Effect of high-temperature steam on the mechanical properties of PAEK polymers & alloy

Energy Rubber Group, 2014 Fall Technical Meeting
San Antonio, TX
September 18, 2014

By Tim Hsu, Ph.D.
Outline

- Introduction & Background
  - Statement of the problem for corrosive HPHT fluid handling components.
  - Material options for PEEK & Beyond®: PAEK, Copolymers, Blends & Alloys
  - Effect of processing on properties. INJ, HCM, CAM, EXT.

- Hot water screening of potential polymer candidates

- Steam as corrosive medium for polymers
  - Experimental
  - 500 °F/72 hrs: appearance, water uptake, property retention
  - 600 °F/24 hrs: appearance, water uptake, property retention

- Summary & conclusion

- Discussion
Introduction & Background
Supply Chain of Polymeric Products

Engineering and Application Development

Polymerization  Compounding  Material Conversion  Application Development - Engineering  Manufacturing & Assembly  End User Products / Market Requirements

Polymer:
- PEEK
- PAEK’s
- PAES’s
- TPI
- PBI

Compounds:
- Carbon fiber
- Glass fiber
- Mineral fillers

Stock Shapes:
- Tubes
- Bushings
- Sheet
- Rod
- Films

Manufacturing Steps:
1. Synthesis & Polymerization
2. Compounding
3. Processing & Forming
4. Machining & Secondary Processing

Products:
1. Monomer & Polymer
2. Compounds
3. Shapes / Fiber / Film
4. Parts & Components
Polymer in Oil & Gas Application
Fluid Handling and Other Critical Components

<table>
<thead>
<tr>
<th>Drilling</th>
<th>Logging</th>
<th>Completion</th>
<th>Production</th>
<th>Workover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drill Pipes</td>
<td>Logging Tool</td>
<td>Cementing Tools</td>
<td>Sucker Rods</td>
<td>Bridge Plugs</td>
</tr>
<tr>
<td>Spoolable Tube</td>
<td>Construction</td>
<td>Frac Plugs</td>
<td>Oil Tubing</td>
<td>Frac Plugs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Frac Balls</td>
<td>Seal Components</td>
<td>Injection Tubes</td>
</tr>
</tbody>
</table>

From Baker Hughes
High-temperature steam treatment

- HT steam is a screening medium for evaluating material performance in corrosive, HPHT environments
Typical PEEK Components in Oil/Gas Applications
Benefit & Value of PEEK in Oil/Gas Applications

- High mechanical strength to withstand high pressures and loads.
- High continuous operating temperature –
  Long life at elevated temperatures up to 150°C in critical environment.
- Resistant to chemical attack – provides corrosion resistance.
- Can be compounded with fillers to provide improved properties.

Limitation of Existing PAEK in Oil/Gas Applications

- Limited use in high pressure environment above 180 °C due to reduced creep resistance, even with reinforced grades.
- Existing higher Tg PAEK is cost prohibitive and has various processing concerns and still limited to 200 °C under high pressure environment.
- Many high Tg PAEK lacks PEEK ductility with limited process option.
Industry Requirements:

- High Tg PAEK that maintains high mechanical strength above 200 °C.
- Maintain ease of processing similar to PEEK.
- Maintain chemical resistance at high temperatures.
- Cost Effective.

Potential Solution(s):

- Alternative high temperature polymer family.
- Copolymers of PAEK.
- PAEK Alloy & Blends.
- Crosslinked PAEK system.
Polymers for Corrosive HPHT Application
PAEK, its Blends & Alloys
High Heat Polymers

Temperature

Performance

Price

Chemical Resistance

260°C

220°C

180°C

Amorphous

Semi-Crystalline
# Commercial PAEK’s

<table>
<thead>
<tr>
<th>Generic Name</th>
<th>Trade Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PEEK</strong></td>
<td>Victrex®; Vestakeep® (Evonik); Ketaspire® (Solvay); Generic</td>
</tr>
<tr>
<td><strong>PEK/PEEKK</strong></td>
<td>PEEK-HT® (Victrex); Generic</td>
</tr>
<tr>
<td><strong>PEKEKK</strong></td>
<td>PEEK-ST® (Victrex); Ultracek® (BASF)</td>
</tr>
<tr>
<td><strong>PEKK</strong></td>
<td>Cypek® (Cytec), Oxpekk® (Arkema); Arylmax® K &amp; P (Polymics)</td>
</tr>
</tbody>
</table>

®: tradename of respective company inside parenthesis
Thermal Transitions of Commercial PAEK’s

<table>
<thead>
<tr>
<th>PAEK</th>
<th>$T_g$ °C</th>
<th>$T_m$ °C</th>
<th>$T_c$ °C</th>
<th>$\Delta H$ J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEKEKK</td>
<td>165</td>
<td>384</td>
<td>344</td>
<td>53</td>
</tr>
<tr>
<td>PEK</td>
<td>160</td>
<td>372</td>
<td>333</td>
<td>51</td>
</tr>
<tr>
<td>PEEK</td>
<td>151</td>
<td>338</td>
<td>293</td>
<td>44</td>
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</tbody>
</table>
Arylmax® K Resin
Poly(ether ketone ketone)

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\begin{align*}
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\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
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\text{C} & \quad \text{Tm} = 310 – 380°C
\end{align*}
\]
Arylmax® P Resin

- Arylmax® P is a new family of copolymers
- Generically named PAEKP copolymers
- Each copolymer property is determined by $x : y$ ratio, or

$$B/P \text{ Ratio}$$

- $Z = \text{bisphenyl(di)ketone radical}$
- $Q = \text{bisphenol radical}$
- $C_p = \text{proprietary aromatic radical}$
Comparison of PAEK’s Thermal Transitions

<table>
<thead>
<tr>
<th></th>
<th>T_g °C</th>
<th>T_m °C</th>
<th>T_c °C</th>
<th>Δ H J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAEKP-2A</td>
<td>246</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PAEK</td>
<td>206</td>
<td>369</td>
<td>318</td>
<td>26</td>
</tr>
<tr>
<td>K7500</td>
<td>170</td>
<td>348</td>
<td>288</td>
<td>31</td>
</tr>
<tr>
<td>PEEK</td>
<td>151</td>
<td>338</td>
<td>293</td>
<td>44</td>
</tr>
</tbody>
</table>
Measurements made on annealed samples using 3 point bend fixture
(except Arylmax K7500CF30 measured (annealed) using single cantilever fixture)
PBI and High Heat PAEK Enhanced Blends & Alloys

Why Use Blends & Alloys?

- Enhance strength at high temperature by increasing Tg with high Tg components
- Improve dimensional stability at high use temperature with high melting components
- Enhance chemical and corrosion resistance with more chemical resistance components
- Compatibilizer and Interfacial Agents for composite and coatings applications
- Modify processing characteristics and mechanical properties
Arylmax® P & PEKK Blends

Tg & Tm, °C

<table>
<thead>
<tr>
<th>Property</th>
<th>PEKK/PAEK-2 Weight Ratio</th>
<th>Tg (°C)</th>
<th>Tcc (°C)</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEKK</td>
<td>100/0</td>
<td>160</td>
<td>311</td>
<td>361</td>
</tr>
<tr>
<td>Example 3</td>
<td>80/20</td>
<td>177</td>
<td>288</td>
<td>360</td>
</tr>
<tr>
<td>Example 4</td>
<td>60/40</td>
<td>187</td>
<td>268</td>
<td>358</td>
</tr>
<tr>
<td>Example 5</td>
<td>40/60</td>
<td>204</td>
<td>-</td>
<td>353</td>
</tr>
<tr>
<td>Example 6</td>
<td>20/80</td>
<td>210</td>
<td>-</td>
<td>354</td>
</tr>
<tr>
<td>PAEK-2</td>
<td>0/100</td>
<td>230</td>
<td>-</td>
<td>320</td>
</tr>
</tbody>
</table>
Processing & Properties
Effect of Processing on Morphology
(Neat & Reinforced)
Effect of Machining on Components

Feed Rate: 0.035mm
RPM: 650

Feed Rate: 0.035mm
RPM: 300
Effect of Compounding on Mechanical Properties

• Compounding conditions has significant impact on tensile properties

PEEK/PBI \((\text{Celazole® TU-60})\) Tensile Properties

- Above Spec
- Below Spec
Effect of Compounding on Mechanical Properties

PEKK/PBI
(Arylmall K7522PB60)

- Tensile Strength (MPa)
- Flexural Strength (MPa)
- Tensile Modulus (GPa)
- Flexural Modulus (GPa)

Above Spec
Below Spec
Steam & Hot Water Performance
Average of three Specimen immersed in Water @ 60 °C; Dimensions and Hardness was also checked.
Average of three Specimen immersed in Water @ 60 °C; Dimensions and Hardness was also checked.
### Experimental Plan for Steam Treatment

Material matrix by PAEK family:

<table>
<thead>
<tr>
<th></th>
<th>PEEK</th>
<th>PEKK (Arylmax® K)</th>
<th>PAEK blends &amp; alloys (Arylloy®)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEEK (Victrex 450G)</td>
<td></td>
<td>PEKK (K7522)</td>
<td>[PEKK/PAEK (Arylmax K7520/P3000)]</td>
</tr>
<tr>
<td>PEEK HMW (Vestakeep)</td>
<td></td>
<td>PEKK HMW (K7500)</td>
<td>[PAEK/PBI (Arylmax P3000/PBI)]</td>
</tr>
<tr>
<td>PEK (Victrex PEEK HT)</td>
<td></td>
<td>PEKK/PBI</td>
<td></td>
</tr>
<tr>
<td>PEEK/PBI (Celazole TU-60)</td>
<td></td>
<td>[PEKK/PBI (Arylmax K7522PB10)]</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>PEKK/PBI</td>
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<tr>
<td></td>
<td></td>
<td>[PEKK/PBI (Arylmax K7522PB50)]</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>PEKK/PBI</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[PEKK/PBI (Arylmax K7522PB60)]</td>
<td></td>
</tr>
</tbody>
</table>

**Condition I.** Steam treatment at 500°F (260 °C) for 72 hrs

**Condition II.** Steam treatment at 600°F (315 °C) for 24 hrs
Experimental Set-up for Steam Treatment

- High pressure, high temperature autoclave with temperature control
- ASTM tensile bar specimens
Steam Treatment @ 500°F/72 hrs
**PEEK**  
(Victrex PEEK 450G)

**PEEK HMW**  
(Vestakeep)

**PEK**  
(Victrex PEEK HT)
PEKK HMW
(Arylmax K7500)

PEKK
(Arylmax 7522)

PEKK/PAEK
(Arylmax KP)

Control 500°F, 72hr
Water Absorption
(Stream Treated PAEK @ 500°F/72 hrs)

Moisture Absorption (%)

PEK (Victrex PEEK HT)  PEEK HMW (Vestakeep)  PEEK (Victrex 450G)  PEKK (Arylmax K7522)  PEKK HMW (Arylmax K7500)  PEKK/PAEK (Arylmax KP)
Mechanical Property Retention
(Steam Treated PAEK @ 500 °F/72 hrs)

Note:
Absolute property value for 100% retention shown in red for PEEK (Victrex 450G)
Mechanical properties
(Steam Treated PAEK @ 500 °F/72 hrs)

- Ultimate tensile stress (MPa)
- Elongation @ break (%)
- Tensile modulus (GPa)
- Yield flex strength (MPa)
- Flex modulus (GPa)

Materials:
- PEEK (Victrex 450G)
- PEKK (Arylmax K7522)
- PEKK HMW (Arylmax K7500)
- PEEK HMW (Vestakeep)
PEEK
(Victrex® 450G)
PEKK/PBI
(Arylmax K7522PB)

PEKK/PBI (K7522PB10)

PEKK/PBI (K7522PB50)

PEKK/PBI (K7522PB60)
PAEK (Arylmax P3000)

PAEK/PBI (Arylmax P3000/PBI)
Water Absorption
(Stream Treated PAEK/PBI Blends @ 500°F/72 hrs)
Mechanical Properties Retention
(Steam Treated PAEK/PBI Blends @ 500 °F/72 hrs)

- Ultimate tensile strength (%)
- Elongation (%)
- Flex modulus (%)
- Yield flex strength (%)
- Tensile modulus (%)

- PEEK/PBI (TU-60)
- PEKK/PBI (K7522PB10)
- PEKK/PBI (K7522PB50)
- INJ condition 1
- PEKK/PBI (K7522PB50)
- INJ condition 2
- PEKK/PBI (K7522PB60)
<table>
<thead>
<tr>
<th></th>
<th>Ultimate tensile stress (MPa)</th>
<th>Elongation @ break (%)</th>
<th>Tensile modulus (GPa)</th>
<th>Yeild flex strength (MPa)</th>
<th>Flex modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Control</strong></td>
<td>90.2</td>
<td>2.0</td>
<td>5.4</td>
<td>187.0</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>115.7</td>
<td>2.8</td>
<td>5.6</td>
<td>176.2</td>
<td>5.6</td>
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<tr>
<td></td>
<td><strong>Steam treated, 500°F, 72hrs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.9</td>
<td>1.2</td>
<td>4.6</td>
<td>102.2</td>
<td>4.8</td>
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<tr>
<td></td>
<td>62</td>
<td>1.4</td>
<td>4.8</td>
<td>110</td>
<td>4.9</td>
</tr>
</tbody>
</table>
PBI
(Celazole® U60)
PEEK/PBI
(Celazole® TU-60)

![Graph showing storage modulus (MPa) versus temperature (°C). The graph compares PEEK/PBI Exp500F, 72hr and PEEK/PBI Control.](image-url)
PEKK/PBI (Arylmax K7522PB50) vs. PEEK/PBI (Celazole® TU-60)

Control

Steam Treated @ 500F/72 hrs

Graphs showing storage modulus (MPa) vs. temperature (°C) for PEKK/PBI and PEEK/PBI samples.
PEKK/PBI  
(Arylmax K7522PB60)  

vs.  

PEEK/PBI  
(Celazole® TU-60)
PEKK/PBI (Arylmax K7522PB60) vs. PEEK/PBI (Celazole® TU-60)
Steam Treatment @ 600°F/24 hrs
PEEK
(Victrex PEEK450G)
(Steam Treated @ 600 °F/24 hrs)
PAEK CF Compound
(Steam treated @ 600°F/24 hrs)

PAEK (CF reinforced)

30% CF Filled PEEK (KD2250)
PAEK/PBI
(Steam Treatment @ 600°F/24 hrs)

PEKK/PAEK
(Arylmax KP)

PEKK/PBI
(Arylmax K7522PB60)

PEKK HMW
(Arylmax K7500)

PEKK
(Arylmax K7522)

PEEK/PBI
(TU-60)

PAEK/PBI
(Arylmax P3000PB20)

PEKK/PBI
(Arylmax K7522PB60)
Enhance Thermal Performance of PAEK Through Cross-linking

- Preliminary results of cross-linked PEEK
  - DMA (control, 600F)

- Cross-linked PAEK
Cross-linked PEEK (Control)
PEKK/PAEK
(Arylmax® KP)
PEKK/PBI
(Arylmax K7522PB60)
PAEK/PBI
(Arylmax P3000PB20)
Summary & Conclusions

- It’s possible to further enhance PAEK thermal and mechanical properties by blending with high Tg polymers such as PBI.

- Arylmax® P can be potential high heat modifier for other PAEK to enhance performance by forming miscible blends (Alloys).

- Miscibility may play an important role in the proper design of high Tg polymer alloys with improved plateau moduli, and enhanced environmental resistance for corrosive HPHT conditions.

- While most PAEK & it’s blends or alloys survives 500 °F/72 hrs steam treatment, further optimization may depend on actual application requirements.

- Only very limited family of PAEK alloys survive 600 °F/24 hrs steam treatment. Additional modification will be needed to further optimize performance as potential candidates for application in similar environment.
ACKNOWLEDGEMENT

- Department of Chemical Engineering, The Pennsylvania State University,
  - Equipment Support
- PBI Performance Products Inc.
- Polymics® Development Team
  - Mike Logsdon
  - Jeremy Johnson
  - Marcus Lancaster
  - Blanca Cruz