Advantages of Aliphatic Polyketones in Automotive Applications

ITB Automotive Energy Storage Systems Conference

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March 1, 2017

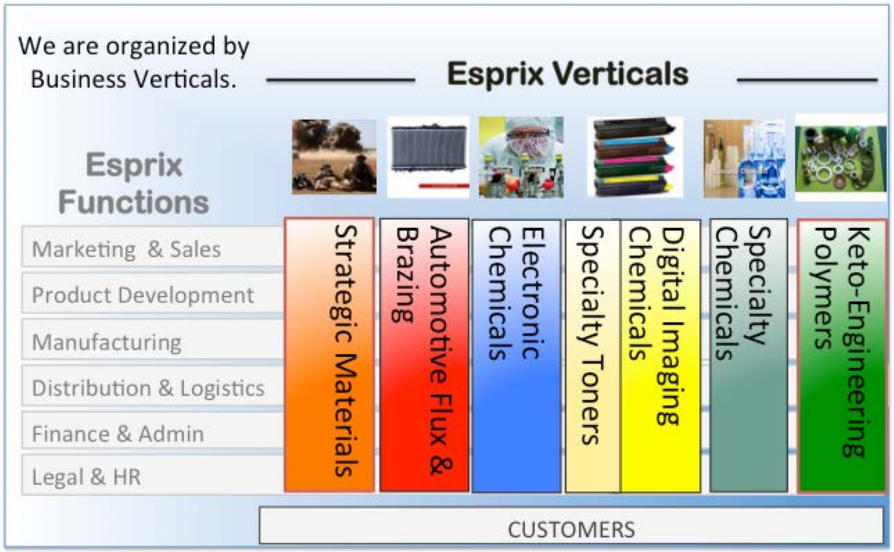
Discussion Topics

- Background of Esprix Technologies
- Light-weighting Trend in Automotive
  - What's required for Auto Energy Systems?

    => Good **chemical resistance**, **mechanical** and **transport** properties
- Overview of Aliphatic Polyketone (PK)
- Ketoprix™ PK Properties
  - Mechanical
  - 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



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".***

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.

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

… founded 2000, Sarasota, FL

a proud member of nacd
National Association of Chemical Distributors

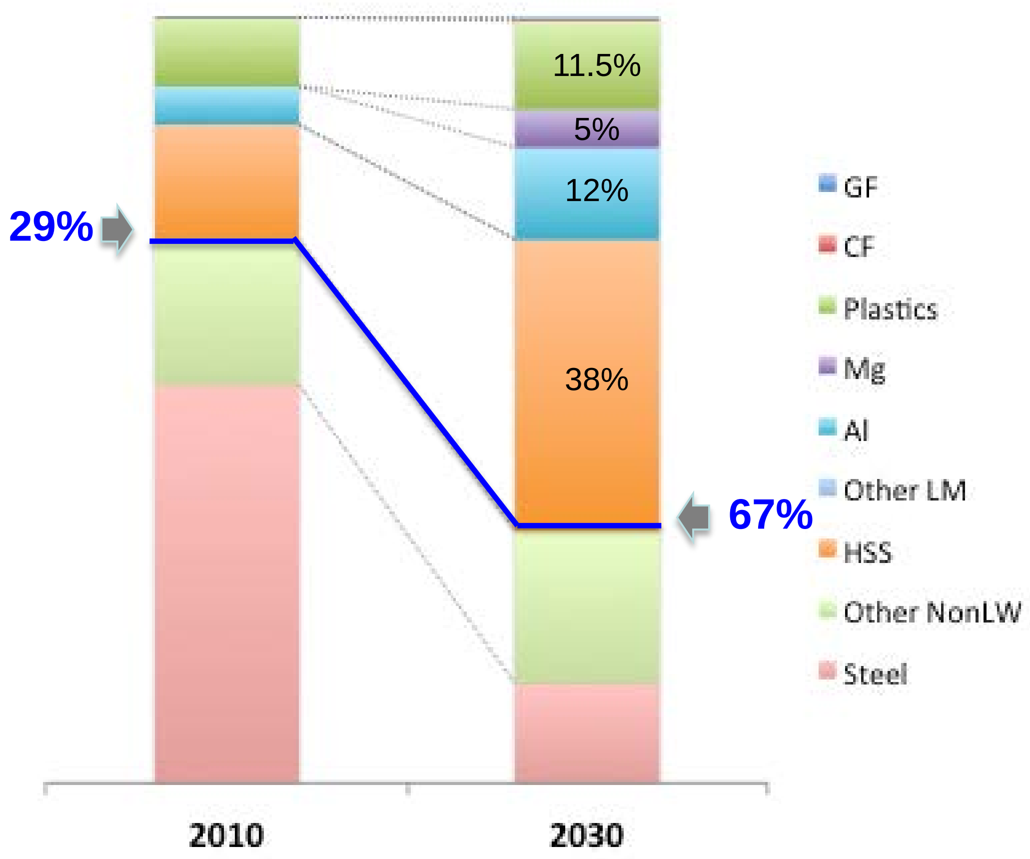
Esprix Distribution & Warehouses

Esprix WH

Esprix HQ

Light-weighting in Automotive

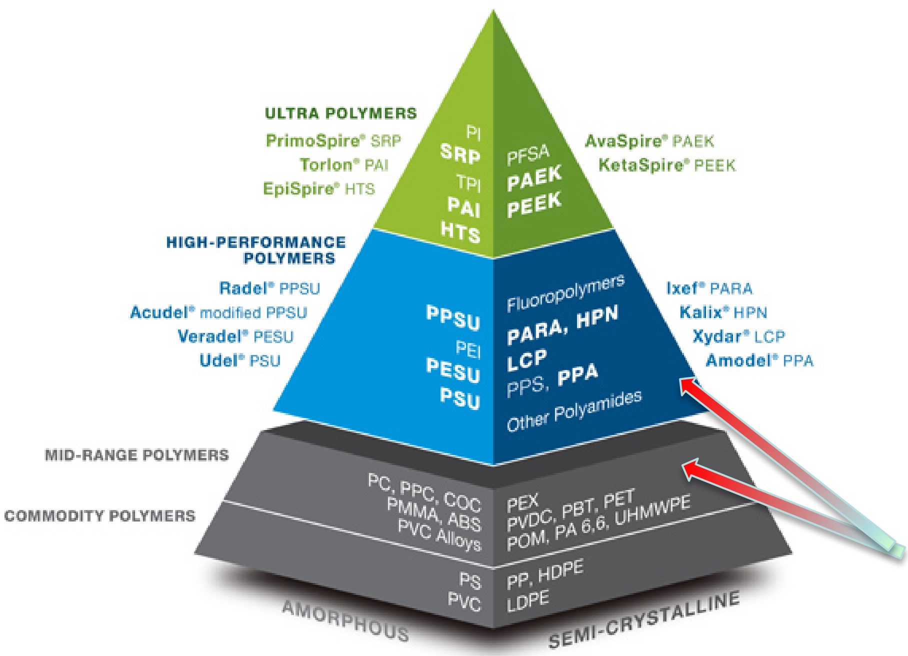
- **Light-weighting trend in Automotive has existed for decades**
  - Fuel efficiency
  - Environmental benefit
- **Different LW Packages will emerge**
  - Conventional
    - HS Steel
  - Moderate
    - More LW materials
    - Al, Mg, CF Composites
  - Extreme
    - High CF Composites share
- **Overall, LW share will grow from 29% to 67% by 2030**



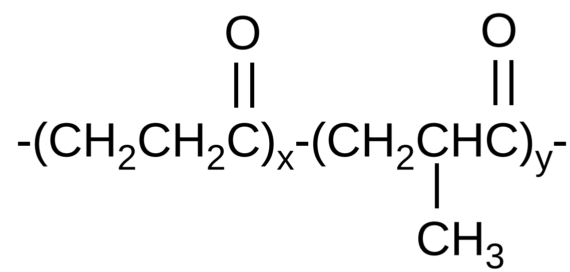
Adapted from McKinsey & Co, "Lightweight_heavy_impact.pdf" publication, Advanced Industries, February 2012.

What is Aliphatic Polyketone?

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.



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

Ketoprix™ polyketone

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

PK vs. Other ETPs – Mechanical

Items		Unit	POK	PA6	PA66	PBT	POM
Density		g/cm^3	1.24	1.14	1.14	1.30	1.41
Melting Temperature		℃	220	220	260	220	160
Impact Strength		KJ/m^2	12	5.2	4.1	5.0	6.5
Tensile Strength	Dry Conditioned Wet	MPa	70 70 60	80 55 35	80 70 50	55 - -	65 - -
Elongation at Break	Dry Conditioned Wet	%	270 270 390	17 40 360	19 60 370	16 - -	35 - -
Flexural Modulus	Dry Conditioned Wet	MPa	1,800 1,800 1,450	2,600 1,200 600	2,900 2,200 1,100	2,400 - -	2,500 - -

* Dry: 23℃, 50% RH, 24hrs Conditioned: 23℃, 50% RH, 60days Wet: 23℃, 90% RH, 60days
** POK : Hyosung M330A properties.

Glass Fiber Reinforced Ketoprix

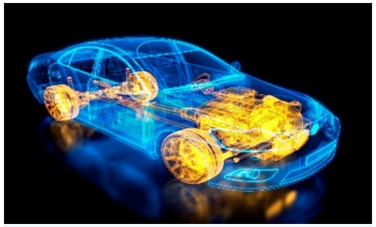
Glass Content, %w		20	30	33	40
	Standard	**EK33G2P**	**EKT33G3P**	**EKT23G3BP**	**EKT23G4P**
Physical					
Density (g/cm³)	ASTM D792	1.35	1.47	1.49	1.56
Mold Shrinkage (Flow Direction, %)	ASTM D955	0.3	0.2	0.2	0.2
Thermal					
Melting Temperature, (°C)	ASTM D1525	220	220	220	220
Viscosity, (Pa-s, 280°C)		100-300	100-300	250-350	300-400
Deflection Temperature	ASTM D648				
HDT 0.45MPa (°C)			205	205	210
HDT 1.82MPa (°C)			205	205	210
Mechanical					
Tensile Strength, 23°C (MPa)	ASTM D638	120	155	160	190
Nominal Strain at Break, (%)	ASTM D638	2-4	2-4	2-4	2-4
Tensile Modulus, 23°C (GPa)	ASTM D638	7	10	10.5	13
Flexural Strength, 23°C (MPa)	ASTM D790	150	240	240	270
Flexural Modulus 23°C (GPa)	ASTM D790	6	8	8.5	11
Impact Strength 23°C (kJ/m²)*	ISO 179	13.5	14.8	12.6	13.3

PK Benefits and Value Proposition

esprix technologies

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

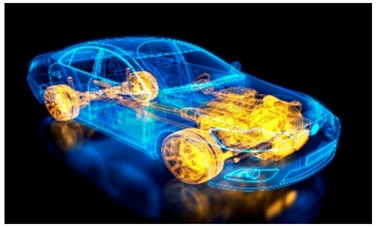
Fibers

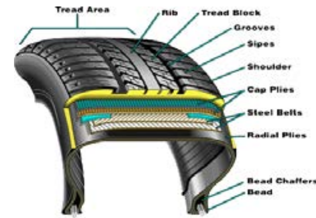
- Toughness
- High Strength
- High Yield Elongation
- Low Moisture Sensitivity

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
- Agricultural

Auto

- Fuel Tank
- Fuel Lines
- UTH Connectors
- Structural – Composites replace metal

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

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

IM = Injection Molding
X = Extrusion

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

Technical information available on our website landing page:
http://www.esprixtech.com/landing-page/engineering-polymers/

Ketoprix PK - Easy Processability

- **Pre-drying generally not needed prior to molding**
- **Easy mold filling (low melt viscosity)**
- **Low clamp tonnage requirements**
- **Lower density compared to PBT, POM, PPS & PVDF**
- **Same mold shrinkage rates as PA and POM → no retooling needed**
- **Shorter molding cycles & high mold definition vs. competitive resins**
- **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 (Santoprene)**

PK Dimensional Stability

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

(from J.W. Kelly, "Materials Selection and Design for Gears in Stalled Conditions", ANTEC Proceedings, 1998, p. 3028)

TABLE 1. COMPARATIVE DATA
Water Uptake & Dimensional Changes

Polymer	Equilibrium Water Uptake @50% RH (% by Wt)	Dimensional Changes (%)
PK	.30	.05 - .15
PA	2.5	.70 - .80
POM	.20	.10 - .20

Ketoprix PK - Chemical Resistance

Ketoprix™ polyketone resins exhibit excellent resistance to a broad range of chemicals including:

- Aromatic & Aliphatic Hydrocarbons
- Ketones, Esters & Ethers
- Inorganic Salt Solutions
- Weak Acids & Bases
- There are in fact few known solvents for Ketoprix™ 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 and under-the-hood components

Ketoprix PK - Hydrolysis Resistance

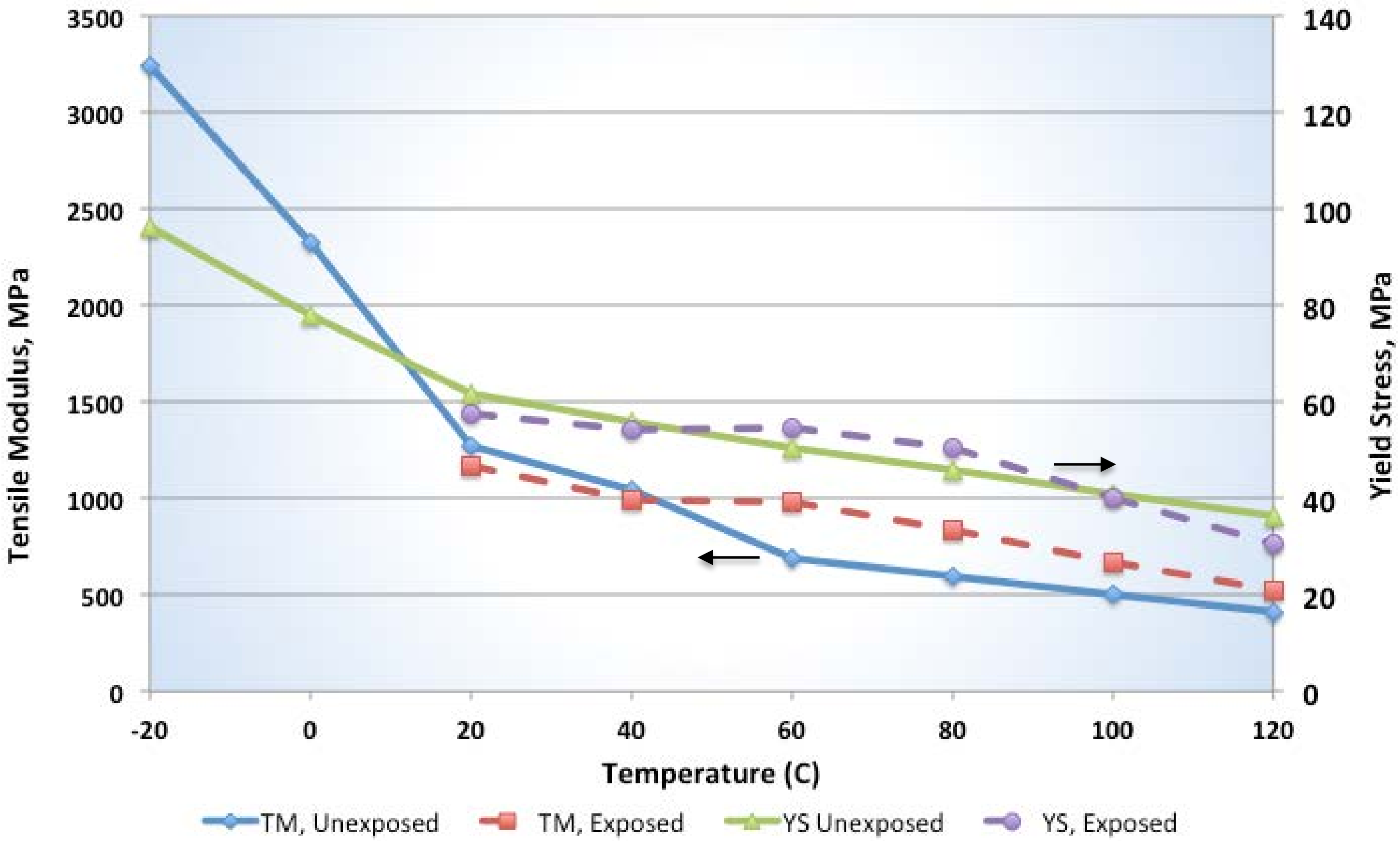
Tensile Strength at Yield at 23C after 25-day exposure to various aqueous environments:

Chemical	POLYKETONE M630A MPa	Polyamide 66 MPa
Control (50% Rh)	60.0	57.2
Water	59.2	33.1
Seawater	60.0	33.1
5% w/w Acetic Acid	54.9	33.8
5% w/w Calcium Chloride	60.0	33.8
50/50 Antifreeze	59.2	35.8

Tensile testing to ASTM D638 was conducted at 23°C

With its C-C backbone, PK has excellent hydrolytic & chemical resistance

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

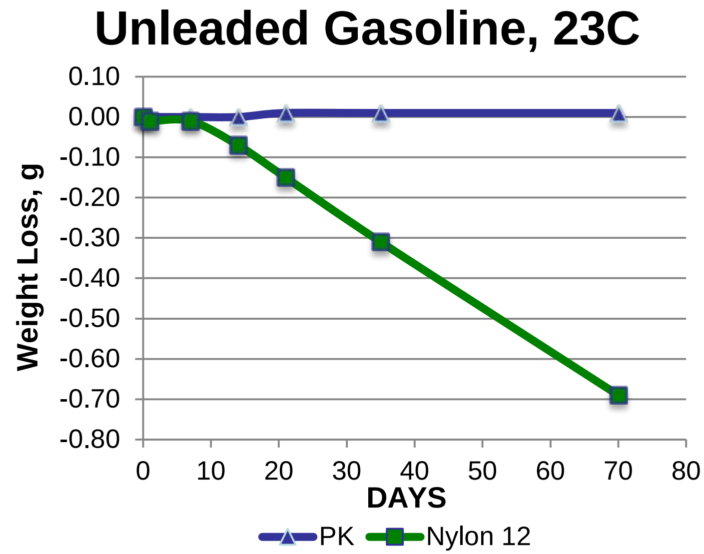
Fuel Permeation Resistance

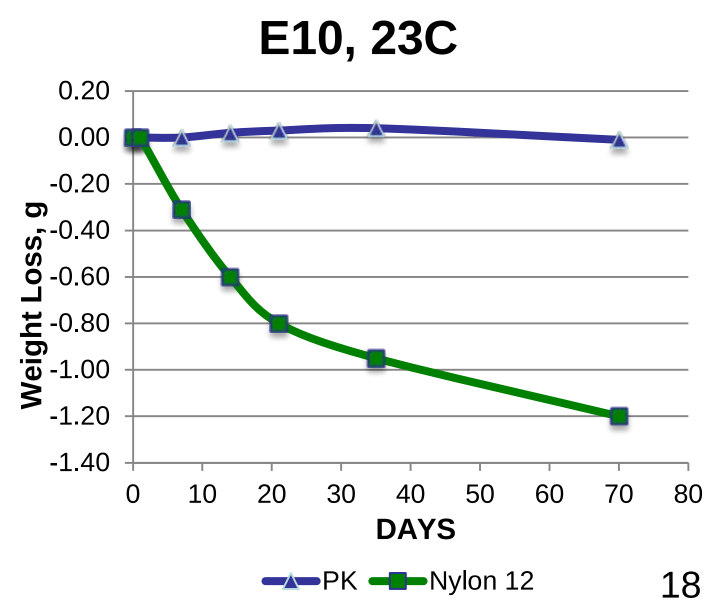
Lower Fuel Permeation

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

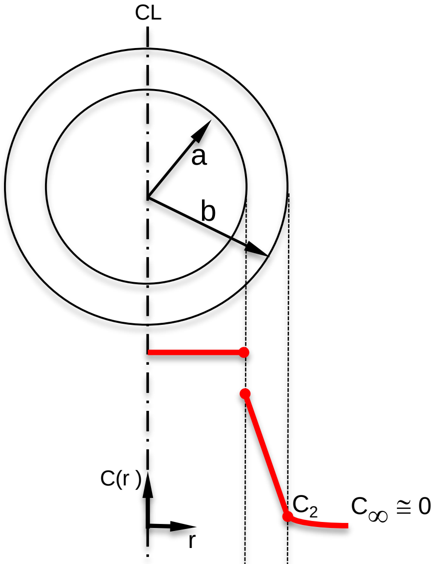




Data from Shell Chemical, 1996

PK Permeability - Theory

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



$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right)$$

Constitutive Equation for Conservation of Mass, Cylindrical Geometry

Boundary & Initial Conditions

BC1: At r = a (inner radius), $C = C_1 = Sp^*$ where $P = D^*S$

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

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

Solving the PDE for the concentration profile:

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

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

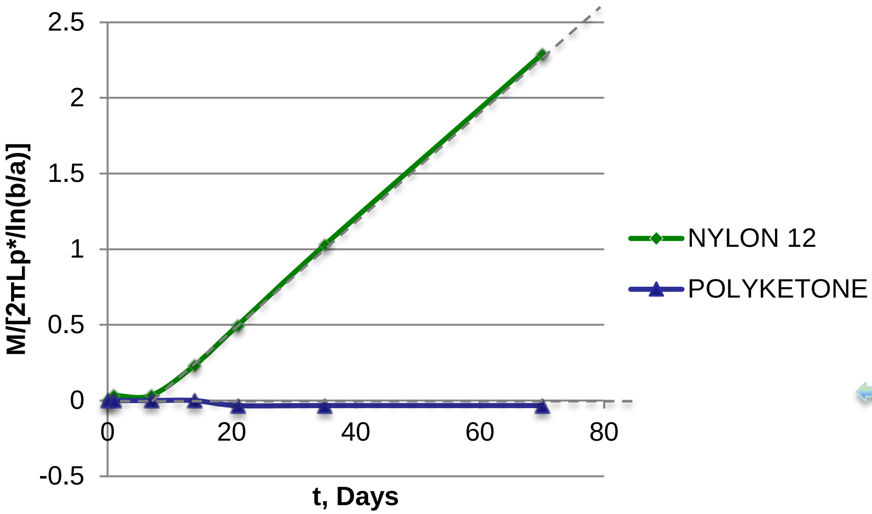
$$M(t) = -2\pi LD \int_0^t r\, \partial C/\partial r \,\Big|_{r=b}\, dt = \frac{2\pi L p^* P}{\ln(b/a)}\ t$$

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

Fuel Permeability Results

UL Gasoline 23C



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

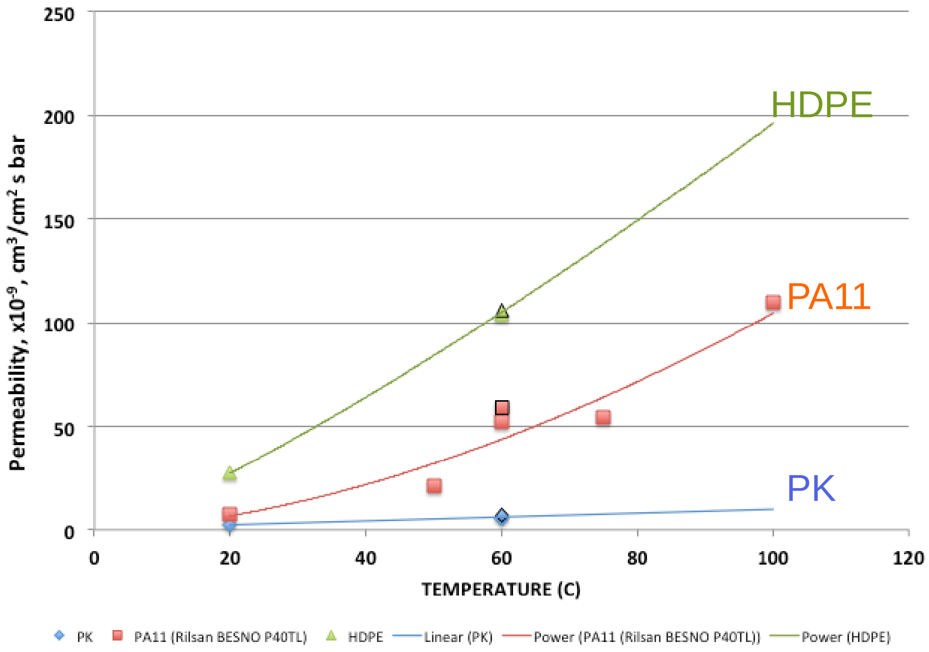
See UL Gasoline, 23C as example.

CALCULATIONS SUMMARY of FUEL PERMEABILITY and LOSS

		Permeability, P (cm/s) (x 10^{-6})			Steady-state Loss, g/(m^2-day)		
Type of Fuel	**Temperature, oC (oF)**	**PK**	**PA12**	**PTFE**	**PK**	**PA12**	**PTFE**
UL Gasoline	23 (73)	≈ 0	3,171	No Data	≈ 0	1.4	No Data
UL Gasoline	93 (200)	328	86,152	2,428	0.9	243.1	6.9
E10	23 (73)	47	2,281	No Data	0.02	0.9	No Data
E10	93 (200)	1,084	6,504	2,168	3.1	18.7	6.2

CO_2, CH_4 Gas Permeability

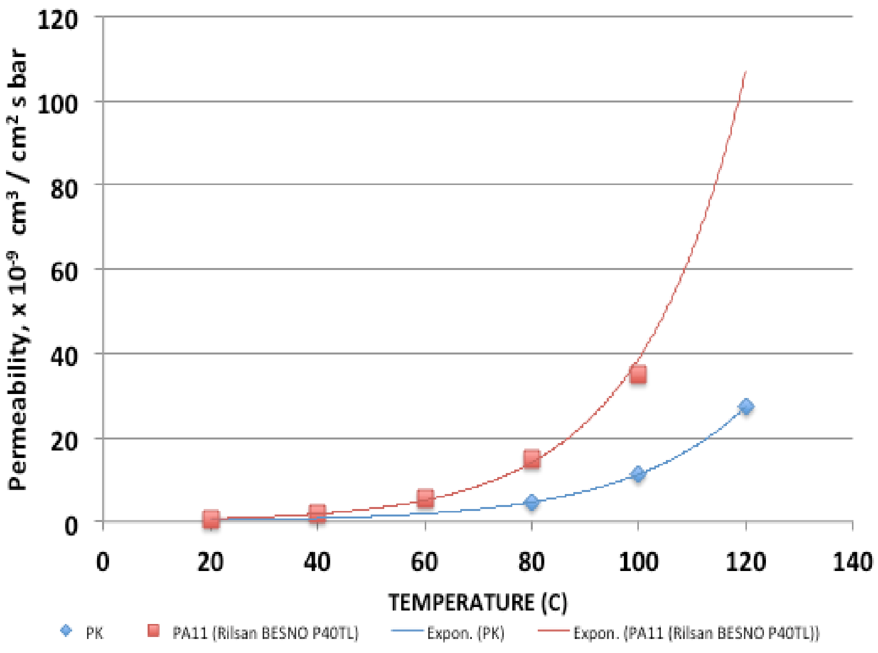
PK has much better gas barrier resistance than PA11, HDPE



CO_2 Permeability:
PK, PA11, HDPE
DAM;
Black outline data point: 50%RH

Data from Shell Canada, 1998

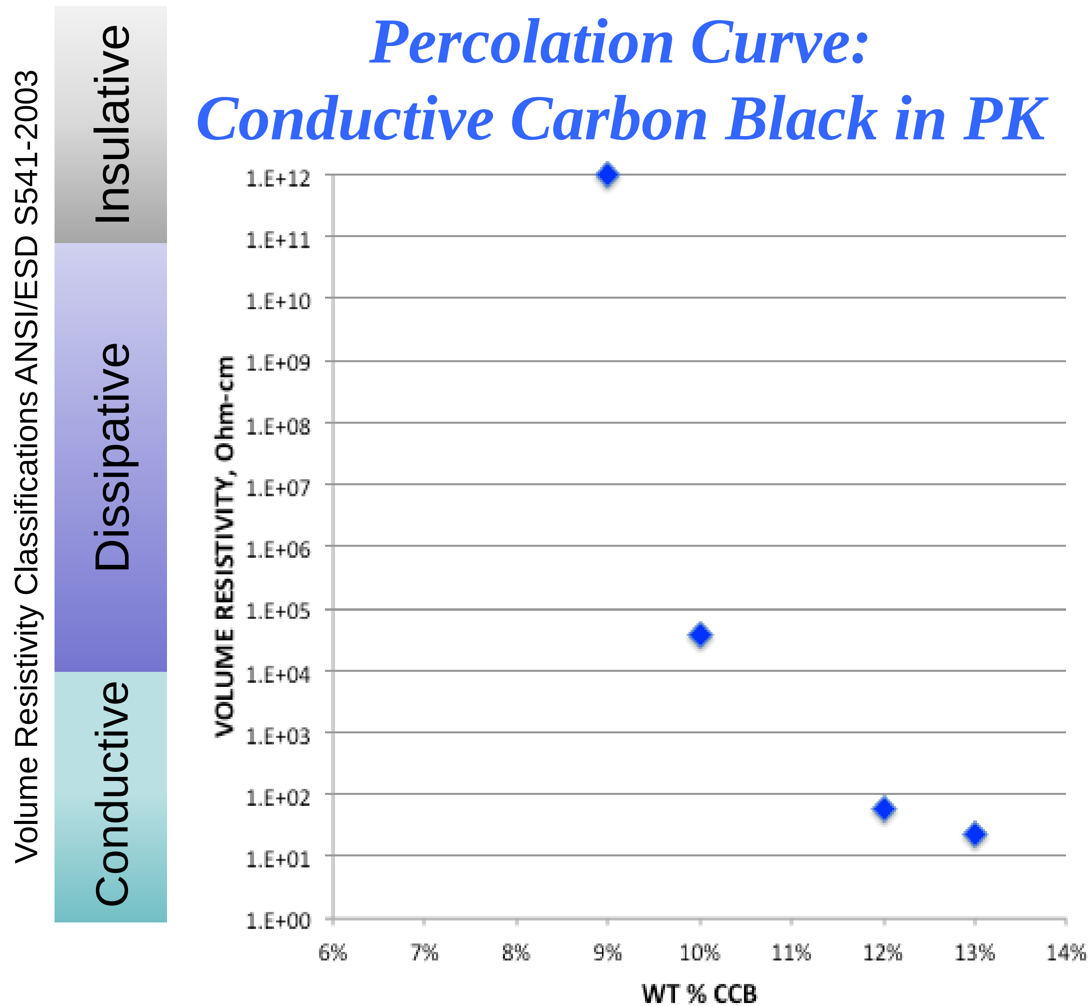
CH_4 Permeability:
PK, PA11
DAM;



Ketoprix polyketone

Electrical Conductivity

Compounded PK with conductive carbon black for ESD applications in extruded Automotive Fuel Lines and IM Fuel Components

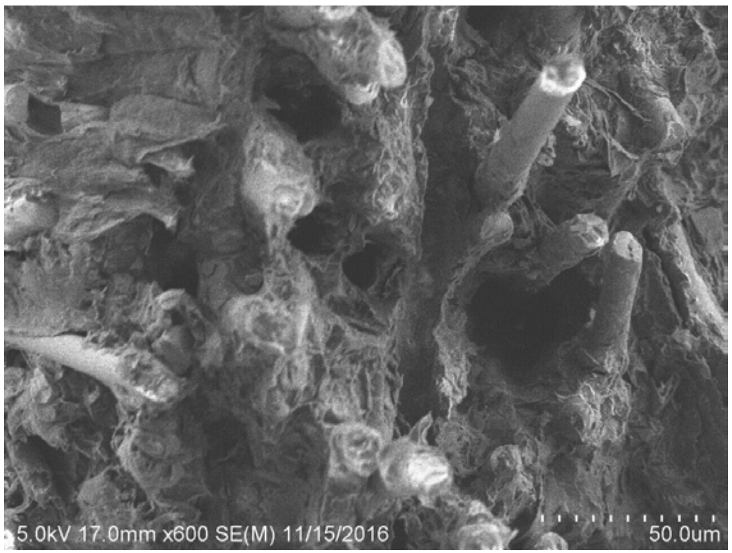


Resistivity measurements courtesy of Imerys R&D

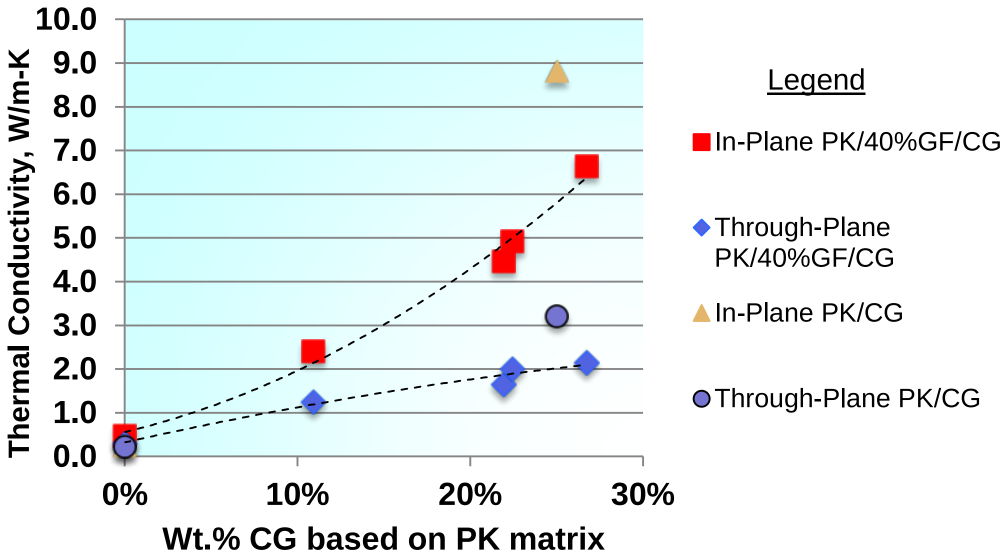
Thermal Conductivity

TC Loading Curves: GF and Neat PK with CG

40%w GF PK with
Conductive Graphite



SEM courtesy of Applied Nanostructured Solutions, LLC



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

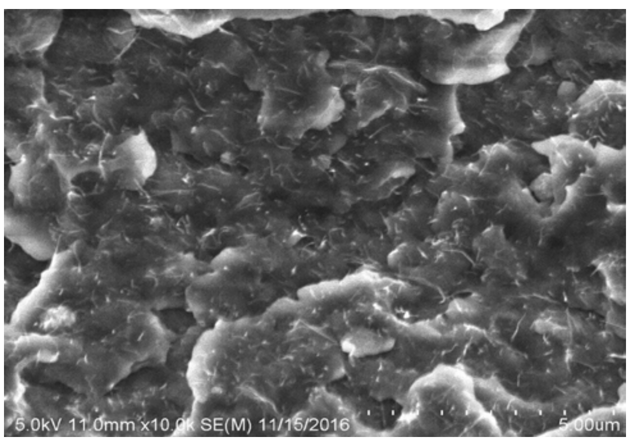
PK can be compounded with fibers and additives for improved strength and thermal conductivity

Nanostructures

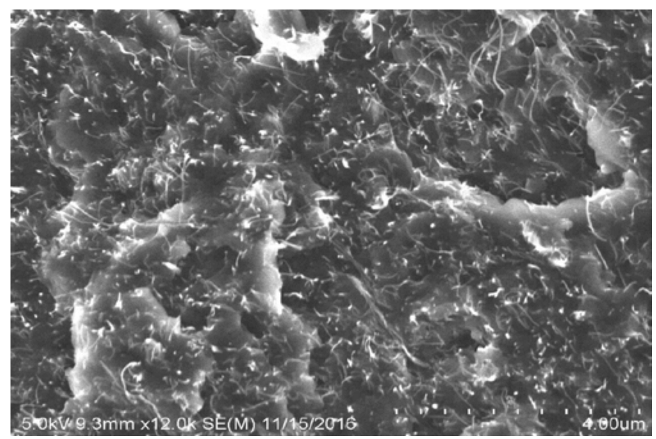
Carbon Nanotube modified Polyketone

Material	Yield Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Volume Resistivity (Ω-cm)	Thermal Conductivity (W/m-K)
PK	60	68	1.6	10^{15}	0.22
PK + 1% CNT	82	108	3.3	20	0.4
PK + 2.5% CNT	100	128	4.6	2	0.5

1% CNT / PK



2.5% CNT / PK



SEM micrographs 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

Connector Junction Box

- Current Material: mPPO
- KPI's:
  - Dimensional Stability
  - Thin Wall IM Processability
- Value Proposition:
  - Economics
  - Able to mold thin-walled parts
  - Shorter Cycle Time

Fuel Lines

- Current Material: PA11/12
- KPI's:
  - Greater fuel resistance
  - Good impact resistance
  - Electrical Conductivity
- Value Proposition:
  - Better Impact Strength
  - Lower fuel permeation
  - Higher Strength, down-gauging wall thickness

Bumper Bracket

- Current Material: PA66
- KPI's:
  - Impact Strength
  - Dimensional Stability
- Value Proposition:
  - Better Impact Strength
  - Higher Strength, down-gauging wall thickness
  - Less moisture sensitivity

Summary & Conclusions

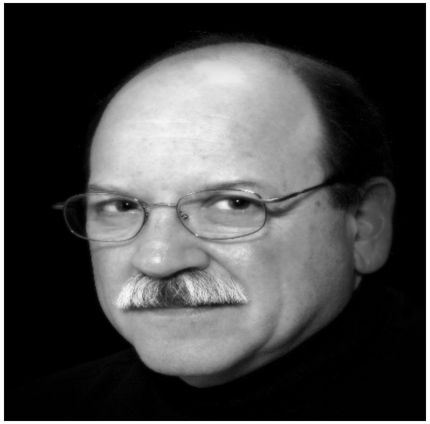
- **Polyketone is a new engineering resin now commercially available with the following benefits:**
  - **Melt processability in extrusion, injection and blow molding**
  - **High strength, toughness / impact strength, resilience**
  - **Better dimensional & hydrolytic stability than polyamides**
  - **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
June 2016

Tim Morefield – TS Consultant
July 2016



Bob Pilotti – Sales Consultant
August 2016

Thank You

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Ketoprix PK vs PA & POM

Tensile Elongation @ Yield, 23C

Resin	POM	PA66, dry	GF PPS	PVDF	Ketoprix™
Tensile Elongation @ yield, 23C,%	10	4.5	1.2	7	~25

Tensile Elongation @ Break, 23C

Resin	POM	PA66, dry	GF PPS	PVDF	Ketoprix™
Tensile Elongation @ break, 23C,%	45	25	1.2	35	>350

Unlike nylon & acetal, PK offers unique combination of strength and resilience

Notched Izod Impact at 23C & -40C

Resin	POM	PA66, dry	GF PPS	PVDF	Ketoprix™ EK63
Notched Izod Impact, J/m,23C	64	53	91	160	240
Notched Izod Impact, j/m, -40C	43	27	N/A	N/A	50

PK has higher impact resistance than nylon and acetal at both 23C and -40C

Ketoprix PK 33GF vs. PA 33GF

Properties	Standard	PK/33%GF	PA66 / 33%GF* DAM	PA66 / 33%GF* 50%RH	PA 610/ 33% GF
Density (g/cm^3)	ASTMD792	1.49	1.37	1.37	1.31
Glass Content, %w	ASTM D5630	33	33	33	33
Equilibrium Water Content, 24 hr, %	ASTM D570	0.30	-	1.9	2.0
HDT, 1.8MPa, °C	ASTM D648	218	250		
Tensile Strength, MPa, 23°C	ASTM D638	167	190	140	110
Strain at Break, %	ASTM D638	3	3	5	6
Tensile Modulus, GPa, 23°C	ASTM D638	11	10	7.2	6.2
Flexural Strength, MPa, 23°C	ASTM D790	240	270	110	160
Flexural Modulus, GPa, 23°C	ASTM D790	9	9.6	4	5.6
Charpy Impact, kJ/m^2	ISO 179	14	12		14

* PA66/33%GF and PA610/33%GFproduct data from internet sources

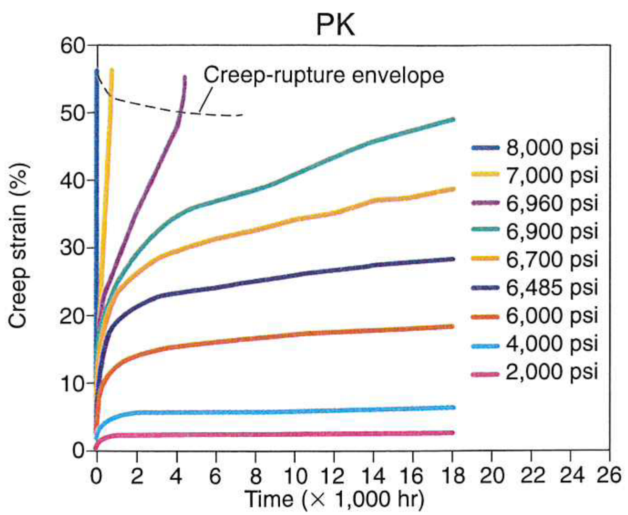
Ketoprix PK vs PA & POM – Friction & Wear

Wear tests run against steel thrust washers in pure sliding contact show that PK has better wear resistance than nylon & acetal

TABLE 2. COMPARATIVE DATA
TRIBOLOGICAL PERFORMANCE
(Data from Testing Polymer Thrust Washers on Steel)

Polymer	Wear Factor (0.28 MPa, 0.25 M/S) 10^{-15} m^3/N-m	Static Coefficient of Friction (0.17 MPa)	Dynamic Coefficient of Friction (2.07 MPa, .05 m/s)	Limiting PV (0.5 m/s) (MPa - m/min)
PK	4.33	0.07	0.49	67.67
PA	16.01	0.09	0.64	56.75
POM	13.09	0.04	0.30	48.35

Creep Resistance Neat PK



- PK has excellent Creep-Rupture resistance
- Superior creep resistance vs. POM, PA66