Stockage et transport de l’hydrogène : solutions matériaux composites pour les réservoirs d’hydrogène haute pression

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Material Science Director - Arkema
Solutions matériaux composites pour les réservoirs d’hydrogène haute pression

1. Arkema’s hydrogen initiatives
2. Liners for High pressure vessels
3. Thermoplastic Composites Shell
   - Elium® tank type IV
   - UDX® tapes type V
4. SHM sensors
5. Conclusion
Hydrogen – European Roadmap & Arkema Initiatives

Arkema $M^2H_2$ project is part of "IPCEI Hy2Tech", the first ever Important Project of Common European Interest in the hydrogen sector.

**Materials for Hydrogen Mobility**

- Thermoplastic recyclable type IV & type V high pressure vessels for cars, trucks, buses and trailers
- Membranes for fuel cells
- Coatings and composites for bipolar plates
- Piezoelectric sensors for high pressure vessels SHM
Rilsan® Liners for High Pressure Vessels
Arkema’s flagship Rilsan® PA11 - overview

1. High performance material with 30+ year track record in many demanding markets
   - Transport
   - O&G pipes

2. 100 % biobased with secure availability and responsible sourcing of castor beans

3. A lower carbon footprint and ambitious decarbonization goals

4. Global production network with 2 monomer plants (Europe, Asia) and 4 polymer plants

5. Demonstrated capacity to invest: >450M€ announced in last years to increase capacity by +50%

6. Leading recycler of high performance polymers Acquisition of Agiplast in 2021
Arkema is reducing the carbon footprint of Polyamide 11

**Cradle to Gate**

*Climate change*² (comparative data vs standard fossil based polyamides)

- **Standard ISO 14040/44 (kg eq. CO₂/kg)**

2023

- 70%

2030 target

- 50%

Fossil-based polyamides

Bio-based PA11

**Biogenic** carbon impact and **Biomethane** energy use

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**Boxes and Arrows Diagram:**

- **Castor Plant** -> **Castor Beans** -> **Castor Oil**

- **Polyamide 11**
Rilsan® PA11 Hydrogen Tank Liner

A balanced set of properties

- Low H2 permeation
- Low moisture uptake
- Impact resistant

Adapted to main processes

**Rotomoulding**
- All tank sizes
- Low CAPEx
- High processability
- Mechanical performance
- Techno for boss-to-liner adhesion

**Blow Molding**
- High productivity
- Multi-layer structures
- No oxidation (high quality weld line)
- Stable process for large liners

**Extrusion - Welding**
- Long tanks
- Thickness control
- Wide portfolio of solutions
- Weldability
- Large tube extrusion experience (O&G)
Thermoplastic Composites for High Pressure Vessels
Advanced Materials: High Performance Thermoplastic Composites

Main thermoplastic polymer base chemistry

**Rilsan® Matrix**
- Carbon fiber / PA & PPA UDX® Tapes
- Main Market: Automotive & Hydrogen

**Elium®**
- Liquid reactive acrylic resins
- Main Markets: Wind energy, Transportation, Building & Infrastructure, Sport & Leisure

**Kynar®**
- PVDF powders for composite manufacturing
- Arkema/Barrday® JV UD tapes for Oil and Gas

**Kepstan®**
- PEKK powders for composite manufacturing
- Collaboration agreement Carbon/PEKK UD tapes for Aeronautics & Space

ARKEMA/BARRDAY® JV UD tapes for Oil and Gas.
Thermoplastic composites solutions

→ **ELIUM**<sup>®</sup>

**Thermoplastic composites with thermoset like processing technologies**

- Substituting thermoset resins for high level of **recyclability** (chemical or mechanical)

- A **large range of composites processing** technologies: RTM, SMC, Pultrusion, wet-winding...

- Thermoplastic process possibilities: post forming welding...

→ **UDX<sup>tapes</sup>**

**High performance polyamide-based unidirectional fibers tapes for demanding applications**

- Unique **biobased high-performance polymers** or PEKK and fibers **impregnation** process for high mechanical performances tapes

- Fast development of **automatized thermoplastic tapes processing technologies**: robotized fiber placement (AFP, ATL..), and hollow body (winding, braiding...) associated with injection molding productive process.
ARKEMA material choice for Type IV & V tanks

Type IV : TP Liner + TP Composites

Material
- Carbon / Elium® winding
- Rilsan® Liner

Process
- Tape winding + UV / Heat (dual cure)
- Rotomoulding
- Blow molding or injection + welding

Type V : TP Continuous – monolithic structure

Material
- Carbon / PA or PPA tapes
- Rilsan® Liner

Process
- Tape winding + heat (Laser, IR,....)
- Tape winding or molded + heat for 1st layer miscibility

TP COMPOSITES ADVANTAGES
- Better fatigue / resistance to cycling vs thermosets
- No explosion at burst test : melting & H2 jets (directional)
- Recycling abilities
- Manufacturing : important lead time reduction

L’Hydrogène vecteur énergétique et réactif chimique - CNC
Elium® wet winding

ELIUM® C599 E resin

- UV Photoiniator and Peroxide
- Productivity improvements: low viscosity and low post curing time

UDX® polyamide tapes winding

High Payload Hydrogen Trailers with New Composites Cylinders - European Roadtrhyp project

- New thermoplastic composite tubes (Type V) to maximise the quantity of H2 transported
  - payload of 1.5 ton of H2 with 700 bar tubes
  - Recyclable thermoplastic material
  - https://road-trhyp.eu/
Elium® the liquid thermoplastic resin designed for recycling

**CHEMICAL RECYCLING**

- Unique property of Elium® resins to be **de-polymerized** thanks to a thermolysis process
- Separation of resin and fiber reinforcement
- Collection of the original monomer of the resin
- Possibility to reuse the monomer to create the new resin in a close loop recycling process

**MECHANICAL RECYCLING**

- Grinding and blending with a virgin thermoplastic (PMMA, ABS, PVC...)
- Reuse in deposition or extrusion process
- **Enhanced properties** compared to host matrix
Mechanical Properties of Elium® materials

**Depolymerisation**

**Circularity**

**Mechanical Compounding**

**Upcycling**

- **Tensile Modulus in GPa**
- **Tensile Strength in MPa**

<table>
<thead>
<tr>
<th>Elium®</th>
<th>Recycled Elium®</th>
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<tbody>
<tr>
<td>200</td>
<td>206</td>
</tr>
<tr>
<td>11</td>
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</table>

- **Flexure Modulus in GPa**
- **Flexure Strength in MPa**

<table>
<thead>
<tr>
<th>PolyPro GF Mat</th>
<th>PolyPro GF 50</th>
<th>Elium® Panel 50%</th>
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</thead>
<tbody>
<tr>
<td>128</td>
<td>72</td>
<td>104</td>
</tr>
<tr>
<td>57</td>
<td>6.2</td>
<td>8.8</td>
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</tbody>
</table>

- **Traction Modulus in GPa**
- **Traction Strength in Mpa**

<table>
<thead>
<tr>
<th>ABS GF20</th>
<th>ABS-Elium® 40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9</td>
<td>6.9</td>
</tr>
<tr>
<td>69</td>
<td>76</td>
</tr>
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</table>

*Properties are based on Elium®, Glassfiber NCF Biax 600 +/- 45°, Fiber content 46.7%.

*Properties are based on Elium®, Coupons made by compression.

*Properties are based on Elium®, Coupons made by injection.
Structural health monitoring of hydrogen tanks

PIEZOTECH
Piezotech® FC

**3 MAIN FEATURES**

**Piezoelectric**
Conversion of mechanical energy (stress, strain) into electrical energy (voltage, current) and vice versa.

**Printable**
We develop a range of high purity polymers and inks adapted to various printing techniques to obtain thin and homogeneous layers.

**Customizable**
Flexibility of Piezotech products is paving the way for high degrees of freedom in terms of size, shape, number of sensing elements and substrates.
**WHAT**

Record and localize **acoustic waves** resulting from mechanical modifications of the composite using **piezo-active polymers (SHM)**.

Detection of a **brutal event** (impacts/shocks, strain, pressure etc.).
Detection of a **premature wear/degradation** (delamination, cracks, fatigue etc.).

**WHEN**

When the tank **fills/empties**.
When the tank **suffers a shock** (damage from an object on the road etc.).

**WHY**

- **Security**: Increasing the security of tanks by **fatigue identification**.
- **Optimal costs**: Optimizing the cost by **optimizing the amount of carbon**.
- Realizing the **requalification** of the tank in real time.
- Measuring the residual life of the tank for **second life use**.

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Flex PCB with piezo acoustic sensors

**FOR SMART COMPOSITES (H₂ tanks use case)**
Conclusions

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   3.1. Elium® tank type IV
   3.2 UDX® tapes type V
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As a conclusion – Hydrogen mobility and Sustainability

→ LCA FCEV – ADEME 2020*

→ FCEV improvements expected

**Lightweighting**
- Less materials
- Less processing / energy for manufacturing
- Reduce energy consumption.
  (today FCEV 16% heavier vs Diesel)

**Reduce use of materials with high environmental impacts**
- Carbon fibers
- Lithium and cobalt for batteries
- Platinum for FC

**Increase equipment’s durability / lifespan**
- 300 000 km vs 200 000 km
  =1/3 less abiotic resources

**Recycle**
- Decrease abiotic resource impact by 50% (platinum and carbon fiber)

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*ADEME, Luc Bondineau, Prestataires : SPHERA, Cécile Querleu, Alexander Stoffregen, ; GINGKO 21, Hélène Teulon, Analyse du Cycle de Vie relative à l’Hydrogène – Production d’Hydrogène et Usage en Mobilité Légère, Septembre 2020*