KEPSTAN™ PEKK Polymer

Tim Spahr – Business Manager

Arkema, Inc
An Introduction to the Polyether Ketone Ketone Ketone (PEKK) Co-Polymer

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KEPSTAN PEKK
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Polyether ketone ketone (PEKK) is not a new polymer, but has recently seen more widespread industrial use.

Prior to 2011, PEKK’s primary use was for captive production of thermoplastic composites.

It was sold in limited quantities of PEKK to a few small compounding companies. These companies offered PEKK for melt processing, as well as other specialty and composite processes.

In 2011, Arkema began industrial PEKK production, providing a PEKK source and reliable supply chain.

The additional supply of PEKK to the market has created a growing interest in PEKK for a variety of industrial sectors and applications.
What is PEKK?

- PEKK is the abbreviation for Polyether Ketone Ketone
- PEKK is a part of the high Performance of Poly Aryl Ether Ketone (PAEK) polymer family.
- The other PAEK polymers are PEEEEK, PEK and PEEK.
- The difference in the characteristics of the PAEK polymer family is a result of the sequence and ratio of keto (k) to ether (e) synthetic linkages.
The PAEK Polymer Family

- Keto linkages are less flexible than Ether linkages
  Stiffer polymer chains = Higher Tg
- Keto linkages enhance packing efficiency of unit-cells
  Larger crystal binding energy = Higher Tm

PEEEK = 25% keto linkages

\[
\text{PEEEK} = \begin{array}{c}
\text{O} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} \_n
\]

\[Tm = 324^\circ C \quad Tg = 129^\circ C\]

PEEK = 33% keto linkages

\[
\text{PEEK} = \begin{array}{c}
\text{O} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array} \_n
\]

\[Tm = 343^\circ C \quad Tg = 143^\circ C\]

PEK = 50% keto linkages

\[
\text{PEK} = \begin{array}{c}
\text{O} \\
\text{O} \\
\text{C} \\
\end{array} \_n
\]

\[Tm = 374^\circ C \quad Tg = 152^\circ C\]

PEKK = 67% keto linkages

\[
\text{PEKK} = \begin{array}{c}
\text{O} \\
\text{O} \\
\text{C} \\
\text{O} \\
\end{array} \_n
\]

\[Tm \geq 400^\circ C \quad Tg = 170^\circ C\]
**What is PEKK?**

PEKK= 67% keto linkage

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\end{array}
\]

\[
\text{Tm} \geq 400^\circ \text{C} \quad \text{Tg} = 170^\circ \text{C}
\]

- The melt temperature for the PEKK homo-polymer would be approximately 400° C
- This is very near the degradation temperature for PAEK polymers.
- Melt processing a polymer with nearly the same melt and decomposition temperature would clearly be a challenge.
- What makes PEKK unique among the other PAEKs, is the ability to synthesize isomeric copolymers to affect the Tm and significantly widen the melt processing window.
What is PEKK

- The various PEKK copolymers are created and identified by the ratio of the percent Terephthaloyl (T) to Isophthaloyl (I) moieties in the polymer chain.
- This ratio is commonly known as the PEKK T/I ratio.
- Varying the T/I ratio can produce PEKK copolymers with Tm ranging from 305°C to 360°C, each with unique crystallization kinetics and very little attenuation of the glass transition temperature (160°C to 165°C).

![Graph showing the relationship between Terephthaloyl and Temperature](image)

**Increasing the Isophthaloyl moieties**
- Decreases the Tm
- Retains Tg at a high level
- Increases chain flexibility
- Decreases crystallization rate
An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer

The PEKK Co-Polymer

- Illustrated below are the terephthaloyl and isophthaloyl repeating units of PEKK copolymers.
- The terephthaloyl moieties are straight and rigid
- While the isophthaloyl moieties create a structural variation, or “kink”, in the chain, that affects chain flexibility, mobility and crystallization.

**Terephthaloyl**  Aka: Para (keto) linkage

**Isophthaloyl**  Aka: Meta linkage
The PEKK Co-Polymer

Co-Polymer system
- Variable isomer ratio Terephthalic moieties (T) & Isophthalic moieties (I)
- Structural variation with T/I ratio

Current PEKK Co-polymers:
- T/I = 80/20, Semi-Crystalline  Tg = 165°C  Tm = 360°C
- T/I = 70/30, Semi-Crystalline  Tg = 162°C  Tm = 332°C
- T/I = 60/40, Semi-crystalline  Tg = 160°C  Tm = 303°C
PEKK Co-Polymer
Crystallization Kinetics
An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer

PEKK Co-Polymer Crystallization Kinetics

- 80/20 PEKK
- 70/30 PEKK
- 60/30 PEKK

Half-Time (Minutes)

Temperature °C
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Flexural DMTA of 60/40 PEKK and 80/20 PEKK at 1 Hz and 5°C/min

Storage Modulus E' (MPa)

Tan Delta

- 60/40 PEKK
- 80/20 PEKK
An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer

Flexural DMTA of 60/40 PEKK at 1 Hz

- 60/40 PEKK DTMA @ 5° C/min
- 60/40 PEKK DTMA @ 1° C/min

Storage Modulus E' (MPa)
Processes Compatible with PEKK
PEKK Compatible Processes

- The PEKK copolymers are processable in all of the traditional melt processes (injection molding, Compression molding and extrusion), thermoforming, laser sintering and in processes related to composite tape and fabrics.

- Because each of the PEKK polymers have a unique melt temperature and crystallinity kinetics, one or more of the polymers might be better suited for a specific process than the others.
PEKK Injection Molding
An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer

80/20 PEKK Injection Molding Process Temperatures

Mold temperatures to lower molded-in stresses
(These mold temperatures require longer process time)

- **Front Zone**: 620–630°F (327–332°C)
- **Rear Zone**: 595–605°F (313–318°C)
- **Center Zone**: 610–620°F (321–327°C)
- **Nozzle**: 630–640°F (332–338°C)

**Melt Temperature**: Min 610°F (321°C) – Max 640°F (338°C)

**DO NOT**:
- exceed a sustained melt temperature of 650°F (343°C)
- set barrel or nozzle temperature below 595°F

**Mold Temperature**: 200°F (93°C) - 250°F (121°C)

60/40 PEKK Injection Molding Process Temperatures

- **Front Zone**: 700–720°F (371–382°C)
- **Center Zone**: 690–710°F (365–377°C)
- **Rear Zone**: 680–705°F (360–374°C)
- **Nozzle**: 710–720°F (377–382°C)

**Melt Temperature**: Min 700°F (371°C) – Max 725°F (385°C)

**DO NOT**:
- exceed a sustained melt temperature of 725°F (385°C)
- set barrel or nozzle temperature below 680°F

**Mold Temperature**: 400°F (205°C) - 420°F (216°C)

Parts thicker than 0.300 inches (7.62 mm) and processing the KEPSTAN 6000 series materials using mold temperatures greater than 320°F (160°C) may allow the polymer to crystallize.
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An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer

Flexural DMTA of KEPSTAN at 1 Hz and 5°C/min

- 80/20 PEKK - Unfilled
- 80/20 PEKK w/ 30% Glass fiber
- 80/20 PEKK w/ 30% Carbon fiber

Storage Modulus $E'$ (MPa)
Thermoforming PEKK
PEKK Sheet/Film

- 60/40 PEKK has been successfully cast extruded in sheets/film in thicknesses from 6µ to 1.5 mm.
- 70/30 PEKK has been successfully cast extruded in sheets/film in thicknesses from 50µ to 400µ.
- Sheet/films made using these polymer are used as cover films, laminating and thermoformed parts.
• Unlike the other Polyaryletherketone polymers the 60/40 PEKK will not crystallize in the thermoforming process

• It also can be thermoformed at much lower temperatures
  • Sheet temperature = 155° C to 180° C
  • Form temperature of 23° C to 100° C.

• The results of laboratory tests have shown that the 60/40 PEKK has the ability of up to a 20 to 1 draw ratio (shown below)

• Film of the 70/30 PEKK and 80/20 PEKK have been produced but have not yet been evaluated for their ability to be thermoformed.
Laser Welding PEKK
Laser Welding PEKK

- Due to its slow crystallinity kinetics, the 60/40 PEKK is ideally suited for laser welded assembly.
- 60/40 PEKK can be laser welded to any black PAEK polymers.
- Unlike most semi-crystalline polymers, the 60/40 PEKK maintain its amorphous condition after welding.
- Not crystalizing during the laser welding process minimizes shrinkage and stress induced warpage.
- Unlike other Polyaryletherketone materials, the 60/40 PEKK maintains its clarity after the laser welding process.
An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer

Laser Welding PEKK

- Laser radiation
- Weld seam
  - 60/40 PEKK unfilled or
  - 60/40 PEKK w/30% Glass fiber
- Melt zone
  - Any Black PAEK, the use of LASER absorption compound or black PAEK film

Courtesy of LEISTER Technologies, LLC
Laser Sintering PEKK
Laser Sintering PEKK Copolymers

- The 60/40 PEKK copolymers are being used in the selective laser sintering process due to:
  - Lowest Melt Temperature of the PAEK polymers at 305° C
  - Glass Transition Temperature = 160° C
  - Heat Deflection Temperature = ~170° C
  - Continuous use Temperature (CUT) = 260° C
  - Exposure at the SLS chamber temperatures for extended period of time does not degrade the PEKK

- The laser sintering process requires a chamber temperature and a cycle time that inherently allow the 60/40 PEKK parts to approach their full crystalline potential.

- In the laser sintering process, PEKK does not degrade like other PAEKs.

- Instead the process temperatures alter the crystalline structure of the non-sintered polymer powder, making it more favorable for re-use/recycling in consecutive laser sintering processes.
Laser Sintering Process

An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer

PEKK in Composites
PEKK in Composites

- All three grades of the PEKK copolymer (60/40, 70/30 and 80/20) have been used to make unidirectional tape and fabric composites.

- Having the lowest melt temperature the initial target for the PEKK composites was the 60/40 PEKK.

- Although it had a desirable process temperature its crystallinity kinetics did not allow it to form the crystallinity require of the polymer to achieve the mechanical properties needed in structural applications.

- Composites made using the 80/20 PEKK showed a marked improvement in strength but required higher than desirable processing temperatures, 370°C - 385°C.

- If the PEKK polymer was going to be applicable to composites it would need faster crystallinity kinetics than the 60/40 PEKK and processing temperatures lower than the 80/20 PEKK.

- The 70/30 PEKK polymer has a process temperature between the 60/40 PEKK and the 80/20 PEKK and crystallinity kinetics that are close to the 80/20 PEKK.

- The 70/30 PEKK was developed as the ideal candidate for thermoplastics composites.
When compared to PEEK AS4 type composites the 70/30 PEKK AS4 type composites has:
- A lower melt temperature (-11°C),
- A processing temperature (-20°C),
- Higher glass transition temperature (+19°C)
- Higher compression after impact strength (+16%)

<table>
<thead>
<tr>
<th>Material:</th>
<th>Data Compliments of TenCate</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Cetex TC 1320</td>
</tr>
<tr>
<td>PolyetherKetone Ketone (PEKK)</td>
<td>PolyetherEther Ketone (PEEK)</td>
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<tr>
<td>Property:</td>
<td>Min</td>
</tr>
<tr>
<td>Glass Transition Temperature</td>
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<tr>
<td>Melt Temperature</td>
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<td>Operating Temperature (Composite)</td>
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<tr>
<td>Continuous Use Temperature (Polymer)</td>
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<tr>
<td>Process Temperature (Composite)</td>
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<td>Limiting Oxygen Index (polymer only)</td>
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<td>Open Hole Tensile (RT)</td>
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<tr>
<td>Open Hole Compression (RT)</td>
<td>328 MPa</td>
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<tr>
<td>Compression After Impact</td>
<td>308 MPa</td>
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Comparison of PEKK and PEEK base composites (Data Courtesy of TenCate Advanced Composites)
PEKK Hybrid Composite Molding
Hybrid Press Forming Process

• Composites are generally relatively flat and formed sheets.
• Forming complex geometry in a composites part is extremely difficult.
• Thermoplastics offer the capability to overmold complex geometry on to a composite part in a secondary operation or a hybrid press-form and injection molding process.
• The PEKK Copolymer is ideally fit for this technology:
  • A composite made using the 70/30 PEKK (332°C Tm) can be overmolded with a glass or carbon filled 80/20 PEKK (360°C Tm).
  • Having a higher melt and processing temperature, over molding the 80/20 PEKK on a 70/30 composite will raise the surface temperature of the 70/30 PEKK composite high enough to insure a cohesive bond.
  • The ability to overmold two thermoplastics with similar temperature performance characteristics is unique to the PEKK polymer family.
• Press-forming is a hybrid process in which forming the composite laminate and the injection molding processes are performed simultaneously in the same operation.

• Two specialty molding companies in France, Cogit and Sintex NP group have proven the compatibility of press forming and overmolding by creating demonstrator boxes using the 70/30 PEKK composite laminate overmolded with the 30% chopped carbon fiber filled 80/20 PEKK.
Demonstrator Box: Press formed and overmolded in one tool and in one process by the Sintex NP Group

Press Formed 70/30 Carbon Fiber Fabric

30% Chopped Carbon fiber filled 80/20 ribs and sides

An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer
Demonstrator Box: Press Formed and overmolded in one tool and in one process

An Introduction to the Polyether Ketone Ketone (PEKK) Co-Polymer

- 30% Chopped Carbon fiber filled
- 80/20 PEKK Ribs and Base
- 70/30 Carbon Fiber Fabric
- Threaded Inserts
Conclusion

- PEKK is a co-polymer that is part of High Performance Poly Aryl Ether Ketone (PAEK) polymer family.

- The PEKK copolymers are identified by the ratio of the terephthaloyl and Isophthaloyl (T/I ratio) used during their synthesis.

- There are three available polymer grades; the 60/40 PEKK, 70/30 PEKK and 80/20 PEKK.

- These polymers can be used in injection molding, sheet/film extrusion, extrusion of stock shape powder coating, additive manufacturing-laser sintering and for thermoplastics composites.

- Due to their unique characteristics, the PEKK copolymers are enabling the use of new process technologies and allowing for create use of older processes, including improvements of thermoplastic composites.
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