Environmentally Friendly Polyurethane (PU) Materials for Space Applications

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General target

- Development of novel eco-friendly polyurethane materials avoiding use of toxic non-isocyanate based PU materials for versatile applicability in aerospace industry:
  a/ potting systems (spacecrafts manufacturing),
  b/ conformal coating (spacecrafts manufacturing), and
  c/ thermal insulation foams (launchers manufacturing).

Requirements

- Elimination of toxic isocyanates used in traditional production of PU materials
- Minimization of health and ecological risks
- Sustainability aspect – use of renewable resources such as non-edible vegetable oils
Development of „Green” Polyurethane Materials for Use in Spacecraft and Launcher Applications

ESA Contract No. 4000119685/17/NL/KML
2017 - 2019
Targeted TRL = 3-4

TOSEDA s.r.o. (CZ)
- SME
- Prime-Contractor
- Design, formulation, preparation and testing of HNIPU materials

ArianeGroup GmbH (DE)
- Large Systems Integrator (LSI)
- Sub-Contractor
- Definition of industrial requirements and evaluation of HNIPU materials

Latvian State Institute of Wood Chemistry (LV)
- Non-profit organization
- Sub-Contractor
- Semi scale of HNIPU foams by spraying and testing
TOSEDA s.r.o.

- 2010 - SME (Czech Republic)
- 2012 - Custom design, development and commercialization of polymeric and nanocomposite materials for hi-tech applications
- 2012 - registered at ESA
- 2013 - membership at Czech Space Alliance
- Space projects:
  - Study of the LH2 Protective Layer Performance (2013)
  - Development of Epoxy Based Syntactic Foam Encapsulant: 3rd Call for Outline Proposals under the Czech Industry Incentive Scheme (2013-2016)
  - Design of Inner Wetted Thermal System for LH₂ Metallic Tank: FLPP3 program (2014-2016)
  - Electrically Conductive „Black Primer“: TRP program (2017-2018)
  - Thermal Joint Development for NEOSAT - Phase C: ARTES Neosat Phase C program (2017-2019)
  - Extended Pot Life Resins for Out of Autoclave Processing for Large and Complex Part: GSTP program (2018-2020)
Latvian State Institute of Wood Chemistry

**LS IWC** mission is the development of knowledge-based, environment friendly low-waste technologies for obtaining competitive materials and products from wood and other plant biomass for sustainable utilisation of natural resources for economic, social and ecological benefits.

- Founded in 1946
- 118 employees;
- 38 Dr.

Cooperation with ArianeGroup (former Airbus DS; Airbus SL; ... ) since 2004: development of ETI and IWTI

- Rigid Polyurethane Foams for External Tank Insulation for Launcher Upper Stages (**CRYOFOAMS**), 2015 – 2017
- Light Weight Polyurethane Insulation for the Bulkhead of Ariane Rocket, Produced with Next Generation Blowing Agents and Environmentally Friendly Catalysts (**CRYOFOAMS-LW**) 2018 - 2020

Development of Biobased Cryogenic Insulation Modified with Nanocrystalline cellulose

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ArianeGroup

- A world leader in access to space, serving institutional and commercial customers and supporting Europe’s strategic independence
- 9000 employees, 11 subsidiaries & main affiliates
- 50/50 joint company between Airbus & Safran
- Main projects:
  - Ariane 5
  - Launch Services
  - Ariane 6
- Development and industrial application of the External Thermal Insulation (ETI) for the application on the Ariane 6 launch vehicle
- In the frame of the “Green” PU project:
  - Providing LSI inputs, as well as support in testing
Approach

Traditional polyurethane synthesis

\[ R_1\text{NCO} + HO-R_2 \rightarrow \overset{\text{isocyanate}}{R_1\overset{\text{urethane}}{\text{NCO}}} \overset{\text{alcohol}}{\text{O}} \overset{\text{R_2}}{\text{O}} \text{urethane} \]

Non-isocyanate polyurethane synthesis

\[ R_1\text{NH}_2 + \overset{\text{CO}_2}{\text{epoxide}} \rightarrow \overset{\text{amine}}{\text{R}_1\text{NCO}} \overset{\text{cyclocarbonate}}{\text{O}} \overset{\text{O}}{\text{R}_2} \text{urethane} \]

\[ \overset{\text{epoxide}}{\text{O}} \overset{\text{CO}_2}{\text{O}} \overset{\text{O}}{\text{R}_2} \text{HNIPU} \]

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Synthesis of cyclocarbonates

- Pressure: 40 bars (CO₂ inlet)
- Temperature: 110 °C (inside of the reactor)
- Mixing: by magnetic bar
- Raw materials loading: 100 g
- Catalyst: Quaternary ammonium salt
- Co-catalyst: Catechol based hydrogen bond donor
- Reaction time: ca 24 - 48 h

Photo of TOSEDA's laboratory pressure reactor set-up.
**HNIPU rigid thermoinsulation foams**

Laboratory testing

<table>
<thead>
<tr>
<th></th>
<th>PU CRS 127 reference</th>
<th>HNIPU F 1</th>
<th>HNIPU F 2</th>
<th>HNIPU F 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [g/cm³]</td>
<td>-</td>
<td>0.05</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>Compression strength at 10% deformation [MPa]</td>
<td>&gt; 0.45*</td>
<td>0.16</td>
<td>0.17</td>
<td>0.35</td>
</tr>
<tr>
<td>Thermal conductivity [W/m.K]</td>
<td>&lt; 0.035*</td>
<td>0.033</td>
<td>0.037</td>
<td>0.038</td>
</tr>
</tbody>
</table>

*Benchmark targets
Requirements for components of rigid thermoinsulation foams obtained by spraying equipment

Glascraft VR
Ratio 1 : 2.5 – 2.5 : 1
Viscosity <400 mPas
Temperature <80°C

Graco Reactor 10
Ratio 1 : 1
Viscosity <300 mPas
Temperature <40°C
HNIPU F 1

Laboratory preparation of the HNIPU foam in paper cup

Cut through the HNIPU foam prepared in paper cup

Renewables = 45 %
Non-isocyanates urethane bonds = 42 %

- Best candidate HNIPU foam
- White color
- Fine cell structure
- No shrinkage
- HFC free blowing agent
- Mixing ratio A/B = 1/1

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### HNIPU conformal coatings

Renewables = 59 %  
Non-isocyanates urethane bonds = 36 %

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Tg (DSC) [°C]</th>
<th>Surface hardness [Shore A]</th>
<th>Tensile strength (25 °C) [MPa]</th>
<th>Elongation at break (25 °C) [%]</th>
<th>Thermal conductivity (27 °C) [W/m.K]</th>
<th>Surface resistivity [Ω]</th>
<th>Volume resistivity [Ω.m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference C*</td>
<td>1</td>
<td>72</td>
<td>2.8</td>
<td>99</td>
<td>0.251</td>
<td>1.5 x 10⁹</td>
<td>5.7 x 10¹¹</td>
</tr>
<tr>
<td>HNIPU C 1</td>
<td>-30</td>
<td>62</td>
<td>0.4</td>
<td>12</td>
<td>0.252</td>
<td>1.3 x 10¹¹</td>
<td>5.2 x 10⁷</td>
</tr>
<tr>
<td>HNIPU C 2</td>
<td>-6</td>
<td>65</td>
<td>0.6</td>
<td>15</td>
<td>n.a.</td>
<td>1.0 x 10¹¹</td>
<td>1.4 x 10¹¹</td>
</tr>
<tr>
<td>HNIPU C 3</td>
<td>22</td>
<td>86</td>
<td>5.0</td>
<td>166</td>
<td>n.a.</td>
<td>1.4 x 10¹²</td>
<td>1.7 x 10⁹</td>
</tr>
</tbody>
</table>

* Reference system (Solithane S113 + Solithane C113-300; Crompton, US)

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# NIPU potting systems

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Tg (DSC) [°C]</th>
<th>Surface hardness [Shore A]</th>
<th>Tensile strength (25 °C) [MPa]</th>
<th>Elongation at break (25 °C) [%]</th>
<th>Thermal conductivity (27 °C) [W/m.K]</th>
<th>Surface resistivity [Ω]</th>
<th>Volume resistivity [Ω.m]</th>
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</thead>
<tbody>
<tr>
<td>Reference P*</td>
<td>52</td>
<td>72</td>
<td>37.4</td>
<td>18</td>
<td>0.164</td>
<td>6.1 x 10^{10}</td>
<td>3.2 x 10^{12}</td>
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<tr>
<td>NIPU P 1</td>
<td>52</td>
<td>80</td>
<td>31.5</td>
<td>4.6</td>
<td>0.242</td>
<td>6.9 x 10^{13}</td>
<td>2.1 x 10^{9}</td>
</tr>
</tbody>
</table>

* Reference system (Solithane S113 + TIPA; Crompton, US)

Renewables = 57 %
Non-isocyanates urethane bonds = 100 %
Conclusions

• Hybrid non-isocyanates polyurethanes as new environmentally friendlier alternative to traditional PU materials
  ➢ Up to 100% replacement of toxic isocyanate hardeners
  ➢ Up to ca 60% renewable raw materials

• HNIPU rigid foam potentially applicable as external thermal insulation of Ariane 6 launcher upper stage tanks for liquid propellants
• HNIPU resins suitable candidates for application in space vehicles electronics such as potting and conformal coating materials
Thank you for attention!