Advances in Aliphatic Polyketone Composites

SPE ACCE Presentation

Cary A. Veith, PhD
President, Esprix Technologies
September 8, 2017
Discussion Topics

- Background of Esprix Technologies
- Light-weighting Trend in Automotive
  - Need for Thermoplastic Composites
- Overview of Aliphatic Polyketone (PK)
- Ketoprix™ PK Properties
  - Mechanical, including glass fiber reinforcement
  - Moisture Sensitivity
  - Chemical Resistance
  - Fuels Permeability
  - Thermal and Electrical Conductivity
- Other Applications
- Summary and Conclusions
Who is Esprix Technologies?

Esprix is a private, specialty chemical & performance products company

Company Values:
- Practice Safety in Everything We Do
- Act with Integrity
- Demonstrate Highest Ethical Behavior
- Have Respect for People
- Treat Customers as Kings
- Treat Esprix Assets as if they were Your Own

OUR MISSION: Esprix Technologies is dedicated to the creation of innovative products and services through partnership with our customers thereby enabling us to provide technical development, manufacturing and distribution of performance materials solutions.

OUR VISION: To be the global market leader in the sale, development and application of performance products, fine chemicals and technical services to improve people's quality of life by “touching lives everyday”.

...founded 2000, Sarasota, FL
Light-weighting in Automotive

Light-weighting trend:

Use of LWM will grow from 29% to 67% by 2030


Polymer & Polymeric Composites Requirements:

To achieve metal replacement, polymers/composites must have:

CHEMICAL RESISTANCE
- Fuels, Fluids, Salts
- Broad T range

MECHANICAL PROPERTIES
- Strength, Stiffness
- Impact

TRANSPORT PROPERTIES
- Thermal Conductivity
- Electrical Conductivity
Esprix has its own line of aliphatic Polyketone polymers and compounds called Ketoprix™

Aliphatic Polyketones (PK) are linear, perfectly alternating terpolymers of α-olefins, such as ethylene and propylene and CO.

\[-(\text{CH}_2\text{CH}_2\text{C})_x-(\text{CH}_2\text{CHC})_y-\]

\[-\text{CH}_3\]

EPCO terpolymers are semi-crystalline engineering resins which play in the upper end of mid-range ETPs or in the lower end of the upper-range ETPs.
PK Benefits and Value Proposition

Industrial
- Excellent Chemical Resistance
- High Service Temperature
- Good Toughness
- Low Moisture Sensitivity

Auto
- Excellent Chemical Resistance
- Elevated Service Temperature
- Low Moisture Sensitivity
- Lower Density (than steel)
- Light Weight Composites

E&E / CAM
- Good Tribology (low friction)
- Good Toughness
- High Strength
- Low Dielectric
- Low Moisture Sensitivity

Fibers
- Toughness
- High Strength
- High Yield Elongation
- Low Moisture Sensitivity

Cpds & Distrib
- Processable
- Colorable
- Moldable
- Flame Retardant
- Fillers
- Fiber Reinforced
- Low Moisture Sensitivity
PK Applications

**Industrial**
- Oil & Gas
  - Pipeliners
- Retail Forecourt
- CPI
  - Valves
  - Pumps
- Plumbing
- Conveying
- Agriculture

**Auto**
- Fuel Connectors
- Fuel Lines
- UTH Connectors
- Radiator End Caps
- Structural Composite Parts

**E&E / CAM**
- Gears
- Wear Plates
- Bearings
- Bushings
- Dielectric Hardware
- Molded parts

**Fibers**
- Monofilament
- Multifilament
- Tires
- Textiles

**Compounds and Distribution**
- Fiber Reinforced
  - Glass
  - Carbon
- Flame Retardant
- Conductive
- Lubricated
- Colors
- Profiles

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Hyosung - Resin Manufacturer

- New PK plant, Ulsan, Korea
- 50 kta expandable to 100 kta
- PK neat resin pellets, powder products
- Special grades available
- Esprix provides Application Development, Marketing, Sales, Compounding, Warehousing & Distribution, Technical Support in North America
Polyketone - Easy Processability

- Pre-drying generally not needed prior to molding
- Easy mold filling (low melt viscosity)
- Low clamp tonnage requirements
- Lower density vs. PBT, POM, PPS & PVDF
- Same mold shrinkage rates as PA and POM => no retooling needed
- Shorter molding cycles & high mold definition
- No conditioning or annealing required after molding
- Properly molded parts are ductile and can be assembled right after molding
- isotropic shrinkage in flow and transverse directions => Parts free of warpage
- Good surface adhesion in over-molding with thermoplastic urethanes and thermoplastic elastomers (e.g. Santoprene)
## Basic Mechanical Properties

<table>
<thead>
<tr>
<th>Items</th>
<th>Unit</th>
<th>POK</th>
<th>PA6</th>
<th>PA66</th>
<th>PBT</th>
<th>POM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>1.24</td>
<td>1.14</td>
<td>1.14</td>
<td>1.30</td>
<td>1.41</td>
</tr>
<tr>
<td>Melting Temperature</td>
<td>°C</td>
<td>220</td>
<td>220</td>
<td>260</td>
<td>220</td>
<td>160</td>
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<tr>
<td>Impact Strength</td>
<td>KJ/m²</td>
<td>12</td>
<td>5.2</td>
<td>4.1</td>
<td>5.0</td>
<td>6.5</td>
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<tr>
<td>Tensile Strength</td>
<td>MPa</td>
<td>70</td>
<td>80</td>
<td>80</td>
<td>55</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>55</td>
<td>70</td>
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<td>-</td>
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<td></td>
<td>60</td>
<td>35</td>
<td>50</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Elongation at Break</td>
<td>%</td>
<td>270</td>
<td>17</td>
<td>19</td>
<td>16</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>270</td>
<td>40</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>390</td>
<td>360</td>
<td>370</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>MPa</td>
<td>1,800</td>
<td>2,600</td>
<td>2,900</td>
<td>2,400</td>
<td>2,500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,800</td>
<td>2,600</td>
<td>2,900</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,450</td>
<td>1,200</td>
<td>2,200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td>1,100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Dry: 23°C, 50% RH, 24hrs  
Conditioned: 23°C, 50% RH, 60days  
Wet: 23°C, 90% RH, 60days  
** POK: Hyosung M330A properties.
## Glass Fiber Reinforced PK

### Glass Content, %w

<table>
<thead>
<tr>
<th></th>
<th>Standard</th>
<th>EK33G2P</th>
<th>EKT33G3P</th>
<th>EKT23G3BP</th>
<th>EKT23G4P</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>ASTM D792</td>
<td>1.35</td>
<td>1.47</td>
<td>1.49</td>
<td>1.56</td>
</tr>
<tr>
<td>Mold Shrinkage (Flow Dir, %)</td>
<td>ASTM D955</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting Temperature, (°C)</td>
<td>ASTM D1525</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>220</td>
</tr>
<tr>
<td>Viscosity, (Pa-s, 280°C)</td>
<td></td>
<td>100-300</td>
<td>100-300</td>
<td>250-350</td>
<td>300-400</td>
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<tr>
<td>Deflection Temperature</td>
<td>ASTM D648</td>
<td></td>
<td></td>
<td></td>
<td>210</td>
</tr>
<tr>
<td>HDT 0.45MPa (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>205</td>
</tr>
<tr>
<td>HDT 1.82MPa (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>205</td>
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<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength, 23°C (MPa)</td>
<td>ASTM D638</td>
<td>120</td>
<td>155</td>
<td>160</td>
<td>190</td>
</tr>
<tr>
<td>Nominal Strain at Break, (%)</td>
<td>ASTM D638</td>
<td>2-4</td>
<td>2-4</td>
<td>2-4</td>
<td>2-4</td>
</tr>
<tr>
<td>Tensile Modulus, 23°C (GPa)</td>
<td>ASTM D638</td>
<td>7</td>
<td>10</td>
<td>10.5</td>
<td>13</td>
</tr>
<tr>
<td>Flexural Strength, 23°C (MPa)</td>
<td>ASTM D790</td>
<td>150</td>
<td>240</td>
<td>240</td>
<td>270</td>
</tr>
<tr>
<td>Flexural Modulus 23°C (GPa)</td>
<td>ASTM D790</td>
<td>6</td>
<td>8</td>
<td>8.5</td>
<td>11</td>
</tr>
<tr>
<td>Impact Strength 23°C (kJ/m²)*</td>
<td>ISO 179</td>
<td>13.5</td>
<td>14.8</td>
<td>12.6</td>
<td>13.3</td>
</tr>
</tbody>
</table>
PK Dimensional Stability

*PK undergoes 3-5X less dimensional change than Polyamide, and is comparable to Polyacetal*


**TABLE 1. COMPARATIVE DATA**

Water Uptake & Dimensional Changes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Equilibrium Water Uptake @50% RH (% by Wt)</th>
<th>Dimensional Changes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK</td>
<td>.30</td>
<td>.05 - .15</td>
</tr>
<tr>
<td>PA</td>
<td>2.5</td>
<td>.70 - .80</td>
</tr>
<tr>
<td>POM</td>
<td>.20</td>
<td>.10 - .20</td>
</tr>
</tbody>
</table>
Effects of Moisture on Neat Resins

Neat resins, PK vs. PA66, Flex Modulus, Tensile Strength

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Effects of Moisture on GF Resins

GF Resins, PK(20%) vs. PA66(33%), Flex Modulus, Tensile Strength

For humid applications, PK20GF offers 2% weight savings at comparable properties to PA66(33GF).
Polyketone resins exhibit excellent resistance to a broad range of chemicals:

- Aromatic & Aliphatic Hydrocarbons
- Ketones, Esters & Ethers
- Inorganic Salt Solutions
- Weak Acids & Bases
- There are in fact few known solvents for PK resins.

The resin structure also confers excellent permeation resistance to aliphatic and aromatic hydrocarbons.

Good utility in automotive fuel tanks, fuel lines, fuel filler necks, UTH components and powertrain structural parts.
PK - Hydrolysis Resistance

Tensile Strength at Yield at 23°C after 25-day exposure to various aqueous environments:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>POLYKETONE M630A MPa</th>
<th>Polyamide 66 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (50% Rh)</td>
<td>60.0</td>
<td>57.2</td>
</tr>
<tr>
<td>Water</td>
<td>59.2</td>
<td>33.1</td>
</tr>
<tr>
<td>Seawater</td>
<td>60.0</td>
<td>33.1</td>
</tr>
<tr>
<td>5% w/w Acetic Acid</td>
<td>54.9</td>
<td>33.8</td>
</tr>
<tr>
<td>5% w/w Calcium Chloride</td>
<td>60.0</td>
<td>33.8</td>
</tr>
<tr>
<td>50/50 Antifreeze</td>
<td>59.2</td>
<td>35.8</td>
</tr>
</tbody>
</table>

Tensile testing to ASTM D638 was conducted at 23°C

*With its C-C backbone, PK has excellent hydrolytic & chemical resistance*
# PK Chemical Resistance

*After exposure to CaCl$_2$ and EG...*

## 6. Chemical Exposure Data for PK M630A

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Conc.</th>
<th>Temp. (°C)</th>
<th>Days Exposed</th>
<th>Appearance</th>
<th>Change from Original, %</th>
<th>Yield Strain</th>
<th>Change</th>
<th>Yield Stress</th>
<th>Break Strain</th>
<th>Chg %</th>
<th>psi</th>
<th>%</th>
<th>Chg %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>23</td>
<td>100</td>
<td>No Change</td>
<td>Length: 1  Thickness: 0</td>
<td>1.6</td>
<td>-23</td>
<td>30</td>
<td>20</td>
<td>-7</td>
<td>248</td>
<td>-17</td>
<td>13996</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>23</td>
<td>365</td>
<td>Light Cream</td>
<td>Length: 1  Thickness: 0</td>
<td>1.7</td>
<td>-27</td>
<td>28</td>
<td>12</td>
<td>10</td>
<td>301</td>
<td>0</td>
<td>16195</td>
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<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>23</td>
<td>730</td>
<td>Yellow</td>
<td>Length: 1  Thickness: 1</td>
<td>1.1</td>
<td>-41</td>
<td>24</td>
<td>-4</td>
<td>-8</td>
<td>251</td>
<td>-16</td>
<td>13430</td>
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<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>23</td>
<td>1095</td>
<td>Yellow</td>
<td>Length: 1  Thickness: 1</td>
<td>1.6</td>
<td>-11</td>
<td>21</td>
<td>-16</td>
<td>-4</td>
<td>277</td>
<td>-8</td>
<td>15031</td>
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<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>80</td>
<td>25</td>
<td>No Change</td>
<td>Length: 1  Thickness: 1</td>
<td>2.2</td>
<td>-29</td>
<td>21</td>
<td>-16</td>
<td>8</td>
<td>219</td>
<td>-36</td>
<td>14113</td>
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<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>90</td>
<td>25</td>
<td>Very Light Off-White</td>
<td>Length: 1  Thickness: 1</td>
<td>2.2</td>
<td>-41</td>
<td>29</td>
<td>16</td>
<td>5</td>
<td>271</td>
<td>-10</td>
<td>15205</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>80</td>
<td>100</td>
<td>Cream Tan</td>
<td>Length: 1  Thickness: 1</td>
<td>1.1</td>
<td>-19</td>
<td>28</td>
<td>12</td>
<td>12</td>
<td>229</td>
<td>-24</td>
<td>13951</td>
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<tr>
<td>Ethylene Glycol</td>
<td>100%</td>
<td>80</td>
<td>25</td>
<td>Light Yellow</td>
<td>Length: 0  Thickness: -4</td>
<td>-7</td>
<td>30</td>
<td>20</td>
<td>9801</td>
<td>18</td>
<td>172</td>
<td>-43</td>
<td>11825</td>
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<tr>
<td>Ethylene Glycol</td>
<td>100%</td>
<td>80</td>
<td>100</td>
<td>Gold Yellow</td>
<td>Length: 3  Thickness: 2</td>
<td>-6</td>
<td>30</td>
<td>20</td>
<td>9744</td>
<td>17</td>
<td>39</td>
<td>-87</td>
<td>7966</td>
</tr>
</tbody>
</table>

## 7. Chemical Exposure Data for PA66 (Zytel 101)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Conc.</th>
<th>Temp. (°C)</th>
<th>Days Exposed</th>
<th>Appearance</th>
<th>Change from Original, %</th>
<th>Yield Strain</th>
<th>Change</th>
<th>Yield Stress</th>
<th>Break Strain</th>
<th>Chg %</th>
<th>psi</th>
<th>%</th>
<th>Chg %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Chloride</td>
<td>6%</td>
<td>23</td>
<td>100</td>
<td>No Change</td>
<td>Length: 2  Thickness: 2</td>
<td>7.72</td>
<td>-67</td>
<td>37</td>
<td>48</td>
<td>-44</td>
<td>322</td>
<td>44</td>
<td>13391</td>
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<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>23</td>
<td>365</td>
<td>No Change</td>
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<td>37</td>
<td>48</td>
<td>-43</td>
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<td>30</td>
<td>11809</td>
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<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>23</td>
<td>730</td>
<td>No Change</td>
<td>Length: 3  Thickness: 2</td>
<td>7.65</td>
<td>-73</td>
<td>32</td>
<td>28</td>
<td>-46</td>
<td>288</td>
<td>29</td>
<td>11431</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>23</td>
<td>1095</td>
<td>No Change</td>
<td>Length: 3  Thickness: 2</td>
<td>7.63</td>
<td>-81</td>
<td>30</td>
<td>20</td>
<td>-44</td>
<td>249</td>
<td>12</td>
<td>10478</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>5%</td>
<td>80</td>
<td>25</td>
<td>No Change</td>
<td>Length: 2  Thickness: 2</td>
<td>6.69</td>
<td>-56</td>
<td>30</td>
<td>20</td>
<td>-40</td>
<td>298</td>
<td>34</td>
<td>13338</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>100%</td>
<td>80</td>
<td>25</td>
<td>No Change</td>
<td>Length: 2  Thickness: 2</td>
<td>13.38</td>
<td>-73</td>
<td>42</td>
<td>68</td>
<td>-38</td>
<td>223</td>
<td>0</td>
<td>10131</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>100%</td>
<td>80</td>
<td>100</td>
<td>Slight Yellow</td>
<td>Length: 4  Thickness: 2</td>
<td>13.51</td>
<td>-68</td>
<td>42</td>
<td>68</td>
<td>-39</td>
<td>164</td>
<td>-26</td>
<td>7412</td>
</tr>
</tbody>
</table>

**Lower Weight Gain for PK vs PA66**

**Retention of Higher Yield Stress for PK vs PA66**
Hydrocarbon Resistance of PK

Excellent property retention after exposure to hydrocarbon fuels

Exposure: 4 months in Multicomponent Hydrocarbon Liquid:
Benzene 1%; Toluene 7%; Xylene 11%; Cyclopentenes 6%; Cyclohexanes 6%; C4-C5 17%; C6-C10 42%; C11 10%

Data provided by Shell Canada, 1999
Fuel Permeability Results

Linear regression of the slopes of weight loss curves at steady-state vs. time gives the Permeability, $P$, of fuel through the polymer tubing.

CALCULATIONS SUMMARY of FUEL PERMEABILITY and LOSS

<table>
<thead>
<tr>
<th>Type of Fuel</th>
<th>Temperature, °C (°F)</th>
<th>Permeability, $P$ (cm/s) ($\times 10^6$)</th>
<th>Steady-state Loss, g/(m$^2$-day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PK</td>
<td>PA12</td>
</tr>
<tr>
<td>UL Gasoline</td>
<td>23 (73)</td>
<td>≈ 0</td>
<td>3,171</td>
</tr>
<tr>
<td>UL Gasoline</td>
<td>93 (200)</td>
<td>328</td>
<td>86,152</td>
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<tr>
<td>E10</td>
<td>23 (73)</td>
<td>47</td>
<td>2,281</td>
</tr>
<tr>
<td>E10</td>
<td>93 (200)</td>
<td>1,084</td>
<td>6,504</td>
</tr>
</tbody>
</table>
CO₂, CH₄ Gas Permeability

**CO₂ Permeability:**
- **PK**, PA11, HDPE
- DAM;

Black outline data point: 50%RH

Data from Shell Canada, 1998

PK has much better gas barrier resistance than PA11, HDPE

**CH₄ Permeability:**
- PK, PA11
- DAM;

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Thermal Conductivity

TC Loading Curves: GF and Neat PK with CG

40\%w GF PK with Conductive Graphite

Conductivity measurements courtesy of Imerys R&D; Compression molded samples

PK can be compounded with fibers and additives for improved strength and thermal conductivity

SEM courtesy of Applied Nanostructured Solutions, LLC
Proper dispersion in compounding of GF and CG is critical for improved strength and thermal conductivity.
Compounded PK with conductive carbon black for ESD applications in extruded Automotive Fuel Lines and IM Fuel Components.

Percolation Curve:
Conductive Carbon Black / PK

Resistivity measurements courtesy of Imerys R&D

Volume Resistivity Classifications ANSI/ESD S541-2003

Conductive
Dissipative
Insulative

VOLUME RESISTIVITY, Ohm-cm

WT % CCB

Resistivity measurements courtesy of Imerys R&D
# Nanostructures

## Carbon Nanotube modified Polyketone

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield Strength (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Volume Resistivity ($\Omega\cdot$cm)</th>
<th>Thermal Conductivity (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK</td>
<td>60</td>
<td>68</td>
<td>1.6</td>
<td>$10^{15}$</td>
<td>0.22</td>
</tr>
<tr>
<td>PK + 1% CNT</td>
<td>82</td>
<td>108</td>
<td>3.3</td>
<td>20</td>
<td>0.4</td>
</tr>
<tr>
<td>PK + 2.5% CNT</td>
<td>100</td>
<td>128</td>
<td>4.6</td>
<td>2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

CNT, mechanical and thermal conductivity measurements courtesy of Applied Nanostructured Solutions, LLC
Other PK Automotive Applications

UTH Radiator Tank End Cap

- Current Material: PA66/PA612, 33%GF, K
- Incumbent Performance Issues: Warpage, Hydrolysis, Susceptibility to CaCl$_2$ exposure
- KPI’s of PK:
  - Chemical Resistance to Antifreeze, Road Salt, Aqueous solutions
  - Impact Strength
  - IM Processability
- Value Proposition:
  - Superior Chemical Resistance
  - Less Warpage, Faster Mold Cycle Time
  - Better long-term mechanical properties
  - Lower Total Cost
Other PK Automotive Applications

**Structural Components**
- Current Material: Aluminum
- Incumbent Performance Issues: Corrosion, Heavy Weight
- KPI’s of GF/TC PK:
  - Chemical Resistance to Antifreeze, Road Salt, Aqueous solutions, Hydrocarbons
  - Tensile Strength per unit Weight
  - 5X Improvement in TC
- Value Proposition:
  - Superior Chemical & Corrosion Resistance
  - Lighter Weight
  - Comparable Total Cost Manufacture (TCM)
Polyketone is a new engineering resin now commercially available with the following benefits:

- Melt processability in extrusion, injection and blow molding
- High strength, toughness / impact strength, resilience
- Better dimensional & hydrolytic stability than polyamides
- Excellent chemical resistance
- Low permeation rates to hydrocarbon fuels
- Can be compounded with fibers for added strength …
- And/or with improved electrical and thermal conductivity for use as metal replacements
- Excellent matrix for specialty nanostructure additives to build strength, chemical resistance and stiffness into Auto parts
Ketoprix Team

Cary Veith – President & CEO

Dang Le – Product Manager
Tim Morefield – TS Consultant
Bob Pilotti – Sales Consultant

SPE ACCE Sep 8, 2017
Thank You

Cary A Veith, PhD
Esprix Technologies, LP
7680 Matoaka Rd.
Sarasota, FL 34243
cveith@esrixtech.com
www.esrixtech.com
Effects of Moisture on GF Resins

GF Resins, PK(40%) vs PA66(33%), Flex Modulus, Tensile Strength

SPE ACCE Sep 8, 2017
Creep Resistance Neat PK

• PK has excellent Creep-Rupture resistance

• Superior creep resistance vs. POM, PA66
Creep Resistance GF PK

- 40%w GF PK
- 120C Creep resistance

**EKT23G4P Creep Rupture, 50% RH, 248F**

- Strain, % 2.5
- Time, hours

<table>
<thead>
<tr>
<th>Load (MPa)</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log (20 MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (40 MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log (60 MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 60
- 40
- 20

**EKT23G4P Tensile Creep, 50% RH, 23 C**

- Strain, %
- Time, hours

- 36 Mpa

- 36

SPE ACC
Fuel Permeation Resistance

Lower Fuel Permeation
PK vs. PA-12

- GM 9061-P Permeability Test protocol
- Gravimetric analysis of sealed polymeric tubing
- Electrically conductive PK compounds => extrusion of fuel tubing lines

KPI’s:
- Excellent Chemical Resistance to Hydraulic Fluids, Antifreeze, Road Salt, Aqueous Solutions
- Greater Impact Strength
- Anti-stat / electrically conductive extrusion grades

Data from Shell Chemical, 1996
PK Permeability - Theory

Based on gravimetric analysis from PK tube according to Spec GM-9061P

\[ \frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (rD \frac{\partial C}{\partial r}) \]

Constitutive Equation for Conservation of Mass, Cylindrical Geometry

**Boundary & Initial Conditions**

BC1: At \( r = a \) (inner radius), \( C = C_1 = S \cdot p^* \) where \( P = D \cdot S \)

BC2: At \( r = b \) (outer radius), \( C = C_2 \rightarrow C_\infty \approx 0 \)

IC: At \( t = 0 \), \( a < r < b \), \( C(r,0) = 0 \)

Solving the PDE for the concentration profile:

\[ C(r,t) = \frac{p^*P}{D \ln(b/a)} \ln(b/r) + \pi \sum_{n=0}^{\infty} \frac{p^*P}{D} \frac{J_0(b \lambda_n)}{J_0(a \lambda_n)} \frac{U_0(r \lambda_n)}{J_0^2(a \lambda_n) - J_0^2(b \lambda_n)} \exp[-D \lambda_n^2 t] \]

For \( t >> 0 \), integrating Fick’s law equation at outer surface gives the mass lost over time,

\[ M(t) = -2\pi LD \int_0^t r \frac{\partial C}{\partial r} \bigg|_{r=b} dt = \frac{2\pi Lp^*P}{\ln(b/a)} t \]

Plotting mass lost as a function of time gives the Permeability, \( P \) as the slope...

Note: \( U_0(r \lambda_n) = J_0(r \lambda_n)Y_0(b \lambda_n) - J_0(b \lambda_n)Y_0(r \lambda_n) \); \( L= \)tube length; \( p^*= \)vapor pressure; \( D= \)diffusivity; \( S= \)solubility constant; \( C= \)solute concentration

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Ketoprix Compounds & Grades

**Natural**
- Ultra High MF IM
- High MF IM
- Low MF IM/X
- Low MF X
- All available with additional thermal stabilizers, colors

**Fiber Reinforced**
- Chopped Glass Fiber
  - Natural
  - Black
- Chopped Carbon Fiber
- Aramid Fiber
- Carbon Nano-Structures

**Conductive**
- Thermally conductive
- Electrically conductive

**Flame Retardant**
- UL 94 V0
- UL 94 V1

**Compounds and Distribution**
- Stock Shapes
- Sheets
- Plaques
- Colors (Pantone)
- Filled Compounds

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Technical information available on our website landing page:

SPE ACCE Sep 8, 2017
Aq ZnCl$_2$ Solution Tests on PK

**PK PASSES the SAE J2044 Specification Test in aq Zinc Chloride**

PK POLYMER - ZINC CHLORIDE TESTING

- 50% ZnCl$_2$ testing
  - automotive specific (nylons)
  - accelerated screening test (cracking)
- Initial PK studies - 10% & 50% ZnCl$_2$
  - good resistance observed
    (hydrolytic, property retention)
- Tier I supplier testing
  - PK Passes

From Shell WTC Report, 1998
PK shows NO Signs of Cracking after Exposure to 50% aq Zinc Chloride

HYOSUNG: 50% ZnCl₂ Exposure Test for PK Tube, GMW14638

- **Test Conditions:**
  - Grade: M630A for 6 ea. M620A for 6 ea.
  - Dimension: OD=8.0mm, Thickness=1.0mm, extruded by Hyosung
  - Condition: Polyketone tube exposure in the tank of 50% ZnCl₂, 200Hrs, 23°C
  - Pass or Fail: good surface quality, no cracking after drying for 24 hrs at 23°C => **PASS**

From Shell WTC Report, 1998