Polyketone Polymers – A Resin Portfolio with Unique Value Propositions for Flexible Packaging Applications

SPE FlexPackCon 2017

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October 18,2017

Discussion Topics

- Background of Esprix Technologies
- Overview of Aliphatic Polyketone (PK)
- Ketoprix™ PK Properties
  - Mechanical
  - Thermal
  - Permeability
  - Chemical Resistance
  - Sterilization Resistance
  - Regulatory Considerations
  - Example 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

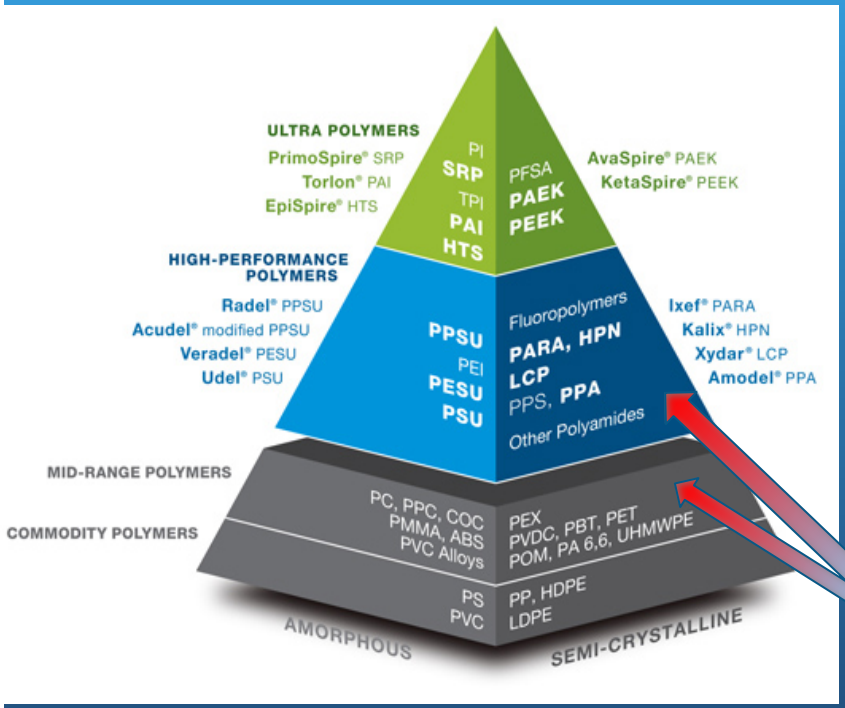
… founded 2000, Sarasota, FL

a proud member of nacd National Association of Chemical Distributors

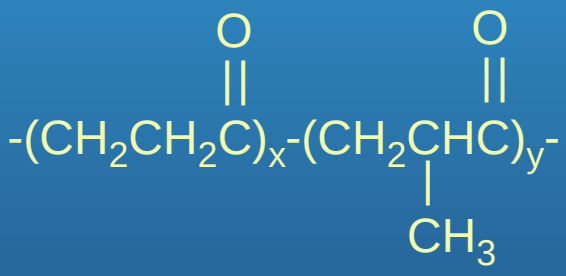
Responsible Distribution nacd

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

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

Basic Mechanical Properties

Property *		Units	PK	EVOH 32% PE	PVDC	PA6
Density		g/cm^3	1.24	1.19	1.70	1.14
Tensile Strength	Conditioned Wet	MPa	70 60	34	40	80 35
Break Strain	Conditioned Wet	%	270 390	15	70	17 360
Flexural Modulus	Conditioned Wet	MPa	1800 1450	2700**	400**	2000 675
Charpy Notched Impact Strength Charpy Unnotched Impact Strength		kJ/m^2	NB NB	- 2.0	- -	18 NB

Conditioned: 23C, 50% RH, 24hr; **Wet**: 23C, 90%RH, 60 days
** Tensile Modulus

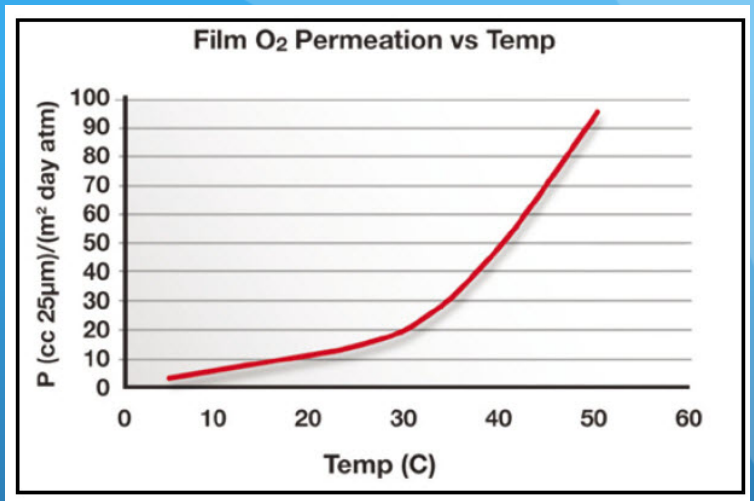
Thermal Properties

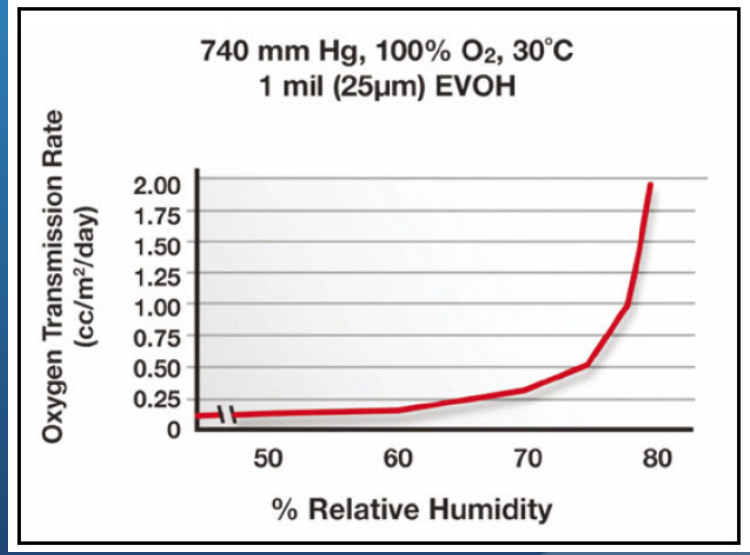
Property	PK	EVOH 32% PE	PVDC	Type 6 Nylon
Melt Temperature, C	220	158-183	158	220
Glass Transition, C Dry Wet	 15 -15	 57 -	 -17 -	 47 8
Peak Crystallization Temperature, C	178	161	77	175

Permeability

- Concentration Gradient
- Temperature
  - 5-7% increase in permeation per degree C[1]
  - Test data derived in controlled conditions vs. field conditions (variable)
  - Relative Humidity
    - Significant effect for some resins
  - Material thickness variations
- Specific material composition

The net result is that it is difficult to accurately compare permeability data from various sources – permeability is the nightmare of units!





1. Permeation and its impact on packaging, Michelle Stevens, Mocon Inc

Oxygen Permeability Values

Material	Temperature, °C	Relative Humidity	Permeability cc-mil/100in²-day-atm
$EVOH_{32}$	20	65	0.02
$EVOH_{32}$	20	85	0.076
$EVOH_{48}$	20	65	3.2
$EVOH_{48}$	20	90	8.0
PVDC	23	65	0.5
PA6 (oriented)	25	60	2.1
PA6(oriented)	23	90	3.8
PK	23	65	2.5
PK	20	65	2.0

$EVOH_{32}$ = 32% Mol PE content; $EVOH_{48}$ = 48% mol PE content

Moisture Vapor Transmission Rates

Material	Temperature, °C	Relative Humidity	MVTR g-mil/100 in^2-day-atm
$EVOH_{32}$	40	90	3.4
$EVOH_{48}$	40	90	1.8
PVDC	38	90	0.2
PA6 (oriented)	40	90	9
PK	40	90	3.7

$EVOH_{32}$ = 32% Mol PE content; $EVOH_{48}$ = 48% mol PE content

Permeability of other gases

Material	H2	CO2	N2
$EVOH_{32}$	30	0.81	0.017
$EVOH_{48}$	200	7.1	0.13
PVDC	-	0.1-2.4	0.01-0.2
PK	11	9.9	2.4

Units for all other than N2 for PK are cc-mil/100in^2-day-atm
Units for N2 for PK are 10^9 cc/cm^2-s-bar measured on 0.5 mm thick sheet

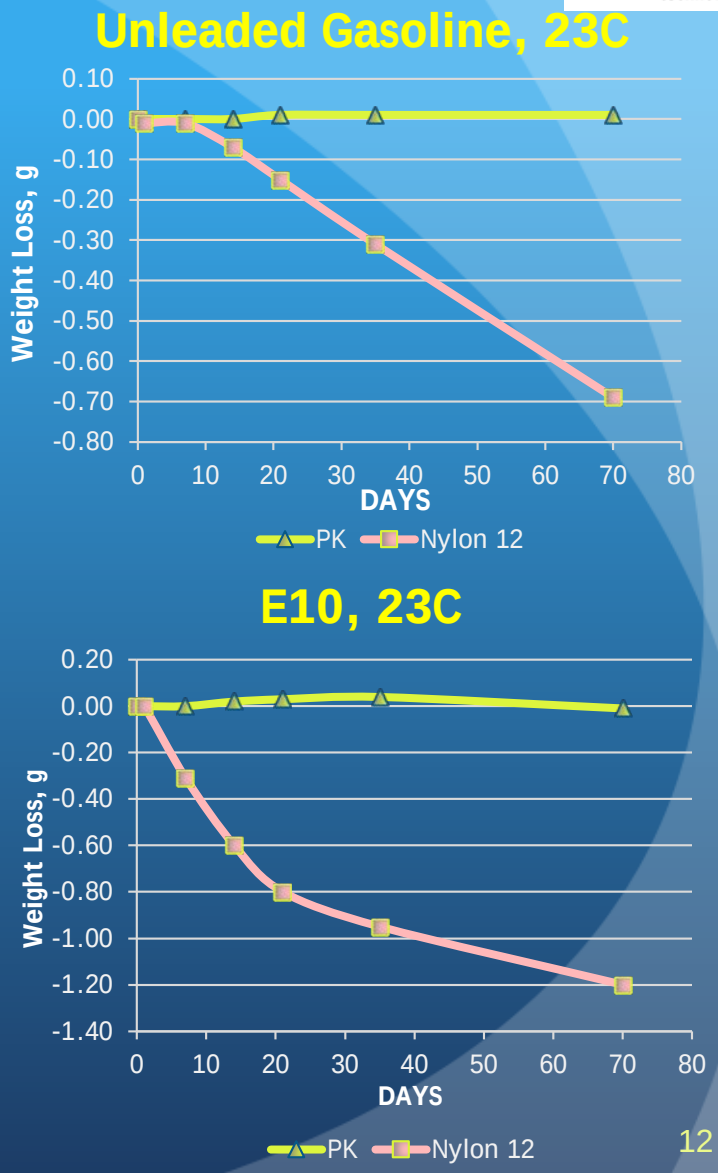
Fuel Permeation Resistance

Lower Fuel Permeation

PK vs. PA-12

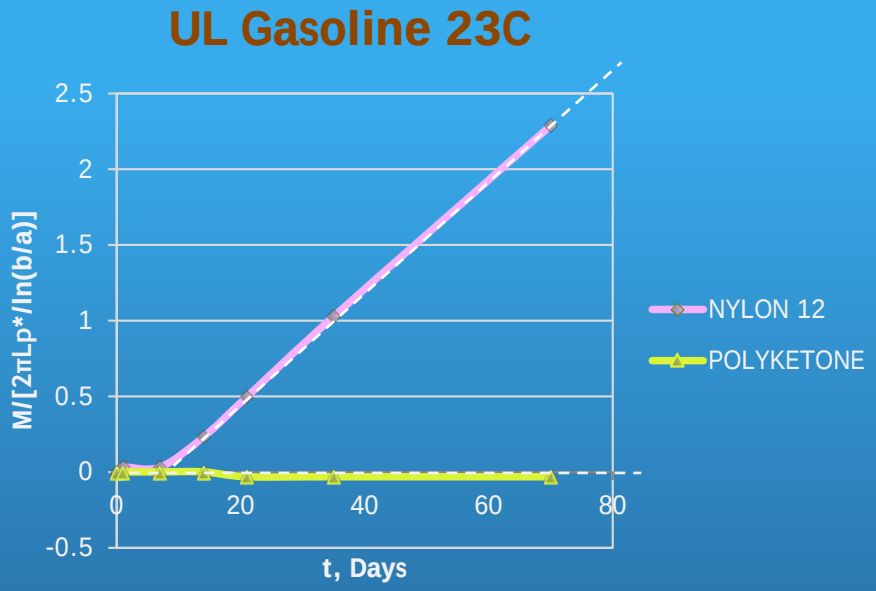
- GM 9061-P Permeability Test protocol
- Gravimetric analysis of sealed polymeric tubing
- Electrically conductive PK compounds

  => 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

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

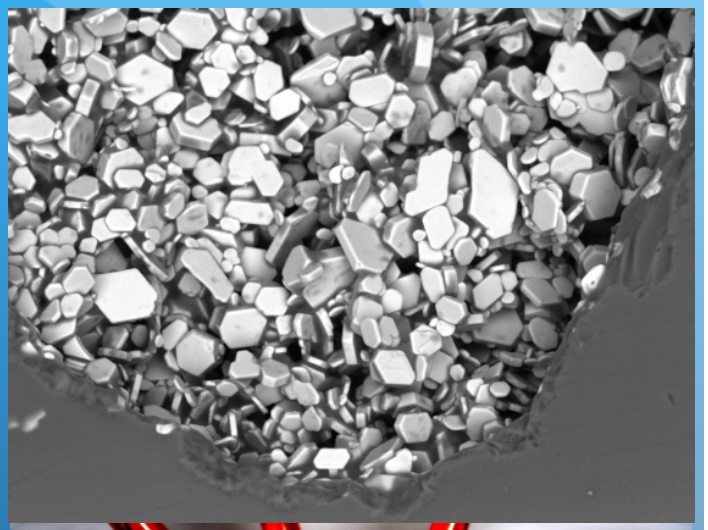
Type of Fuel	Temperature, oC (oF)	Permeability, P (cm/s) (x 10^{-6})			Steady-state Loss, g/(m^2-day)		
		PK	PA12	PTFE	PK	PA12	PTFE
UL Gasoline	23 (73)	≈ 0	3,171	No Data	≈ 0	1.4	No Data
UL Gasoline	93 (200)	328	86,152	2,428	0.9	243.1	6.9
E10	23 (73)	47	2,281	No Data	0.02	0.9	No Data
E10	93 (200)	1,084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

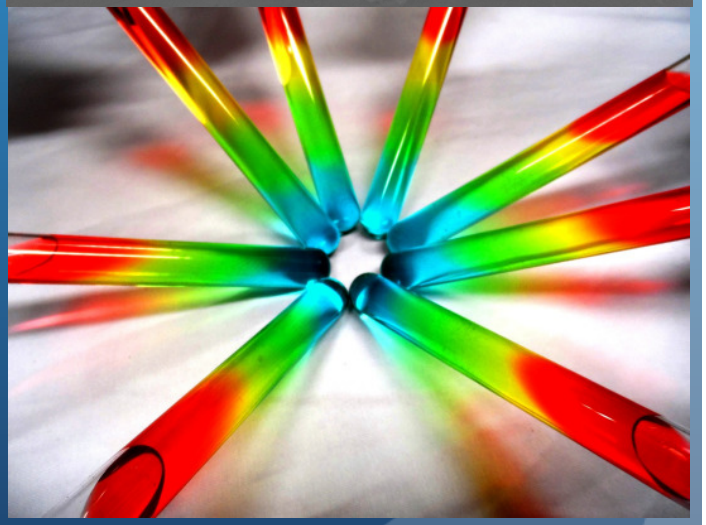
PK - Chemical Resistance

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.





Chemical Resistance of PK v. Barex® in films

: Observed Change after 10 days and 20 days Immersion

Solvent/Source	Temp.	10day	20day	
		POK	POK	BAREX
Ethyl Alcohol	23℃	None	None	None
	38℃	None	None	None
Ethylene Glycol	23℃	None	None	None
	38℃	None	None	None
Isopropyl Alcohol	23℃	None	None	None
	38℃	None	None	None
Benzene	23℃	None	None	None
	38℃	None	None	None
Toluene	23℃	None	None	None
	38℃	None	None	None
Xylene	23℃	None	None	None
	38℃	None	None	None
D-Limonene	23℃	None	None	None
	38℃	None	None	None
Acetone	23℃	None	None	Frosted, Softened
	38℃	None	None	Frosted, Softened
Methyl Ethyl Ketone	23℃	None	None	Frosted, Softened
	38℃	None	None	Frosted, Softened
Methyl Isobutyl Ketone	23℃	None	None	None
	38℃	None	None	None
Soy sauce	23℃	Discolored	Discolored	Discolored
	60℃	Discolored	Discolored	Discolored, Shrunk
Tabasco sauce	23℃	Little Discolored	Little Discolored	Little Discolored
	60℃	Little Discolored	Little Discolored	Discolored, Swell
Mustard sauce	23℃	Discolored	Discolored	Discolored
	60℃	Discolored	Discolored	Discolored, Shrunk
Iodine solution	23℃	Discolored	Discolored	Discolored
	60℃	Discolored, Brittle	Discolored, Brittle	Discolored, Shrunk

Data courtesy of Hyosung Corporation

PK Chemical Resistance vs. Barex®

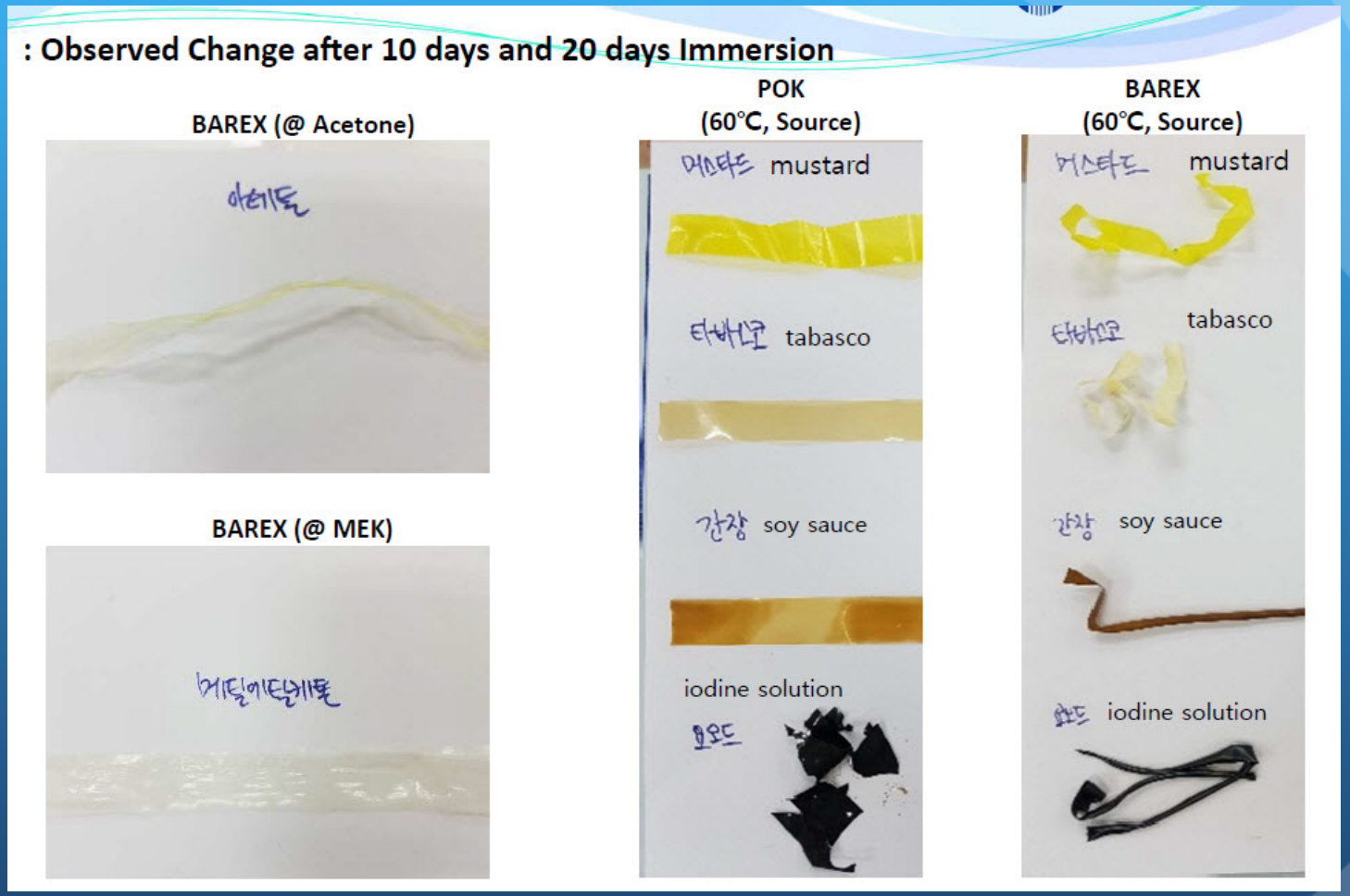


Image courtesy of Hyosung Corporation

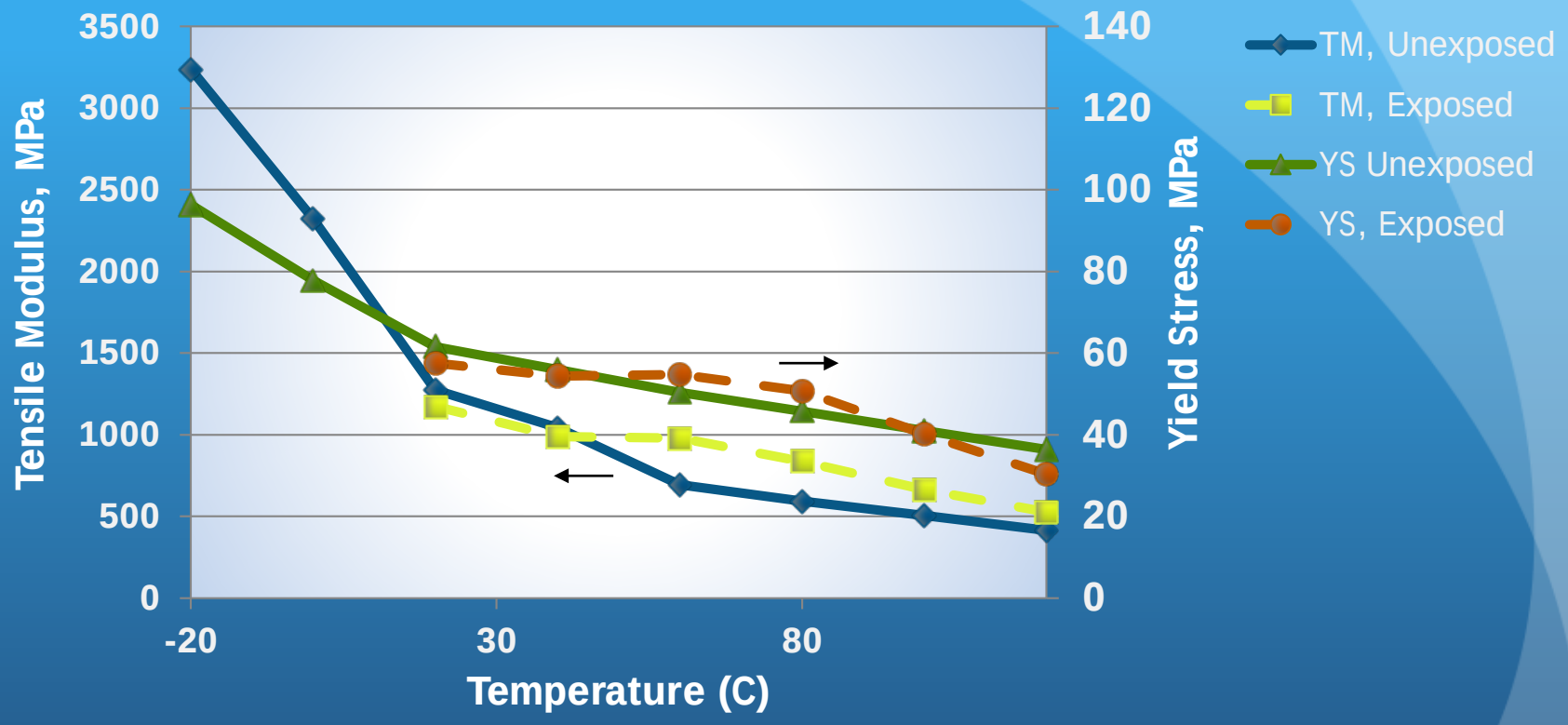
PK & Barex® Tensile Strength Retention after chemical exposure

Solvent/Source	% of Retained Elongation after 20 days Immersion		Conclusion
	POK	BAREX	
Ethyl Alcohol	100 91	54 30	Better
Ethylene Glycol	104 96	81 92	Better
Isopropyl Alcohol	95 19	79 89	POK 38℃ worse
Benzene	94 52	93 36	Better
Toluene	93 91	49 10	Better
Xylene	83 75	56 17	Better
D-Limonene	99 80	92 69	Better
Acetone	100 80	178 122	Better (BAREX Swell)
Methyl Ethyl Ketone	76 12	148 27	Better (BAREX Swell) POK 38℃ worse
Methyl Isobutyl Ketone	100 97	100 100	-
Soy source	97 55	20 -	Better
Tabasco sauce	91 92	68 -	Better
Mustard sauce	100 80	99 -	Better
Iodine solution	8 0	30 -	Bad (All sample)

+ 0 day The value of elongation at Break : POK 366%, BAREX 121% , The data after 20day immersion.
+ BAREX (Source, 60℃) : Not available for tensile test due to badly deformed shape.

Data courtesy of Hyosung Corporation

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

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

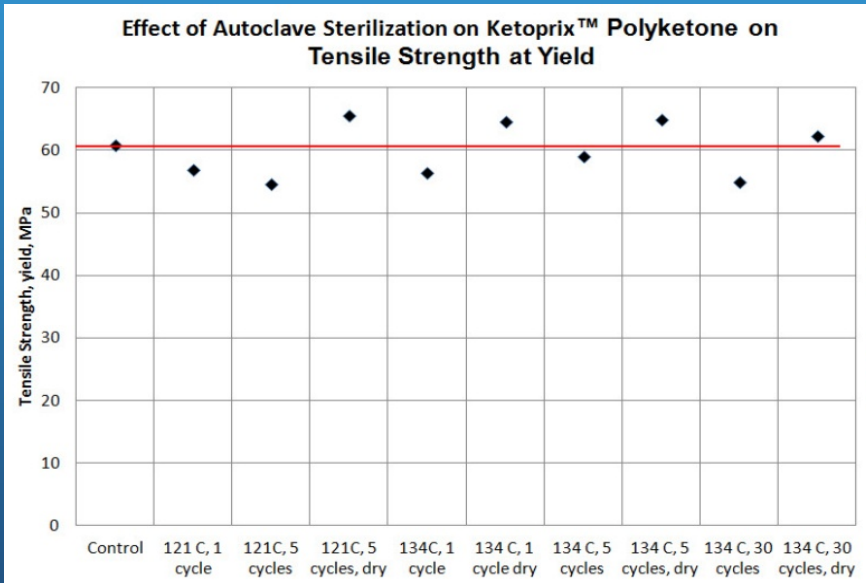
With its C-C backbone, PK has excellent hydrolysis & chemical resistance

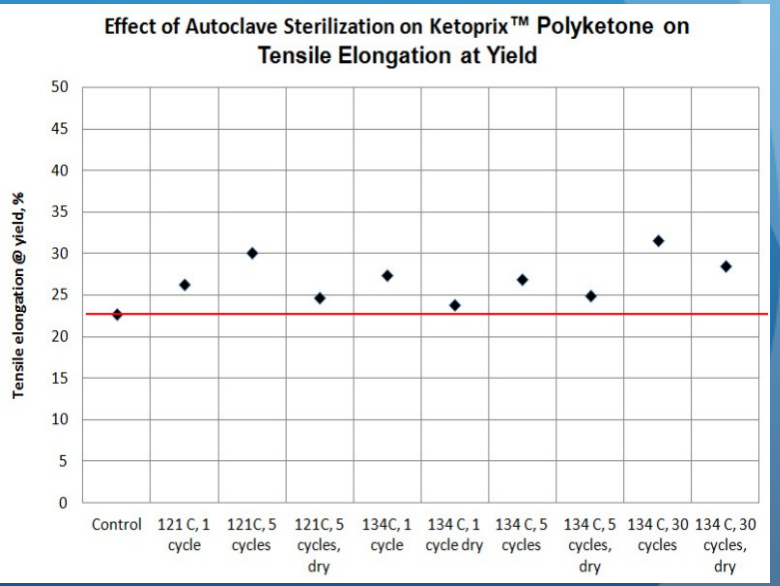
PK resistance to common sterilization and disinfection techniques

- PK is resistant to effects of all common sterilization techniques
  - Autoclave
    - Repeat exposures
  - Irradiation
    - E-beam
    - Cobalt (C_{60})
  - Gaseous Chemicals
    - Ethylene Oxide (EtO)
- Resistant to effects of common disinfectants
  - Quarternary ammonium compounds

Effects of autoclave sterilization

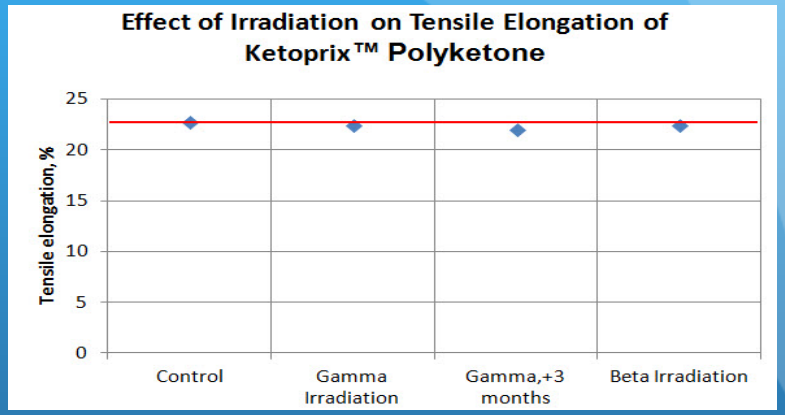
Strength and ductility of PK are virtually unaffected by sterilization after 30 autoclave cycles @ up to 134C with the wet or dry technique

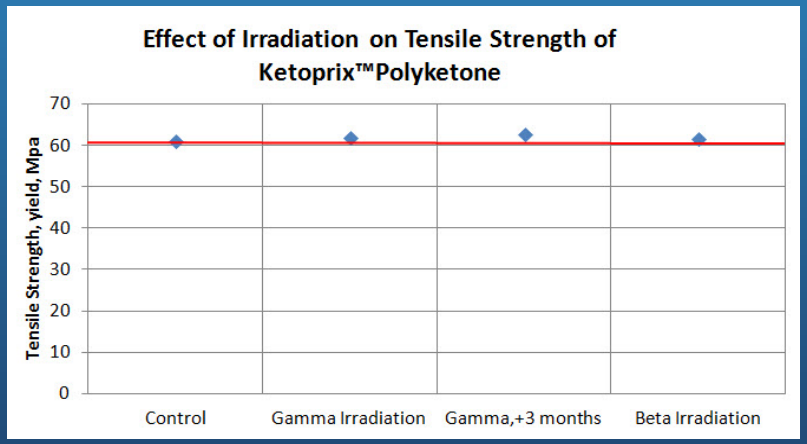


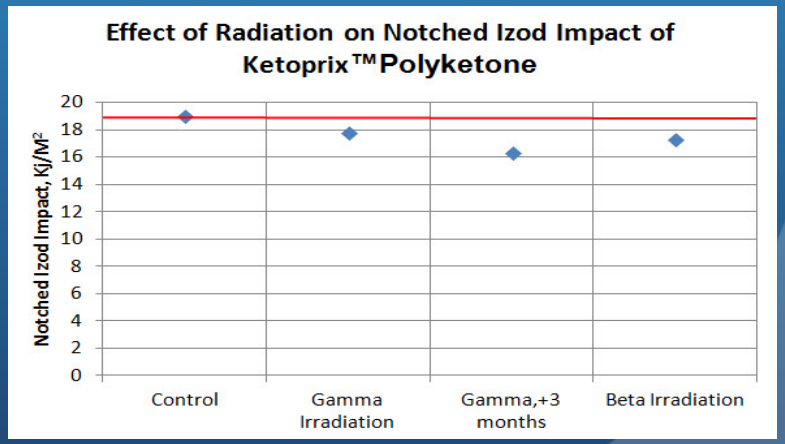


Effects of irradiation sterilization

Strength & ductility of PK are virtually unaffected by either Gamma or Beta irradiation







Effects of common disinfectants

- PK exhibits excellent resistance to attack by a broad range of chemicals including quarternary ammonium compounds which are commonly used as/in disinfectants
- Immersion in a 10% aqueous solution of ammonium hydroxide at 23C for 100 days had virtually no effect on the tensile strength or ductility of PK

Sample	Tensile Strength, psi	Tensile elongation, yield, %
Control	8,294	25
Exposed	8,294	23

Regulatory Approvals

- NSF 61 approval for potable water
  - Up to 170 in^2/L contact area
- FDA FCN# 1562
  - Approved for use in articles intended for repeated use in food processing establishments, for multilayer flexible packaging for refrigerated food products and for reheatable or microwaveable rigid retort packaging for food, except in contact with infant formula and breast milk
  - Currently limited to a maximum thickness of 0.010”. Approval for larger thicknesses expected 4Q17
- E/U 10/2011 approval for food contact applications

NSF 61 approval for PK

NSF International

OFFICIAL LISTING

NSF International Certifies that the products appearing on this Listing conform to the requirements of NSF/ANSI Standard 61 - Drinking Water System Components - Health Effects

This is the Official Listing recorded on February 6, 2015.

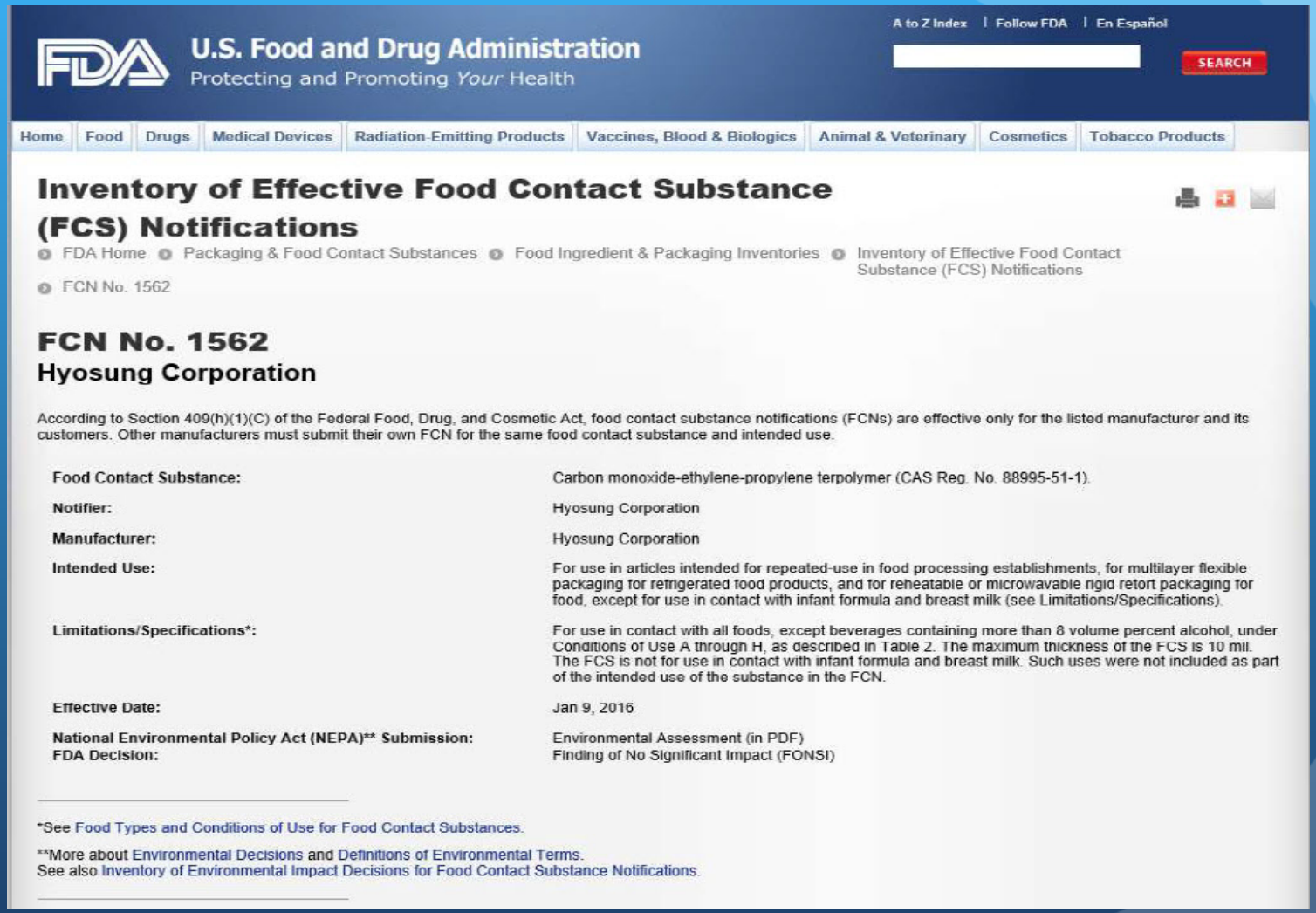
Hyosung Corporation
183, Hogey-dong, Donan-Gu
Anyang-Si, Gyeonggi-Do
431-080
Republic of Korea
82 31 428 1352

Facility: Ulsan, Republic of Korea

	Potable Water Materials		
Trade Designation	**End Use**	**Water Contact Temp**	**Water Contact Material**
Potable Water Materials			
Polyketone M230A [1]	F,P	C. HOT	OTHER
Polyketone M330A [2]	F,P	C. HOT	OTHER
Polyketone M630A [3]	F,P	C. HOT	OTHER

[1] Certified for a maximum surface area to volume ratio of 500 sq. in./L.
[2] Certified for a maximum surface area to volume ratio of 400 sq. in./L.
[3] Certified for a maximum surface area to volume ratio of 170 sq. in./L.

FDA approval for PK



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Inventory of Effective Food Contact Substance (FCS) Notifications

FDA Home › Packaging & Food Contact Substances › Food Ingredient & Packaging Inventories › Inventory of Effective Food Contact Substance (FCS) Notifications › FCN No. 1562

FCN No. 1562
Hyosung Corporation

According to Section 409(h)(1)(C) of the Federal Food, Drug, and Cosmetic Act, food contact substance notifications (FCNs) are effective only for the listed manufacturer and its customers. Other manufacturers must submit their own FCN for the same food contact substance and intended use.

Food Contact Substance:	Carbon monoxide-ethylene-propylene terpolymer (CAS Reg. No. 88995-51-1).
Notifier:	Hyosung Corporation
Manufacturer:	Hyosung Corporation
Intended Use:	For use in articles intended for repeated-use in food processing establishments, for multilayer flexible packaging for refrigerated food products, and for reheatable or microwavable rigid retort packaging for food, except for use in contact with infant formula and breast milk (see Limitations/Specifications).
Limitations/Specifications*:	For use in contact with all foods, except beverages containing more than 8 volume percent alcohol, under Conditions of Use A through H, as described in Table 2. The maximum thickness of the FCS is 10 mil. The FCS is not for use in contact with infant formula and breast milk. Such uses were not included as part of the intended use of the substance in the FCN.
Effective Date:	Jan 9, 2016
National Environmental Policy Act (NEPA) Submission:**	Environmental Assessment (in PDF)
FDA Decision:	Finding of No Significant Impact (FONSI)

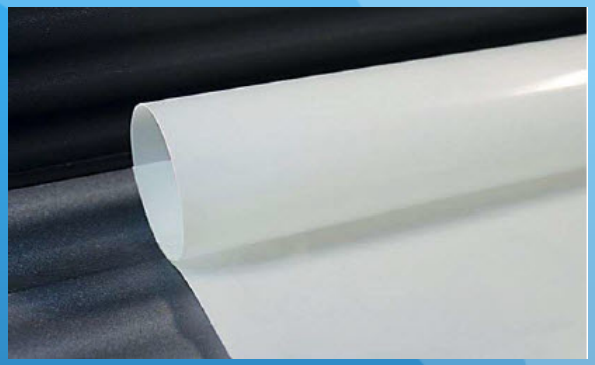
*See Food Types and Conditions of Use for Food Contact Substances.

**More about Environmental Decisions and Definitions of Environmental Terms.
See also Inventory of Environmental Impact Decisions for Food Contact Substance Notifications.

Tie layer resin development

- Effort underway to develop an Esprix proprietary tie layer resin suitable for use with PK & PE resins
  - Based on MAPE chemistry
  - Early success achieved in trial quantities
  - Development ongoing targeting commercialization 4Q17-1Q18

PK film for packaging & industrial applications



- Incumbent Material: PE-EVOH
- Film thickness: 0.5-20 mils
- Customer requirements:
  - Effective gas barrier for N_2, H_2SO_4, CH_4, CO_2,O_2,H_2O
  - Chemical Resistance – Crude Oil, Fuel, acids, alkalai
  - Low moisture absorption
  - Dimensional Stability
  - Good scratch & mar resistance
- Value Proposition:
  - Better physical property retention than PE-EVOH
  - Gas Barrier performance similar to PE-EVOH at significantly lower cost
  - Better resistance to attack by fuels than PA11 & PA12 at significantly lower cost
  - Ability to achieve performance of multi-layer EVOH structure with a single layer of PK

Polyketone flexible packaging in medical application

- Application Laminates for ringer bag (Film)
- Application Description Transparent packaging laminates for ringer solution
- Processing Co-extrusion with PP (sealing temperature: 150~160℃)
- Incumbent material PP(25㎛) / PP+Rubber(150㎛) / PP(25㎛)
- Drivers for conversion Oxygen gas barrier performance and system cost vs. EVOH
- Key Requirements
  - Transparency(Haze 5↓ at 200㎛)
  - Gas barrier, low temperature impact resistance, flexibility
  - Non-PVC, processability of adhesion with PP
- Compelling Value Propositions
  - Low oxygen permeability with mono layer(0.1 cc.mm/m^2/day/atm)
  - Cost reduction with thinner layer
  - FDA approval

Summary & Conclusions

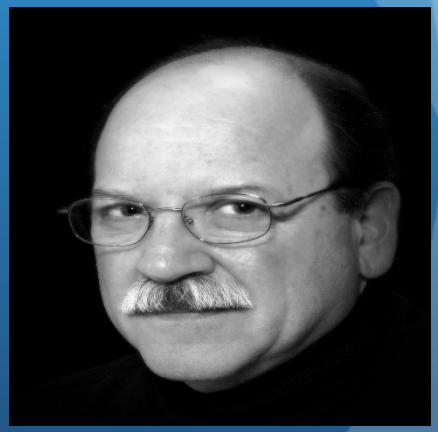
- **Polyketone is a new engineering resin now commercially available with the following benefits:**
  - Unique combination of high strength and good ductility
    - Excellent resilience
    - Excellent puncture resistance
  - High heat resistance
  - Good permeation and vapor transport characteristics
  - Excellent chemical resistance
  - Excellent hydrolysis resistance
  - Virtually impervious to the effects of common sterilization & decontamination techniques
  - Excellent adhesion to PP
  - Regulatory (FDA & NSF) approvals in place
  - Appealing economics vs. EVOH, PVDC, PA11,PA12

Ketoprix Team

Cary Veith – President & CEO

Dang Le – Product Manager

Tim Morefield – TS Consultant



Bob Pilotti – Sales Consultant

Thank You

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