KETOPRIX™
ALIPHATIC POLYKETONE

High Performance Engineering Thermoplastic Polymer Resin
Injection Molding Guide

from Esprix Technologies
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What are Ketoprix™ polymers?
KETOPRIX™ aliphatic polyketones are a new class of revolutionary engineering thermoplastics that are changing people’s perceptions about the future in plastics and composite materials.

These tough, semi-crystalline polymers were originally made possible as the result of an important catalyst discovery at the Shell Research Laboratories in Amsterdam; however, commercialization could not be continued after 2000.

In 2004, HYOSUNG Corporation, Seoul, Korea started the research of new technology to produce this unique polymer at commercial level and succeeded in 2013.

KETOPRIX™ POLYKETONES have a perfectly alternating structure made of carbon monoxide and alpha-olefins such as ethylene and propylene. KETOPRIX™ POLYKETONES offer a unique balance of processing and performance properties that can satisfy a very broad range of applications. This potential stimulates innovative thinking in product designers, expanding their horizons in an unprecedented way.

By challenging conventional thinking about the use of engineering thermoplastics, KETOPRIX™ POLYKETONES are capable of turning the unexpected into reality. As you will discover by using this Injection Molding Guide, their applications could be as diverse as your imagination will allow.
A global market perspective
The commercialization of aliphatic polyketones has been widely acknowledged in the polymer industry as one of the most significant developments since the introduction of polyamides and polycarbonate.

Previously, the global market for engineering thermoplastics consisted of the so-called "Big Five": polyamides, polyesters, polyacetals, polycarbonates and modified polyphenylene oxide. The introduction of aliphatic polyketones means that the "Big Five" is set to become the "Big Six". Because of their enormous potential for new applications, KETOPRIX™ POLYKETONES are expanding the global market for engineering thermoplastics into new areas.

Initial market development quantities were supplied from a pilot production facility operating at capacity of 1,000MT/Year. The first commercial production at a nameplate capacity of 50,000MT/Year has already come on-stream in mid-2015.

A broad range of properties
KETOPRIX™ POLYKETONES are characterized by a carbon-carbon backbone consisting of carbon monoxide and alpha-olefins. Their perfectly alternating structure between CO and olefin gives rise to a unique combination of performance properties:

- Short molding cycles and good mold definition
- Low warpage and no need for conditioning
- Superior resilience and snap-fit
- Very good impact performance over a broad temperature range
- High chemical resistance and barrier performance
- Very good hydrolytic stability
- Good friction and wear characteristics.

These polymers are suitable for injection molding, extrusion, rotational molding and blow molding as well as the production of coatings, films and fibers. In most cases, KETOPRIX™ POLYKETONES can be processed using standard equipment.
SUMMARY of PROPERTIES

A. Strong and ductile

- Tensile yield stress, approximately 60-65 MPa or 8700-9400 psi at 23°C
- Tensile yield strain, approximately 25 % at 23°C
- Tensile and flexural moduli, approximately 1.8-2.3 GPa or 260 – 330 kpsi at 23°C
- Deflection temperature under load, 100°C at 1.8 MPa or 260 kpsi for unfilled or natural resin

B. Injection molders benefit from:

- Easy mold filling
- Short cycle times
- Low clamp-force requirements
- Low warpage and high dimensional stability

C. Superior resilience

- Elongation at yield is very high: 25 %
- KETOPRIX™ POLYKETONES can be subjected to larger, cyclic, deformations than other ETPs
- Perfect for connectors in Electrical & Electronics, Consumer, Appliance, Medical End Uses

D. Impact resistance & toughness

- KETOPRIX™ POLYKETONES exhibit a high level of ductility over a broad temperature range
- Elongation at break is approximately 300 percent at 23°C
- Notched Izod impact strength is 20-50 kJ/m or 4.5-11.25 ft-lb/in at 23°C; Charpy I.S. is 15-50 kJ/m²

E. Superior chemical resistance and barrier properties

KETOPRIX™ POLYKETONES are resistant to swelling and attack in a broad range of:

- Aliphatic and aromatic hydrocarbons
- Ketones, esters and ethers
- Inorganic salt solutions
- Weak acids and bases
- Good Hydrolytic Stability
- They can also provide a good barrier to automotive fuels and other solvents.

There are only a few known solvents for KETOPRIX™ POLYKETONES such as Hexafluorisopropanol and phenolic solvents.
**Tough, semi-crystalline structure**

\[ \text{-CH}_2\text{-CH-} \rightarrow \text{-CH}_2\text{-CH-} \]

Where -R may represent for example either H or CH₃

KETOPRIX™ POLYKETONES chains are flexible and possess the molecular symmetry and cohesive energy, derived from the perfectly alternating monomer groups to give 1,4 di-ketone groups in the backbone. This symmetry produces a tough, high-melting-point, semi-crystalline thermoplastic suitable for a broad range of applications.

In the polymerization process, a second olefinic monomer such as propylene may be randomly substituted with ethylene to produce a terpolymer.

The controlled addition of termonomers facilitates the related properties.

**Excellent chemical resistance**

The excellent and broad chemical resistance exhibited by KETOPRIX™ POLYKETONE is strongly influenced by their di-polar and semi-crystalline morphology.

KETOPRIX™ POLYKETONES are widely used in hydrocarbon barrier applications. This is a consequence of their dipolar nature that confers resistance to attack and permeation by aliphatic and aromatic hydrocarbons.

In addition, the symmetry and chain flexibility of KETOPRIX™ POLYKETONES promote crystallization, which, in turn, promotes resistance to swelling and dissolution in all but the strongest polar environments.

In aqueous environments, KETOPRIX™ POLYKETONES absorb a limited amount of water that results in mild plasticization, yet their carbon-carbon backbone ensures that they also exhibit good hydrolytic stability.
**Average molecular weight**

The molecular weights of KETOPRIX™ POLYKETONES are summarized in Table 1. These values are obtained by gel permeation chromatography, GPC. Hexafluoro-Isopropyl alcohol is used as the solvent and molecular weights are determined relative to polymethylmethacrylate standards.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Mn</th>
<th>Mw</th>
<th>Mz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resins</td>
<td>119,000</td>
<td>276,000</td>
<td>652,000</td>
</tr>
<tr>
<td>EK63</td>
<td>92,000</td>
<td>185,000</td>
<td>399,000</td>
</tr>
</tbody>
</table>

Table 1. Average molecular weight

- Mn: Number average molecular weight
- Mw: Weight average molecular weight
- Mz: Z average molecular weight

Test conditions:
- Instrument: Waters 1515 pump
- Column: Shodex HFIP-806M (8mm * 300mm) * 2 at 35°C
- Eluent: HFIP 0.7ml/min(10mM TFA) with degassing and 0.2 μm suction Filtering
- Detection: Waters 2414 RI detector (30°C)
- Material: 0.1% (0.001g/1ml)
- Narrow STD: PMMA (903K, 608K, 366K, 287K, 182K, 93.3K, 58.7K, 31.6K, 10.9K, 2.58K)
- Injection: 25μL

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**Limiting viscosity number**

The intrinsic viscosity or limiting viscosity number, LVN, of KETOPRIX™ POLYKETONES is summarized in Table 2. These values are obtained measured in a capillary viscometer using m-cresol at 60°C as the solvent.

<table>
<thead>
<tr>
<th>Grade</th>
<th>LVN dL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resins EK63</td>
<td>2.1</td>
</tr>
<tr>
<td>EK33</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 2. Limiting viscosity numbers
Density ISO 1183
The density of KETOPRIX™ POLYKETONES, \( \rho \) (g/cm\(^3\)) at 23°C, were measured in accordance with ISO 1183. These values are summarized in Table 3.

Table 3. Density

<table>
<thead>
<tr>
<th>Grade</th>
<th>Density g/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resins</td>
<td>1.24</td>
</tr>
<tr>
<td>EK63</td>
<td>1.24</td>
</tr>
<tr>
<td>EK33</td>
<td>1.24</td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
</tr>
<tr>
<td>GF 15% Filled</td>
<td>1.34</td>
</tr>
<tr>
<td>GF 30% Filled</td>
<td>1.46</td>
</tr>
<tr>
<td>FR(V-0)</td>
<td>1.45</td>
</tr>
<tr>
<td>FR(V-0) GF 20%</td>
<td>1.60</td>
</tr>
<tr>
<td>FR(V-1) GF 15%</td>
<td>1.60</td>
</tr>
<tr>
<td>Wear Resistant</td>
<td>1.22</td>
</tr>
<tr>
<td>Advanced WR</td>
<td>1.29</td>
</tr>
<tr>
<td>WR GF 30%</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Bulk density ISO 60:1977
The bulk densities for KETOPRIX™ POLYKETONE granules were measured in accordance with ISO 60:1977. These values are summarized in Table 4.

Table 4. Bulk Density

<table>
<thead>
<tr>
<th>Grade</th>
<th>Density kg/m(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resins</td>
<td></td>
</tr>
<tr>
<td>EK63</td>
<td>700</td>
</tr>
<tr>
<td>EK33</td>
<td>700</td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
</tr>
<tr>
<td>GF 30% Filled</td>
<td>660</td>
</tr>
</tbody>
</table>

Note: EK63 was formerly M630A; EK33 was formerly M330A.

Amorphous and crystalline densities
The crystalline densities of KETOPRIX™ POLYKETONES were determined at 23°C using wide angle X-ray diffraction analysis. The amorphous densities are then derived from the measured crystalline density and the measured degree of crystallinity.

The values measured and calculated are summarized in Table 5.

Table 5. Amorphous and crystalline densities of KETOPRIX™ POLYKETONE, EK63

<table>
<thead>
<tr>
<th>Phase</th>
<th>Density g/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>1.206</td>
</tr>
<tr>
<td>( \alpha )-Crystalline</td>
<td>1.382</td>
</tr>
<tr>
<td>( \beta )-Crystalline</td>
<td>1.297</td>
</tr>
</tbody>
</table>
Density temperature relationship

The influence of temperature on density is illustrated in Figure 1. These data were derived from PVT data, at a pressure of 1 bar, 0.1 MPa.

Figure 1. Density as a function of temperature

Note: EK63 was formerly M630A; EK33 was formerly designated M330A
Thermal Properties

Differential Scanning Calorimetry
Figure 2 shows typical heat flow curves as a function of the temperature for the grade EK63.
These curves were obtained on a DSC during the course of a first heating up to 280°C, a cooling down to 30°C followed by a second heating.

Figure 2. DSC curves for KETOPRIX™ POLYKETONE EK63
Thermophysical data
The thermophysical data for KETOPRİX® POLYKETONES are derived from DSC analysis, and DTMA analysis.
The glass transition temperature, Tg, was determined for dry material at a frequency of 1 rad/sec with strain amplitude of 0.2 percent in the torsional testing mode.

DSC analysis consisted of heating to 280°C followed by cooling to 30°C and then reheating to 280°C all at a rate of 20°C/min. The melting temperature, Tm, is determined as the peak of the second heating cycle and the crystallization temperature, Tc, is determined as the peak of the first cooling cycle.

These values are summarized in Table 6.

Table 6. **Thermophysical data**

<table>
<thead>
<tr>
<th></th>
<th>EK63</th>
<th>EK33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg °C</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Tm °C</td>
<td>220</td>
<td>220</td>
</tr>
<tr>
<td>Tc °C</td>
<td>178</td>
<td>178</td>
</tr>
<tr>
<td>$\Delta H_f$ J/g</td>
<td>84</td>
<td>91</td>
</tr>
<tr>
<td>$\Delta H_{f100}$ J/g</td>
<td>227</td>
<td>-</td>
</tr>
</tbody>
</table>

Tg       Glass transition temperature  
Tm       Crystalline melting point  
Tc       Crystallization temperature  
$\Delta H_f$ Typical heat of fusion for molded material  
$\Delta H_{f100}$ Heat of fusion for 100% crystalline material
Heat distortion temperature under load: ISO 75/A and ASTM D648

The heat distortion temperature is an index of the short-term thermal behavior of a material under load. The heat distortion temperatures for various KETOPRIX™ POLYKETONES were determined in accordance with ISO 75/A and ASTM D648, HDT values for KETOPRIX™ POLYKETONES are summarized in Table 7.

Table 7. Heat distortion temperatures

<table>
<thead>
<tr>
<th>Grade</th>
<th>HDT ISO 75/A, 1.80 MPa °C</th>
<th>HDT ASTM D648, 66psi °C</th>
<th>HDT ASTM D648, 264 psi °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resins</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EK63</td>
<td>100</td>
<td>210</td>
<td>218</td>
</tr>
<tr>
<td>EK33</td>
<td>100</td>
<td>203</td>
<td>218</td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF 15% Filled</td>
<td>-</td>
<td>218</td>
<td>218</td>
</tr>
<tr>
<td>GF 30% Filled</td>
<td>215</td>
<td>218</td>
<td>218</td>
</tr>
<tr>
<td>FR(V-0) Comp.</td>
<td>105</td>
<td>-</td>
<td>105</td>
</tr>
<tr>
<td>FR(V-0) GF 20%</td>
<td>210</td>
<td>-</td>
<td>210</td>
</tr>
<tr>
<td>FR(V-1) GF 15%</td>
<td>200</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>Wear Resistant</td>
<td>96</td>
<td>204</td>
<td>96</td>
</tr>
<tr>
<td>Advanced WR</td>
<td>96</td>
<td>199</td>
<td>96</td>
</tr>
<tr>
<td>WR GF 30%</td>
<td>207</td>
<td>213</td>
<td>207</td>
</tr>
</tbody>
</table>
**Coefficient: linear thermal expansion**

The coefficient of linear thermal expansion $\alpha$ (K-1) of KETOPRIX™ POLYKETONE is measured by TMA, thermal mechanical analysis, according to the requirements of ASTM E831.

Measurements are carried out on injection-molded samples with LTE measured both parallel and perpendicular to the direction of flow to account for anisotropy in the molded product.

The coefficient of linear thermal expansion is expressed as a mean value taken over the temperature range 25°C to 55°C for each direction. These values are summarized in Table 8.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Parallel to Flow</th>
<th>Perpendicular to Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EK63</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>EK33</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF 30% Filled</td>
<td>2</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 8 **Coefficient of linear thermal expansion**
Specific heat capacity
The thermal dependence of the specific heat capacity at constant pressure, $C_p$ (J/g.K), is shown in Figure 3 for KETOPRIX™ POLYKETONES. The specific heat capacity is measured by adiabatic calorimeter on a DSC under a constant heating rate of 20°C/min. These values are summarized in Table 9.

The $C_p$ increases gradually up to 180°C. Above this temperature the $C_p$ reaches a peak, corresponding with the melting point of the polymer. Beyond this peak the variation of $C_p$ as a function of temperature is re-established.

Table 9. Specific heat capacity

<table>
<thead>
<tr>
<th>Grade</th>
<th>$C_p$(J/g.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 50 °C</td>
</tr>
<tr>
<td>Resins</td>
<td></td>
</tr>
<tr>
<td>EK63</td>
<td>1.84</td>
</tr>
<tr>
<td>EK33</td>
<td>1.81</td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
</tr>
<tr>
<td>GF 30% Filled</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Note: EK63 was formerly M630A; EK33 was formerly M330A.
**Melt flow rate, ISO 1133, ATM D1238**

Typical melt flow rates for KETOPRIX™ POLYKETONES are summarized in Table 10, measured at 240°C with a load of 2.16kg, in accordance with the above standards.

### Table 10. Melt Flow Index rates

<table>
<thead>
<tr>
<th>Grade</th>
<th>ISO 1133 ml/10 mins</th>
<th>ASTM D1238 g/10 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EK33</td>
<td>60</td>
<td>64</td>
</tr>
<tr>
<td>EK63</td>
<td>5.4</td>
<td>5.8</td>
</tr>
<tr>
<td>EK73</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Apparent melt viscosity
The following Figure 4 illustrates the apparent melt viscosities, $\eta$ (Pa.s), for various KETOPRIX\textsuperscript{TM} POLYKETONES. The data are presented as a function of shear strain rate, $\gamma$ (s\textsuperscript{-1}), over a range of temperatures. The flow curves were generated using a constant shear strain rate capillary rheometer and all data were corrected using the Bagley and Rabinowitz methods. Data were not corrected for shear heating or pressure effects.

Figure 4. Melt Viscosity vs Shear Rate

Note: EK63 was formerly M630A; EK33 was formerly M330A.
Effect of temperature on apparent melt viscosity

Figure 5 demonstrates the relative insensitivity of apparent viscosity to melt temperature for KETOPRIX™ POLYKETONES.

Figure 5. Effect of temperature on apparent melt viscosity measured at a shear strain rate of 500 s⁻¹
Injection molding operation

Before molding, thoroughly dry the KETOPRIX™ POLYKETONE for at least two hours at 90°C or for four hours at 60°C.

Mold shrinkage will be about 0.022 cm/cm in the Machine Direction (MD) vs. 0.021 cm/cm in the Transverse Direction (TD).

Mold temperature depends on the details of the part being molded. For bulk parts without much intricacy and without narrow sections, mold temperatures as low as 80°C will give rapid crystallization and reduce cycle time. For other parts where fast crystallization and solidification are not desired, higher mold temperatures are required. KETOPRIX™ POLYKETONE crystallizes very rapidly.

IM Temperature Profile Across Barrel:

Feed Temperature = 240°C (464°F)
Middle Temperature = 240°C (464°F)
Discharge Temperature = 240-260°C (464-500°F)

For heavily filled grades, these temperatures, particularly the discharge temperature, will need to be higher by some 10-12°C (18-20°F) to keep the material flowing through the nozzle and into the mold.

Injection pressure should be at least 600-1000 psig, although higher injection pressures are acceptable.

Backpressure must be at least 50 – 100 psig, although higher pressures are acceptable.

Screw speed should be about 50-100 rpm and the screw L/D should be 18-20:1, with a compression ratio of 2.5:1 (ideal).

Use free-flow check rings to minimize material holdup. Streamlined nozzle design with polished bores is preferred.

Do everything possible to keep KETOPRIX™ POLYKETONE moving from feed hopper through the barrel and into the mold. Avoid designs that will allow the KETOPRIX to collect and pool in the machine. It is best to use larger diameter runners and gates than those used for polyacetal, and/or nylon molding, if possible. If this is not possible, KETOPRIX™ POLYKETONES can be processed in molds designed for POM and PA.

If there are interruptions of up to 30 min, retract nozzle and take sufficient number of air shots to clear barrel before resuming.

For process interruptions of 30-120 min: decrease barrel temperature (e.g. 50-70°C), shut off hopper feed and purge barrel with low melt flow PP with screw in forward position; then when resume, raise barrel temperature, reintroduce KETOPRIX resin and take air shots prior to resuming molding.
Mold conditions

Molding conditions vary substantially depending on the part design, geometry and type of resin (filled vs unfilled). Provided below are some typical times for a 25g part:

Injection: 2-4 sec

Hold time: 2-6 sec

Cool/Discharge: 6-10 sec.

It is preferred to balance shot size and barrel capacity to give residence times of KETOPRIX in barrel of 2-10 min max.

Clamp force is not critical, typically 3-6 tons/sq. in. will be adequate.

Sticking of molded parts to the mold tooling is rare with KETOPRIX and standard mold release agents can be applied or mold release agents can be compounded into the polymer. Esprix can provide you with the best solution for mold release.

Do NOT injection mold KETOPRIX™ POLYKETONES right behind other nylon (polyamides) as crosslinking in the melt can occur leading to a thermoset in the barrel, nozzle or mold.

Use low MF polypropylene to purge out KETOPRIX after the run is complete.
Thank you!
If you have any questions, please contact Esprix Technologies:

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USA
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Email: cveith@esprixtech.com