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Technical Paper

Long Term Compression Stress Relaxation Evaluation of Elastomers OAT Coolants

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Acknowledgements

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Executive Summary

This study was initiated to screen currently used hydrocarbon rubbers against various Fluoroelastomers (FKM) via 3000 hour Compression Stress Relaxation (CSR) in Organic Acid Technology (OAT) coolant and ethylene glycol at 150°C. FKM is not traditionally used for coolant systems; however, requirements are emerging demanding longer and higher temperature conditions that necessitate changes to both the coolant and materials used in the seals and hoses. Longer and hotter test requirements and changes to coolant compositions could reveal opportunities.

All the polymers tested were more affected by the Prestone® Cor Guard and its incorporated OAT additive package compared to just ethylene glycol. Most of the polymers retained sealing force around 20% in this coolant with the exception of the 3M™ Dyneon™ Fluoroelastomer FPO 3820. This high fluorine, peroxide cured terpolymer fluoroelastomer showed exceptional resistance, retaining 57% sealing force, after long term CSR testing at elevated temperatures. This makes FPO 3820 an ideal candidate for higher temperature coolant applications in ICE, Hybrid and BEV.

Background

Battery Electric vehicles (BEV) will use more coolant than vehicles with traditional Internal Combustion Engines (ICE). The indirect liquid cooling systems for electric vehicles and ICE cooling system are very similar: both circulate coolant throughout a series of metal pipes to transfer heat away from the battery pack or engine. Therefore, coolant requirements for indirect liquid cooling systems will be very similar to traditional ICE coolants.

Cooling e-motors is key to ensure peak operational efficiency. Indirect cooling systems allow the usage of cooling fluid that is optimized for heat transfer only as the fluid circulates in isolated cooling channels. Water/glycol-based fluids are often used in indirect cooling systems as they have excellent thermal conductivity and capacity properties. Effective thermal management of the area between the stator and rotor in an e-motor is critical, as the bearings reach a temperature of 150°C and can hit 170°C for short periods.[1]

Automotive gaskets are mechanical seals used to fill the gap between two components to stop any leakage that may occur during the compression stage. The gaskets are manufactured with a diverse set of materials, including rubber. Cooling system gaskets are effective at fixing or sealing the pipe joints and matched components to ensure that there is no fluid leakage.

Compressive Stress Relaxation (CSR) is a means of estimating the service life of a rubber seal over an extended period of time. This is opposed to measuring the permanent loss of thickness of a compressed rubber specimen as is done in compression set testing. CSR testing directly measures the load force generated by a compressed specimen and how it drops over time. In a standard compressed seal design, a rubber seal is deformed between two parallel surfaces to roughly 75% of its original thickness. Because the material is elastic in nature, the seal pushes back against the mating surfaces, and this contact force prevents fluid flow past the seal, thus achieving a leak-free joint. Over time, the material will slowly relax. The amount of force with which the seal pushes against the mating surfaces will drop, and the seal will become permanently deformed into the compressed shape. In compression set testing, the residual thickness of the specimen is measured, and it is assumed that this residual thickness is valid proxy for the amount of residual load force generated by the compressed seal. In CSR testing, the residual load force is measured directly.[4]

Specifications are often written such that a minimum of 10% of the initial contact load force must remain for a passing result. In practice, there is nothing special about 10%. This is a semi-arbitrary value that ensures a material continues to apply some non-zero load force to the mating surfaces, with some safety factor to ensure that it does so even after all normal test variations are considered.

This study was initiated to screen currently used hydrocarbon rubbers against different 3 various Fluoroelastomers (FKM's) via 3000 hour Compression Stress Relaxation (CSR) in Organic Acid Technology (OAT) coolant and ethylene glycol at 150°C. The study was designed to have two distinct components: CSR in coolant to determine sealing force retention over time at temperature, and compression set in air at 150°C to see the effects of heat over time.

Table 1: Examples of Coolant Compositions

OAT Coolant Compositions			
Properties - Concentrate		**GM GMW3420**	**FORD WSS-M97B57-A1**
Properties	**Test Methods**	**Requirement (Weight %)**	**Requirement (Weight %)**
Ethylene Glycol	ASTM E202	85 Minium	85 Minimum*
Other Glycols	ASTM E202	10 Maximum	NR
Water (Note 1)	ASTM D1123	5 Maximum (including water by hydration)	NR
Ash	ASTM D1119	5 Maximum	NR
Chloride	ASTM D3634 ASTM D5827	25 ppm Maximum	25 ppm Maximum
Silicon (from Silicate)	ASTM D5185	10 ppm Maximum	10 ppm Maximum
Phosphorous	ASTM D5185	10 ppm Maximum	Report Results**
Boron	ASTM D5185	10 ppm Maximum	5 ppm Maximum
Sulfates	ASTM D5827	NR	30 ppm Maximum
Glycolate	ASTM D5827	NR	10 ppm Maximum
Nitrite	ASTM D5827	NR	5 ppm Maximum
Calcium	ASTM D6130	NR	Report Results
Copper	ASTM D6130	NR	5 ppm Maximum
Iron	ASTM D6130	NR	5 ppm Maximum
Lead	ASTM D6130	NR	5 ppm Maximum
Magnesium	ASTM D6130	NR	Report Results
Strontium	ASTM D6130	NR	Report Results

* Virgin monoethylene glycol per ASTM E1177, Type EG-1
** Phosphate

Note 1: Water may be used to aid in the dissolution of the inhibitor salts, but the amount must be controlled so that the finished product conforms to the limits specified for freezing point.

Coolants Evaluated

Ninety nine percent of coolant compositions are commonly based on glycol or polyglycol, but the 1% additive package is what separates good from great engine protection and performance. Additive packages, commonly referred to as Organic Acid Technology (OAT), can be blended with the ethylene glycol base to form a coolant that protects against rust, scale, and corrosion. The additive packages used in ICE vehicles contain corrosion inhibitors to protect the many types of metals found in cooling systems, such as pipes, gaskets, connections, radiator, etc.[2] Examples of OAT coolant compositions can be seen in Table 1.

The useful life of any coolant is largely determined by the makeup of the inhibitor package and the depletion rates of the coolant's inhibitors. During use of a vehicle with ethylene glycol-based coolants, the ethylene glycol and other glycols in the engine coolants can generate acidic degradation products, such as glycolic acid, formic acid, and acetic acid. The generation of acidic glycol degradation products can affect both metals and the elastomeric seals and hoses.

Prestone® Cor-Guard (#AF2100) and ethylene glycol were selected for this study. The Prestone® coolant contains proprietary OAT additives and the ethylene glycol (Sigma Aldrich, Anhydrous, 99.8%, lot# SHBL0617) is representative of the base of most commercially available coolants. Both fluids were evaluated in a diluted form. The Prestone® coolant was obtained prediluted and the ethylene glycol was diluted 50:50 with water. By using these two coolants we will be able to see how the OAT additive package affects the polymers.

Polymers Evaluated

The Hydrogenated Nitrile Rubber (HNBR) was obtained as fully compounded material. The Ethylene Propylene Diene terpolymer (EPDM) was also obtained as compounded material. These hydrocarbon rubbers are both representative grades used in coolant sealing applications and were optimized for performance in coolant applications. 3M™ Dyneon™ FPO 3820, 3M™ Dyneon™ LTFE 6400ZC, 3M™ Dyneon™ FPO 3520, and 3M™ Dyneon™ BRE 7231X were chosen to represent a variety of FKM chemistries varying in monomer composition, percent fluorine level, cure type and low temperature capabilities. The fluoroelastomer samples were compounded in their respective quality control formulas and were not optimized for coolant applications. Table 2 summarizes the polymers used.

Sample Preparation

Each of the FKM polymers were mixed in-house as QC formulations using a standard 2-roll laboratory mill in a 400-gram batch size. The HNBR and EPDM were received fully compounded from their suppliers and were refreshed on the mill before use. Rheology was run using the Monsanto MDR to establish the cure rate of the compounds as well as the final state of cure.

Test slabs were produced using an ASTM 6" × 6" × 0.08" test slab mold and triplicate 0.139 O-rings and 13 mm CSR buttons were also produced. The polymers were all press and post cured as appropriate for the polymer type. Tensile data was gathered using an MTS Tensometer employing ASTM Die D dumbbells, in triplicate, and the results averaged for reporting. Hardness was

Table 2: Polymer Summary

	HNBR	EPDM	3M™ Dyneon FPO 3520	3M™ Dyneon FPO 3820	3M™ Dyneon LTFE 6400ZC	3M™ Dyneon BRE 7231
Polymer Type	Hydrocarbon	Hydrocarbon	Low Fluorine	High Fluorine	Low Temperature	Base Resistant
Fluorine Content	0%	0%	66%	70.1%	67.1 %	60%
Cure Type	Peroxide	Peroxide	Peroxide	Peroxide	Peroxide	Bisphenol
Mooney Viscosity, MU	78-92	NA	25	24	100	34
Glass Transition, T_g	-27°C	NA	-19°C	-6°C	-40°C	-9°C
Upper Use Temperature	165°C	120°C	220°C	220°C	220°C	175°C
Formula	Coolant Grade	Coolant Grade	QC	QC	QC	QC

measured on the Type A scale. An overview of equipment and ASTM procedures can be found in Table 3. The primary focus was on good sealing force retention in coolant as determined by CSR. Formulations and detailed rheological and physical property data, including specific cure times and temperatures, for all samples can be found in Appendix 1.

Results and Discussion

Coolant Grade HNBR

Initially, the HNBR does not appear affected much by the OAT additives. After 504 hours, it becomes noticeable that the HNBR is more resistant to the Prestone® Cor-Guard coolant than the ethylene glycol base fluid. However, upon removal from the jigs after 3024 hours, the Prestone® samples showed severe delamination and some embrittlement as can be seen in Figure 1. The final CSR data point of the Prestone® sample is suspect and may not be accurate due to sample degradation. The HNBR is likely being affected by the 150°C temperatures which is near the recommended upper use temperature of 160°C. That, in combination with the attack from the OAT additive package and its degradation components, could be a possible cause of the failure.

Table 3: Test Methods

Test	Instrument	ASTM Method
Rheology	Monsanto MDR 2000	D6204
Physical Properties	MTS Transometer	D412
Durometer/Hardness	Shore Convoloader	D2240
Compressive Stress Relaxation	ASD CSR Jigs and Paar Bombs	D6147
Compression Set	O-rings	D395-18

Graph 1: HNBR CSR Comparison of Prestone® to Ethylene Glycol

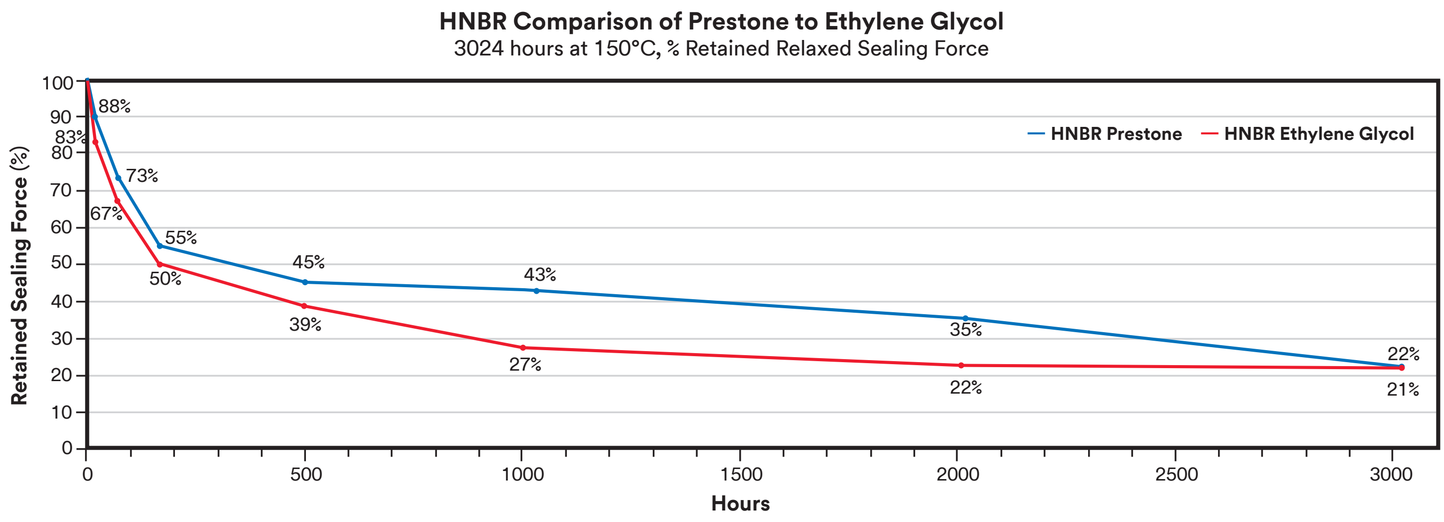
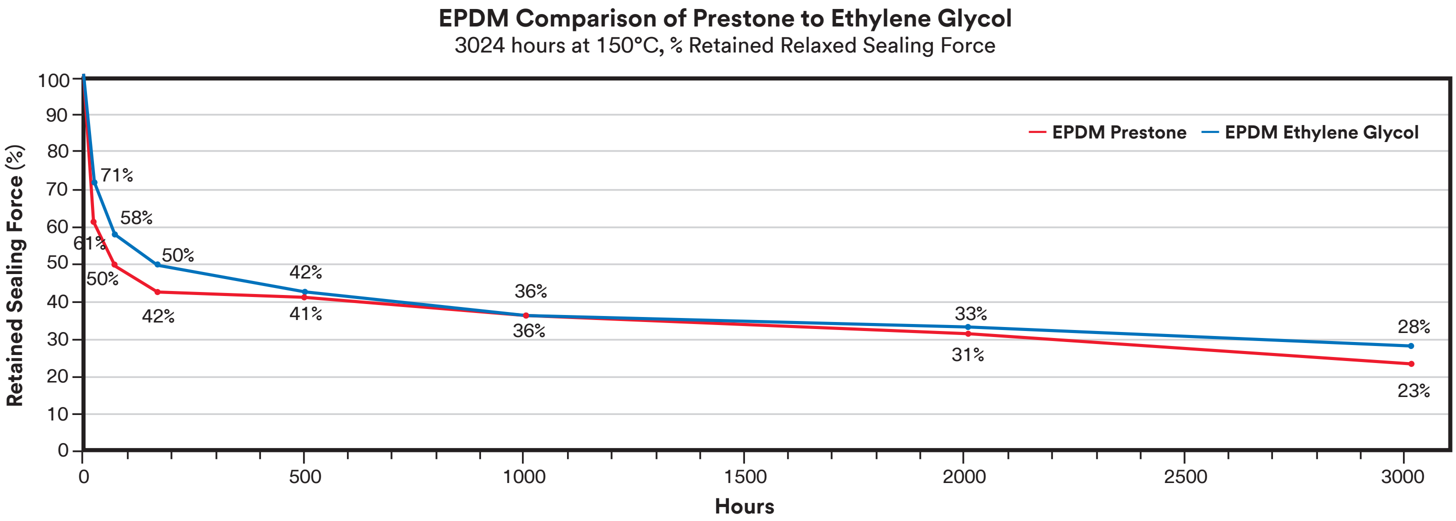


Figure 1: HNBR CSR buttons after 3024 hours exposure in Prestone® Coolant

Graph 2: EPDM CSR Comparison of Prestone® to Ethylene Glycol



Coolant Grade EPDM

The initial data points for the EPDM shows, after 3024 hours of testing, a 23% retained sealing force. After completion of the 3024 hours of testing the buttons looked unblemished and were still supple.

3M™ Dyneon™ BRE 7231X

The BRE 7231X was the most affected of all the polymers tested. It showed the largest initial drop in sealing force overall due to the heat alone, which is typical of TFE/P comprising elastomers. Both BRE 7231X samples were removed from testing after 504 hours and 1008 hours due to the inability to accurately measure the CSR breakpoints in the Testworks software. Upon removal from the CSR jigs there were no signs of visible degradation. The BRE 7231X is bisphenol cured, requiring 9 phr of metal oxide in order to activate cure system. This cure mechanism creates sites of unsaturation which are vulnerable to hydrolysis and nucleophilic attack from the water and acidic degradation components form during coolant aging.

3M™ Dyneon™ FPO 3520

The FPO 3520 showed similar results to BRE in OAT additives within the first 504 hours of testing, and most of the sealing force has been lost at 2016 hours. The rise in sealing force in the OAT coolant at 3024 hours is suspect because the samples showed extreme extrusion, delamination and embrittlement when removed from the CSR jig which can be seen in Figure 2.

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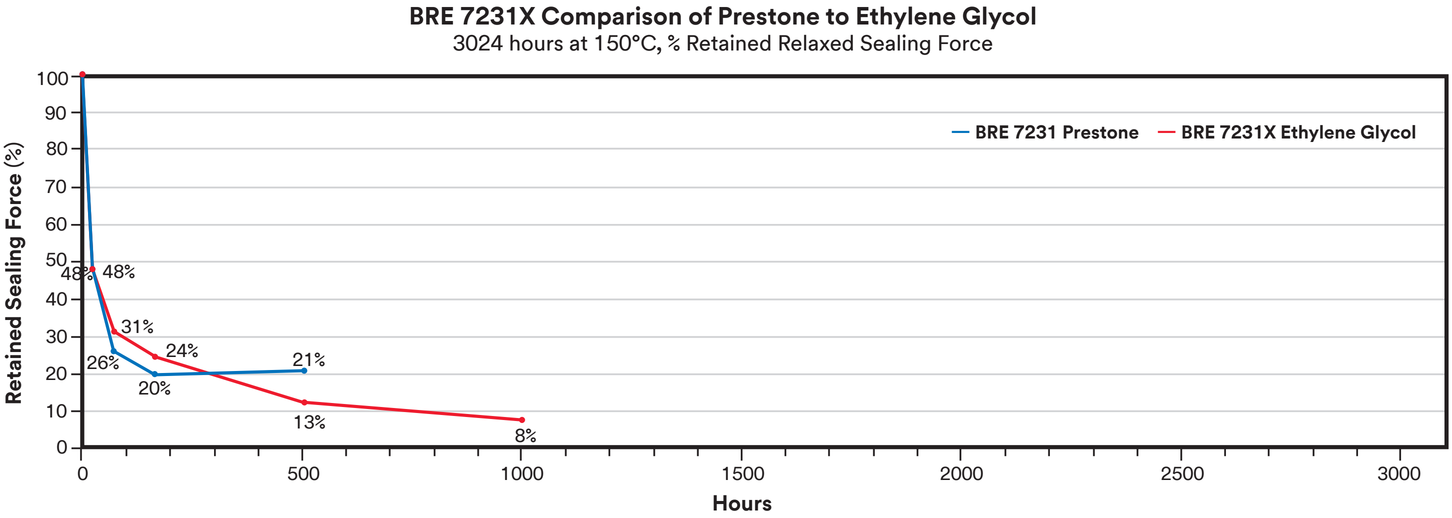
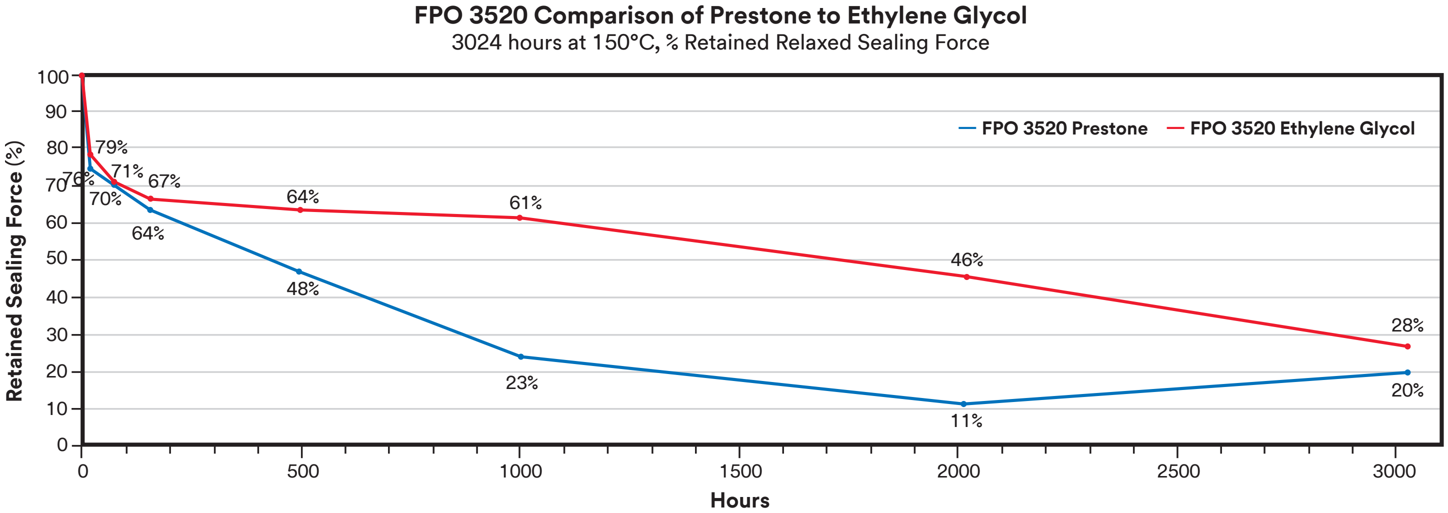
3M™ Dyneon™ FLTFE 6400ZC

LTFE 6400 looks better overall in the ethylene glycol. The LTFE 6400 still retains ~ 20% RSF in the OAT coolant and may be a candidate for applications where low temperature sealing properties are needed.

Graph 3: 3M™ Dyneon™ BRE 7231X CSR Comparison of Prestone® to Ethylene Glycol



Graph 4: 3M™ Dyneon™ FPO 3520 CSR Comparison of Prestone® to Ethylene Glycol



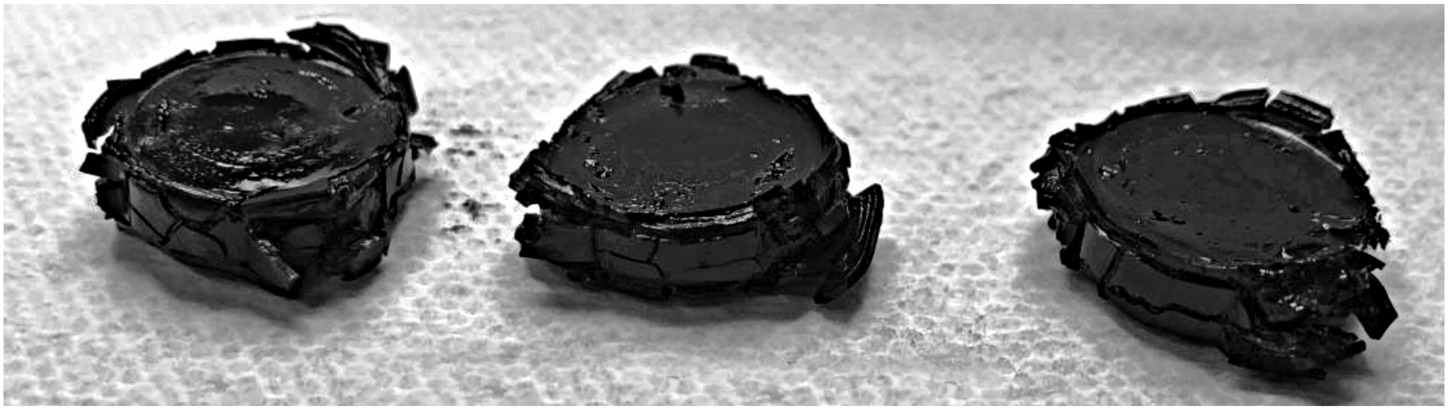
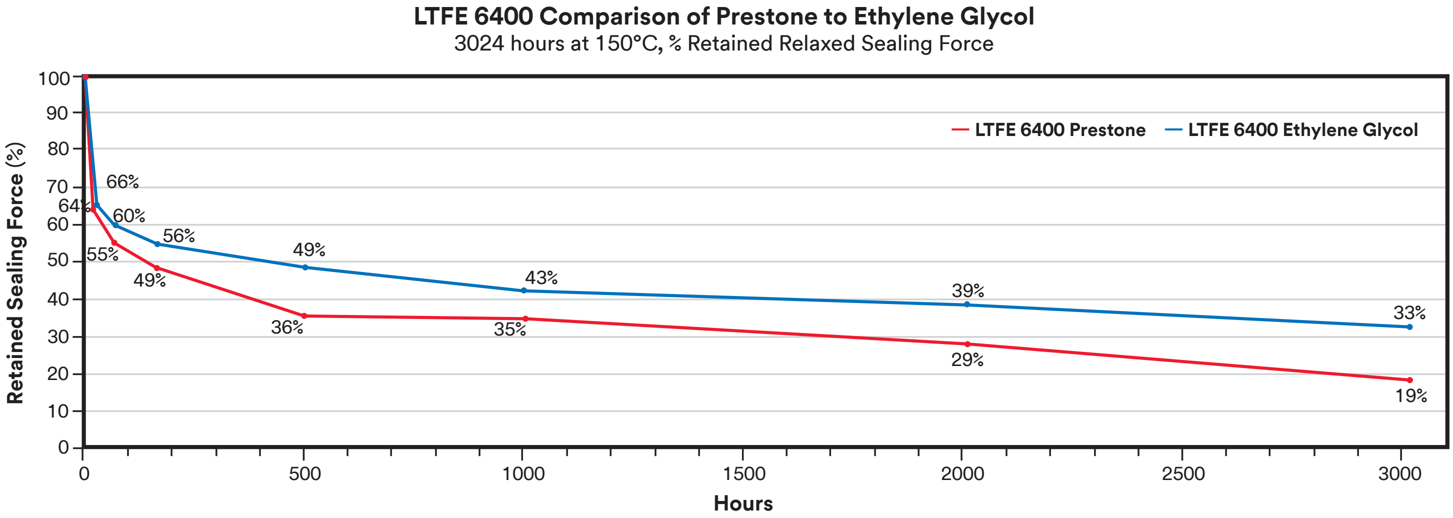
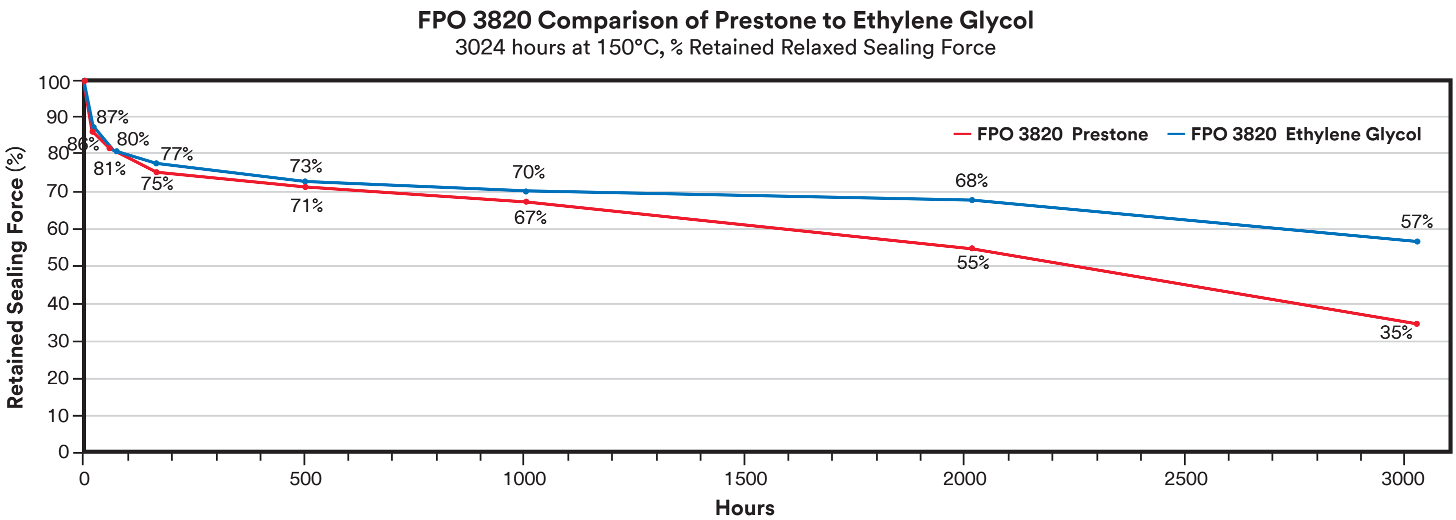


Figure 2: Dyneon™ FPO 3520 CSR buttons after 3024 hours in Prestone® Coolant

Graph 5: 3M™ Dyneon™ LTFE 6400ZC CSR Comparison of Prestone® to Ethylene Glycol



Graph 6: 3M™ Dyneon™ FPO 3820 CSR Comparison of Prestone® to Ethylene Glycol



3M™ Dyneon™ FPO 3820

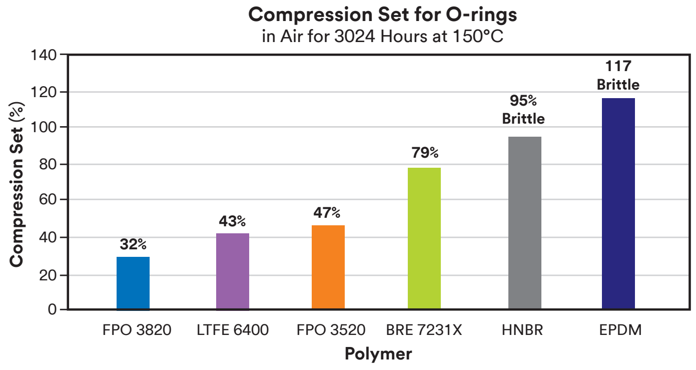
FPO 3820 was the best of all the polymers tested in this study, retaining the most sealing force in both coolants. Little difference is seen in either coolant out to 1008 hours. At 2016 hours the OAT additives appear to have an effect on the FPO 3820 but to a much lesser extent than the other samples.

Compression Set

Compression set testing measures the ability of rubber to return to its original thickness after prolonged compressive stresses at a given temperature and deflection. As a rubber material is compressed over time, it loses its ability to return to its original thickness. This loss of resiliency (memory) may reduce the capability of an elastomeric gasket or seal to perform over a long period of time. The resulting set that a seal or gasket takes over time could potentially cause leakage. Compression set results for a material are expressed as a percentage. The lower the percentage, the better the material resists permanent deformation under a given deflection and temperature range.

Compression set for this study was run on 0.139 inch o-rings, in air, for 3024 hours at 150°C to see only the effects heat over time. As can be seen in Figure 3, the HNBR and EPDM are quite affected by the heat without any coolant present. These two samples were also found to be brittle after testing. As expected of FKM's, the higher fluorine content polymers showed the best overall compression set over time with the 3M™ Dyneon™ FPO 3820 having the best compression set result at 32% making it the most suitable for sealing applications.

Figure 3: Compression Set, O-rings, 3024 Hours in Air at 150°C



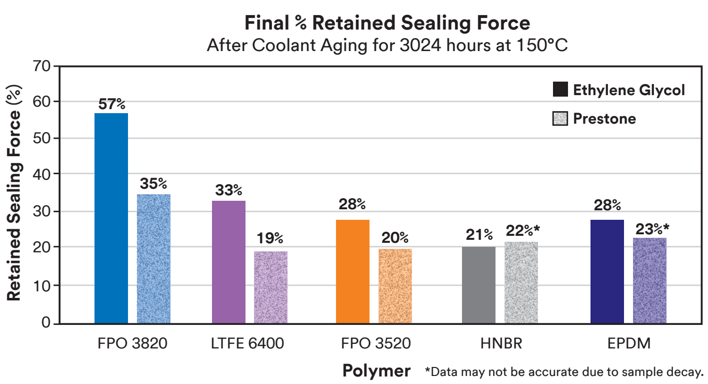
Conclusions

In conclusion, Compressive Stress Relaxation is a powerful tool for comparing the performance of two or more materials in a particular application, provided it is done on an apples-to-apples basis. This test measures the sealing force exerted by a seal or O-ring under compression between two plates, and more closely resembles end use applications than traditional Compression Set testing.

It provides definitive information for the prediction of the service life of materials by measuring the sealing force decay of a sample as a function of time, temperature, and environment. With this information, Arrhenius plots can be used to provide service life predictions, where a minimum "load to seal" is needed for a particular design. Material designers can also use this as a tool for continuous improvement of compound designs.

In summary, all of the polymers tested in this study were more affected by the Prestone® Cor Guard and its incorporated OAT additive package. All of the polymers retained sealing force around 20% in this OAT coolant with the exception of the 3M™ Dyneon™ FPO 3820. This commercially available high fluorine, peroxide cured terpolymer FKM showed exceptional resistance retaining 57% sealing force in ethylene glycol after long term CSR testing at elevated temperatures. This makes the FPO 3820 an ideal candidate for higher temperature coolant applications in both ICE and BEV applications.

Figure 4: Final Percent Retained Sealing Force Coolant Comparison



Coolant

The useful life of any coolant is largely determined by the makeup of the inhibitor package and the depletion rates of the coolant's inhibitors. During use of a vehicle with ethylene glycol-based coolants, the ethylene glycol and other glycols in the engine coolants can generate acidic degradation products, such as glycolic acid, formic acid, and acetic acid. The generation of acidic glycol degradation products will gradually reduce the pH of the engine coolant and can eventually lead to a substantial increase of metal corrosion rates in the engine cooling system and attack of elastomeric seals and hoses.

To confirm this the pH values of each solution were measured and are listed below in Table 6. pH measurements were made directly on coolant samples using a Metrohm gel pH electrode (P/N 6.0221.100), calibrated against solutions buffered at pH 4, 7, and 9.

Notably, the unaged samples give weakly basic pH values, but upon aging become significantly acidic, particularly in the case of the ethylene glycol/water mixtures. The fact that the pH values decrease with aging does not correlate with the increase in glycolate, formate, and acetate that we observe for these samples, and likely is indicative of the fact that there are other acidic species that we are not observing in this chromatogram. It's possible that the increase in the unknown peak at 12 minutes accounts for this increase in acidity, but we cannot confirm this hypothesis without knowing more about what the species is that is appearing at 12 min.

Table 6: Test Methods

Sample	Identification	pH
1	Unaged Ethylene Glycol: Water 50:50 (Control)	7.52
2	Unaged Prestone® Cor Guard Coolant Prediluted 50:50 with Water (Control)	8.35
3	Aged Prestone® Cor Guard #1	6.81
4	Aged Prestone® Cor Guard #2	6.56
5	Aged Ethylene Glycol:Water 50:50 #1	4.64
6	Aged Ethylene Glycol:Water 50:50 #2	4.46

Conclusions from Analytical Results

Through analytical testing we have confirmed that the aged samples are more acidic than the unaged samples, especially the aged ethylene glycol. This change overall pH affects the elastomer seals the effect confirmed by the results seen in the CSR aging at elevated temperatures.

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4. Parker Hannifin, http://blog.parker.com/how-much-do-you-know-about-compressive-stress-relaxation-csr-part-1, (February 2020)

Appendix 1: Polymer Formulations and Physical Properties

Polymer Type	HNBR	EPDM	3M™ Dyneon™ FPO 3820	3M™ Dyneon™ FPO 3820	3M™ Dyneon™ LTFE 6400	3M™ Dyneon™ BRE 7231X
Formulation, phr						
3M™ Dyneon™ FPO 3520	Coolant Grade Used as Received		100			
3M™ Dyneon™ FPO 3820				100		
3M™ Dyneon™ LTFE 6400ZC					100	
3M™ Dyneon™ BRE 7231X						100
N990 MT Carbon Black			30	30	50	30
Elastomag® 170 (MgO)						9
ZnO			3		5	
TAIC, 72%DLC			4	1.5	1.8	
Varox® DBPH 50			4	2.5	2.5	
Struktol® WS280						2
Formula Weight			141	134	159.3	141
MDR, 0.5" arc, time/temperature	40'/170°C	30'/180°C	12'/177°C	12'/177°C	12'/177°C	12'/177°C
Minimum Torque, ML, in-lb	0.76	1.90	0.51	0.64	3.31	1.04
TS2, minutes	0.52	0.60	0.43	0.49	0.07	2.95
T50, minutes	2.19	1.41	0.65	0.76	0.98	4.02
T90, minutes	9.01	4.62	2.19	1.49	3.11	7.84
Maximum Torque, MH, in-lb	35.63	14.95	17.5	24.91	12.46	11.45
Tan Δ ML	1.079	1.079	1.235	1.047	0.520	0.712
Tan Δ MH	0.017	0.106	0.086	0.054	0.140	0.101
Press Cured, time/temperature	40'/170°C	30'/180°C	10'/177°C	10'/177°C	10'/177°C	10'/177°C
Post Cured, time/temperature	No Post Cure	No Post Cure	16h/232°C	4h/232°C	16h/232°C	16h/232°C
Tensile, psi	1848	1927	3555	3727	1806	2122
Elongation, %	52	290	131	181	141	242
100 % Modulus, psi	-	848	2751	2340	1291	644
Hardness, Type A	71	63	66	67	64	70
Press Cured, time/temperature						
3024 hours at 150°C, in Air, % Set	95	117	47	32	43	79
	Brittle	Brittle				

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