

Ketoprix[™] aliphatic polyketones are novel, engineering thermoplastic resins that provide superior toughness, strength, resilience and chemical resistance. Ketoprix[™] polymers exhibit very high permeation resistance to fuels and hydrocarbons. Fuel transport systems can utilize Ketoprix[™] polymers in single layer or as the inner barrier layer in multilayer pipe/tube.

Esprit Ketoprix[™] White Paper on Fuel Permeation Resistance of Aliphatic Polyketone

Natural Grades, EK33, EK63

Engineered Resins for Fuel Transport Systems

1

POLYKETONE PRODUCT INTRODUCTION

Ketoprix[™] resins are thermoplastic aliphatic polyketones containing a 1,4-diketone backbone structure. They are produced from ethylene, propylene and CO and perfectly alternate olefin and CO monomers in the backbone.

The resins are very tough, strong and have high permeation resistance to hydrocarbons making them well suited for use as a barrier layer to many different fuels and hydrocarbons, including oxygenated fuels. This white paper estimates fuel permeability through Ketoprix Polyketone resins using experimental data developed by Shell in the late 1990's [1].

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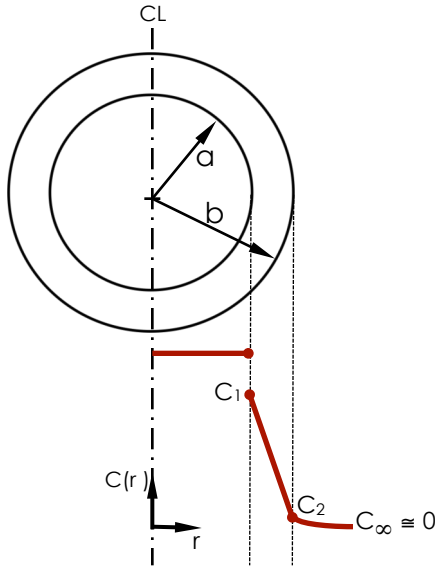
BACKGROUND

The task of designing automotive and retail forecourt (gasoline service station) fuel transport components and complete piping systems has been made more difficult by new fighter emissions standards and uncertainty about the composition of future fuels. A variety of oxygenated fuels may be required to reduce exhaust emissions as mandated in many areas throughout the country. Polymers used in fuel system components must be compatible with these new oxygenated fuels.

The testing herein has followed the procedures outlined by General Motors specification GM 9061-P, "Permeability Test for Fuel Hose and Tubing." The extruded tubing tested had a nominal OD of 8.51 mm (0.34 in.), and a wall thickness of 1.07 mm (0.042 in.). The total effective length of the tubing with both ends plugged was 300 mm (11.8 in.).

Because of the multi-component nature of the new fuel systems, we tested several different types of fuels, including the most prevalent oxygenated fuel, E10. The tubing is filled with the target fuel and then maintained at constant temperature, and the weight loss of the fuel/tube system was measured as a function of exposure time.

Next we develop the diffusion theory used in this analysis. Then the raw data are shown in Figures 1-4, in the Testing Results section. Permeability coefficient calculations follow including a summary of daily loss rates and discussion.



KETOPRIX™ polymers have excellent barrier properties to gasoline and oxygenated fuels. In order to solve for the Permeability of various fuels through polymeric tubing using experimental gravimetric data, we begin with the fundamental differential diffusion equation (constitutive equation for conservation of mass) in cylindrical geometry. Neglecting end effects and assuming angular symmetry (only transient radial diffusion), we have:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (rD \frac{\partial C}{\partial r}) \quad \text{Eq 1}$$

Assuming diffusivity is not concentration dependent, and with the following Boundary and Initial Conditions, gaseous diffusion of fuel through the polymeric tubing wall can be defined as:

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

where S = the Henry's Law solubility constant for the given fuel and the polymer matrix and p^* is the vapor pressure of the fuel at given temperature. P is the Permeability coefficient which equals the product of the Diffusivity coefficient, D and the Henry's Law Solubility constant, S , at given T , such that $P = D \cdot S$.

BC2: At $r = b$ (outer radius), $C = C_2 \rightarrow C_\infty \approx 0$, where the outer wall fuel concentration is going to be very small due to the rapid diffusion away from the outer cylinder wall into an essentially infinite air medium. Essentially we are assuming the Mass Transfer Biot number ($= k_c b / D$) is very large, or the film transfer coefficient, $k_c \gg D$, the diffusivity of the fuel vapor through the polymer, in order for this simplifying assumption to hold. This assumption makes the solution of the PDE simpler (homogenous BC) and will not measurably impact the resulting estimates of the Permeability coefficient.

IC: At $t = 0$, $a < r < b$, $C(r,0) = 0$, i.e. there is no fuel anywhere in the tube at the start of the experimental observation.

Recognizing that: 1) solving this 2D PDE involves lengthy variable manipulation (dimensionless variables, SOV, IBP, normalization equations to get the eigenfunctions and root solving to get the eigenvalues of the Bessel functions, orthogonality checks, etc), and 2) the fact that we are most interested in the Permeability after steady state has been reached, we solve the steady-state 1D ODE to give:

$$C(r) = Sp^* \frac{\ln(b/r)}{\ln(b/a)} \quad \text{Eq 2}$$

As noted in *The Mathematics of Diffusion* by J. Crank [2], the full 2D solution for this problem has the steady-state solution in Eq 2 plus another term consisting of the infinite series of Bessel functions times the exponential decay term, $\exp(-D\lambda_n^2 t)$, where λ_n represents the eigenvalues of the normalization equations involving Bessel functions for a given root number, n . For large times, this second term decays away to a very small value and leaves us with the steady state solution shown in Eq 2.

If we integrate across the outer surface of the cylindrical tube and evaluate the fuel concentration flux gradient (first derivative) at the outer surface $r=b$, (following Fick's Law) we get the total mass that has diffused out of the tube in time, t .

$$Q(t) = -2\pi LD \int_0^t r \frac{\partial C}{\partial r} \Big|_{r=b} dt = 2\pi Lp^* P t / \ln(b/a) \quad \text{Eq 3}$$

This suggests that a plot of $Q \cdot \ln(b/a) / (2\pi Lp^*)$ versus time will give the Permeability coefficient, P as the slope of the graph for large times when steady state has been reached.

The raw data are shown in plots of weight loss versus time in Figures 1-4 for two different fuels, an unleaded (UL) gasoline and an oxygenated fuel, E10 for two different temperatures, 23°C and 93°C (200°F). In the ambient tests, polyketone (PK) is compared against a commonly used polymer, polyamide-12 (PA-12). For the elevated temperatures, polytetrafluoroethylene (PTFE) is also compared in the tests.

The summary of these plots and slope calculation via linear regression for each fuel tested is shown in Table 1.

SUMMARY OF CALCULATIONS of FUEL PERMEABILITY and LOSS

Type of Fuel	Temperature, °C (°F)	Permeability, P (cm/s) (x 10 ⁻¹²)*			Steady-state Loss, g/(m ² -day)			Comments
		PK, EK63	PA12	PTFE	PK, EK63	PA12	PTFE	
UL Gasoline	23 (73)	≈ 0	0.425	No data	≈ 0	1.4	No data	PK P too low to measure in 70 d
UL Gasoline	93 (200)	0.044	1.860	0.325	0.9	39.2	6.9	
E10	23 (73)	0.006	0.306	No data	0.02	0.9	No data	
E10	93 (200)	0.145	0.871	0.290	3.1	18.7	6.2	

* We convert pressure to kg_f/m² units to get Permeability in units of cm/s

Table 1. Summary of Permeability Coefficient and Steady-State Loss estimates for various fuels.

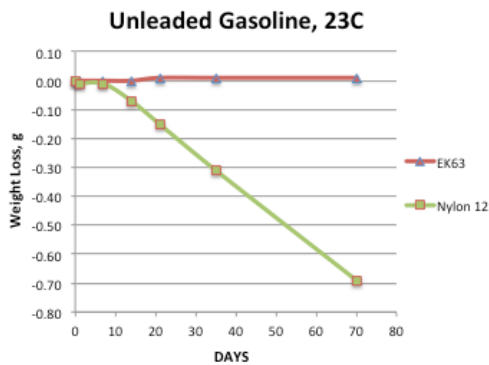


Figure 1: UL Gasoline at 23°C

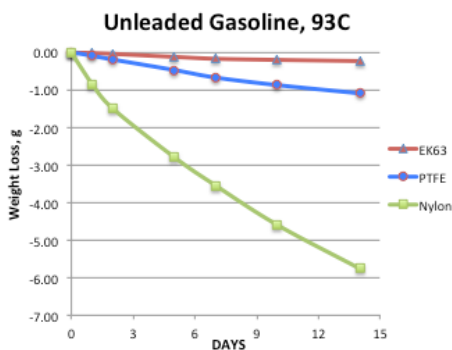


Figure 2: UL Gasoline at 93°C

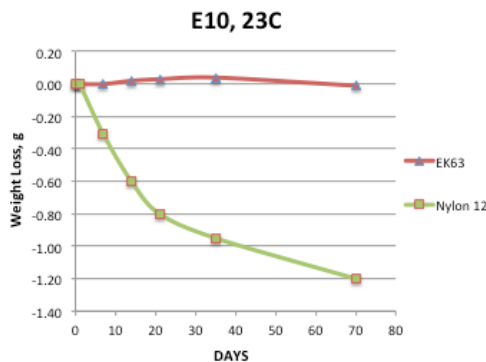


Figure 3: E10 at 23°C

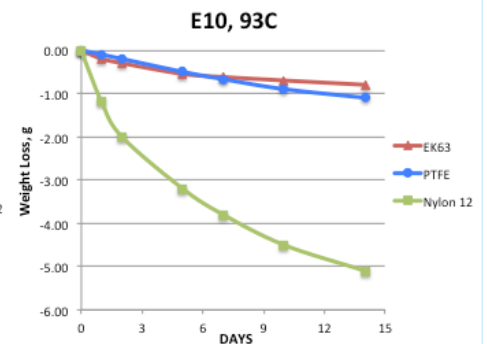


Figure 4: E10 at 93°C

The vapor pressures for the various fuels were calculated from EPA publication AP-42, "Compilation of Air Pollution Emission Factors" [3] for a RVP10 UL fuel. Vapor pressures at 93°C were estimated from Antoine's equation. For E10, Raoult's Law was assumed in estimating total vapor pressure assuming 10% EtOH addition by volume with the balance being the UL fuel. No correction was made for the removal of lower boilers in E10 as this adjustment is outside the scope of accuracy of these calculations. While this approach may not be completely accurate, it will suffice for our purposes here, which is to gain a preliminary understanding of the diffusion behavior of various fuels through polyketone as compared with other conventional materials.

For unleaded gasoline at room temperature, PK performs superior to PA-12 with substantially lower fuel permeability. For UL Gasoline at 93°C, PK performs far better than PA-12 and even better than PTFE in terms of fuel permeation resistance.

For E10 fuel, permeability of fuel through polyketone is very low at ambient temperature and for elevated temperature, fuel permeability through PK is comparable to that through PTFE. For E10, PK performs better than PA-12 at all temperature ranges.

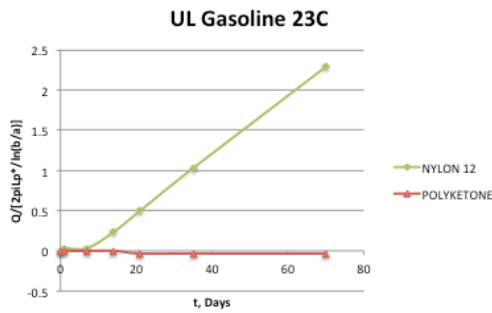


Figure 5. Classical diffusion behavior for PA-12

In examining the steady state permeabilities and flux loss through the tube wall, the PK tubing had losses well under the UL971 limit of 4 g/(m²-d) for both UL and E10 fuels at both ambient and elevated temperatures of 200°F [4]. Fuel permeation through PK is even slightly less than fuel permeation through PTFE, although the values are quite similar when comparing orders of magnitude.

In examining the shape of the permeation curves as a function of time, one notices changes depending on the type of fuel tested. For UL gasoline diffusing through PA-12 at ambient temperature, the curve perfectly fits the type of molecular diffusion depicted in Eq 1-3, as shown in Figure 5. Here, we see that the unsteady-state diffusion process governs for the first 8-10 days or so. After that time, the process has reached steady-state and the theoretical development suggested here applies very nicely with the data fitting the theory. This further supports that the assumptions in the numerical derivation of the diffusion / permeation theory shown in Equations 1-3 are acceptable.

However, the shapes of the other curves are not the same (compare PA-12 data in Figures 2-4 with Figure 1 as illustrative examples). In looking at E10 at ambient temperature in PA-12, the rate of permeation of the fuel seems to be higher in the initial times and then slows to a steady state rate after 20 days or so. This suggests that there could be some molecular changes occurring in the PA resin possibly due to plasticization effects by the EtOH. Or perhaps the rates of diffusion of the EtOH and hydrocarbons are different and that the composition of the fuel in the tube is changing with time, with the EtOH diffusing very quickly out of the tube in early times followed by a steady state diffusion of mostly the remaining hydrocarbons in the fuel at long times.

Regardless of these differences, the overall permeability coefficients and amount of fuel lost through the tube wall is shown in comparison of Figures 1-4 and the calculated values for PK, PA12 and PTFE. Clearly, permeation of gasoline fuels through Polyketone is far less than through Polyamide-12 and slightly lower than fuel permeation through PTFE. From these experiments, Polyketone appears to have improved fuel permeation resistance over conventional materials and would make an excellent candidate material for further testing as the inner liner in multi-layer pipe and tube composites.

Tie layer polymers are commercially available for providing good adhesion of Polyketone to HDPE outer layers in multi-layer pipe and tube constructions.

1. Shell Chemical Co., Polymer Fuel Permeation Information Sheets, ca. 1998.
2. The Mathematics of Diffusion, J. Crank, Brunel University, Uxbridge, 2nd Ed., Clarendon Press, Oxford, (1975) pp. 84.
3. U.S. Environmental Protection Agency's publication "AP-42: Compilation of Air Pollution Emission Factors", Chapter 7, Table 7.1-2
4. UL Standard "Safety for Nonmetallic Underground Piping for Flammable Liquids", revision dated March 2, 2006, ISBN: 1-55989-910-7.

KETOPRIX™ Polyketone resins are not hazardous. For information on handling and storage of KETOPRIX™ Polyketone resins, please consult our Safety Data Sheets, available from Esprit Technologies. For more detailed information, please contact your representative at Esprit Technologies.

KETOPRIX™ Polyketone resins comply with all regulatory statutes in the USA. For more detailed information on regulatory compliance outside the USA, please contact your representative at Esprit Technologies.

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