-PMA-co-PAN)
Time Temperature Superposition Results

Master Curve - Surlyn

22nd ICSHM 2009
Puncture Self-Healing Mechanism

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