Elastomers for Steam Service

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ABSTRACT

Steam injection for enhanced oil recovery is a mature technique that will likely increase to satisfy future demand for crude oil. Graphite impregnated yarns have been successfully used to pack well-heads and injectors in such projects. Nevertheless, engineers still inquire on the use of high-temperature elastomers for ease of assembly, replacement, and the promise of less compression-set than impregnated cords.

In 1979, Brookhaven National Laboratory was commissioned by the Department of Energy “to determine the best elastomers for use in medium temperature geothermal wells – with emphasis on binary plants in which isobutane is the working fluid.” The final stage of testing was conducted in brine, isobutane, and ASTM No. 1 oil in temperatures as high as 265˚C (510˚F). The tests, involving static o-rings with a 20.7 MPa (3000 psi) differential across the seal, lasted 46 hours. “The major conclusion was that the EPDM O-rings (L’Garde Y267…) are superior to the others tested in each of the three fluids.”

A few years later, a paper titled “A proven Elastomer Compound for Extremely Hostile Geothermal and Oilfield Environments” was present at the IADC/SPE 1983 Drilling Conference (New Orleans, LA). The presentation concluded that “…Y267 EPDM is the superior elastomer for high temperature aqueous reducing environments. There is one environment where Y267 EPDM is not a good choice, where there is free access to air or oxygen at high temperatures.” This material has come to be known as a L’Garde EPDM.

In the twenty-plus years since this noteworthy compound introduction, additional developments have taken place in FEPM and FFKM polymer compounds that warrant

consideration for use in steam. The objective of this paper is to examine some relatively recent elastomers as well as the “famed” L’Garde EPDM.

INTRODUCTION

Water possesses unique properties. Relevant to this study are some thermal properties of water. The boiling point, or the conditions at which it can exist as a liquid and vapor, is 100˚C when at 1 atm. Elementary data, but it gets more interesting. At 100˚C, the theoretical internal energy of the saturated liquid is 418.9 kJ/kg while the theoretical internal energy of the saturated vapor is 2506.5 kJ/kg.[1] Thus, there is roughly six times more energy in a saturated vapor (steam) than there is in the saturated liquid! As the pressure of the system increases, steam tables indicate a substantial increase in internal energy of the saturated liquid and only marginal increases in the same for the saturated vapor. For instance, the vapor pressure of water at 100˚C is 0.1 MPa. However, for a system at 5.0 MPa pressure, the internal energy values of the saturated liquid and vapor are 1147.8 kJ/kg and 2597.1 kJ/kg respectively. Hence, boiler operators deliver more energy with steam than with hot water. For purposes of this study, aging the test specimens in the vapor phase was of considerable importance.

Water, also known as the universal solvent, has the ability to act as both an acid and a base. Although a very weak electrolyte on its own, water nevertheless undergoes ionic dissociation to a small extent by means of autoprotolysis[2]:

Eq. (1) $2H_2O\ (l) \leftrightarrow H_3O^+\ (aq) + OH^-\ (aq)$

Many so-called high temperature elastomers are susceptible to degradation in the presence of a base. Temperature merely accelerates the inevitable reaction. The mechanism of dehydrohalogenation of the vinylidene fluoride monomer within an FKM composition is well documented.

Hertz III, in his paper titled “Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers Evaluated using Strain Energy Density” observed that FKM Type 1 and Type 2 polymers failed within 168 hours in deionized water at temperatures of 250˚C (482˚F) and higher. In this same study, Hertz III also concluded “[t]he BPAF cure system is characteristically unstable in deionized water at temperatures of 225˚C and above.”[3] Thus, FKM class polymers and BPAF cured polymers have been excluded from the study.

The ASTM D 2000[4] defines a framework for elastomers to be classified for automotive applications. Heat resistance, under this specification, is determined by change in (1) tensile strength (i.e. +/- 30% max), (2) change in elongation (i.e. -50% max), and (3) change in hardness (i.e. +/- 15 points max) at a given temperature after 70 hours of aging. These three attributes can be calculated by even the most uninitiated rubber laboratory. These attributes taken individually, do not reflect the mechanical properties that determine whether an elastomer will function properly subsequent to thermal aging. Auda and Hazelton instead adopted Fractional Strain Energy at Break (Eq.1), simultaneously taking into account tensile and elongation, as a means of examining the thermal stability of EPDM compositions[5].

Eq. (2) $$\text{Fractional Strain Energy at Break} = (\text{TAB x EAB})_{\text{aged}} / (\text{TAB x EAB})_{\text{original}}$$

where TAB is tensile at break and EAB is elongation at break. The author has taken liberty to apply this same framework in examining the aged samples.

Objective

The primary objective was to provide data on the effects of high temperature saturated steam on elastomers recommended for high temperature service. It should be noted that these materials are being aged at temperatures exceeding their recommended limits. One exception is the PFR 95 HT which is designed to handle service at 300˚C (572˚F).

Scope

Elastomers:

Four proprietary compounds formulated, using commercially available elastomers, were selected. All four compounds utilize a peroxide induced cure. Only polymers that might be recommended for use in steam were examined. The compound attributes, or baseline data, as compiled from D412 dumbbells, is reported in Table 1.

Base Polymer	Designation	D412Stress @ Break	D412 Elongation @ Break	Shore-A Durometer
Aflas® 100H	TFE/P	23.1 MPa (3349)	49%	92
EP terpolymer	EP (Y-267)	21.5 MPa (3124)	138%	84
Viton® “Extreme”	TFE/E/PMVE	20.1 MPa (2919)	157%	84
PFR 95HT	FFKM	17.2 MPa (2498)	99%	87

Table 1.

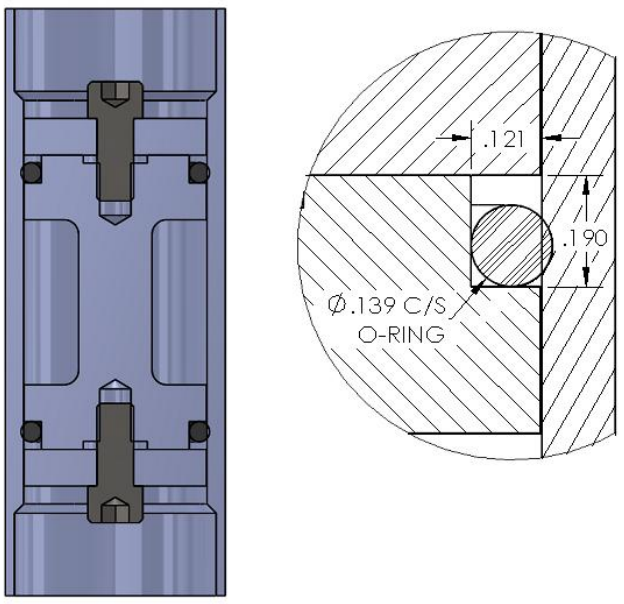
Environment:

The thermal stability of the elastomers in Table 1 was examined in saturated steam. The materials were aged at temperatures known to represent or exceed the outer thermal limit of their respective ASTM category, with the exception of the FFKM. Testing temperatures were 250°C (482°F) and 275°C (527°F).

EXPERIMENTAL

Method

AS568-214 o-rings of the subject materials were mounted on mandrels with accommodating glands and were then subsequently installed in a bore (see fig 1) to act as static rod seals. These fixtures were then placed in gray iron vessels with carbon steel caps atop a positioning device whose function was to maintain the fixture within the vapor phase (see fig 2). The test vessels were partially filled with de-ionized water.



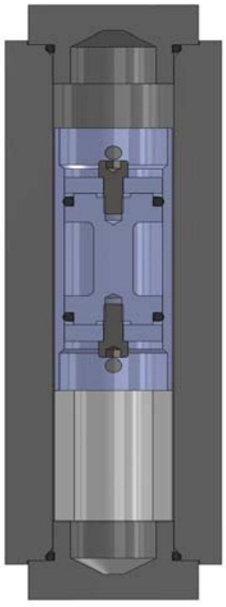


Fig. 1 – O-ring Mandrel, compression sleeve, and gland; Fig 2 – Complete assembly.

ASTM dumbbells were suspended, in the vapor phase, of similar gray iron test vessels that were partially filled with de-ionized water.

Test Parameters

Variables such as sample size, test conditions, temperatures, aging period and specimens tested are presented in Table 2.

Aging period	• 168 hours • 336 hours
Test Specimen	• ASTM D412 dumbells, n = 4[6] • AS568-214 O-rings, n = 4
Test media	• Deionized Ultra Filtered water
Test Temperature	• 250˚C • 275˚C

Table 2: Experiment test matrix

Measurements

The experiment was designed to age AS568-214 o-rings in a saturated steam subject to the mechanical demands that seals within a steam injector would experience. Using o-rings would allow relevant visual examination, compression set measurement, and strain energy measurements. The aging of ASTM dumbbells would facilitate DMRT analysis for changes in viscoelastic response under shear and the compilation of conventional stress-strain data under tension.

DMRT / Shear Modulus

At its simplest level, an elastomer ages individually or through some combination of three basic mechanisms: chain scission, crosslink scission, and/or crosslink addition. Kuhn developed an equation (Eq.3) for shear modulus that describes the effect of these mechanisms.[7]

Eq. (3) $G = NkT = \rho RT / M_c$

Under this equation, shear modulus (G) is directly proportional to the number of polymer chains per unit volume (N) at a given temperature (T - Kelvin), where (k) equals Boltzmann’s constant. Similarly, shear modulus is proportional to the material’s density (ρ) at a given temperature and inversely proportional to the molecular weight between crosslinks (M_c) where (R) is the universal gas constant.

DMRT Thermal Sweeps were run from 0C to 200C at a frequency of 0.1Hz, at a 0.1% strain. The temperature change was run at 5C/min.

Strain Energy:

Fractional strain energy (Eq.2) describes an aged vulcanizate in terms of both its integrity (retained tensile) and its extensibility (retained elongation). Use of fractional (or retained) strain energy has been shown to be a reliable means of characterizing and projecting aging behavior of EP rubbers as previously demonstrated by Auda and Hazleton.

We have defined fractional strain energy (Eq.4) in the same manner as Auda and Hazelton. We calculated the fractional strain energy of the AS568-214 o-rings as the ratio of retained strain energy after aging to the strain energy of the material prior to aging.

Eq. (4)

$$TE_f = (\text{Retained Tensile x Retained Elongation})_{aged} / (\text{Tensile x Elongation})_{original}$$

Tensile Stress-Strain (at break), M25, and Compression Set

Traditional ASTM stress-strain attributes of dumbbells include tensile at break (“TAB”) and elongation at break (“EAB”). However, it is our opinion that the energy potential of an elastomer is better evaluated at low strains, staying within the hyperelastic (linear) region of the stress-strain curve. On a basic level, the modulus of a formulated elastomer will be a function of the elastomer’s molecular constitution, the cross-link density, and the elastomer’s interaction with reinforcing filler. Reinforcing filler, such as carbon black, will affect an elastomer’s modulus as a function of the filler’s particle size, surface energy, and loading. Generally speaking, the smaller the particle size, holding all else constant (including particle structure), the higher the modulus. Hertz, in his chapter on Sealing Technology[8], observed this logical increase in modulus as particle size decreased when evaluated using strain energy calculated at twenty percent strain. This relationship, however, failed when stress was examined at strains in excess of 100% presumably due to rupture at the polymer-filler interface. At high strain, polymer-filler interactions become increasingly complex and unpredictable as reflected in the broad range of stress values. For instance, the standard deviation of stress data points is increasingly larger as strain increases. Thus, chemically and thermally induced changes to the vulcanizate’s structure will be best reflected by changes in stress at 25% strain rather than higher levels of strain.

Compression set (“radial compression set”) calculations were measured from the AS568-214 o-rings.

FTIR

FTIR analysis was conducted to examine alterations to organic species associated with the cure systems.

Caveats

Contrary to normal protocol, proprietary compounds were examined. All the compounds utilize a peroxide cure. The TFE/P and the TFE/E/PMVE utilize a TAIC co-agent. The compounds also utilize carbon black reinforcement but of different grades (particle size and structure) and loadings. Nevertheless, the author contends that gross differences in respective performance will largely be a function of the polymer. Thus, the data reported reflects and emphasizes the respective changes for individual materials rather than their absolute values for a more relative evaluation.

RESULTS AND DISCUSSION

Absent a mechanical apparatus whose functional operation determines a seals success or failure, the market tends to embrace arbitrary thresholds defining the same. For instance, ASTM D2000 prescribes that a “type” designation, for service temperature, is determined by “changes in tensile strength of not more than +/- 30%, elongation of not more than – 50%, and hardness of not more than +/- 15 points after heat aging for 70 hours at an appropriate temperature.”[9] Obviously, any material not conforming to these limits at a specific temperature cannot be identified as the corresponding “type”. That is, the material has effectively failed under the logic of D2000. Accepting ASTM’s methodology in this regard, we can establish an upper and lower fractional strain energy value that considers such change in the area defined under a stress-strain curve.

Figure 3 – Hypothetical Stress Strain Curves

To calculate a failure point, we simplified the area under the stress strain curve as a rectangle with two transverse corners defined at the origin and at the point of breakage as in Figure 1. This area can be subsequently defined as percent strain at break multiplied by the stress at break. First we assumed an un-aged material having a stress at break of 10MPa (1,450 psi) and an elongation at break of 100%. The area under the stress-strain curve would be 10MPa (1,450 psi). Next we assumed that stress and elongation declined to the extent permissible in ASTM D2000 for establishing “type”. Specifically, stress at break declined 30 percent to 7MPa (1015 psi) and elongation declined 50 percent to 50% at break. The area is now 3.5MPa (507.5 psi). The fractional value is 3.5MPa over 10MPa or 0.35. Thus we assigned .35 as our lower fractional strain energy failure point. Using the same logic, we derived 1.3 as our upper fractional strain energy failure point.

Fractional (Retained) Strain Energy of AS568-214 o-rings

Tables 3 and 4 contain the tabulated results of fractional strain energy of AS568-214 o-rings after aging in 250˚C and 275˚C saturated steam respectively. Changes in retained strain energy that would otherwise “fail” ASTM D2000 criteria as discussed *supra* are marked with “** **”.

AS568-214 o-rings : % Retained Strain Energy after 250°C soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
Un-aged	100%	100%	100%	100%
168 hours	64%	65%	86%	** 30% **
336 hours	45%	94%	** 27% **	39%

Table 3

AS568-214 o-rings : % Retained Energy after 275°C soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
Un-aged	100%	100%	100%	100%
168 hours	61%	104%	** 5% **	51%
336 hours	50%	62%	** 6% **	46%

Table 4

Compression Set of AS568-214 o-rings

Compression set (“radial compression set”) calculations were measured from the AS568-214 o-rings. The 3.53 mm (.139 inch) cross-section o-rings were deflected .457mm (.018 inches), or 13%. The most remarkable resistance to compression set was noted in the Y-267 type EP.

AS568-214 o-rings : Percent Compression Set after soak in 250C Saturated Steam				
Aging Time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168 hours	90.5%	37.3%	79.3%	51.4%
336 hours	88.0%	38.1%	69.2%	73.8%

Table 5

AS568-214 o-rings : Compression Set after soak in 275C Saturated Steam				
Aging Time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168 hours	104.9%	66.5%	92.0%	88.1%
336 hours	115.6%	67.4%	106.1%	118.5%

Table 6

Stress-Strain Analysis and Durometer using ASTM D412 dumbbells

Stress-strain analysis was compiled to ASTM D412 standards using a sample size of 4. Change in “tensile at break” and change in “elongation at break” were compiled for purposes of fractional strain energy computation. Change in modulus at 25% strain (“M25”) is reported since the strain is within normal design limits. Changes in value of tensile at break, elongation, and durometer that would otherwise “fail” ASTM D2000 criteria for temperature type are marked with “** **”.

Missing values were not available at the time of printing.

Tensile (at break) Change after 250°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	-27%	-28%	** -83% **	
336	-25%	-19%	** -89% **	

Table 7

Elongation (at break) Change after 250°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	39%	-28%	** -52% **	
336	61%	-19%	** -69% **	

Table 8

M25 Change after 250°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	-36%	7%	-62%	
336	-40%	3%	-59%	

Table 9

Fractional Strain Energy after 250°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	101%	51%	8%	
336	121%	66%	4%	

Table 10

Shore-A Durometer change after 250°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	0	0	** -16 **	
336	-1	-1	** -17 **	

Table 11

Tensile Change after 275°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	** -32% **	** -42% **	** -87% **	** -72% **
336	** -43% **	** -62% **	** -83% **	** -84% **

Table 12

Elongation Change after 275°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	120%	-13%	** -69% **	31%
336	141%	-40%	** -71% **	38%

Table 13

M25 Change after 275°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	-48%	-22%	-51%	-59%
336	-52%	-24%	-31%	-73%

Table 14

Fractional Strain Energy after 275°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	** 151% **	51%	** 4% **	37%
336	** 138% **	23%	** 5% **	22%

Table 15

Shore-A Durometer change after 275°C Saturated Steam Soak				
Aging time	(TFE/P)	EP (Y-267)	(E/TFE/PMVE)	FFKM
168	-1	-4	** -19 **	-9
336	-6	-5	-9	-12

Table 16

FTIR Analysis

FTIR spectroscopy scans were taken of the four test materials. Un-aged spectra are shown in blue. Spectra associated with material aged in steam at 250˚C are shown in red. Spectra associated with material aged in 275˚C steam are shown in green.

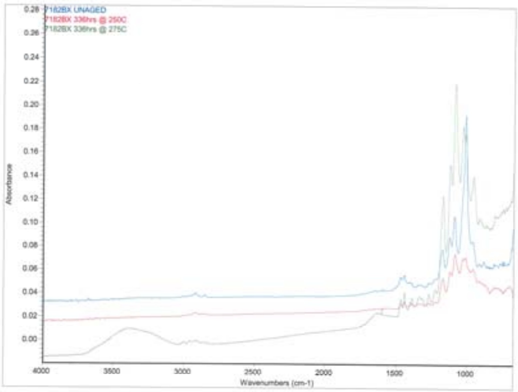


Figure 4 – TFE/P FTIR

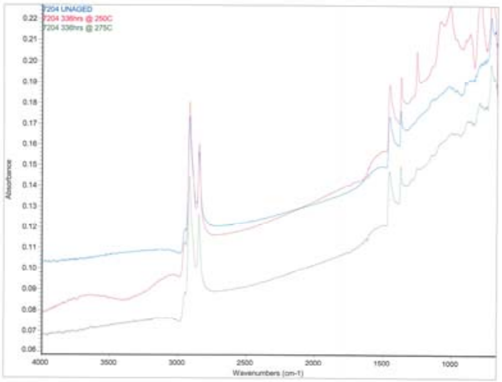


Figure 5 – Y-267 EP FTIR

Changes in the TFE/P spectra (fig.4) at 250˚C are unremarkable. However at 275˚C the presence of an alcohol (3300 cm^{-1}) and carboxylic acid (1600 cm^{-1}) are noted. We would attribute these groups with water absorption and degradation of the co-agent, respectively. Similar absorbance is noted in the Y-267 EPDM spectra (fig 5).

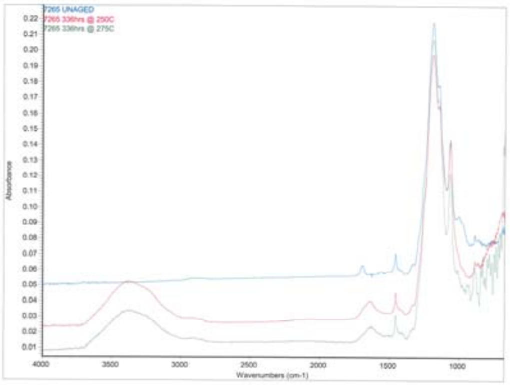


Figure 6 – TFE/E/PMVE FTIR

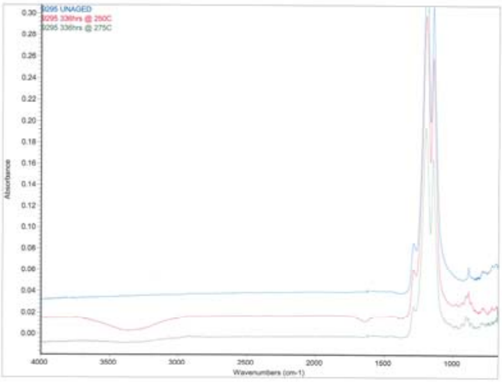


Figure 7 – FFKM FTIR

The TFE/E/PMVE spectra (fig.6) exhibits marked absorbance at 3300 cm^{-1} and 1600 cm^{-1}, indicative of water absorption and co-agent degradation.

The FFKM spectra (fig.7) exhibits remarkable stability. We surmise the loss of mechanical properties is attributable to bond scission rather than chemical alteration of the composition.

DMRT Analysis

All dynamic mechanical rheological thermal analysis (“DMRT”) sweeps were run at 0.1Hz, 0.1% strain running from 0˚C to 200˚C. The sweeps displayed herein are to document changes in elastic modulus, attributable to aging in 250˚C saturated steam, across a range of operating temperatures.

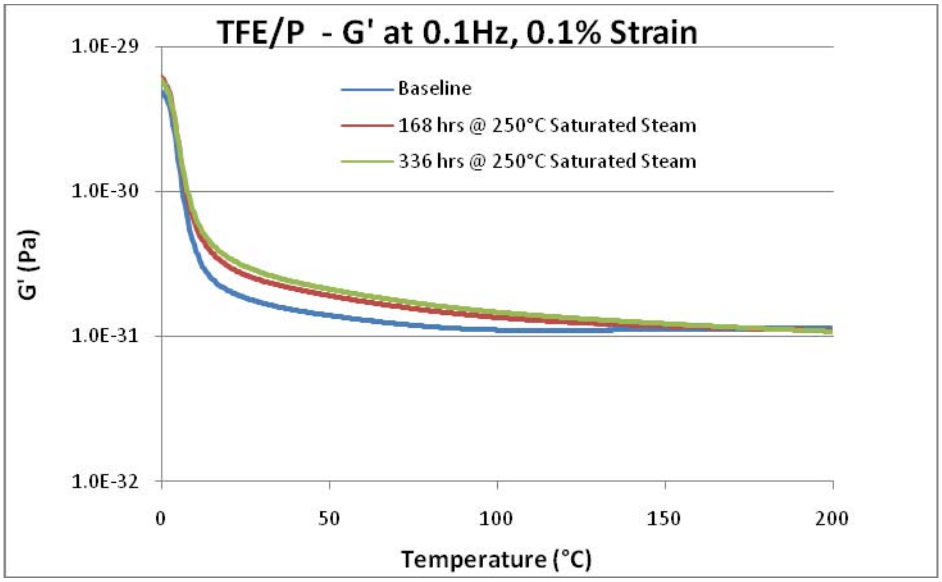


Figure 8 – TFE/P Elastic Modulus (G’)

Examination of the TFE/P thermal sweep (fig.8) exhibits a mostly stable composition whose aging in steam caused a minor increase in modulus measureable at temperatures below 150˚C.

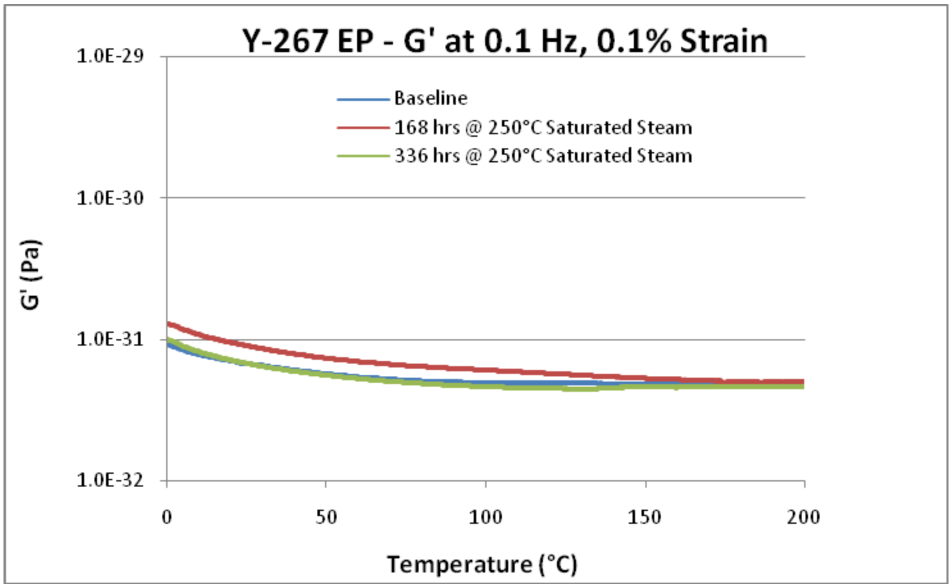


Figure 9 – Y-267 type EP Elastic Modulus (G’)

Examination of the Y-267 thermal sweep (fig.9) exhibits a mostly stable composition whose aging in steam caused a minor increase in modulus measureable at temperatures below 150˚C.

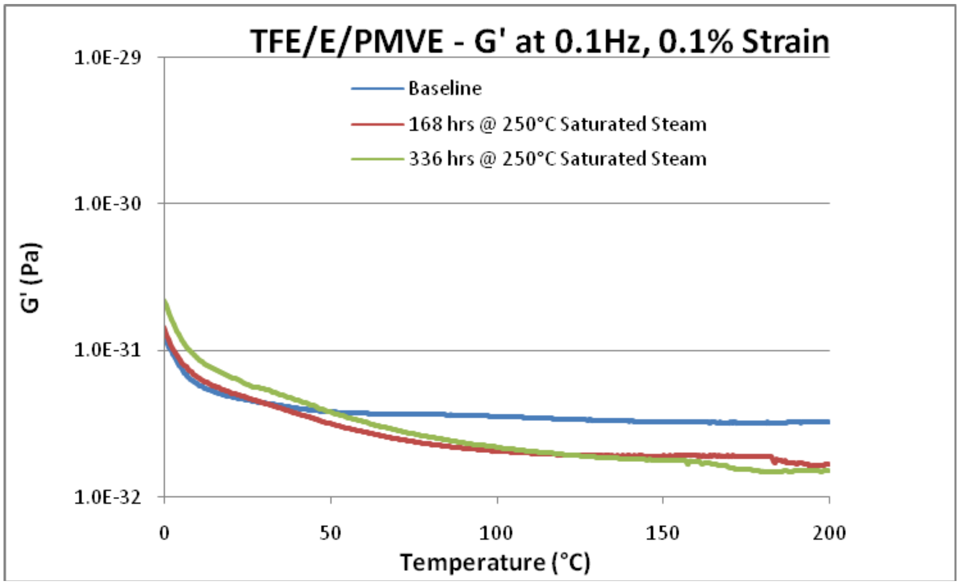


Figure 10 – TFE/E/PMVE Elastic Modulus (G’)

Examination of the TFE/E/PMVE sweep (fig.10) exhibits a composition whose aging in steam caused a degradation in modulus measureable at temperatures above 50˚C.

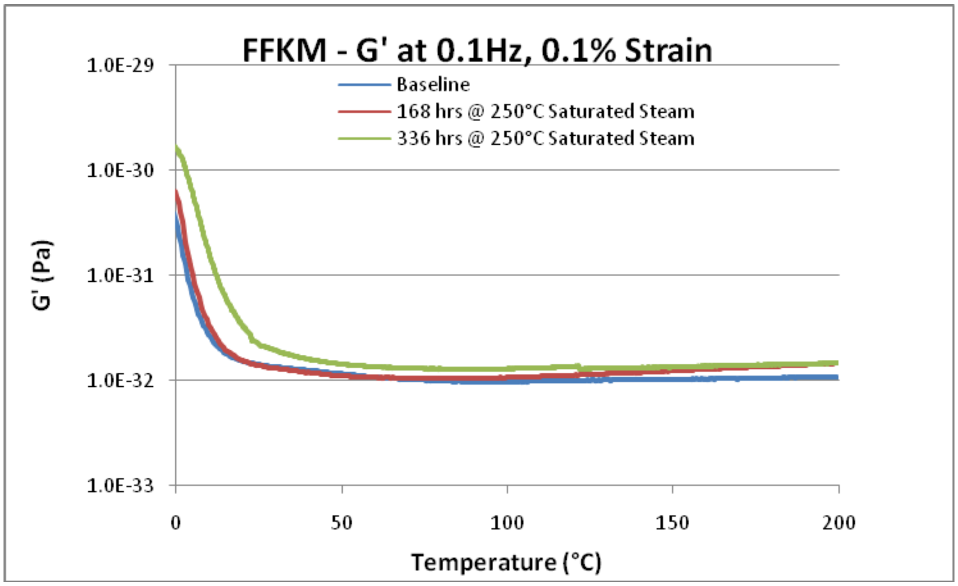


Figure 11 – FFKM Elastic Modulus (G’)

Examination of the FFKM sweep (fig.11) exhibits a composition whose aging in steam caused a minor increase in modulus measureable at all temperatures. The apparently stable elastic modulus is surprising in context of the severely diminished mechaincal properties observed in higher strain testing.

CONCLUSIONS

1) The Y-267 type EP, by the measurement standards herein, exhibits remarkable stability in saturated steam up to 275˚C for at least the 336 hours evaluated.
2) Based upon the measurement standards herein, Viton® ETP (E/TFE/PMVE), an otherwise high performance elastomer, should not be used in a saturated steam application.
3) A premium 100H TFE/P composition while suitable in 250˚C saturated steam, is demonstrably unstable in 275˚C saturated steam based upon the measurement standards herein.
4) Based upon the measurement standards herein, the high temperature FFKM (CSM containing) is marginally viable in steam at and exceeding 250˚C.

ACKNOWLEDGEMENTS

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[3] Hertz, III, D.., “Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers Evaluated using Strain Energy Density”, RAPRA High Performance & Specialty Elastomers, Geneva, (2005).

[4] ASTM Standard D 2000 – 08, “Standard Classification System for Rubber Products in Automotive Applications”, “Table X1.1 Polymers Most Often Used In Meeting Material Requirements”, *Annu. Book ASTM Stand.* **09.02**, 115 (2009). “X1.1 This appendix is intended to assist the users of Classification System D 2000-SAE J200 *and is not to be considered as part of the system*.” (emphasis added), 116.

[5] Auda, R.S. and Hazelton, D.R,”Ethylene Propylene Elastomer Technology for Improved High Temperature Serviceability”, Elastomers Technology Div., Exxon Chemical Co., Paper No. 750962

[6] Exception: sample size (n) = 2 for the FFKM o-rings and dumbbells.

[7] Hertz, Jr., Daniel, “Sealing Technology”, Rubber Products Manufacturing Technology, p.790, Marcel Dekker, Inc. (1994).

[8] Hertz, Jr., D, “Sealing Technology”, Rubber Products Manufacturing Technology, p.781, Marcel Dekker, Inc. (1994).

[9] ASTM Standard D 2000 – 08, “Standard Classification System for Rubber Products in Automotive Applications”, Section 4.2, *Annu. Book ASTM Stand.* **09.02**, 65 (2009).

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