New Frontiers for Thermoplastics in Oilfield Applications

Burak Bekisli, PhD
06/14/2016
Burak Bekisli has a PhD degree in Mechanical Engineering from Lehigh University and has been employed by Greene Tweed since 2011. He was part of the R&D team that developed company’s latest thermoplastic, Arlon® 3000 XT, and he is now managing the Product Development, Testing and Simulation Group in Houston. His expertise is in testing, numerical analysis and structure-property relationships of advanced polymers for oilfield and other applications.
Greene, Tweed has a rich history grounded in 150+ years of innovation:

- **1863** – company began as distributor of hardware and mill supplies
- **Today** – a global technology leader in the design and manufacture of high-performance materials and custom-engineered solutions
- **Passion for innovation** – advancing next generation of technologies to solve critical industry challenges for our customers
Our Beginnings & Beyond

1863: Founded
1870s: Palmetto® Distributor
1950s-1960s: Customized Seals
1970s-2000s: Global Expansion of Offices, Manufacturing & Capabilities
2010 & Beyond: Continued Growth of Custom-Engineered Solutions
2013: 150th Anniversary
2014: Arlon® 3000 XT
2014 – 2015: Chemraz® 678/694
2016: Christian Rheault, New President & CEO.

Oilfield
Arlon® 3000 XT by Greene, Tweed based on VESTAKEEP®, an Evonik product.
Global Presence, Local Service

Greene, Tweed has 1,600 employees across 11 countries – delivering local support on a truly global scale.
Oilfield Plastics: Extreme Challenges

- Performance in load bearing applications – critical for sealing
- Performance in HPHT and Ultra-HPHT conditions that exceed 30,000 psi and 500°F
- Broad chemical resistance to oilfield chemicals (common exposure to steam, CO₂, H₂S, drilling and production fluids)
- Creep and aging resistance for long-term reliability
- Strong electrical insulation capability – critical for connectors
- Most often, all needed at the same time
• Extreme-temperature amorphous plastics generally have higher $T_g$ than semi-crystalline counterparts.

• Semi-crystalline polymers can be used above $T_g$.

• Imide group reacts *irreversibly* with water (hydrolysis) at temperatures above $90^\circ C/194^\circ F^{1,2}$. This leads to significant property drops.

• PEEK and polyketone family is closest to satisfying the broad requirements in our target applications.

Polyketone Family

- Improved high temperature and creep properties
- Reduced chemical resistance (especially with water-based fluids over 200°C)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ketone / Ether ratio (K/E)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td>0.5</td>
<td>143</td>
</tr>
<tr>
<td>PEK</td>
<td>1</td>
<td>152</td>
</tr>
<tr>
<td>PEKEKK</td>
<td>1.5</td>
<td>162</td>
</tr>
<tr>
<td>PEKK</td>
<td>2</td>
<td>162</td>
</tr>
</tbody>
</table>

Ketone (polar) → Ether (non-polar) → Aromatic rings

Polymer Ketone / Ether ratio (K/E) Tg (°C)
Improving Properties of Polyketones

- **Increase crystallinity via thermal post-treatments**
  - Improves thermal, chemical and mechanical resistance
  - (Limited, most often already in place, 35-45% crystallinity typical)

- **Use of fillers**
  - **Carbon**: Improves mechanical properties and creep resistance
    - Elongation drops to 1-2% (BUR installation issues)
    - Electrical resistance drops
  - **Glass**: Improves mechanical properties and creep resistance
    - Elongation drops to 3-5%
    - Compatibility with water drops significantly
  - **PTFE** and others mainly used for different purposes (friction, wear reduction, etc.)

Installation of a BUR on a connector
High molecular weight PEEK (Vestakeep 5000G by Evonik)

- Longer chains, more entanglements, higher Tg
- PEEK chemical structure
- Highly improved ductility

<table>
<thead>
<tr>
<th>Grade</th>
<th>Mn</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK 1</td>
<td>43900</td>
<td>106000</td>
</tr>
<tr>
<td>Vestakeep 5000G</td>
<td>56700</td>
<td>125000</td>
</tr>
</tbody>
</table>

[Graphs showing tensile modulus and strain over temperature for PEEK 2 and Vestakeep 5000G]
Arlon 3000 XT: First and only commercially available cross-linked PEEK

- Patented cross-linking technology. Significantly enhanced high temperature and creep properties.
- High-temperature resistant (aromatic) cross-linking system on amorphous and crystalline regions.
Oilfield
Arlon® 3000 XT by Greene, Tweed based on VESTAKEEP®, an Evonik product

- Best-in-class polyketone
- PEEK chemical structure, enhanced mechanical properties with cross-linking (excellent chemical compatibility, improved thermal stability, improved creep resistance)
Arlon® 3000 XT Back-up rings

14-Day Back-Up Ring Testing

Testing at 350˚ F & 25 ksi

- Arlon 3000 XT shows improved extrusion resistance versus virgin and filled versions of PEEK.

PEEK Total Extrusion ~0.0075”
GF-PEEK Total Extrusion ~0.0055”
CF-PEEK Total Extrusion ~0.004”
Arlon 3000 XT Total Extrusion ~0.002”
### All-Plastic Multi-Pin Connectors

<table>
<thead>
<tr>
<th>Material</th>
<th>New Connector</th>
<th>Post Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEK (tan)</td>
<td><img src="PEK.jpg" alt="Image" /></td>
<td>Extrusion 0.049” Extrusion 0.049” Splayed pins</td>
</tr>
<tr>
<td>Arlon® 3000XT (black)</td>
<td><img src="Arlon.jpg" alt="Image" /></td>
<td>Extrusion 0.013”</td>
</tr>
</tbody>
</table>

*Testing at 20,000 psi and 400°F, for 100 hours*

- Arlon 3000 XT improves connector ratings and provides higher reliability.
New Frontiers with Arlon® 3000 XT

HVHT (High Voltage, High Temperature Applications)

- Insulation of high power electricity
- Mostly subsea applications
- Requires high voltage (> 5kV) resistance on top of other general requirements (high temperature, chemical compatibility, creep resistance and even high pressure)

- High Voltage Connector, Application requirements: 350°F, 20,000 psi, 24 kVDC
- High Voltage Insulator Sleeves Application requirements: compliance to IEC60502-4 (4 hours survival under 4 times the application voltage of 5 kVAC), 400°F
New Frontiers with Arlon® 3000 XT

Volume Resistivity Testing at 400°F (per ASTM D257)

- Significant insulation resistance improvement over PEEK and PEK at high temperatures and over a range of voltages.
- Chemical structure of cross-links help increase resistance.

\[ R = \frac{V}{I} \quad \rho = \frac{RA}{t} \]
New Frontiers with Arlon® 3000 XT

- Insulation improvement with Arlon 3000 XT persists at 400°F - 500°F and with applied voltages up to 5kV.
- Higher voltages and higher temperatures reduce the resistivity of materials significantly.
New Frontiers with Arlon® 3000 XT

Proving the effect of cross-linking (400°F test data)

- Crystallinity has no influence in the improvement.
- Level of cross-linking seems to influence the resulting resistivity.
New Frontiers with Arlon® 3000 XT

4-hour Dielectric Breakdown Testing
(Test sample thickness: 0.020”, voltage: 10 kVDC)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>PEEK</th>
<th>PEK</th>
<th>Arlon 3000XT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temp</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>400°F</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>450°F</td>
<td>28.5 s</td>
<td>297.5 s</td>
<td>None</td>
</tr>
<tr>
<td>500°F</td>
<td>Not tested</td>
<td>Not tested</td>
<td>None</td>
</tr>
</tbody>
</table>

• Highly improved dielectric breakdown resistance
• Excellent candidate for high power insulation

Oilfield
Arlon® 3000 XT by Greene, Tweed based on VESTAKEEP®, an Evonik product
New Frontiers with Arlon® 3000 XT

Fire Safe Seals

• Utilization of non-melting, rubbery behavior of Arlon 3000 XT at extremely high temperatures

Flame test on sealing arrangement containing Arlon 3000 XT back-up rings.

Max internal temperature: 850°F
Flame temperature: 2012°F±176°F
Flame duration: 15 minutes
N₂ gas at 3000 psi sealed
Arlon 3000® XT back-up ring maintains sealing integrity and acts as a seal at higher temperatures.
Future Improvements

Carbon-filled Cross-linked PEEK

- Not commercialized yet
- Ideal for metal replacement
- Ultra-high stiffness at high temperatures
- No-melt behavior, similar to Arlon 3000 XT

![Graph showing the comparison of G' (Pa) vs. T (°C) for 30% Carbon filled X-PEEK, 30% Carbon filled PEEK, and Arlon® 3000 XT.]

**Oilfield**
Arlon® 3000 XT by Greene, Tweed based on VESTAKEEP®, an Evonik product
## Carbon-filled, Cross-linked PEEK

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Unit</th>
<th>30% Carbon filled Crosslinked PEEK</th>
<th>30% Carbon filled PEEK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>23°C 75°F</td>
<td>93°C 200°F</td>
</tr>
<tr>
<td>Elongation @ Break</td>
<td>ASTM D638</td>
<td>%</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>ASTM D638</td>
<td>MPa</td>
<td>248</td>
<td>212</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>ASTM D638</td>
<td>GPa</td>
<td>23</td>
<td>22.7</td>
</tr>
<tr>
<td>Flex Strength</td>
<td>ASTM D790</td>
<td>MPa</td>
<td>347</td>
<td>310</td>
</tr>
<tr>
<td>Flex Modulus</td>
<td>ASTM D790</td>
<td>GPa</td>
<td>19.0</td>
<td>18.7</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>ASTM D695</td>
<td>MPa</td>
<td>304.7</td>
<td>240.6</td>
</tr>
</tbody>
</table>

Oilfield
Arlon® 3000 XT by Greene, Tweed based on VESTAKEEP®, an Evonik product
Conclusions

- Polyketone family is still the most ideal thermoplastic for a broad range of demanding oilfield applications.

- Enhancements in properties of polyketones can be achieved in several ways; carefully optimized cross-linking is one example.

- Unique properties of Arlon 3000 XT, the first commercially available cross-linked PEEK, have been utilized successfully in HPHT applications such as back-up rings, electrical connectors and fire safe seals.

- Cross-linking is proven to enhance the electrical resistivity of PEEK, a critical property especially for HVHT applications.

- Filled grades of Arlon 3000 XT have a potential to expand the capability window of polyketones to further extremes.
Greene, Tweed Oilfield

**USA:** Houston, TX
1930 Rankin Road
Houston, TX 77073

**Tel:** +1.281.765.4500
**Fax:** +1.281.821.7771
**Toll Free:** +1.800.927.3301

**Website**
www.arlon3000xt.com

**Email**
arlon3000xt@gtweed.com

**LinkedIn**
www.linkedin.com/company/greene-tweed-&-co