

Fluoroelastomer Compatibility with Bioalcohol Fuels

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ABSTRACT

Global acceptance and use of biofuels is growing rapidly in the transportation sector. Diminishing reserves of limited and costly fossil fuel resources and a growing realization that world peak oil production will most likely occur within the next decade is driving significant investment in sustainable biofuels. Legislative, regulatory and market forces are driving developments which seek to reduce vehicle emissions, improve fuel efficiency, lower environmental greenhouse gases and strengthen the economy. The use of alternate, sustainable, renewable fuels, preferably of domestic origin, is fostering considerable investment in new technologies. One promising technology is the addition of aliphatic alcohols to gasoline and diesel fuels.

The compatibility of seal and hose materials commonly used in automotive fuel systems with conventional hydrocarbon fuels is well known. Over the past forty-five years fluorohydrocarbon elastomers have been successfully used in passenger car and truck and off-highway gasoline and petrodiesel fuel delivery and metering systems. More recently, biofuels such as ethanol have become technically and economically attractive blending constituents for gasoline and diesel fuels. These biomass fuels present their own set of material compatibility challenges to automotive fuel storage, delivery, and metering system component hardware.

In this presentation the compatibility of selected fluoroelastomers with ethanol and butanol, and their respective alcohol-based blend fuels, will be reviewed. Fluoroelastomers that have historically been used for petroleum based fuels will be compared to several new types that display improved compatibility and sealing functionality with alcohol-based fuels. Accelerated long

term testing results will be presented that characterize physical properties and property retention in bioalcohols through 1008 hours at 40°C. Properties relevant to sealing applications and hose will also be discussed and best in class elastomers will be highlighted, so that, in gaining a better understanding of the respective capabilities of high performance fluorohydrocarbon elastomers, the engineer may design more robust sealing systems for bioalcohol service.

INTRODUCTION

For nearly half a century fluorohydrocarbon elastomers (FKM) have demonstrated excellent performance in aerospace and automotive sealing applications. FKM's have demonstrated broad compatibility with petroleum-based fuels since their adoption in the automotive sector in 1961 (fuel metering components for carburetion) and are preferred elastomers for today's sophisticated common rail fuel injection systems.

Market forces are driving spark ignition (SI) and compression ignition (CI) engine developments to decrease vehicle emissions, improve fuel efficiency and reduce environmental greenhouse gases (primarily CO₂). The use of alternate, sustainable, renewable fuels, preferably of domestic origin, is driving significant investment in new technologies. Biofuels, such as ethanol and butanol, are technically and economically attractive blending constituents for gasoline.

Ethyl alcohol, or ethanol, is a common, oxygen-containing, pollution control additive used in automotive gasoline, typically at the 6-10% level. Ethanol usage has been largely limited to the mid-western part of North America, due in part to supply and price constraints. As new manufacturing technology makes this alcohol more plentiful and government incentives continue to

encourage further production and use, there is a drive to use ethanol in automotive fuel at higher percentages, for example at 85%, in E85 flex fuel. In 2007 it is estimated that 6.5 billion gallons of ethanol was produced in North America for the transportation sector [1].

Ethanol offers high performance in SI engines due to its inherently high research octane number (RON). This property, together with its high latent heat of vaporization, enables internal combustion engines running on this fuel to achieve high thermal efficiency and high performance levels. Engines optimized to exploit these beneficial properties are prevalent in today's world of high performance motorsports. In 2007 the IndyCar Series moved to 100% ethanol and in 2009 the V8 Supercar Championship will move to E85. Further confidence in the performance attributes of ethanol is evident with Lotus Engineering's noteworthy efforts to optimize engine performance with E85 in flex-fuel vehicles [2, 3].

The rapidly increasing use of ethanol derived from corn has contributed to a growing controversy and debate about food vs. fuel [4]. Technology breakthroughs have been recently announced by DuPont and Genencor to develop and commercialize low-cost cellulosic ethanol utilizing proprietary enzyme technologies and production platforms enabling high biomass-to-sugar conversion rates [5]. Equally significant, General Motors announced a partnership with Coskata to use the company's technology to affordably and efficiently produce ethanol from a wide variety of renewable sources, garbage, old tires and plant waste [6]. These new technologies hold great potential in bringing low cost ethanol to the market, where the fuel will not be derived from, or compete with, grain-based food sources.

In 2006 DuPont and BP announced the creation of a partnership to develop, produce and market biobutanol to meet the increasing global demand for renewable transportation fuels [7].

EXPERIMENTAL

The materials evaluated in this study were prepared using commercial grades of fluoroelastomers. ASTM D1418 designations are used to describe each material.

FLUOROLEASTOMERS EVALUATED

Typically, fluoroelastomers are differentiated by their monomer composition and the cure system employed. Traditional copolymer and terpolymer compositions, based on vinylidene fluoride (VF₂), hexafluoropropylene (HFP) and tetrafluoroethylene (TFE), are considered "standard" products within the rubber industry. Other products offering some special aspect of functionality not provided for by the standard products are considered "specialty" types. For example, FKM- GLT-S and FKM-GFLT-S contain the monomer perfluoromethylvinylether (PMVE) to provide enhanced low temperature flexibility.

Recently, advanced polymerization and curing technology designed to manufacture specialty fluoroelastomers with end use properties that meet evolving market needs was developed and commercialized [8,9]. These polymers, called Viton[®] fluoroelastomer made with Advanced Polymer Architecture (APA Polymers), were designed to provide an excellent balance of processing and physical properties [10, 11]. These improvements are due to the modified molecular weight distributions, improved cure site monomers and unique polymer end group chemistry that were applied to the manufacture of these polymers.

While the basic building blocks (monomers) are the same, polymer architecture has advanced considerably. The APA polymers have superior properties and processing characteristics when compared to their predecessors. These advances in polymer design have been necessary to keep pace with automotive seal fabricators quest to optimize part quality and manufacturing yields, in order to maintain competitive position, without sacrificing end-use properties.

Table 1 lists those fluoroelastomers evaluated in this study and describes some of their attributes.

Table 1 - Fluoroelastomers Evaluated	
Product	General Description
FKM-A601C	Viton [®] A-601C, VF ₂ /HFP, 66.0% fluorine, bisphenol cure
FKM-B601C	Viton [®] B-601C, VF ₂ /HFP/TFE, 68.0% fluorine, bisphenol cure
FKM-VTR9209	VTR-9209, VF ₂ /HFP/TFE, 69.0% fluorine, bisphenol cure
FKM-F605C	Viton [®] F-605C, VF ₂ /HFP/TFE, 70.0% fluorine, bisphenol cure
FKM-GLT-S	Viton [®] GLT-600S, VF ₂ /TFE/PMVE/CSM, 64.5% fluorine, peroxide cure
FKM-GBLT-S	Viton [®] GBLT-600S, VF ₂ /TFE/PMVE/CSM, 66.0% fluorine, peroxide cure
FKM-GFLT-S	Viton [®] GFLT-600S, VF ₂ /TFE/PMVE/CSM, 67.0% fluorine, peroxide cure
FKM-GF-S	Viton [®] GF-600S, VF ₂ /HFP/TFE/CSM, 70.2% fluorine, peroxide cure
Monomer Description: VF ₂ = vinylidene fluoride HFP = hexafluoropropylene TFE = tetrafluoroethylene PMVE = perfluoromethylvinylether CSM = proprietary cure-site monomer APA polymers are designated with an "S" suffix	

FUELS EVALUATED

Table 2 lists those fuels evaluated in this study and describes their general composition.

Table 2 - Fuels Evaluated	
Fuel	General Description
Fuel C	Blend of 50% isooctane and 50% toluene
Ethanol	Ethyl alcohol (denatured with 5% methanol)
CE-10	10% ethanol blended with 90% Fuel C
CE-25	25% ethanol blended with 75% Fuel C
CE-50	50% ethanol blended with 50% Fuel C
CE-85	85% ethanol blended with 15% Fuel C
E-100	100% ethanol
Butanol	1-Butyl alcohol (99.4% A.C.S Reagent)
UTG-91	Unleaded test gasoline – 91 octane
Fuel C / Butanol	80% Fuel C blended with 20% butanol
UTG91 / Butanol	80% UTG-91 gasoline blended with 20% butanol

Test Protocols - Standard Property and Aging Tests

Sample Preparation: Compounding of the fluoroelastomers was carried out using standard rubber lab equipment (internal mixer and two-roll mill.) Standard processing techniques commonly practiced in the industry were employed in preparation of test specimens. Compound formulations, with the exception of FKM-VTR9209, were typical of those recommended for sealing service. FKM-VTR9209 has been designed for fuel hose service. All fluoroelastomers contained 30 pph MT carbon black (N-990) to produce a nominal 70-80 durometer hardness. Standard ASTM slabs were prepared by compression molding as follows:

- FKM-A601C FKM-B601C FKM-F605C
Press Cure: 7 min/177°C
Post Cure: 16 h/232°C in air circulating oven
- FKM-GLT-S FKM-GBLT-S FKM-GFLT-S FKM-GF-S
Press Cure: 7 min/177°C
Post Cure: 16 h/232°C in air circulating oven
- FKM-VTR9209
Press Cure: 30 min/162°C

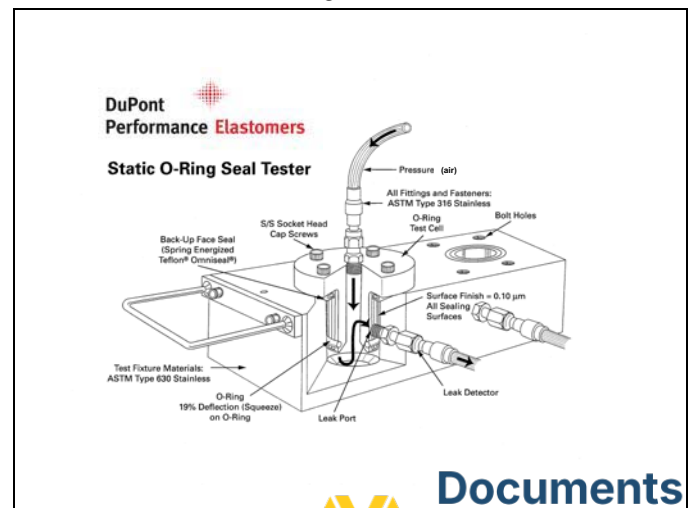
Following post cure, the FKM test specimens used for physical property and aging tests were die-cut from the molded slabs and tested per ASTM methods.

Test Methods: The fluoroelastomers were characterized using the test methods described below:

- Stress-strain in accordance with ASTM D 412-98a, Die C.
- Hardness in accordance with ASTM D 2240-02.

- Compression set in accordance with ASTM D 395-01.
- Temperature retraction (TR-10) in accordance with ASTM D 1329-88.
- Glass transition temperature (T_g) by Differential Scanning Calorimetry in accordance with ASTM D 7426-08. Measurements were made with a TA Instruments Differential Scanning Calorimeter, Model Q200, and run in sub-ambient, modulated mode, at a scanning rate of 5°C/min.
- Fluid immersion in accordance with ASTM D 471-98 – all fuel testing was conducted in sealed 1 liter 316 stainless steel Parr pressure vessels.
- Permeation testing in accordance with SAE J2665 using the Thwing Albert cup weight loss method.
- Compression Stress Relaxation measurements in accordance with ASTM D 6147-97 using an MTS Model 830 and modified Wykeham-Farrance evaluation jigs designed to apply a constant compressive strain to a molded pellet test specimen.
- Static O-ring Seal Testing - This test method utilizes a special test rig and protocol developed by DuPont. No established ASTM test method yet exists. This test rig has been previously described [12, 13] and has been routinely used to screen the low temperature functionality of elastomeric sealing materials. The apparatus consists of a 316 stainless steel block and plugs as shown in Figure 1, along with associated fasteners, valves, fittings and tubing. This apparatus was adapted, with major modifications, from SAE Aerospace Material Specification 7273B [14]. The gland design conforms to SAE Aerospace Recommended Practices 1231 and 1232A [15, 16]. A radial squeeze of 19% is provided within three separate cells of the test block. The surface finishes are of industry standard (0.1µm / 4µin). Apparatus cooling is provided by a low temperature environmental chamber capable of achieving -70°C.

Figure 1



Documents

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The test procedure consists of selecting three AS568-214 O-rings [17] of excellent visual surface quality (parting line quality is critical) being lightly lubricated with a low temperature Krytox® perfluorinated polyether grease prior to installation in the test plug gland. The plug is fastened into the block with socket head screws until finger tight. A spring-energized Teflon® PTFE face seal provides secondary backup directly above the leak port. The apparatus is placed into the environmental chamber, internally pressurized with dry air to 0.4 MPa (60 psi), then cycled down to -70°C at ~0.5°C per minute until leakage is detected via IGLS flow meters. The temperature is monitored continuously by RTD platinum thermocouples. The test reports the median temperature of the three cells at 1.5 Cubic Centimeter per Minute (CCM) leakage. All data is captured via a computerized data acquisition system. The rig then auto-cycles back to room temperature and the procedure is repeated with another set of O-rings. The time to run the test varies, depending upon the Tg of the material. With the FKM polymers, 3-4 hours is typical.

In our study denatured ethanol and respective blends with Fuel C were evaluated. Also, 1-butanol and respective blends with Fuel C and UTG-91 unleaded gasoline were evaluated. 1-butanol was selected as a surrogate for BP butanol, since commercial quantities of biobutanol are not yet available. Testing was conducted in Parr pressure vessels at 40°C for a period through 1008 hours (6 weeks) with fuel refreshed weekly. Fuel C, ethanol, and four different blend ratios of Fuel C with ethanol (CE-10, CE-25, CE-50 and CE-85) were evaluated. Three different butanol fuels were tested ranging from neat butanol to blends of 80% Fuel C / 20% butanol and 80% unleaded gasoline / 20% butanol. 20% blends of butanol with fuel were chosen for our study based on the maximum amount of butanol permitted by law – currently, 10% in European Union (EU 228) and 11.5% in the USA. EPA regulations require fuel manufacturers to produce fuels that are substantially similar (“sub-sim”) to fuels used for vehicle certification.

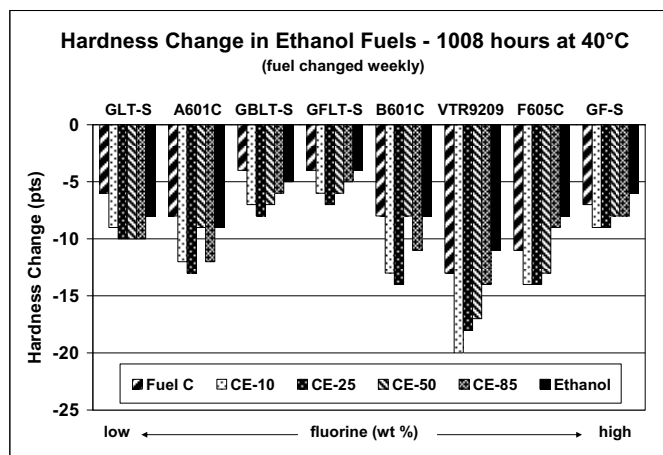
RESULTS AND DISCUSSION

Compatibility of elastomeric components with service fluids is typically ascertained by accelerated aging under laboratory conditions evaluating volume swell and physical property retention after exposure. The testing performed in this study employed methods typically used to characterize elastomeric sealing performance. Hardness changes, retention of stress-strain properties (tensile strength and elongation), volume swell, compression set, compressive stress relaxation, and low temperature tests were performed. Vulcanizates of the FKM materials were subjected to immersion in the various alcohol-fuel blends.

Historically, elastomer compatibility testing has shown that FKM has generally been judged to be resistant to ethanol and methanol fuels based on accelerated fluid aging [18, 19].

Hardness Change: Typically, one of the effects of fluid swell in elastomers is a corresponding loss of hardness (softening). This generally holds true for the materials reported in this study. Figures 2-4 indicate a strong relationship exists between hardness loss and the volume swell values shown later in this presentation.

Figure 2



Some softening (loss of hardness) was also observed as a function of predicted swell; however the correlation was not as strong as with swell. Noteworthy was the softening observed with FKM-VTR9209 (a high fluorine content FKM developed for fuel hose). Here we observe low swell, but high softening (Figures 2-4). Since FKM-VTR9209 was not postcured in this study, its crosslink network is not as tight as the other postcured FKM polymers evaluated, and shows a higher loss in hardness (20 points) after fuel immersion that is neither unexpected nor surprising.

Figure 3

