

Long Term Fuel Aging of Peroxy Cured “APA” Fluoroelastomers

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ABSTRACT

Peroxide cured fluoroelastomers have been increasingly used in automotive fuel systems for the past 15 years. Now refined, peroxide cured Advanced Polymer Architecture (APA) technology fluoroelastomers (FPM) have arrived with their enhanced properties. Documenting the long-term aging properties of these APA technology types and how they compare to conventional peroxide cured FPM is the focus of this presentation.

5,000 hour agings in CM-15A fuel @ 60°C were conducted on both standard hexafluoropropylene (HFP) containing fluoroelastomers: GF, GF-S, GBL, and GBL-S as well as low temperature perfluoromethylvinylether (PMVE) containing fluoroelastomers: GLT, GLT-S, GBLT-S, GFLT and GFLT-S. Tensile and volume swell data was collected periodically during the 5,000 hour test to see trends over this extended exposure period. Additional data such as fuel permeation and sour gasoline testing was also conducted and will be reported.

INTRODUCTION

Sealing needs in automotive fuel system have continued to evolve. With the advent of Euro 5 and the current California Air Resources Board's (CARB) Low Emission Vehicle Part II (LEV II) requirements the demands on materials in the automotive fuel systems has risen to an all time high. These demands will require not only low permeation materials, but also will require robust systems that can maintain the original design intent for 12 to 15 years. All this must be accomplished with elastomers resistant to today's gasoline fuels, as well as bio and alcohol fuels we are likely to use in the next decade (1).

Fluoroelastomers have long been recognized as the rubber sealing material of choice for premium fuel systems. Peroxide cured fluoroelastomers are a specialty niche of the FPM market used in fuel systems. Fluoroelastomers such as Viton® GF for excellent fuel and permeation resistance, Viton® GFLT for improved low temperature and methanol/fuel resistance, and Viton® GLT for the best low temperature flexibility have gained an excellent reputation in fuel system applications. Now an improved generation of peroxide cured **Advanced Polymer Architecture (APA)** technology fluoroelastomers (FPM) has arrived offering further enhanced properties.

The objective of this paper is to document the long-term fuel resistance of APA technology

fluoroelastomers and show how they compare to the older, peroxide cure technology FPM polymers.

EXPERIMENTAL

Ten fluoroelastomer polymers were mixed in a laboratory scale internal mixer into a standard 30 MT black (N990) recipe.

Standard HFP containing FPM peroxy types

- 1- **VTR-8675** “GAL-200S”, 66% fluorine, APA technology peroxy cured FPM
- 2- **Viton® GBL-900**, 67% fluorine, conventional peroxy cured FPM
- 2- **Viton® GBL-600S**, 67.5% fluorine, APA technology peroxy cured FPM
- 4- **Viton® GF**, 69.5% fluorine, conventional peroxy cured FPM
- 5- **Viton® GF-600S**, 70.2% fluorine, APA technology peroxy cured FPM

Low temperature FPM peroxy types

- 6- **Viton® GLT**, 64% fluorine, conventional low temperature peroxy cured FPM
- 7- **Viton® GLT-600S**, 64% fluorine, APA technology, low temperature peroxy cured FPM
- 8- **Viton® GBLT-600S**, 66% fluorine, APA technology, low temperature peroxy cured FPM
- 9- **Viton® GFLT**, 67% fluorine, conventional low temperature peroxy cured FPM
- 10- **Viton® GFLT-600S**, 67% fluorine, APA technology, low temperature peroxy cured FPM

ASTM test slabs were cured 5 minutes @ 177°C in a compression mold. The conventional technology polymers were then postcured in an air circulating oven for 16 hours at 232°C whereas the Advanced Polymer Architecture products were postcured for only 4 hours at 232°C. Tensile samples were then cut and either tested or immersed in fuel as noted. Testing was done at several time intervals so trends could be noted.

Test fuels used were CM-15A and sour fuel (PN180). CM-15A is a blend of 85% Fuel C with 15% methanol. The methanol was contaminated with “aggressive” water containing trace amounts of salts such as sodium chloride, sodium sulfate, and formic acid. Five ml of aggressive water was added to one liter of methanol which was then blended with the Fuel C when the fuels were prepared for testing. The fuel was changed weekly during the 5,000 hour aging with CM-15A. Aging was conducted in a Parr pressure vessel

placed in a Class A air oven at 60°C. Tensile testing was done after time intervals of 168, 672, 2,000, 3,000, 4,000, and 5,000 hours. After 5,000 hours of fuel immersion, samples were dried 4 hours @ 100°C and tested to investigate the overall effect of the fuel on the FPM. The sour fuel was made using a 80% Fuel C/15% methanol/5% t-butyl alcohol blend with copper ion and t-butyl hydroperoxide added to increase the peroxide number to 180. Sour fuel aging was also done in a Parr pressure vessel placed in an air oven at 60°C.

RESULTS AND DISCUSSION

After the slabs of the ten FPM test compounds were cured and postcured as noted, the original physical properties were determined. The results of that testing can be seen in Tables 1 and 2.

Table 1

Original physical properties of standard peroxy FPM polymers

	GF	GF-600S	GBL	GBL-600S	VTR-8675 "GAL-S"
Compound # 2226	A50-01	A50-02	A50-03	A50-04	A50-05
Physical Properties @ R.T. - Original (Cure 5' @ 177°C - postcure @ 232°C as noted)					
postcure time:	16 hr	4 hr	16 hr	4 hr	4 hr
M-25, MPa	1.6	2.0	1.4	1.3	1.2
M-100, MPa	7.2	6.8	7.6	4.0	3.3
Tensile (T-B), MPa	19.0	20.4	22.2	17.9	18.7
Elongation (E-B), %	204	278	186	289	349
Hardness, A, pts	73	77	72	70	69
Compression Set, Method B, Plied					
70 Hrs @ 200°C	46	16	30	27	26

Table 2

Original physical properties of low temp. "LT" polymers

	GLT	GLT-S	GBLT-S	GFLT	GFLT-S
Compound #	A44-01	A44-02	A44-03	A44-04	A44-05
Physical Properties @ R.T. - Original (Cure 5' @ 177°C - postcure @ 232°C as noted)					
postcure time:	16 hr	4 hr	4 hr	16 hr	4 hr
M-25, MPa	1.2	1.3	1.3	1.4	1.3
M-100, MPa	6.1	3.7	4.6	8.8	5.5
Tensile, MPa	21.7	17.5	17.1	20.3	17.7
Elongation, %	205	290	245	166	223
Hardness, A, pts	69	68	71	71	71
Compression Set, Method B, Plied					
70 Hrs @ 200°C	31	23	20	39	19

The FPM compounds were all nominally 70-75 durometer. The tensile strength of the conventional technology FPMs was slightly higher than that of the APA technology FPMs. The elongation of the APA technology compounds was higher and the 100% modulus was lower. These trends in physical properties have been observed previously when comparing conventional and APA technology peroxide cured FPM (2, 3, 4) and were not unexpected. Compression set resistance was tested on plied discs cut from the same slabs and included in Tables 1 and 2. In this test the APA technology polymers show superior performance with lower compression set values compared to the conventional types.

The ten FPM polymers were immersed for 360 hours @ 60°C in sour fuel (PN180), then tested. The results are shown in Figures 1 and 2. The lower fluorine VTR-8675, GLT and GLT-S show the largest tensile and elongation changes and higher volume swell whereas the higher fluorine GF, GF-S, GBL, GBL-S, GBLT-S,

GFLT, and GFLT-S polymers have slightly lower properties changes and lower volume swell.

Figure 1

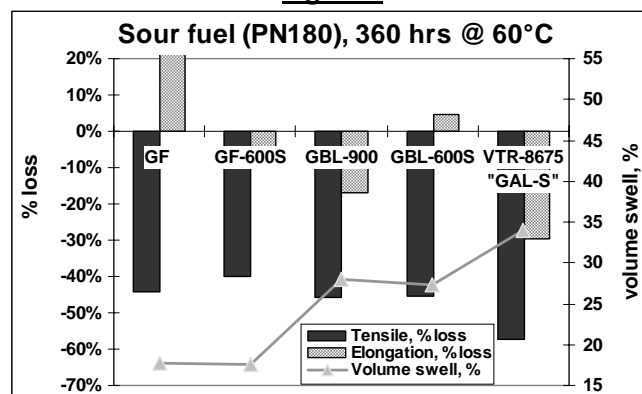
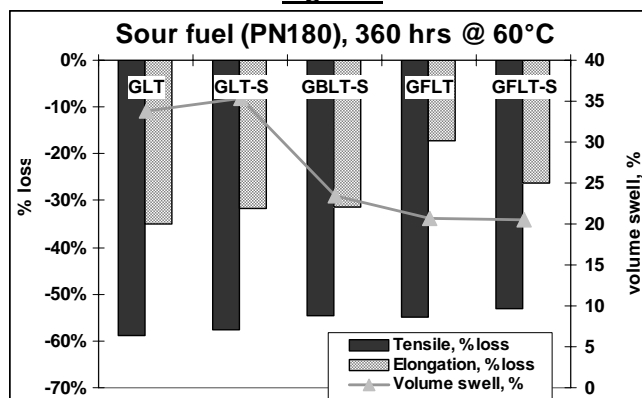


Figure 2



The performance of conventional polymers was similar to that of APA technology polymers with the exception that GF gained elongation after immersion while GF-S lost elongation. The volume swell coupons of all ten FPMs were examined after the sour fuel testing and no sign of cracking, a common failure mode with many fuel resistant elastomers, was seen in any of the samples.

Next, the performance of the ten peroxide cured FPMs was evaluated in CM15A. As previously mentioned, CM-15A is a blend of 85% Fuel C with 15% methanol which has some trace salt water contaminants. Figure 3 shows on a bar chart the volume swell of standard, hexafluoropropylene (HFP) containing GF, GF-S, GBL900, GBL-600S, and VTR-8675 after 168, 672, 2,000, 3,000, 4,000, and 5,000 hours of immersion in the CM15A fuel. The data indicate that the swell properties of conventional and APA technology polymers are quite similar throughout the entire 5,000 hour test period with the exception that GF-S exhibited a somewhat lower volume swell than conventional GF. Likewise Figure 4 below graphically illustrates on a bar chart the volume swell of low temperature, perfluoromethylvinylether (PMVE) containing GLT, GLT-S, GBLT-S, GFLT, and GFLT-S respectively after immersion in the CM15A fuel. The data indicates that the swell properties of conventional and APA technology polymers are similar throughout the entire 5,000 hour test period

Figure 3

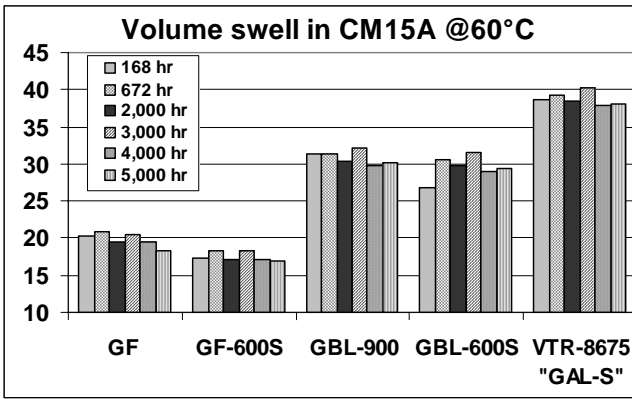
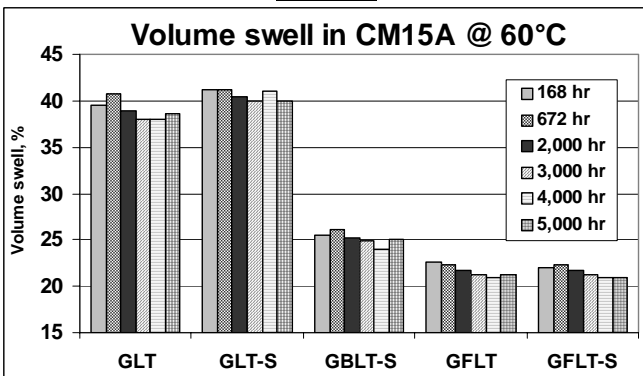


Figure 4



Figures 5 and 6 illustrate the percent change in tensile and elongation exhibited by the standard peroxide types while Figures 7 and 8 show the tensile and elongation loss of the low temperature types. Both sets of polymers have an initial loss in tensile strength early in the test. The rate of change in tensile strength then stabilizes and remains fairly constant throughout the remainder of the 5,000 hour immersion. The only result that is a bit different is for GF which gains elongation after fuel immersion, whereas all the other polymers lose elongation. At the end of the test, the fuel aged tensile samples were placed in an oven, and dried for 4 hours at 100°C. The tensile strength and elongation largely recovered to their original values after this drying procedure. Overall the fuel aged tensile results for both the standard and the low temperature polymers are similar.

Figure 5

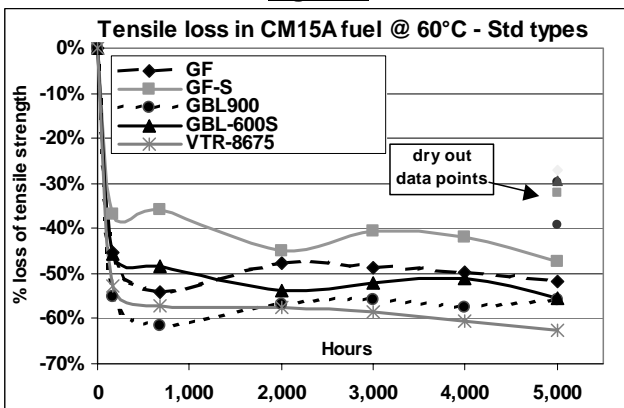


Figure 6

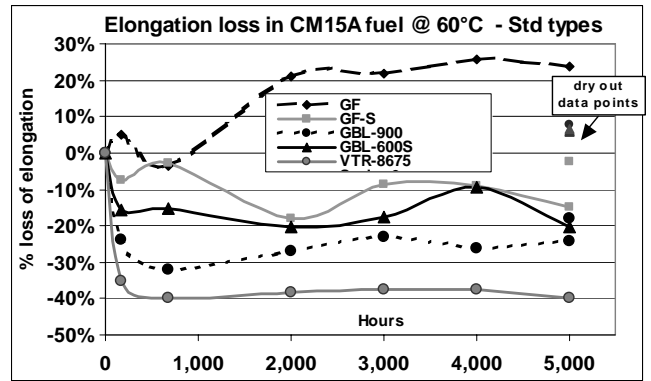


Figure 7

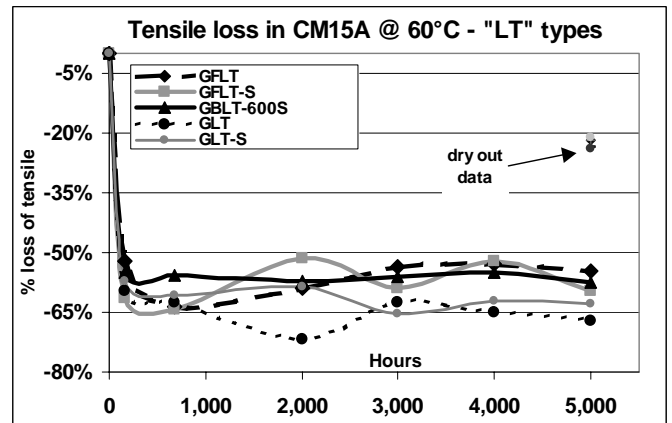
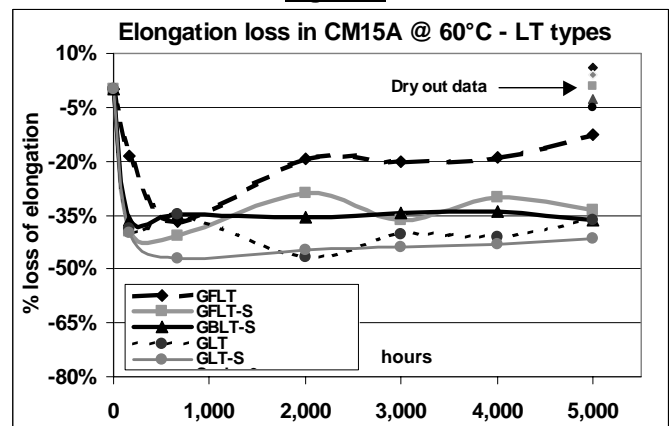


Figure 8

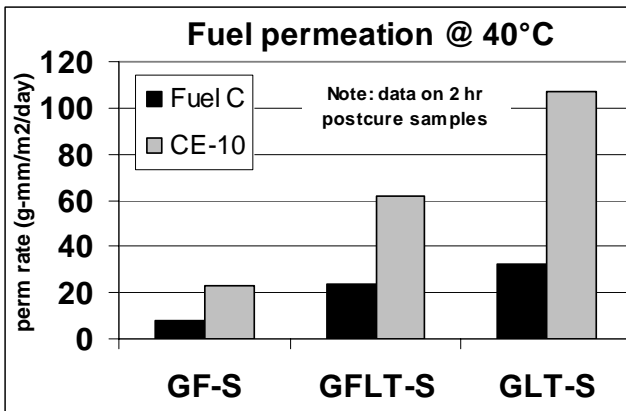


In summary, the data indicate that there is an initial plasticizing effect as the fuel swells these FPM polymers lowering the tensile strength and elongation. However, this effect is substantially reversible when the fuel aged tensile samples are dried for 4 hours @ 100°C with the % loss in tensile strength and elongation diminishing to very low values. The data suggest that the fuel immersion had limited long-term effect on any of the ten FPM polymers tested. It was noted that the 4 hour @ 100°C dry out is not a long enough period to completely drive off all the fuel as the samples still had a positive volume swell after this short dry out routine.

PERMEATION PROPERTIES

The permeation resistance of GF-S, GFLT-S, and GLT-S was evaluated in Thwing Albert cups by ASTM E96 test method. The results of that testing are shown in Figure 9.

Figure 9



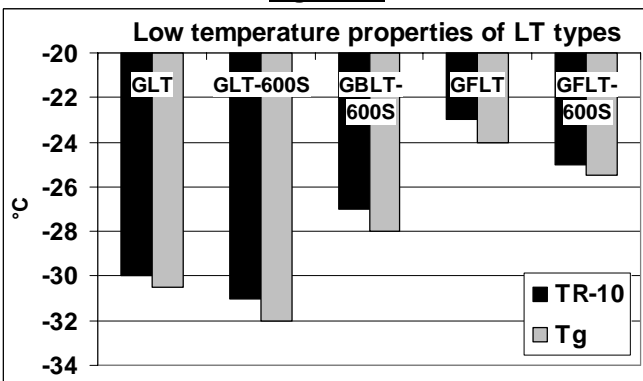
It should be noted that in subsequent permeation testing it was observed that additional postcure time improved the permeation resistance of all of the APA technology polymers. For example, postcuring GF-S for 16 hours @ 232°C brought the CE-10 permeation down from 22 to 16 g-mm/m²/day

LOW TEMPERATURE PROPERTIES

Much of the long-term testing reviewed here involved low temperature FPM types, so it is appropriate to review the low temperature properties of the five LT polymers tested in the long-term fuel agings

Figure 10 shows the Temperature Retraction (TR-10) and Glass Transition temperature (Tg) measured by a DSC for conventional GLT and GFLT and APA technology GLT-S, GBLT-S, and GFLT-S. The general trend observed is that the APA technology GLT-S and GFLT-S show a modest improvement in low temperature properties compared to GLT and GFLT. GBLT-S is well positioned between these products with a TR-10 of -27°C and a Tg of -28°C.

Figure 10



CONCLUSIONS

In conclusion, peroxide cured APA technology types of Viton® fluoroelastomer are now available in both standard and low temperature grades. Extensive long-term testing has been conducted and the results show that:

APA technology standard and low temperature polymers have similar volume swell and physical property retention to their conventional counterparts when aged in

- Sour gasoline (PN180) @ 60°C for 360 hrs
- CM15A fuel @ 60°C for 5,000 hours
- Dry out properties after CM15A fuel immersion

Compared to their conventional technology counterparts, APA technology polymers exhibit

- Better compression set resistance @ 200°C
- Slightly better low temperature TR-10 and Tg
- Good fuel permeation resistance

Results presented here may not be indicative of the performance of other low temperature fluoroelastomers not tested in this program.

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TEST METHODS

Compression Set	ASTM D395, Method B (25% deflection)
Stress/Strain Properties (Tensile, Elongation)	ASTM D412, pulled at 8.5 mm/s
Temperature Retraction (TR-10)	ASTM D1329
Volume Change In Fluids	ASTM D471